

# University of St Andrews



Full metadata for this thesis is available in  
St Andrews Research Repository  
at:

<http://research-repository.st-andrews.ac.uk/>

This thesis is protected by original copyright

School of Geography and Geosciences

University of St Andrews

St Andrews

**Water quality functioning of an upland  
reservoir and its catchment area – with  
particular emphasis on iron and manganese**

By

Corinna Abesser

A thesis submitted for the degree of  
Doctor of Philosophy from the University of St Andrews

May 2003



TH E473

## Declarations

- i. I, Corinna Abesser, hereby certify that this thesis, which is approximately 85,000 words in length, has been written by me, that it is record of work carried out by me and that it has not been submitted in any previous application for a higher degree.

Date : St Andrews, 9th May 2003  
Signature :

- ii. I was admitted as a research student in October 1999 and as a candidate for the degree of a PhD. in October 1999; the higher study for which this is a record was carried out in the University of St Andrews between 1999 and 2003.

Date : St Andrews, 9th May 2003  
Signature :

- iii. I hereby certify that the candidate has fulfilled the conditions of the Resolution and Regulations appropriate for the degree of a PhD. in the University of St Andrews and that the candidate is qualified to submit this thesis in application for that degree.

Date :  
Signature : 17/10/03

### Copyright Declaration

In submitting this thesis to the University of St Andrews I understand that I am giving permission for it to be made available for use in accordance with the regulations of the University Library for the time being in force, subject to any copyright vested in the work not being affected thereby. I also understand that the title and abstract will be published, and that a copy of the work may be made and supplied to any bona fide library or research worker.

Date :

Signature :

## Abstract

---

Water quality problems associated with high iron and manganese concentrations in the water column are a common feature in many upland water supplies and have been experienced at the Megget Reservoir during a period of major draw down in 1997/98. The peaty soils covering such upland catchments favour metal mobilisation processes resulting in high iron and manganese loading in the streams draining into lakes and reservoirs. When removed from the water column by sedimentation, the metals accumulate in the bottom sediments from where they can be remobilised when conditions in the water body change.

In this thesis, extensive investigations at the reservoir body and its surrounding catchment area have been carried out to study the hydrological processes in the catchment, the reservoir and processes operating at the sediment-water interface in the reservoir. The temporal and spatial variability in iron and manganese concentrations in the water column of the reservoir and in the feeder streams is a particular focus of the study. A combination of analytical techniques and process-based laboratory experiments has been employed to investigate the relative importance of physical and chemical processes in determining iron and manganese mobilisation within, and release from, the bottom sediments of the Megget Reservoir.

Evaluation of the catchment data reveals that stream chemistry is influenced by flow pathways through the catchments and by catchment characteristics, in particular soil

type distribution, which control the iron and manganese fluxes into the reservoir, especially during high rainfall episodes. Evidence is presented that sediment release and re-suspension processes can introduce large amounts of iron and manganese into the reservoir water column and appear to have contributed significantly to the experienced water quality problems. The results of this study have significant implications for the management of the water supply itself and also highlight the importance of catchment-based management strategies for water supplies in other upland regions.

## Acknowledgements

---

I would like to express my sincere gratitude to Dr Ruth Robinson and Dr Richard Bates for providing me with the opportunity to undertake this research in the first place, for offering their guidance throughout the project and for co-ordinating links with the sponsors of the project at East of Scotland Water, the financial assistance of whom is gratefully acknowledged.

I thank Professor Chris Soulsby for his generous assistance and advice during the project, and for the stimulating discussions on many aspects of the catchment work. Similarly, I would like to thank Professor Colin Neal for his enthusiastic support and the illuminating discussions on hydrogeochemistry, and for his generosity in providing me with the use of the CEH library and analytical facilities. I am very grateful to both Chris and Colin for giving up their time to help me throughout the project, and for their encouragement and direction during times of difficulties.

My sincere gratitude is extended to Alexander Kirika, without whom the planning and realisation of the laboratory experiments would have been unthinkable. His ongoing interest in my research, but, above all, his assistance in the technical design of the experiments and in the collection of the sediment cores has been invaluable.

I would also like to thank Margaret Neal for her assistance with the ICP-OES analysis at the CEH laboratory and her patience in dealing with my samples, as well as for the

great hospitality with which Margaret and Colin welcomed me during my visits to Wallingford.

There have been many other people without whom my research could not have proceeded. Many thanks to CJ for sharing her knowledge and for her support during the early stages of the PhD. I would also like to express my gratitude to Dr Olivia Bragg for making the automatic samplers available for my field studies. Furthermore, I am grateful to everyone who accompanied me on my field visits, in particular Stuart Alison, for his help during many stormy hours on the reservoir; Dean for his willingness to spend his free time collecting water samples and testing field equipment, and Thomas for not letting me down during the sampling of torrential storm events. Many thanks to Rab and Dave for their reliability in supplying the boat, for helping out during the sampling programme and for the many cups of tea, which were always welcome after a long, cold day on the reservoir.

My friends and family have been of immense support in enabling me to keep going. I particularly thank my parents for their continued encouragement and support throughout my education. Finally, I would like to thank Dean for his curiosity and interest in my research and for his unwavering support during the last few years.

# Table of Contents

---

ABSTRACT.....	3
ACKNOWLEDGEMENTS.....	5
TABLE OF CONTENTS .....	I
LIST OF FIGURES .....	IV
LIST OF TABLES.....	IX
<b>1 INTRODUCTION.....</b>	<b>1</b>
1.1 <i>Water quality and water supply in upland regions</i> .....	1
1.2 <i>Water quality history of the Megget Reservoir</i> .....	8
1.3 <i>Aims of the study</i> .....	13
<b>2 BACKGROUND.....</b>	<b>18</b>
2.1 <i>Important processes affecting water quality in upland reservoirs</i> .....	18
2.1.1 <i>Iron and manganese in the water column of lakes and reservoirs</i> .....	20
2.1.2 <i>Water–sediment interactions</i> .....	26
2.2 <i>Important processes in upland catchments and their effect on stream water quality</i> .....	37
2.2.1 <i>Effect of soil processes on iron and manganese mobilisation</i> .....	38
2.2.2 <i>Role of hydrological pathways</i> .....	42
2.2.3 <i>Catchment characteristics that affect iron and manganese runoff in upland catchments</i> .....	48
<b>3 THE MEGGET CATCHMENT .....</b>	<b>53</b>
3.1 <i>Introduction</i> .....	53
3.2 <i>Hydrology and land use</i> .....	54
3.3 <i>Geology and geomorphology</i> .....	65
3.4 <i>Iron and manganese sources in bedrock</i> .....	70
3.5 <i>Soils</i> .....	71
<b>4 RESERVOIR WATER QUALITY .....</b>	<b>79</b>
4.1 <i>Sampling design and data collection</i> .....	79
4.1.1 <i>Sample collection</i> .....	82
4.2 <i>Water Analysis</i> .....	84
4.2.1 <i>Terms and definitions</i> .....	84
4.2.2 <i>ESW Laboratory, Edinburgh</i> .....	86
4.2.3 <i>CEH Laboratory, Wallingford</i> .....	88
4.2.4 <i>Gatty Marine Laboratory, St Andrews</i> .....	93
4.3 <i>Summary of data collected</i> .....	93
4.4 <i>Reservoir water quality – Temporal variations</i> .....	98
4.4.1 <i>Temperature distribution</i> .....	98
4.4.2 <i>Water chemistry</i> .....	102
4.5 <i>Reservoir water quality -Spatial pattern</i> .....	113
4.5.1 <i>Temperature distribution</i> .....	113
4.5.2 <i>Water chemistry</i> .....	114
4.6 <i>Discussion</i> .....	114
4.7 <i>Summary</i> .....	120

<b>5</b>	<b>STREAM WATER QUALITY.....</b>	<b>123</b>
5.1	<i>Sampling design and methods .....</i>	<i>123</i>
5.1.1	<i>Sample collection and analysis .....</i>	<i>125</i>
5.1.2	<i>Stream flow monitoring and discharge calculations.....</i>	<i>127</i>
5.2	<i>Summary of data collected.....</i>	<i>129</i>
5.3	<i>Stream hydrochemistry -Temporal patterns.....</i>	<i>133</i>
5.4	<i>Stream hydrochemistry - Spatial patterns.....</i>	<i>144</i>
5.5	<i>Discussion.....</i>	<i>149</i>
5.6	<i>Summary.....</i>	<i>158</i>
<b>6</b>	<b>EPISODIC HYDROLOGICAL RESPONSE .....</b>	<b>160</b>
6.1	<i>Introduction.....</i>	<i>161</i>
6.2	<i>Sampling design and methods .....</i>	<i>163</i>
6.2.1	<i>Sample collection and analysis .....</i>	<i>167</i>
6.2.2	<i>Hydrological monitoring.....</i>	<i>170</i>
6.3	<i>Summary of data collected.....</i>	<i>171</i>
6.4	<i>General patterns of stream response during storm events .....</i>	<i>172</i>
6.5	<i>Statistical data analysis: R-mode and Q- mode factor analysis .....</i>	<i>182</i>
6.5.1	<i>Introduction .....</i>	<i>182</i>
6.5.2	<i>Method adopted and data analysis.....</i>	<i>184</i>
6.5.3	<i>Data interpretation.....</i>	<i>190</i>
6.6	<i>End-member mixing analysis .....</i>	<i>208</i>
6.6.1	<i>Introduction .....</i>	<i>209</i>
6.6.2	<i>EMMA- conceptual model and assumptions .....</i>	<i>213</i>
6.6.3	<i>Selection of end-member chemistries .....</i>	<i>219</i>
6.6.4	<i>Hydrograph separation using EMMA.....</i>	<i>222</i>
6.7	<i>Discussion.....</i>	<i>238</i>
6.8	<i>Summary.....</i>	<i>245</i>
<b>7</b>	<b>SEDIMENT STUDIES .....</b>	<b>247</b>
7.1	<i>Introduction.....</i>	<i>247</i>
7.2	<i>Sampling design and methods .....</i>	<i>248</i>
7.2.1	<i>Sample collection.....</i>	<i>250</i>
7.3	<i>Sediment analysis.....</i>	<i>253</i>
7.3.1	<i>Physical analysis .....</i>	<i>253</i>
7.3.2	<i>Chemical analysis.....</i>	<i>263</i>
7.4	<i>General results and spatial pattern .....</i>	<i>270</i>
7.4.1	<i>Physical sediment properties.....</i>	<i>270</i>
7.4.2	<i>Sediment chemistry.....</i>	<i>279</i>
7.5	<i>Discussion.....</i>	<i>284</i>
7.6	<i>Summary.....</i>	<i>289</i>
<b>8</b>	<b>PROCESS STUDIES.....</b>	<b>291</b>
8.1	<i>Experimental design .....</i>	<i>291</i>
8.1.1	<i>Introduction .....</i>	<i>291</i>
8.1.2	<i>Core collection .....</i>	<i>294</i>
8.2	<i>Sediment re-suspension .....</i>	<i>298</i>
8.2.1	<i>Methods and materials .....</i>	<i>299</i>
8.2.2	<i>Results.....</i>	<i>300</i>
8.3	<i>Sediment release.....</i>	<i>307</i>
8.3.1	<i>Methods and materials .....</i>	<i>308</i>
8.3.2	<i>Results.....</i>	<i>309</i>
8.4	<i>Core metal distribution .....</i>	<i>319</i>

8.4.1	<i>Methods and materials</i> .....	321
8.4.2	<i>Results</i> .....	321
8.5	<i>Discussion</i> .....	326
8.6	<i>Summary</i> .....	336
<b>9</b>	<b>SUMMARY AND CONCLUSIONS</b> .....	<b>338</b>
9.1	<i>Summary</i> .....	338
9.1.1	<i>Main research findings</i> .....	339
9.1.2	<i>Limitations</i> .....	345
9.1.3	<i>Future research</i> .....	348
9.1.4	<i>Management perspectives and wider implications</i> .....	350
9.2	<i>Conclusions</i> .....	354
<b>10</b>	<b>REFERENCES</b> .....	<b>357</b>
	<b>APPENDIX I – SAMPLING PROTOCOLS</b> .....	<b>379</b>
	<b>APPENDIX II: WATER ANALYSIS METHODS – ESW LABORATORY</b> .....	<b>379</b>
	<b>APPENDIX III – ICP-OES STANDARDS</b> .....	<b>390</b>
	<b>APPENDIX IV – CHLOROPHYLL-A ANALYSIS USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)</b> .....	<b>402</b>
	<b>APPENDIX V - DISCHARGE: CALCULATED VERSUS MEASURED VALUES</b> .....	<b>404</b>

## List of Figures

Figure 1.1: Variations in water volume (as percentage full) of the Megget Reservoir between 1987 and 2001, including the excessive artificial draw down of the reservoir in 1997/98. ....	9
Figure 1. 2 a: Relationship between reservoir drawdown and iron levels in the reservoir water monitored at the Marchbank water treatment works during the event. ....	12
Figure 1. 3: Factors affecting iron and manganese concentrations in the water column of the Megget Reservoir. ....	14
Figure 2. 1: Conceptual model for the redox-driven cycling of iron and manganese at a redox boundary showing schematic concentration profiles of particulate and soluble forms (after Davison, 1985). ....	27
Figure 2. 2: Schematic representation of near-surface pathways (after Hensel and Elsenbeer, 1997). ....	45
Figure 3. 1: Location of the study area (map taken from <a href="http://www.multimap.co.uk">www.multimap.co.uk</a> ) .....	53
Figure 3. 2: Map of the Megget catchment and its main subcatchments. ....	55
Figure 3. 3: The Megget Reservoir (view from the northside towards the tower). ....	56
Figure 3. 4: Bathymetry of the Megget Reservoir (surveyed on 27/09/1999). ....	56
Figure 3. 5: Winterhope Burn catchment and sampling site for regular and event sampling at low flow (looking downstream) and during storm event (looking upstream). ....	57
Figure 3. 6: Catchment of Megget Water and sampling site (at Meggethead) for regular sampling (looking towards the reservoir). ....	58
Figure 3. 7: Catchment of Linghope Burn and sampling site for regular and event sampling (looking downstream). ....	59
Figure 3. 8: Site for regular sampling and stage measurements at Shielhope Burn and iron leaching from organic gleys at the stream banks. ....	60
Figure 3. 9: Sampling site at Cramalt Burn (looking upstream and downstream). ....	61
Figure 3. 10: Sampling site at Craigierig Burn looking towards the reservoir and downstream of sheep shed. ....	62
Figure 3. 11: Solid and drift geology of the Megget catchment (taken from Geological Survey of Great Britain, Sheet 16). Inset map (after Chapman et al. 2000). ....	67
Figure 3. 12: Outcrops of greywackes (top) and shales (bottom) in the Megget catchment. ....	68
Figure 3. 13: Soil map of the Megget catchment (based on Soil Survey of Scotland, 1:50,000 soil map, Sheets 71, 72, 77, 78). ....	75
Figure 3. 14: Leaching of iron from near-stream soils and precipitation on clasts in the oxidising stream environment. ....	76
Figure 3. 15: Blanket peat in the upper parts of the Winterhope catchment (top) and in the Megget Water catchment (bottom). ....	77

Figure 3. 16: Eroded peat and coarse drift deposits underlying peat horizons.....	78
Figure 4. 1: Megget Reservoir sampling sites .....	80
Figure 4. 2: Variations in reservoir water level during the sampling period.....	100
Figure 4. 3: Piper diagram for water samples from the Megget Reservoir collected between September 1999 and November 2000. ....	100
Figure 4. 4: Spatial and temporal pattern of temperature distribution at the Megget Reservoir.....	101
Figure 4. 5: Thermocline development at site A in (a) 2000 and (b) 2001. ....	101
Figure 4. 6: Distribution of (a) silica, (b) manganese and (c) iron in the water column of the Megget Reservoir during the sampling period (September 1999- December 2001).....	105
Figure 4. 7: Distribution of (a) TOC, (b) nitrate and (c) total phosphorous in the water column of the Megget Reservoir during the sampling period (September 1999- December 2001).....	106
Figure 4. 8: Concentrations of dissolved oxygen (DO) in the water column of the Megget Reservoir as measured by the ESW laboratory. Error bars indicate the relative standard deviation (RSD) of the data. The inlet shows the thermocline development during the sampling period. ....	109
Figure 4. 9: Oxygen profiles measured at the three sampling sites during summer 2001. ....	110
Figure 5. 1: Map of regular stream sampling sites in the Megget catchment.....	124
Figure 5. 2: Sampling frequency during the regular sampling programme (September 1999 to December 2001). ....	134
Figure 5. 3 (a-b) Plots of monthly stream water TP concentrations during regular sampling programme at all six streams, (c) daily rainfall and discharge for Winterhope Burn. ....	134
Figure 5. 4: (a-d) Plots of monthly (fortnightly) stream water pH and conductivity levels during the regular sampling programme at all six streams, (e) daily rainfall and discharge for Winterhope Burn. ....	135
Figure 5. 5: (a-d) Plots of monthly (fortnightly) stream water alkalinity and colour values during the regular sampling programme at all six streams, (e) daily rainfall and discharge for Winterhope Burn. ....	136
Figure 5. 6: (a-d) Plots of monthly stream water Na and Cl levels during the regular sampling programme at all six streams, (e) daily rainfall and discharge for Winterhope Burn. ....	137
Figure 5. 7: (a-d) Plots of monthly stream water NO <sub>3</sub> and TN concentrations during the regular sampling programme at all six streams, (e) daily rainfall and discharge for Winterhope Burn. ....	138
Figure 5. 8: Concentration-discharge relationship for selected determinants at Winterhope Burn during regular sampling programme (graphs only include data for which discharge measurements are available: August 2000 to December 2001). ....	139
Figure 5. 9: Sheep shed located ~100m upstream of sampling site at Craigierig Burn. .....	140
Figure 5. 10 Piper diagram for (a) precipitation data collected at Sourhope (ECN data) and (b) stream water samples from the Megget catchment between September 1999 and December 2001. ....	145

Figure 5. 11: Plot of (a) Ca ( $\text{mg L}^{-1}$ ) versus conductivity ( $\mu\text{S cm}^{-1}$ ) and (b) Cl ( $\text{mg L}^{-1}$ ) versus Na ( $\text{mg L}^{-1}$ ) concentrations for samples collected during the regular sampling programme. ....	153
Figure 6. 1: Sampling Location during intensive sampling programme .....	164
Figure 6. 2: Sampling and storm event frequency at individual streams during intensive sampling (18 October 2000 – 30 October 2000).....	165
Figure 6. 3: Automatic sampler (American Sigma Portable Wastewater Sampler) and bottle arrangement. ....	165
Figure 6. 4: Automatic sampling site at Peaty Muckle Burn.....	170
Figure 6. 5: Changes in flow (cumecs), pH, alkalinity ( $\mu\text{Eq L}^{-1}$ ), conductivity ( $\mu\text{S cm}^{-1}$ ) and concentrations ( $\text{mg L}^{-1}$ ) of sulphate and silica during the event sampling programme. ....	176
Figure 6. 6: Changes in flow (cumecs), colour ( $^{\circ}\text{Hazen}$ ) and concentrations ( $\mu\text{g L}^{-1}$ ) of iron, manganese, aluminium and zinc during the event sampling programme. ....	177
Figure 6. 7: Relationship between flow (cumecs), colour ( $^{\circ}\text{Hazen}$ ), pH, Alkalinity ( $\mu\text{eq/L}$ ) and concentrations ( $\text{mg/L}$ ) of Fe, Al, Ca and $\text{SO}_4$ for all streams sampled during intensive programme (18 October 2000 - 30 October 2000).....	180
Figure 6. 8: Scatter plots showing relationship between (a) colour and Al ( $\mu\text{g L}^{-1}$ ) and (b) alkalinity ( $\mu\text{Eq L}^{-1}$ ) and Ca ( $\text{mg L}^{-1}$ ).....	181
Figure 6. 9: Variable factor loadings in the factor space derived from analysis of entire data set .....	193
Figure 6. 10: Distribution of stream water samples in factor space of factor 1 and factor 2 derived from analysis of entire data set.....	198
Figure 6. 11: Sample loadings of all streams on factor 1 and their relation to flow. ....	199
Figure 6. 12: Sample loadings of all streams on factor 2 and their relation to flow. ....	200
Figure 6. 13: Shielhope Burn sample factor loadings. ....	204
Figure 6. 14: Shielhope Burn sample factor loadings for rainfall events on 18 October. ....	205
Figure 6. 15: Winterhope Burn sample factor loadings. Inlet shows magnitude of the five sampled storm events. Vertical (small) arrows indicate maximum F2 loading at individual events (gradual Fe and Mn depletion), horizontal (small) arrows indicate maximum F1 loadings at individual events (effect of storm event magnitude) (see text for explanation). ....	206
Figure 6. 16: Estimation of end-member chemistry from Shielhope Burn alkalinity data. Circle encloses points that were averaged to calculate end-member chemistry.....	219
Figure 6. 17: Hydrograph split for Winterhope Burn based on event data (18 October 2000-30 October 2000).....	222
Figure 6. 18: Hydrograph split for Shielhope Burn based on event data (18 October 2000- 30 October 2000).....	222
Figure 6. 19: Hydrograph split for Peaty Muckle Burn based on event data (18 October 2000- 30 October 2000).....	223
Figure 6. 20: Hydrograph split for Black Burn based on event data (18 October 2000- 30 October 2000) .....	223
Figure 6. 21: Hydrograph split for Linghope Burn based on event data (18 October 2000 - 30 October 2000).....	224

Figure 6. 22: Relationship between groundwater proportion and flow at Winterhope Burn. ....	227
Figure 6. 23: Hydrograph split for (a) Shielhope Burn and (b) Winterhope Burn using time series flow data and (c) stream hydrograph for Winterhope Burn. ....	229
Figure 6. 24: Hydrograph split for (a) Peaty Muckle Burn, (b) Black Burn and (c) Linghope Burn using time series flow data. ....	230
Figure 6. 25: Hydrograph split for Linghope Burn based on end-member with higher alkalinity (+70 $\mu$ Eq L <sup>-1</sup> ) and using time series flow data. ....	233
Figure 6.26: Relationship between proportion of groundwater and Ca at Winterhope Burn (5% steps seen in the groundwater proportion data are remnants of alkalinity values being reported as mgCaCO <sub>3</sub> ·L <sup>-1</sup> in the original data). ....	234
Figure 6. 27: Regression relationships between predicted and measured Ca concentrations for (a) Shielhope Burn, (b) Winterhope Burn, (c) Peaty Muckle Burn, (d) Black Burn and (e) Linghope Burn. Heavy lines are fitted trendlines; lighter lines indicate a slope of one (1:1 lines). ....	235
Figure 7. 1: Location of sampling sites during sediment survey.....	248
Figure 7. 2: Sediment sample collection .....	251
Figure 7. 3: Cumulative frequency distribution curves (all locations). ....	272
Figure 7. 4: Frequency distribution curves (Locations MS1, MS2, MS5, MS7, MS8, MS9, MS11, MS13, MS14). ....	273
Figure 7. 5: Frequency distribution curves (Locations MS3, MS6). ....	274
Figure 7. 6: Concentrations of acid-extractable (weakly bound) iron and manganese extracted from the sediments (HOAc extraction). ....	278
Figure 7. 7: Relationships between total concentrations (determined by XRF) of selected metals in the sediment samples collected at sites MS1-MS9 (full diamonds) and MS10-MS14 (open diamonds). ....	280
Figure 7. 8: Relationship between weakly bound iron and manganese (derived from HOAc extraction) and loss on ignition (~organic content) of the sediment samples. ....	281
Figure 7. 9: Relationship between weakly bound iron and manganese (derived from HOAc extraction) and specific surface area of the sediment samples....	282
Figure 8. 1: Experiment Design.....	291
Figure 8. 2: Experimental set-up: Re-suspension.....	291
Figure 8. 3: Experimental set-up: Diffusion.....	291
Figure 8. 4: Location of core collection sites at the Megget Reservoir.....	293
Figure 8. 5 : Collection and preparation of sediment cores for laboratory experiments and for the analysis of metal distribution in the sediments (04/10/01)...	294
Figure 8. 6: Iron concentrations in the water column overlying re-suspended cores: (a) C3-5 re-suspended to 1-2 cm depth for 4 hours and (b) C3-1 re-suspended to 4-5 cm depths for 1 hour. (Arrows mark intervals of core re-suspension). ....	301
Figure 8. 7: Manganese concentrations in the water column overlying re-suspended cores: (a) C3-5 re-suspended to 1-2 cm depth for 4 hours and (b) C3-1 re-suspended to 4-5 cm depths for 1 hour. (Arrows mark intervals of core re-suspension). ....	302
Figure 8. 8: Temporal variations in pH values in the incubated cores during the re-suspension experiments. ....	303

Figure 8. 9: Temporal variations in redox potential during the re-suspension experiments.....	303
Figure 8. 10: Documentation of re-suspension experiments.....	304
Figure 8. 11: Iron concentrations in water column overlying incubated cores: (a) C3-3, incubated at 9°C (±1°C) and (b) C3-6, incubated at 22°C (±2°C). .....	310
Figure 8. 12: Manganese concentrations in water column overlying incubated cores: (a) C3-3, incubated at 9°C (±1°C) and (b) C3-6, incubated at 22°C (±2°C). .....	311
Figure 8. 13: Temporal variations in pH values in the incubated cores during diffusion experiments.....	312
Figure 8. 14: Temporal variations in redox potential in the incubated cores during diffusion experiments. ....	312
Figure 8. 15: Stability relation in the system Fe-O-H <sub>2</sub> O-S-CO <sub>2</sub> at 25°C, assuming ferrihydrite as the ferric oxide phase, $\Sigma S=10^{-2}$ m and $P_{CO_2}=10^{-3}$ atm. Solid-solution boundaries are drawn for an activity of dissolved Fe species of $10^{-6}$ (after Drever, 1997). ....	313
Figure 8. 16: Inter-relationships between selected elements in the water column of the incubated cores C3-3 and C3-6 during the sediment release (diffusion) experiment. ....	314
Figure 8. 17. Experimental cores at the end of the experiments prior to core segmentation. ....	315
Figure 8. 18: Vertical distribution of weakly bound iron and manganese in the sediment cores (open symbols) and concentrations of (total) iron and manganese in the overlying water column (full symbols) of the Megget cores analysed (a) immediately after collection, (b) after incubation and (c) after re-suspension experiments [note the differences in units for water column concentrations in (a)]. ....	322

## List of Tables

Table 3. 1: Rainfall composition for the period between September 1999 to May 2001 derived from weekly composites collected at ECN monitoring site at Sourhope (concentrations in mg L <sup>-1</sup> ).....	63
Table 3. 2: Catchment characteristics of the Megget sub-catchments .....	72
Table 4. 1: Analysis suites for regular sampling programme (ESW laboratory).....	87
Table 4. 2: Elements analysed by the method and lower detection limits of the Optima 3300.....	89
Table 4. 3: Chlorophyll-a content (Nov-99 to Aug-00) and transparency (Sep-99 to Dec-01) of the Megget Reservoir during stratification and mixing periods	94
Table 4. 4: General water chemistry of the Megget Reservoir (mean values).....	95
Table 4. 5: Mean metal concentrations in the Megget Reservoir.....	95
Table 4. 6: Nutrient concentrations in the reservoir between Sep-99 and Dec-01 during stratification and mixing periods.....	95
Table 4. 7: Mean values of general water chemistry of the three reservoir sites between September 1999 and December 2001 at different depths and stratification regimes .....	96
Table 4. 8: Mean metal concentrations of the three reservoir sites between September 1999 and December 2001 at different depths and stratification regimes.....	97
Table 5. 1: Sampling undertaken during the different sampling programmes.....	129
Table 5. 2.: Summary of stream chemistry for regular ( <sup>(m)</sup> -monthly, <sup>(f)</sup> - fortnightly) sampling programme (September 1999 – December2001) [Parameters were only included: * until October 2000, ** from October 2000 onwards ; † after October 2000 calculated from colour values] .....	131
Table 5. 3 Summary of stream chemistry for regular ( <sup>(m)</sup> -monthly, <sup>(f)</sup> - fortnightly) sampling programme (September 1999 - December 2001) [Parameters were only included: * until October 2000, ** from October 2000 onwards; † after October 2000 calculated from colour values] .....	132
Table 5. 4: Stream concentrations of chlorophyll-a (µg L <sup>-1</sup> ) measured during regular sampling December 1999 to August 2000) [* no data for winter period available].....	142
Table 6. 1: Details of sample collection at individual sites during the intensive sampling programme .....	166
Table 6. 2: Summary of stream chemistry data for the intensive sampling programme (18 October 2000 to 30 October 2000) [AA=acid available].....	173
Table 6. 3: Combined R- and Q-mode analysis: computational steps .....	188
Table 6. 4: Factor loadings resulting from analysis of entire data set (all streams).....	194
Table 6. 5: Factor loadings for individual streams resulting from separate analysis of water chemistry data.....	195

Table 6. 6: End-member alkalinities ( $\mu\text{Eq L}^{-1}$ ) .....	221
Table 6. 7: Equations describing relationship between %gw and flow, used for hydrograph split based on flow data time series .....	229
Table 6. 8: Slopes and coefficients of determination ( $R^2$ ) derived from the regression relations between predicted and measured Ca concentrations .....	237
Table 6. 9: Coefficient of determination ( $R^2$ ) for linear regression between stream metal concentrations and stream soilwater proportion.....	238
Table 7. 1: Physical sediment characteristics (SD=Standard deviation).....	271
Table 7. 2: Statistical grain size parameters and estimated sampling error .....	272
Table 7. 3: Sediment chemical composition determined by XRF analysis.....	281
Table 8. 1: Description of collected cores.....	297

# 1

## **Introduction**

---

This thesis examines the factors controlling the mobilisation of iron and manganese in upland environments, in response to a specific water quality problem in an upland reservoir in Scotland. The following chapter contextualises the work and provides an overview of the water quality problems related to iron and manganese mobilisation in upland catchments and water supplies. A detailed account of the water quality problems experienced at the Megget Reservoir in 1997/98 during a period of extensive reservoir draw down is given, the needs for research and the aims of the current study are identified.

### **1.1 Water quality and water supply in upland regions**

Uplands are economically marginal areas, which constitute an important component of the natural heritage of Scotland and also provide the source area for many major river systems. As such, upland catchments are of crucial importance as a source of potable, industrial and agricultural water supplies, particularly in Scotland where 96% (by volume) of the public water supplies are derived from surface waters (MacDonald, 1994), most of which are sourced from upland catchments.

While generally regarded as relatively pristine natural environments, increasing environmental pressures on upland water quality arise from: (1) acidification through

sulphur and nitrogen deposition (e.g., Langan, 1985; Neal *et al.* 1998), (2) high sediment loads from forestry and overgrazing (Carling *et al.* 2001) and (3) mobilisation of colour and metals (Heal *et al.* 1997; Mitchell and McDonalds, 1995). These factors have provided a major impetus for water quality research in the UK during the last few decades. Much research has been undertaken in upland catchments in Wales (e.g., Foster *et al.* 1997; Neal *et al.* 1997a – Plynlimon) and North-east Scotland (e.g., Reid *et al.* 1981; Rees *et al.* 1989 – Glendye; Ferrier *et al.* 1990a, b- Allt a’Mharcaidh), and the results have significantly improved the understanding of the water quality functioning in such upland environments, as is discussed in more detail in Chapter 2.

While iron and manganese have been included in many studies on upland catchment hydrogeochemistry (e.g., Reid *et al.* 1985; Giusti and Neal, 1993; Heal, 2001), the main research focus has been on the impact of acid deposition and aluminium mobilisation. Comparatively little work has been dedicated to water quality problems related to the occurrence of (naturally) high loadings of iron and manganese, probably because of their, generally, less harmful effect compared to inorganic aluminium species; however, when in excess, manganese toxicity to fish (Nyberg *et al.* 1995) and humans (Kondakis *et al.* 1989) have been suggested, and ecological impacts of high iron levels, such as destruction of fish spawning grounds (Marsden and Mackay, 2001) and smothering of benthos with iron hydroxides (Younger, 2001), have also been reported.

Naturally elevated manganese and iron concentrations in streams and water bodies are commonly observed in upland regions and have been reported in a number of studies in Scotland (Reid *et al.* 1981; Giusti and Neal, 1993, Gavin *et al.* 2001), Northern England

(Heal *et al.* 1995, 1997; Stunell and Younger, 1995) and Wales (Neal *et al.* 1997a). The high concentrations of manganese and iron are generally associated with the acidic pH and the organic nature of upland catchments soils, which favour mobilisation of manganese and iron.

Iron and manganese are provided by weathering and mobilisation processes in the underlying bedrock and in the soils, rather than anthropogenic pollution, and in the Moffat region of the Southern Upland stream-sediment concentrations of up to 2% manganese and >20% iron in form of secondary oxides (BGS, 1993) were found. However, it usually is the mobility of manganese and iron within the soils, which control the concentrations of these elements in surface waters. As such, the mineral assemblage in the underlying geology may be a less important factor compared to the accumulation of organic matter in the soils, which encourages mobilisation and release of manganese and iron from the soils; however, the bedrock base content may affect the metal mobility indirectly as it determines the buffer capacity, and thus the pH, of the soils. Various studies have indicated that differences in soil type strongly influence the mobilisation of manganese and iron; Mitchell and McDonald (1995), for example, demonstrated the positive relationship between concentration of iron and manganese and percentage peat cover in an upland catchment in northern England. A variety of direct and indirect connections between upland land-use and manganese and iron concentrations in surface waters have been suggested (Heal, 2001), with afforestation probably being the most important influence, as it significantly increases the mobilisation of (manganese and) iron from the soils through increased leaching of Dissolved Organic Carbon (DOC) (Hughes *et al.* 1990; Grieve and Marsden, 2001).

However, catchment hydrology is, without doubt, the dominant control on stream water quality and metal loading. Upland catchments, underlain by crystalline basement rocks and with high precipitation totals, tend to exhibit ‘flashy’ runoff responses, and storm events usually promote rapid changes in stream water chemistry associated with high loadings in colour (TOC), iron and manganese (Muscutt *et al.* 1990; Giusti and Neal, 1993; Neal *et al.* 1997a; Reid *et al.* 1981; Heal *et al.* 1997, in press). Consequently, much of the annual load of iron and manganese in the streams is transported during hydrological events (Peters, 1994a; Longabucco and Rafferty, 1998; Jarvie *et al.* 2001), and these high loadings can affect the water quality of the receiving water body, both transiently (Zaw and Chiswell, 1998) as well as permanently (Longabucco and Rafferty, 1998), as the water body acts as a concentrator and digester of the chemical and physical inputs from the surrounding catchment areas. Knowledge about stream water loading pattern is therefore a prerequisite for establishing cause and effect relationships for water quality problems in lakes and reservoirs.

Manganese and iron are present in water supplies as a result of natural processes involving both, catchment erosion and dissolution of iron and manganese containing minerals at or near the sediment-water interface. Increased presence of these elements concerns many water authorities in the UK (Little and McFadzean, 1991; Schofield *et al.* 1991; Heal *et al.* 1995; Graham *et al.* 2002), but has also caused problems in Australia (Zaw and Chiswell, 1998), the Ukraine (Linnik and Zubenko, 2000) and in the United States of America (Hsiung and Tissue, 1994), where approximately 40% of the public water supply systems are affected (AWWA, 1987).

The EC Drinking Water Directive (CEC, 1980) has set the mandatory maximum admissible concentration of manganese and iron in drinking water at  $50 \mu\text{g L}^{-1}$  and  $200 \mu\text{g L}^{-1}$ , respectively. Although only 1.03 per cent of the drinking water samples tested across Scotland in 1996 failed to meet these EC Standards for manganese, the majority of failures occurred in upland water bodies (Heal, 2001). Mobilisation from poorly drained, peaty upland soils probably provides the initial source for these high manganese and iron levels reported in water treatment works and supply reservoirs, which receive runoff from upland catchments. Temporary deterioration in water quality has occurred in raw waters from the Ellan valley in Wales (Schofield *et al.* 1991) and in Loch Bradan, south-west Scotland (Little and McFadzean, 1991), and was also experienced at the Megget Reservoir during an excessive draw down of the reservoir water level in 1997/98 as is detailed in Section 1.2. The actual concerns for many water authorities arise from both, the potential for impairment caused by high levels of manganese and iron in drinking water (e.g., through oxide precipitation and clogging of the distribution system, staining and aesthetic problems) and the difficulties related to its removal from the drinking water by conventional treatment procedures (AWWA, 1987). Where the problem persists, cost-intensive upgrading of the treatment works may be required, as was the case at the Loch Bradan waterworks in south-west Scotland, where the installation of an ozonation treatment facility was necessitated to comply with the EC drinking water standards for manganese (Little and McFadzean, 1991).

Other concerns for upland water supplies located in peaty source areas arise from the colouration of the raw water, indicative of high organic contents. This not only causes aesthetical problems, but may also lead to increased levels of trihalomethanes (THM's)

in the treated supply water. THM's are a class of chemicals formed by reactions between chlorine and organic compounds in the water, and since chlorine is used as an effective means for disinfecting drinking water in the UK, there is a propensity of THM's to form during the treatment of peaty upland waters with chlorine. Due to the rising concerns that THM's may be toxic, carcinogenic or mutagenic at subchronic exposure (Robinson *et al.* 1998), drinking water standards now require THM concentrations to be kept as low as possible (CEC 1980), and the 1989 Water Supply (Water Quality) Regulations for England and Wales have introduced a standard of  $100\mu\text{g L}^{-1}$  for total THM's.

Besides catchment erosion and stream inputs, a number of internal processes, both biochemical and physical, may contribute to high iron and manganese concentrations in standing waters. High concentrations of manganese in Loch Bradan (Gavin *et al.* 2001), for example, have been attributed to the dissolution of (iron and) manganese containing minerals at or near the sediment water interface. Such dissolution and diffusion processes can provide a constant input of dissolved species into the overlying water column (Warnken *et al.* 2001; Hsiung and Tissue, 1994; Davison *et al.* 1982), and manganese release from sediments has also been suggested by sediment core studies in a number of Scottish freshwater lochs (Bryant *et al.* 1997). Where high concentrations of iron and manganese have accumulated, sediment may become a strong source of secondary water pollution as was experienced at the Dnieper reservoirs in the Ukraine (Linnik and Zubenko, 2000).

The operation of sediment re-suspension has also been linked to increased metal concentrations in the water column of aquatic systems (Davison *et al.* 1982; Hulscher *et*

*al.* 1992, Brassard *et al.* 1994; Caetano *et al.* 2003) and such processes may be promoted in reservoirs due to large water level fluctuation and/or coupled to draw down events (Effler *et al.* 1998a). In fact, excessive reservoir draw down was also held responsible for the increased metal release at the Dnieper reservoirs (Linnik and Zubenko, 2000), illustrating the close link between aspects of water quality and the operation of reservoirs.

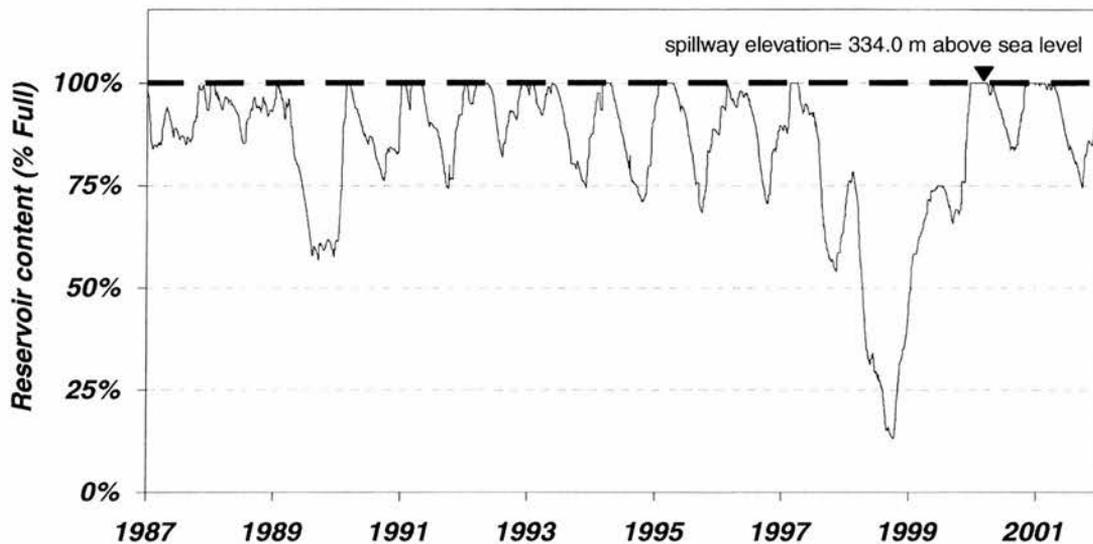
The above discussion has demonstrated the close linkage between catchment processes, reservoir processes and reservoir water quality. It also underlines the importance of adopting a catchment-integrated (holistic) approach to develop coherent reservoir management strategies, which promote sustainable water use and provide long-term protection of the available water resource as required by the EC Water Framework Directive (CEC, 2000). These stringent guidelines set out for surface water bodies and for water bodies providing water for human consumption include measures to 'ensure their necessary protection with the aim of avoiding deterioration in their quality in order to reduce the level of purification treatment required in the production of drinking water'. Hence, the guidelines not only affect the water regulators and authorities, such as SEPA, but also have direct implications for the operators of impoundments and water supply reservoirs through the integration of long-term water supply protection strategies and the promotion of sustainable management strategies for such water bodies in Community policies. It is therefore essential that scientifically based knowledge about the functioning of such water bodies and their catchment area is available to serve as a basis for the development of future protection, management and operation strategies for such regulated water bodies.

So far, comparatively little hydrological catchment studies have been undertaken in the Southern Uplands of Scotland, and the few hydrogeochemical process studies have mostly concentrated on the Galloway region in the south-west (Giusti and Neal, 1993; Grieve and Marsden, 2001). Given the variability in geological settings across the Southern Upland region and the remarkable west/east gradient in climatic conditions (Fox and Johnson, 1997) the processes identified in these studies may be quite different from those operating in other parts of the region. Moreover, the general focus on acidification and forested catchments has created an imbalance with regards to non-forested catchments. Clearly, insight into the water quality functioning of these non-forested upland environments is essential for estimating future impacts of climate change, predicted to bring stormier conditions and warmer temperatures to temperate climate, but also to establish suitable management strategies for such catchments, which in turn is a prerequisite for the successful implementation of the EU Water Framework Directive.

## **1.2 Water quality history of the Megget Reservoir**

The Megget Reservoir lies in the Southern Uplands between Peebles and Moffat, about 50km south of Edinburgh (*Figure 3. 1*). The reservoir is owned and operated by *Scottish Water* as a supply of drinking water and to augment flow downstream of the reservoir. The reservoir has been in operation since 1983 and its supply covers 40% of the demand in the area between Livingston in the west and Tranent in the east, including the whole of Edinburgh and Midlothian. With a yield of  $102.3 \text{ ML day}^{-1}$  (Jowitt and Hay-Smith, 2002) and a monthly average supply of  $80.1 \text{ ML day}^{-1}$  (averaged for 1992-2001) it used

to be *East of Scotland Water's (ESW)* largest supply reservoir prior to the amalgamation of the three Scottish water authorities (North, East and West) into *Scottish Water (SW)* in 2001. To date it is the fifth largest water supply body in Scotland (MacDonald, 1994). The seasonally varying compensation releases provided by the reservoir comprise quantities of up to  $41 \text{ ML day}^{-1}$  during summer and  $14 \text{ ML day}^{-1}$  during winter, and whenever feasible the reservoir level is kept drawn down by at least 1m for flood mitigation purposes (Fox and Johnson, 1997).



*Figure 1.1: Variations in water volume (as percentage full) of the Megget Reservoir between 1987 and 2001, including the excessive artificial draw down of the reservoir in 1997/98.*

Wide variations in water surface elevation (WSE) and water volume occur in the Megget Reservoir on an inter-annual and seasonal basis, as a result of the combined effects of natural variations in inflow and the operational demands for water supply as well as downstream releases, and variations in reservoir water content of 25% within a year are common (*Figure 1.1*). During normal reservoir operation (reservoir content

~75% full) the water quality at the Megget Reservoir fulfils the criteria required for highest standard drinking waters (iron < 300  $\mu\text{g L}^{-1}$ , colour < 20 mg  $\text{L}^{-1}$  Pt Scale) as set by the 1990 Surface Water (Classification) (Scotland) Regulations and the EEC Directive 75/440, and the abstracted water usually requires no additional treatment other than chlorination.

During the course of 1997/1998, however, the water level of the Megget Reservoir was artificially lowered to 13% of its full capacity (28 m below maximum water surface elevation (WSE)) to facilitate remedial repairs to the riprap on the dam wall. This dramatic draw down, illustrated in *Figure 1.1*, resulted in a severe deterioration of the water quality noted by high iron and manganese levels and discolouration of the water. The problem was first detected at the Marchbank water treatment works, which observed iron levels in the range of 300-400  $\mu\text{g/l}$  and manganese concentrations of up to 50  $\mu\text{g/l}$  in the water supplied by the Megget Reservoir. Further investigations of the problem revealed that iron and manganese levels were even higher in the reservoir water itself. For example, samples collected by ESW staff on 7 March 1998 contained 467  $\mu\text{g/l}$  iron at the reservoir bottom (30 m below WSE) and between 226  $\mu\text{g/l}$  and 246  $\mu\text{g/l}$  in the upper parts of the water column (15-3 m below WSE). These samples were taken directly from the overflow works at the Megget Dam and at a time when the water level was down to about 18 m below normal. Subsequent statistical analysis on the water chemistry data revealed that there is a significant correlation between iron and manganese levels in the water and reservoir draw down, and the regression relation between the water content (expressed in % full) of the reservoir and iron and manganese

concentrations is illustrated in *Figure 1. 2a,b<sup>1</sup>*. Based on these findings it was concluded that the increase in iron and manganese levels was a result of the abnormal draw down conditions at the Megget Reservoir. The problem finally ceased as the reservoir water level was raised to its normal elevation, and following the refilling of the reservoir the water quality improved, and quickly reverted to the high drinking water quality usually observed at the Megget Reservoir.

Despite the positive outcome, the poor water quality experienced during this draw down event greatly concerned *ESW*, the responsible water authority at the time, as such high levels of iron and manganese render the Megget water unsuitable for drinking water supply unless further treatment is applied. Thus, the reoccurrence of such problems may not only cause significant delays and/or shortage in water supply, but also implies a dramatic increase in the water treatment costs, in particular at the Megget Reservoir since appropriate treatment facilities are not available at the Marchbank water treatment works. It is therefore in the interest of both the water authorities as well as the consumers to avoid such problems in the future, but this, in turn, requires a better understanding of the underlying processes that may have triggered the dramatic decline in water quality. It was this realisation that provided the motivation to initiate and support a scientific research project at the Megget Reservoir and to gain deeper insight into the water quality functioning of the reservoir.

---

<sup>1</sup> Unfortunately, the original data collected during the event were lost during repeated re-structuring of *East of Scotland Water* and during the final amalgamation to *Scottish Water*, so that only summary copies of the original data are available.

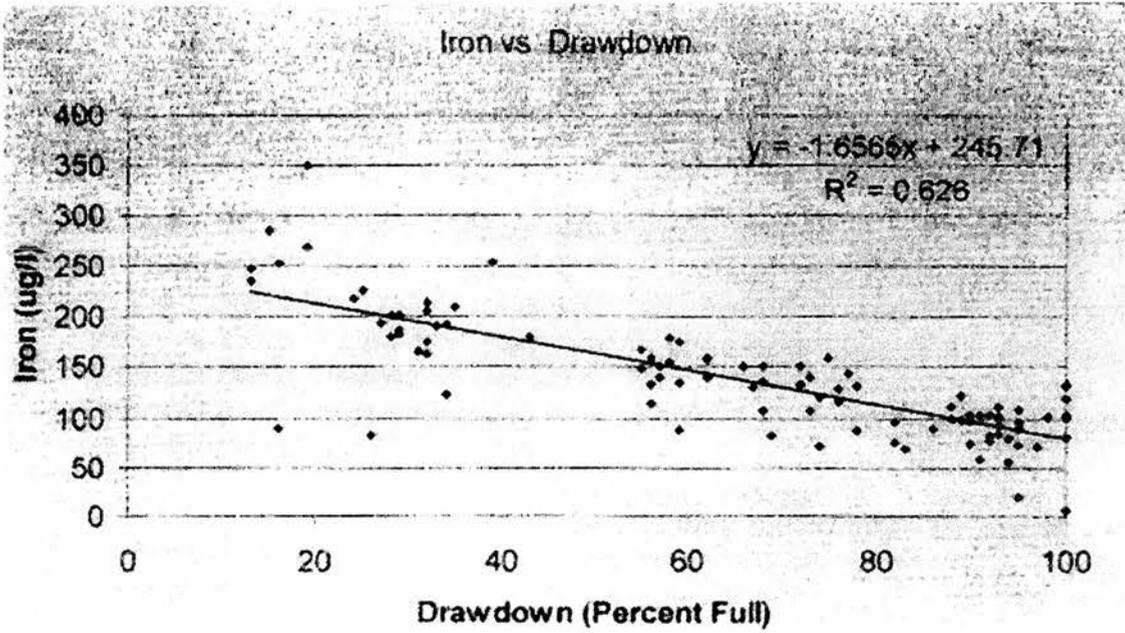


Figure 1. 2 a: Relationship between reservoir drawdown and iron levels in the reservoir water monitored at the Marchbank water treatment works during the event.

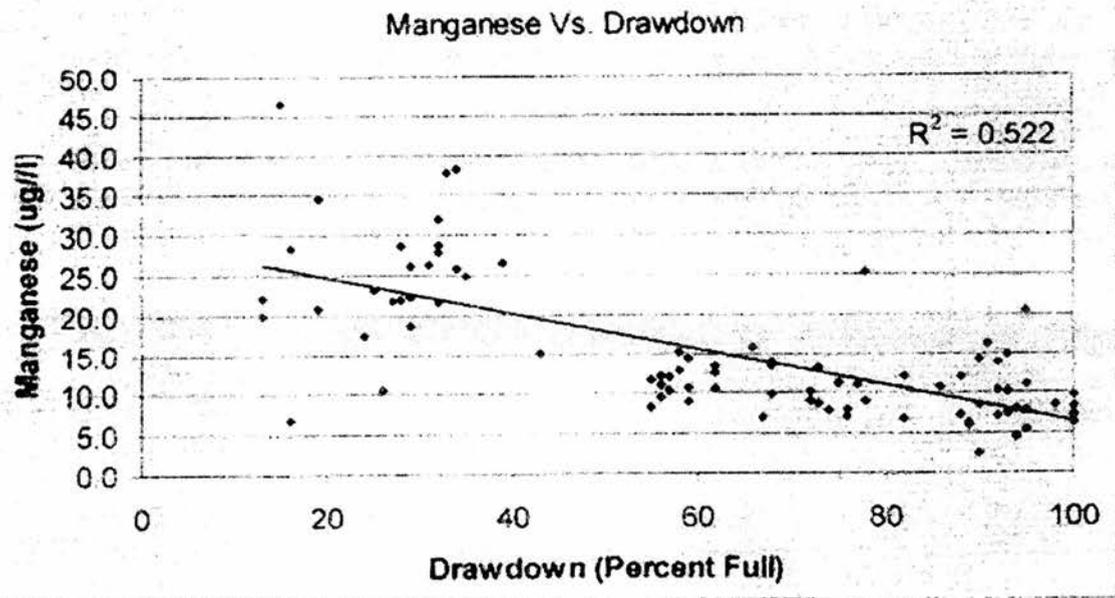


Figure 1.2b. Relationship between reservoir drawdown and manganese levels in the reservoir water monitored at the Marchbank water treatment works during the event.

### 1.3 Aims of the study

This study is motivated by the water quality problems experienced at the Megget Reservoir in 1997/98, which in many ways are similar to problems that occur in other upland regions. As reservoir systems and processes are interlinked with the surrounding catchment system, water quality and any changes may be functions of catchment and reservoir behaviour and cannot be looked at in isolation. The three main compartments that affect reservoir water quality are pictured in *Figure 1. 3* and will be considered in more detail in this thesis. The specific aims for this study are therefore:

- i. to assess the general characteristics of the Megget Reservoir with regards to its trophic status, physical and chemical properties and any spatial and temporal variability,
- ii. to monitor background levels of stream water chemistry and investigate the temporal and spatial variability of water composition in the aquatic environment,
- iii. to investigate flow related variations in stream chemistry during individual storm events in order to assess the range of iron and manganese loading in the streams and to examine the contribution of different runoff source areas to stream flow during rainstorm episodes,
- iv. to investigate the physical and chemical characteristics of the bottom sediments of the Megget Reservoir and their spatial distribution in order to identify areas of metal accumulation and potential sites for increased metal release, and
- v. to examine the importance of sediment re-suspension and diffusion processes for internal iron and manganese loading and assess their effect on reservoir water

quality, to identify processes which are responsible for iron and manganese mobilisation within the sediments and to relate them to those in the water column.

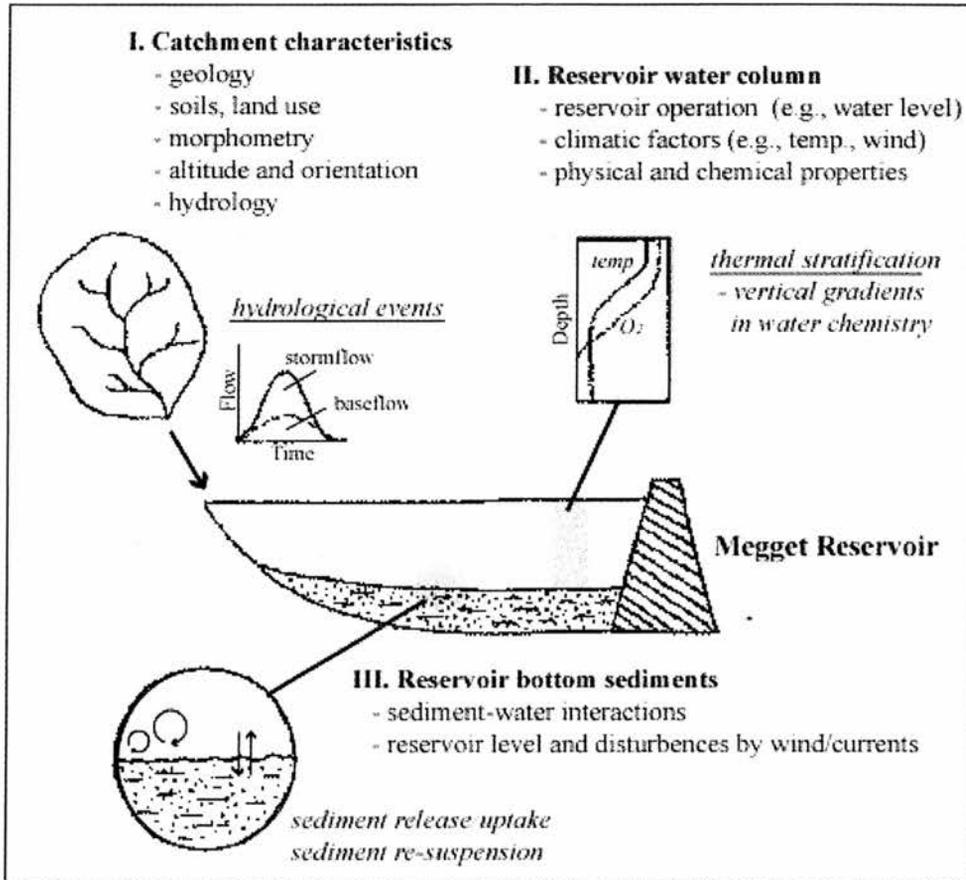


Figure 1. 3: Factors affecting iron and manganese concentrations in the water column of the Megget Reservoir.

It is anticipated that the outcomes of this study will provide *Scottish Water* with a scientific basis on which they can base future management strategies for the Megget Reservoir and its catchment area. The results are generally applicable to other upland catchments with similar catchment characteristics.

The structure of the thesis, in which these objectives are addressed, is as follows:

Chapter 1 provides an introduction to the study presented in this thesis and outlines the water quality issues specific to water supplies in upland regions in general and to the Megget Reservoir in particular.

In Chapter 2, important processes that control the water quality in upland reservoirs are introduced and processes in the surrounding upland catchment area are considered. Particular attention is paid to processes that influence the iron and manganese chemistry and their impact on stream water chemistry is discussed. The close link between reservoir and catchment factors is emphasised.

An introduction to the study area is provided in Chapter 3 and the physical characteristics of the catchment are described. The high proportion of organic rich soils in the Megget catchment and high precipitation rates promote mobilisation and runoff of iron and manganese in the area and these processes vary depending on geological settings and soil coverage. The characteristics of the individual sub-catchments are outlined.

Chapter 4 presents the spatial and temporal variability in water chemistry in the Megget Reservoir observed during the monthly sampling programme. The data show distinct temporal and spatial variations in physical and chemical properties of the reservoir and provide insight in the annual cycling of such elements as iron and manganese.

In Chapter 5, the temporal and spatial variability in stream water chemistry across the catchment area is investigated. Analysis of the data shows that temporal variations in stream chemistry are strongly influenced by changing flow conditions while catchment characteristics, such as soil type, appear to control the spatial variability.

The episodic hydrochemical response of selected streams with contrasting soil type distribution is evaluated in Chapter 6. Factor analysis techniques are applied to the data and inferences are made about the sources of different waters contributing to flow. The data also support the use of a simple two-component mixing model, which assumes stream water composition, at least to a first approximation, to result from mixing of 'soilwater' and 'groundwater' sources. This simple conceptual model is then utilised to model the episodic variability in stream chemistry.

The physical and chemical characteristics of the reservoir bottom sediments are investigated in Chapter 7. The results provide insight in the spatial variability in the bottom sediment characteristics, but also demonstrate the problems associated with determining the sediment chemical properties, in particular when dealing with redox sensitive elements like iron and manganese.

Chapter 8 investigates the effects of in-reservoir processes, namely re-suspension and diffusion, on the reservoir water quality by means of laboratory experiments on undisturbed sediment cores. Analysis of the data allowed identification of different mechanisms responsible for the release of iron and manganese from the sediments into

the overlying water column, although the limitations of such an laboratory approach have to be recognised.

In the final chapter, Chapter 9, the major findings and achievements are summarised within the context of this study. The limitations of the chosen approach are discussed and areas of further work and future research are identified. Finally, management perspectives for the Megget Reservoir are outlined based on the findings of this study and the wider implications are discussed.

# 2

## Background

---

### 2.1 Important processes affecting water quality in upland reservoirs

Water quality in aqueous systems such as lakes and reservoirs is an integral function of a variety of physical, chemical and biological processes. The most important physical event in the annual cycle of a water body is thermal stratification, caused by temperature-induced density differences between upper and lower water layers, which influences many biological and chemical aspects in the functioning of the aqueous system. During thermal stratification the vertical circulation and mixing of the system is limited and oxygen supply to the bottom water layers, the hypolimnion, is restricted. As oxygen in the hypolimnion is permanently consumed in biochemical processes, the deeper waters of the system may become depleted in oxygen, and where stratification persists over longer periods, the redox potential in the water may decline to levels suitable for iron and manganese mobilisation. In deeper water bodies (>30 m) with large hypolimnic water volumes, however, time during stratification may not be sufficient for bottom waters to de-oxygenise (Davison, 1993), in which case oxic conditions in the water column are maintained throughout the stratification period.

The iron and manganese chemistry is closely linked to redox conditions in the water column (Stumm and Morgan, 1981), which in turn are determined by the balance between decomposition of organic matter and the supply of oxygen. The physical

characteristics of water bodies, in particular circulation and vertical mixing of the water, therefore, strongly affect the cycling and fate of iron and manganese in aqueous systems, as will be discussed in the following section.

The ability of manganese and iron to be oxidised and reduced closely links the cycle of these elements with that of oxygen (oxidant) and organic carbon (reductant). The sediment-water interface is a particularly active site for decomposition of organic matter and thus for oxygen and carbon cycling. The low oxygen content together with high concentrations of organic reductants create favourable conditions for the dissolution of manganese and iron oxyhydroxides<sup>1</sup> and support the mobilisation and release of soluble iron and manganese into the overlying water column. These processes are fuelled by the more or less constant supply of organic matter and iron/manganese particles supplied to the sediment-water interface by the overlying water column and since the settled particles are captive they must reside there until they are either decomposed/reduced or incorporated into the sediment. However, there are other mechanisms by which iron and manganese can be mobilised from the sediments, including physical processes, such as re-suspension, in which case mainly particulate forms of these elements enter the water column. The importance of the various sediment processes has been widely recognised (Mortimer, 1941, 1942; Hulscher *et al.* 1992; Davison, 1985, 1993; Blösch, 1995; Bryant *et al.* 1997; Effler *et al.* 1998a, b; Erickson and Auer, 1998; Linnik and Zubenko, 2000) and will be discussed in the second part of this section.

---

<sup>1</sup> The term 'oxyhydroxides' is used to refer to hydrous oxides and hydroxides in general.

### 2.1.1 Iron and manganese in the water column of lakes and reservoirs

#### General aquatic chemistry of iron and manganese

The dynamics of iron and manganese in lakes and reservoirs are largely governed by the system's pH and redox status (Stumm and Morgan, 1981; Sholkovitz, 1985; Hamilton-Taylor and Davison, 1995), which determine metal speciation and partitioning between the solution and the solid phase. In well-oxygenated, circum-neutral waters the thermodynamically stable forms of iron and manganese are their higher oxidation states, Fe(III) and Mn(III, IV), which are usually completely hydrolysed oxyhydroxides present as particles or colloids. Where oxygen is depleted or absent, the lower redox states, Fe(II) and Mn(II) are favoured, which in the pH range of most natural aqueous systems (pH 4-8) are very soluble (Hamilton-Taylor and Davison, 1995). As a consequence, in well-mixed, fully oxygenated waters, iron and manganese are typically present as particles and at low concentrations. In seasonal or permanently stratified lakes, however, Fe(II) and Mn(II) can accumulate to high concentrations, especially when the bottom waters become anoxic (Mortimer, 1941, 1942; Davison *et al.* 1982; Balistrieri *et al.* 1992; Hongve, 1997).

Generally, the biogeochemistry of iron and manganese are very similar, but appreciable differences in the behaviour of the two elements arise from the differences in oxidation rate between Mn(II) and Fe(II). In well-oxygenated, neutral (pH~7) waters, the half time of Fe(II) is approximately 4h (at 10°C) (Davison and Seed, 1983), while for the same conditions Mn(II) oxidation was found to take between 1 to 130 days (Tipping *et al.* 1984). There is strong evidence that oxidation of Mn(II) to Mn(IV) is brought about by microbial activity (Tipping *et al.* 1984; Nealson *et al.* 1989) and this may also be the reason for the relatively large variations in oxidation rates. Iron oxidation, however, is

believed to proceed abiotically (Warren and Haack, 2001), although catalysis by particles, e.g., trace elements (Davison and Seed, 1983), and microbial mediation (Tipping *et al.* 1981) have been observed.

Manganese oxyhydroxides are also more readily reduced in comparison to their iron counterparts. Laboratory studies on lake sediments, for example, have shown that reduction of Mn(IV) to Mn(II) begins at dissolved oxygen (DO) concentrations of 2-3 mL·L<sup>-1</sup>, in contrast to Fe(III) reduction, which occurred at essentially anoxic (DO concentrations ~ 0 mL·L<sup>-1</sup>) conditions (Sholkovitz, 1985). Pathways suggested for the reduction of iron and manganese in natural waters and sediments are numerous (see review discussions in Nealson *et al.* 1989; Hering and Stumm, 1990; Stumm and Sulzberger, 1992; Davison, 1993), and include the reductive dissolution through complexation with humic substances, which in surface water may be photocatalysed (Collienne, 1983). Such complex-formation reactions with organic and inorganic ligands are also believed to be responsible for the fact that redox transformations, e.g., Fe(II) - Fe(III), are not only limited to low redox conditions, as thermodynamics would suggest, but can occur throughout the entire redox range encountered in natural waters (Stumm and Sulzberger, 1992; Davison, 1993). Other reduction pathways are the direct reduction by micro-organisms and the chemical reduction by reactions with inorganic or organic reductants, whereby the latter is often regarded as indirect microbial reduction since most reductants themselves are produced as a result of microbial decomposition processes (see Nealson *et al.* 1989; Hering and Stumm, 1990; Warren and Haack, 2001). Dissolution of iron oxyhydroxides may also proceed via non-reductive reaction pathways, mainly through the formation of dissolved Fe(II) complexes with organic

ligands although such processes may be more significant in soils (Davison and DeVitre, 1992).

While redox processes in aquatic systems are largely governed by biological activity related to organic matter decomposition (Davison, 1993; Warren and Haack, 2001), humic substances themselves also play an important role in the reduction and oxidation of iron and manganese. They are not only responsible for the transformation of oxyhydroxides to their reduced forms, but can also inhibit the loss of dissolved species from the water column by slowing down scavenging (Curtis, 1993) and oxidation processes (Davison and Seed, 1983) at neutral pH and/or by effectively stabilising dissolved species against oxidation through complexation (Theis and Singer, 1973; Hem, 1985). The latter process is probably more important for iron, as complexation by humic material is generally thought to be unimportant for manganese (Chiswell and Mokhtar, 1986), although significant complexation with organic ligands has been observed in organic rich waters (Hsiung and Tissue, 1994; Graham *et al.* 2002), sediments (Bryant *et al.* 1997) and soils (see Livens, 1991).

Depending on pH and redox conditions of the aquatic system, iron and manganese compounds can provide an important carrier phase for nutrients (Mortimer, 1941; Hongve, 1997; Baccini, 1985) and trace elements (Sigg, 1985; Bendell-Young and Harvey, 1992a,b; Balistrieri *et al.* 1992), mediating uptake and release of these elements from the sediments (Farmer *et al.* 1994; Gomez *et al.* 1999; Ciceri *et al.* 1992; Erickson and Auer, 1998), and thereby regulating their presence in the water column. The exact role of iron and manganese particles in the overall pathway of these elements, however, is still being debated (Tessier, 1992; Davison, 1993).

Iron and manganese cycling in the water column of well oxygenated, neutral water bodies

Most iron and manganese supplied to lakes and reservoirs via streams and surface runoff is in particulate form (Salomons and Förstner, 1984), although significant proportions of manganese may also be input in dissolved form where leaching of soluble reduced species from oxygen-deficient soils, e.g., in peat bogs, and groundwater sources occurs (Davison, 1993). Some inputs may be associated with atmospheric sources (Salomons and Förstner, 1984) or derived from phytoplankton in the surface waters, but such sources are probably of minor importance in oligotrophic systems situated in pristine upland environments. Iron and manganese particles entering the aquatic system are of various size and reactivity comprising (1) particulate iron and manganese in form of oxyhydroxides, either associated with clay minerals or as free particles, and (2) iron and manganese incorporated into clay mineral lattices, in which case they are unavailable for reactions in solution. The relative distribution between these phases differs for the two elements and also controls their fate in the water column and in the sediments.

Most of the iron entering the aqueous systems is well bound within the lattice of clay minerals (Nembrini *et al.* 1982) or associated with clay minerals in form of oxyhydroxides (Linnik and Zubenko, 2000) via adsorption and sinks quickly to the sediment, as do the free iron oxyhydroxide particles. While iron within clay minerals accumulates within the sediment without reaction, amorphous iron oxyhydroxides can be reduced to soluble Fe(II) if the sediments are sufficiently reducing. This only affects the very reactive oxyhydroxides of iron, and sequential extraction schemes have shown that a large fraction of iron within lake sediments is inert, bound within mineral lattices

(Warnken *et al.* 2001; see Davison and DeVitre, 1992) and/or present in form of relatively unreactive iron oxides that are not reduced (Hamilton-Taylor and Davison, 1995). Consequently, iron is usually retained within the sediments with minimal loss (Davison *et al.* 1982).

Particulate manganese is present mainly in the form of reactive oxyhydroxides, which are often associated with surfaces and only a small proportion of manganese is well bound within mineral lattices (Davison, 1993). As for iron, the particulate fractions quickly sink to the bottom and the reactive oxyhydroxides are readily reduced at the (reducing) sediment-water interface. Consequently, most of the manganese is rapidly returned to the overlying water column and only a small proportion of manganese is permanently incorporated into the sediments; in Esthwaite Water, for example, less than 10% is retained in the sediment (Davison *et al.* 1982). Similarly, sediment core studies have shown that manganese is concentrated in surface sediments, mostly present in the form of reactive manganese oxyhydroxides, while manganese concentrations in deeper sediments are rather low (Bryant *et al.* 1997; Warnken *et al.* 2001), mostly comprising manganese in the refractory/insoluble phase.

In the water column the mobilised Fe(II) and Mn(II) species are subjected to random transport by eddy diffusion, and while Fe(II) is quickly oxidised and for the most part returned to the sediment (Campbell and Torgersen, 1980), Mn(II) may be transported some distance prior to oxidation. Once mixed into the overlying water column, particulate and dissolved species may eventually be flushed from the system and removal of remobilised Mn(II) via the outflow was commonly observed at Esthwaite Water (Davison *et al.* 1982). At the bottom of deeper basins, however, whose waters do

not become anoxic, an isolated manganese cycle of release, oxygenation and deposition may exist (see Davison, 1993), which does not affect the rest of the water body. Such isolated cycles are not only restricted to deep basins. Core studies at the shallow and eutrophic Loch Leven, for example, indicated that during the summer period, re-precipitation and sedimentation of manganese outweigh any release processes from the sediment (Bryant *et al.* 1997) and this was attributed to the higher O<sub>2</sub> production during an algal bloom, which favoured manganese oxidation. However, once the primary productivity had decreased, redox-driven release of manganese prevailed over re-deposition and manganese was removed from the system by hydraulic flushing from the loch, hence sharing the same fate as manganese in Esthwaite Water.

In summary, the above section illustrates the dynamic and complex nature of iron and manganese cycling in the aquatic system, and highlights the differences between the two elements. It is shown that redox transformations tend to dominate behaviour of manganese in lakes, and also have some effect on iron, although interactions of particulate iron are more dependent on the presence of humic material.

Despite the high proportion of iron present in clay minerals, and as relatively unreactive oxides, there is usually a plentiful supply of readily reducible iron oxyhydroxides. In contrast, the supply of less abundant manganese oxyhydroxides may quickly become depleted, in particular where suboxic and anoxic conditions predominate. However, the extent to which the individual processes influence iron and manganese cycling in a given system strongly depends on system specific characteristics, and the relative importance of different mobilisation/de-mobilisation processes may vary depending on factors like biological productivity, loading pattern or climatic influences.

## 2.1.2 Water–sediment interactions

### *Diffusion processes*

The sediment-water interface is a particularly active site for decomposition of organic material, continually recruited from the overlying waters, and plays a key role in the cycling of iron and manganese in the aquatic system (Sholkovitz, 1985; Davison, 1985, Hamilton-Taylor and Davison, 1995), not least because the settled iron and manganese particles are captive and must reside there until they are either reduced or incorporated into the sediment. Due to the rapid oxygen consumption caused by increased microbial activity and the slow rate of oxygen diffusion into the sediment, reducing conditions in the surface sediments are generally established earlier than in the water column. As a result, oxygen is completely consumed in the first few millimetres of most fine-grained freshwater sediments (Davison and DeVitre, 1992) and a redox boundary is developed at which reduced metal ions are supplied by reductive dissolution of oxides and hydroxides, which have settled from the water column to the sediment surface. Manganese oxyhydroxides are usually most readily reduced, followed by iron oxyhydroxides, but this may vary locally as the reactions depend on local elemental concentrations and are mostly controlled by microorganisms (Stumm and Morgan, 1981). Davison (1993) suggests that this rapid reduction of oxyhydroxide particles at the sediment water interface is the dominant mechanism responsible for iron and manganese sediment release. Still, there can be times when Fe(II) and Mn(II), formed at depth within the sediment rather than at the interface, accumulates in the pore water of the sediments and diffusional fluxes into the overlying, mostly anoxic, bottom waters occur.

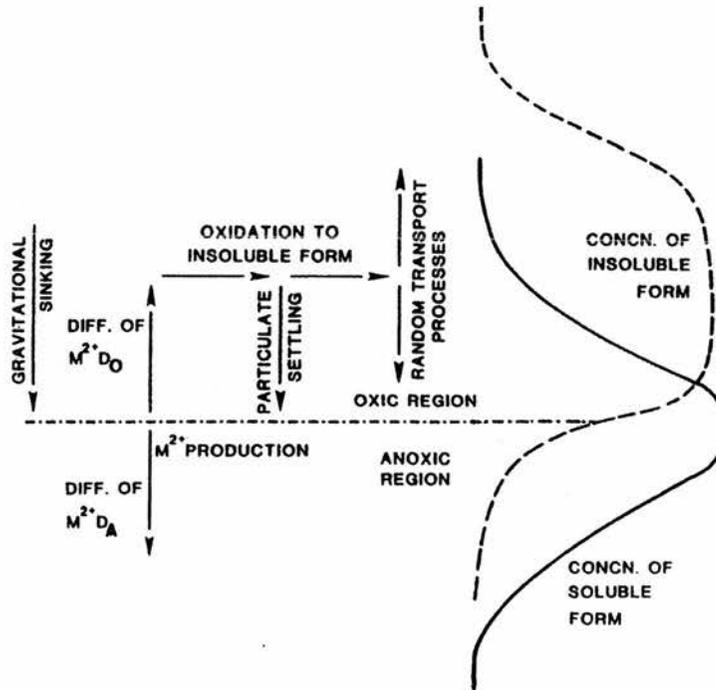


Figure 2. 1: Conceptual model for the redox-driven cycling of iron and manganese at a redox boundary showing schematic concentration profiles of particulate and soluble forms (after Davison, 1985).

A generalised conceptual model for the transport of iron and manganese at such redox boundaries has been proposed by Davison (1985) and is illustrated in *Figure 2. 1*. The model assumes the establishment of a well-defined boundary between oxidising and reducing conditions, at which oxidised particulate material is reduced to its divalent soluble form. Soluble Fe(II) and Mn(II) species then diffuse upwards or downwards away from the point of maximum solution. Where sediment-water interface and redox boundaries coincide: dissolved species move downwards to establish equilibrium with sulphides and/or carbonates at depths in the sediment (Bryant *et al.* 1997) and upwards into the oxic water column to re-precipitate as oxides/hydroxides once favourable redox conditions are reached. Due to the differences in the redox behaviour of the two elements, peak concentrations of particulate manganese are often found higher up in the water column, overlying those of particulate iron (Balistrieri *et al.* 1992). The redox

cycle is completed where larger, re-precipitated particles sink to the bottom due to gravity.

As time progresses and depending on the characteristics of the aqueous system, the anoxic/oxic interface may move up through the sediment surface, causing anoxic conditions to develop in the hypolimnion of the water column. In Esthwaite Water, for example, a moving anoxic/oxic boundary was found, which changed with the seasonal cycles in temperatures, stratification and dissolved oxygen concentrations, resulting in dynamic iron and manganese redox cycles and high concentration levels in the water column during summer stratification (Mortimer, 1941; Sholkovitz, 1985; Davison, 1985). Similar developments are commonly observed in other systems (Zaw and Chiswell, 1999; Hsiung and Tissue, 1994; Balistrieri *et al.* 1992) and it is suggested that under such conditions of hypolimnic anoxia, dissolution of settling manganese and iron particles in the anoxic water column becomes important. It may, in fact, present a major source of dissolved iron and manganese in the water column of lakes with a seasonally anoxic hypolimnion (Davison, 1981). The seasonality in the importance of the different iron and manganese sources in such systems is demonstrated by DeVitre *et al.* (1988) at Lake Bret, Switzerland, where high fluxes from the sediment constitute an important Mn(II) source earlier in the year, whereas dissolution of sinking manganese particles controls the supply later in the year. In comparison, inter-annual changes in concentrations of dissolved substance in the hypolimnion of Lake Windermere, where de-oxygenation of the bottom water does not occur, were definite but extremely small (Mortimer, 1941) and supply of soluble manganese and iron from reductive dissolution in the water column is probably of little importance.

However, redox cycling of iron and manganese is not restricted to the anoxic water column; in fact, reductive remobilisation and subsequent loss of manganese and iron is a common phenomena at the sediment-water interface of well-oxygenated waters (Warnken *et al.* 2001; Hsiung and Tissue, 1994; Davison *et al.* 1982). Reduced forms originating from rapid reduction of oxyhydroxide particles, which have settled from the water column, can be released from the sediment-water interface whether the overlying water is oxic or anoxic (Davison, 1993).

Where the redox boundary is sufficiently close to the sediment-water interface, reduced ferrous iron, formed at depth within the sediment and accumulated in the pore water of the sediments, can also diffuse into the overlying water column as has been reported by Warnken *et al.* (2001). This suggests that not only the conditions in the water column, but also the position of the redoxcline (i.e., the maximum change in redox potential with depth) in the sediment profile appears to be an important determinant for the behaviour of manganese and iron. Davison *et al.* (1982) suggest that this is because of faster eddy diffusion, as opposed to the slow molecular diffusion in the sediment, is dominating the transport regime near the sediment-water interface. Thus, elemental cycling is more rapid the closer the redox-boundary is situated to the sediment-water interface and differences of only a few millimetres can prove to be critical in regulating the chemical exchange across the sediment water interface (Mortimer, 1971). Release at the sediment-water interface may be further enhanced by turbulence and stirring action in the upper few millimeters of the sediment (Mortimer, 1971).

The above examples imply that release of iron and manganese from the sediment is not necessarily associated with anoxic conditions in the water column, but may also occur in the oxidised water column and during periods at which the water body is completely

mixed. Nonetheless, because vertical dispersion is pronounced during the periods of complete mixing, it may be difficult to detect the release until the onset of stratification when the bottom water is isolated (Sholkovitz, 1985), and the dilution effect by the high-volume surface water is sufficiently reduced to not mask the effect of any release of iron and manganese from the sediments. However, in the oxidising water column  $\text{Fe}^{2+}$  is rapidly oxidised and although  $\text{Fe}^{2+}$  is instrumental for the release of iron from the sediments, it can generally not be detected in the water column (Davison, 1993).

In any case, rapid oxidation of the released metals in the oxygenated water column may result in very high concentrations of solid-phase iron and/or manganese at the sediment surface and red-brown coloration of surface sediments caused by large concentrations of particulate iron and manganese in surface sediments has been widely reported (Mortimer, 1941, 1971; Gorham and Swaine, 1965; Farmer and Lowell, 1986). The enriched layer may appear as a loose association of freshly precipitated material or occasionally can form a solid crust. Such oxidised surface layers are believed to prevent the release of dissolved species from the sediments (Mortimer, 1941; Hutchinson, 1957) due to a variety of trapping mechanisms (Mortimer, 1971), although preferential manganese release may still be possible due to its slow rate of oxidation (Davison *et al.* 1982).

In regulated water bodies, such as reservoirs, draw down events were reported to have similar effects to that of thermal stratification, in that the volume of the water column and consequently, the dilution effect of the overlying water column are reduced (Linnik and Zubenko, 2000). At the Dnieper reservoirs, for example, a significant increase in the concentrations of heavy metals in the water was experienced after draw down of the

reservoir. Linnik and Zubenko (2000) concluded that the main reason for the rise in concentration was accelerated oxygen depletion in the water column and the development of reducing conditions in the surface layer of the sediments, causing the release of heavy metal ions into the overlying water column as iron and manganese hydroxides are reduced.

### Re-suspension processes

Sediment re-suspension has long been recognised as an important and ubiquitous internal process in lakes. It has been identified as the dominant process of generating particles in the water columns of most lakes, contributing up to 85% to the total flux of particulate matter (Evans, 1994). Re-suspension occurs in water bodies of various depths and sizes and has been defined as the reconvening of particles, which have been deposited on bottom sediments, into the overlying water column (Blösch, 1995). The primary and most important driving force of re-suspension is wind, acting on the water surface and generating waves and currents. Other forces include internal seiches and turbidity currents. A comprehensive review of the processes and mechanisms related to re-suspension of bottom sediment has been given by Imboden and Wüest (1995) and Evans (1994).

Sediment is re-suspended when the current-induced shear stress at the sediment- water interface is sufficient to overcome the cohesion of the sediment and the gravity. The critical shear stress for re-suspension depends on the characteristics of the sediments, including parameters such as grain size and shape, type of sediment material, organic content and water content, as well as on the *in situ* conditions of the sediment (fresh or compacted) (Blösch, 1995). Thus, sediment re-suspension is a function of the properties

of the bottom sediment. Re-suspension further depends on wind speed, duration of disturbance, effective lake fetch and lake morphometry (Evans, 1994) and can be a whole lake process or a local, episodic event (Blösch, 1995). Such local and episodic events, for example, are observed at Esthwaite Water. Davison *et al.* (1982) conclude that re-suspension is not an important process in the hypolimnion of the lake, but can significantly affect water quality in the epilimnion during the turnover and may, in fact, account for the high iron loadings in the lake during that period. Other examples of temporal re-suspension events are found at Lake Balaton, Hungary (Luettich *et al.* 1990), the Hinze Dam reservoir in Queensland, Australia (Zaw and Chiswell, 1999) and the Eau Galle Reservoir in Wisconsin, USA (James and Barko, 1993), where re-suspension is mostly related to episodic wind events, extreme runoff inputs during storm events and to autumn overturn, respectively.

#### *Effect of re-suspension on water quality*

Processes related to sediment re-suspension may affect the water quality of a specific water body in many different ways. They could cause significant increase in water column turbidity, which in turn decreases the light penetration in the water body. This can have a major impact on the lake metabolism and affect the ecosystem of the water body significantly (see Blösch, 1995). Increased turbidity is also of concern for managers of water supplies because it regulates the clarity and light attenuation of the water as well as its visual aesthetics, and thus has implications for the public perception of water quality and the feasibility of meeting turbidity limits for water supplies (Effler *et al.* 1998a,b).

However, the ecological importance of sediment re-suspension is found in the intense cycling of particulate material, such as clay minerals or organic matter, and associated nutrients, metals and contaminants (Hulscher *et al.* 1992; see Blösch, 1995 and Evans, 1994; Effler *et al.* 1998a). Due to their high surface to volume ratio (large specific surface area) the re-suspended particles provide effective adsorption surfaces to which metals, nutrients and contaminant can be bonded (Förstner and Wittmann, 1981). Thus, rapidly settling particles may act as removal agents for these elements leading to their accumulation in the sediment, which in this case acts as a sink. However, due to their small fall velocities these fine-grained particles can be kept in suspension in the water column over long periods and are also easily re-suspended, in which case the sediment becomes an internal source of nutrients, metals and contaminants. This was experienced in a variety of lake and reservoir systems, where re-suspension of bottom sediment and subsequent desorption was found to release significant amounts of nutrients (Luettich *et al.* 1990; Gálvez and Niell, 1992; Pierson and Weyhenmeyer, 1994) and metals (Hulscher *et al.* 1992) into the water column.

When the shear stress diminishes the re-suspended sediment particles become subject to resettling. As the process may take place repeatedly, the particles may be recycled several times (Blösch, 1995). However, the sedimentation rate of fine particles can be significantly reduced by turbulence, so that these particles may be retained in the water column for a considerable time (Thornton, 1990b), causing prolonged periods of high turbidity and increased metal and nutrient concentrations in the affected water body. This effect is probably even more pronounced when the re-suspended material largely consists of organic matter, rather than of heavier clay minerals, as was observed by Gloor *et al.* (1994) and Hicks *et al.* (1994). Moreover, repeated recycling of the particles along with the longer exposure in the water column may increase the size of the contact

zone between particle surfaces and the water, probably due to disaggregation processes (Lick and Lick, 1988 cited in Brassard *et al.* 1994) and this further augments the quantity of material sorbed onto particle surfaces. It can, however, also have the opposite effect and metal release associated with flocculation and decrease in specific particle surface area has been reported by Brassard *et al.* (1994). In either case, the fluxes from, and to, the suspended particles are enhanced, and this exchange may be appreciable when compared to molecular diffusion into/out of the sediment (Imboden and Wüest, 1995). Nonetheless, these sorption processes and the resulting exchange (partitioning) of the elements (metals, nutrients, contaminants) between solution and solid phase are dependent on the physico-chemical conditions (e.g., redox and pH) of the aqueous system and thus, are strongly influenced by the inherently dynamic nature of the of aquatic systems (Warren and Haack, 2001).

#### *Areas of re-suspension and implication for reservoir water quality*

Blösch (1995) has identified two basic zones of re-suspension in lakes: shallow areas where wave action has a direct influence on bottom sediments and deeper areas located below the direct impact of the wave base. In the latter wave-induced currents and internal seiches, are expected to be the most relevant source for re-suspension during stratification (Gloor *et al.* 1994; Pierson and Weyenmeyer, 1994). In the absence of stratification (e.g., during turnover periods) increased water motions may occur at these depths, directly generated by the forcing wind. However, in reservoirs subject to substantial draw down, the settings of re-suspension are more dynamic than in lakes (Effler *et al.* 1998a, b), as the (shallow) areas exposed to wave action and turbulence move deeper into the reservoir as the water level of the reservoir declines. As a

consequence, proportions of the lake bottom which were previously below the wave base become subject to re-suspension as the reservoir water level drops. A comprehensive study at the Cannonsville Reservoir, for example, demonstrated that increase in non-phytoplanktonic turbidity in the water body coincided with, and was coupled to, the draw down of the reservoir (Effler *et al.* 1998a). Based on these results it was hypothesised that the re-suspension process is promoted, and related turbidity problems exaggerated, by greater draw down of the reservoir surface. Moreover, as draw down proceeds the reservoir shoreline can be expected to become progressively more susceptible to re-suspension and the imparted turbidity, caused by particles with reduced settling velocity, to be more persistent (Effler *et al.* 1998a). Thus, water level fluctuations in reservoirs and resulting sediment erosion and re-suspension may result in significant transport, exchange, and re-deposition of the sediments and their associated constituents causing enhanced sediment-water interactions and increased solids and nutrient concentration in the water column (Thornton, 1990b). Where the draw down is significant this may lead to prolonged periods of water quality deterioration, which is of major concern where the water is needed for drinking water supply purposes. Hence, from a management point of view this could mean that there is a water quality cost for the operation of the reservoir for its intended use.

Further to the physical disturbance, water level fluctuations and the recurring drying and re-flooding of the coastal regions of regulated water bodies may also alter the chemical and biological properties of the sediment and thereby influence mobility and release of nutrients and metals into the water column (Calmano *et al.* 1993, Stigliani, 2001; Lau and Chu, 1999), not least because of the rapid conversion from anaerobic to aerobic

sediments and vice versa (Thornton, 1990b) and the related changes in redox conditions and pH.

In summary, from this section it becomes apparent that sediment is of fundamental importance for the aquatic cycle of iron and manganese as it mediates uptake, release and re-cycling of these elements. In particular, the processes at the sediment-water interface need to be considered, since the reducing intensity is likely to be greater at the sediment interface due to accumulation of organic material. Consequently, significant amounts of iron and manganese can be re-mobilised and released into the overlying water column, even when oxidising, although the release may be masked by the dilution effect of the high-volume surface water and is most pronounced during stratification.

It has also been demonstrated, that re-suspension of bottom sediment can significantly affect water quality. Such processes may be further enhanced in reservoirs, due to the large water level fluctuation, thereby linking aspects of water quality to the operation of the reservoir.

Again, while the main features of elemental cycling related to diffusion and re-suspension processes will be similar in most lakes and reservoirs, it should be appreciated that the importance of the different sediment processes will vary between systems as a function of system specific factors, including sediment properties, biological productivity and trophic state, basin morphometry, exposure to winds, effective fetch and others.

## 2.2 Important processes in upland catchments and their effect on stream water quality

Over the last decades numerous studies have been carried out in upland regions throughout the UK, many of which are concerned with the increasing amount of pollution associated with agriculture, industry and urbanisation (e.g., Langan *et al.* 1997; Petry *et al.* 2002; Reynolds *et al.* 1997; Younger, 2001) and its impact on the catchment ecosystem. In many studies the focus is directed towards the contribution of atmospheric deposition and catchment management practices to changes in water quality of streams draining the catchment area (e.g., Langan, 1985; Harriman *et al.* 1994; Robson and Neal, 1996; Foster *et al.* 1997; Neal *et al.* 1998; Heal, 2001; Miller *et al.* 2001), or more specifically towards the runoff behaviour of nutrients and metals under changing environmental and hydrological conditions (Heal *et al.* 1997; Jarvie *et al.* 2001; Chapman *et al.* 2001; Grieve and Marsden, 2001; Graham *et al.* 2002; Petry *et al.* 2002). Considerable effort has been made to model and conceptualise catchment characteristics and to shed light on internal processes such as runoff generation, hydrological pathways and interactions between processes occurring at different levels in the soil, vegetation cover, groundwater and stream water zone, and detailed discussion of these plentiful approaches are given in Jenkins *et al.* (1994b), Buttle (1994), Soulsby (1997) and Church (1997).

Iron and manganese runoff in surface waters is controlled by soil and hydrological processes, as well as by catchment characteristics, which also influence the spatial variability of iron and manganese loading across the catchment area. Thus, the following sections intend to outline processes and factors influencing mobilisation and transport of iron and manganese, demonstrating how varying runoff patterns during

changing hydrological conditions and the various catchment characteristics affect the behaviour of iron and manganese in upland stream waters.

(In the following text dissolved organic matter, total organic carbon and dissolved organic carbon are abbreviated by DOM, TOC and DOC, respectively.)

### 2.2.1 Effect of soil processes on iron and manganese mobilisation

In upland catchments iron and manganese are mainly derived from natural sources (e.g., bedrock), through chemical weathering of soil minerals in the acidic soil zone and the breakdown of oxides and hydroxides (Neal *et al.* 1997a) that are also released from decomposing organic residue, although this aspect of cycling is generally secondary (Cresser *et al.* 1993).

The presence of organic matter has a strong influence on iron and manganese cycling and was found to control the chemistry, solubility and transport of iron and manganese in the upper horizons of many upland soils (Hughes *et al.* 1990; Graham *et al.* 2002) as well as affecting the fate of these elements in streams (Tipping *et al.* 2002 and references within). There are a number of ways in which organic matter affects processes of iron and manganese mobilisation in the soil environment.

Decomposition of plant material, for example, produces significant concentrations of dissolved organic material (DOM), including fulvic and humic acids, which in turn provide persistent binding agents (ligands) for amorphous iron (and manganese) in soils (Mulder and Cresser, 1994; Cresser *et al.* 1993) and thus encourage the formation of

organo-metal complexes of high stability known as chelates. Such chelation processes not only promote the dissolution of metals from soil minerals (Mulder and Cresser, 1994), thus aiding weathering processes, but also enhance the mobility of these elements in the soil environment (Livens, 1991). This process is most apparent in podzolic soils where organic chelation results in leaching of these elements from upper soil horizons and deposition in deeper horizons (as DOM is removed) (Soulsby, 1997; Drever, 1997). The amount of organic matter decreases sharply with depth, in particular between the organic and the mineral soil horizons (Mulder and Cresser, 1994). Hence, processes of metal complexation are most important in organic rich surface soil horizons and contribute significantly to the high rates of iron and manganese mobilisation and flushing from peats (Graham *et al.* 2002). Complexation to humic substances also plays an important role in stabilising the dissolved iron and manganese species against oxidation compared to the free species (Hem, 1985; Grieve, 1984b; Gavin *et al.* 2001; Tipping *et al.* 2002 and references within), as a result of which the complexed elements can potentially be transported greater distances downstream and are removed only slowly from solution by oxidation and precipitation. Despite the evidence that manganese is less readily complexed by organic ligands (LaZerte and Burling, 1990; Chiswell and Mokthar, 1986), humic complexation was found to be an efficient removal agent for iron and manganese from peaty catchment soils (Graham *et al.* 2002).

As well as affecting trace element mobility through complexation and chelation processes, the decomposition and processing of organic matter, together with other activities carried out by soil organisms, can also alter the redox potential and pH of the soil. The pH of the soil solution is an important factor in controlling mobilisation and

transport of iron and manganese as it determines the dissolved speciation of the metals and also controls dissolution and precipitation processes through hydrolysis reactions (Stumm and Morgan, 1981). While low at neutral pH, the solubility of metal oxide phases increases under acidic conditions, resulting in high iron and manganese mobility in acidic soils (Cresser *et al.* 1993). Since abiotic oxidation rates at low pH are very slow (see Tipping, 1984) higher concentrations of dissolved metals are often observed in naturally acidic streams and/or in acidic mine drainage (McKnight and Bencala, 1990; Sullivan and Drever, 2001).

Redox reactions can also dominate the soil solution chemistry of iron and manganese, as both elements exist in more than one oxidation state in soils (iron in Fe (II) and Fe (III) states and manganese in form of manganese (II), manganese (III) and manganese (IV)). Such redox processes are often microbially mediated, i.e. related to the decomposition of organic matter in the soils, which shows a clear seasonality (Grieve, 1984a; Robson and Neal, 1996; Reynolds *et al.* 1997). In peat dominated catchments, maximum metal loadings often occur in late summer/early autumn storm events (Heal *et al.* 1995) and/or after long dry spells (Hughes *et al.* 1997), where high soil temperatures promote high microbial activity in the soil and along with drier conditions in the catchment, produce a store of soluble and readily reduced manganese and iron in the upper soil horizons.

Seasonal variations in microbial decomposition rates in peaty soils were also apparent from iron concentrations in stormflow runoff in the Plynlimon catchment in Wales (Neal *et al.* 1997a), and the associated high DOC levels highlight the close association between metal mobilisation and organic matter decomposition. However, which process

is more important in determining the solubility of iron, supply of natural organic ligands or redox effects, is unclear and appears to depend on antecedent and present conditions in the catchment as demonstrated by Hughes *et al.* (1997).

Cyclic seasonal variations in manganese concentrations at Plynlimon were less apparent and, unlike DOC and iron, were not biologically influenced. Neal *et al.* (1997a) conclude that the amount of manganese reaching the stream is purely determined by wetting and drying of gleyed layers in the soils, where the associated changing redox conditions govern the transition of immobile to mobile forms of manganese (and vice versa) and thereby, increase its mobility. One would expect that such abiotic redox changes also affect the iron mobility in the soils, but in the case of Plynlimon this appears to be overridden by microbially mediated processes. In fact, the abiotic reduction (of manganese) is probably only one of a range of processes related to such drying-rewetting cycles, and changes in metal binding forms and soil pH may also contribute to increased metal mobility (Calmano *et al.* 1993).

In the majority of upland studies concentrations of iron and manganese in streams display a positive relationship to DOC and flow (e.g., Grieve, 1984a, b; Reid *et al.*, 1981; Neal *et al.* 1997a, Foster *et al.* 1997), suggesting a source linked to processes in organic rich surface soils and to storm runoff. However, high loadings of these elements may also originate from deeper soils and/or bedrock sources. Heal *et al.* (1995), for example, report that manganese maxima occur during summer low flows in a small mineral soil-dominated catchment in North Yorkshire, suggesting deep-water sources associated with bedrock weathering and/or dissolution of manganese in the anaerobic groundwater zone.

From the above discussion it becomes clear that (microbial) decomposition of organic matter is the key chemical factor affecting iron and manganese mobilisation in organic rich soils, as it influences the pH and redox conditions and also determines the relative abundance of natural organic ligands for metal complexation. As such it controls the speciation and complexation of iron and manganese, and thus their solubility and mobility, but also affects dissolution and precipitation processes in organic rich soils. These processes are most important in organic rich surface soils, owing to the dramatic OM decrease in the mineral horizons, and different in-soil processes appear to determine metal solubility at different times depending on the prevailing catchment conditions. Abiotic redox processes in the soils associated with the rapid conversion from anaerobic to aerobic conditions during drying/re-wetting cycles are a further influence, and appear more important for manganese, while in the case of iron these abiotic processes are overridden by microbial mediated mobilisation processes. In catchments dominated by mineral soils, deep soilwaters and groundwaters may be the more important source of manganese (and iron) released during bedrock weathering.

### 2.2.2 Role of hydrological pathways

The temporal composition of stream water is highly dynamic. Its physical and chemical loads exhibit a clear annual cycle, which reflects changes in the seasonal discharge regime and/or biological processes that may occur in-stream or in the surrounding catchment area. The most significant changes in stream flow and associated chemistry occur during individual rainfall or snowmelt events when the source of runoff generation in the catchment changes rapidly (Soulsby, 1997) and short-term variations

in transport along hydrological pathways occur. In upland catchments these changes are often rapid, due to the 'flashy' runoff regime, and distinct chemical changes are noted by a decrease in pH, alkalinity and base cation concentration, and an increase in dissolved organic matter (DOM) and associated metals, such as iron, manganese and aluminium.

The temporal response of stream flow to hydrological events has traditionally been attributed to variations in the importance of different hillslope processes and the flowpath, and the variable significance of different hydrological pathways, each with a distinct chemical composition, and the influence of local geology, topography and climate has been recognised in a variety of upland studies (Reid *et al.* 1981; Christophersen *et al.* 1990, 1994; Giusti and Neal, 1993; Muscutt *et al.* 1993; Heal *et al.* 1995; Neal *et al.* 1997a, Jarvie *et al.* 1997, Foster *et al.* 1997). Different chemical patterns are observed at different flows as hydrological pathways vary.

At low flows, stream water is fed mainly by drainage from lower mineral sub-soils and groundwater sources, which are derived from waters that have followed relatively slow and deep transport pathways through the catchment. On its passage to the stream various interactions and processes occurring within the soil system, such as mineral weathering, cation exchange, decomposition of organic material, anion adsorption and oxidation/reduction processes, alter its chemical composition producing the characteristic low acidity baseflow chemistry, rich in weathering products such as calcium and silica, but depleted in transition metals and aluminium (Ferrier *et al.* 1990b; Neal *et al.* 1997a). During intensive rainfall or snowmelt events, as flow rates increase, runoff generation pattern and prevailing hydrological pathways are changing from

deeper baseflow sources to the upper organic and organo-mineral soil horizons, and stream water chemistry becomes dominated by chemical equilibria with organic matter (Cresser *et al.* 1993). Thus, the routing of water through the catchment and its residence times in different soil layers determine the interaction between percolating water and soils, and thus the water's chemical composition.

Within any particular catchment, a variety of different hydrological pathways may exist, controlled by the catchment's bedrock geology, soil type distribution, topography and the prevailing hydrometeorological conditions and several conceptual approaches have been advanced to describe mechanisms by which stream flow, in particular short-term event response, is generated from rainfall (or snowmelt) events (see review discussions in Sklash and Farvolden, 1979; Buttle, 1994; Jenkins *et al.* 1994b and Church, 1997). In general, however, four basic pathways can be distinguished which participate in stormflow generation: (a) overland flow, (b) sub-surface flow, (c) return flow and (d) deep flow. Here (a) to (c) are regarded as 'near-surface' pathways as suggested by Hensel and Elsenbeer (1997), drawing attention to the fact that 'the anthropocentric concept of soil or land surface is not applicable in catchment hydrology because of the difficulty to define the hydrologically relevant soil surface'. These near-surface pathways are summarised in *Figure 2. 2* together with the respective conditions prerequisite for their occurrence, and will be explained below.

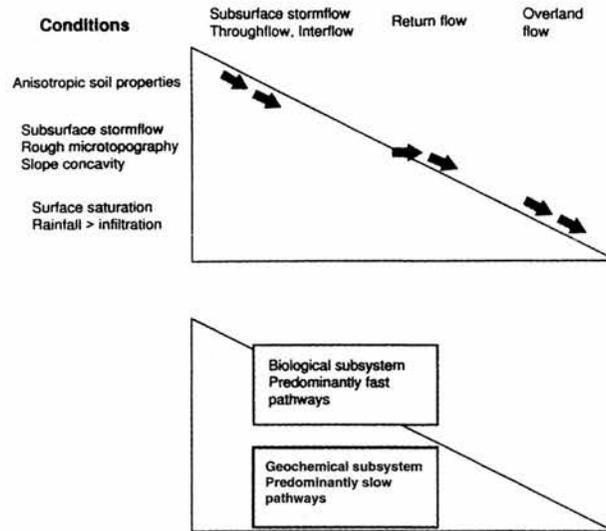


Figure 2. 2: Schematic representation of near-surface pathways (after Hensel and Elsenbeer, 1997).

Overland flow can arise when rainfall intensity exceeds soil infiltration rate causing rapid surface runoff across saturated soils. In upland catchments this, so called *Hortonian overland flow*, is unlikely to be an important hydrologic pathway (Jenkins *et al.* 1994b), although it may contribute significantly to event runoff in catchments with extensive rock outcrops, as was established at the Panola Mountain Research Watershed (Burns *et al.* 2001). Usually, *saturation overland flow*, where rainfall is unable to infiltrate the saturated soil surface and results in water moving down slope, is more commonly observed (e.g., Kirnbauer and Haas, 1998; Becker and McDonnell, 1998). Such flows may occur in saturation areas adjacent to the streams (Hoeg *et al.* 2000) and in valley bottoms but also on the hillslopes (Kirnbauer and Haas, 1998), wherever flow convergence occurs within the catchment. As the storm (snowmelt) event progresses, these saturated areas expand, leading to greater expanses of directly contributing zones of runoff generation, which subsequently shrink as rainfall (snowmelt) dissipates. This conceptualisation of runoff generation is termed '*variable source area concept*'

(Hewlett and Hibbert, 1967 cited in Church, 1994) and is, at present, probably the most widely accepted conceptual model. During storm events, however, the saturated soil zone does not necessarily occur at the soil surface. In fact, it may occur at any depth below the surface at which the vertical hydraulic conductivity suddenly falls significantly, e.g., at less permeable or impervious soil layers and/or at the bedrock interface (Becker and McDonnell, 1998), resulting in *sub-surface flow*, which during storm events contribute substantially to runoff volumes (e.g., Kirnbauer and Haas, 1998; Brown *et al.* 1999). In situations where perched water tables occur, such sub-surface flows may break back through to the surface, e.g., where slope concavity drops, where impervious layers are laterally discontinuous or due to the hydraulic head at the bottom of extended slopes (Cresser *et al.* 1993), at which point *return flow* arises.

The flow velocity of these near-surface flows depends on both vegetative cover and soil properties, but will in any case be considerably lower than open channel flow. This provides sufficient time for the near-surface runoff to equilibrate with the surface soil cation complex (Cresser *et al.* 1993), thus acquiring the soil's geochemical signature. Clearly, travel times and reactivity of the medium through which the water moves control the type of chemical reactions that alter the water's composition (Peters, 1994b).

Another potential sub-surface flow path that should be considered in upland areas is pipeflow and macropore flow, the importance of which in rapidly transferring rainwater during storm events both, vertically and laterally downslope has been widely recognized (Beven and Germann, 1982; Holden *et al.* 2001; Jones, 2002; see review discussion in Buttle, 1994). Pipeflow may provide a major source of stream acidity even under baseflow conditions and pipe runoff at high flows is generally enriched in colour

(DOM) and aluminium (Jones, 2002), while generally depleted in base cations, although ion exchange reaction along the pipe water pathways may alter its composition (Chapman *et al.* 1997).

Views differ on the mechanisms by which rapid stormflow is generated within a catchment and a range of complementary, rather than contradictory processes are suggested (see review discussions in Sklash and Farvolden, 1979; Buttle, 1994; Jenkins *et al.* 1994b and Church, 1997). These may be responsible for the rapid delivery of largely pre-event and groundwater contributions to stormflow widely observed in isotope (e.g., Sklash and Farvolden, 1979; Hangen *et al.* 2001; Hoeg *et al.* 2000) and hydrochemical (Hooper *et al.* 1990; Jenkins *et al.* 1994a; Peters and Radcliffe, 1997) tracer studies, as well as for the mixing of pre-event and event water. However, it generally appears that during hydrological events, there is little direct evidence that the whole catchment contributes to stream flow (Peters, 1994b; Peter and Radcliffe, 1997; Hooper, 2001), although an important control on stream water chemistry during storm episodes are the upper, more organic rich soil horizons (Hooper *et al.* 1990; Brown *et al.* 1999), as well as the riparian zone (Fiebig *et al.* 1990; Burns *et al.* 2001; Hooper, 2001).

The above section has illustrated the potential variations in hydrological pathways within a catchment. It is, however, important to realise that only a relatively small number of hydrological routes and sources may be important in a particular catchment, the contribution of which to stream flow generation is governed by such properties as soil type, topography, geology and land-use (Buttle, 1994).

### 2.2.3 Catchment characteristics that affect iron and manganese runoff in upland catchments

Although hydrological processes strongly control temporal variability in streamwater chemistry, catchment characteristics such as topography, altitude, climatic factors, soil type, solid and drift geology, vegetation, land-use and anthropogenic influences, all of which vary spatially across the catchment, also affect stream chemistry by influencing catchment hydrology and hydrological pathways (Buttle, 1994). It was previously shown (Section 2.2.1) that soil processes are of considerable importance for iron and manganese mobilisation, and are strongly influenced by soil type characteristics, including soil organic matter content, depths and structure. The direct effect of soil type on stream DOC loading has been demonstrated by Dawson *et al.* (2001) and also by Aitkenhead *et al.* (1999), who found that percentage peat cover is a good predictor of stream DOC concentrations. Hydrological pathways through soils may be affected by formation of iron pans diverting flow laterally in podzols, while soil permeability and texture (which is a function of clay content and mineralogy) determines the depth to which water percolates in a soil, its residence time as well as the existence of preferential pathways, such as macropores (Foster, 2000). The effects of storm events and timing of maximum metal loading in stream runoff may also differ between different soil types. Heal *et al.* (1995), for example, compared runoff pattern in two neighbouring catchments. They found that in the catchment dominated by mineral soils maximum manganese concentrations occurred during summer low flow and were associated with groundwater inputs. In the peat-dominated catchment, however, maximum manganese loading occurred during late-summer/early-autumn storm events when readily soluble manganese was flushed from the organic-rich catchment soils.

Such knowledge is of particular interest from a water management perspective, e.g., for water supply management or to predict periods of potential fish toxicity in upland catchments.

Topography and altitude are important for determining which soils develop as they are closely related to altitude and slope (Bown and Shipley, 1982). Topographic factors not only determine the flow pathways that water takes (Becker and McDonnell, 1998), but may also influence the dissolved organic matter content of the soils. Grieve and Marsden (2001), for example, found that there is a significant inverse relationship between concentrations of total organic carbon (TOC) and slope angles at different upland sites in Scotland. Increasing altitude can also affect the stream chemistry due to the effect of lower temperatures and greater precipitation (orographic effect) on decomposition rates in the soils. The altitude effect is generally associated with the greater accumulation of organic matter (TOC) in soils at higher altitudes, and Grieve and Marsden (2001) found soilwater TOC in upland peats to increase by  $26 \text{ mg L}^{-1}$  per 100 m increase in elevation.

Geology may also be an important factor in controlling metal concentrations in catchment soils and stream runoff, as it determines weathering rates and influences processes of soil development. Bedrock composition also determines the nature of the soils, since in most Scottish landscapes many properties of the parent material, little altered by soil formation, are inherited directly by the soils (Bown and Shipley, 1982). Thus, the base cation availability in the bedrock controls the buffering capacity of the overlying soils and hence the acidity of the drainage water. Billet and Cresser, (1996) demonstrated that stream chemistry in catchments developed on base-poor bedrock

(granites and acid schists) clearly reflect the lower pH and lower exchangeable base cation concentrations of the soils compared to catchments dominated by base-rich bedrock (metabasic rock and base-rich meta-sediments). Moreover, bedrock consisting of weatherable and acid-soluble inorganic components, such as calcite and layer lattice silicates, has the capacity to neutralise acid soilwaters and to precipitate the easily hydrolysable trace metals (Neal *et al.* 1997b). Conversely, bedrock mineralogy characterised by high concentrations of pyrite may produce naturally acidic streams, which often have unusually high metal concentrations (McKnight and Bencala, 1990).

Geology may also evoke a certain type of land-use such as mining, which has profound implications for stream chemistry (see discussion in Soulsby, 1997; Younger, 2001) resulting from seepage of acidic and metal-enriched mine drainage into streams and surface water bodies (Sullivan and Drever, 2001; McKnight and Bencala, 1990). Another land-use practice, which has been shown to influence iron and manganese runoff, is conifer afforestation/ deforestation (Neal *et al.* 1997b; Harriman *et al.* 1994) causing soil and water acidification in acid sensitive upland catchments and promoting enhanced manganese (and iron) concentrations in surface water runoff (Heal, 2001 and references within). Upland pasture improvement practices, including liming, drainage ditch construction and ploughing, may also increase DOC, manganese (and iron) runoff in the catchment (Heal, 2001; Harriman *et al.* 1994), although the evidence is less clear-cut.

Climatic variables like precipitation and temperature regime exert a strong control on soil development, including the depths of peat and the degree of humification, and clearly are key factors controlling catchment hydrology, in terms of flow and catchment

moisture content. Antecedent hydrometeorological conditions and storm intensity are important in determining the type and sources of water reaching the stream during storm episodes (Giusti and Neal, 1993; Robson *et al.* 1993; Hoeg *et al.* 2000; Burns *et al.* 2001). Dry periods can generate soilwaters with very high solute concentration of manganese (Heal *et al.* 1995), iron (Hughes *et al.* 1997) or dissolved organic matter (DOM) (Hughes *et al.* 1997, Neal *et al.* 1997a) due to the longer contact times and enhanced microbial activity. As rainfall events occur the soilwater is flushed into the streams causing high concentration peaks of these elements in the streamwater (Neal *et al.* 1997a; Heal *et al.* 1995). These events are typically found at the end of summer when the first autumn storms occur. Later in the season the soilwater is diluted by the high volume of rainfall received during the winter and spring period (Neal *et al.* 1997a).

In summary, this section has established the fundamental importance of different in-catchment hydrological and soil processes in controlling iron and manganese cycling in upland catchments and streams. It has been shown that the presence of organic matter in the soils has a strong influence on iron and manganese cycling and a variety of ways in which organic matter controls chemistry, solubility and transport of iron and manganese have been introduced. However, the most significant changes in stream chemistry occur during individual storm events when runoff sources in the catchment change rapidly and the variable significance of different hydrological pathways, each with a distinct chemical composition, has been demonstrated.

Again, while the underlying processes and controls related to the mobilisation and transport of iron and manganese will be similar in most upland environments, the importance of the individual processes may vary greatly between catchments and the

strong control exerted by catchment characteristics such as local geology, topography and climate should also be considered.

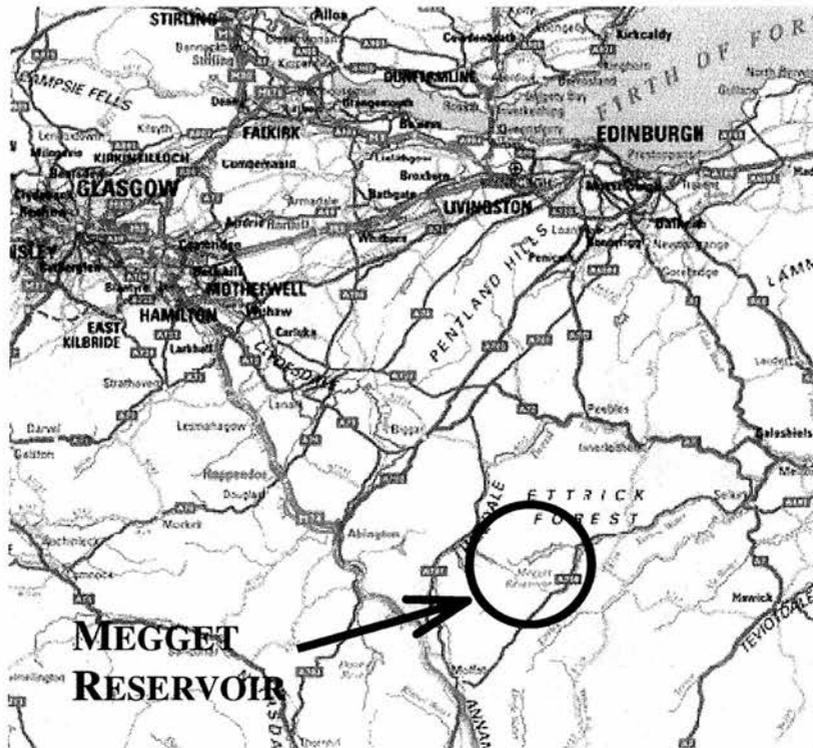
# 3

## The Megget Catchment

---

### 3.1 Introduction

The Megget catchment is a headwater catchment located in the Scottish Uplands, between Peebles and Moffat, about 50km south of Edinburgh (see *Figure 3. 1*). It is part of the greater Tweed catchment whose water resources have been exploited significantly by water supply interests.



*Figure 3. 1: Location of the study area (map taken from [www.multimap.co.uk](http://www.multimap.co.uk))*

The Megget catchment comprises an area of about 45 km<sup>2</sup> with altitudes ranging between 330 m and 840 m above sea level. It is an important source of drinking water and holds *East of Scotland Water's* (now part of *Scottish Water*) largest supply reservoir. Scotland-wide the Megget Reservoir is the fifth largest supply water body (MacDonald, 1994), providing until recently 40% of the water demand in the area between Livingston in the west and Tranent in the east, including the whole of Edinburgh and Midlothian.

### 3.2 Hydrology and land use

The Southern Uplands have a predominantly cool and temperate climate that is dominated by frontal systems with strong winds from the west (Chapman *et al.* 2001). Average annual rainfall in the catchment area is 1524 mm (calculated from daily rainfall data for period 1987-2001) with higher rainfalls occurring in autumn and winter and annual temperatures ranging between -10°C and 29°C (measured daily at the Megget dam). Highest runoffs in the area are reported during December and January, while lowest values occur in July, August and September. There is, however, evidence that since the 1980's seasonal precipitation has become more variable with trends towards wetter winters and drier summers (Fox and Johnson, 1997). Potential evapotranspiration in the area is about 230 mm at 300 m altitude, but declines with increasing altitude (Bown and Shipley, 1982).

Rainfall chemistry monitored at the Environmental Change Network (ECN) research site at Sourhope, located about 50km east of the Megget catchment, suggests that atmospheric deposition predominantly results from inputs of maritime origin, rich in chloride (Cl) and sodium (Na).

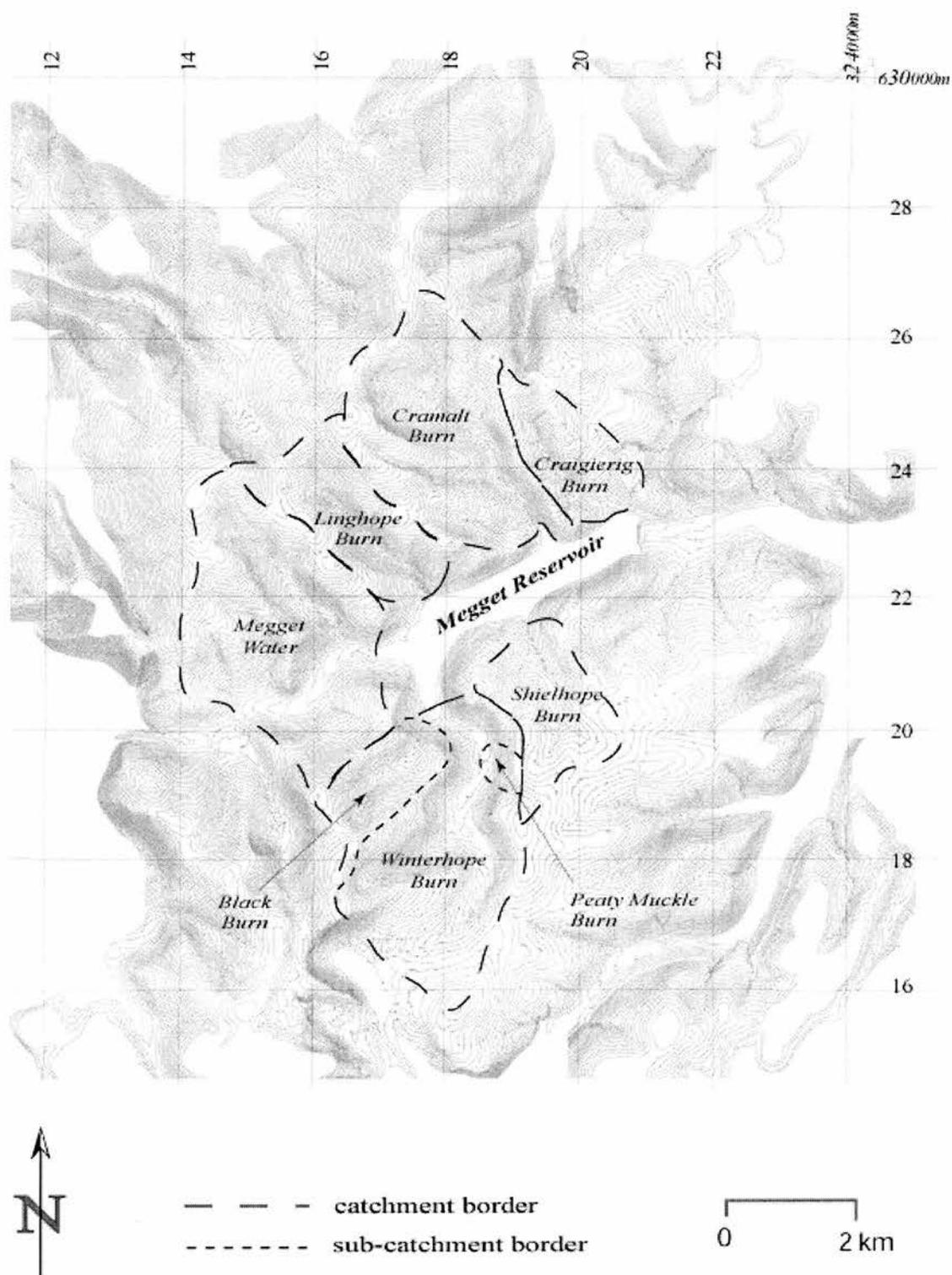


Figure 3. 2: Map of the Megget catchment and its main subcatchments.

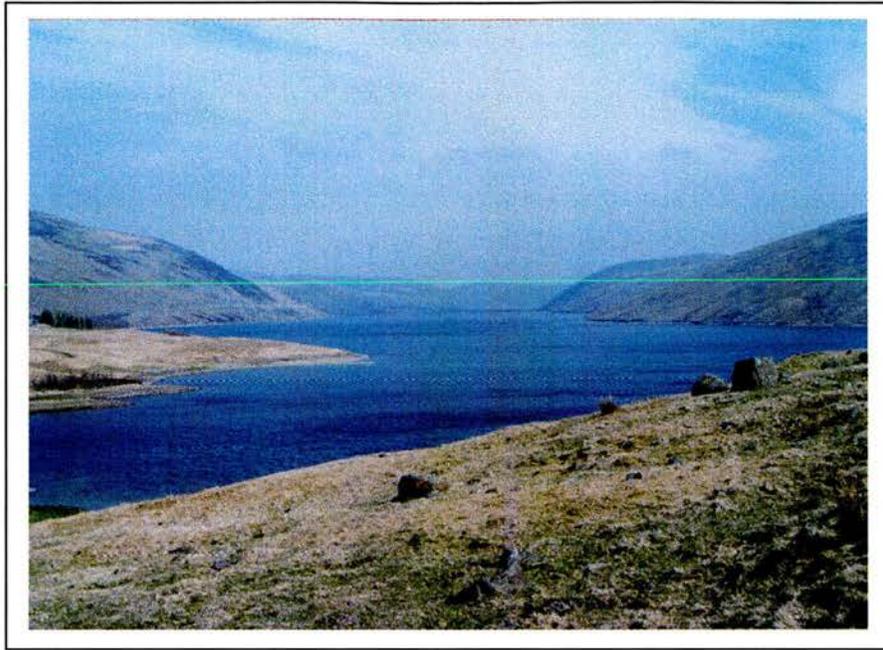


Figure 3. 3: The Megget Reservoir (view from the northside towards the dam).

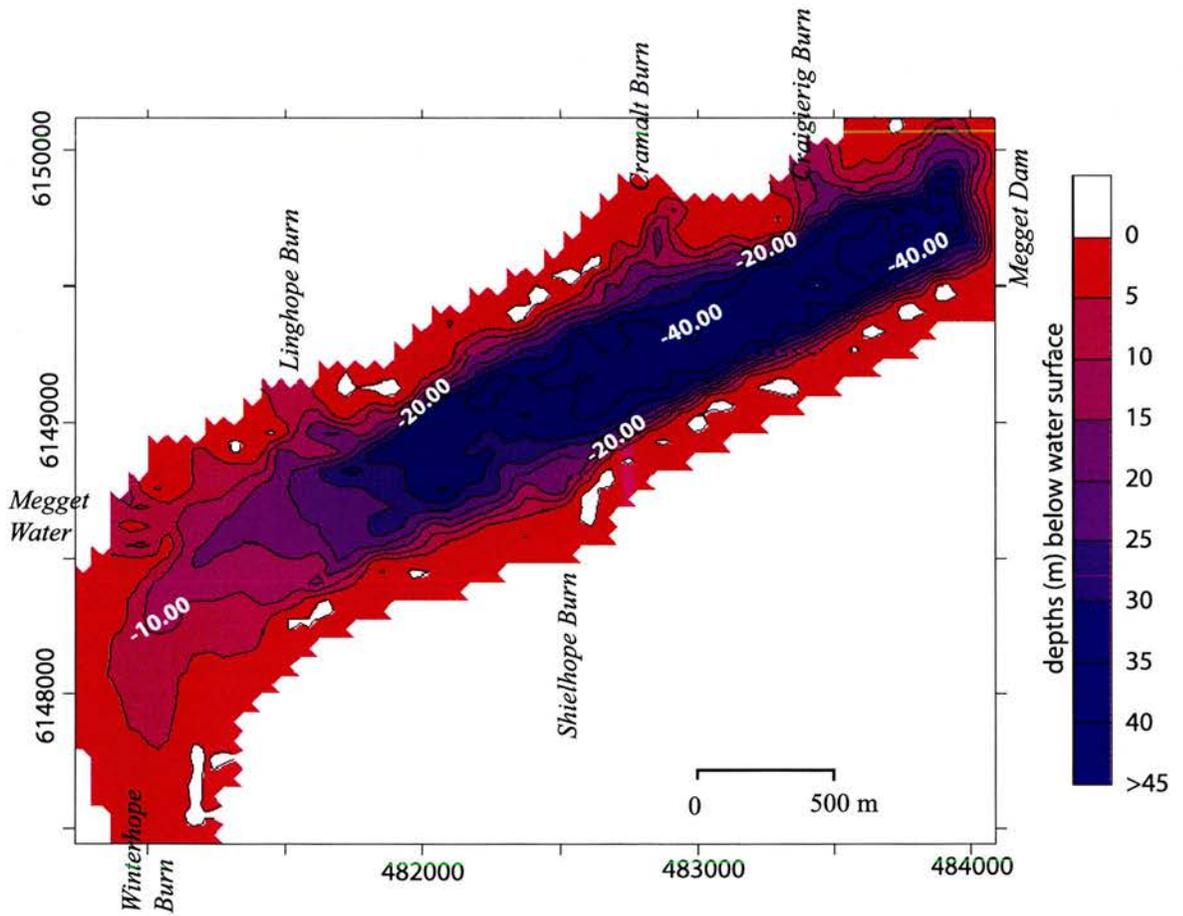
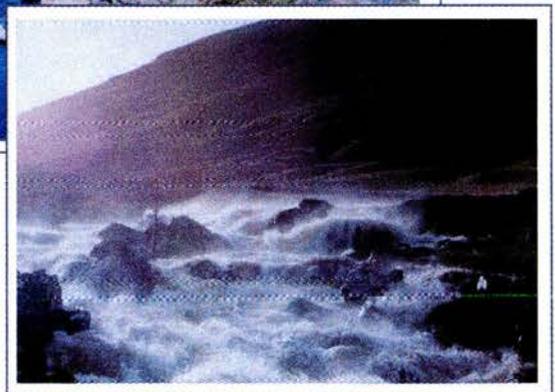
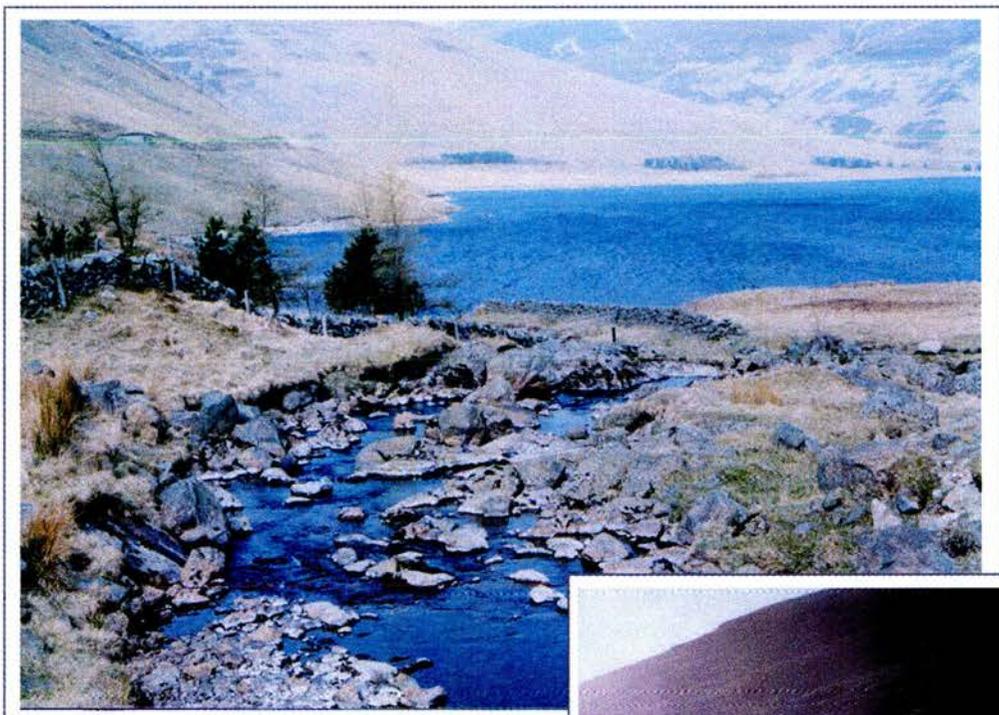
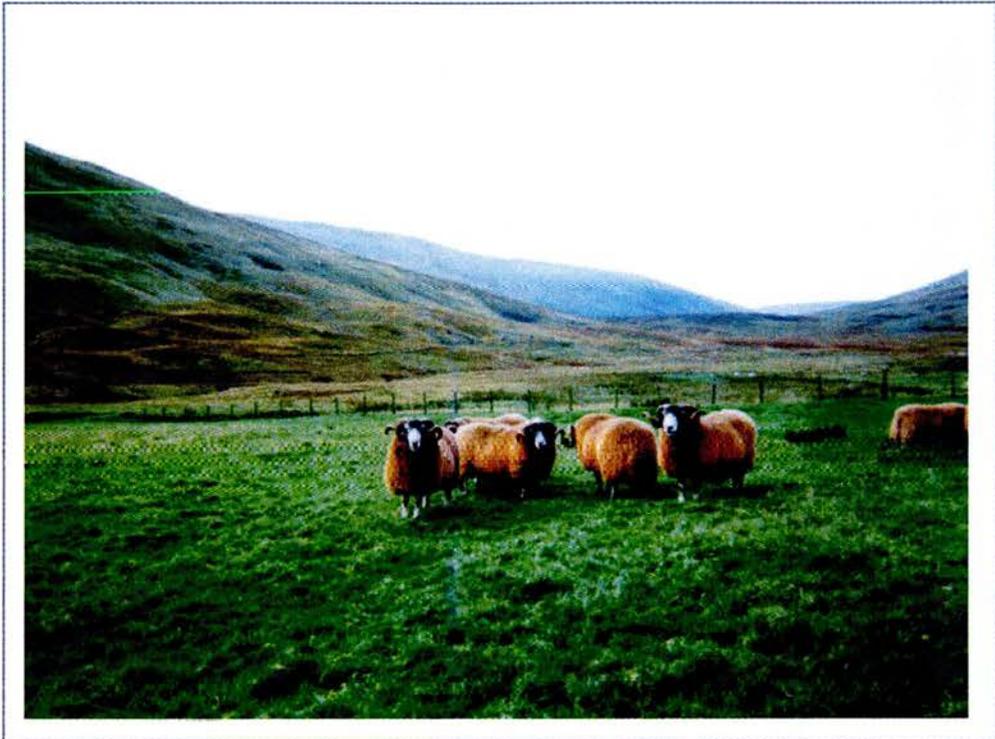


Figure 3. 4: Bathymetry of the Megget Reservoir (surveyed on 27/09/1999).



*Figure 3. 5: Winterhope Burn catchment and sampling site for regular and event sampling at low flow (looking downstream) and during storm event (looking upstream).*



*Figure 3. 6: Catchment of Megget Water and sampling site (at Meggethead) for regular sampling (looking towards the reservoir).*

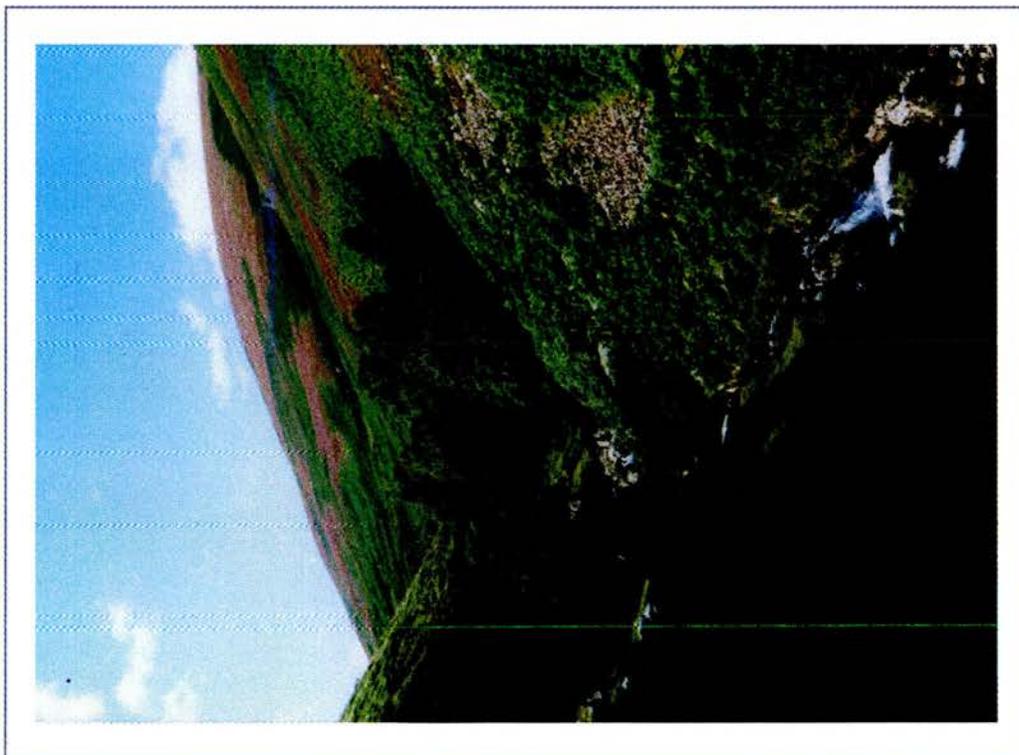
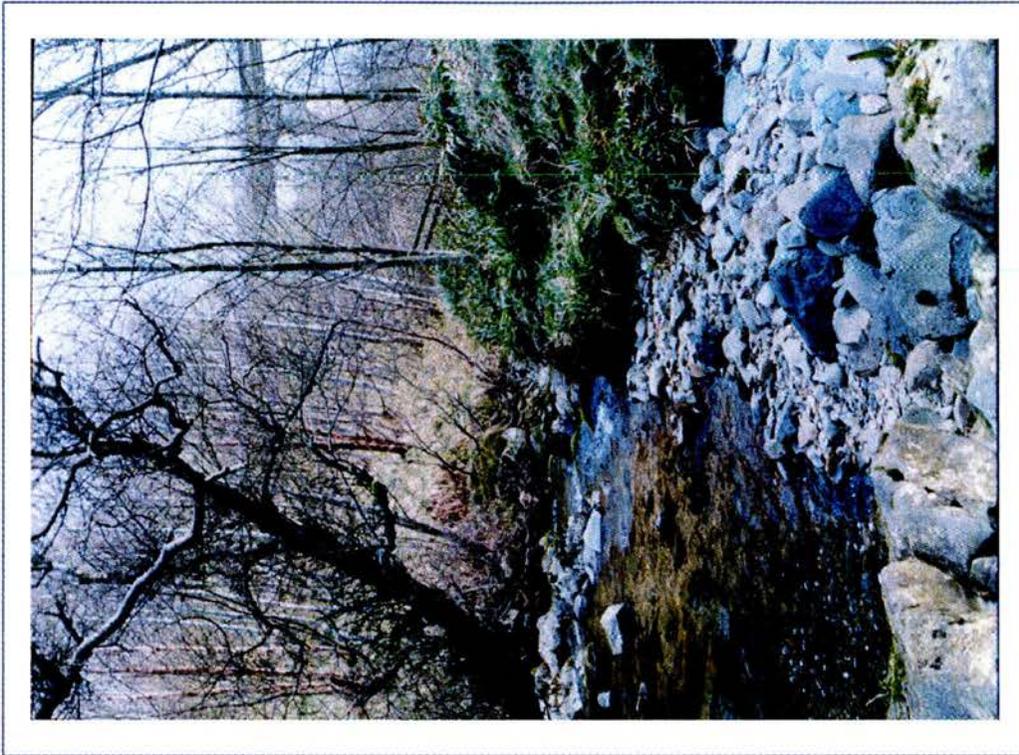
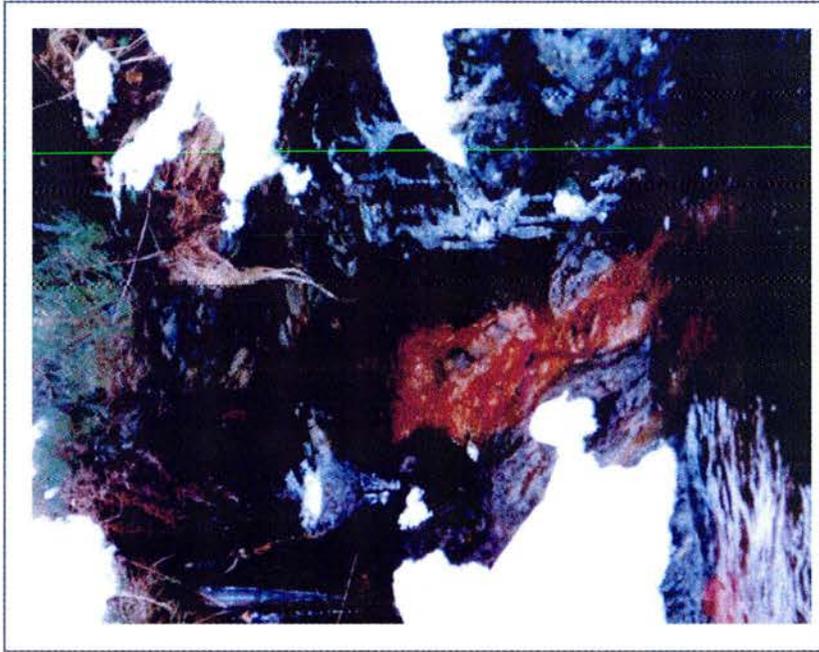
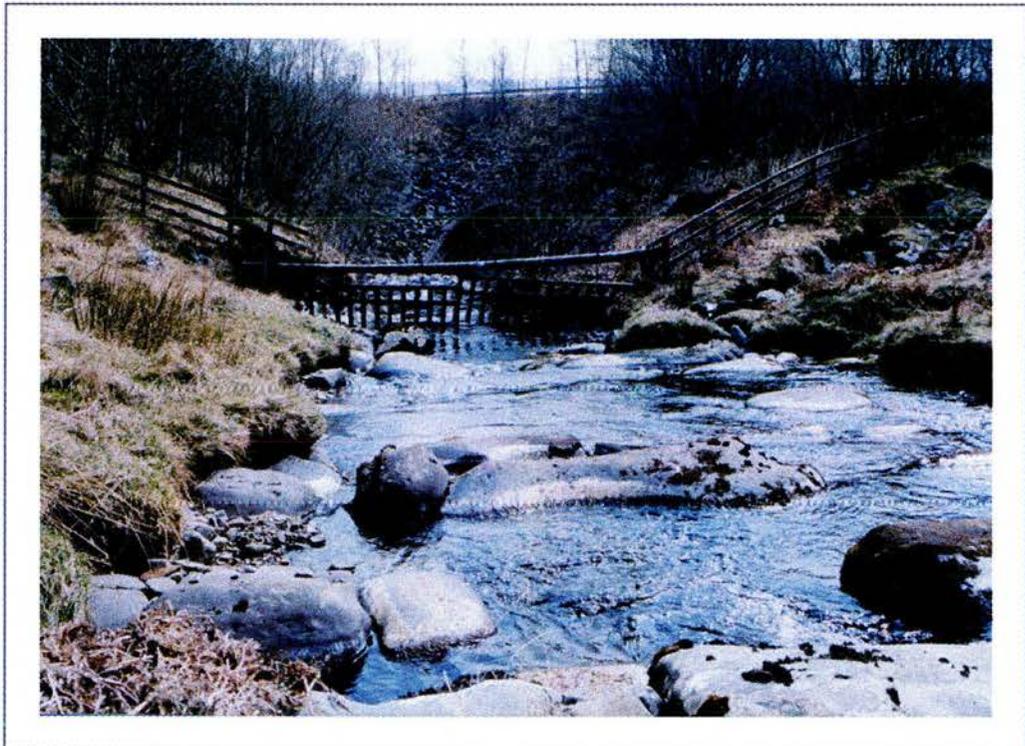
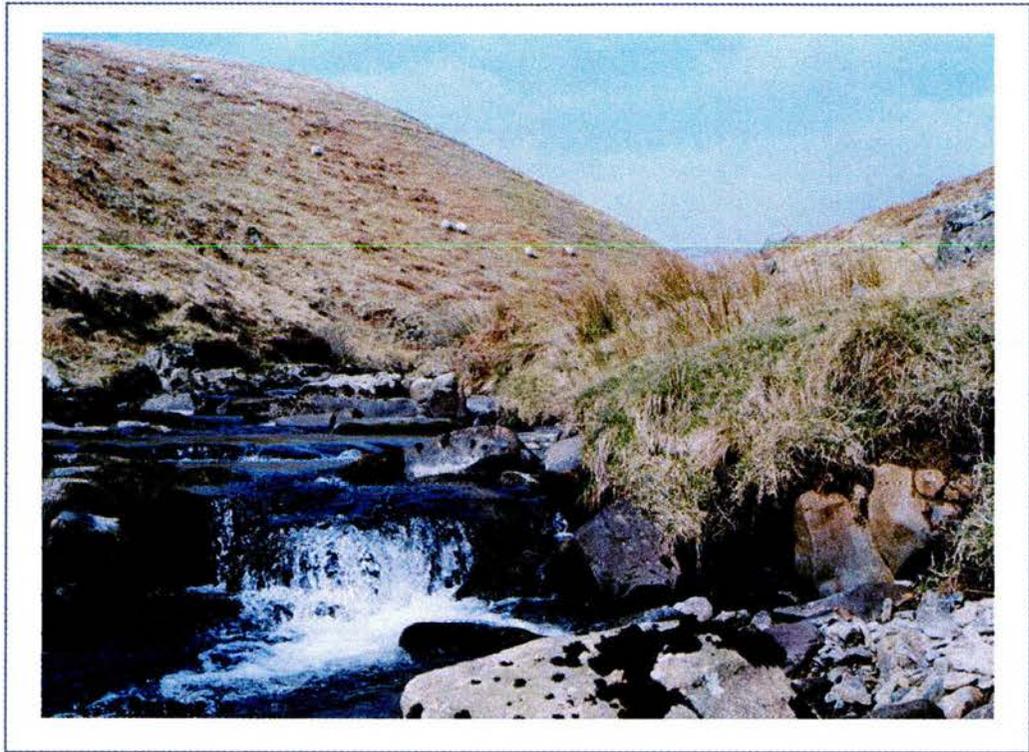


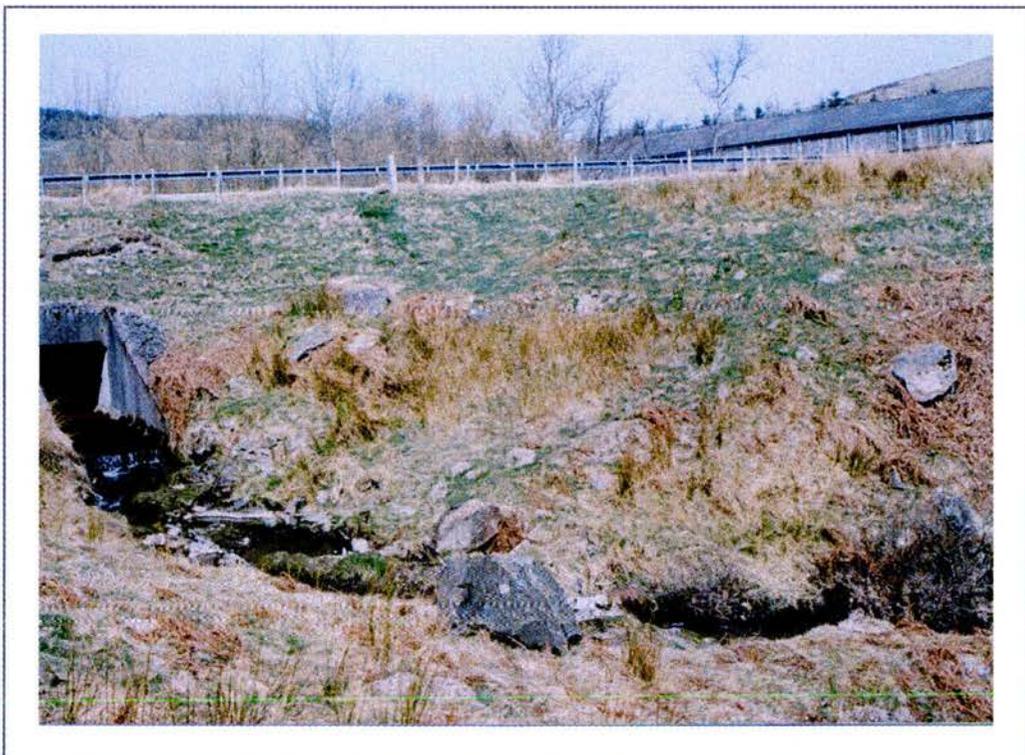
Figure 3. 7: Catchment of Linghope Burn and sampling site for regular and event sampling (looking downstream).



*Figure 3.8: Site for regular sampling and stage measurements at Shielhope Burn and iron leaching from organic rich gleys at the stream banks.*



*Figure 3. 9: Sampling site at Cramalt Burn (looking upstream and downstream).*



*Figure 3. 10: Sampling site at Craigierig Burn looking towards the reservoir and downstream of sheep shed.*

Inputs of anthropogenic pollutant origin (nitrate (NO<sub>3</sub>), ammonium (NH<sub>4</sub>), sulphate (SO<sub>4</sub>), metals, dissolved organic carbon (DOC)) are generally low (see *Table 3. 1.*) reflecting the remoteness of the area, as well as the general Atlantic source (mainly westerly direction) of prevailing weather systems (ECN data).

	<i>Mean</i>	<i>Range</i>
<i>PH</i>	4.92	4.03- 6.32
<i>Conductivity</i>	28	4- 241
<i>Alkalinity</i>	4.4	0.0- 65.1
<i>Na</i>	3.06	0.01- 37.93
<i>K</i>	0.39	0.024- 5.810
<i>Ca</i>	0.43	0.01- 8.43
<i>Mg</i>	0.4	0.02- 4.59
<i>Cl</i>	5.8	0.11- 66.2
<i>Fe</i>	0.006	0- 0.036
<i>Al</i>	0.03	0- 0.15
<i>PO<sub>4</sub>-P</i>	0.013	0- 0.325
<i>NO<sub>3</sub>-N</i>	0.398	0.057- 1.897
<i>NH<sub>4</sub>-N</i>	0.328	0.005- 1.835
<i>SO<sub>4</sub>-S</i>	0.64	0.11- 3.76
<i>DOC</i>	2.45	0.33- 32.77

*Table 3. 1: Rainfall composition for the period between September 1999 to May 2001 derived from weekly composites collected at ECN monitoring site at Sourhope (concentrations in mg L<sup>-1</sup>)*

The reservoir, depict in *Figure 3. 3*, has a surface area of 2.59 km<sup>2</sup> and its yield to supply (at time of construction) is estimated as 102.3 ML d<sup>-1</sup> (Jowitt and Hay-Smith, 2002). Six major tributaries feed the Megget Reservoir: Megget Water, Winterhope Burn, Shielhope Burn, Cramalt Burn, Craigierig Burn and Linghope Burn (*Figure 3. 2*,

*Figure 3. 5 to Figure 3. 10*). The main inflow is Megget Water. The deepest part of the reservoir is situated towards the east with a maximum depth of 55 m at the dam (at full capacity), and is enclosed by steep slopes, matching the steep valley sides, typical for river valley reservoirs. The western part of the reservoir is relatively shallow with alluvial fans developed around areas of stream inflow as illustrated in the bathymetric map of the reservoir given in *Figure 3. 4*.

Low bedrock permeability and shallow soils together with the steep slopes result in a relatively flashy hydrological regime for the input streams, and a separate study on Linghope Burn, Winterhope Burn and Megget Water (Grzybowski, 2001) has clearly demonstrated the influence of a rapid runoff component and a delayed runoff component, associated with different flow pathways (see Chapter 2) on the storm hydrograph. The discharge rating curves obtained during this study have also established similarities in the hydrological response of these streams to storm events, despite the differences in catchment size and soil coverage (*Table 3. 2*). Lag times of 9.5 hours and 8.5 hours were obtained for Megget Water and Winterhope Burn.

Several natural springs drain the hill slopes around the reservoir. These are likely to indicate joints or fractures in the bedrock since the thick sequences of greywacke and grits, shales and mudstones as a whole are only weakly permeable (Robins, 1990) and groundwater storage and transport is confined to the shallow weathered zone, in which cracks and fissures are dilated (Lawrie and MacGregor, 1946; Robins, 2002). Alternatively, peat soils and mire systems covering much of the high ground around the reservoir can hold large quantities of water and probably provide small but perennial baseflow (Bragg, 2002) which feeds some of these springs and also supplies water for

the small streams draining the peat areas above the reservoir. Other potential sources of water in the catchment area are the superficial glacial and post-glacial deposits (Robins, 2002). While the stony, medium-textured drifts mantling the steep slopes of the area allow rapid run-off of water and free internal drainage (Bown and Shipley, 1982), significant amounts of drainage water from the upper parts of the catchment may accumulate in the valley bottom alluvium and in lower slope drift deposits. Upland studies in the Allt'a Mharcaidh catchment, north-east Scotland, for example, have confirmed that such deposits can provide effective groundwater storage and may present a significant source of active water in upland catchments (Soulsby *et al.* 1997).

Land use in the catchment area is generally confined to hill farms and semi-natural moorland. Sheep farming is the dominant agricultural activity in the area and is concentrated along the hill slopes of the reservoir. A number of small farms are situated in the lower reaches of the catchment at Winterhope Burn, Meggethead, Cramalt Burn and Craigierig Burn (*Figure 3. 9*). Most of the higher grounds are covered by peat, while moorland and (semi) natural grassland communities form the dominant vegetation of the steep hill slopes. Small patches of forest are located along the north side of the reservoir between the boathouse (Linghope Burn) and Meggetknowes and also at the mouth of Shielhope Burn. A small patch of plantation forest is located between Cramalt Burn and Craigierig Burn.

### **3.3 Geology and geomorphology**

The Megget catchment lies in the Central belt of the Southern Uplands, delineated by the Southern Upland fold in the north, within the region of the ancient Silurian

Tableland. The bedrock consists predominantly of Silurian greywackes, siltstone and shales that have been intensively folded (*Figure 3. 12c*) during the Grampian Orogeny. Siltstones and shales are thinly bedded (*Figure 3. 12b*) while the greywackes often form thick beds with poorly preserved bedding planes (*Figure 3. 12a*). Bedding strikes NE-SW and the tracts are delimited by a series of major strike parallel faults (Chapman *et al.* 2000) as illustrated in *Figure 3. 11* (inset map). The greywackes and shales dip at high angles towards the NW or SE although local variations in dip and strike occur widely within the catchment (Creig, 1969). Moreover, Chapman *et al.* (2000) point out that the position of the major strike parallel faults is largely conjectural, since they are difficult to define in the field. Hence, the traces given in *Figure 3. 11* (inset map) may, therefore, be in error by some tens or even hundreds of meters.

Stratigraphically, most rocks in the catchment belong to the lower part of the Gala Group of Llandovery age (Chapman *et al.* 2000), often referred to as the Abbotsford Flags, which were deposited from medium to high-density turbidity currents (BGS, 1993). Near Shielhope Burn, Craigierig Burn and Cramalt Burn narrow slivers of older Silurian Moffat shales outcrop (*Figure 3. 11*). These formations stratigraphically underlie the greywackes and are described as a condensed sequence dominated by graptolitic, carbonaceous black shale (locally pyritic with nodules of ironstone and manganese) and siliceous mudstone with occasional metabentonite horizons (BGS, 1993; Peach and Horne, 1899). Condensed marine sequences with a volcanic arc source (Walton and Weir, 1974) such as this are typically enriched in organic content, metals, heavy minerals and ferromanganese nodules.

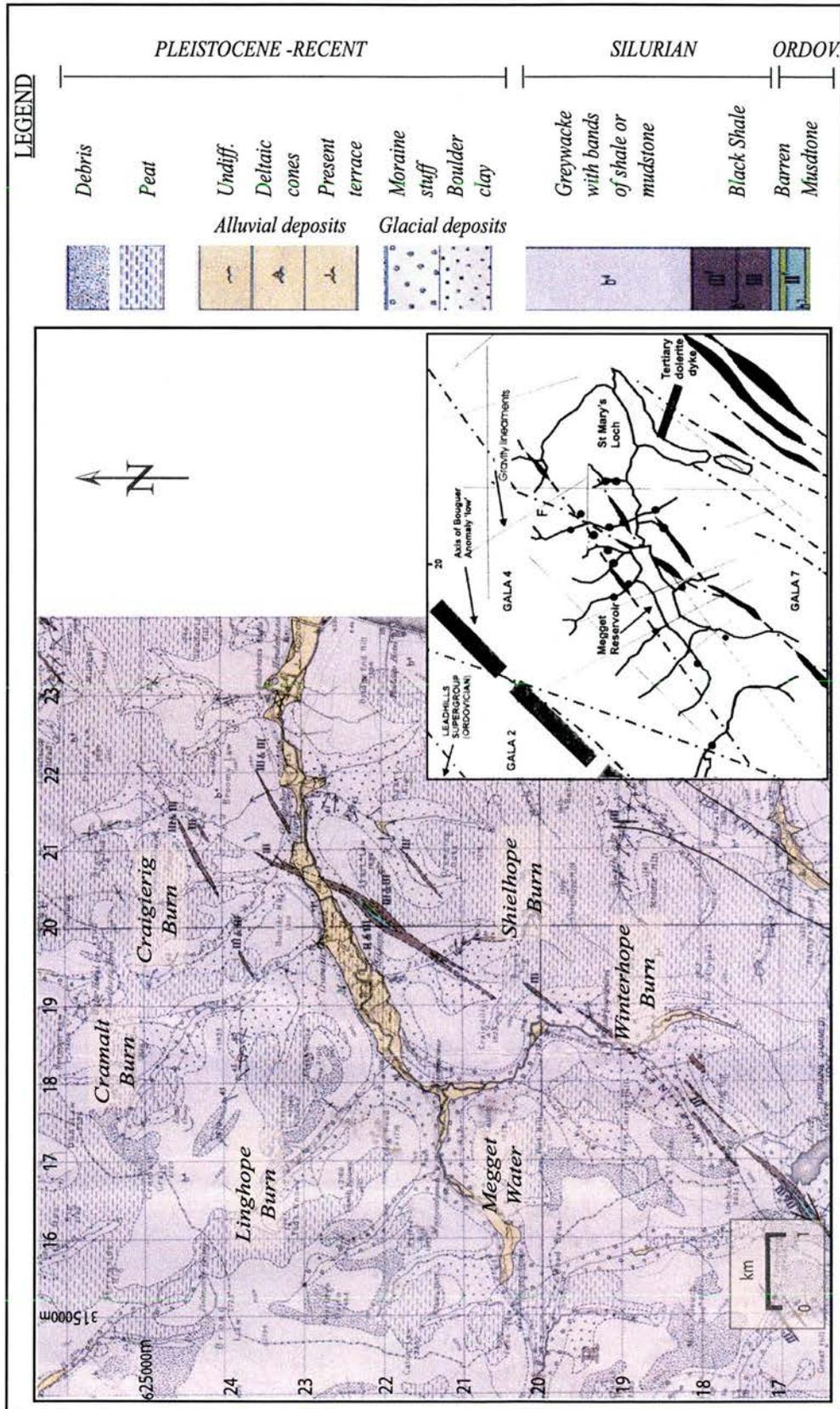


Figure 3.11: Solid and drift geology of the Megget catchment (taken from Geological Survey of Great Britain, Sheet 16); Inset map (after Chapman et al., 2000) shows the tectonical structures of the catchment: major strike parallel faults ( dash-dot lines), gravity lineaments (thin solid lines) and axis of Bouguer Anomaly (fat dashed line).



Figure 3.12: Outcrops of greywackes (top) and shales (bottom) in the Megget catchment.

The solid geology is widely covered by superficial or drift deposits of Pleistocene and recent age. Glacial and post-glacial superficial deposits in the Megget catchment include morainic drift and boulder clay (till), alluvial cones and terraces (for the most part now flooded), valley floor alluvium (flooded), colluvial accumulations (such as scree), hillwash and landslip, as well as peat.

Repeated glaciation of the area during the Pleistocene has strongly contributed to the formation of the recent landscape. Smoothed hillsides, moraine hummocks and ridges and glacial deposits as well as the U-shape of the Megget valley show the results of severe glacial erosion and depositional processes in the area (BGS, 1993). The higher ground is often free of drift, but sometimes the bedrock is loosened or mantled by scree and periglacial deposits. The stony, medium textured drifts (*Figure 3. 16*) mantling much of the steep slopes of the area, allow rapid run-off of water and free internal drainage (Bown and Shipley, 1982). Postglacial peat deposits are occupying most of the hilltops in the Megget catchment (*Figure 3. 15*) while moraines and boulder clay (till) mantle much of the lower ground. Moraine hummocks and ridges are most clearly developed at the mouth of Winterhope Burn and also at Glengaber. As the present drainage system developed, drift deposits occupying the valleys were partially reworked and modern stream profiles are primarily incised into post-glacial drift due to isostatic rebound and high flow energies during glacial retreat. The valley floors in the Megget valley are characteristically underlain by sandy gravely alluvium and the lower part of the valley sides are mantled by older alluvial and glacial deposits (Cuthbertson and Partners, 1977); both are now mostly covered by the reservoir body.

### 3.4 Iron and manganese sources in bedrock

A study on the geochemistry of stream sediments in Southern Scotland (BGS, 1993) has shown enrichment of iron ( $\text{Fe}_2\text{O}_3$ ) in the sediments of the southern Gala Group (prevalent in the study area) relative to those in the north, which is related to a change in the grain size (Pringle, 1948) and petrography of the greywackes (a decrease in volcanic components, such as detrital grains of hornblende and pyroxene) (BGS, 1993). The pattern of manganese enrichment in the area appears to be strongly controlled by the distribution of Moffat Shales, and the lithological description of this formation (Peach and Horne, 1899) suggests that the diagenetic formation of pyrite and ferromanganese nodules has further promoted the enrichment of iron and manganese in bedrock and sediments. The increased presence of iron bearing minerals in the bedrock may also explain the anomalous high hematite ( $\text{Fe}_2\text{O}_3$ ) (>20%) and manganese values that have been found in the area northeast of Moffat, close to the line of the Moffat Valley fault (BGS, 1993). While manganese and iron enter the stream sediments in a variety of solids and phases, the prevalence of acidic and reducing conditions around peat areas with impeded drainage can also result in the mobilisation of large quantities of manganese (and iron) in soluble form (Williams, 1992 in BGS, 1993). The scale of the BGS study does not allow detailed conclusions about the iron and manganese distribution in the Megget catchment, although some enrichment of iron and manganese may be expected at Shielhope Burn, Cramalt Burn and Craigierig Burn where the iron and manganese enriched Moffat Shales crop out.

There has been a long tradition of gold production in the Southern Upland area, dating back to the sixteenth century. Old gold workings are reported on Glengaber Burn, east

of the Megget dam, and independent references of gold findings at that stream have also been given by Atkinson (1619) as cited in Chapman *et al.* (2000):

*'Upon Glengabere Water in Inderland, within the forest of Atrick, Mr Bulmer gott the greatest gold, the like to it in no other place before of Scotland...And he had there sometimes great gold, like Indian wheate or pearle, and black eyed like to beanes'.*

Recent field studies have confirmed that alluvial gold is present in the Megget catchment, probably derived from proximate gold bearing mineralisation (Chapman *et al.* 2000). The abundance of gold grains was found to be higher in the north of the catchment (Craigierig Burn, Cramalt Burn, Linghope Burn, Megget Water and Glengaber Burn), compared to the south (Winterhope Burn and Shielhope Burn) and this may also have implications for the distribution of iron in the catchment area as these local occurrences of gold mineralisation are often associated with iron sulphides, such as pyrite ( $\text{FeS}_2$ ), chalcopyrite ( $\text{CuFeS}_2$ ) and tetrahydrite ( $(\text{Cu,Fe})_{12}(\text{Sb,As})_4\text{S}_{13}$ ) (Chapman *et al.* 2000). The authors conclude that the Glengaber area is the local centre of mineralisation in the area, probably controlled by deep seated concordant NNW trending structures which reveal themselves by the intersection of different structural features as seen in *Figure 3. 11*.

### **3.5 Soils**

The soils are typical of upland areas and are usually highly responsive to hydrological events due their generally limited available storage. A number of different soil types are present in the catchment area including rankers, podzols and brown forest soils, peaty

podzols, peaty gleys and peats as well as subalpine soils, and their distribution throughout the catchment is given in *Figure 3. 13*. The distinguishing features between these catchment soils are the differences in leaching intensity and organic matter content present in the upper layers of the soils (Bown and Shipley, 1982), which also influence the chemical composition of the soil drainage water. Under the high average rainfall leaching of mineral elements from the soils is intense and as a result pH levels in the soils are low, due to the base poor nature of the underlying parent material, in particular in areas around coniferous forests or peatlands.

	Catchment characteristics*			Slope angle (°)*			Average daily flow (cumeCS)**	Soil type proportions (%)			
	Catchment Area (km <sup>2</sup> )*	Length/width ratio*	Maximum elevation* (m above sea level)	Maximum	Mean	Standard deviation		Blanket peat	Peaty podzols	Peaty gleys / some peaty podzols	Others
<i>Craigierig Burn</i>	2.9	1.65	643	n.a.	n.a.	n.a.	0.5	43	49	0	8
<i>Cramalt Burn</i>	7.2	1.73	831	n.a.	n.a.	n.a.	1.3	7	42	8	43
<i>Linghope Burn</i>	4.4	2.08	831	40.5	15.9	7.02	0.8	12	42	0	36
<i>Megget Water</i>	14.7	0.58	840	47.3	15.5	7.5	2.6	6	44	9	41
<i>Winterhope Burn</i>	10.3	2.04	801	43.8	15.6	8.7	1.8	38	31	2	29
<i>Peaty Muckle</i>	0.5		588				0.1	50	50	0	0
<i>Black Burn</i>	1.8		761				0.3	0	46	0	54
<i>Shielhope Burn</i>	4.1	2.03	588	27.7	9.5	5.08	0.7	52	0	46	2

\* derived from Digimap Digital Elevation Model (DEM)

\*\* estimated from flow measurements at Winterhope Burn between 7 Aug 2000 and 9 April 2002

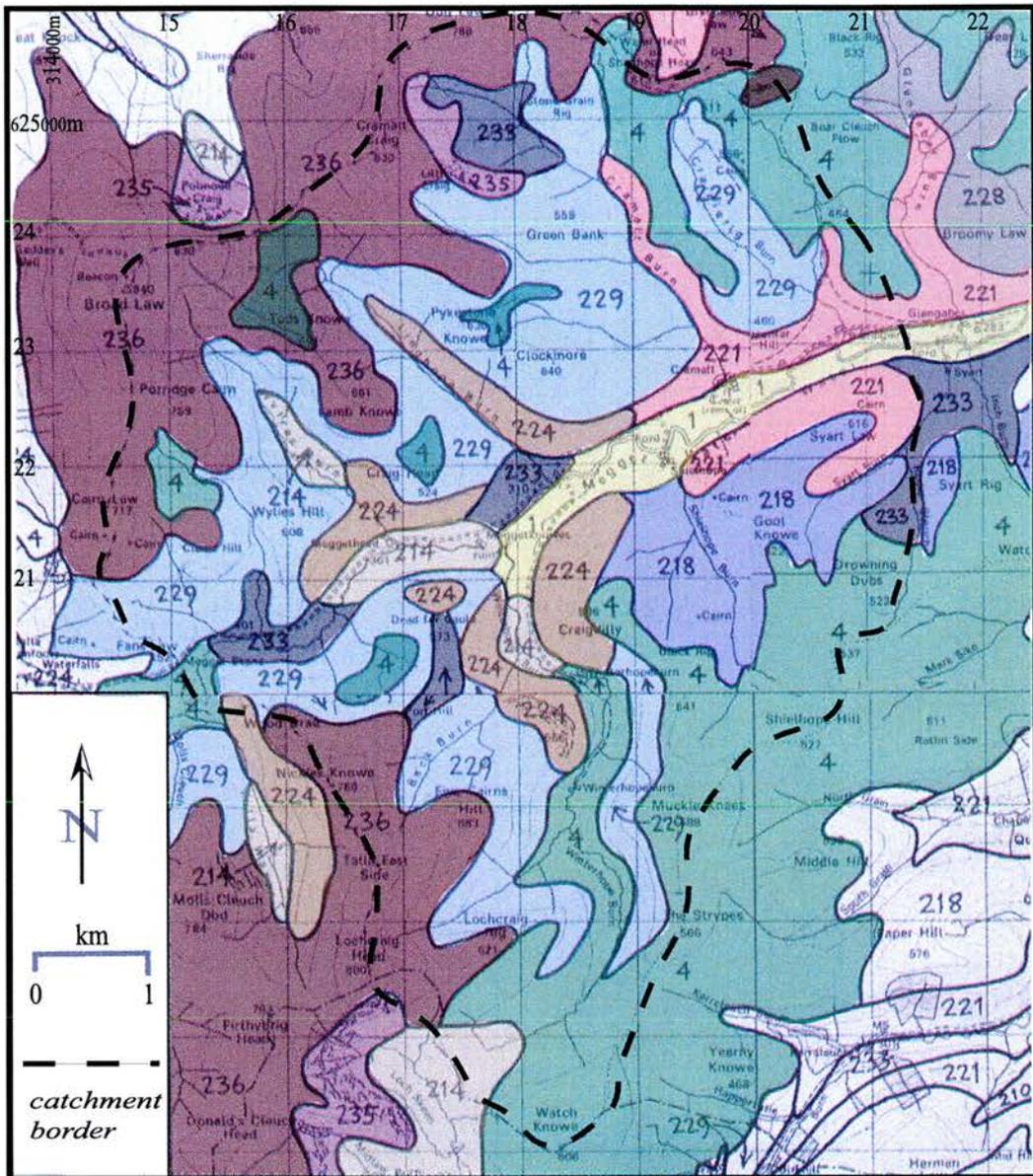
Table 3. 2: Catchment characteristics of the Megget sub-catchments

The soils are closely related to altitude and slope, and their distribution throughout the catchment varies widely (*Figure 3. 13*). On the soliflucted stony drift and on the stabilised scree of the lower parts of the steep slopes, brown forest soils have developed

together with rankers and podzols. These free-draining soils cover most of the narrow valleys at Cramalt Burn and Linghope Burn, but also occupy some of the steeper slopes around Winterhope Burn, Meggethead and Shielhope Burn. The mid and upper slopes of the catchment are dominated by peaty podzols, which are the most abundant soil type in the catchment area and also cover the loamy sand moraines occurring as hummocks and mounds at the lower reaches of Winterhope Burn and Meggethead. Leaching processes during soil genesis (podzolisation) have resulted in the mobilisation of aluminium and iron from the upper soils by organic acids (leached from decomposing organic matter) and displacement to the lower mineral horizons (Hughes *et al.* 1990), where they form a weakly indurated deeper soil horizon. Such horizons may promote the occurrence of perched water tables (Jenkins *et al.* 1994a), although this was not further investigated in the Megget catchment. Peaty gleys have locally developed on boulder clay and clayey till deposits, occupying the gentle slopes of Shielhope Burn as well as the lower reaches of Linghope Burn. Downslope drainage from the valley sides has promoted saturated, waterlogged conditions, especially at Shielhope Burn, where peaty gleys occupy valley bottom locations. The exclusion of oxygen from the soil pores by water regularly leads to the development of anaerobic conditions and the prevalence of reducing and slightly acidic conditions in the soils. This often leads to the mobilisation of iron and manganese from the soils, as is apparent from the presence of hydrous oxide coatings on stream clasts in the aerated environment of Shielhope Burn (see *Figure 3. 14*). The high grounds are widely covered by intensely leached subalpine soils, although blanket peats of 0.5-1m thickness (Bown and Shipley, 1982) often predominate, especially in the southern part of the catchment, where peats cover much of the hill plateaux (*Figure 3. 15*). The peat is in many areas eroded (*Figure 3. 16*), but

evidence of soil pipe development has not been observed, despite their common occurrence in such upland environments (Jones, 2002; Jenkins *et al.* 1994a).

From *Figure 3. 13* it is apparent that soil types vary largely between individual sub-catchments of the Megget area, and their distribution is closely linked to topographical features, including slope angle and altitude range. Both, soil type distribution as well as topography play an obvious role in influencing the hydrological and hydrochemical response of these catchments and a summary of the most relevant characteristics of the catchments considered in this study is given in *Table 3. 2*, and illustrations of individual sampling sites and characteristic catchment views are provided in *Figure 3. 5* to *Figure 3. 9*.



1	Alluvial soils	228	Peaty podzols: some humus-iron podzols
4	Blanket peat	229	Peaty podzols: some peaty gleys, peat
214	Peaty podzols, brown forest soils, peat, peaty gleys	233	Peaty gleys, noncalcareous gleys
218	Peaty podzols, peaty gleys, peat	235	Rankers
221	Brown forest soils	236	Subalpine soils: some peat, peaty podzols
224	Rankers, podzols, brown forest soils		

Figure 3.13: Soil map of the Megget catchment (based on Soil Survey of Scotland, 1:50,000 soil map, Sheets 71, 72, 77, 78).

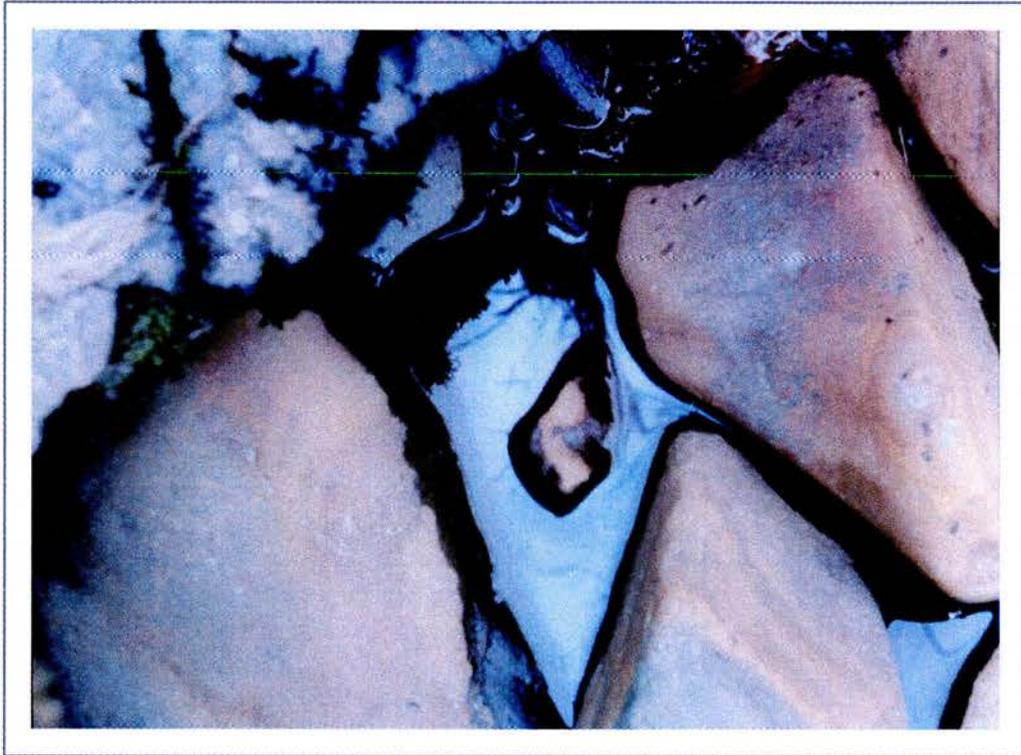
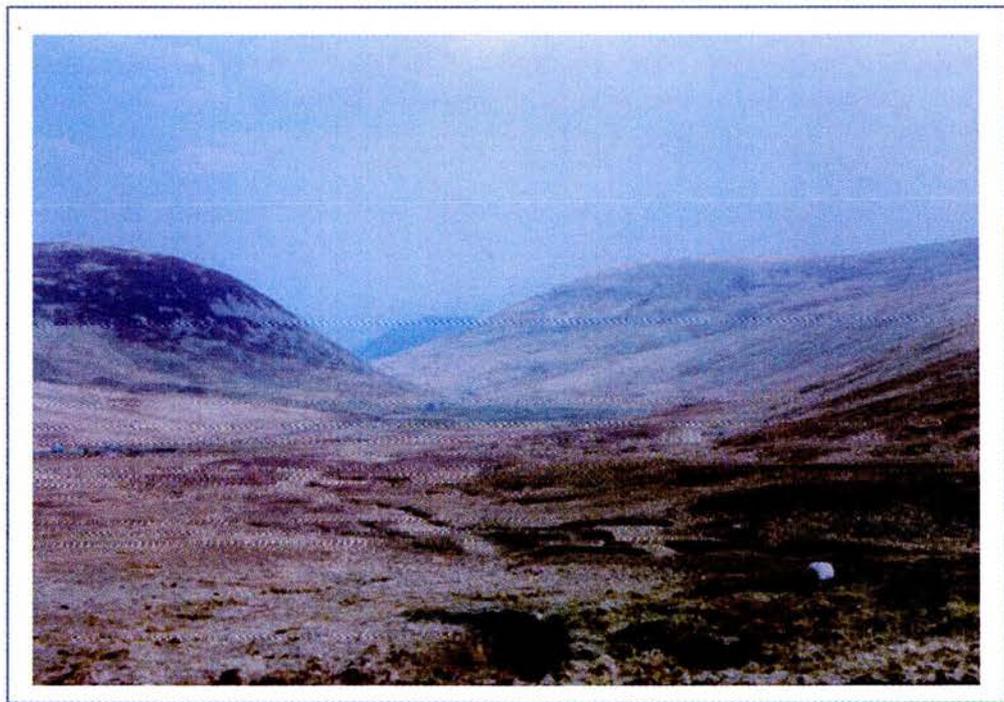


Figure 3. 14: Leaching of iron from near-stream soils and precipitation on clasts in the oxidising stream environment.



*Figure 3.15: Blanket peat in the upper parts of the Winterhope catchment (top) and in the Megget Water catchment (bottom).*



*Figure 3.16: Eroded peat (left) and coarse drift deposits (above) underlying peat horizons.*



# 4

## **Reservoir Water Quality**

---

The following chapter is intended to summarise the findings from the regular reservoir sampling and to describe strategies and methodologies of sample collection and analysis. During the initial period of the sampling programme, and in order to minimise errors related to sample collection and sample handling, all sampling operations were standardised to follow a defined sequence. Detailed descriptions of each procedure are summarised in sampling protocols provided in the Appendix I.

### **4.1 Sampling design and data collection**

Prior to designing the sampling programme an inventory of general water quality, chemical constituents and their variability as well as trophic status and biological productivity of the reservoir was acquired through an initial survey. The survey comprised of a bathymetric survey of the reservoir, sampling of the feeder streams as well as sample collection at five locations along the longitudinal axis of the reservoir at various depth, employing a suite of chemical, biological and physical measurements.

Based on these initial findings a sampling strategy for the regular sampling programme was devised. Appropriate sampling sites, frequency of sampling and parameters to be determined were selected to adequately capture spatial and temporal variability in physical, chemical and biological reservoir characteristics. Although limited with

respect to the ecological dynamics of the system, it was envisaged that the regular sampling would highlight significant seasonal changes and provide a scientific background on which more detailed reservoir process studies could be based.

Regular sampling was undertaken between October 1999 and December 2001 on three main sampling sites, aligned along the length of the reservoir, including:

- Station A:* the deep end of reservoir at the dam  
*Station C:* the middle of the reservoir  
*Station E:* the shallow end of the reservoir

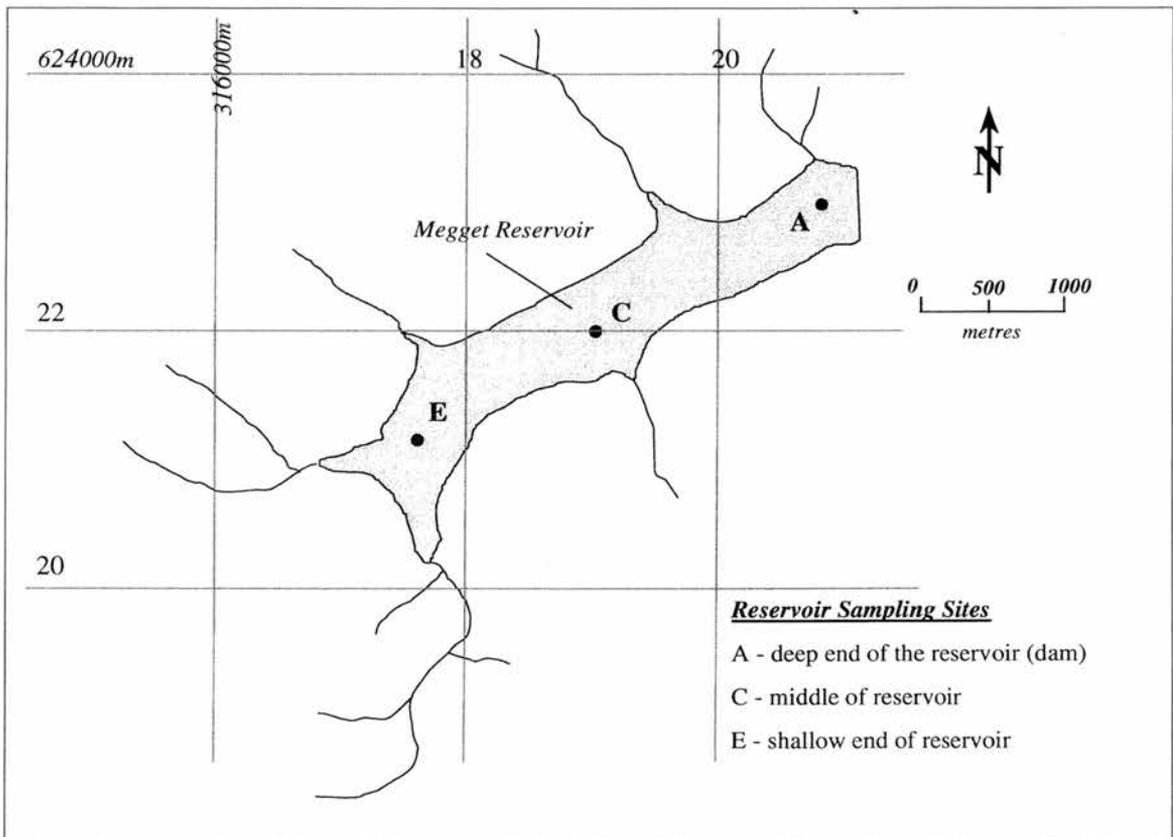


Figure 4. 1: Megget Reservoir sampling sites

The location of the sampling sites on the reservoir is illustrated in *Figure 4. 1* and detailed site descriptions are provided in Appendix I. At each station samples were collected at 2 to 4 strategic depths, depending on the reservoir depths at the sampling site.

Weather permitting; reservoir samples were taken at monthly intervals, providing a time series of twelve samples per year. If the weather was considered unsuitable for launching the boat, samples were taken indirectly by abstraction from the sampling taps at the water supply tower or directly by lowering the sampling tube from the top of the tower into the reservoir and collecting samples at appropriate depths. During data analysis these samples were considered separately from those selected from the boat due to the possible influence of turbulences around the tower and/or precipitates formed within the abstraction pipes on the water chemical composition. Other problems encountered during the sampling programme were related to financial concerns brought forward by the ESW laboratory, which resulted in the modification of the original suite of analysis performed on the samples, and is detailed elsewhere in this chapter. Some changes in the preservation procedures of the water samples occurred during the sampling programme and will be discussed where relevant. Most importantly, however, the sampling programme at the Megget Reservoir was interrupted due to a nationwide outbreak of Foot and Mouth disease, which began in late February 2001. As a precaution, and to prevent the spread of the disease, a general ban on fieldwork was suggested by several national organisations, societies and institutions, including the University of St Andrews, and was later enforced locally by the Scottish Border Council as well as by the ministry of Agriculture, Fisheries and Food. As a consequence, access

to the Megget Reservoir was denied in February 2001. Limited access to the area was allowed in mid June 2001 and reservoir sampling was resumed at the end of that month.

#### 4.1.1 Sample collection

Water grab samples were taken at three locations along the longitudinal axes of the reservoir (*Figure 4. 1*) and from discrete depths using a graduated hose and an electric pump ('*Geopump*'). Samples were taken from the surface to the bottom, at two to four depths depending on the water depth at the sampling site and the depth of the thermocline. At the deep sampling sites (*locations A, C*), a minimum of three samples were collected to include sampling at:

- 0.2 m below water surface
- above the thermocline
- below the thermocline
- close to the bottom without disturbing the sediment

At the shallow end of the reservoir (*location E*) a minimum of two samples were taken. Since the water at this location is too shallow for a thermocline to fully develop, samples were collected from:

- 0.2 m below the water surface
- close to the bottom without disturbing the sediment.

During sample collection the boat was anchored at the appropriate sampling position and the engine was switched off to avoid contamination of the samples.

Water samples for the analysis of general chemistry were collected in clean 1 L polyethylene bottles. Samples for the analysis of total and dissolved metals were collected in clean 250 mL polyethylene. All sample bottles were provided by the ESW laboratory. Before taking a water sample, each bottle was thoroughly rinsed with reservoir water withdrawn from the depth at which the sample was taken.

The sample containers were filled and tightly capped. In the 1 L sample bottles the air space was kept to a minimum in order to minimise CO<sub>2</sub> exchange with the headspace, as this affects the pH of the sample. The 250 mL bottles were filled to the bottleneck leaving space for mixing and for addition of preservatives.

During the first year of the project, an additional sample was collected for the analysis of the chlorophyll-*a* content of the water. Chlorophyll-*a* samples were taken by filtering a volume of 1 litre of water through an in-line Whatman GFC-filter. The filter paper with the chlorophyll-*a* was folded, enclosing the sample, and wrapped in tin foil to keep it dark. After labelling, the sample was kept in a cooling box and when on-shore was stored in liquid nitrogen until transferral to the deep freeze in the Gatty Marine Laboratory in St Andrews.

At each sampling site, *in situ* readings of water temperature and conductivity were taken at the surface and at discrete depth intervals (2 m) throughout the profile. Measurements were made using a digital thermometer and a conductivity meter respectively, with the probes attached to a weighted, graduated hose. Secchi depth transparency was measured over the lee side of the boat using a 30-cm diameter weighted disk. The depth at which the disk disappeared from sight was recorded as the depth of transparency together with water surface characteristics, time of day and percentage of cloud cover.

During sampling, all bottles were labelled by location, date and time of sample collection. GPS co-ordinates, time of sampling and other readings taken at individual sampling sites were recorded in the field log book along with observations about weather conditions, air temperature, reservoir level and any other observations relevant to sample quality.

## **4.2 Water Analysis**

A number of different water analysis techniques were applied during this study. While the majority of water analyses, essential for the realisation of this study, were performed within the ESW Analytical Facility, some analyses that required special sample preparation, treatment and/or analysis procedures were carried out elsewhere and are described in the following sections. Furthermore, important terms used repeatedly throughout this study are defined and issues of data quality, data completeness and delivery of the results by the ESW laboratory are discussed.

### **4.2.1 Terms and definitions**

A number of definitions are necessary to assure the unambiguous understanding of the terms used in the following text and throughout this thesis.

I In the following text, all elements (e.g., calcium, iron, manganese) are abbreviated using their symbols (e.g., Ca, Fe, Mn), referring to both, particulate and dissolved species. Where the distinction between different redox states is important, the valence state of the considered species is given in brackets (e.g., Fe(II), Mn(II)),

while charge notation ( $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ) is used to emphasise the presence of these species in dissolved form.

- II For the purpose of this discussion, calcium (Ca), magnesium (Mg), sodium (Na) and potassium (K) are summarised as ‘major cations’. They are also referred to as ‘base cations’, but in this thesis this term is mainly used to refer to Ca and Mg, as will be specified in the individual chapters. The term ‘major anions’ is generally applied to sulphate ( $\text{SO}_4$ ), chloride (Cl) and nitrate ( $\text{NO}_3$ ), although the latter is also referred to as ‘nutrients’, along with total phosphorous (TP), soluble reactive phosphorous (SRP) and total nitrogen (TKN).
- III Silicon is usually non-ionic and thus, is reported in terms of an equivalent concentration of the oxide, silica ( $\text{SiO}_2$ ).
- IV For practical purposes the term ‘alkalinity’ is used to refer to the value determined by single acidimetric titration to the bicarbonate endpoint at approximately pH 4.5 (see Appendix II), which in more correct terms represents the ‘bicarbonate alkalinity’ of the water samples. Thus, the following correction term was applied to the data (*cf.* Neal, 2001):

$$\text{Alk}(\mu\text{Eq L}^{-1}) = \left( \text{Alk}(\text{mgHCO}_3 \text{ L}^{-1}) \times \frac{1000}{61} \right) - 31.4 \mu\text{Eq L}^{-1}$$

(Eq 4. 1)

in order to (1) to standardise the alkalinity units by converting the data from  $\text{mgHCO}_3 \text{ L}^{-1}$  to  $\mu\text{Eq L}^{-1}$  (first term of (Eq 4. 1)), and (2) to convert the data from ‘bicarbonate alkalinity’ values to ‘alkalinity’ values (second term of (Eq 4. 1)) as defined by Neal (2001).

- V Metals are distinguished between ‘total’ and ‘filterable’ concentrations, and these fractions are operationally defined. Where not stated otherwise, the term ‘total metals’ refers to the total amount of metals present in the water as determined on unfiltered and acidified samples. ‘Filterable’ metals are determined on filtered and acidified samples and the term ‘filterable’ is used to indicate compounds that pass through a filter with a pore size of 0.45  $\mu\text{m}$ . For some practical purposes, these may also be referred to as ‘dissolved’ metals, although such components often include colloidal species (Hem, 1985; Davison, 1993), and thus present the dissolved-colloidal fraction of metals rather than the ‘truly dissolved’ species.
- VI For reasons discussed elsewhere in this chapter, total organic carbon (TOC) was only analysed during the first year of the sampling programme. Thereafter, stream water TOC values were inferred from colour data using linear regression. In some instances and in order to avoid confusion, the term ‘TOC’ may be used even if values were determined from colour data.

Other constituents and properties are included in the water analysis and will be discussed in the following sections and in Appendix II.

#### 4.2.2 ESW Laboratory, Edinburgh

Water samples collected during the field programme, including samples from regular sampling at streams and reservoir as well as from intensive catchment sampling, were analysed by the ESW laboratory in Edinburgh, which is a commercial laboratory dedicated to water quality assurance and performing to a set of standard procedures. The methods used for sample analysis are detailed in the *Organic and Inorganic Procedure Manual for the Analysis of Raw and Portable Water* available at the Scottish Water

(former ESW) laboratory in Edinburgh. A brief summary of the applied procedures, detection limits and precision data for the applied methods are provided in Appendix II.

<i>Analysis suites</i>	
<i>I</i> <i>(before October 2000)</i>	<i>II</i> <i>(after October 2000)</i>
<u><i>General parameters</i></u>	
colour conductivity pH turbidity	colour conductivity pH turbidity alkalinity
<u><i>Major ions</i></u>	
magnesium calcium potassium sodium chloride nitrate sulphate	magnesium calcium sulphate
<u><i>Metals</i></u>	
filterable iron total iron filterable manganese total manganese total copper	filterable iron total iron filterable manganese total manganese total aluminium total zinc
<u><i>Nutrients</i></u>	
total phosphorous soluble reactive phosphorous total nitrogen ammonia	total phosphorous total nitrogen
<u><i>Others</i></u>	
silica total organic carbon	silica

*Table 4. 1: Analysis suites for regular sampling programme (ESW laboratory)*

However, during the study period there have been a number of internal changes in the organisation of ESW, which indirectly affected the current study as the restructuring

also concerned the internal distribution of finances. As a consequence, the original analysis suite (Suite I, *Table 4. 1*) was modified in order to save analysis costs and also to allow the inclusion of other relevant parameters and resulted in the 'new' analysis suite (Suite II, *Table 4. 1*). Other problems encountered during the sampling programme were related to changes in the reporting limits of some parameters, mainly nutrients. For example, the reporting limits for total nitrogen (TKN) and soluble reactive phosphorous (SRP) were changed from  $<0.2 \text{ mg L}^{-1}$  to  $<1.0 \text{ mg L}^{-1}$  and  $<5 \text{ } \mu\text{g L}^{-1}$  to  $<50 \text{ } \mu\text{g L}^{-1}$ , respectively. This not only obscured seasonal dynamics in these parameters in the water body, but also introduced some inconsistency in the data set, although general trends can still be inferred.

#### 4.2.3 CEH Laboratory, Wallingford

Water samples collected during the laboratory experiments (Chapter 8) and samples obtained from sediment leaching (Chapter 7 and 8) were analysed using Inductively Coupled Plasma Optical Emission Spectrometry (I.C.P.O.E.S) to determine dissolved and total metal concentrations. The analysis was carried out at the Centre of Ecology and Hydrology (CEH) in Wallingford with the assistance of Margaret Neal, using an *OPTIMA 3300 (DV) ICP-OES system*. The system is well suited for the analysis of sample mixtures that demand both, low detection limits (see *Table 4. 2*) and/or extended working ranges, which are defined by the method applied during analysis. Information regarding system specifications, functioning and operation of the instrument can be found in the *Perkin Elmer Optima 3000 Family Hardware Guide (1997)* and the *Perkin Elmer ICP Winlab Software Guide (1997)*, respectively. The following section provides an overview of the steps undertaken during sample preparation and outlines the adopted

analysis procedure. The main focus of the analysis lay on the determination of the Fe and Mn contents of the samples, but the applied method also determined the concentrations of the elements listed in *Table 4. 2*, which also provides the detection limits for each analyte.

#### Sample preparation

Due to the different nature of the samples different sample preparation procedures were applied to provide samples that fulfil the standard requirements of the applied method.

All samples had to be free of sediment and acidified to 1 %-vv to avoid blockage of the system and to optimise the performance of the instrument (plasma), respectively.

Furthermore, the concentrations of the analysed elements in the sample had to be within the calibration range of the method in order to obtain reliable results.

<i>Element</i>	<i>Unit</i>	<i>Detection limit</i>
Na	mg/l	0.1
K	mg/l	0.05
Ca	mg/l	0.05
Mg	mg/l	0.1
B	mg/l	0.005
Li	mg/l	0.001
Sr	mg/l	0.001
Be	mg/l	0.001
Ba	mg/l	0.001
Mn	mg/l	0.001
Co	mg/l	0.001
Fe	mg/l	0.002
Zn	mg/l	0.003
V	mg/l	0.002
Cd	mg/l	0.001
Cu	mg/l	0.002
Cr	mg/l	0.003
Ni	mg/l	0.005
Mb	mg/l	0.002
Al	mg/l	0.01
Pb	mg/l	0.01

*Table 4. 2: Elements analysed by the method and lower detection limits of the Optima 3300*

Samples collected during the laboratory experiment (incubation and re-suspension experiments) had been acidified to 1 %-vv immediately after sample collection and the unfiltered samples were left upright in the sample stands to allow the suspended sediment to settle before transferring 5 mL of the sample into the appropriate analysis vials. Where metal concentrations of the sample were expected to be significantly higher than the calibration range of the method dilution of the samples was necessary. On these samples a 20-fold dilution was carried out by adding 1 %-vv nitric acid to 0.25 mL sample to make up 5 mL of diluted sample solution. Nitric acid was chosen as the dilutant in order to maintain the required 1%-acidity of the samples.

Samples derived from the acetic acid extraction of the sediment were diluted in two steps. During the first dilution the acidity of the sample was reduced from 10-12 %-vv to about 1 %-vv according to the standard requirements of the method. This was achieved by a 10-fold dilution of 1 mL original sample extract with de-ionised water to make up 10 mL of 1 %-vv acidic sample solution. Subsequently, an analysis test run was performed on the diluted samples, which showed that some metal concentrations, in particular Fe and Mn were still significantly higher than the calibration standards used within the applied method. As a consequence, a second dilution was carried out to reduce the metal concentrations in the samples. For that 0.5 mL of 1 %-vv sample extract was diluted with 1 %-vv nitric acid to give 5 mL of 1 %-vv diluted sample solution. All dilutions were carried out on a scale rather than by volumetric dilution with a pipette in order to increase the accuracy of the dilution.

### Sample analysis

Prior to analysis a set of standard solutions as defined within the method and summarised in *Tables 1* and *2* of Appendix III was made up and used for calibrating the instrument. A linear calibration method was applied, namely the line forced through zero method, by which the calibration curve is established assuming that the relationship between the concentration (X) of the analyte and the intensity (Y) of the plasma emission is linear and can be described by the following relationship:

$$Y = MX$$

(Eq 4. 2)

with M being the slope of the calibration curve. During calibration the correlation coefficient for each element included in the analysis was calculated to give an indication of the quality of calibration. Where poor correlation for one or more elements was observed the calibration process could be repeated until acceptable calibration results were obtained; however, high correlations were recorded and re-calibration was not necessary during this analysis.

After successful calibration of the instrument the samples were analysed automatically. Within the method each sample was analysed as a replicate of three from which the mean emission intensities and concentration values of the analytes were derived. Standard deviation (SD) and the relative standard deviation (RSD) were automatically calculated based on the following formulas:

$$SD = \sqrt{\frac{\sum (c_i - c_{mean})^2}{n - 1}}$$

(Eq 4. 3)

and

$$RSD(\%) = 100 \times \frac{SD}{mean}$$

(Eq 4. 4)

The samples were arranged in sets of ten, whereby a set of standard solutions and quality control samples were analysed after each sample set. In doing so the performance of the instrument was monitored and correction factors required for the subsequent drift correction were obtained.

During the analysis it was found that the metal concentration range in many samples was higher than the one used for the instrument calibration even after the samples had been diluted. Thus, a set of additional high concentration metal standards with known concentrations (see *Table 3* in Appendix III) was made up. The standards were then analysed as samples to give the deviation of the analysis results from the actual concentrations present in the standards.

After completion of the analysis all results were downloaded including the quality control and standard data and the data were corrected for any errors caused by drift of the instrument that has occurred during data analysis.

Concentrations that lay outside the calibration range were corrected using the relationship between the elemental concentrations present in the high standards and those measured by the instrument. The corrections were only applied to elements with a  $RSD < 5\%$ , and the used equations are provided in *Table 3* in Appendix III. For the other elements, namely Zn, V, Pb, Ni, Mo, Li, Cu, Co and Cd the RSD exceeded 5%,

probably because of their low concentrations in the samples, and to assure high data quality these elements were discarded from the analysis.

#### 4.2.4 Gatty Marine Laboratory, St Andrews

##### Chlorophyll-a

Samples collected for determining the chlorophyll-*a* content of the water were analysed by CJ Colby at the Gatty Marine Laboratory. The applied procedure used *High Performance Liquid Chromatography (HPLC)* and is briefly described in Appendix IV. Further details on the methodology can be found in Colby (2000) and in the general literature on standard procedures in water analysis, e.g., APHA (1998).

### **4.3 Summary of data collected**

The results from physical and chemical monitoring carried out on three sites at the Megget Reservoir (*Figure 4. 1*) from September 1999 to December 2001 are summarised in *Table 4. 4* to *Table 4. 8* and are presented in the following section.

These data cover two years of stratification and mixing cycles including the development of a thermocline in spring, the mixing in autumn and the maintenance of well-mixed conditions during winter. Data collection was interrupted from January 2001 to June 2001, when the sampling site was inaccessible due to a nation-wide outbreak of Foot and Mouth disease in the UK.

Depth integrated temperature (profile) data are derived from the monthly sampling programme and weekly thermistor readings taken at nine depths (20-60 m below

maximum water surface elevation (WSE) outside the draw off tower at the dam are available from June 2000 onwards.

The collected data set provides a basis for assessing the general characteristics of the Megget Reservoir with regards to nutritional status, chemical and physical properties as well as their annual and inter-annual cycling (Table 4. 4, Table 4. 5, Table 4. 3). The data also allow comparison between chemical and physical characteristics at the different sampling sites representative of the shallow inflow area (site E), the deeper middle part (site C) and the dam area (site A) of the reservoir (Table 4. 3-Table 4. 7). In classical reservoir studies these areas are often referred to as riverine zone, transition zone and lacustrine zone of the reservoir (Thornton, 1990b), which, when well established, represent different depositional and chemical environments.

	Zone A		Zone C		Zone E		Total mean
	mixed	stratified	mixed	stratified	mixed	stratified	
Chlorophyll-a ( $\mu\text{g/l}$ )							
0-8m	0.123	1.037	0.161	1.102	0.152	0.792	<b>0.766</b>
09-28m	0.164	1.001	0.147	0.898	-	0.870	<b>0.783</b>
29-50m	0.175	0.912	-	0.766	-	-	<b>0.700</b>
Secchi Depth (m)	3.5	3.7	3.4	4.0	3.3	4.0	<b>3.7</b>

Table 4. 3: Chlorophyll-a content (Nov-99 to Aug-00) and transparency (Sep-99 to Dec-01) of the Megget Reservoir during stratification and mixing periods

	mixed			stratified			total		
	0-8m	09-28m	29-50m	0-8m	09-28m	29-50m	0-8m	09-28m	29-50m
Colour (Hazen)	19	18	19	16	17	16	17	17	17
Conductivity ( $\mu\text{S}/\text{cm}$ )	41	41	42	40	39	40	40	40	40
PH	7.0	7.2	7.1	7.1	7.0	6.9	7.1	7.0	7.0
Alkalinity ( $\mu\text{Eq L}^{-1}$ )	149	149	149	149	149	133	149	149	133
Turbidity (NTU)	0.9	0.8	1.0	0.7	0.8	1.1	0.7	0.8	1.0
Mg (mg/l)	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
Ca (mg/l)	2.7	2.8	2.6	2.8	2.8	2.8	2.8	2.8	2.7
K*(mg/l)	0.4	0.5	0.4	0.7	0.6	0.6	0.6	0.6	0.6
Na*(mg/l)	3.42	3.43	3.39	3.31	3.43	3.41	3.34	3.43	3.41
Cl*(mg/l)	5.6	5.6	5.6	5.5	5.4	5.5	5.5	5.5	5.5
SiO <sub>2</sub> (mg/l)	2.20	2.27	2.22	1.57	1.70	2.08	1.74	1.89	2.11
SO <sub>4</sub> (mg/l)	3.0	2.6	2.6	2.6	2.6	2.6	2.7	2.6	2.6
TOC (mg/l)	3.8	3.6	3.5	3.4	3.6	3.5	3.5	3.6	3.5

\*until Sep-00

Table 4. 4: General water chemistry of the Megget Reservoir (mean values)

	mixed			stratified			total		
	0-8m	09-28m	29-50m	0-8m	09-28m	29-50m	0-8m	09-28m	29-50m
filterable Mn ( $\mu\text{g}/\text{l}$ )	9	7	8	2	9	38	4	8	32
Mn ( $\mu\text{g}/\text{l}$ )	16.7	21.3	36.9	12.7	21.0	76.3	13.8	21.1	68.0
filterable Fe ( $\mu\text{g}/\text{l}$ )	46	44	43	32	45	42	36	45	42
Fe ( $\mu\text{g}/\text{l}$ )	94.9	97.2	116.3	65.8	87.1	109.9	73.7	90.9	111.2
Zn** ( $\mu\text{g}/\text{l}$ )	3.4	3.4	3.4	1.9	2.4	2.2	2.4	2.9	2.4
Al** ( $\mu\text{g}/\text{l}$ )	48.8	45.8	53.3	38.5	46.0	44.5	41.4	45.9	45.8
Cu* ( $\mu\text{g}/\text{l}$ )	4.3	3.3	9.6	1.5	2.6	2.7	2.5	2.8	5.2

\*until Sep-00

\*\* from Sep-00

Table 4. 5: Mean metal concentrations in the Megget Reservoir

	mixed			stratified		
	Min	Max	Range	Min	Max	Range
TP ( $\mu\text{g}/\text{l}$ )	<10	21	21	<10	26	26
SRP* ( $\mu\text{g}/\text{l}$ )	<5	12	12	<5	11	11
TKN (mg/l)	<0.1	0.6	0.4	0.2	0.6	0.4
NO <sub>3</sub> (mg/l)	0.7	1.1	0.4	0.6	1.1	0.5
NH <sub>4</sub> * (mg/l)	<0.02	<0.02	<0.02	<0.02	0.06	0.06

\*until Sep-00

Table 4. 6: Nutrient concentrations in the reservoir between Sep-99 and Dec-01 during stratification and mixing periods

	Zone A				Zone C				Zone E					
	mixed		stratified		mixed		Stratified		mixed		stratified			
	0-8m	09-28m	29-50m	0-8m	09-28m	29-50m	0-8m	09-28m	29-50m	0-8m	09-28m	0-8m	09-28m	
Colour (Hazen)	18	18	19	16	17	16	19	19	16	16	19	19	16	17
Conductivity ( $\mu\text{S}/\text{cm}$ )	41	41	41	40	39	40	41	40	39	40	40	41	41	39
PH	6.9	7.2	7.1	7.2	7.0	7.0	6.9	7.1	7.0	6.9	7.1	7.0	7.2	6.9
Alkalinity ( $\mu\text{Eq}/\text{l}$ )	149	149	149	149	149	133	149	133	133	133	149	149	149	149
Turbidity (NTU)	1.0	0.9	1.0	0.7	0.7	1.1	0.6	0.7	0.7	0.8	0.9	0.8	0.6	0.9
Mg (mg/l)	1.0	1.0	1.0	1.1	1.1	1.1	1.2	1.1	1.1	1.1	1.1	1.2	1.1	1.1
Ca (mg/l)	2.6	2.7	2.5	2.8	2.8	2.8	2.8	2.8	2.7	2.7	2.9	2.8	2.8	2.7
K*(mg/l)	0.4	0.5	0.4	0.7	0.6	0.5	0.3	0.3	0.6	0.7	0.4	0.4	0.3	0.5
Na*(mg/l)	3.36	3.41	3.35	3.39	3.47	3.40	3.56	3.52	3.29	3.36	3.56	3.60	3.23	3.42
Cl*(mg/l)	5.7	5.7	5.7	5.4	5.4	5.5	5.4	5.3	5.5	5.5	5.3	5.5	5.5	5.4
SiO <sub>2</sub> (mg/l)	2.28	2.27	2.26	1.68	1.81	2.09	2.29	2.38	1.58	1.63	2.10	2.14	1.45	1.70
SO <sub>4</sub> (mg/l)	3.3	2.5	2.6	2.6	2.7	2.6	2.6	2.5	2.6	2.6	2.7	2.6	2.6	2.6
TOC (mg/l)	3.8	3.6	3.5	3.5	3.7	3.4	3.8	3.6	3.4	3.5	3.5	3.7	3.3	3.6

\*until Sep-00

Table 4. 7: Mean values of general water chemistry of the three reservoir sites between September 1999 and December 2001 at different depths and stratification regimes

	Zone A				Zone C				Zone E							
	mixed		stratified		mixed		Stratified		mixed		stratified					
	0-8m	09-28m 29-50m	0-8m	09-28m 29-50m	0-8m	09-28m 29-50m	0-8m	09-28m 29-50m	0-8m	09-28m	0-8m	09-28m				
filterable Mn ( $\mu\text{g/l}$ )	6	6	7	2	3	40	8	6	12	2	14	26	10	8	2	11
Mn ( $\mu\text{g/l}$ )	14	17	43	17	18	65	18	26	20	9	23	66	16	16	10	23
filterable Fe ( $\mu\text{g/l}$ )	38.5	37.6	38.8	31.6	37.3	40.4	55.3	45.6	54.0	32.8	46.1	38.1	51.2	52.0	31.3	57.0
Fe ( $\mu\text{g/l}$ )	95	96	119	70	79	109	100	98	108	62	81	96	94	96	62	108
Zn** ( $\mu\text{g/l}$ )	4.5	3.7	3.6	2.0	2.1	2.1	2.8	3.2	3.1	0.9	2.7	2.8	3.1	3.8	2.6	2.2
Al** ( $\mu\text{g/l}$ )	47.5	48.3	50.5	38.7	39.4	45.1	47.5	44.6	59.0	39.2	38.7	41.3	50.0	46.5	37.7	67.0
Cu* ( $\mu\text{g/l}$ )	5.4	4.1	11.0	1.3	5.5	3.8	3.5	3.8	4.2	1.1	1.1	1.5	3.5	2.5	2.5	1.3

\*until Sep-00

\*\* from Sep-00

Table 4. 8: Mean metal concentrations of the three reservoir sites between September 1999 and December 2001 at different depths and stratification regimes

## 4.4 Reservoir water quality – Temporal variations

### 4.4.1 Temperature distribution

*Figure 4. 4a* shows the temperature distribution in the Megget Reservoir at site A during the sampling period as measured during the monthly sampling programme and derived from thermistor readings installed at the draw off tower at the dam. Temperature data are plotted as depth below surface; variations in reservoir water surface elevation during this period are not included in *Figure 4. 4*, but are displayed separately in *Figure 4. 2*. Also displayed are individual temperature profiles collected at station A during the regular sampling programme.

For stations C and E a complete set of temperature data, covering build up of temperature stratification, thermocline and turnover is only available for the first year of this study as the sampling programme was interrupted in the beginning of 2001. Temperature distribution plots for these sites, therefore, only include data collected during the year 2000 as illustrated in *Figure 4. 4b* and *Figure 4. 4c*.

The seasonal progression of the temperature profiles at site A as seen in *Figure 4. 4a* displays typical pattern for monomictic water bodies, which develop thermal stratification during summer period, but remain fully mixed during winter. The figure shows the warming of the surface waters from spring to late summer associated with the development of a thermocline. During summer, the thermocline deepens and progressive warming of the hypolimnion occurs. In late summer, decreasing air temperatures and increasing winds cause cooling of the surface waters and causes the

epilimnion to deepen before complete mixing of the reservoir body occurs. The latter is also illustrated in the individual temperature profiles displayed in *Figure 4. 5*.

An important feature of thermal stratification is the depth of the thermocline, which in this study is assumed to be located where the vertical temperature gradient is maximum. Thermocline depths in both years were similar at around 30 m (when fully developed), despite the greater draw down of the reservoir in 2001 (*Figure 4. 2*). The most significant difference in the temperature distribution for the years 2000 and 2001 is that thermal stratification was established later in spring 2000 but persisted longer in autumn compared to 2001 (*Figure 4. 4 and Figure 4. 5*). Given the similar reservoir levels (*Figure 4. 2*) during the spring period of 2000 and 2001 the differences in thermocline establishment are probably the result of differences in meteorological conditions. Meteorological factors are also the driving force for reservoir mixing in autumn, although the greater temperature gradient established in the water column in September 2000 may have delayed the response to surface cooling and wind mixing in that year.

Another important factor is the reservoir water level and Owens (1998) suggests a potential linkage between reservoir draw down and thermal stratification. In his study at the Cannonsville Reservoir, he concludes that the volume reduction related to abstraction of cold water from the hypolimnion reduces the stability of the hypolimnion, allowing mixing to occur more easily. Thus, it could be hypothesised that the lower reservoir level in autumn 2001 (~3m) and the smaller hypolimnion (*Figure 4. 5*) have promoted the earlier turnover of the reservoir that year. However, a more detailed exploration between meteorological conditions, management operation and reservoir temperature stratification is required.

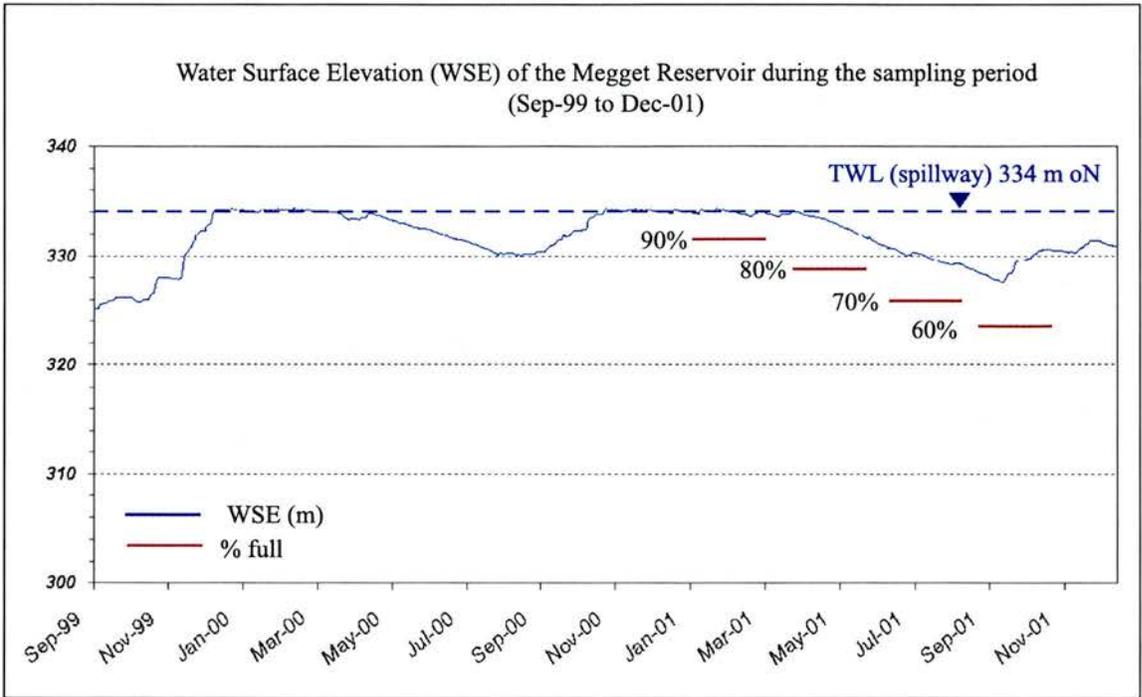


Figure 4.2: Variations in reservoir level during the sampling period.

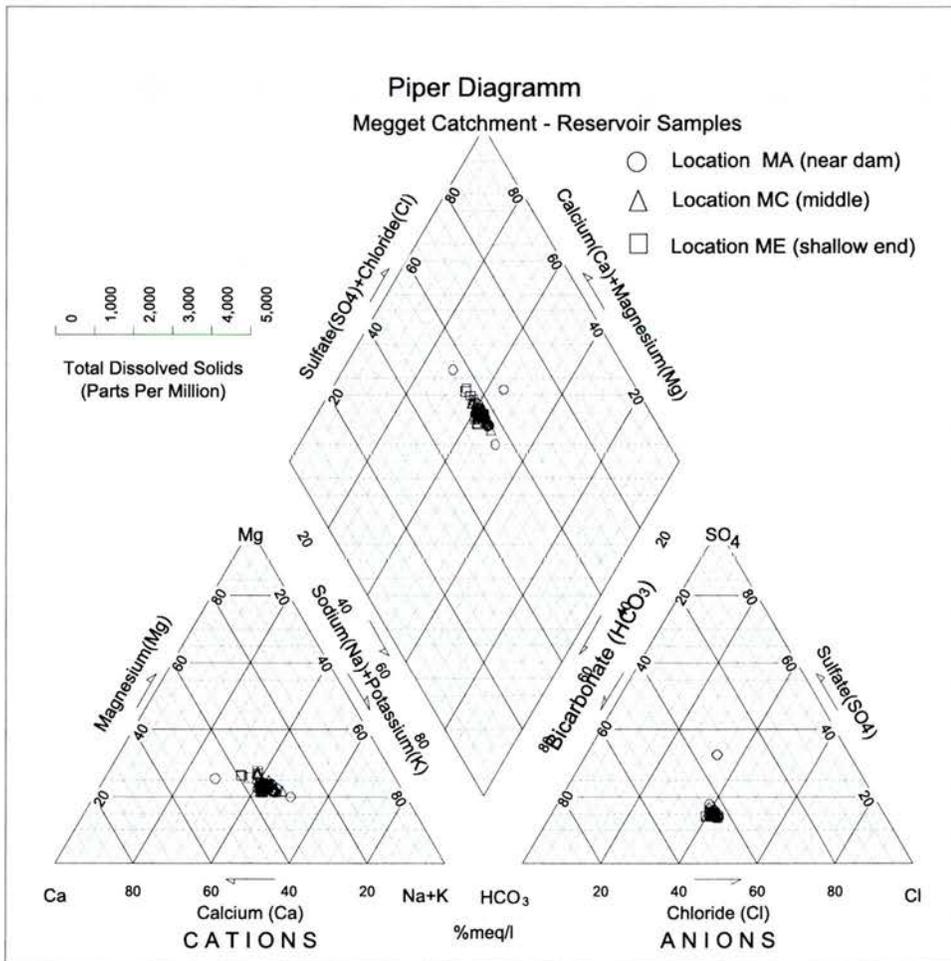


Figure 4.3: Piper Diagram for water samples from Megget Reservoir collected between September 1999 and November 2000.

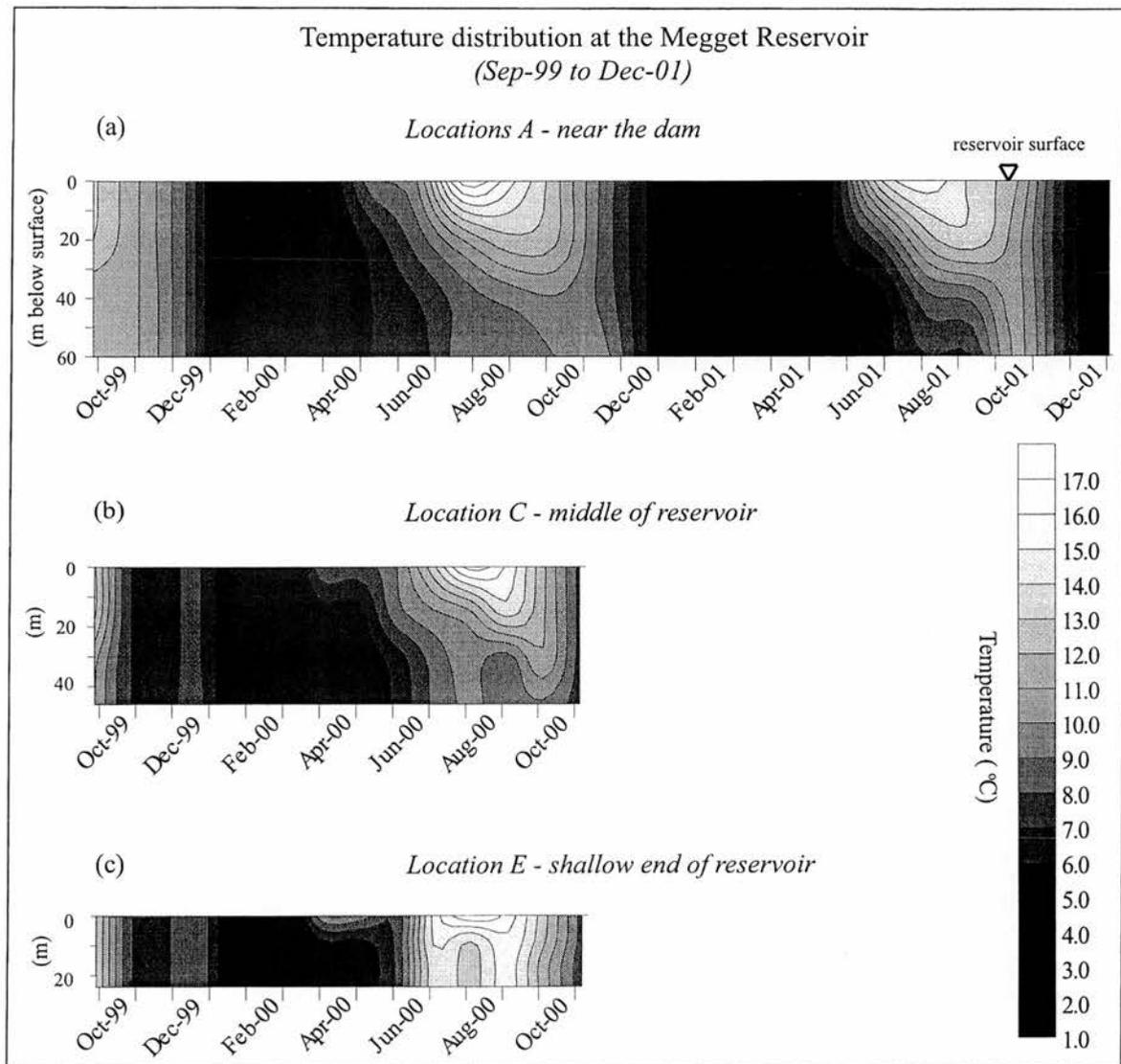


Figure 4.4: Spatial and temporal pattern of temperature distribution at the Megget Reservoir.

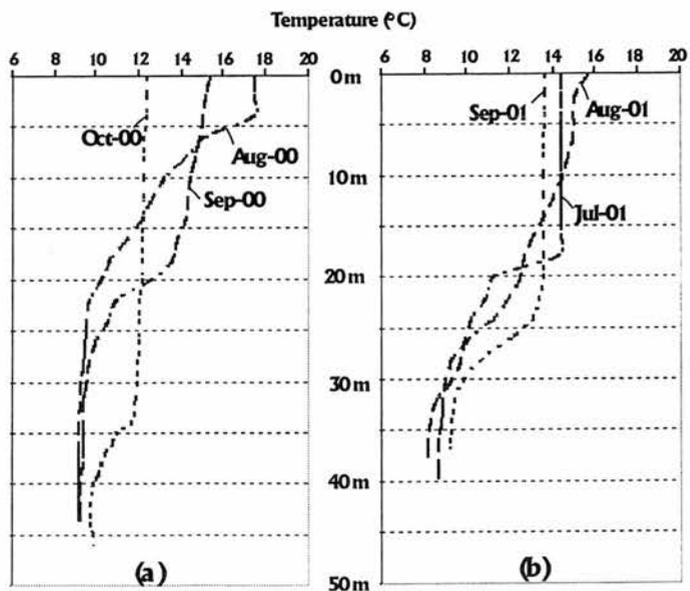


Figure 4.5: Thermocline development at site A in (a) 2000 and (b) 2001.

#### 4.4.2 Water chemistry

##### General chemistry

Mean values of the most important chemical parameters obtained during the regular sampling programme are summarised in *Table 4. 4*. For most parameters spatial and temporal variability is low, but distinctive seasonal patterns are observed for some elements, reflecting the changing importance of internal processes on the reservoir water composition.

Colour values measured during the routine sampling at the reservoir range from 14° to 18° Hazen, with higher values during autumn and winter. Colour is mainly associated with inputs of dissolved humic substances (as summarised in Wetzel, 1975; Nürnberg and Dillon, 1993), accumulated in the soils during the drier summer period. Thus, the observed increase in autumn reflects higher runoff from the tributaries and is also noted by higher TOC levels in the water column. Turbidity values increase by about 0.2-0.3 NTU (*Table 4. 4*) during turnover and mixing of the reservoir, indicating increased amounts of suspended sediment particles (tripton) in the water column. As this may be related to the higher tributary loading, re-suspension of fine sediments in inflow areas and shallow parts of the reservoir is likely to have contributed to the observed increase. Moreover, a vertical turbidity gradient develops during thermal stratification of the reservoir, with maximum differences of 0.4 NTU between top and bottom waters.

The range of pH values measured during the regular sampling lies between pH 6.3 and pH 7.9, underlining the near neutral character of the reservoir. Between autumn and spring, when the reservoir is well mixed, pH values are similar throughout the reservoir

and do not show significant variations with depth. On some occasions, pH values in the surface waters of the deeper reservoir sites (site A and C) are slightly lower (0.1-0.2 pH units) compared to those of the remaining water column. This may be due to excess CO<sub>2</sub> production in the upper part of the water column related to respiration by aquatic organism.

Distinct vertical differences in pH emerge in the reservoir during the stratification period. Values are highest in the upper water layers of the epilimnion and gradually decrease towards the hypolimnion. In productive systems the temporal and vertical distribution of pH are primarily mediated through consumption and production of CO<sub>2</sub> (Wetzel, 1975) and may be an important control on pH variations in the Megget Reservoir. The vertical differences in pH are at maximum towards the end of the stratification season (0.5-1.2 pH units) when values as low as pH 6.3 occur in the hypolimnion near the sediment.

Concentrations of major ions (Ca, Mg, K, Na, Cl, SO<sub>4</sub>) and alkalinity are given in *Table 4. 4*. The low concentrations of these elements in the reservoir water are typical for soft water systems and are also reflected in the low conductivity values. Alkalinity values range between 100 µEq L<sup>-1</sup> to 182 µEq L<sup>-1</sup> indicating the limiting buffering capacity of the water with regards to pH changes. Samples for which a complete set of anion/cation data are available are also displayed in the form of a Piper Diagram (*Figure 4. 3*), which is used to present the relative proportions of major ions rather than absolute concentrations. This not only allows a general characterisation of the water composition but also provides a good basis for comparing individual sampling sites. Bicarbonate (HCO<sub>3</sub>) concentrations used in the plots were directly inferred from the original

alkalinity values, which are quoted in terms of bicarbonate concentrations ( $\text{mgHCO}_3\text{L}^{-1}$ ) (see *Section 4.2.1*). The graph shows that proportions of major ions are similar at the three sampling locations and that the overall variations in major ion concentrations in the Megget Reservoir are small.

The temporal distribution of silica ( $\text{SiO}_2$ ) concentrations in the upper waters of the Megget Reservoir is illustrated in *Figure 4. 6a* and clear seasonal variations are apparent. The graphs show that silica content in the water column is highest during winter and early spring when the reservoir is well mixed and inputs from the tributaries are high. With onset of summer stratification concentrations in the water decrease and a distinct vertical gradient between upper (low  $\text{SiO}_2$ ) and lower (high  $\text{SiO}_2$ ) layers of the water column is observed, indicating uptake of  $\text{SiO}_2$  by micro-organisms (e.g., diatoms) in the photic zone and silica depletion in the upper water layers. Minimum concentrations are reached in September prior to reservoir turnover, when the  $\text{SiO}_2$  content in the water column is replenished during mixing and increased runoff from the catchment area.

#### Metal concentrations

Seasonal differences are also seen in the distribution of iron and manganese in the reservoir as summarised in *Figure 4. 6b* and *Figure 4. 6c* and in *Table 4. 5*. From the data it can be seen that manganese (Mn) concentrations are significantly less than those of iron (Fe); on average by a factor of 5-6, although on one occasion (27 September 1999) hypolimnetic Mn concentrations exceeded those of Fe by about  $65\text{-}75\mu\text{g L}^{-1}$ . Most Mn is present in particulate form and the ratio of particulate to 'dissolved' (filterable) species often exceeds that found for Fe. Given the slower oxidation rate of Mn this is

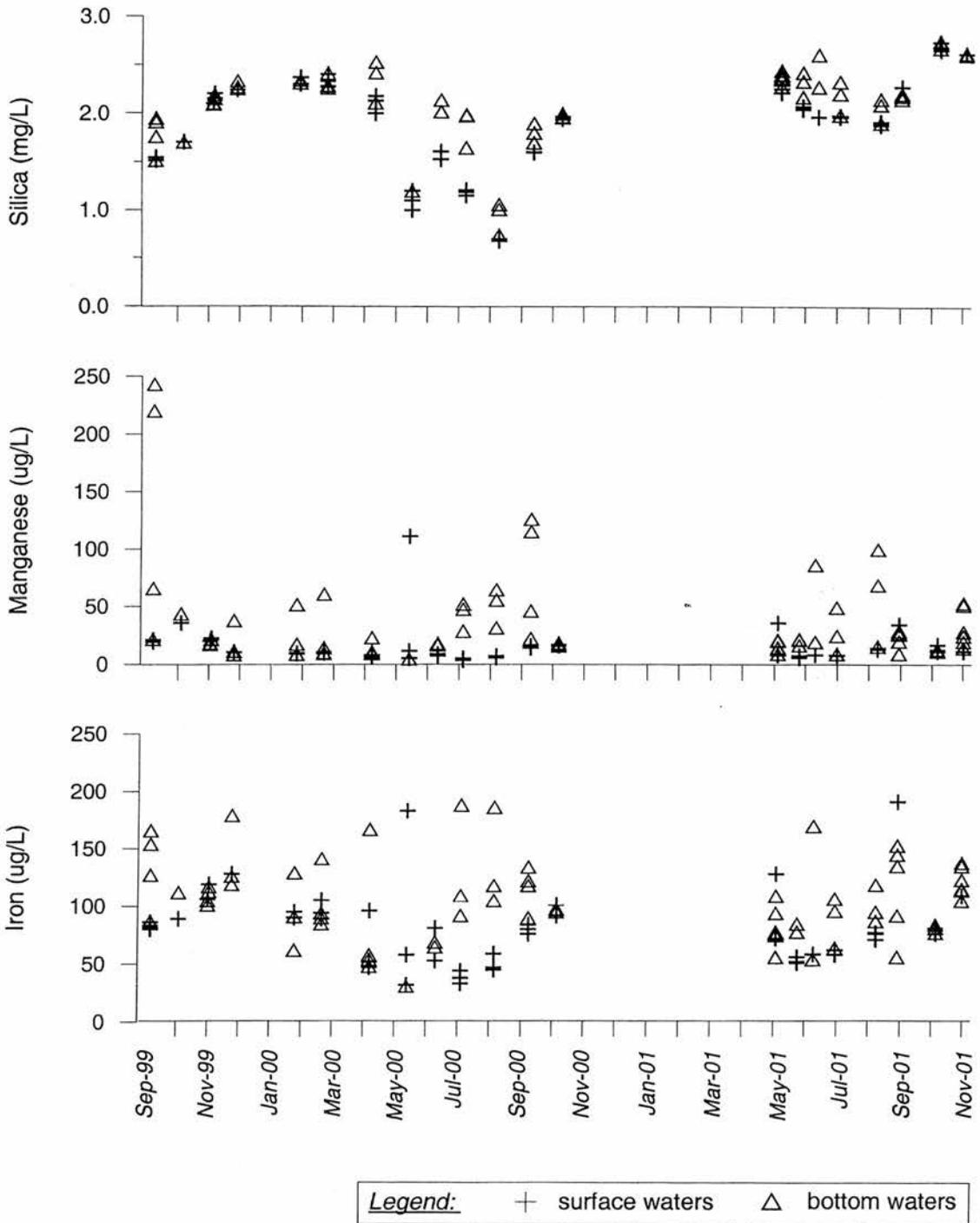


Figure 4. 6: Distribution of (a) silica, (b) manganese and (c) iron in the water column of the Megget Reservoir during the sampling period (September 1999- December 2001).

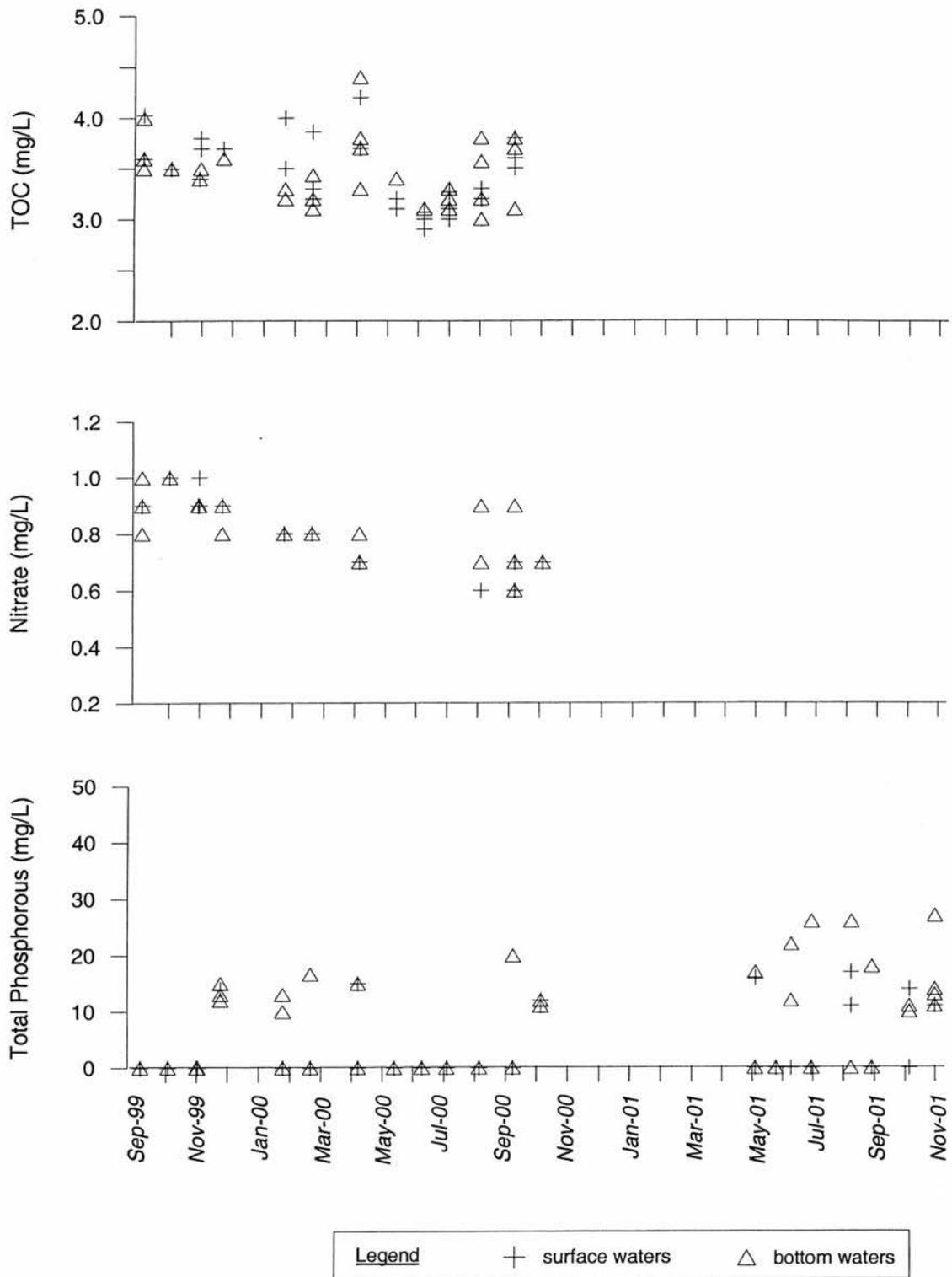


Figure 4. 7: Distribution of (a) TOC, (b) nitrate and (c) total phosphorous in the water column of the Megget Reservoir during the sampling period (September 1999-December 2001).

surprising, as the opposite (high dissolved Mn and low dissolved Fe) would be expected in the well-oxygenated water column of the reservoir.

Also seen in the plots is the development of distinct vertical Fe and Mn gradients during summer stratification. Concentrations are highest in the lower parts of the water column, near the sediment water interface and coincide with low pH and dissolved oxygen (DO) values, presented elsewhere in this chapter. The gradient develops during mid summer, when the thermocline is fully established and declining oxygen levels in the bottom waters promote the release of Fe and Mn from the sediments into the overlying water column. The maximum gradient occurs during late summer/early autumn prior to mixing of the reservoir when oxygen concentrations in the bottom waters are lowest (*Figure 4. 8, Figure 4. 9*). At this time concentration differences as high as  $146\mu\text{g L}^{-1}$  for Fe and  $90.3\ \mu\text{g L}^{-1}$  for Mn are observed between surface and bottom waters and maximum hypolimnetic concentrations of  $188\ \mu\text{g L}^{-1}$  and  $126\ (248)\ \mu\text{g L}^{-1}$  for Fe and Mn, respectively. After complete turnover of the reservoir and throughout the mixing period, variations in Fe and Mn concentrations in the water column are generally small and probably result from tributary inputs and/or local re-suspension events.

The concentration ranges of copper (Cu), aluminium (Al) and zinc (Zn) (*Table 4. 5*) are measured during the regular sampling at the reservoir are generally low and lie below the limits recommended by the WHO drinking water standards (WHO, 1993), which are  $3\ \text{mg L}^{-1}$ ,  $0.2\ \text{mg L}^{-1}$  and  $3\ \text{mg L}^{-1}$  for Cu, Al and Zn, respectively. Distribution of these metals and variations observed in the water column during the sampling season show no temporal or spatial pattern.

Dissolved oxygen, secchi depth and nutrients

Chlorophyll is the most widely used measure of phytoplankton standing crop, and in the Megget Reservoir showed very little variability. The average chlorophyll-*a* concentrations for the upper waters proximate to the dam (site A) over the sampling interval (November 1999 to July 2001) were between  $0.123 \mu\text{g L}^{-1}$  (during the winter mixing period) and  $1.037 \mu\text{g L}^{-1}$  (during summer stratification) and are indicative of the oligotrophic conditions at the reservoir. Similar values were observed at site C and site E as summarised in *Table 4. 3*. All stations record a decrease in chlorophyll-*a* content with depth during summer stratification due to the exponential decrease in light intensity with depth, which limits most photosynthetic activity to the upper water layers. During winter, the chlorophyll-*a* content in the reservoir water was lower and equally distributed throughout the water column due to the constant mixing of the water column.

Clarity of the reservoir was measured by Secchi disc transparency (SD) and showed only little spatial and temporal variability (*Table 4. 3*). SD values were somewhat higher during stratification (May-August), ranging from about 3.7 m to 4.0 m. Thereafter clarity slightly decreased to about 3.4 m, indicating increased inputs of organic material (colour) or tripton particles from the tributaries as well as sediment re-suspension during the mixing. In many lakes, SD is approximately one third of the depth of the photic zone (Horne and Goldman, 1994). Accordingly, the photic zone in the Megget Reservoir extends to an average depth of 10 m to 12 m during the winter mixing and summer stratification, respectively.

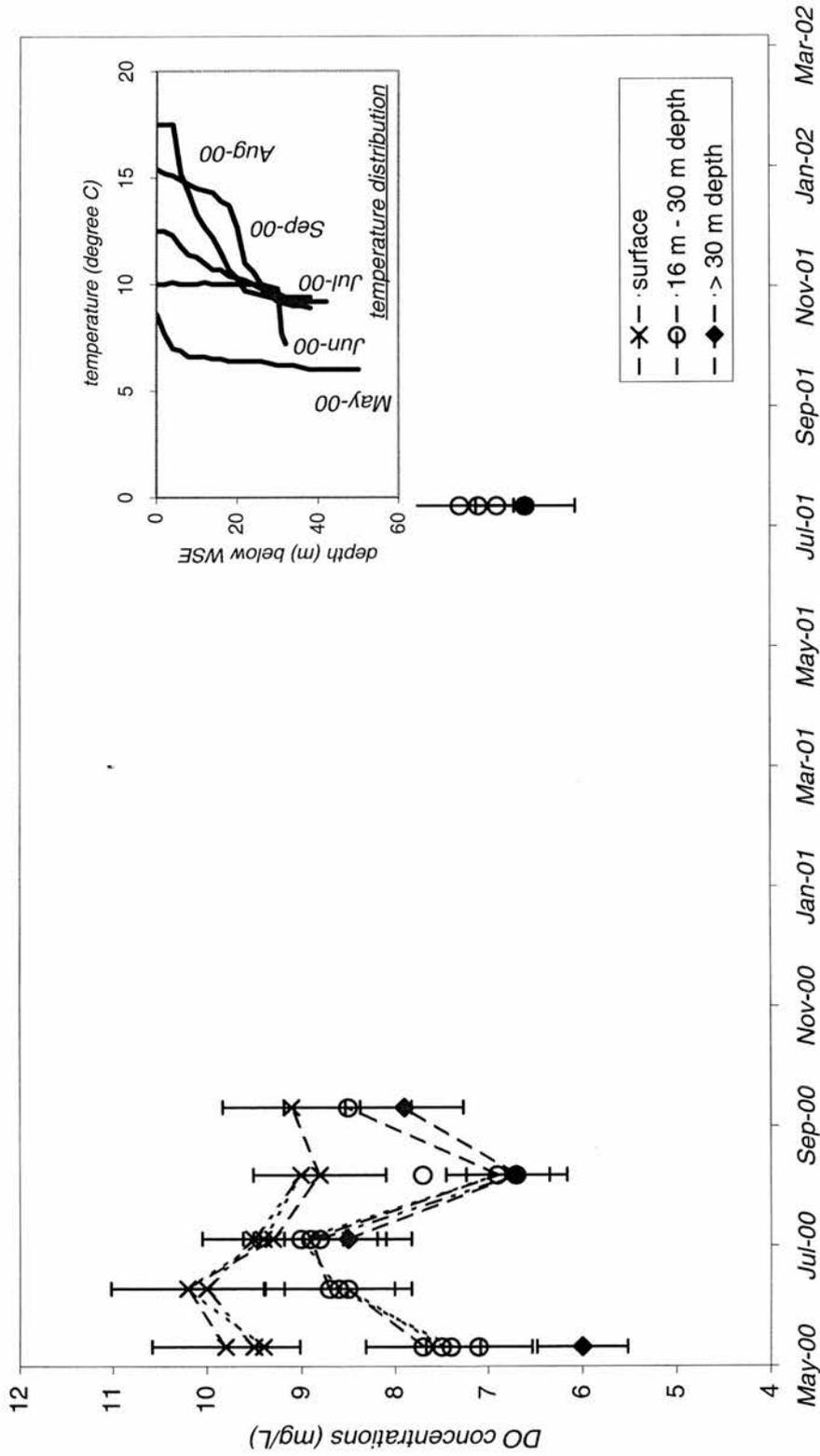


Figure 4. 8: Concentrations of dissolved oxygen (DO) in the water column of the Megget Reservoir as measured by the ESW laboratory. Error bars indicate the relative standard deviation (RSD) of the data. The inset shows the thermocline development during the sampling period.

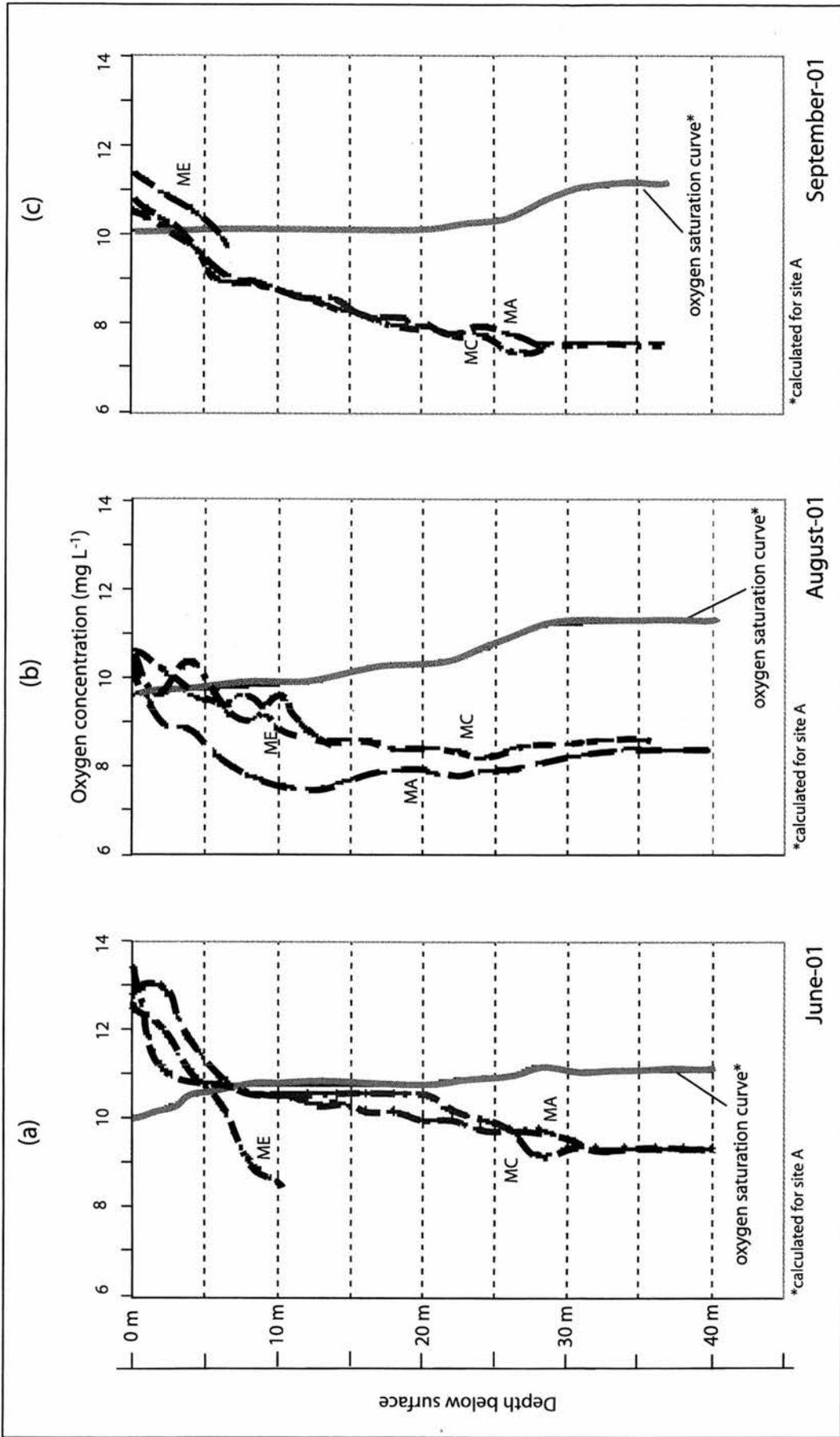


Figure 4. 9: Oxygen profiles measured at the three sampling sites during summer 2001.

*In-situ* dissolved oxygen (DO) profiles for the Megget Reservoir are only available for three sampling dates in summer 2001 and are displayed in *Figure 4. 9*. In addition, DO concentrations were measured in the laboratory as part of the regular sampling programme in summer 2000. Most laboratory results produced similar trends to those observed by field measurements in summer 2001, and the data are illustrated in *Figure 4. 8* together with the temperature distribution in the reservoir. The graphs show that distinct differences in DO concentrations between top and bottom waters develop during stratification and this phenomenon will be discussed in more detail using the field oxygen data. Oxygen profiles measured at three dates in summer 2001 are displayed in *Figure 4. 9* and show relatively orthograde (uniform) oxygen curves, although a tendency towards clinograde distributions (high concentrations in the epilimnion, decreases with depth) is apparent. Oxygen saturation concentrations were estimated for the three sampling dates, based on the temperature profiles of site A and using the nomograph given in Horne and Goldman (1994). The resulting depth-saturation curves are plotted as solid lines in *Figure 4. 9*. The graphs show that dissolved oxygen concentrations in the upper-well mixed waters of the epilimnion tend to track concentrations that are at equilibrium with air (i.e., saturation concentrations) mediated by exchange at the air-water interface. The saturation curves indicate that oversaturation occurs in the upper few meters of the water column reflecting the effect of photosynthesis. The reductions in DO seen in the upper waters during summer are largely attributable to the increase in temperature, which in cold water can account for loss of 50% dissolved oxygen content (Horne and Goldman, 1994). Undersaturation and progressive decrease of oxygen concentrations in the lower parts of the reservoir can be partly explained by temperature changes, but also reflects the demand of oxygen associated with natural respiration and oxidation

processes, such as decomposition of organic matter, which depletes the limited oxygen supply in the hypolimnion. However, bottom waters of the Megget Reservoir remained oxygenated throughout the summer period and development of anoxic (zero oxygen) conditions were not detected. The lowest oxygen concentrations were  $7.6 \text{ mg L}^{-1}$ , observed in the bottom waters of the reservoir towards the end of the stratification period in September.

Average nutrient concentrations for the Megget Reservoir are given in *Table 4. 6* and *Figure 4. 7*. Phosphorous is of fundamental importance as nutrient and major cellular constituent and is a common growth limiting factor for phytoplankton in aquatic systems because it is often present in low concentrations. Concentrations of total phosphorous (TP) found in the Megget Reservoir were very low, in most cases below the detection limit of  $10 \text{ } \mu\text{g L}^{-1}$ . When detected, concentrations ranged between  $11 \text{ } \mu\text{g L}^{-1}$  and  $26 \text{ } \mu\text{g L}^{-1}$ , falling in the typical range for oligotrophic to mesotrophic lakes (Vollenweider, 1982; Wetzel, 1975). Detectable concentrations were mainly found in the upper and middle parts of the water column, suggesting that catchment inputs are the main phosphorus source (rather than input from the sediments). On only four occasions TP was detected during the summer (growth) period and the relatively high TN:TP ratios ( $>10$ ) indicate a deficiency of phosphorous (Horne and Goldman, 1994). Similar behaviour was found for soluble reactive phosphorous (SRP) (measured between September 1999 and November 2000), which was generally not detectable ( $<5 \text{ } \mu\text{g L}^{-1}$ ) in the water column.

Nitrogen, as phosphorous, is a nutrient required in moderate quantities in the aquatic ecosystem and may become limiting for plant growth in the reservoir. Concentrations of nitrogen, measured in the form of total nitrogen (TN), ammonia ( $\text{NH}_4$ ) and nitrate

(NO<sub>3</sub>) were generally low in the Megget Reservoir, and show seasonal cycling typical for these elements. However, there appear to be some discrepancy in the data, related to different analysis techniques used for determination of the individual nitrogen species, causing concentrations of TN to be smaller than those measured for NO<sub>3</sub>. Ammonia concentrations (available for September 1999 to November 2000) in the water column are generally <0.02 mg L<sup>-1</sup> and could only be detected during the turnover period in autumn September 2000, when concentrations between 0.02 mg L<sup>-1</sup> and 0.06 mg L<sup>-1</sup> were observed. Nitrate concentrations range between 0.6 mg L<sup>-1</sup> and 1.0 mg L<sup>-1</sup> and, on average, are higher during the mixing period where NO<sub>3</sub> is mixed up from the hypolimnion and loading from precipitation and stream inputs exceeds uptake by algae. During summer stratification highest concentrations are found in the hypolimnion (0.9 mg L<sup>-1</sup>) while the lower concentrations (0.6 mg L<sup>-1</sup>) in the upper layers of the reservoir indicate uptake by algae. A similar trend is seen in the distribution of TN with low concentrations during the productive summer period (0.2 mg L<sup>-1</sup>) and higher concentrations (0.2-0.6 mg L<sup>-1</sup>) during autumn and winter.

## 4.5 Reservoir water quality -Spatial pattern

### 4.5.1 Temperature distribution

While strong vertical variations in temperature were observed, longitudinal temperature variations were small and did not show a consistent trend. Occasionally temperature differences between individual stations were measured but were less than 2°C and limited to the surface layer of the water column. Generally, temperatures were higher at the shallow parts of the reservoir, but the opposite case was also found.

Differences in stratification pattern were observed between the deeper sampling sites and those at the shallow end of the reservoir. The temperature distributions found at site C (*Figure 4. 4b*) are similar to those previously discussed for site A, while at site E (*Figure 4. 4c*), the temperature gradient is less well established and therefore stratification at this site is less stable and prone to disturbance by wind-induced mixing events.

#### 4.5.2 Water chemistry

Mean water chemistry data collected at the different reservoir sites during the sampling programme are listed in *Table 4. 7* and *Table 4. 8*. The data show no clear longitudinal gradients in water quality as is widely observed in other reservoirs (e.g., Effler and Bader, 1998) and a zonation of the reservoir into riverine, transition and lacustrine zone as suggested by Thornton (1990a) is not obvious from the collected data. However, systematic changes in the vertical distribution of elements such as Fe, Mn, SiO<sub>2</sub>, as well as DO and pH are observed during thermal stratification of the reservoir and have been discussed in the previous section.

### 4.6 Discussion

The spatial and temporal patterns in temperature distribution observed during monthly sampling at the Megget Reservoir are typical for monomictic water bodies, which develop thermal stratification during summer but remain mixed during the winter period. It is suggested that the observed inter-annual variability in thermocline depth and length of stratification period is attributable primarily to meteorological factors and variations in catchment runoff, but variations in reservoir operations (e.g., draw

down level) may also have an influence as was found to be the case at other reservoirs (Effler and Bader, 1998). However, the importance of the individual factors for the thermocline development in the Megget Reservoir remains unclear and more detailed investigations relating meteorological conditions, management operations and temperature distribution in the reservoir would be beneficial.

The regular sampling has shown that concentrations of major ions (Ca, Mg, K, Na, Cl, SO<sub>4</sub>) and alkalinity values in the reservoir waters are generally low and this would be expected given the base-poor nature of the Silurian bedrock of the catchment area. Concentrations of Ca average about 2.8 mg L<sup>-1</sup> and mean alkalinity values lie around 149 µEq L<sup>-1</sup>, indicating that the Megget Reservoir is a softwater system with limiting buffering capacity. Nutrient levels in the reservoir are also very low, in most cases below detection and the low concentrations may be limiting for phytoplankton growth during summer. Both, the low nutrient levels as well as the low chlorophyll-*a* content (0.091 mg L<sup>-1</sup> – 1.529 mg L<sup>-1</sup>) of the water indicate that the Megget Reservoir tends towards an oligotrophic system according to the trophic state classification system suggested by Vollenweider (1982).

Most distinct changes in reservoir water chemistry occur during the period of thermal stratification, where substantive vertical gradients in the distribution of DO, Fe, Mn, chlorophyll-*a* and pH develop, and concentration changes in these elements are often closely related.

During stratification oxygen is depleted progressively from the lower layers of the reservoir and this is linked to a decrease in pH with depth observed in the hypolimnion of the Megget Reservoir in summer. Both, oxygen depletion as well as

decrease in pH are mainly caused by respiration and decomposition processes (Effler and Bader, 1998; Wetzel, 1975), which usually control oxygen consumption and CO<sub>2</sub> release in the lower parts of the water column. CO<sub>2</sub> production resulting from microbial decomposition of organic material is particularly high near the sediment water interface, where organic material settles out from the water column. Accordingly, the sediment-water interface is also the zone of highest oxygen demand (Davison, 1993, Mortimer, 1942), where DO concentrations are lowest and anoxia is observed first. However, establishment of anoxia (absence of oxygen) in the hypolimnion of the Megget Reservoir has not been observed during the sampling programme, which suggests that the duration of stratification is insufficient to deoxygenise the bottom waters, as is often the case in lakes deeper than 30 m (Davison, 1993).

While depleted in the hypolimnion, oxygen oversaturation was observed in the upper meters of the water column due to increased photosynthetic O<sub>2</sub> production in the photic zone during summer, and pH values also increased owing to the photosynthetic uptake and utilisation of CO<sub>2</sub> in excess of inputs from respiration. The pH peak observed in July 2000, for example, is coincident with a chlorophyll-*a* maximum. This chlorophyll-*a*-pH relationship is relatively well established at site A and can also be seen at site C. No such relationship is found at the shallow end of the reservoir, suggesting that other factors, such as tributary inflow may be controlling pH variations in this part of the reservoir, although the available chlorophyll-*a* data are too limited to allow more detailed conclusions.

Distinct seasonal cycling is seen in the chlorophyll-*a* concentrations of the Megget water reflecting the annual growth cycle of phytoplankton. Concentrations are lowest during the mixing period, distributed uniformly throughout the water column, but increase in spring when environmental conditions for phytoplankton growth become more favourable. The resulting increase in biomass not only affects the chlorophyll-*a* content of the water column, but also mediates pH and O<sub>2</sub> content in the upper layers of the water column as was seen before. It is also responsible for the observed decline in silica levels, which is required in large quantities by diatoms as it makes up 25% to 60% of the dry weight of their cells (Horne and Goldman, 1994).

It has further been shown that, despite of the oxygenated conditions in the hypolimnion, Fe and Mn accumulate in the lower layers of the reservoir during stratification, which suggests that processes like dissolution of Fe and Mn oxyhydroxides at the sediment water interface or release from the sediment are occurring. The high proportion of filterable Fe observed in the water column is somewhat surprising, but results from various studies as discussed in Davison and DeVitre (1992) and Davison (1993), using electron microscopic techniques, ultrafiltration, and use of ion exchange resins have indicated that not all filterable Fe or Mn is necessarily Fe<sup>2+</sup> and Mn<sup>2+</sup> and that 'dissolved' Fe (<1 μm) is predominantly present as negatively charged colloids, which may or may not be associated with humic substances. A similar size range was found by Tipping *et al.* (1981) who observed that much of the ferric oxyhydroxides in the water column of Esthwaite Water were present as amorphous particles with mean diameters in the range of 0.05-0.5 μm. Many substances, like humic and tannic acids, surfactants, inorganic ions, silicate and phosphate are capable of stabilising these colloids in the water column

(Cameron and Liss, 1984) and laboratory experiments have indicated that aggregation rates of Fe colloids produced by natural oxidation processes can be slow where adsorption of humic substances occurs (Tipping and Ohnstad, 1984), which may explain their prolonged (and abundant) presence in the water column of the reservoir. Therefore, it can be anticipated that the high proportion of filterable Fe found in the water column of the reservoir is indicative of Fe in colloidal form (stabilised by association with humic substances), small enough to pass through 0.45  $\mu\text{m}$ -sized filters, rather than of 'truly dissolved', electroactive  $\text{Fe}^{2+}$  species. Laboratory experiments with reservoir water and sediments, discussed in Chapter 8, indicate that this hypothesis is true for Fe but not entirely for Mn. The comparatively low proportion of filterable Mn present in the water column of the Megget Reservoir indicates that much of the dissolved Mn entering the system is rapidly removed from the water column through (microbially mediated) oxidation processes (Davison, 1993) or incorporation into living biomass (Hsiung and Tissue, 1994), but high Mn concentrations accumulate in the hypolimnion of the reservoir during summer stratification.

Despite the generally low Fe and Mn content of the water column, hypolimnic Fe and Mn reach high concentrations during late summer/early autumn prior to mixing of the reservoir. While the observed concentrations still fulfil the requirements set by the WHO (Fe = 300  $\mu\text{g L}^{-1}$ ; Mn = 500  $\mu\text{g L}^{-1}$ ) (WHO, 1993), they may cause problems where drinking water standards are based on the stricter EC regulations (Fe = 200  $\mu\text{g L}^{-1}$ ; Mn = 50  $\mu\text{g L}^{-1}$ ) (CEC, 1980), as is the case in Scotland.

Vertical turbidity gradients developed during reservoir stratification and have been reported in other studies (Blösch, 1995; Effler *et al.* 1998a). A variety of possible causes have been suggested for the gradients, including near-shore re-suspension and sediment focusing (Blösch, 1995), internal seiche motion, density underflows and local re-suspension (see Effler *et al.* 1998a for references). Given the complexity of (sediment) transport processes the data collected during routine sampling are insufficient to identify the causes of the observed turbidity gradient. Thus, the origin of the observed gradient will remain unresolved, though contributions from one or more of the above processes are likely.

The overall increase in turbidity and colour observed during the mixing period and the decrease in transparency (SD) are attributed to inputs of organic matter and fine sediments from the tributaries, rather than from increase in biomass, but sediment re-suspension may at least in part be responsible for introducing fine sediment particles (tripton) into the water column. One may argue that increased biomass production may also have contributed to the observed decrease in transparency, and SD is often used as an indicator of chlorophyll-*a* contents in the water column as significant inverse correlations between both parameters have been repeatedly observed (Vollenweider, 1982). However, SD not only depends on the biomass (biotic light extinction) present in the water column, but is also dependent on colour and mineral turbidity. Based on the fact that transparency of the water was higher during summer when phytoplankton productivity and chlorophyll-*a* contents should be highest, two conclusions can be reached:

- (1) Biomass and phytoplankton productivity in the reservoir during summer are low (also seen by low chlorophyll-*a* content)

- (2) Factors other than phytoplankton are important in regulating water clarity of the reservoir, for example tributary inputs of organic particles or re-suspension of tripton particles (Owens, 1998).

Two different methods were used to measure dissolved oxygen (DO) concentrations in the water column of the reservoir: *in-situ* measurements and laboratory analysis. While both methods showed similar trends in DO distribution, the absolute DO values differed, and the relative standard deviation (RSD) of nearly 9%, calculated from replicate samples indicated a relatively high sampling error associated with the laboratory method. This discrepancy is probably caused by the sampling method applied in this study, and two potential error sources can be identified: (1) Sample collection using the hydraulic pump may promote aeration of the sample and oxygen exchange in the sampling hose, and (2) further alterations in the DO content of the sample may have resulted from photosynthetic/respiratory processes in the sample bottles during transport to the ESW laboratory. It is therefore concluded that *in situ* sampling methods are more appropriate for the determination of DO concentration.

## 4.7 Summary

Monthly sampling was carried out on three sites at the Megget Reservoir between September 1999 and December 2001 and various physical and chemical parameters were determined. The data show that the Megget Reservoir exhibits a monomictic stratification cycle and can be classified as an oligotrophic system, low in nutrient and

chlorophyll-*a* content. The relatively low alkalinity and base cation (Ca, Mg, Na, K) content of the water indicates a limited buffering capacity with respect to pH changes.

Temporal variations in reservoir water chemistry are closely linked to the thermal properties of the water body. Summer stratification is the most important event in the reservoir's annual cycle, as it promotes the development of substantive vertical concentration gradients, illustrated by a number of chemical determinants.

During stratification oxygen is depleted progressively from the lower layers (hypolimnion) of the reservoir, due to decompositional processes near the sediment-water interface associated with a decrease in pH. Although establishment of hypolimnic anoxia has not been observed in this study, release from the sediment-water interface and built up of high concentrations of Fe and Mn in the bottom waters during the stratification period was apparent. In the upper water column (epilimnion) of the reservoir a decrease in nutrient concentrations and SiO<sub>2</sub> content is observed during summer stratification caused by restricted water mixing, but mainly due to increased uptake of these elements by biota. The increased primary productivity is also apparent from the rise in chlorophyll-*a* levels in the upper water layers as well as from high pH values and oxygen supersaturation, which are related to high rates of photosynthesis.

Catchment runoff also affects the reservoir quality. Increased loading of organic matter and fine sediments in the streams during autumn and winter may contribute to the overall increase in turbidity and colour observed during the mixing period.

However, processes of sediment re-suspension may at least in part be responsible for introducing fine sediment particles into the water column.

The study has further shown that Fe and Mn contents in the water column are generally low, but during summer stratification high concentrations built up in the bottom waters of the reservoir, regularly exceeding the drinking water requirements set by the EC (CEC, 1980). This could have important implications for the future management of reservoir use on a daily basis and especially during times of excessive draw down.

# 5

## Stream Water Quality

---

In the following chapter the findings from regular stream sampling are summarised and strategies and methodologies of sample collection are described. Sample collection followed the procedures given in Appendix I, while the analysis of the samples was carried out using the methods described in Section 4.2 and in Appendix II.

### 5.1 Sampling design and methods

Stream water samples were collected from the six streams that supply the Megget Reservoir: Winterhope Burn (MF), Meggethead (MG), Linghope Burn (MH), Cramalt Burn (MI), Craigierig Burn (MK) and Shielhope Burn (MJ) (*Figure 5. 1*). Collection sites at these streams were located in relatively straight channel reaches, close to the inflow mouth into the reservoir but upstream of the stream sections that are affected by fluctuations of the reservoir water level. Where possible, samples were taken midstream. At gauged streams, sampling sites were located near the gauging stations.

The determination of appropriate sampling sites and frequencies and the selection of the parameters to be determined were based on the objectives to monitor background levels of the stream water chemistry as well as to investigate the temporal and spatial variability of water composition in the aquatic environment. Although limited in respect of the dynamics of extreme events, it was envisaged that the regular sampling would

highlight significant changes related to changing runoff conditions in the catchment area.

Regular stream sampling was carried out between October 1999 and December 2001. Initially water samples from all streams were collected on a monthly basis, but in September 2000 this was increased to fortnightly sample collection at Shielhope Burn, Winterhope Burn and Linghope Burn, to provide better coverage of the temporal variability in stream chemistry related to runoff variations.

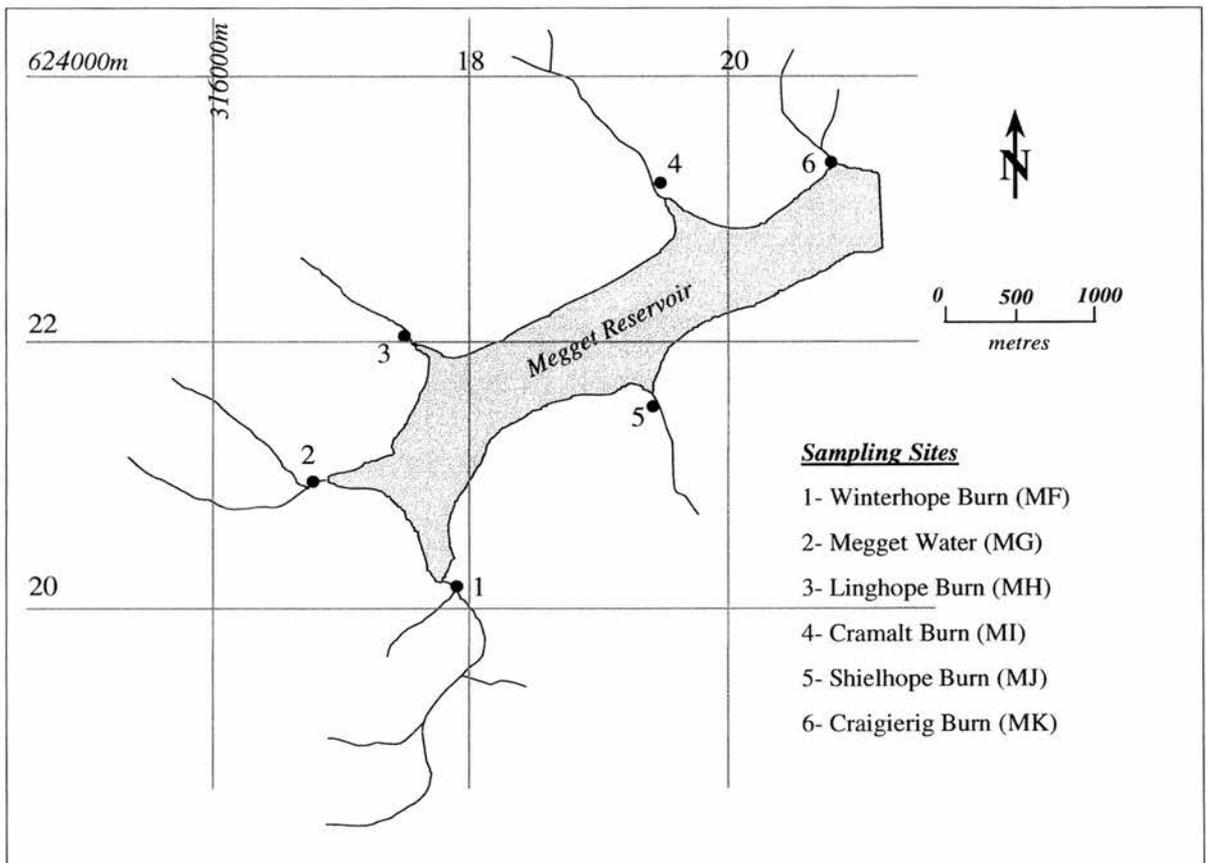


Figure 5. 1: Map of regular stream sampling sites in the Megget catchment

A second, more intensive sampling programme was undertaken between 16 October and 30 October 2000, as detailed in Chapter 6, where samples were collected on selected streams at 2-4 hourly intervals. The main objective of this intensive sampling

period was to investigate flow-related variations in stream chemistry during individual storm events and periods of increased stream runoff.

Problems encountered during the sampling programme were mainly related to weather conditions (snow and strong winds), which impeded access to the catchment (e.g., in January 2000) and/or to individual sampling sites (e.g., Shielhope Burn). Furthermore, it was necessary to make adjustments to the initial sample analysis suites due to financial concerns of the ESW laboratory and changes in the sample handling procedure will be pointed out later in this chapter. Most importantly, however, was a nation-wide outbreak of Foot and Mouth disease in the UK, which occurred during the sampling period and resulted in a general ban on fieldwork. As a consequence, access to the Megget catchment was denied from February 2001 onwards. Limited access to the area was re-gained in mid June 2001 but the area around the reservoir remained closed off and the stream sampling programme had to be postponed until the issue was resolved in August 2001. An overview of all sampling dates for the regular sampling is given in *Figure 5. 2*.

### 5.1.1 Sample collection and analysis

Stream samples were collected at each sampling site by immersing the clean hand-held bottle into the flow. Prior to collection of each sample the sample bottle was thoroughly rinsed with stream water. Samples for the analysis of general chemistry were taken in clean 1 L polyethylene bottles while metal samples were collected in clean 250 mL polyethylene bottles. Initially, an additional sample was collected for the analysis of the chlorophyll-*a* content of the water, but the collection was terminated after no significant chlorophyll-*a* levels could be detected. At each sampling site stream water temperature,

air temperature and conductivity of the water were measured at the time of sample collection.

Samples collected for analysis of dissolved metals were filtered and preserved with concentrated AristaR grade nitric acid to suppress precipitation of the metals or sorption. This was initially done at the reservoir boathouse, immediately after sample collection, by filtering a 20-ml sub-sample into small vials using a syringe and disposable 0.45µm pore diameter filter disks. Both, the filtered and the unfiltered sample were then acidified to 1 %-vv with concentrated AristaR grade nitric acid. This was necessary to lower the pH of the sample to pH 1-3, which is sufficient to prevent the precipitation of iron and other metals (Golterman *et al.* 1983) as well as metal adsorption to the walls of the storage container. Due to time limitations and because of the high degree of cleanliness, which is required in sample handling and is difficult to achieve in the field, it was later agreed with ESW that filtration and preservation of the metal samples would be undertaken by the ESW laboratory immediately after admittance of the samples. In doing so, the turn around time between sample collection in the field and delivery to the laboratory could be reduced from 4-5 hours to 3-4 hours. No preservation was applied to the 1 L water samples. The ESW laboratory performed a full suite of analysis on the samples including pH, conductivity, turbidity, major cations (Mg, Ca, K, Na) and anions (Cl, SO<sub>4</sub>, NO<sub>3</sub>), nutrients (TP, TN, SRP, NH<sub>4</sub>), dissolved and total metals (Fe, Mn, Cu<sup>1</sup>), TOC and SiO<sub>2</sub>. However, during the sampling programme some modifications of the original analysis suite were required resulting in a reduced parameter set (see Chapter 4, *Table 4.1*), and related issues of data quality, data completeness and delivery of results have already been discussed in Section 4.2.2.

---

<sup>1</sup> Only total concentrations analysed.

Chlorophyll-*a* samples were stored in liquid nitrogen and taken to the Gatty Marine Laboratory at St Andrews where they were kept in the deep freeze (-81°C) prior to processing by *High Performance Liquid Chromatography* (HPLC).

Further details on sampling procedures are given in Appendix I and sample preparation and analysis followed the procedures described in Section 4.1 and 4.2 and in Appendix II and IV, respectively.

### 5.1.2 Stream flow monitoring and discharge calculations

A separate study was undertaken, beginning in August 2000, to measure stream flow variations at three tributaries in the catchment area. This included continuous stage recording as well as measurements of channel morphology and velocity under different runoff regimes.

Three initial sites were chosen for monitoring stream levels at Linghope Burn, Winterhope Burn and Meggethead. At each site automatic depth level recorders developed by ISODAQ Systems Limited were installed in stilling wells and stream stage was recorded at 30-minute intervals. Additionally, the data logger installed at Winterhope Burn was provided with dual channel capability, and a stream temperature sensor was employed to work alongside with the pressure transducer.

During the project, the water level of the reservoir rose significantly, so that the reservoir body affected the stage measurements at the Linghope Burn site. The site, therefore, had to be abandoned in October 2000 and the depth level recorder was moved to Shielhope Burn in November 2000.

Relevant findings of this study have been presented in Chapter 3, and a complete discussion of the results as well as further information and technical details on stream flow measurements are provided in Grzybowski (2001).

In this study, stage-discharge ratings and stage measurements recorded at the three streams were used to determine the discharge characteristics during the sampling period. To estimate discharge at the ungauged streams, a variety of different approaches were attempted, but the best results were obtained by using the simple catchment area to stream flow ratio (Eq 5. 1). Generally it was assumed that the discharge time series in the gauged catchments was similar to that in the ungauged catchments, and discharge at the ungauged sites was then calculated from the gauged flows at Winterhope Burn weighted by catchment area, using the following relationship:

$$\frac{flow_{ungauged}}{A_{ungauged}} = \frac{flow_{gauged}}{A_{gauged}} \quad (\text{Eq 5. 1})$$

where  $A$  represents the catchment area of the gauged and ungauged sites, respectively. This method is undoubtedly an over-simplification and comparison of calculated discharge data with measured flow data available in Appendix V for Linghope Burn and Meggethead showed that discharge is clearly overestimated by the method, in particular under high flow conditions. However, the comparison also shows that the general runoff trends are well captured by the calculated data, and since relative changes are the important factor in the current application rather than absolute values, these simple discharge calculations were found to be sufficient for the purpose of this study, although

some uncertainty remains in the hydrological response of the different streams, in particular during storm events.

## 5.2 Summary of data collected

A summary of the collected data is provided in *Table 5.1*, *Table 5.2* and *Table 5.3* as well as in *Table 6.2* and chemical analysis methods are outlined in Chapter 4 and in Appendix II.

<u>Sampling Programme</u>	<u>Sampling period</u>	<u>Sampling interval</u>	<u>Sampling sites</u>	<u>no of samples per site</u>
<i>Regular Sampling</i>	October 1999 - December 2001*	monthly	All	18-32
	September 2000 - December 2001*	Fortnightly	Winterhope Burn, Linghope Burn, Shielhope Burn	
<i>Initial survey</i>	17 August 2000	once	Winterhope Burn, Linghope Burn, Peaty Muckle Burn, Black Burn	1-3
<i>Intensive sampling</i>	16-(23) 30 October 2000	2-hourly, 4-hourly	Shielhope Burn, Winterhope Burn, Peaty Muckle Burn	53-70
	16-(23) 30 October 2000	1-3 samples per day	Linghope Burn, Black Burn	14-25

\* *sampling programme interrupted from Feb-01 to Aug 01 due to fieldwork ban*

*Table 5.1: Sampling undertaken during the different sampling programmes*

*Table 5.2* and *Table 5.3* summarise the results from the regular sampling programme between September 99 and December 2001 for all six streams. From these data comparisons between the chemical compositions of the sampled streams can be made

and temporal variations in stream chemistry during the monitoring period can be considered.

As the sampling intervals differ between Winterhope Burn and Linghope Burn on the one hand, and Megget Water, Cramalt Burn and Craigierig Burn on the other hand there are limitations in comparing the results directly, but a number of conclusions can be made. For the streams Winterhope Burn, Shielhope Burn and Linghope Burn, sampled during both programmes, the range of most solutes is wider during the intensive sampling in October 2000 than during the regular sampling programme, probably because of the more frequent sampling, during which 2-5 storm events of intermediate intensity were covered.

The data collected during the regular sampling include a wide range of hydrological conditions and, despite their relatively low temporal resolution, allow some insight into the response of the individual catchments to changing hydrological conditions. Low flow conditions were sampled on 24 July 2000 following a dry summer period; highest flows occurred on 4 December 2000 where sampling was carried out during a period of prolonged and heavy rainfalls. Most of the time samples were collected during smaller rainfall events or in between high rainfall events. Where samples were taken during or shortly after major storm events or prolonged rainfalls (21 August 2000, 19 September 2000, 05 October 2000, 16 August 2001, 02 October 2001, 17 October 2001 and 05 December 01) the changes in stream chemistry were considerable although discharge varied widely for each sampled event. On some occasions changes in stream discharge

Catchment	Colour °Hazen	Cond µS/cm	pH	Alk** µEq/l	Turb NTU	Mn (filt.) µg/l	Mn µg/l	Fe (filt.) µg/l	Fe µg/l	Al ** (filt.) µg/l	Al** µg/l	Zn** µg/l	Cu* µg/l
<i>Meggethead</i> <sup>(m)</sup>	Minimum	29	6.3	67	0.0	3	4	18	28	20	24	0.0	1.6
	Maximum	51	7.9	346	2.9	29	31	188	366	178	299	4.8	4.9
	Mean	17	7.3	226	0.3	5	7	70	101	48	61	2.8	3.3
<i>Cramalt Burn</i> <sup>(m)</sup>	Minimum	4	6.4	165	0.0	2	2	13	22	16	18	0.0	1.0
	Maximum	48	8.0	362	3.5	13	11	122	205	54	86	3.3	6.5
	Mean	11	7.3	260	0.2	4	5	43	64	29	39	2.3	3.2
<i>Craigierig Burn</i> <sup>(m)</sup>	Minimum	6	6.8	198	0.0	3	3	25	34	18	19	0.0	1.8
	Maximum	41	7.8	1526	1.5	8	16	135	236	108	198	4.5	9.9
	Mean	17	7.4	573	0.2	4	6	59	82	36	56	1.6	4.8
<i>Linghope Burn</i> <sup>(l)</sup>	Minimum	2	6.5	83	0.0	1	1	4	11	12	14	0.0	1.9
	Maximum	42	8.0	395	4.3	18	23	138	505	183	437	4.2	9.7
	Mean	9	7.3	262	0.3	2	4	26	62	35	56	2.2	5.5
<i>Shielhope Burn</i> <sup>(l)</sup>	Minimum	18	6.2	51	0.0	4	7	41	42	16	34	0.0	1.6
	Maximum	176	7.7	428	2.4	31	46	495	592	257	286	19.5	8.4
	Mean	66	7.1	203	0.6	14	18	209	253	105	137	4.6	3.8
<i>Winterhope Burn</i> <sup>(l)</sup>	Minimum	10	6.3	51	0.0	1	1	30	19	11	14	0.0	1.1
	Maximum	80	7.7	280	3.0	25	31	295	496	123	150	11.2	8.0
	Mean	33	7.2	157	0.4	9	14	145	211	55	95	3.3	4.1

Table 5. 2.; Summary of stream chemistry for regular ( <sup>(m)</sup>-monthly, <sup>(l)</sup>- fortnightly) sampling programme (September 1999 – December 2001) [Parameters were only included: \* until October 2000, \*\* from October 2000 onwards; † after October 2000 calculated from colour values]

Catchment	TSS** mg/l	Mg mg/l	Ca mg/l	SiO <sub>2</sub> mg/l	Na* mg/l	Cl* mg/l	K* mg/l	TOC <sup>†</sup> mg/l	SO <sub>4</sub> mg/l	TP µg/l	SRP** µg/l	TKN* mg/l	NO <sub>3</sub> * mg/l
Meggethead	Minimum	0.0	0.5	1.1	1.83	2.41	3.8	0.20	1.5	0	0	0.1	0.0
	Maximum	12.5	1.7	5.2	6.47	3.84	6.4	0.65	8.5	27	21	0.5	0.7
	Mean	1.7	1.3	3.5	4.60	3.35	4.8	0.38	3.1	4	1	0.2	0.3
Cramalt Burn	Minimum	0.0	0.6	1.2	1.97	2.40	4.0	0.23	1.1	0	0	0.0	0.0
	Maximum	10.0	3.5	5.4	6.70	3.88	6.0	1.30	7.8	14	7	0.5	0.8
	Mean	1.6	1.5	3.9	5.03	3.46	4.9	0.51	2.0	2	1	0.2	0.3
Craigierig Burn	Minimum	0.0	1.5	4.0	2.86	4.18	4.2	0.30	1.5	0	0	0.1	0.4
	Maximum	8.0	3.6	9.4	7.15	5.10	7.0	1.75	6.0	26	5	0.5	1.6
	Mean	1.3	2.9	7.5	5.87	4.71	5.3	0.55	2.8	4	1	0.3	0.8
Linghope Burn	Minimum	0.0	0.7	1.3	2.59	2.51	4.1	0.28	0.7	0	0	0.0	0.0
	Maximum	17.0	3.6	5.4	7.36	3.82	5.4	1.60	7.3	29	21	0.6	0.8
	Mean	1.1	1.6	3.9	5.45	3.47	4.6	0.52	1.8	3	1	0.1	0.3
Shielhope Burn	Minimum	0.0	0.5	0.9	2.08	2.23	3.3	0.20	3.0	0	0	0.1	0.0
	Maximum	9.0	2.3	5.7	7.49	4.52	7.7	0.72	22.9	33	9	0.6	0.4
	Mean	0.6	1.4	3.0	4.68	3.56	4.8	0.40	8.9	8	1	0.3	0.1
Winterhope Burn	Minimum	0.0	0.5	0.9	0.83	2.13	3.1	0.17	2.0	0	0	0.1	0.0
	Maximum	11.0	3.0	5.4	6.57	4.15	7.2	0.83	10.8	33	9	0.4	0.5
	Mean	1.3	1.1	2.7	3.30	3.19	4.2	0.37	5.0	4	1	0.2	0.1

Table 5. 3 Summary of stream chemistry for regular ( <sup>(m)</sup>-monthly, <sup>(f)</sup>- fortnightly) sampling programme (September 1999 - December 2001) [Parameters were only included: \* until October 2000, \*\* from October 2000 onwards; <sup>†</sup> after October 2000 calculated from colour values]

were not dramatic, but significant changes were noted in stream chemistry, and this occurred where samples were collected during lower flow events following dry periods (24 November 1999). A number of large rainfall events were sampled in more detail during the intensive sampling programme (18 - 30 October 2000), but these data are not considered here and will be discussed in Chapter 6.

### **5.3 Stream hydrochemistry -Temporal patterns**

Temporal patterns in stream chemistry show seasonal variations typical for many Scottish upland catchments and are best illustrated by assessing changes in pH, conductivity, alkalinity and colour in the individual streams, as shown in *Figure 5. 4* and *Figure 5. 5* as well as their relation to flow (*Figure 5. 8*). The graphs show that average pH, conductivity and alkalinity values in the stream water are highest during summer periods and periods of little rainfall, where stream flow is dominated by baseflow from deeper mineral soil and groundwater sources. When rainstorm frequency and thus stream flow, increases depression of those parameters is observed, indicating the higher contribution of acidic, base-poor surface and subsurface flow to the stream runoff. Minimum pH values observed during the regular sampling programme ranged between pH 6.2-6.8 and show the streams are relatively well buffered compared to other upland catchments (Giusti and Neal, 1993; Billet and Cresser, 1996), most likely due to base-rich groundwaters.

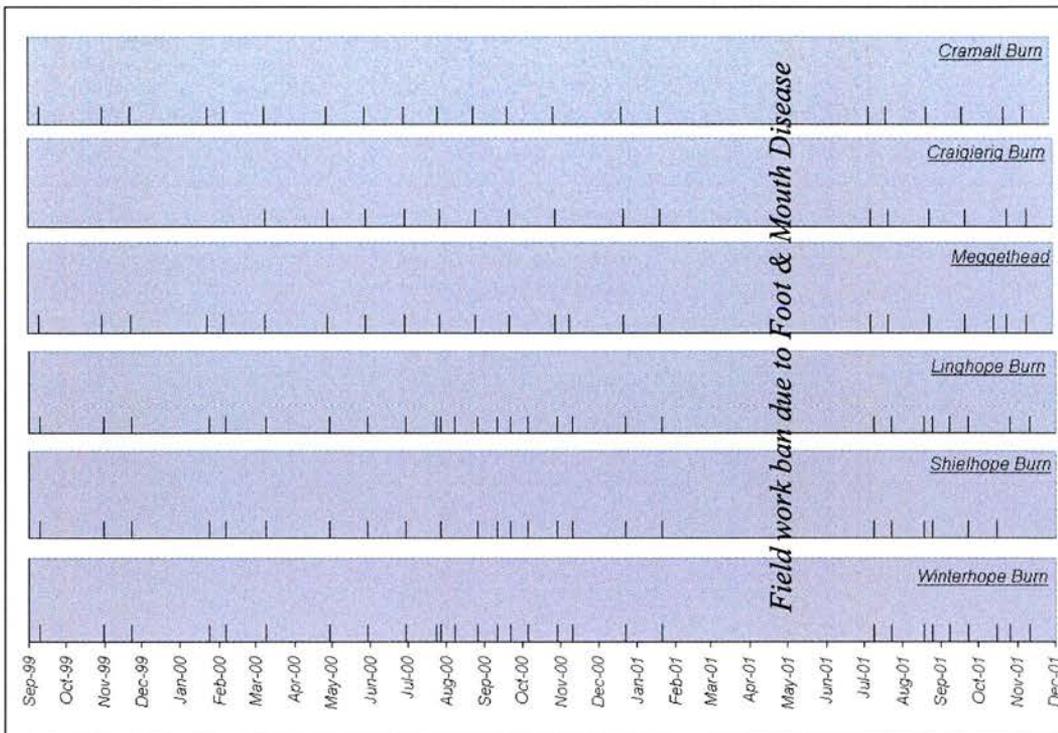


Figure 5.2: Sampling frequency during regular sampling programme (September 1999 to December 2001).

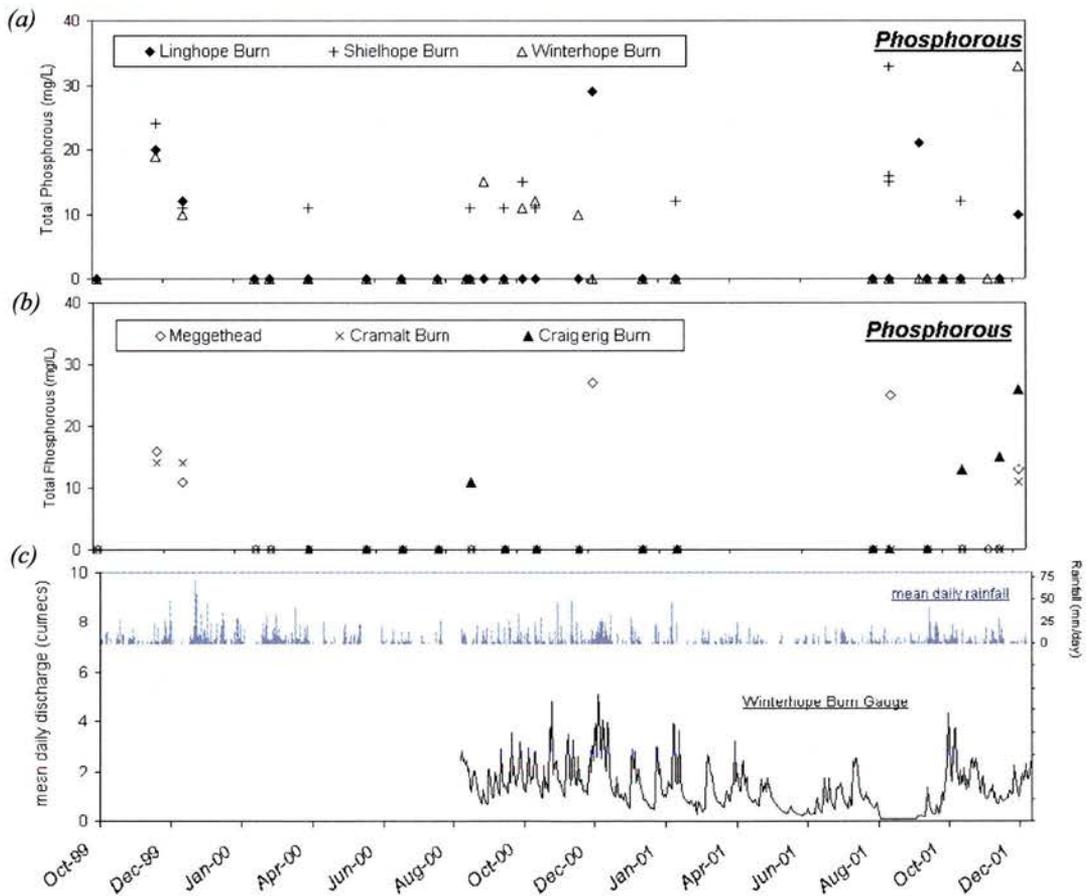


Figure 5.3: (a-b): Plots of monthly stream water TP concentrations during regular sampling programme at all six streams. (c): daily rainfall and discharge for Winterhope Burn.

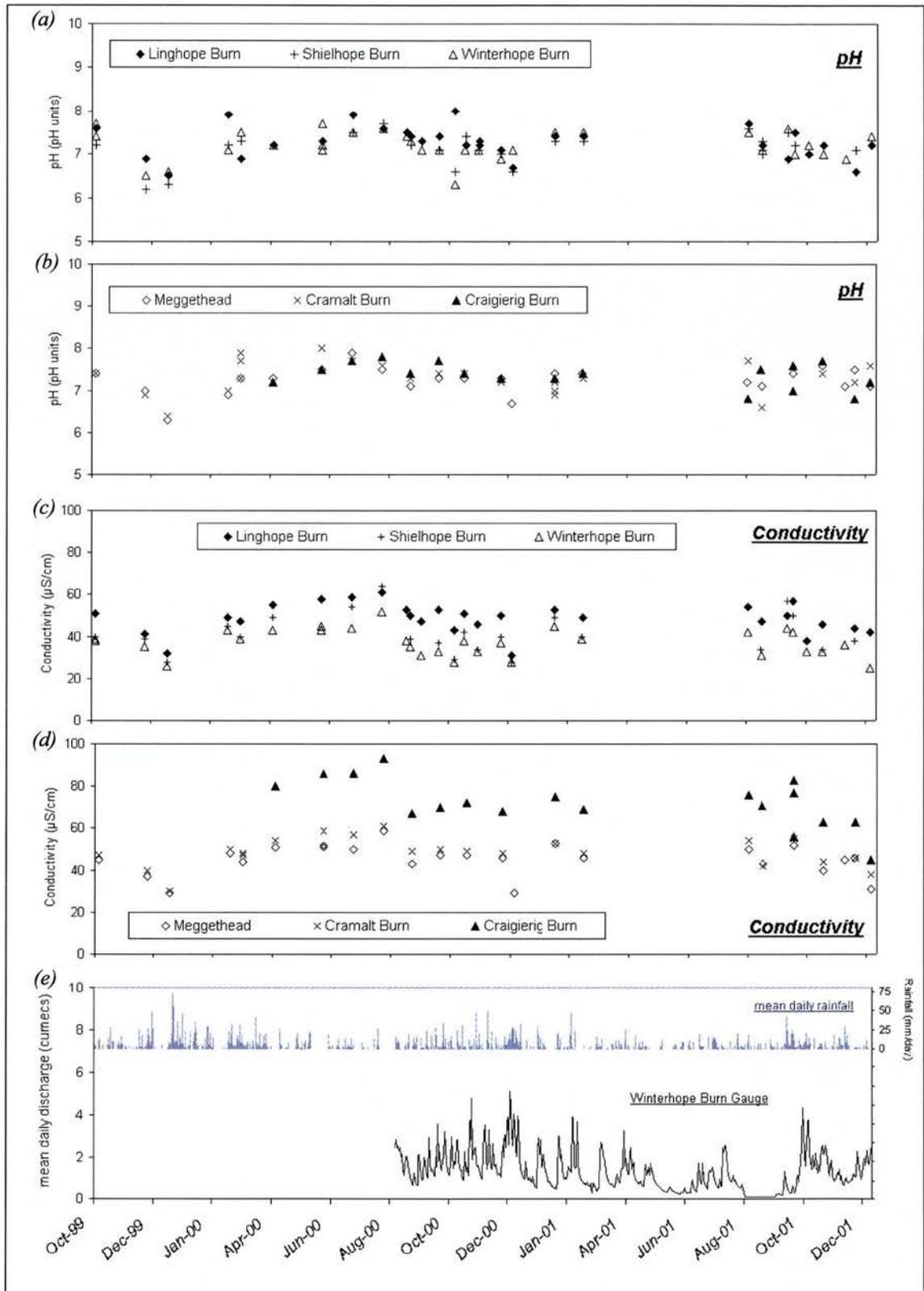


Figure 5.4: (a-d): Plots of monthly (fortnightly) stream water pH and conductivity levels during regular sampling programme at all six streams. (e): daily rainfall and discharge for Winterhope Burn.

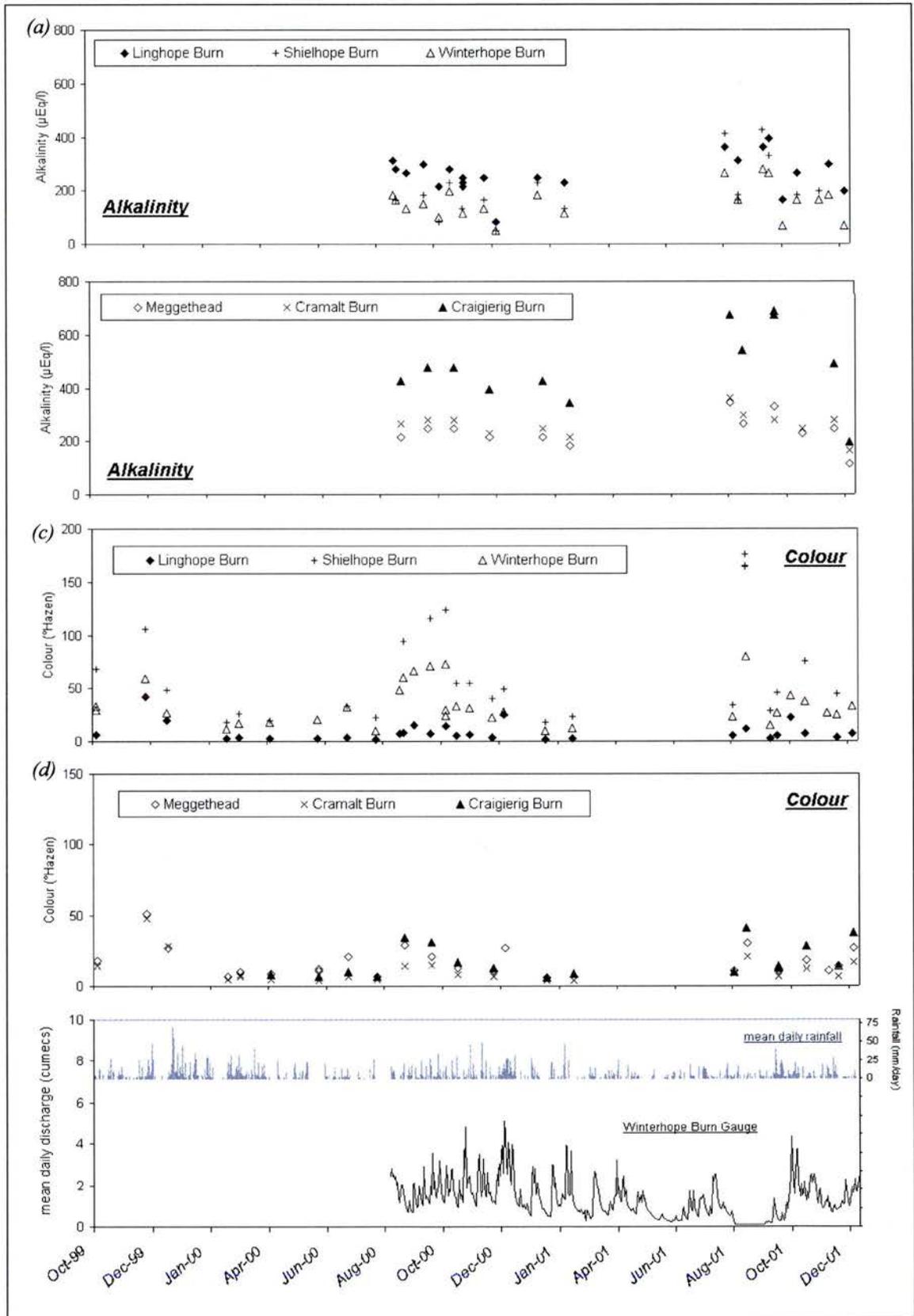


Figure 5.5: (a-d): Plots of monthly (fortnightly) stream water alkalinity and colour values during regular sampling programme at all six streams. (e): daily rainfall and discharge for Winterhope Burn.

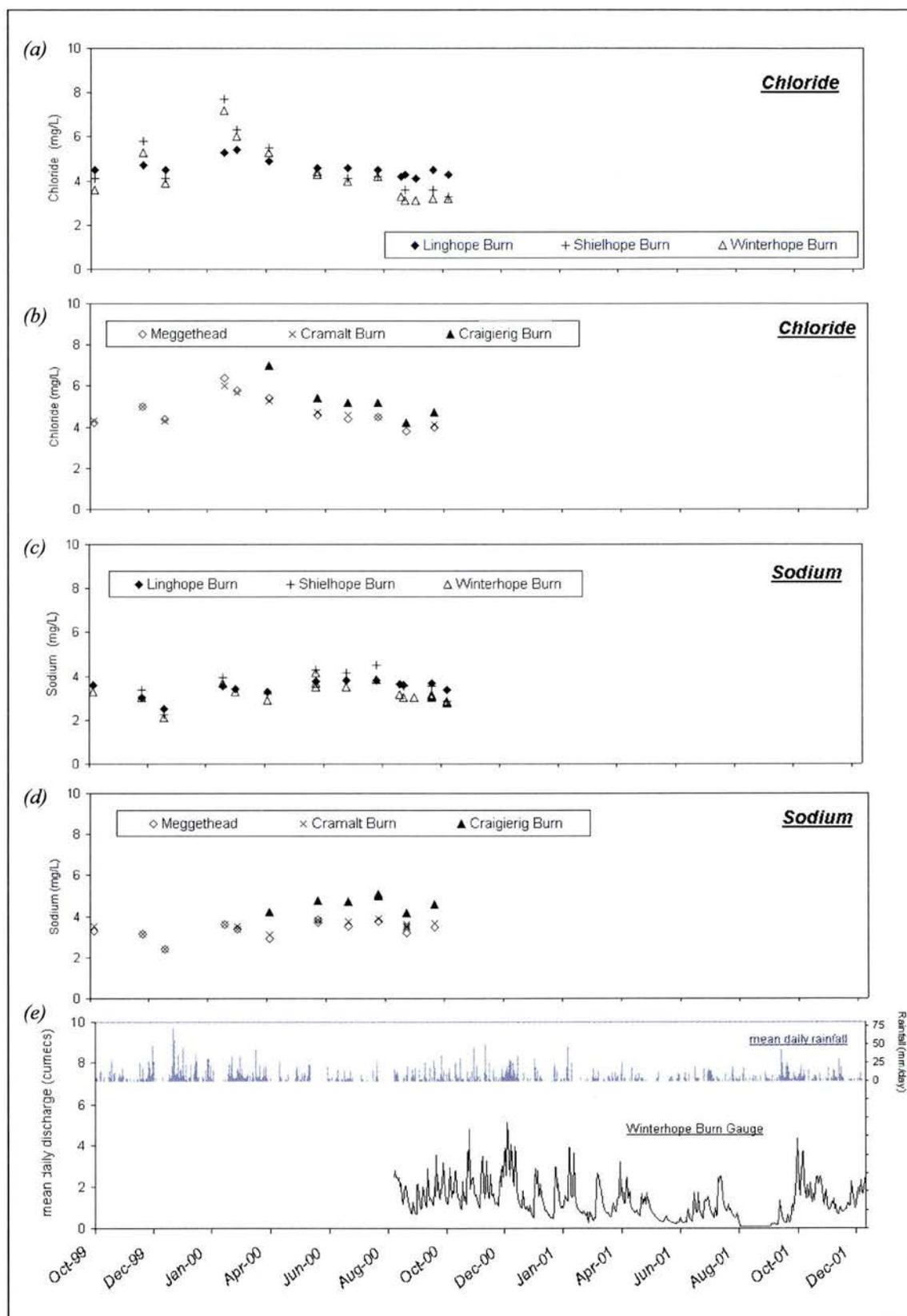


Figure 5.6: (a-d): Plots of monthly stream water Na and Cl levels during regular sampling programme at all six streams. (e): daily rainfall and discharge for Winterhope Burn.

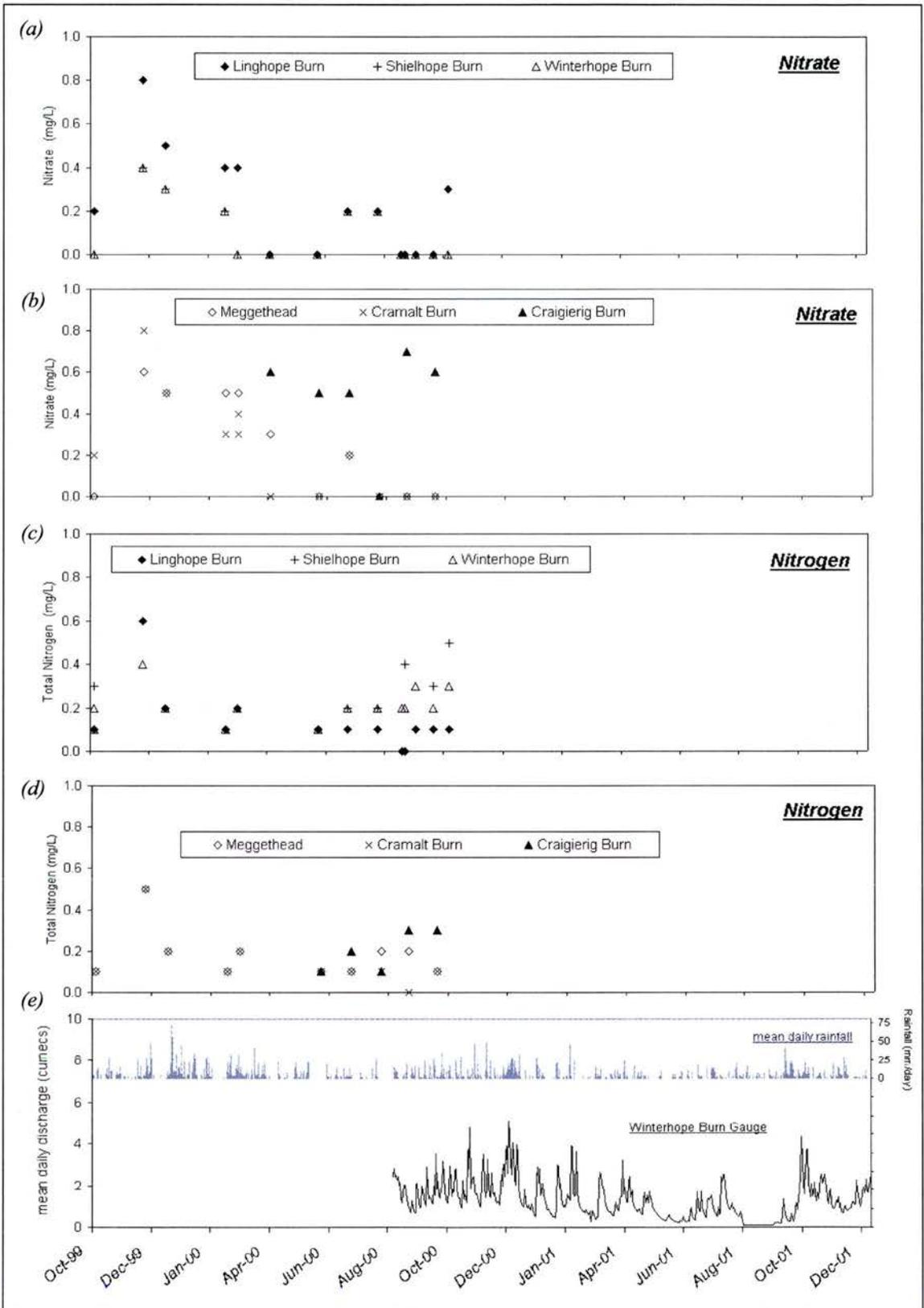


Figure 5.7: (a-d): Plots of monthly stream water  $\text{NO}_3$  and TN concentrations during regular sampling programme at all six streams. (e): daily rainfall and discharge for Winterhope Burn.

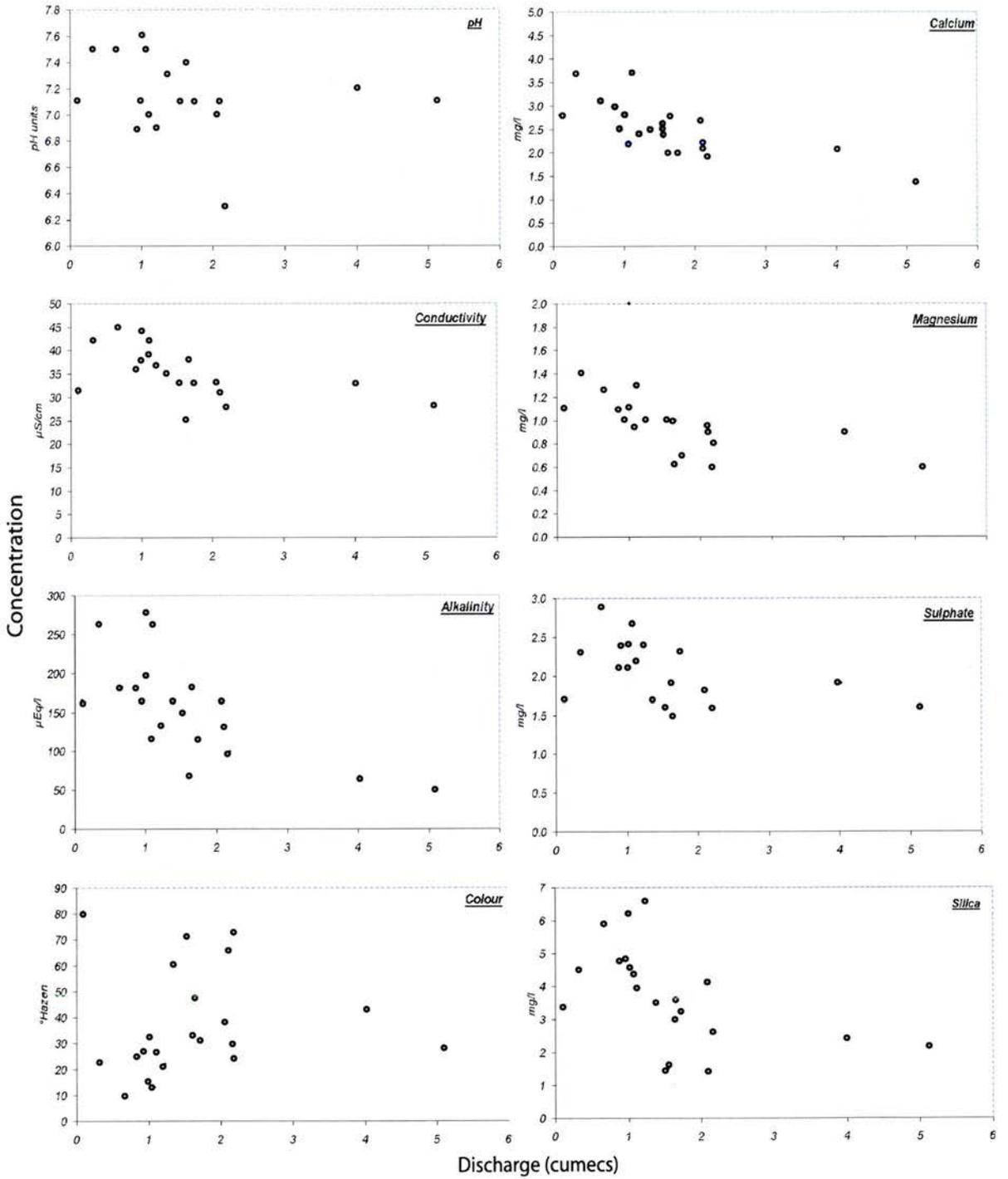


Figure 5.8: Concentration- discharge relationship for selected determinants at Winterhope Burn during regular sampling programme (graphs only include data for which discharge measurements are available (August 2000 and December 2001)).

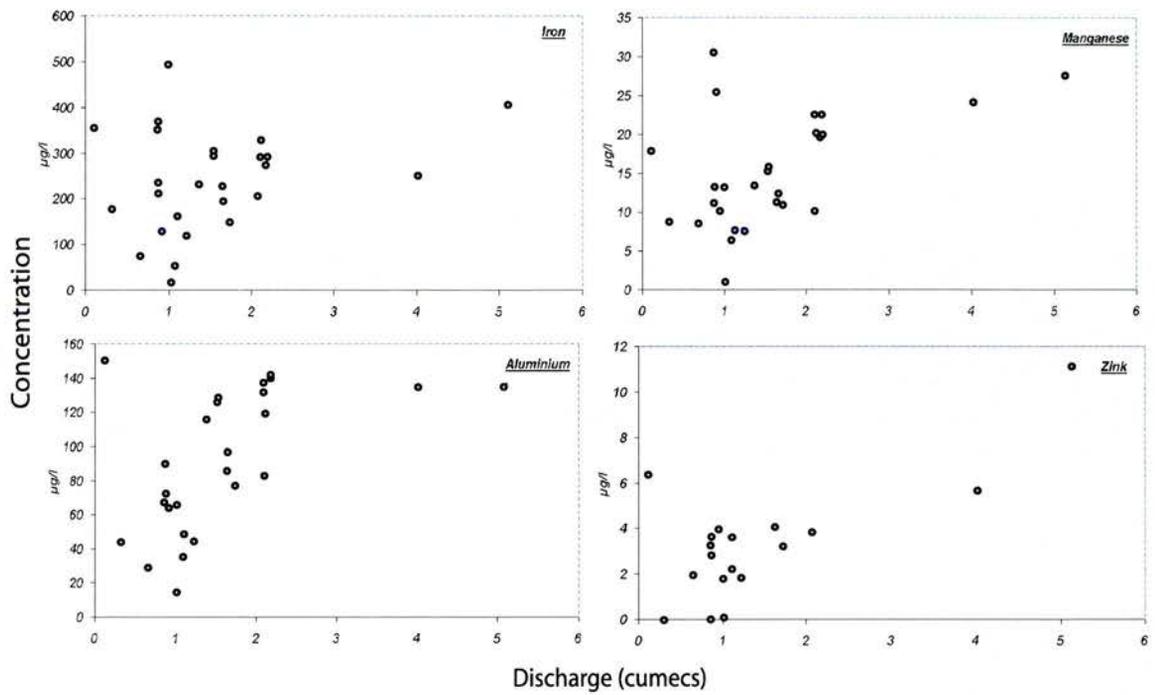


Figure 5.8 (continued): Concentration- discharge relationship for selected determinants at Winterhope Burn during regular sampling programme (graphs only include data for which discharge measurements are available (August 2000 and December 2001)).

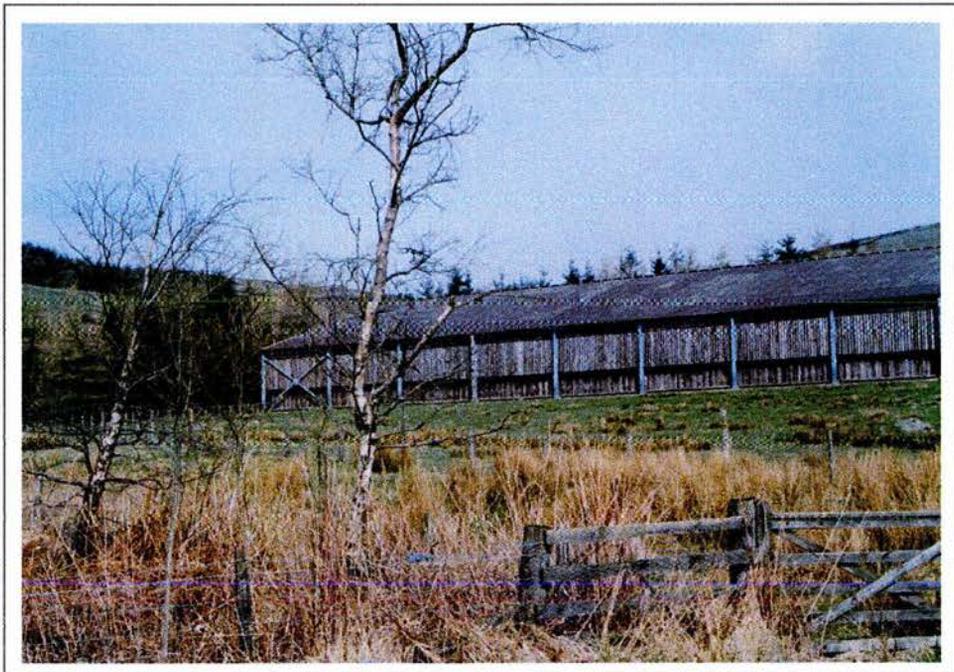


Figure 5.9: Sheep shed located ~100 metres upstream of sampling site at Craigierig Burn.

Calcium (Ca) and magnesium (Mg) concentrations also decrease during periods of increased runoff (*Figure 5. 8*) as both elements are mainly derived from alkaline baseflow, dominated by processes of bedrock weathering, which during storm events is diluted by more acidic, organic rich runoff from the upper soil horizons.

The increasing influence of organic rich soilwater inputs during storm events is exhibited in the high colour (and total organic carbon (TOC)) loadings, which have been observed at all streams during periods of high flow (*Figure 5. 8*) and are found to vary depending on the magnitude of the storm event. A seasonal component in TOC concentrations resulting from higher summer temperatures and increased decomposition rates as found in other upland catchments (Miller *et al.* 2001) is not obvious from the data.

Concentrations of iron (Fe), manganese (Mn), aluminium (Al) and zinc (Zn) in stream waters also increase with flow (*Figure 5. 8*) and Fe and Al show particularly positive correlations with TOC ( $R^2_{Fe} = 0.90$ ;  $R^2_{Al} = 0.84$ ) and colour, thus demonstrating a close association between metals and (dissolved) organic matter. A high proportion of the metals are present as filterable species ( $<0.45 \mu\text{m}$ ), suggesting a possible role of dissolved and/or colloidal organic matter in metal complexation in the Megget streams, since uncomplexed dissolved species of Fe and Al, and to a lesser degree Mn, are relatively unstable in well-aerated natural waters of near-neutral pH (Hem, 1985).

Sodium (Na) and chloride (Cl) appear to be derived from atmospheric deposition. Concentrations of Cl ions in the stream water are found to be highest during winter storm events (*Figure 5. 6*) reflecting the high precipitation totals and the general Atlantic source (mainly westerly direction) of prevailing weather systems (ECN data),

which can bring high concentrations of marine-derived ions, such as chloride. The high Cl concentrations in the stream waters observed in February 2000, for example, coincided with a sea-salt deposition episode during which unusually high rainfall Cl occurred with concentrations of up to  $51.3 \text{ mg L}^{-1}$  (ECN data). Although Na concentrations in rainfall generally mirror those of Cl (*Figure 5. 6*), Na ions in the stream waters do not reflect the increase in Na in the rainfall, even during periods of sea-salt deposition and high Na loading in the rainfall. This may indicate that Na is at least partly retained within the catchment, e.g., due to competitive ion exchange, whereby Na ions replace hydrogen, Fe and Al ions at cation exchange sites (Cresser *et al.* 1993). However, the positive correlations with elements like Mg and Ca indicate some Na inputs from sources other than atmospheric deposition, most likely associated with bedrock weathering. Cl concentrations are unrelated to Mg and Ca, as well as to flow.

	<i>Minimum</i>	<i>Maximum</i>	<i>Mean</i>
<i>Winterhope Burn</i>	0.07	0.27	0.16
<i>Meggethead</i>	0.10	0.57	0.29
<i>Linghope Burn</i>	0.05	0.30	0.20
<i>Cramalt Burn</i>	0.10	0.90	0.30
<i>Shielhope Burn</i>	0.05	0.39	0.15
<i>Craigierig Burn*</i>	0.23	0.59	0.40

*Table 5. 4: Stream concentrations of chlorophyll-a ( $\mu\text{g L}^{-1}$ ) measured during regular sampling December 1999 to August 2000) [\* no data for winter period available]*

Temporal patterns in silica ( $\text{SiO}_2$ ) exhibit characteristic variations with flow (*Figure 5. 8*); with concentrations rising during low flow periods as groundwater derived from deeper sources sustains the flow and declining during high flow periods when shorter-residence water derived from upper soil horizons predominates. Annual variations

related to increased uptake of silica by diatoms and benthic algae in summer (Soulsby *et al.* 2002a, Neal *et al.* 2000) was not evident from the data and would not be expected given the low abundance of these organism in these oligotrophic streams (see *Table 5. 4*; Colby, 2000).

Sulphate (SO<sub>4</sub>) ion concentrations in the stream waters are generally low and decrease with flow (*Figure 5. 8*), suggesting either point sources or groundwater sources as the major source of SO<sub>4</sub>. Atmospheric inputs of this compound are generally very small (on average < 1mg L<sup>-1</sup>, ECN data) owing to the remote nature of the site and appear to have no effect on the stream chemistry directly.

Nitrate (NO<sub>3</sub>), total nitrogen (TN) and total phosphorous (TP) concentrations in the streams are generally low (*Figure 5. 3*, *Figure 5. 7*), often below the detection limits of 0.2 mg L<sup>-1</sup> for NO<sub>3</sub> and TN and 10 µg L<sup>-1</sup> for TP. The actual values vary between <0.2 mg L<sup>-1</sup> and 1.6 mg L<sup>-1</sup> for NO<sub>3</sub>, <0.2 mg L<sup>-1</sup> and 0.6 mg L<sup>-1</sup> for TN and <10 µg L<sup>-1</sup> and 29 µg L<sup>-1</sup> for TP. Concentrations tend to be highest during the winter period, reflecting the low biotic uptake, and appear to decrease with flow, suggesting input from point or groundwater sources rather than from surface runoff and diffuse sources. At Craigierig Burn, however, NO<sub>3</sub> levels are up to 1 mg L<sup>-1</sup> higher than at the other streams and were also detectable during the summer months (0.4-0.7 mg L<sup>-1</sup>). This may be due to pollution caused by the close locality of sheep pens upstream of the sampling site (*Figure 5. 9*).

The limited nutrient availability is reflected in low chlorophyll-a concentrations (*Table 5. 4*), ranging between 0.05 µg L<sup>-1</sup> to 0.9 µg L<sup>-1</sup>, where lowest concentrations occur in winter due to reduced biological activity in the streams.

Concentrations of Cu and K in the stream waters are generally low and show no discernable variations throughout the year.

#### 5.4 Stream hydrochemistry - Spatial patterns

The concentration ranges observed for individual solutes during regular sampling are summarised in *Table 5. 2* and *Table 5. 3* and may be used to investigate the spatial variability in stream chemistry in the Megget catchment. The data show that stream waters throughout the catchment are generally weakly mineralised and have low conductivity ( $<65 \mu\text{S cm}^{-1}$ ) and alkalinity ( $<450 \mu\text{eq L}^{-1}$ ) values and near neutral pH (pH 6.2-8.0). Only at Craigierig Burn are somewhat higher ranges observed with conductivities of up to  $93 \mu\text{S cm}^{-1}$  and alkalinity values ranging between 350 and 700  $\mu\text{Eq L}^{-1}$ .

To better illuminate spatial variations in the contribution of major ion components in the catchment area results from the chemical analysis of all stream water samples are presented in form of a Piper trilinear diagram (*Figure 5. 10b*) together with the ECN precipitation data (*Figure 5. 10a*). To display data in a Piper diagram, the concentrations ( $\text{mg L}^{-1}$ ) of each constituent are converted to milliequivalents ( $\text{mEq L}^{-1}$ ) and normalised such that the proportions of the three variables displayed in the triangular graphs sum up to 100 % ( $\% \text{mEq L}^{-1}$ ). Thus, the resulting graphs show the relative proportions of the major ions and not their absolute concentrations. Bicarbonate ( $\text{HCO}_3$ ) concentrations used in the plots were directly inferred from the original alkalinity values, which are quoted in terms of bicarbonate concentrations ( $\text{mgHCO}_3 \text{ L}^{-1}$ ) (see Section 4.2.1). The graph illustrates that the major ion composition of the stream water is similar in all streams and it can be seen that

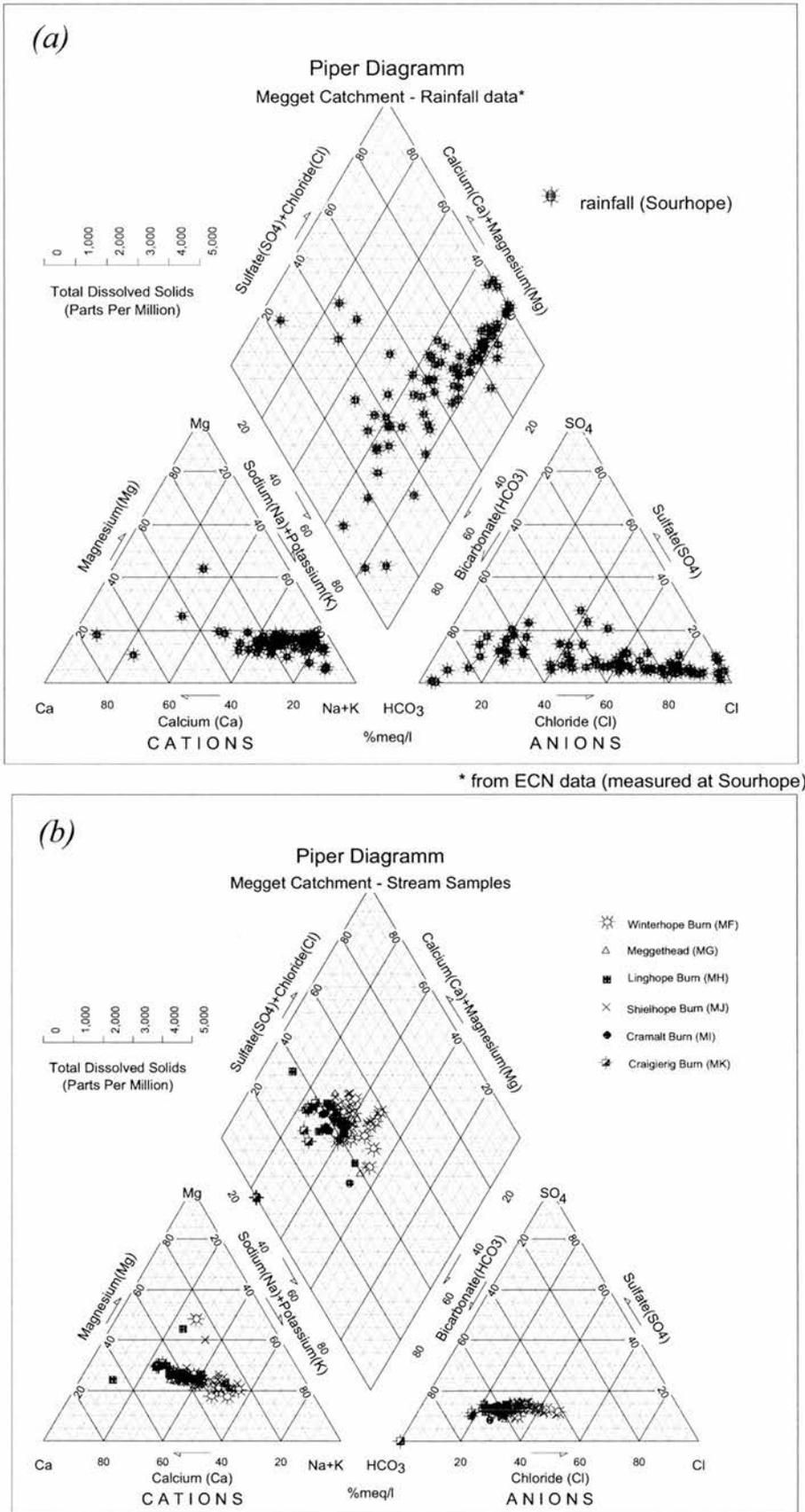


Figure 5.10: Piper diagrams showing (a) rain water samples from Sourhope and (b) stream water samples from Megget catchment for period between September 1999 and December 2001.

samples cluster in the field typical for Ca-HCO<sub>3</sub> dominated waters, which, in the Southern Upland Region of Scotland, is the common groundwater type (Robins, 2002). Variations within these clusters are in part due to changes in stream flow regime and the resulting mixing of waters from different runoff sources, as is indicated by the straight lines in the triangular cation and anion plots along which the samples assemble (Hem, 1959). These mixing lines illustrate the flow related changes in contributions from groundwater sources, enriched in Ca, Mg, HCO<sub>3</sub> and precipitation sources, dominated by Cl and Na (see *Figure 5. 10*) to stream water composition.

Despite the flow related mixing, it can be seen that samples collected at Winterhope Burn and Shielhope Burn in general display lower proportions of Ca, Mg and HCO<sub>3</sub> and higher proportions of Cl, Na and K relative to the other streams (see also *Figure 5. 5* and *Figure 5. 6*). In contrast, samples from Linghope Burn and, in particular, Craigierig Burn appear to be enriched in Ca, Mg and HCO<sub>3</sub> in relation to Cl, Na and K. This may be due to local variations in bedrock mineralisation within the catchment, for example small-scale predominance of rocks with higher base cation content and/or higher weathering rates, although if SiO<sub>2</sub> concentrations are used as a surrogate measure for weathering (Thornton and Dise, 1997) higher weathering rates seem an unlikely mechanism for high base cation concentrations. However, given the heterogeneous nature of the Silurian bedrock underlying the Megget catchment (see *Section 3.3*), it is quite possible that small-scale variations in bedrock geology occur, and Chapman *et al.* (2000) have found evidence for the presence of a local centre of mineralising activity north-east of the reservoir, probably associated with tectonic structures as has been discussed in Chapter 3. Alternatively, the varying proportions of these elements may indicate differences in the contribution of long- residence time

(ground-) and short-residence time (rain-) water, to stream flow. The higher proportions of atmospherically-derived Cl in the stream waters of Winterhope Burn and Shielhope Burn, for example, may be due to higher contributions of the rainwater component to the stream flow, input directly via rainfall onto the stream and/or routed through the catchment as surface and near surface flow before entering the stream. Where cation distribution on the cation exchange complex is governed by precipitation composition, drainage water chemistry would also be very similar to precipitation chemistry (Billett and Cresser, 1996), thus further adding to the rainfall signal in *Figure 5. 10*.

Beside differences in conductivity, alkalinity and relative amounts of major ions, spatial patterns mainly emerge from variations in colour (TOC) and metal loadings in the individual streams. Water chemistry in Shielhope Burn and Winterhope Burn, low in base cation concentrations, conductivity and alkalinity, is characterised by high concentrations and wide ranges in colour and TOC concentrations (*Table 5. 2*). Values observed during regular sampling are up to 2-3 times higher than those observed in the other streams with maximum values of 176° Hazen and 22.9 mg L<sup>-1</sup> at Shielhope Burn and 80° Hazen and 11.8 mg L<sup>-1</sup> at Winterhope Burn, respectively. On average, Shielhope Burn and Winterhope Burn also exhibit the highest concentrations in Fe, Mn and Al of all streams. Fe concentrations at Shielhope Burn range between 42-592 mg L<sup>-1</sup> and are consistently higher than those in Winterhope Burn, which lie between 19-496 mg L<sup>-1</sup>. The pH values in both streams are on average 0.1-0.2 units lower than in the other streams. Given the low concentrations of base cations and based on previous observations it may be hypothesised that these stream water compositions reflect the higher proportion of organic soils in these catchments, seen

in *Figure 3. 13*, and/or the predominance of water sourced from upper soil horizons. Peaty gleys and podzols in the lower reach of the streams and blanket peats in the headwater areas provide a probable source of low pH waters rich in TOC and associated metals.

In comparison, spatial variability in stream water compositions of Cramalt Burn, Linghope Burn, Meggethead and Craigierig Burn is generally small (*Table 5. 2*). Except for the constantly higher values at Craigierig Burn, conductivity, alkalinity and concentrations of elements derived from bedrock weathering are low, although still higher than those at Shielhope Burn and Winterhope Burn. Water chemistry is characterised by low TOC and colour values averaging around 1.4-2.4 mg L<sup>-1</sup> and 6-13°Hazen, respectively. Some spatial variations occur in the distribution of TOC and colour and also in the metal distribution; Meggethead and Craigierig Burn show the highest loadings of these elements (*Table 5. 2*), probably reflecting the higher proportion of organic soils in their catchments. Concentrations of TOC and metals are generally lowest at Linghope Burn and Cramalt Burn (*Table 5. 2*), dominated by brown forest soils and rankers near the stream area (see *Figure 3. 13*). High loadings occur during storm events and the response is generally highest in Meggethead and Craigierig Burn. However, despite these generally low TOC and metal values unusually high loadings of Fe, Mn and Al were encountered on 4 December 2000, where sampling was carried out during a storm event following a prolonged rainfall period. Most notable were elevated levels of Fe, Mn and Al at Linghope Burn and Meggethead with concentrations up to 10 times higher than those usually observed; Linghope Burn even exceeded the concentrations observed at Shielhope Burn and Winterhope Burn during that event. A similar event occurred on 5 December 2001,

where sampling followed a night of heavy rains and snowfall and highest metal concentrations were determined at Craigierig Burn.

While these observations mainly illustrate differences in catchment response during prolonged rainfall periods it is suggested that the higher loadings at Linghope Burn and Craigierig Burn relative to Winterhope Burn and Shielhope Burn are also due to differences in the timing of sample collection with respect to storm event progression. For example, sampling on 4 December 2000 coincided with the onset of a storm event (on a very wet catchment). The rise in metal concentrations in the samples mirrors the order of sample collection on the rising limb of the hydrograph; streams sampled first (at the onset of the storm event) show the lowest concentrations, and highest concentrations occur in streams sampled last, when the hydrograph had risen. Similar pattern, but in reverse order, are seen on 5 December 2001, where samples were collected towards the end of a storm event; on the falling limb of the hydrograph.

## 5.5 Discussion

Results from the regular sampling programme demonstrate that temporal variations in the stream chemistry of the Megget catchment are mainly influenced by changes in flow pattern, while spatial variability in stream chemistry appears to be mainly related to the distribution of soil types.

The most distinct changes in stream chemistry occur during hydrological events when hydrological pathways in the upland catchment change, resulting in the dilution of base-rich groundwater sources by overland and shallow subsurface flow through acidic organic rich soils. Similar temporal pattern have been observed in numerous studies of upland regions of Scotland (Reid *et al.* 1981; Jarvie *et al.* 2001; Soulsby *et*

*al.* 1998), England (Miller *et al.* 2001; Stunell and Younger, 1995, Thornton and Dise, 1997) and Wales (Neal *et al.* 1997a,c; Foster *et al.* 1997).

Evaluation of the episodic response of the streams shows that conductivity and pH are largely controlled by discharge and hydrological pathway and are highest during periods of low flow, dominated by inputs from base-rich groundwater sources. Other elements associated with processes of bedrock weathering also decrease with discharge.

Waters rich in TOC (as indicated by the high colour values) dominate the stream composition during periods of increased runoff (*Figure 5. 8*), reflecting the greater contribution of waters from shallow organic soil horizons to the stream flow. The distinct rise in TOC and colour coincides with an increase in Al, Fe and Mn concentrations in all streams. Concentrations of these elements are directly related to the acidity of the water, and in the case of Mn and Fe also depend on the redox conditions of the aqueous system. However, Hughes *et al.* (1990) argue that DOC determines the chemistry, solubility and transport of Al and Fe in the O horizon of soils and DOC has also been linked to the mobilisation of Al (Tipping *et al.* 1989) as well as Fe and Mn (Gavin *et al.* 2001; Graham *et al.* 2002) in peaty upland catchments. Concentrations of Al, Fe and Mn in the stream waters are predominantly present as filterable species (<0.45µm), probably in association with micro-particulates that pass through the filter disks, rather than in 'true solution' (Neal *et al.* 1996), and also exhibit strong positive correlations with TOC. Thus, it appears that the rise in Fe, Al and Mn was of organic form.

Atmospherically derived elements are higher during periods of high rainfall and can be related to sea-salt deposition events. While atmospheric inputs of Cl are reflected in the stream water composition, the Na signal is less clear and it appears that Na concentrations in the streams are affected by in-catchment processes, like bedrock weathering and/or cation-exchange in the soil. The latter has been suggested to occur in peats and organic topsoils (Cresser *et al.* 1993; Giusti and Neal, 1993) as well as in acidic woodland soils (Soulsby, 1997), where mineral weathering plays a minor role in the generation of soluble salts. During high precipitation inputs, Na ions exchange with hydrogen ions in the organic surface horizons and Al ions in the deeper mineral soils. According to Shotyk and Steinmann (1994) however, the preference for Na ions on exchange sites in peats is fairly low and on the catchment scale Na has often been reported to show high loss rates (Ferrier *et al.* 1990b) or conservative behaviour (Neal *et al.* 1997a). It appears that competitive ion exchange of Na is only important where availability of ion exchangers like Ca, Mg and K is limited, which is likely to be the case in the organic rich soils of the Megget catchment given the low concentrations of these elements in the rainfall (see *Table 3. 1*), as well as the slow rates of bedrock weathering. There is probably some Na input from groundwater sources, originating from deeper weathering sites (e.g., weathering of plagioclase feldspar:  $\text{NaAlSi}_3\text{O}_8$ - $\text{CaAl}_2\text{Si}_2\text{O}_8$ ), as indicated by the positive correlations with elements like Ca and  $\text{SiO}_2$ . The somewhat lower Cl/Na ratio in the stream waters relative to that of the bulk precipitation supports this hypothesis, and the two mixing lines in the Na-Cl plot (*Figure 5. 11b*) also suggest a second Na source. However, Na inputs from weathering sources only appears to be important during the summer period, where baseflow conditions dominate and precipitation inputs are low. This is consistent with Peters *et al.* (1998) who show that two different Na sources, atmospheric inputs and a

feldspar-weathering source, dominate the different parts of the hydrograph. Thus, it appears that Cl and Na behave differently within the catchment and damping of high atmospheric Na inputs (mainly during winter rain storms) indicates processes of differential retention of these elements within the catchment (Giusti and Neal, 1993).

Potassium concentrations do not exhibit a clear relationship with flow. It is commonly fixed in specific clay minerals after being released during primary weathering reactions (Sposito, 1984) and therefore exhibits different behaviour to other weathering-derived ions. K is also taken up by, and recycled in plant biomass (Billett and Cresser, 1996) and is often largely retained within the root zone (Hooper *et al.* 1990).

Generally, concentrations of nutrients in the catchment are very low, owing to the remoteness of the site and the small amount of agricultural activity (mainly rough grazing ground). Concentrations are lowest during summer, as expected, due to biological uptake. The higher NO<sub>3</sub> values at Craigierig Burn may be due to effluent inputs at the sheep pans upstream of the sampling site (*Figure 5. 9*) and Thornton and Dise (1997) have related increased NO<sub>3</sub> concentrations in streams draining unfertilised lands to pollution from animal waste. The inverse relationship to flow supports the assumption of point source inputs. However, this finding is somewhat surprising and the nature of the NO<sub>3</sub> source should be further investigated, in particular since (chemical) waste from the farms draining into Megget Reservoir is, in theory, removed by Scottish Water to reduce the risk of pollution of the water supply (Virtue, 2003, personal communication).

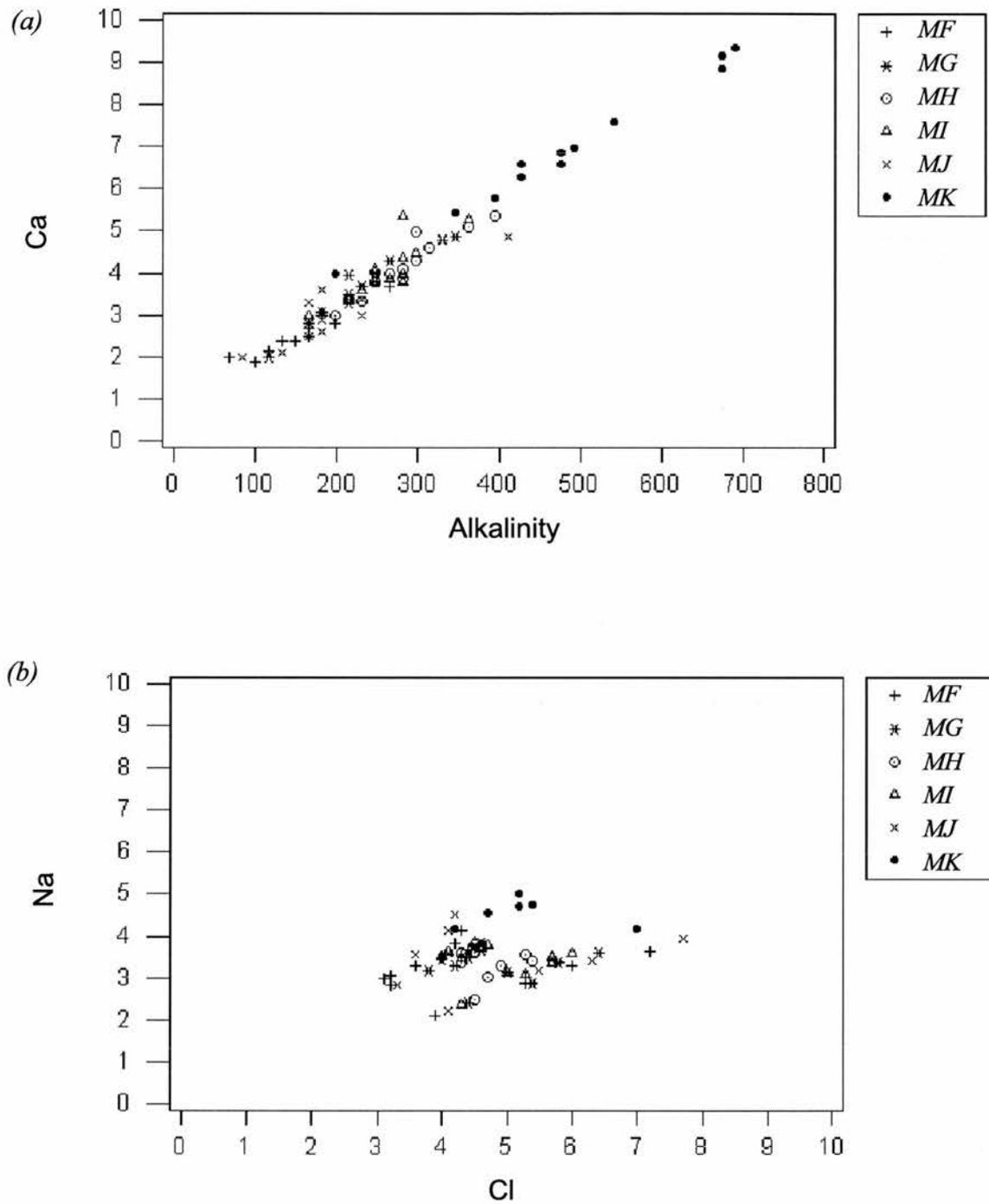


Figure 5.11: Plot of (a) Ca (mg/L) versus conductivity ( $\mu\text{S/cm}$ ) and (b) Na (mg/L) versus Cl (mg/L) for samples collected during regular sampling programme (for better comparability the plot only contains data for dates on which all six stream were sampled).

Monitoring all streams in the catchment area allows the assessment of the spatial variability in the stream chemistry and the result have shown that spatial patterns in stream chemistry in the Megget catchment are manifested in considerable differences in colour (TOC) and metal loadings as well as in base cation concentrations in individual streams.

Although factors like topography, altitude and slope angle may be linked to TOC in soils (Grieve and Marsden, 2001), spatial variations in TOC concentrations in the streams are most likely related to soil changes within the catchment area (Rees *et al.* 1989) and many studies have successfully linked stream chemistry with soil type attributes (Billett and Cresser, 1996; Foster, 2000). Dawson *et al.* (2001), for example, have demonstrated that DOC concentrations vary as streams pass through different soil types and DOC concentrations decreased in the order of peat > peaty podzols > rankers. Highest TOC concentrations in the Megget catchment are seen in Winterhope Burn and Shielhope Burn, and this reflects the predominance of organic soils (blanket peat) within these catchments (see *Figure 3. 13, Table 3. 2*). TOC concentrations in these streams are variable (as seen in the colour values in *Figure 5. 5*), mainly due to changes in hydrological pathways, but on average are  $>3.5 \text{ mg L}^{-1}$  reflecting the acidic nature of the streams (Dawson *et al.* 2001) and the high soilwater inputs, even during low-flow periods.

Mobilisation of Fe, Mn and Al is principally controlled by the availability of water-soluble complexing agents (Grieve, 1984b, Hughes *et al.* 1990), so that the high metal concentrations in Shielhope Burn and Winterhope Burn are a logical consequence of

the high colour (and thus TOC) values in these streams, as well as the organic nature of the stream metal inputs as discussed above.

While TOC/colour and metal concentrations in Meggethead, Linghope Burn, Cramalt Burn and Craigierig Burn are generally much lower, due to the higher proportion of brown forest soils and rankers and/or peaty podzols near these streams and in their catchment areas, the high loadings observed during two storm events on 4 December 2000 and 5 December 2001 demonstrate the importance of storm duration and intensity on flow pathways and on stream water composition. During these intense and long duration events, where catchment soils are well wetted and the groundwater table is high, more water is derived from the upper soil zone and acidic soil layers (Neal *et al.* 1997b). These changes in flow path become apparent from the high TOC/colour and metal loadings observed in Meggethead, Linghope Burn and Craigierig Burn, which reflect the increasing influence of the organic soils in the catchments. During small storm events and during baseflow conditions, however, groundwater inputs and drainage water from the near stream areas and riparian zone (Neal *et al.* 1997b) appear to dominate stream flow, and TOC and stream metal concentration in these catchments remain relatively low as runoff from the organic soils has little impact on stream chemistry.

Although dilution of groundwater inputs by soilwater runoff during storm events is obvious at all streams, base cation concentrations and pH values remain relatively high compared to those found in soilwater solutions of peaty podzols, peats and alpine soils (Soulsby *et al.* 1998; Ferrier *et al.* 1990b; Billett and Cresser, 1996) suggesting that groundwater inputs buffer the stream waters at high flow. The role of

groundwater in influencing stream chemistry during storm events has also been observed in other upland catchments (Chapman *et al.* 1997; Haria *et al.* 2002) and detailed isotopic and chemical tracer studies during storm events in the Allt A' Mharcaidh have demonstrated that groundwater can contribute as much as 46% of runoff during events (Jenkins *et al.* 1994a), although such large contributions appear inconsistent with respect to the high TOC/colour loadings at Shielhope Burn and Winterhope Burn during storm events. Contributions of groundwater to runoff events in the Megget streams will be investigated in Chapter 6.

Spatial trends in conductivity, alkalinity, base cations (mainly Ca and Mg) and SO<sub>4</sub> within the catchment are best seen during baseflow conditions when groundwater inputs are more important, but in most cases are also traceable at higher flows. Although the underlying bedrock geology is similar throughout the catchment it is not unreasonable that the distinctively higher concentrations of Ca, Mg and SO<sub>4</sub> at Craigierig Burn result from local predominance of shales with higher rates of flow in heavily fractured units and enriched in Ca, Mg, SO<sub>4</sub> and Na (BGS, 1993) relative to the greywackes. It has been shown that stream chemistry is strongly influenced by the underlying geology (Billett *et al.* 1996) and that even adjacent streams with similar geology, soil type and vegetation cover may have different chemistries (Hill and Neal, 1997) due to small-scale changes in bedrock mineralogy (Reynolds *et al.* 1986).

An alternative hypothesis might be that baseflow in the comparatively base-poor streams, Shielhope Burn and Winterhope Burn, does not represent a true deep-water composition (Robson and Neal, 1990), but is composed of groundwater inputs and varying contributions from the upper soil horizons. Studies in upland catchments in Northern England (Stunell and Younger, 1995) and SW Scotland (Giusti and Neal,

1993) have shown that seepage from peaty soils can contribute significantly to stream baseflows. Blanket peats, for example, despite their usually flashy runoff regime, can provide a perennial baseflow component (Holden and Burt, 2000; Bragg, 2002), although the discharges involved are usually very small.

The hypothesis that differences in chemical composition of individual streams are due to variations in the contribution from two main runoff source (simple two-component mixing), rather than due to input from a third source (a different groundwater composition), is supported by *Figure 5. 11a*, showing a plot of Ca versus alkalinity for all streams. The single mixing line for all streams indicates that stream flow consists of two main sources, baseflow and stormflow, and ion concentrations are mainly controlled by hydrological factors, rather than by catchment characteristics such as geology (Jarvie *et al.* 1997).

The stream chemistry in the northern part of the catchment, but in particular at Craigierig Burn, may therefore reflect a greater groundwater influence, derived from shallow drift deposits and fracture flow or from shallow, long residence time groundwater sources within the riparian zone, as identified by Ferrier *et al.* (1990b) in the Allt a' Mharcaidh catchment. Groundwater inputs in the Megget catchment may also be associated with inputs from the fault system cutting across the upper reaches of the streams (*Figure 3. 11*).

However, testing the above hypothesis will be difficult without detailed field investigation and analysis of the contributing soilwater and deep-water sources. Within this study the question of which factors control spatial variability in base cation concentrations remains untested, although a combination of both, geological and hydrological/hydrogeological factors appears most likely.

## 5.6 Summary

Data presented in this chapter were collected during the regular (monthly, fortnightly) sampling programme at Winterhope Burn, Meggethead, Linghope Burn, Cramalt Burn, Craigierig Burn and Shielhope Burn and show that surface waters in the Megget catchment are of low ionic strength and of slightly acidic or circum-neutral nature, reflecting the geology of the area dominated by relatively base-poor greywackes with low weathering rates. The waters are oligotrophic with low nutrient concentrations but during runoff events contain high concentrations of organic carbon, derived from the surrounding organic-rich soils of the catchment area.

It is shown that temporal variations in stream chemistry are for the most part governed by stream flow variations and exhibit the characteristic variations related to changing hydrological pathways during events, illustrated by a number of chemical determinants. During storm events the contribution of water from surface organic horizons was found to increase, causing the lowering of pH, conductivity and alkalinity in the stream runoff and also causing the dilution of weathering components of Ca, Mg and SiO<sub>2</sub>. This coincides with an increase in colour, TOC and organically complexed metals (Al, Fe, Zn and Mn), and the rise in concentrations was on average highest in catchments dominated by peat soils, namely Shielhope Burn and Winterhope Burn. Storm duration and intensity were seen to be important factors in controlling the catchment response to events, in particular in the catchments with high proportions of peaty podzols and brown forest soils/rankers. Unusually high metal loadings occurred after periods of prolonged and heavy rainfall, although temporally

better resolved data are required to improve understanding of the underlying processes.

The results also indicate that spatial variations in stream chemistry between different catchments are mostly due to variations in soil type distributions and stream compositions largely reflect varying proportions of soilwater and groundwater components. However, baseflow chemistry at Craigierig Burn suggests some small-scale variations in bedrock mineralisation, possibly a higher proportion of shale, causing higher Ca, Mg, Na and SO<sub>4</sub> loadings, although more detailed knowledge of groundwater composition and pathways within the bedrock is required to verify this assumption.

# 6

## **Episodic Hydrological Response**

---

The importance of changing flow path and temporal variability of stream chemistry during storm events was introduced in Chapter 2, while regular sampling at all streams, discussed in Chapter 5, has provided a general picture of temporal variations in stream chemistry in the Megget catchment. However, regular sampling has concentrated on the collection of monthly (fortnightly) samples and spot sampling at such large intervals tends to overlook peak values and details of rapid changes in stream chemistry during events (Jarvie *et al.* 2001; Peters, 1994a), thus introducing bias. Hence, short-term sampling during storms is important in documenting changes in stream water quality not readily apparent from routine sampling (Peters, 1994a) and is also essential for capturing the entire range of stream chemical loadings. Such intensive sampling thereby provides insight into the hydrochemical response of individual streams/catchments to changing hydrological conditions and this allows identification of critical periods of acidic runoff and/or high metal (e.g., Fe, Mn) loading, knowledge of which is essential for effective water quality management in upland catchments (Heal *et al.* 1997, in press).

In this chapter, results from the intensive sampling programme are presented. Factors controlling stream chemistry during events are assessed using a factor analysis

technique and a two component conceptual mixing model (EMMA) is introduced to investigate the contribution of different sources of stream flow generation to stream runoff during events.

## 6.1 Introduction

In upland catchments, it has been recognised that during heavy rain events the source of runoff generation changes (e.g., Robson and Neal, 1990; see review in Soulsby, 1997) and the contribution of through flow from surface soil horizons and overland flow to stream discharge increases dramatically. During such events stream water chemistry becomes increasingly dominated by equilibrium with soil organic matter and this often can be linked to rising metal levels in the streams since organic matter and low soil pH increase the solubility and mobility of trace metals and other metal species. Following storm events soilwater contribution to stream flow declines and water from deeper soil horizons and groundwater sources becomes the increasingly dominant component of runoff. These are characterised by high alkalinities and base ion concentrations and are generally low in organically complexed metals. Thus, it is expected in the Megget Reservoir that metal inputs will preferentially occur during periods of high flow, although more detailed knowledge of the underlying controls and the timing of such critical periods is required in order to fully assess the impact of the metal loading on water quality.

The contrasting chemical characteristics of baseflow and stormflow have lead to the assumption that stream flow can be viewed as consisting of two or more 'end-members' with distinct chemistries (e.g., Neal and Christophersen, 1989), the proportion of which change as discharge changes. Hydrograph separation techniques have been developed

---

using conservative chemical tracers for estimating the contribution of different runoff sources to stream flow (e.g., Robson and Neal, 1990). Such knowledge of the range of variations in stream water chemistry and evaluation of the contribution from the different runoff sources to stream flow is an essential prerequisite for assessing the variations in iron and manganese loading and its impact on the reservoir water quality, as well as for designing effective reservoir management strategies.

The contributing source areas and pathways ('end-members') may not always be obvious from the collected data, thus statistical methods may be used to aid the identification of the sources contributing to stream runoff, singling out the factors that control stream chemical response, particularly where knowledge of the hydrological framework of the catchment is limited.

Monthly and fortnightly sampling at the Megget streams has provided a general picture of temporal variations in stream chemistry and metal loadings. The sampling indicated the close relationship between changes in stream chemistry and flow (Chapter 5). During events, however, such changes in stream water chemistry are often rapid, due to the 'flashy' runoff regime characteristic of most upland catchments, and large changes in flow and associated chemistry may occur in a matter of hours or minutes during storm events (Foster *et al.* 1997). Hence monthly sampling is likely to miss these peak values and sampling at smaller time increments is required to capture the main chemical effects associated with the rapid stream response to events.

Event based sampling was carried out over a two week period in October 2000 (18 October to 30 October). The main objective of this intensive sampling period was to

investigate flow-related variations in stream chemistry during individual storm events and periods of increased stream runoff in order to:

- (1) assess the range of chemical loading and material fluxes within the tributaries, especially with regard to iron and manganese, and
- (2) examine the change in contribution of the different sources of runoff generation to the stream flow during rainfall events.

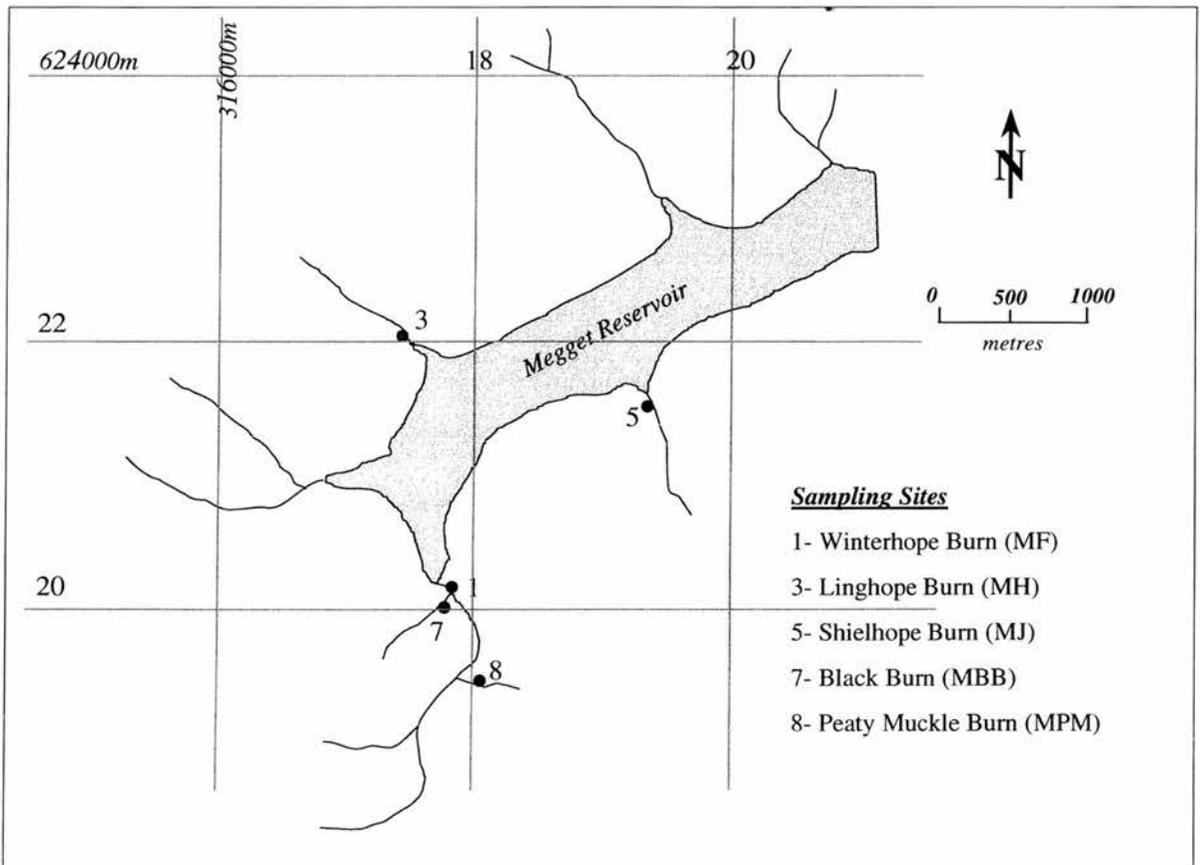
Furthermore, the influence of different soil types on the stream runoff chemistry was investigated. This chapter addresses the episodic hydrochemical response of the Megget catchment by:

- (1) analysing the chemical response of episodic stream chemistry data, collected at small sampling intervals from five streams to evaluate short-term variations in stream chemistry,
- (2) identifying factors controlling stream chemistry during episodes using a combined Q-and R-mode factor analysis technique, and
- (3) introducing a conceptual two-component mixing model (EMMA) to estimate contributions of different in-catchment sources to stream runoff during events.

## 6.2 Sampling design and methods

Stream water samples were collected from five streams in the Megget catchment. These streams were Linghope Burn, Shielhope Burn, Winterhope Burn, and two smaller streams Black Burn and Peaty Muckle Burn, which lie within the Winterhope catchment (*Figure 6. 1*). The selection of sampling sites was based on soil survey maps and geological maps (see *Figure 3. 11* and *Figure 3. 13*) of the area, water chemistry data from the regular sampling programme and was complemented by results from a preliminary stream sampling survey carried out in the Megget catchment in August

2000. Streams of different soil types were selected (*Figure 3. 13*) so that the effect of soil type distribution on stream chemistry and runoff response could be considered. Shielhope Burn catchment is predominated by peat soils with peaty gleys occupying the lower reaches of the stream, Linghope Burn and Black Burn mainly drain peaty podzols with brown forest soils /rankers occupying much of the riparian zone at Linghope Burn, which are further substituted by gleys near the reservoir inflow. The dominant soils in the Winterhope and Peaty Muckle catchments are peats and peaty podzols, but brown forest soils are also developed in the lower reaches of Winterhope Burn near the inflow into the reservoir. A more detailed description of soil type distribution has been given in Section 3.5. The selected catchments also differ in size and slope angle distribution and the catchment characteristics are summarised in *Table 3. 2*.



*Figure 6. 1: Sampling Location during intensive sampling programme*

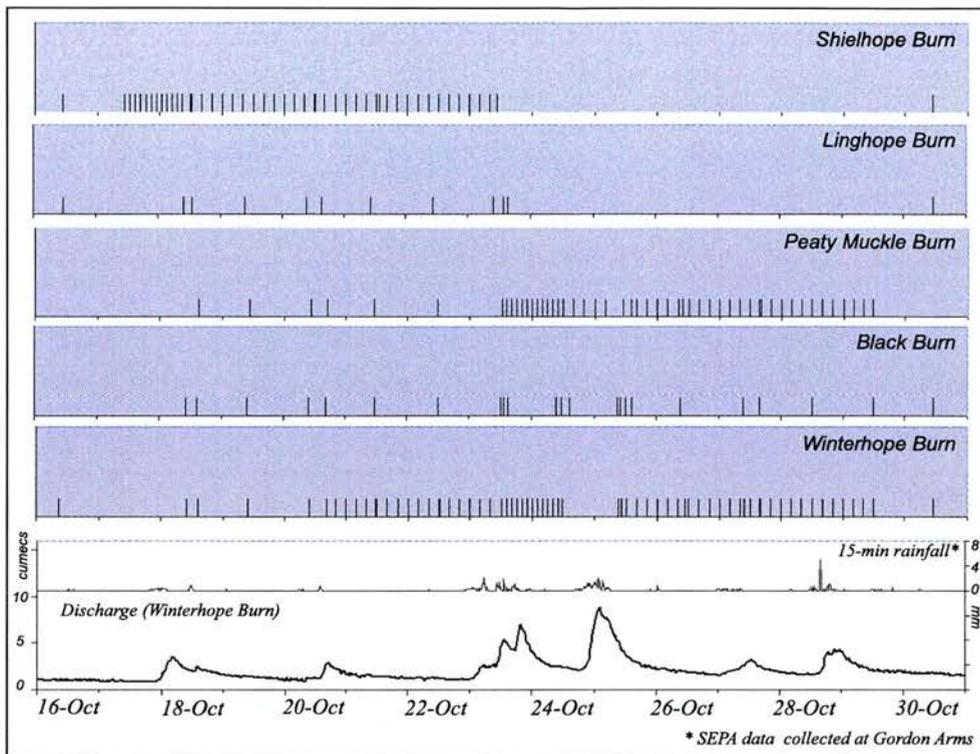


Figure 6.2: Sampling and storm event frequencies during intensive sampling programme (18 October 2000 - 30 October 2000).



Figure 6.3: Automatic sampler (American Sigma Portable Wastewater Sampler) and bottle arrangement.

Two automatic samplers (American Sigma Portable Wastewater Samplers, pictured in *Figure 6. 3*) were available and allowed sampling over a 24h period. Initially, samples were taken at five sampling sites (*Figure 6. 1*). Automatic samplers were installed at Shielhope Burn and Winterhope Burn on the 17 October 2000 and the 20 October 2000, respectively; Linghope Burn, Peaty Muckle Burn and Black Burn were sampled manually. At automated sites, samples were collected at 2 or 4-hourly intervals, depending on the hydrological conditions. At non-automated sites, sampling was carried out by hand, up to four times a day during rainfall events and once a day during dry periods.

	<i>-period</i>	<i>Sampling -frequency</i>	<i>-mode</i>	<i>Total no of samples</i>
Winterhope Burn	18/10/00-30/10/00	2-4 hourly	Automatic	70
Peaty Muckle Burn	18/10/00-23/10/00 23/10/00-29/10/00	1-2 per day 2-4 hourly	Manual Automatic	54
Black Burn	18/10/00-30/10/00	1-4 per day	Manual	25
Shielhope Burn	16/10/00-23/10/00 30/10/00	2-4 hourly once	Automatic Manual	53
Linghope Burn	16/10/00-23/10/00 30/10/00	1-3 per day once	Manual Manual	14

*Table 6. 1: Details of sample collection at individual sites during the intensive sampling programme*

Due to time and accessibility considerations and in response to concerns of commercial costing by the ESW lab, sample collection at Shielhope Burn and Linghope Burn was terminated after the first week of sampling. During the second part of the programme sample collection was reduced to the three sites in the Winterhope catchment (*Figure 6. 1*). The sampling site at Winterhope Burn remained automated and additional samples

were taken by hand in order to compare manual versus automated sampling. The second automatic water sampler was installed at Peaty Muckle Burn on the 23 October 2000 (*Figure 6. 4*). Details on sampling periods and frequencies for each site are summarised in *Table 6. 1* and *Figure 6. 2* and a summary of the collected data is given in *Table 6. 2*.

### 6.2.1 Sample collection and analysis

*Automatic samplers* were installed at suitable positions at the stream bank (see *Figure 6. 4*) and the end of the intake tube was positioned as midstream as possible, ca. 20 cm above the streambed. Each sampler required a 12V battery and was equipped with a high-speed peristaltic sample pump, an internal clock and a control panel consisting of a membrane switch keypad and an alphanumeric display. On installation, the sampler specific parameters (length of intake tube, number and type of bottles) were set and the intake sample volume (575 mL) was calibrated. Once programme parameters were defined, these settings were kept constant throughout the entire sampling programme. Only the sampling intervals varied between 2 and 4 hours, depending on weather conditions.

Prior to start of the programme all sample bottles, numbered from 1-24, were rinsed with stream water and arranged in the sampler accordingly (see *Figure 6. 3*). Samples for metal analysis were collected into unevenly numbered bottles to which 0.5 mL of concentrated AristaR nitric acid was added and the samples were thereby acidified to 0.1-%vv on collection. Immediate preservation had the advantage that processes of precipitation and adsorption were reduced, but this meant that after filtration the acid available metal fraction (AA) was determined, rather than the usually determined colloidal/dissolved metal fraction. After completion of the sampling cycle, full sample

bottles were collected and taken to the boathouse for storage (see below). The sampler was prepared for the next sampling period and before leaving the site a manual sample was taken, where possible immediately before the new sampling cycle started.

*Manual sampling* followed the procedure described in Chapter 5 and sampling protocols are also given in Appendix 1. Where applicable, samples were collected as close as possible to the intake tube of the automatic sampler. Temperature and conductivity of the stream were measured and recorded.

After collection all samples were taken to the boathouse and prepared for storage at the end of each sampling day. Samples collected by automatic samplers were decanted into appropriate sample bottles: general chemistry samples into 1-L bottles and acidified metal samples into 250 mL bottles. Metal samples collected manually were preserved in the boathouse and acidified to 0.1 %-vv by adding 0.25 mL concentrated AristaR nitric acid to the 250 mL sample bottles. Acidification to 0.1 %-vv lowered the pH of the sample sufficiently to suppress metal precipitation and sorption processes. On arrival at the ESW laboratory, the samples were filtered and acidified to 1 %-vv in order to fulfil ESW laboratory standard requirements.

Conductivity and pH were measured on non-acidified samples using a pHOX conductivity meter and a Jenway general purpose pH meter equipped with a BDH combination probe (which does not contain electrolyte solution that could leak into measured sample), respectively.

All sample containers were kept cool and stored in the dark before being transferred to the ESW laboratory for analysis. Storage times varied for individual samples but were kept to a minimum and the turn around time between sample collection and delivery to the laboratory did not exceed 3 days. Analysis of the samples at the ESW laboratory was undertaken according to the ESW standards (see Appendix 2 for the chemical analysis methods) and included the parameters and solutes listed in *Table 6. 2*.

The filtration procedure during the intensive sampling programme differed from that applied during regular sampling as the samples were acidified *before* filtration. This was due to a combination of two facts: firstly, filtration could not be carried out in the field due to contamination concerns and time limitations, and secondly, samples were kept in the field up to three days before being delivered to the ESW laboratory and therefore preservation was necessary to minimise changes in metal concentrations caused by precipitation and adsorption processes. Generally, the lowering of the pH in the acidified sample mobilises the metals adsorbed to clay particles and sediments present in the water. Only strongly adsorbed metal ions and those built into the mineral lattice remain in particulate form. Thus, during the event-sampling programme the fraction of acid-available metals (AA) were determined instead of the colloidal/dissolved metal fraction obtained during the regular programme. However, differences in concentrations of dissolved and acid-available fractions should only be significant in samples containing significant amounts of clay particles and sediments to which metals are adsorbed (Neal, 2000: personal communication). Comparison of Fe and Mn concentrations in samples acidified before and after filtration has shown small variations in the ratio between total and filterable concentrations. The ratio is generally higher in the filtered-acidified samples (Fe: 1.31, Mn: 1.28) compared to the acidified-

filtered samples (Fe: 1.14, Mn: 1.06), indicating some release of metal ions from solid adsorption sites, although their overall contribution to the ‘filterable’ fraction is small.



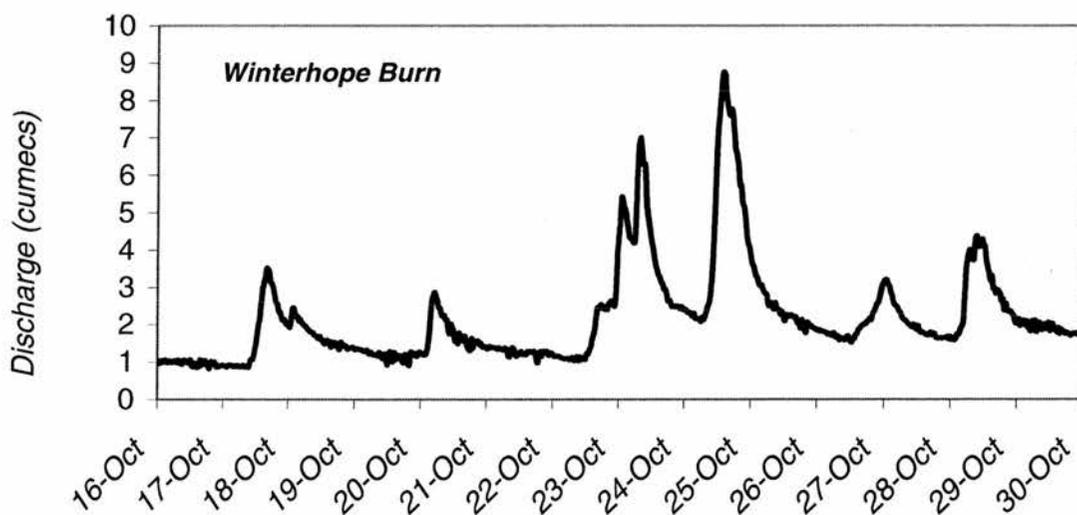
*Figure 6. 4: Automatic sampling site at Peaty Muckle Burn*

### 6.2.2 Hydrological monitoring

During the event sampling period hydrological monitoring in the catchment area was carried out on Linghope Burn and Winterhope Burn, where pressure transducers and automatic data loggers were installed and stream level changes could be recorded in 30-minute interval (see *Chapter 5*). Other hydrological parameters such as wind speed, wind direction, air temperature and (daily) rainfall were recorded at the Megget Dam. More detailed rainfall data were made available from the Scottish Environmental Protection Agency (SEPA), which maintains a rain gauging station at the Gordon Arms Hotel, about nine kilometres east of the Megget Reservoir.

### 6.3 Summary of data collected

A summary of the data collected during the intensive sampling programme is given in *Table 6. 2*. Comparisons can be made between the response of individual streams to storm events and the range of metal loading during high flow events can be assessed. Furthermore, the effects of soil type on stream chemical response during events can be considered. As sampling periods and intervals differ between the streams, there are limitations when comparing stream responses to individual storm events, but nevertheless some conclusions can be drawn and will be discussed in the following sections.



*Figure 6. 5: Flow changes at Winterhope Burn during the event-sampling programme*

There were six rainfall events during the sampling period (see *Figure 6. 5*), which varied in length and magnitude, including one of the largest events of the year. Two large events occurred on 22-23 October and 24-25 October with a total rainfall of 24.8

mm and 28.2 mm and a maximum rainfall intensity of  $8.0 \text{ mm h}^{-1}$ , causing stream flow to increase by a factor of 7 and 5, respectively. Smaller events occurred on 17-18 October (4.4 mm,  $1.6 \text{ mm h}^{-1}$ ), 20 October (2.4 mm,  $2.4 \text{ mm h}^{-1}$ ), 27 October (3.4 mm,  $0.8 \text{ mm h}^{-1}$ ) and 28 October (12.8 mm,  $20 \text{ mm h}^{-1}$ ) and although changes in stream flow were less dramatic significant changes in stream chemistry were observed. As the catchment wetness increased with successive events, the stream discharge gradually increased, and stream levels in-between rainstorm events remained higher than those at the beginning of the programme. For Shielhope Burn and Linghope Burn, only data for the first two events are available as sampling at these sites was terminated on 23 October. Furthermore, during the storm event from 24-25 October the automatic sampler at Winterhope Burn was blown over by the strong winds and all samples collected during the first half of this event were lost.

#### **6.4 General patterns of stream response during storm events**

A summary of the data collected during the intensive sampling period is given in *Table 6. 2.* and the observed variations in stream chemistry are illustrated in *Figure 6. 6* and *Figure 6. 7.*

Despite the different sampling periods and intervals it is immediately apparent that stream composition in all streams is dominated by the dynamic response to individual storm events, characterised by the depression of pH, conductivity, alkalinity and base cation (Ca, Mg) concentrations and the dramatic rise in colour (organic matter) and metal concentrations in the stream runoff at the same time.

Catchment	Colour °Hazen	Cond µS/cm	pH	Alk µeq/l	Turb NTU	Mn (AA) µg/l	Mn µg/l	Fe (AA) µg/l	Fe µg/l	Al (AA) µg/l	Al µg/l	Zn µg/l
<i>Winterhope Burn</i>	Minimum	16	5.7	51	0.0	8	9	110	132	57	60	0.0
	Maximum	83	6.8	215	3.5	88	93	648	686	172	226	18.0
	Mean	43	6.3	112	0.8	16	16	209	237	94	103	4.4
<i>Peaty Muckle Burn</i>	Minimum	16	5.9	34	0.0	10	10	115	142	38	45	0.0
	Maximum	62	6.7	231	4.0	73	84	535	651	169	256	37.1
	Mean	32	6.3	146	0.9	20	22	204	244	87	107	4.4
<i>Black Burn</i>	Minimum	19	6.0	51	0.0	1	2	20	20	16	16	1.9
	Maximum	55	7.3	182	4.1	41	44	376	466	257	256	13.1
	Mean	37	6.5	103	0.8	8	9	117	134	111	119	3.9
<i>Shielhope Burn</i>	Minimum	46	5.7	67	0.4	10	10	180	217	16	71	1.9
	Maximum	155	7.0	378	4.1	102	121	938	1160	242	338	35.9
	Mean	85	6.5	183	0.9	23	26	353	404	142	146	7.1
<i>Linghope Burn</i>	Minimum	4	6.0	133	0.0	1	1	17	19	19	22	0.0
	Maximum	54	7.1	296	2.0	12	15	195	280	165	240	5.3
	Mean	14	6.8	250	0.2	4	4	64	85	58	70	2.1

Table 6. 2: Summary of stream chemistry data for the intensive sampling programme (18 October 2000 to 30 October 2000) [AA=acid available]

Catchment		TSS** mg/l	Mg mg/l	Ca mg/l	SiO <sub>2</sub> mg/l	SO <sub>4</sub> mg/l
<i>Winterhope Burn</i>	Minimum	0.0	0.4	0.8	1.76	1.1
	Maximum	11.3	2.1	2.8	4.56	2.3
	Mean	1.4	0.8	1.8	3.04	1.8
<i>Peaty Muckle Burn</i>	Minimum	0.0	0.4	1.0	2.00	0.0
	Maximum	15.0	1.3	3.2	4.79	2.2
	Mean	1.5	0.9	2.2	3.40	1.7
<i>Black Burn</i>	Minimum	0.0	0.3	0.9	2.16	1.3
	Maximum	18.5	1.7	4.4	6.63	2.4
	Mean	1.2	0.8	1.9	3.79	1.9
<i>Shielhope Burn</i>	Minimum	0.0	0.9	1.9	2.46	1.2
	Maximum	8.0	1.5	3.3	6.16	2.0
	Mean	1.5	1.2	2.6	4.63	1.7
<i>Linghope Burn</i>	Minimum	0.0	0.9	2.0	3.58	2.3
	Maximum	9.5	1.7	4.1	6.93	3.2
	Mean	1.0	1.4	3.6	5.57	3.0

Table 6. 2 (continued): Summary of stream chemistry data for event sampling programme (16 October 2000 – 30 October 2000)

The graphs suggest that the hydrochemical response to rainfall events is similar in all streams, although some differences occur:

- (I) During storm events, most dramatic changes in stream composition occur in Shielhope Burn (*Figure 6. 6* and *Figure 6. 7*), which also shows the highest metal concentrations of all streams (*Table 6. 2*), indicating a predominant water source from the upper soil horizons. The dramatic increase in colour (organic carbon) and metal loadings during storm events arise near the time of peak discharge and is mirrored by a dramatic drop in pH, alkalinity and base ion concentrations.
- (II) Winterhope Burn and Peaty Muckle Burn also show a dramatic rise in colour and metal loadings during high flows, but maximum concentrations are lower than those at Shielhope Burn, even during the large storm event on 23 October 2000 (which has not been monitored at Shielhope Burn).
- (III) Black Burn and Linghope Burn are sampled in less detail and for the most part, concentrations of Fe, Mn, Al and Zn at both streams are low. However, high Al concentrations occur in both streams on 23 October where samples are collected at around peak discharge and measured Al concentrations even exceed those of Winterhope Burn and Peaty Muckle Burn and are probably due to accumulation and flushing from organic rich soils, as indicated by increased Fe, Mn, Zn or colour loadings. Linghope Burn also shows the highest concentrations in weathering components (*Table 6. 2*) and stream chemistry generally appears to be dominated by deeper soil and groundwater inputs.

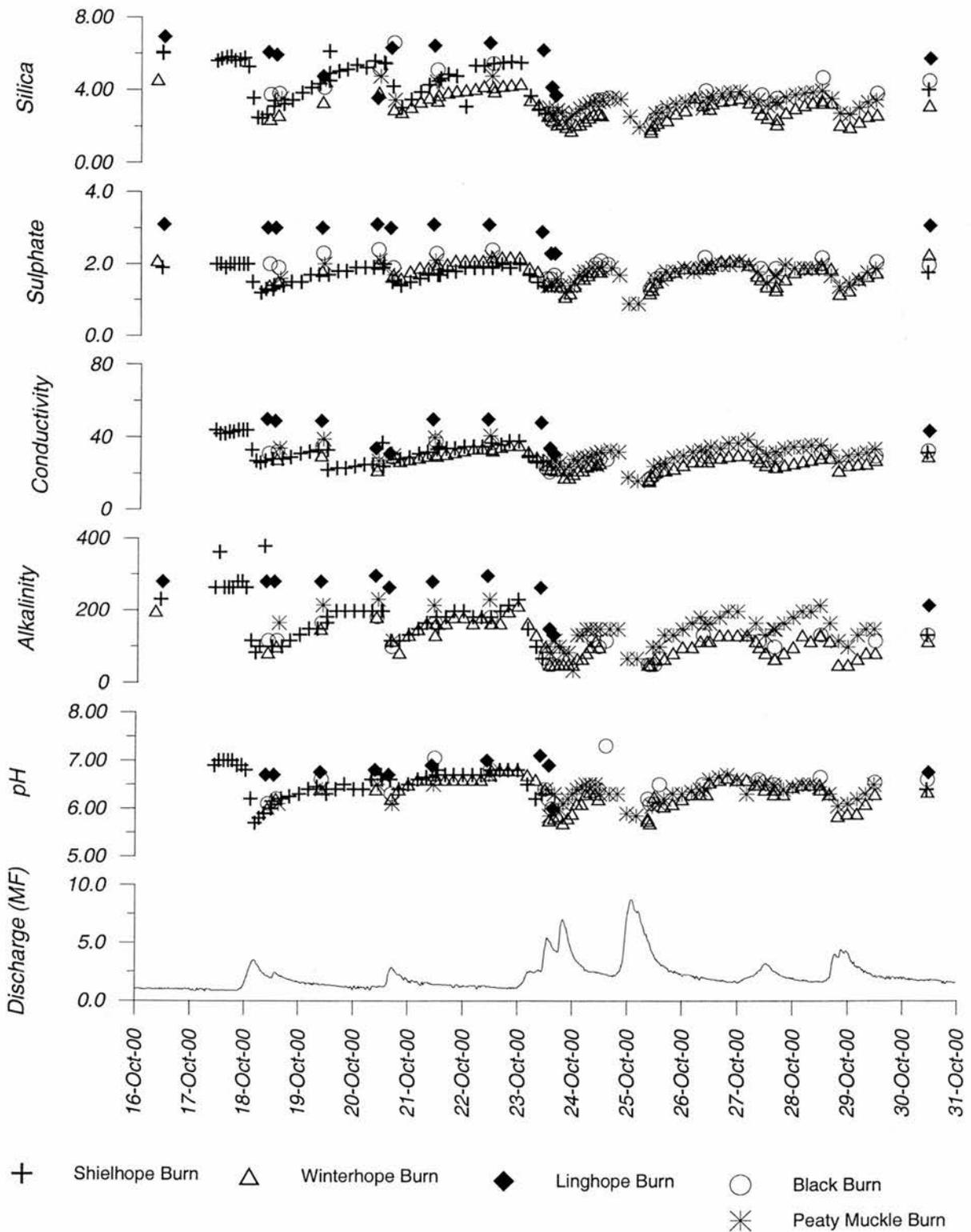


Figure 6. 6: Changes in flow (cumecs), pH, alkalinity ( $\mu\text{Eq L}^{-1}$ ), conductivity ( $\mu\text{S cm}^{-1}$ ) and concentrations ( $\text{mg L}^{-1}$ ) of sulphate and silica during the event sampling programme.

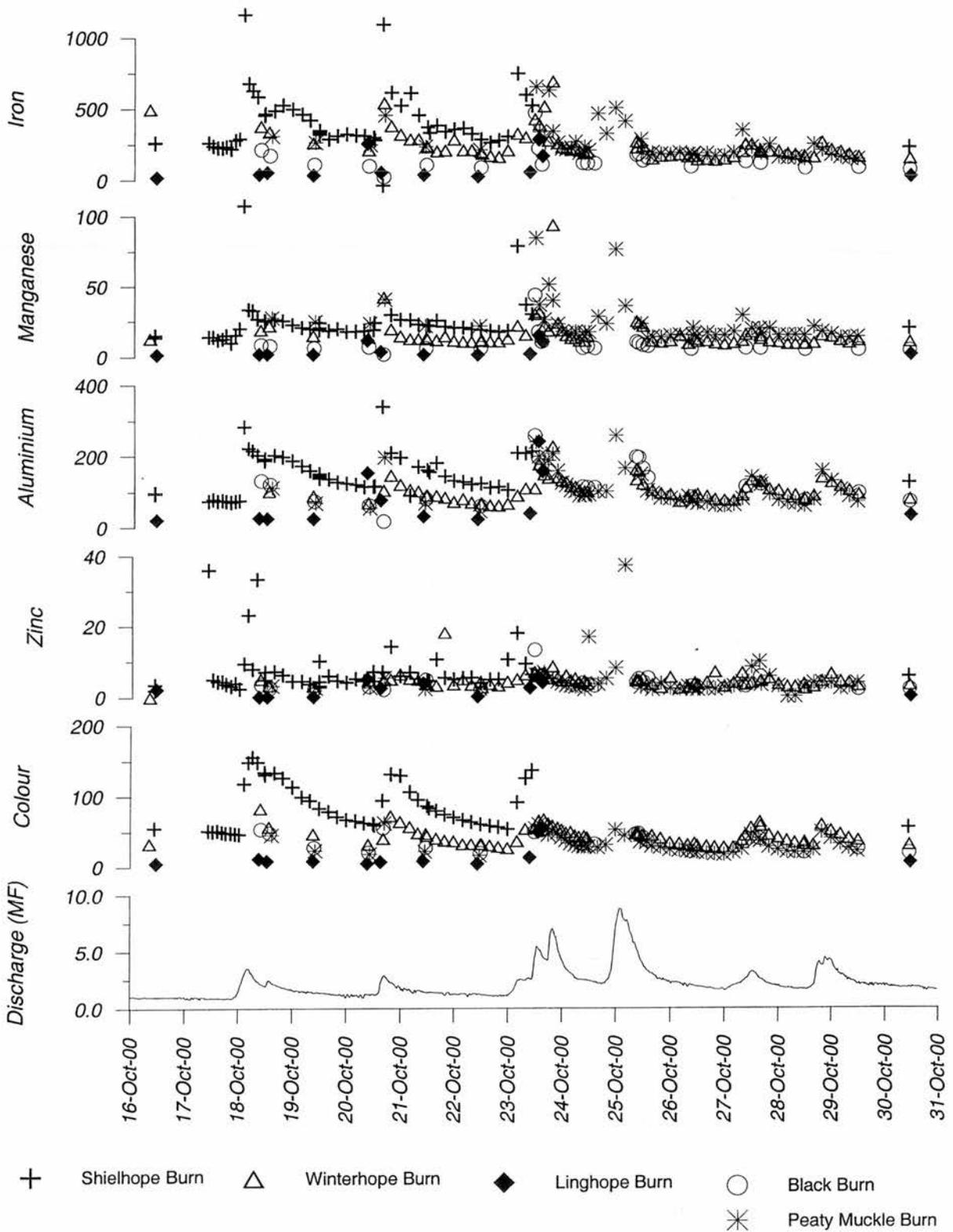


Figure 6. 7: Changes in flow (cumecs), colour ( $^{\circ}\text{Hazen}$ ) and concentrations ( $\mu\text{g L}^{-1}$ ) of iron, manganese, aluminium and zinc during the event sampling programme.

For a more direct comparison of chemical trends and ranges in the different streams the results from stream chemistry analysis are summarised in the form of scatter plots (*Figure 6. 8*) and data for different streams are plotted using different symbols to highlight variations between the samplings sites. The graphs show a range of inter-elemental relationships and it is apparent that hydrological factors (e.g., changes in flow) play an important role in determining the dynamic variations in stream chemistry during storm events.

Components related to weathering (Ca, SO<sub>4</sub>, alkalinity, pH) have an inverse relationship with flow for all the streams and this is consistent with the dilution of base-rich groundwater sources with more acidic soilwater inputs during storm periods. The single straight linear (positive) relationship between these parameters, best seen for Ca and alkalinity, indicates their similar flow-related behaviour for all streams and suggests conservative two component mixing of two main water types (or end-members), one corresponding to typical stormflow waters and another representing baseflow chemistry. Thus, hydrological factors appear more important than the geological factors in determining concentrations of these elements at different flows.

Determinants associated with soilwater sources (colour, Fe, Al) are positively related with flow, although the inter-relationships of these elements show that gradients differ between the streams. The differences are well seen in the relationships between Al and colour (*Figure 6. 9a*) and suggest that high flow chemistry varies between the sampling locations. The gradients are similar for Shielhope Burn and Winterhope Burn as well as for Black Burn and Peaty Muckle Burn, and this paring compares well with the observed variations in soil type distribution between these sub-catchments. No clear

gradient is observed at Linghope Burn, but the plot clearly illustrates the extremely low colour and metal concentrations at baseflow conditions characteristic for that stream.

The effect of soil type on flow pathway and chemistry is also clearly reflected in the high Fe, Mn, Zn, Al and colour loadings in Shielhope Burn, Winterhope Burn and Peaty Muckle Burn, indicating higher contribution of soilwater sources, even during low flow. Alkalinity, Ca, Mg and SO<sub>4</sub> are generally lower in Shielhope Burn and Winterhope Burn compared to Linghope Burn and Black Burn, but high alkalinity values are seen in Peaty Muckle Burn, in particular between storm events. This is probably due to inputs from waters draining the peaty podzols, which make up much of the steep slopes in the catchment and appear to maintain stream flow during baseflow periods.

Despite the high flow contribution of organic rich soilwater in Shielhope Burn, deeper groundwater sources rich in weathering components appear to be important during baseflow indicated by the relatively high SiO<sub>2</sub> concentrations. The constantly high concentrations in weathering components at Linghope Burn also suggest a permanently high contribution of deeper soilwater and groundwater to stream flow.

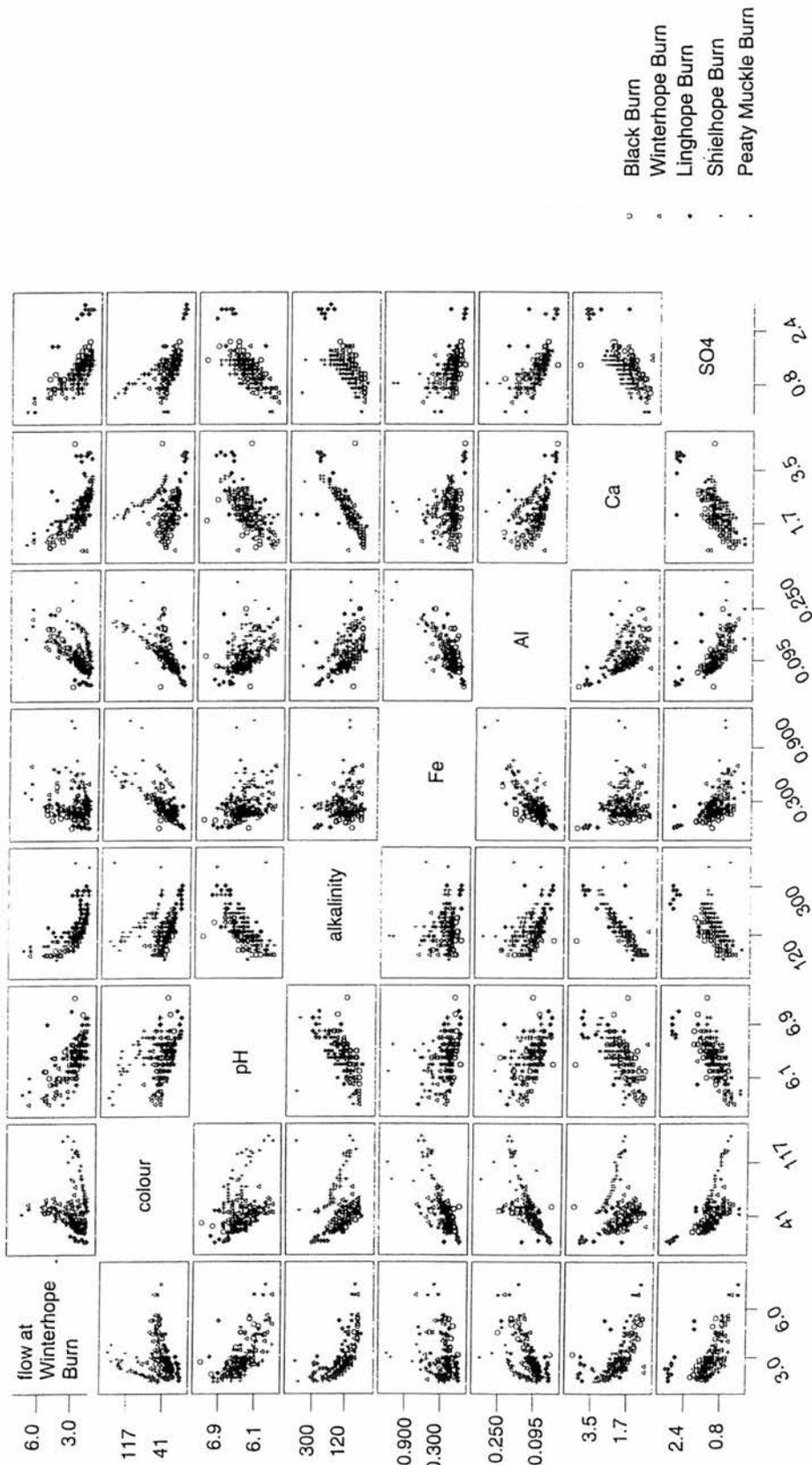


Figure 6. 8: Relationship between flow (cumecs), colour ( $^{\circ}$ Hazen), pH, Alkalinity ( $\mu\text{eq/L}$ ) and concentrations (mg/L) of Fe, Al, Ca and SO4 for all streams sampled during intensive programme (18 October 2000 - 30 October 2000)

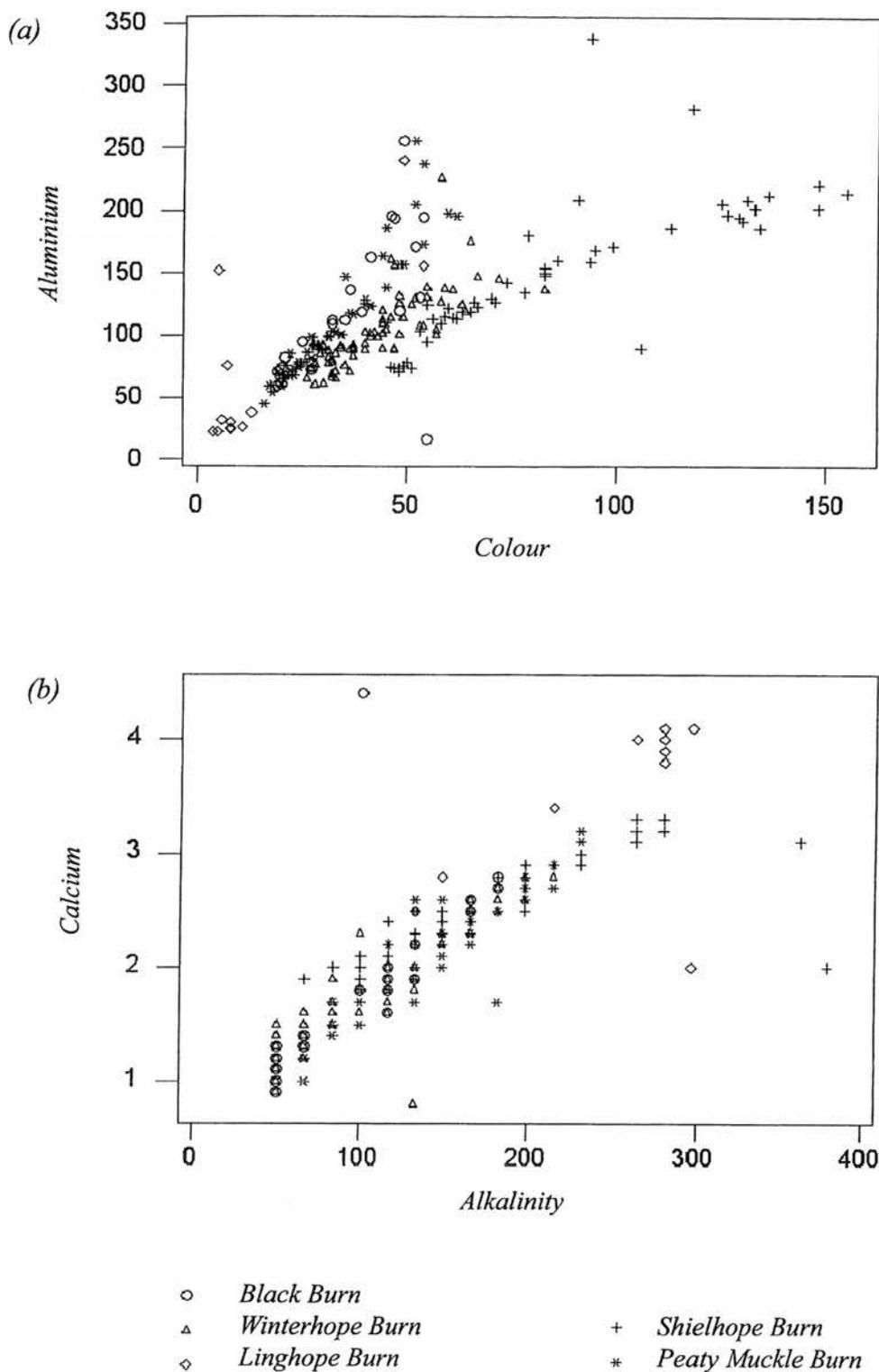


Figure 6. 9: Scatter plots showing relationship between (a) colour and Al ( $\mu\text{g L}^{-1}$ ) and (b) alkalinity ( $\mu\text{Eq L}^{-1}$ ) and Ca ( $\text{mg L}^{-1}$ )

## 6.5 Statistical data analysis: R-mode and Q- mode factor analysis

Scatter plots have been used in *Section 6.4* as a visual tool to investigate the relationships between the measured variables and to compare the runoff chemistries at different streams (*Figure 6. 8*). The plots clearly indicate that inter-relationships exist between some of the variables but not between others and that different patterns of runoff chemistry emerge for the individual streams. However, the relationships within the data are clearly complex and the dependencies cannot be resolved satisfactorily by a purely subjective method such as visual inspection of the scatter plots.

Therefore, a multivariate technique, called factor analysis, has been adopted for analysing the inter-relationships between variables and comparing the respective properties of groups of samples. The aim of the analysis is to improve the understanding of the environmental context responsible for runoff composition and to identify the different sources of, and controls upon, runoff generation.

### 6.5.1 Introduction

Factor analysis is a widely used multivariate method of data reduction and comprises a number of related computational procedures designed for the analysis of inter-relationships within a set of variables or samples. It is sometimes referred to as 'true factor analysis' to discriminate it from principal component analysis, which often is inaccurately termed as 'factor analysis' (Davis, 1986; Jöreskog *et al.* 1976).

The prime objective of factor analysis is to reduce the dimensionality of the original data by looking for underlying trends inherent in the data. It transforms the original

variables (or samples) into a smaller set of mutually uncorrelated 'factors'<sup>1</sup>, which contain the essential information of the original set of variables (or samples) and form the 'new (reduced) dimensions' of the data space.

Factor analysis has been applied in various geological, hydrological and geochemical studies and was found to offer a useful means for exploration of multivariate relationships within suitable data sets (Heal *et al.* in press; Walden and Smith, 1995; Davis, 1986; Reid *et al.* 1981; Jöreskog *et al.* 1976). The technique groups together correlated variables into underlying factors, the most significant of which account for more variation within the data set than any single original variable. If interpretable, these factors can be associated directly or indirectly with a specific source and/or process.

All factor methods are based on eigenvector methods and can be grouped into R-mode and Q-mode techniques, both of which can be performed separately. R-mode factor analysis is applied when the primary objective of the investigation is to understand the inter-correlations among the variables. It is similar to Principle Component Analysis (PCA), but factors are chosen so as to maximise the correlation between the original variables, rather than to maximise the variances as in PCA (Kovach, 1995). Q-mode factor analysis is mathematically similar to R-mode analysis, but it explores relationships among samples (objects) rather than among variables. It is similar to cluster analysis in that it has the objective to group together similar observations

---

<sup>1</sup> The term '*factor*' is commonly used to describe 'some sort of theoretical or hypothetical casual variable' extracted from the data set by factor analysis and refers to the results of the method rather than to the method itself. In older literature, however, the term 'factor' is sometimes related to its mathematical meaning as 'one of a number of things that when multiplied together yields a product', in which case it is referring to the method itself (Klovan, 1975).

(similar columns of data) with the general goal to minimize within-group variation and maximize between group variations.

In this study, a simultaneous R- and Q-mode factor analysis is adopted to detect multivariate patterns in the geochemical data sets collected during an intensive sampling period at different streams in the Megget catchment in October 2000. The method follows a procedure proposed by Walden and Smith (1995) and is also detailed in Zhou *et al.* (1983) and Davis (1986). The following chapter is intended to provide an outline of the applied technique. For a more detailed discussion of the method and underlying mathematical procedures the reader is referred to the references given above.

## 6.5.2 Method adopted and data analysis

### Selection of variables for analysis

The output of factor analysis is a strong function of the input. This means that factors emerging from factor analysis are the ones that best capture the nature of the data set. Thus, if the data set contains many variables that are related to the same source and/or depend on the same controls, they would emerge as the principal factor, simply because so many variables were highly correlated (Rogerson, 2001). This cannot be avoided when dealing with stream chemistry data as the stream water components originate from similar or the same source and all are controlled by a common factor: flow. However, to minimise effects of data redundancy and to facilitate the interpretation of the results, variables such as concentrations of dissolved metals, 'CaCO<sub>3</sub>-hardness' and TOC were removed from the data set. Variables whose concentrations were extremely low (TSS, nutrients) were also omitted. The resulting data set contained the following variables to be included in the factor analysis:

Alkalinity, colour, conductivity, pH, total iron, total manganese, total aluminium, calcium, magnesium, silica and sulphate.

### Data normalisation

For the factor analysis to be valid the raw data have to meet a number of requirements. Firstly, the data should be multivariate normally distributed and secondly, the number of samples should be larger than the number of variables. The technique, strictly speaking, is not a statistical procedure (in the narrow sense) and is not subject to significance testing, so that moderate departures from these assumptions are not thought to be critical (Walden and Smith, 1995). However, normalisation of the data can facilitate analysis of the data and also improve the interpretability of the results (Kovach, 1995). Therefore, the raw data were adjusted to be normally distributed by applying the following *log ratio transformation* to the data matrix prior to analysis:

$$d_{i,j} = \log \frac{a_{i,j}}{\bar{a}_i},$$

(Eq 6. 1)

where  $\bar{a}_i$  is the mean of all  $a_{i,j}$  for  $j=1,n$  and  $d_{i,j}$  is the log ratio transformation for all variables and samples. These logarithm transformations are generally used to adjust non-normal continuous measurements so they are close to being normally distributed (Kovach, 1995). The second criterion ( $n_{samples} > n_{variables}$ ) has been satisfied by all data sets.

Data standardisation

Both, R-mode and Q-mode techniques are sensitive to the scale of the measurements and when applied to non-standardised data, the factors (and the various factor loadings) extracted by the two techniques are not common due to the differences in the underlying scaling procedures (Walden and Smith, 1995). Therefore, it was necessary to standardise the raw (normalised) data matrix prior to R- and Q-mode analysis so they have means of 0.0 and variances of 1.0. The elements of the resulting variance-covariance matrix will then consist of correlations, and thus the extracted factors and/or principal components will be dimensionless (Davis, 1986). A common standardisation procedure was selected, as suggested by Davis (1986) (see also Walden and Smith, 1995), where

$$z_{i,j} = \frac{d_{i,j} - \bar{d}_i}{s_i},$$

(Eq 6. 2)

with  $\bar{d}_i$  and  $s_i$  being the mean and the standard deviation for all  $d_{i,j}$ ,  $j=1, n$ . This procedure removes the effects of variables being measured in different scales (pH, mg L<sup>-1</sup>, µg L<sup>-1</sup>, mmol Eq<sup>-1</sup> etc.) and when applied prior to R- and Q-mode factor analysis, allow extraction of a common set of factors. Both variable and sample factor loadings are then relative to the same underlying factors and for any two of these factors can be plotted in the same two-dimensional factor space.

It has been pointed out by Davis (1986) that standardisation of the raw data tends to inflate variables whose variance is small, and reduces the influence of variables whose variance is large. This is unavoidable if the original variables are measured in different,

incompatible units. However, when interpreting the results of factor analysis it should be remembered that a property that seems relatively insignificant may exert a strong influence on the analysis.

#### Data analysis

Combined R- and Q-mode factor analysis was carried out using Minitab on the standardized data and consisted of a series of matrix algebra manipulations. The techniques will be introduced in the following section and the individual computational steps incorporated in the analysis are summarised in *Table 6. 3*.

The *R-mode technique* adopted for this study presents a principal component approach to factor analysis and as pointed out by Davis (1986) does not lead to a 'true' factor solution. Thus, strictly speaking, the technique is not a statistical procedure; rather, it is a mathematical manipulation. Given an original (standardised) data matrix of  $n$  samples by  $m$  variables the data are transformed into an  $m \times m$  correlation matrix from which the eigenvalues and eigenvectors are extracted. The underlying factors are then derived by multiplying each eigenvector by its singular value (square root of eigenvalue). This transforms each eigenvector into a vector whose length is proportional to the variations it represents. The resulting factor matrix contains 'factor loadings' for each of the original variable on each of the new factors. Each factor loading is therefore related to the amount of variance contributed by that variable to the factor and its size provides a measure of the amount of variance of each variable explained by that particular factor.

The *Q-mode technique* applied in this study follows a procedure similar to principle coordinates analysis (Kovach, 1995, Davis, 1986). Starting from the same standardised

data set of  $n$  samples and  $m$  variables, an  $n \times n$  similarity matrix is constructed, representing the similarities between sample pairs in terms of the way they respond to all variables. Factors are then extracted from the data using the same procedure applied in R-mode analysis and producing a factor matrix of all sample factor loadings. This time, the size of the resulting factor loading is related to the amount of variance of each sample explained by a particular factor [Note that this procedure can be abbreviated to  $[Z].[U]$  as shown below because the data are standardised].

- i. Compilation of *raw data matrix*  $[A]$  of  $n$  samples (rows) and  $m$  variables (columns) to be included in the analysis
- ii. Normalisation of data by *log ratio transformation* to obtain  $[D]$
- iii. *Standardisation* of data by subtracting the means and dividing by the standard deviation resulting in  $[Z]$
- iv. Creating  $[Z]'$  by transposing  $[Z]$
- v. Matrix (pre-) multiplication of  $[Z]'.[Z]$ . gives  $[R]$ , the *correlation matrix* between the variables
- vi. Extraction of *eigenvalues* and *eigenvectors* from  $[R]$ ; Eigenvectors form matrix  $[U]$
- vii. Formation of the diagonal, *single value matrix*  $[\Lambda]$ , whereby square roots of the eigenvalues extracted from  $[R]$  form the diagonal values of the matrix
- viii. Compute matrix of *variable factor loadings*  $[A^R]$  by multiplication of  $[U].[\Lambda]$
- ix. Compute matrix of *sample factor loadings*  $[A^Q]$  by multiplication of  $[Z].[U]$
- x. Plot variable factor loadings  $[A^R]$  and sample factor loadings  $[A^Q]$  in the same factor space

Table 6. 3: Combined R- and Q-mode analysis: computational steps

After the factor loadings for all variables and samples are derived, the original data can be plotted in the 'new' factor space to illustrate relations between sample and variable factor loadings. This is possible since the new factors derived from factor analysis are uncorrelated and occupy a mutually orthogonal axis in a 'multidimensional factor space'. This means that any two factors can be presented as perpendicular axes in two-dimensional space. Using factor loadings, it is therefore possible to plot the position of the original variables in relation to any two of the new factors as a simple scatter plot. Variables that plot in close proximity are generally highly correlated. The same is true for sample factor loadings. Samples plotting in close proximity in factor space can be interpreted as being most similar in terms of their values on all variables. As discussed previously, the data standardisation procedure has led to the extraction of a common set of factors between R-mode and Q-mode analysis, so that for any two factors variable and sample factor loadings can be plotted in the same two-dimensional factor space.

Nonetheless, factor analysis has been criticised for subjectivity of the method (Swan and Sandilands, 1995) mainly related to:

- (i) Selection of the factor rotation method,
- (ii) Preconception of the analyser with regards to the number of factors included in the analysis.

However, the method used in this study is based on a principle component approach, which means that the number of factors is not determined prior to analysis. Instead, all eigenvectors and eigenvalues of a correlation matrix are extracted and the less important ones of these are then discarded after inspection of the data. Furthermore, the applied techniques do not employ factor rotations, so that the main criticism made on the application of factor analysis is avoided by using the method outlined above.

### 6.5.3 Data interpretation

Combined R- and Q-mode analysis was carried out on selected parameters of the entire data set collected during the intensive sampling programme. The aim was to find a set of common (mathematical) factors for all sampled streams, which explain the variations in chemical composition and are interpretable, in order to relate stream chemistry to processes occurring in the streams and the surrounding catchment.

By analysing all streams together, the results for each can be directly compared since variable factor loadings and sample factor loadings for all the streams occupy the same factor space and common processes controlling stream runoff response during storm events can be identified. However, there are two obvious problems with combining data from all tributaries into one data set for factor analysis. First, the large variations in sampling frequency between the individual streams may introduce a strong bias towards processes occurring in more frequently sampled streams, as they contain a larger number of samples and may overly influence the data set. In contrast, processes controlling stream water chemistry in less frequently sampled tributaries have less influence on the data set and may remain obscured in the data. Second, by analysing all streams together, it is assumed that stream runoff and chemistry in all catchments is generated from and controlled by similar sources and processes. This may not be true, as local variations in geological settings and soil type distribution can cause significant differences in stream chemical composition (Reynolds *et al.* 1986; Billet *et al.* 1996; Dawson *et al.* 2001) and may also, alongside other catchment properties like topography and/or size and shape, give rise to different runoff responses and flow pathways (Ferrier *et al.* 1990b). Therefore, R-mode and Q-mode analysis of the entire data set was used as a basis to identify the main processes controlling stream chemistry,

but then was repeated for each stream individually to account for local variations and to test the 'universal' stream response in the Megget catchment.

The Linghope Burn dataset just fulfils the  $n_{\text{samples}} > n_{\text{variables}}$  criterion and when analysed separately the criterion is barely acceptable. Therefore, separate factor analysis is not carried out for Linghope Burn, but the data are included when analysing the entire data set.

### R-mode analysis - Variable factor loadings

From the R-mode analysis of the entire data set two factors are extracted with eigenvalues greater than one so that each factor explains greater variance than the original standardised variables. The eigenvalues (*Table 6. 4*) show that the two factors account for 80% of the variation present in the original data set with 67% and 13% for Factor 1 and 2, respectively. The loadings of individual variables on the two factors are listed in *Table 6. 4* and the positions of the original variables in the newly created factor space are plotted in *Figure 6. 10*, which contains 80% of the variability in the original 11 dimensions.

From *Table 6. 4* it is apparent that factor 1 has very high loadings on all variables and the position of the 11 original variables with respect to the two factors in *Figure 6. 10* also shows that factor 1 clearly divides the original data into two distinct groups of variables, characterised by high negative or high positive factor loadings, respectively. The most dominating variables within these groups are alkalinity and SiO<sub>2</sub> with strong negative loadings, and Al and colour with loadings of similar absolute value but opposite sign. Fe and Mn also have high loadings on factor 1, but are clearly the most dominating control on factor 2 with relatively high positive loadings. The close

proximity of groups of variables in the factor space (*Figure 6. 10*), such as colour, Al, Fe and Mn or SiO<sub>2</sub>, alkalinity, pH and base cations suggests that these variables are highly correlated and the differences in sign imply an inverse correlation between these groups of variables.

The high positive loadings on Al and colour on factor 1 (*Table 6. 4, Figure 6. 10*) suggest a strong influence of the soilwater component. As shown in Chapter 2, soilwater chemistry is dominated by processes of decomposition of plant material in the upper soil horizons and becomes important during rainfall events when stream runoff is derived mainly from overland and through flows generated in the upper soil horizons. Beside high concentrations in organic matter (colour and TOC), soilwater also contains high amounts of organically complexed metals, and this is reflected in the strong loadings on Fe, Mn and in particular Al (*Table 6. 4, Figure 6. 10*), which together with hydrogen (strong negative pH loadings) is the dominant cation in the solution of acidic soils and forms strong complexes with dissolved organic matter (Drever, 1997). SiO<sub>2</sub>, alkalinity and base cations are indicative of bedrock weathering and the high negative loadings on factor 1 are consistent with the dilution of base-rich groundwater inputs with more acidic soilwater sources during storm periods. Hence, factor 1 reflects the flow related changes in stream chemistry and, in this study, is interpreted as the dilution of stream baseflow with soilwater inputs that are high in Al and colour during storm events, where water from the upper soil horizons is displaced as rainfall infiltrates the soils.

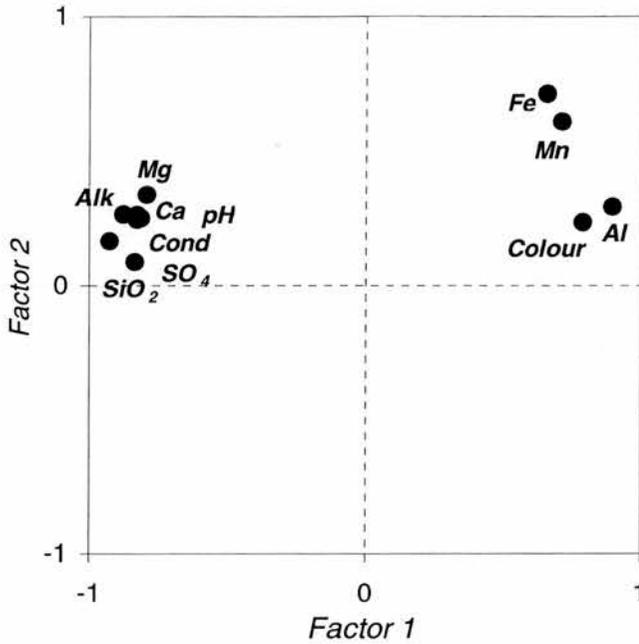


Figure 6. 10: Variable factor loadings in the factor space derived from analysis of entire data set

Factor 2 is clearly an Fe and Mn factor with no important contribution from any of the other elements (Table 6. 4). It is interpreted as the reductive solution of Fe and Mn oxides/hydroxides in the soils under low redox conditions; the important influence of such processes on stream chemistry during events has been pointed out in similar studies (Heal *et al.* in press; Reid *et al.* 1981).

Similar factor loading patterns are found when analysing data from the individual streams separately. Two factors with eigenvalues around or greater than one are extracted which are sufficient to express most of the variation (84 %-90 %) in the original data. Factor loadings for individual streams are listed in Table 6. 5.

Elements	Factor 1	Factor 2	
Colour	<b>0.79</b>	0.23	
Conductivity	<b>-0.83</b>	0.25	
pH	<b>-0.81</b>	0.25	
Alkalinity	<b>-0.88</b>	0.26	
Mn	<b>0.71</b>	<b>0.61</b>	
Fe	<b>0.66</b>	<b>0.71</b>	
Al	<b>0.90</b>	0.29	
Ca	<b>-0.79</b>	0.34	
Mg	<b>-0.83</b>	0.26	
SiO <sub>2</sub>	<b>-0.93</b>	0.17	
SO <sub>4</sub>	<b>-0.84</b>	0.09	
			<b><u>Totals</u></b>
Eigenvalues	7.364	1.427	8.791
Variance	0.67	0.13	0.80

*Factor loading <-0.5 and >0.5 are emboldened*

Table 6. 4: Factor loadings resulting from analysis of entire data set (all streams)

Elements	<u>Shielhope Burn</u>		<u>Peaty Muckle Burn</u>			
	Factor 1	Factor 2	Factor 1	Factor 2		
Colour	<b>0.97</b>	0.10	<b>0.91</b>	-0.19		
Conductivity	<b>-0.97</b>	-0.17	<b>-0.84</b>	-0.16		
pH	<b>-0.87</b>	-0.25	<b>-0.77</b>	-0.01		
Alkalinity	<b>-0.84</b>	0.02	<b>-0.845</b>	-0.14		
Mn	<b>0.73</b>	<b>-0.66</b>	0.49	<b>-0.85</b>		
Fe	<b>0.87</b>	-0.42	<b>0.55</b>	<b>-0.77</b>		
Al	<b>0.92</b>	-0.25	<b>0.94</b>	-0.21		
Ca	<b>-0.94</b>	-0.19	<b>-0.72</b>	<b>-0.59</b>		
Mg	<b>-0.96</b>	-0.15	<b>-0.90</b>	-0.33		
SiO <sub>2</sub>	<b>-0.91</b>	-0.15	<b>-0.93</b>	-0.32		
SO <sub>4</sub>	<b>-0.95</b>	-0.15	<b>-0.93</b>	-0.05		
			<b><u>Totals</u></b>		<b><u>Totals</u></b>	
Eigenvalues	9.032	0.882	9.915	7.343	2.001	9.344
Variance	0.82	0.08	0.90	0.67	0.18	0.85

Continued

*Continued*

Elements	<i>Winterhope Burn</i>			<i>Linghope Burn</i>		
	Factor 1	Factor 2		Factor 1	Factor 2	
Colour	<b>0.77</b>	-0.41		<b>0.76</b>	<b>-0.63</b>	
Conductivity	<b>-0.91</b>	-0.26		<b>-0.89</b>	-0.25	
pH	<b>-0.91</b>	-0.19		<b>-0.62</b>	0.21	
Alkalinity	<b>-0.94</b>	-0.24		<b>-0.78</b>	0.49	
Mn	<b>0.69</b>	<b>-0.57</b>		<b>0.97</b>	0.15	
Fe	0.45	<b>-0.86</b>		<b>0.91</b>	0.11	
Al	<b>0.95</b>	-0.15		<b>0.96</b>	0.13	
Mg	<b>-0.81</b>	-0.24		<b>-0.76</b>	<b>-0.51</b>	
Ca	<b>-0.73</b>	-0.42		<b>-0.83</b>	-0.39	
SiO <sub>2</sub>	<b>-0.97</b>	-0.19		<b>-0.87</b>	-0.14	
SO <sub>4</sub>	<b>-0.95</b>	0.09		<b>-0.82</b>	<b>0.54</b>	
			<b><u>Totals</u></b>			<b><u>Totals</u></b>
Eigenvalues	7.728	1.687	9.415	7.728	1.519	9.247
Variance	0.70	0.15	0.85	0.70	0.14	0.84

Elements	<i>Black Burn</i>		
	Factor 1	Factor 2	
Colour	<b>0.70</b>	-0.42	
Conductivity	<b>-0.87</b>	0.25	
pH	<b>-0.66</b>	0.49	
Alkalinity	<b>-0.91</b>	0.34	
Mn	<b>0.75</b>	<b>0.52</b>	
Fe	<b>0.68</b>	<b>0.66</b>	
Al	<b>0.89</b>	0.41	
Mg	<b>-0.91</b>	-0.05	
Ca	<b>-0.95</b>	-0.12	
SiO <sub>2</sub>	<b>-0.98</b>	-0.05	
SO <sub>4</sub>	<b>-0.90</b>	0.29	
			<b><u>Totals</u></b>
Eigenvalues	7.800	1.571	8.371
Variance	0.71	0.14	0.85

*Factor loading <-0.5 and >0.5 are emboldened*

Table 6. 5: Factor loadings for individual streams resulting from separate analysis of water chemistry data

Factor 1 is by far the most dominant factor in all streams and accounts for 67 % (Peaty Muckle Burn) to 82 % (Shielhope Burn) of the variability in the original variables. In all

streams, it has high positive loadings on Al (0.89 to 0.96) and colour (0.70 to 0.97), indicative of storm event runoff, derived from the upper organic and organo-mineral horizons and high negative loadings on Mg (-0.72 to -0.94), Ca (-0.73 to -0.96), SiO<sub>2</sub> (-0.87 to -0.98), SO<sub>4</sub> (-0.82 to -0.95), alkalinity (-0.78 to -0.94) and conductivity (-0.84 to -0.97) reflecting the dilution of baseflow waters by soilwater inputs during events. Loadings on pH are also high, but somewhat lower values are observed in Black Burn (-0.66) relative to the other streams (-0.83 to -0.91), and this may be due to the generally higher pH of this stream (*Table 6. 2*) and the buffering of stream chemistry by inputs from deeper soilwater sources. There is some contribution of Fe and Mn on factor 1 but loadings are mostly intermediate.

Factor 2 is most clearly influenced by Fe and Mn in all streams (*Table 6. 5*) and captures between 8 % (Shielhope Burn) and 18 % (Peaty Muckle Burn) of the variability within the original data sets. Differences between individual streams mainly occur in the relative contribution of Fe and Mn to that factor and are probably due to local variations in redox conditions in the soils and/or local variations in bedrock mineralisation. The positive correlation between factor scores of Fe and Mn and pH, as seen at Black Burn, suggests that mobilisation of Mn and Fe may occur in less acidic, deeper mineral soil horizons and this explanation is consistent with the negative relationship to colour seen at most streams, and also agrees with the high loadings of Mg on factor 2 seen at Peaty Muckle Burn. It, however, does not explain the intermediate loadings on colour at Winterhope Burn, and this may suggest that some Fe and Mn is being complexed by organic matter during the transport into and/or in this stream. Alternatively, Heal *et al.* (in press) suggests that colour may also result from the formation of finely divided colloidal Fe(III) oxides as deep water enters more oxidising environment of the stream channel as has been found by (Laxen and Harrison,

1981). Somewhat surprising are the low Fe loadings on factor 2 seen at Shielhope Burn, and the dominance of Mn loadings on that factor may indicate a strong influence of gleyed layers in the riparian zone, which promote the transition from immobile to mobile Mn during drying and re-wetting of the soils (Neal *et al.* 1997a).

#### Q-mode analysis - Sample factor loading

Q-mode analysis was carried out on the entire data set as well as on individual streams. As for the R-mode analysis results of the two analyses are very similar, although some features are more pronounced when considering stream sample loadings from separate stream analysis. Therefore, in the following section general features emerging from the analysis are explained on the basis of the results from the analysis of the entire data set and for more detailed illustration the examples from the separate analysis are provided.

The distribution of stream water samples from all streams in the factor space of factor 1 and 2 is shown in *Figure 6. 11* from where it is apparent that sample sets from all streams show a similar spread of values on factor 1 and also on factor 2. Samples with high negative loadings on factor 1, plotting on the far left hand side of the diagram, suggest relatively high alkalinity, SiO<sub>2</sub> and base cation concentrations and/or relatively low Al and colour values. The opposite would be expected for samples with high positive factor 1 loadings, which would plot on the far right hand side of the diagram, close to Al and colour, and this is confirmed by re-inspection of the original data. Samples collected at low flows plot on the left hand side of the diagram and high flow samples on the right and this is consistent with the interpretation that factor 1 represents the dilution of groundwater by more acidic, organic rich storm runoff. Assuming that stream flow consists of two (or more) end-members (Foster, 2000), it appears that the

plot separates the stream flow end members (although the individual end-members itself may not be captured) at opposite ends of the x-axis, and the effect of mixing of two different (main) sources is illustrated by the continuum of the data across the two end-members.

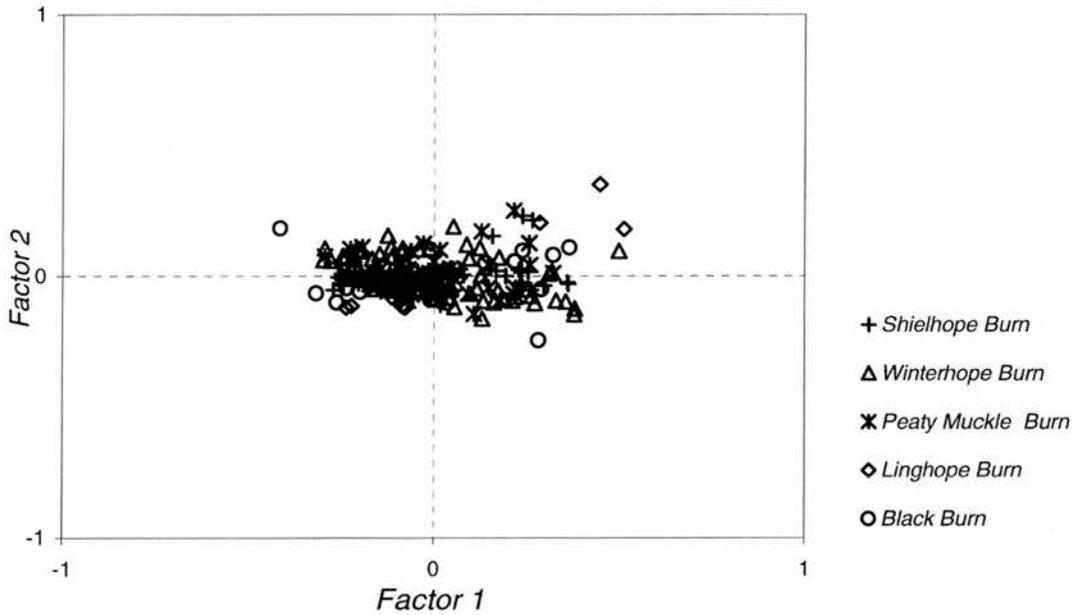


Figure 6. 11: Distribution of stream water samples in factor space of factor 1 and factor 2 derived from analysis of entire data set

As samples from different streams cover different sampling periods and intervals, comparison between streams is difficult by using an universal factor diagram and for the purpose of comparison, variations between streams are better illustrated by considering temporal changes in sample loadings and their relation to flow (Figure 6. 12 and Figure 6. 12). Given that both factors represent stream flow contributions from different, though closely related, runoff sources, the graphs also provide insight into the response of individual streams to particular storm events.

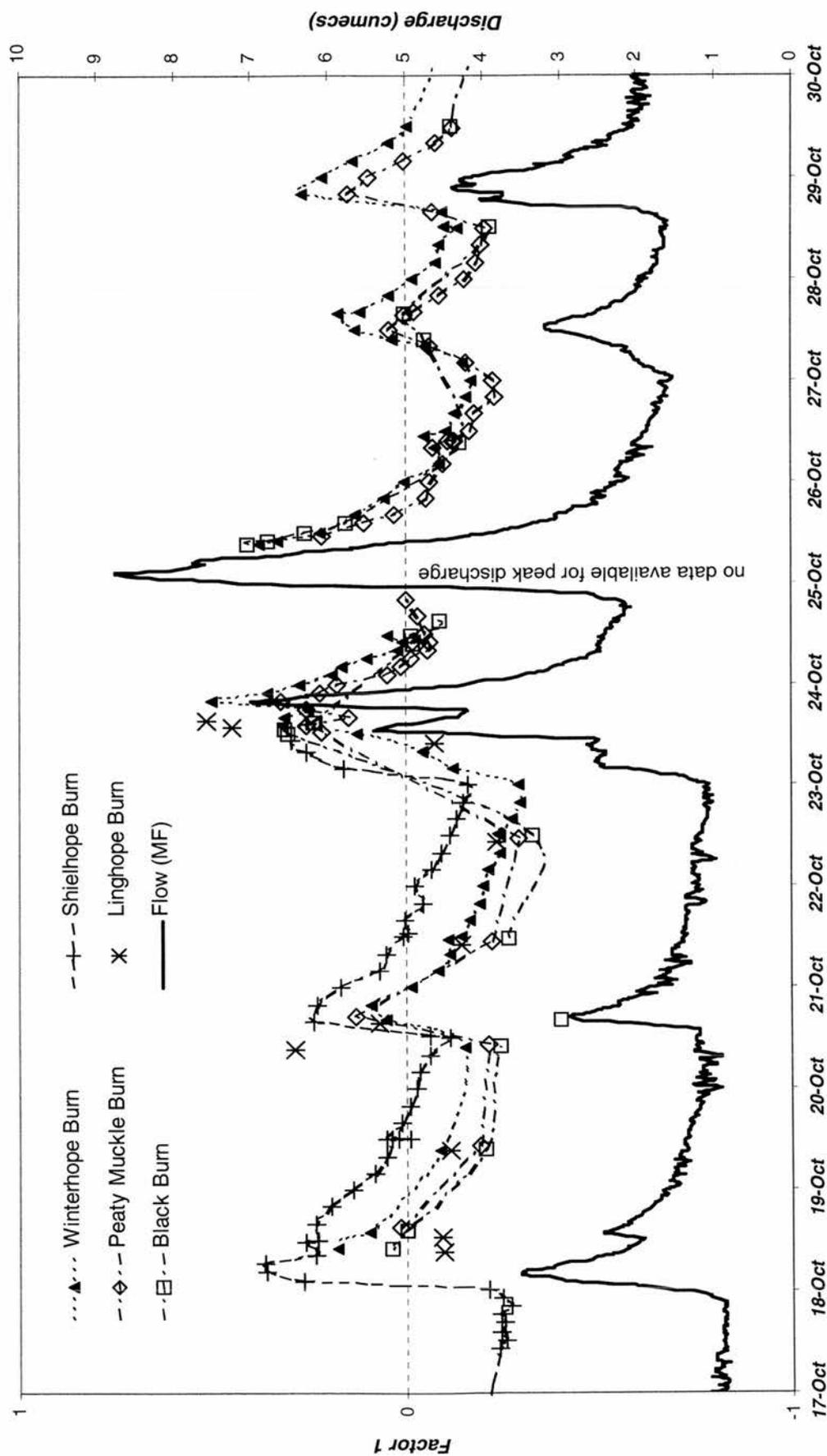


Figure 6. 12: Sample loadings of all streams on factor 1 and their relation to flow.

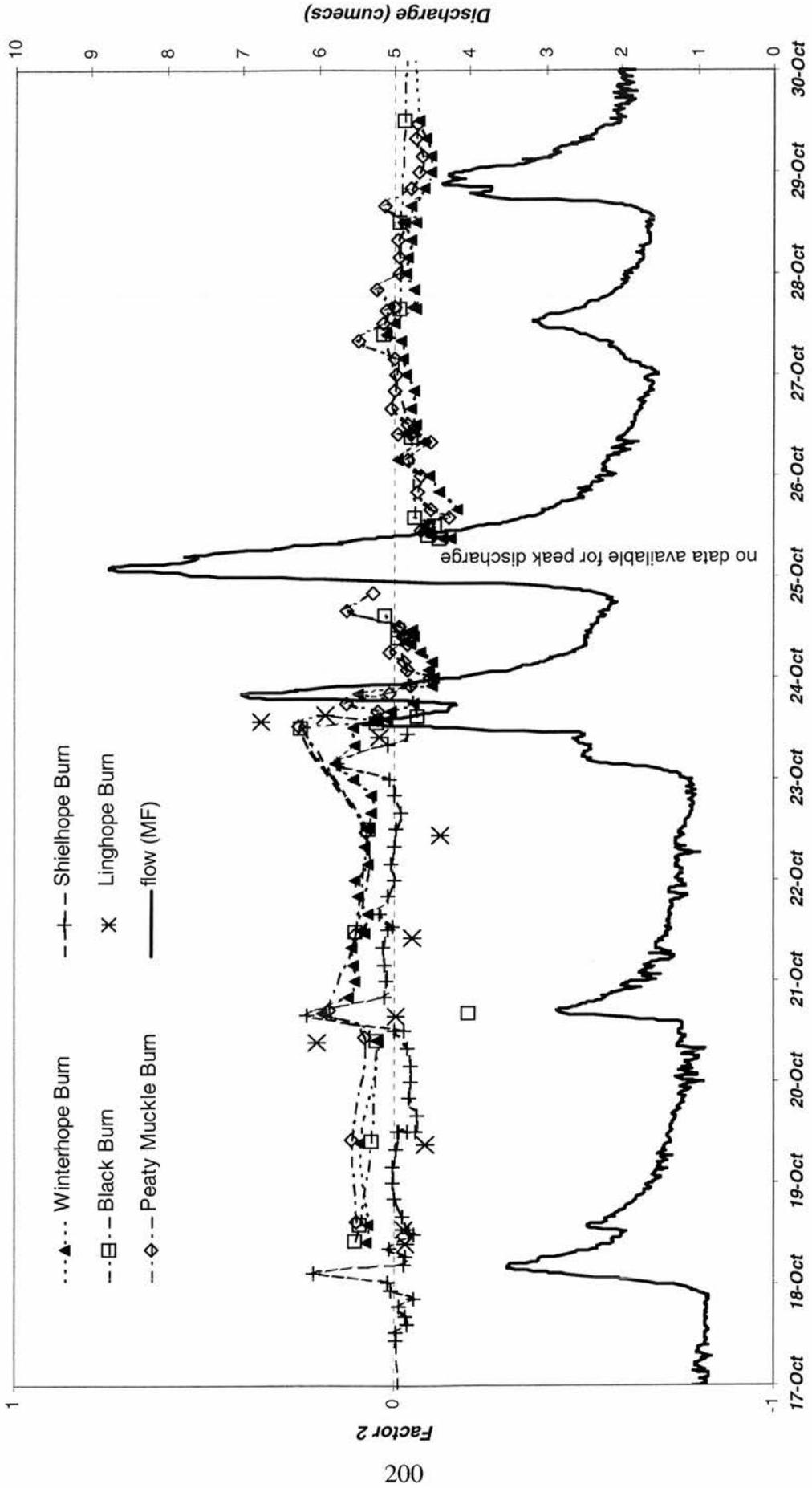


Figure 6. 13: Sample loadings of all streams on factor 2 and their relation to flow.

From *Figure 6. 12* it is apparent that factor 1 is closely related to flow, as would be expected, and similar patterns emerge for all streams, illustrating the general importance of flow path changes during storm events and the increasing influence of soilwater inputs on stream flow composition. Loadings are generally highest at Shielhope Burn (*Figure 6. 12*), probably due to the constantly higher soilwater contribution and the slower regression after storm events also indicates throughflow from slow-draining peat soils. Black Burn, Peaty Muckle Burn and Winterhope Burn have lower loadings, but these increase considerably during storm events. When stream levels are rising, loadings at Peaty Muckle Burn and Black Burn are similar to those at Winterhope Burn, but peak values are generally lower as are the loadings on the falling limb of the hydrograph, reflecting the higher proportion of organic soils in the Winterhope catchment. Linghope Burn also shows dramatic changes in factor 1 loadings, although fine details of runoff dynamics are obscured by the low temporal sampling resolution. Loadings are mostly intermediate, but unusually high values occur during two storm events on October 20 and October 23, where peak factor loadings exceed those of the other streams.

Factor 2, interpreted as the input from (reductive) solution of iron and manganese oxides in the soils, also shows some relation to flow (*Figure 6. 12*), but it appears to be less closely associated than factor 1, and different patterns in sample loadings on factor 2 can be seen for individual streams. Samples from Shielhope Burn generally have very small factor 2 loadings, except for three samples, collected during storm events on 18 October, 20 October and 23 October. Abrupt changes, noted as high factor 2 loadings, occur just before the hydrograph peaks, followed by a rapid decline to pre-storm values, and this is interpreted as the displacement of soilwater, rich in dissolved Fe and Mn, in the gleyed soils near in the riparian zone (Reid *et al.* 1981). Changes of similar

magnitude and abruptness are seen at Linghope Burn, indicating similar processes, although due to the low data coverage at Linghope Burn this can only be speculated.

A somewhat different pattern is seen at Winterhope Burn, Peaty Muckle Burn and Black Burn (*Figure 6. 12*). Initially, factor 2 loadings are intermediate, suggesting a small, but constant contribution of factor 2 to stream flow, and leaching of dissolved Fe and Mn from more freely-draining soils. Increase in loading values is noted during storm events with maximum values foregoing the hydrograph peak; but peak values remain below those at Shielhope Burn and are lowest at Winterhope Burn. Following the storm events on 22-23 October and 24-25 October a dramatic decline in factor 2 loadings is noted at all streams and thereafter factor 2 loadings remain low. Hence, it appears that during these major storm events, the reservoir of dissolved Fe and Mn in the soils is depleted, and while replenishment is slow, contribution of this factor to stream chemistry remains low. For Linghope Burn and Shielhope Burn, there are no data available for these rainfall events, as data collection was terminated on 23 October.

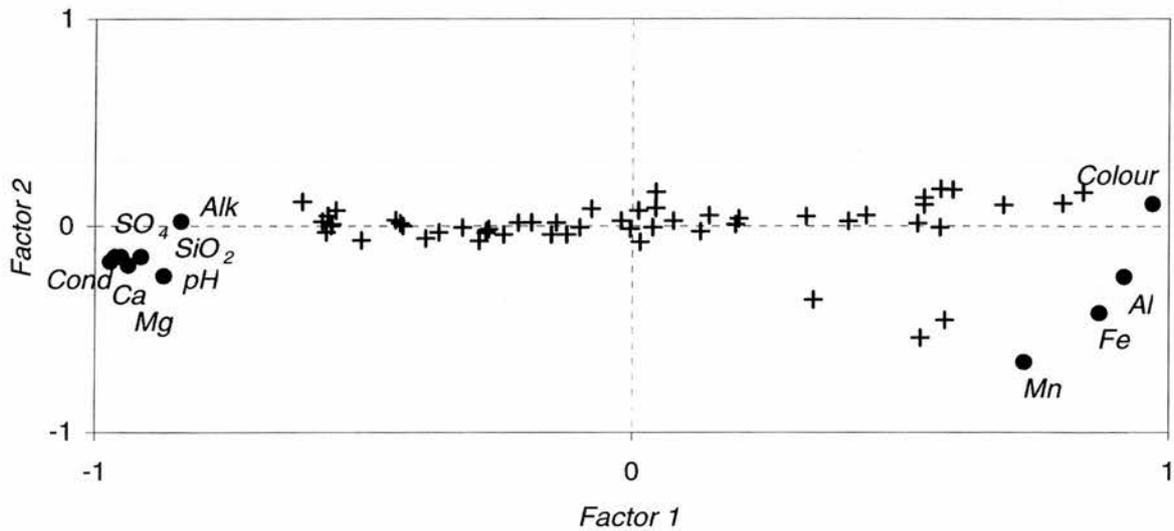
Analysing streams individually and plotting the position of the samples in the form of factor diagrams also shows distinct pattern, as seen in *Figure 6. 14* for Shielhope Burn. The plot shows the distribution of the samples in factor space of factor 1 and factor 2, and also illustrates their relationship to the original variables. The wide range of loadings on factor 1 displayed by the samples may now be explained by reference to the position of the original variables in the same factor space. Besides the clear distinction into baseflow and stormflow samples in factor 1 it is also possible to distinguish a small group of 3 samples with relatively high loadings on factor 2, which, as previously shown (*Figure 6. 12*), are associated with 3 individual storm events. Examining the original data in the context of their position in the factor diagrams it is possible to relate

the observed loading pattern to possible in-catchment processes that control stream chemistry during storm events and to place them in temporal context. A consistent trend emerges among data for individual storm events and is demonstrated in *Figure 6. 15* for the storm event on October 18, where the order of sample collection is indicated by arrows, and the time of sampling is given relative to the beginning of hydrograph rise. The following picture emerges:

- (I) At onset and during the early stage of the event, samples show high negative loadings on factor 1, while loadings on factor 2 are low, and stream chemistry is characterised by high concentrations in  $\text{SiO}_2$ , alkalinity and base ions, thus close to baseflow composition
- (II) As the stream hydrograph rises samples move towards Fe and Mn loadings, and factor 2 loadings reach a maximum after about 8 hours, just before peak flow, and decreasing rapidly thereafter. The change occurs very suddenly, coinciding with maximum Fe and Mn values in the original data, and is probably related to the flushing of Fe and Mn rich waters from the waterlogged riparian gleys
- (III) At peak flow (~10 hours after onset of the storm event), samples move towards colour and Al, and maximum concentrations of these elements in the original data indicate maximum soilwater contribution
- (IV) After peak flow, on the recession limb of the hydrograph, factor 1 loadings and thus soilwater inputs gradually decline and samples return to the original baseflow composition at about 65 hours after hydrograph peak.

Similar patterns are seen in the event data of Winterhope Burn, Peaty Muckle Burn and Black Burn, although factor 2 loadings for these streams increase more gradually during events, suggesting a more gradual displacement of waters in near stream areas. Factor 2

also appears to contribute to stream flow in-between events as previously seen in *Figure 6.12*.



*Figure 6.14: Shielhope Burn sample factor loadings.*

The factor diagrams for individual streams also reflect the effects of antecedent conditions and storm magnitude as is illustrated in *Figure 6.16* for Winterhope Burn, where a succession of five storm events has been sampled. The former is clear from the decrease in factor 2 loadings with successive storm events, indicating gradual depletion of the reservoir of reduced Fe and Mn in the soils, and from the general shift of factor 1 loadings towards higher values resulting from higher soilwater runoff in the wet catchments (see also *Figure 6.12*). The latter is reflected in the variations in factor 1 loadings, thus soilwater inputs are linked to storm magnitude.

The identification of two main factors may also have implications for the End-Member Mixing Analysis undertaken in the next section, where stream chemistry is regarded as a mixture of waters from chemically distinct sources ('end-members'). Statistical techniques similar to the one applied here have been used to aid identification of these

'end-members' (Christophersen and Hooper, 1992; Brown *et al.* 1999), assuming that the distinct properties of the different stream flow sources are reflected in the identified factors. The separation of two main factors, accounting for up to 90 % of the variability in the original data, would imply that at least three different 'end-members' are required to sufficiently explain stream chemistry variations (Christophersen and Hooper, 1992).

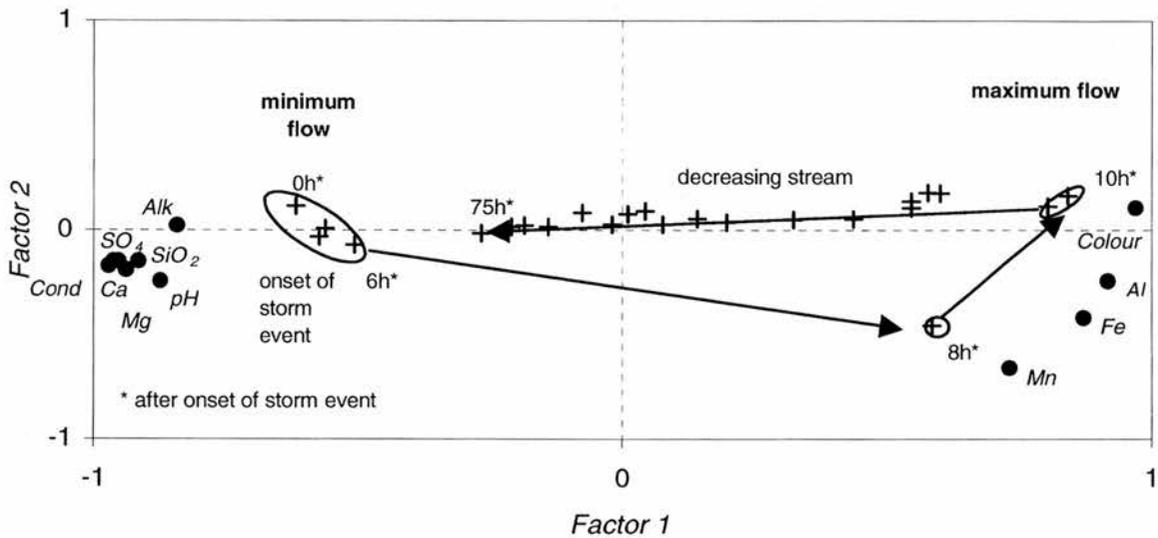


Figure 6.15: Shielhope Burn sample factor loadings for rainfall events on 18 October.

In this study these appear to be (1) a deep water source, (2) an organic soilwater source with high colour loadings and rich in complexed Al, Fe and Mn and (3) a soilwater source rich in dissolved Fe and Mn, although the latter only accounts for 8-15 % of the variability and cannot be distinguished using conservative hydrochemical tracers, such as alkalinity or Ca concentrations, the implications of which will be discussed later (see Section 6.6.3).

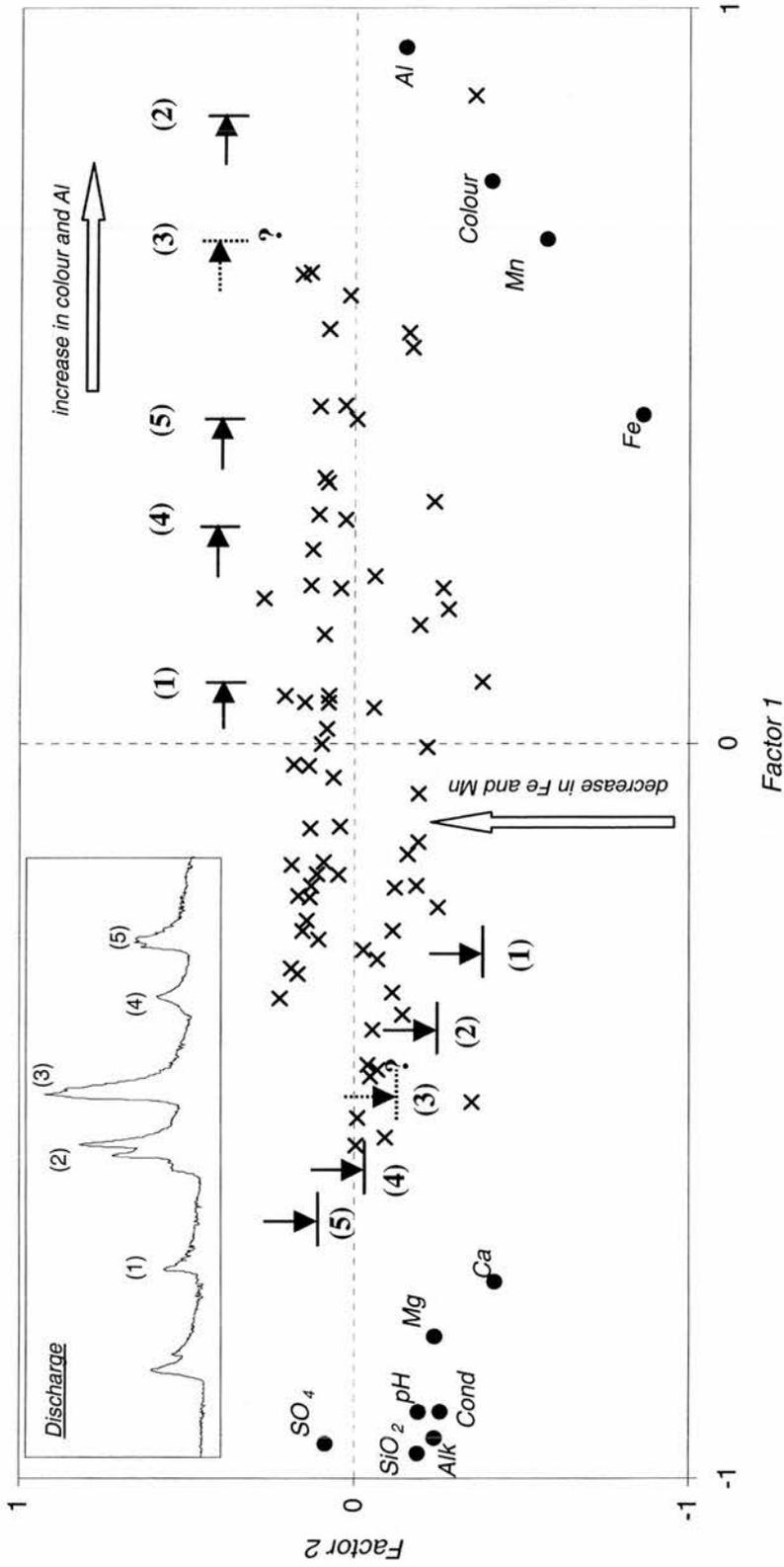


Figure 6. 16: Winterhope Burn sample factor loadings. Inlet shows magnitude of the five sampled storm events. Vertical (small) arrows indicate maximum F2 loading at individual events (gradual Fe and Mn depletion), horizontal (small) arrows indicate maximum F1 loadings at individual events (effect of storm event magnitude) (see text for explanation).

## 6.6 End-member mixing analysis

In this section signatures of geochemical tracers are used to examine the varying hydrological stream flow sources and associated pathways in the Megget catchment over the study period. The relatively simple relationship between flow and alkalinity, seen in all streams, suggests that End-Member Mixing Analysis (EMMA) may offer an useful diagnostic tool for exploring the conceptual hydrological pathways in a more quantitative manner and in this study, the technique is applied to identify the different hydrological pathways and areas of storm runoff generation in the Megget catchment at different flows. Moreover, by assessing the contribution of the different pathways to stream flow, the storm response at individual streams can be described and compared consistently, and this is important to understand processes controlling streamwater chemical variations in the different sub-catchments. Such simple conceptualisation of the catchment behaviour, in particular during high flow periods where contribution from organic rich soil horizons increases sharply, is also important for assessing the cumulative effect of high Fe and Mn loadings in the streams on reservoir water quality and therefore has potential utility as a tool for supporting reservoir management decisions.

Thus, the aim in this section is two-fold:

- (1) identifying the relative importance of hydrological pathways and areas of storm runoff generation in the different sub-catchments using the spatial and temporal variability in streamwater chemistry between streams at different flows, and
- (2) estimating the contribution of the different pathways and sources to stream flow over the sampling period in order to assess the cumulative effect of high Fe and Mn loadings on reservoir chemistry.

### 6.6.1 Introduction

It has been previously shown (Chapter 2) that the pathway which water takes through the catchment determines the water's chemical composition and that different pathways yield different chemical signatures. Conversely, the streamwater characteristics can help to identify the pathways taken and this is one of the basic realisations underlying End-Member Mixing Analysis (EMMA), a tool which has been widely used to investigate processes of stream flow generation and infer runoff sources and flow path (e.g., Christophersen *et al.* 1990; Hooper *et al.* 1990; Chapman *et al.* 1997) based on the observed stream chemistry. This can be accomplished because different soil horizons often have very different chemical properties, and in EMMA theory, the stream is considered as being composed of a mixture of chemically distinct water sources ('end-members'), which relate to distinct soil horizons (e.g., O/A-horizon or soilwater; B/C-horizon or groundwater), the relative proportions of which change depending on hydrological conditions. Inherent in this approach are the assumptions that, fast equilibrium reactions are taking place in the soils between chemical species in the solid phase and in soil solution, by which the latter acquires a fingerprint of that particular soil horizon and that these same chemical species mix conservatively (i.e. do not participate in chemical reactions) on release from the soil and in the stream system itself (Foster, 2000). Their combined concentrations equate to that observed in the streamwater chemistry, an assumption that is sometimes violated (e.g., Christophersen *et al.* 1990).

Using EMMA it is further assumed that, to a first approximation, the end-members are temporally invariant and this is one of the main criticisms of the method since

end-member composition is likely to change (Hoeg *et al.* 2000) over the year as well as during individual storm events as flow paths can vary according to antecedent conditions and storm intensity (Robson and Neal, 1990; Burns *et al.* 2001) and as such the technique has limitation when detailed information of flow pathways in small, heterogeneous catchments are of concern (Chapman *et al.* 1997).

However, the technique is powerful in its simplicity and may be successfully applied as a hydrograph separation technique (e.g., Robson and Neal, 1990; Brown *et al.* 1999; Jarvie *et al.* 2001; Soulsby *et al.* 2002b) using a time series of stream chemistry data and estimates and/or measurements of the end-member chemistries. Conversely, EMMA is also used for the apparent inverse approach to model time series stream chemistry by assigning chemical signatures to the different flow components (e.g., Hooper *et al.* 1990; Wade *et al.* 1999; Foster, 2000). Compared to other models EMMA offers the advantage that it allows an explicit linkage of model compartments to features (e.g., different runoff components) identified in the field and permits the use of direct measurements in the modelling (Seip *et al.* 1995). Such direct field measurements also prove valuable when refining and/or correcting existing models as is demonstrated by Burns *et al.* (2001) and Hooper (2001) in studies at the Panola Mountains Research Watershed (PMRW) in Georgia, US.

The main difficulty in EMMA arises from the identification of viable end-members and this includes defining the number of end-members as well as their chemical composition. The number of end-members is often selected based on results from previous analysis (e.g., factor analysis) and studies in the catchment area (e.g., Soulsby *et al.* 2002b) and/or can be inferred from so-called mixing diagrams (Hooper

*et al.* 1990, Christophersen *et al.* 1990, Hooper, 2001, Christophersen and Hooper, 1992). A variety of studies have required three end-member components, as opposed to the traditional two component models (e.g., Robson and Neal, 1990), to adequately represent stream chemistry. Christophersen *et al.* (1990), for example, suggested that at least three end-members are needed to model stream chemical composition at the PMRW and by re-defining the end-members to include a hillslope-runoff, a (organic-rich) soilwater and a groundwater component, Hooper *et al.* (1990) successfully applied the three-component approach to model stream chemistry in the catchment. Soulsby and Dunn (2003) also employed a simple three-component mixing model to estimate the contributions of overland flow, shallow surface stormflow and groundwater to stream flows in the Allt a'Mharcaidh catchment in northern Scotland. The modelling approach was found to produce consistent results, despite the relatively large uncertainty in the separation between the overland flow and the subsurface flow end-member, probably related to both the continuum of chemistries in the catchment soils and interdependent flow pathways (overlapping end-member chemistries). Such problems of equifinality are discussed by Buttle (1994), and may in part have contributed to the discrepancies in the results observed at PMRW (Hooper *et al.* 1990; Peters and Radcliffe, 1997), beside other factors, such as temporal and seasonal variations in runoff and differences in spatial scales at which these studies were conducted (Burns *et al.* 2001).

As for the end-member composition, direct measurements of end-member composition are often not available and there are major questions as to whether they would be representative given the spatial variability in soilwater (Christophersen *et al.* 1990) and groundwater chemistry (Reynolds *et al.* 1986; Hill and Neal, 1997). Thus,

in many studies (Wade *et al.* 1999; Foster, 2000; Jarvie *et al.* 2002; Soulsby *et al.* 2002b) a more pragmatic approach is chosen, whereby stream chemistries of extreme high and low flow periods are averaged to approximate the composition of a 'notional' catchment-integrated high flow and low flow end-member, respectively.

Moreover, EMMA does not consider the spatial and temporal variability in end-member composition and does not account for spatial distribution of the soils in the catchment area. While the former is assumed to be acceptable as long as these variations are small relative to the variations in stream chemistry and provided that end-members are chemically distinct from one another (Hooper, 2001), the latter may lead to misrepresentation of the catchment runoff processes, in particular since different catchment areas appear to be more important for runoff generation than others (e.g., Billet and Cresser, 1992; Kirnbauer and Haas, 1998; Burns *et al.* 2001; Hooper, 2001).

In summary, EMMA provides a powerful tool to explore the importance of conceptual hydrological pathways in a given catchment area, even when little is known about the hydrological framework. This can provide a good basis for approximating the spatial and temporal pattern in contributions from the different hydrological sources and pathways to stream flow, which in turn may serve as a useful tool for communicating catchment hydrochemical issues in reservoir management decisions. Nevertheless, the validity of the assumptions behind EMMA should rightly be challenged and their appropriateness for the intended application needs to be considered. A discussion of the appropriateness of the technique for this study will be given in the following sections.

### 6.6.2 EMMA- conceptual model and assumptions

EMMA is based on simple mixing and mass balance equations using, in this case, alkalinity as a conservative tracer and as a measure of stream chemistry. For two components, the standard mixing equations are as follows (e.g., Robson and Neal, 1990):

$$Q_{streamwater} \cdot Alk_{streamwater} = Q_{groundwater} \cdot Alk_{groundwater} + Q_{soilwater} \cdot Alk_{soilwater}$$

(Eq 6. 3)

$$Q_{groundwater} + Q_{soilwater} = Q_{streamwater}$$

(Eq 6. 4)

where *Alk* represents the alkalinity and *Q* is stream flow with the subscripts *streamwater*, *groundwater* and *soilwater* referring to those specified sources, the latter two being the identified end-members. By combining (Eq 6. 3) and (Eq 6. 4), the proportion of groundwater ( $\%_{gw}$ ) can then be determined as follows;

$$\%_{gw} = 100 \cdot (Alk_{soilwater} - Alk_{streamwater} / Alk_{soilwater} - Alk_{groundwater})$$

(Eq 6. 5)

Application of this approach is based on a number of assumptions:

- 1) streamwater arises from a mixture of two flow components ('end-members') originating from different sources,

- 2) these end-members equate to a groundwater component which provides hydrograph 'baseflow' and a soilwater component, which contributes to the hydrograph 'peak' (stormflow) (Foster, 2000),
- 3) the source waters (end-members) have distinct chemical signatures and are sufficiently different from each other (Christophersen *et al.* 1990),
- 4) end-members within each sub-catchment are, to a first approximation, temporally and spatially invariant (Christophersen *et al.* 1990, Wade *et al.* 1999) relative to variation between end-members,
- 5) the chemistry of the baseflow end-member can be estimated by sampling stream chemistry at extreme low flows (Wade *et al.* 1999; Foster, 2000),
- 6) stormflow end-member are best represented by a range of soilwater data (Robson and Neal, 1990) and, as a first approximation, can be inferred from soil data (Wade *et al.* 1999, Billet and Cresser, 1992; Smart *et al.* 1998), and
- 7) stream chemistry can be used to uniquely identify the proportions of the two end-members at any given time (Foster, 2000).

These assumptions allow hydrograph separation and modelling of stream composition to be undertaken by greatly simplifying the existing complex environmental system. The simple two-component flow model is deemed appropriate in view of the hydrochemical response of the Megget streams outlined in Chapter 5. For baseflow, stream chemistry reflects the influence of bedrock geology and weathering, and thus, low flow chemistry of the streams can be considered to reflect the signature of streamwater originating from deeper (B/C) soil horizons and groundwater sources within the catchment. Similarly, high flow chemistry tends to show dominance of waters derived from surface and near surface (O/A) soil horizons. Thus, stream flow

can be viewed as a mixture of these two chemically distinct source waters, the relative proportion of which vary during an event and for each individual stream may be estimated using the conceptual EMMA approach.

The assumption that stream chemistry at times of flow extremes is identical to the respective end-member composition is unlikely to hold, and various studies have shown that even at highest and lowest flows, streamwater is still a mixture of the two main components soilwater and deeper groundwater (Smart *et al.* 1998; Robson and Neal, 1990). At high flows, in particular, groundwater can be expected to contribute to stream runoff and the important role of groundwater in storm runoff generation has been widely recognised (Sklash and Farvolden, 1979; Bonell and Fritsch, 1997; Soulsby *et al.* 1998; Burns *et al.* 2001). In this study the soilwater end-member is deduced from literature soil data ( $-50 \mu\text{Eq L}^{-1}$  and  $-75 \mu\text{Eq L}^{-1}$ ), rather than from the high flow stream chemistry of the individual streams, which range between  $+34 \mu\text{Eq L}^{-1}$  and  $+67 \mu\text{Eq L}^{-1}$ . However, at low flow conditions the relative proportion of soilwater compared to groundwater will be at a minimum, in particular when samples are collected during dry summer periods, and thus, sampling of stream chemistry will provide a good approximation of the baseflow end-member.

The method applied here further assumes that the catchment-integrated end-members represent sources from throughout the catchment while, in fact, these end-members may only take on the signature of the soils in the riparian zone and/or near stream areas. Billet and Cresser (1992) demonstrated that the proportions of different soils immediately adjacent to the streams have much greater effect on the stream chemistry than the proportional total coverage of the soils in the catchment. Other studies have

suggested that stream chemistry is the result of displacement of water stored near the stream (Burns *et al.* 2001; Smart *et al.* 2001) by hillslope runoff. The importance of riparian areas in mediating the transfer of these hillslope waters to the stream channels and in modifying the chemistry of the drainage water has been demonstrated by Soulsby *et al.* (1998) and Billet and Cresser (1992). However, because of the uncertainty in determining the importance of different catchment areas in runoff generation, and since the role of the riparian zone in 'resetting' the end-member signature is not yet understood, it appears appropriate to characterise the soil end-member by means of two extreme values enclosing the range of possible end-member compositions rather than by defining a spatially weighted soil component.

Alkalinity is used as the conservative tracer (Soulsby *et al.* 2002b; Wade *et al.* 1999) for establishing the hydrograph split, and since alkalinity values in all streams are always positive, the conversion to Acid Neutralisation Capacity (ANC), which is strictly a more conservative measure (Neal, 2001; Neal *et al.* 1999), does not appear necessary nor does Al have to be taken into account (Hooper *et al.* 1990) as was done for other catchments (Robson and Neal, 1990, Christophersen *et al.* 1990). Conservative behaviour of this parameter can also be inferred from the matrix plots in *Figure 6. 9*, indicated by the straight-line relationship between the plotted, conservative components: Ca and alkalinity (Neal *et al.* 1997b; Jarvis *et al.* 1997; Foster, 2000). When alkalinity is used as the conservative tracer for hydrograph separation the analysis results in a geographic source separation as opposed to a time source separation, i.e., the distinction is drawn between different sources of water, namely soilwater and groundwater, and their contribution to flow rather than between 'new' and 'old' water or 'quick' and 'slow' flow. This allows contribution of the two

sources to stream flow to be approximated and runoff response of individual catchments can be compared.

Inherent in this method are the assumptions that end-members take on the chemical signature of the soils and rocks in which they originate, and that the pathway rainwater takes through the catchment determines the water's chemical signature (e.g., Mulder *et al.* 1991). Rainwater travelling along preferential pathways (e.g., organic horizons) during events acquires the signature of those horizons, while water travelling along longer pathways (e.g., deeper mineral soil horizons) gains a more base-rich composition. This suggests that end-members are more likely to represent a chemical reaction pathway (Robson, 1993 in Foster, 2000) rather than a water body of defined chemistry, whereby the water acquires its signature en route to the stream (Chapman *et al.* 1997; Muscutt *et al.* 1993). Stream chemistry therefore may provide the key to determining hydrological pathways, in particular when considering (chemically inert) solutes that are transported conservatively through the catchment (Peters *et al.* 1998). The rainfall signature itself is not usually observed within stream hydrograph response (Robson *et al.* 1992, 1993; Peart and Fung, 1997), and only rarely during large events or wet antecedent conditions (Robson *et al.* 1993; Neal *et al.* 1997b). The Megget stream data show that the contribution from unchanged rainwater to stream flow is mostly undetectable (see Section 5.3) and does not need to be postulated.

The method applied here therefore assumes that a two-component end-member mixing model is sufficient to represent the stream chemistry in the Megget catchment and this is in agreement with studies carried out in other catchments in the Scottish

Uplands (Giusti and Neal, 1990; Wade *et al.* 1999; Billet and Cresser, 1992, 1996; Soulsby *et al.* 2002b), which demonstrated that the majority of patterns in stream chemistry behaviour are simply linked to variations in soilwater and groundwater inputs, particularly at the sub-catchment level (Smart *et al.* 1998). However, a number of studies have indicated that three components are more appropriate for sufficiently explaining stream chemical variations (Hooper *et al.* 1990; Jenkins *et al.* 1994a; Katsuyama *et al.* 2001; Burns *et al.* 2001), and the influence of a third component on stream chemistry in the Megget streams may also be inferred from factor analysis and factor plots (e.g., *Figure 6. 15*) since identification of two main factors implies at least three end-members to sufficiently explain stream chemistry variation (Christophersen and Hooper, 1992). Yet, there are two main motives for not incorporating a third end-member into EMMA. (1) Although the component identified in factor analysis (*see section 6.5.3*) is characterised by high Fe and Mn loadings, it cannot be sufficiently characterised as a separate end-member as there are no obviously distinct chemical signatures in any of the other, more conservative elements (Ca, Mg, alkalinity), whose mixing behaviour, in general, implies two-component mixing (*Figure 6. 8, Figure 6. 9*). (2) Moreover, this component is clearly an Fe and Mn factor associated with displacement flow (translatory/piston flow) from the near-stream areas, and as such it probably represents reduction processes occurring in the riparian soils rather than a separate runoff source because it acquires its signature by mixing subsurface stormflow from adjoining hillslopes with riparian groundwater. This assumption is consistent with Cresser *et al.* (2000) and the important role of the riparian zone in effectively de-coupling sub-surface stormflow at the hillslope from the stream network has also been demonstrated by other studies (Smart *et al.* 2001, Burns *et al.* 2001; Hangen *et al.* 2001). Therefore, the basic two-component approach is

considered adequate for the purpose of this modelling effort, which aims to provide a simple representation of the changing contribution of the two flow components to stream flow for individual events, and also over the two study years, and allows comparison of runoff patterns in individual sub-catchments.

### 6.6.3 Selection of end-member chemistries

#### Groundwater end-member

In this study, no direct measurements of groundwater chemistry were taken. Instead the chemistry of the groundwater end-member is inferred from observed baseflow characteristics. For each stream the available data are ranked according to flow, as shown in *Figure 6. 17* for Winterhope Burn, and the three lowest flow events are chosen to represent the low flow chemistry of that particular stream. From the selected events, the mean average alkalinity is calculated and assumed to represent the low flow end-member as listed in *Table 6. 6*. There are two obvious limitations to this approach:

- (1) Individual streams were sampled at different frequencies, thus covering different flow conditions, and in particular data collection at Peaty Muckle Burn and Black Burn do not include sampling during dry summer periods. Thus the groundwater end-member is likely to be underestimated compared to that of the other streams as soilwater contribution on that component could be expected to be higher during the wetter autumn period. Low flow chemistries at these streams are therefore assumed to be similar to that of Winterhope Burn and at both Black Burn and Peaty Muckle Burn, the Winterhope low flow end-member is used for the separation.

(2) One or two streamwater alkalinity concentration(s) will be higher than the mean alkalinity derived from the three highest flows. Similarly, the three highest alkalinity values do not necessarily coincide with the three lowest flows. In both cases, groundwater contribution will be overestimated by the model, giving a groundwater contribution greater than 1.0. Although these groundwater contributions are unrealistic, the general trends will be preserved and it is in fact an advantage that the EMMA model is extremely flexible and does not ‘collapse’ when dealing with data outside the defined end-member range (Foster, 2000). In this study there are only three occasions where the observed alkalinity lies outside the end-member range and groundwater contributions are estimated to be 103 %, 105 % and 109 %, respectively.

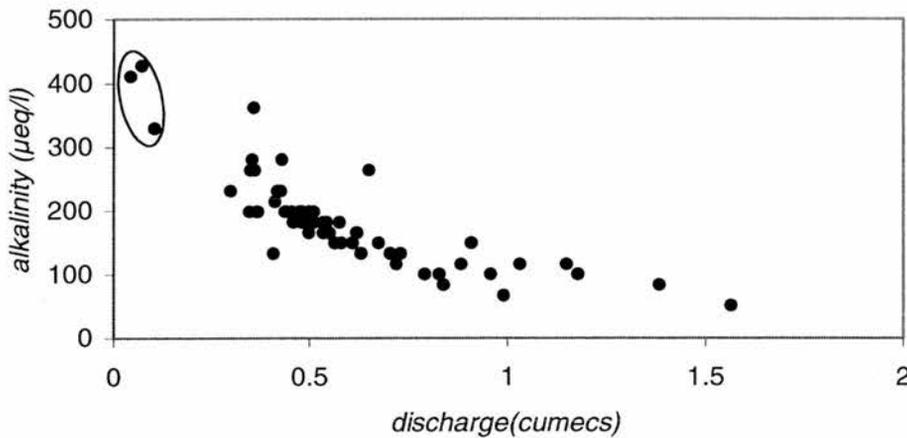


Figure 6. 17: Estimation of end-member chemistry from Shielhope Burn alkalinity data. Circle encloses points that were averaged to calculate end-member chemistry.

Soilwater end-member

Definition of the soilwater end-member is somewhat more difficult, in particular because it is still debated which areas most significantly contribute to stream flow generation and where end-members acquire their signature (see above). To simplify this problem two models are produced assuming the soil end-member alkalinity to lie in the range between peat soils and peaty podzols. The end-member alkalinities are inferred from literature soil data (*Table 6. 6*) collected from sites with similar soil types and catchment characteristics. The value range is chosen to account for the different soil types present in the individual catchments and also to assess the effect of the uncertainty in the soilwater end-member on the hydrograph separation. The limitations of such a pragmatic approach are recognised, but soilwater collection is difficult and labour intensive (Mulder and Cresser, 1994), and it could be argued that results from individual soil analysis may not be representative for end-member definition (Wade *et al.* 1999, Jarvie *et al.* 2001) due to the wide temporal and spatial variation in soilwater composition (Robson and Neal, 1990; Neal *et al.* 1997d).

	<u>Groundwater</u> <u>end-member*</u>	<u>Soilwater</u> <u>end-member **</u>
Winterhope Burn	269	-75 -50
Peaty Muckle Burn	269	-75 -50
Black Burn	269	-75 -50
Shielhope Burn	389	-75 -50
Linghope Burn	373	-75 -50

*Table 6. 6: End-member alkalinities ( $\mu\text{Eq L}^{-1}$ )*

(\* calculated from alkalinities at three lowest flows, \*\* estimated from literature values in Ferrier *et al.* (1990a), Soulsby *et al.* (2002b); Soulsby and Dunn (2003); Soulsby (unpublished data))

Although the use of a range of literature values as a surrogate for soil chemical data is crude, the approach facilitates the reasonable characterisation of a catchment-integrated end-member and considering the two extremes of the soilwater end-members, it is reasonable to assume that the hydrograph separations would provide a first approximation of the upper and lower limits of groundwater and soilwater contribution.

#### 6.6.4 Hydrograph separation using EMMA

Using (Eq 6. 5, together with estimates of the groundwater and soilwater end-members, it is possible to calculate the groundwater proportion for any point in time for which stream alkalinity data are available. Since groundwater proportions are calculated from stream chemistry, irrespective of flow, this has the advantage that some hysteresis (lag in catchment response) can be accounted for (Foster, 2000), as the flow values on the rising and falling limb of the storm hydrograph give rise to different stream alkalinities. Groundwater proportions are then calculated for all streams and the resulting separation is illustrated in *Figure 6. 18* to *Figure 6. 22* for the event-sampling period. Results from Shielhope Burn, Peaty Muckle Burn, Black Burn and Linghope Burn must be interpreted with caution as flows are modelled for these sites (see Section 5.1.2).

Uncertainty in the hydrograph split depends almost entirely upon the end-member selection, which in the case of the soilwater end-member is undertaken somewhat arbitrarily by means of literature data. Therefore, the proportion of groundwater contribution to flow is calculated for both an upper (alkalinity  $-50 \mu\text{Eq L}^{-1}$ ) and a

lower (alkalinity  $-75 \mu\text{Eq L}^{-1}$ ) soilwater end-member and the results are included in the graphs. From there it can be seen that errors in groundwater proportion are small (1-5 %) in all streams and approximately constant with time, with higher divergence occurring at high flows.

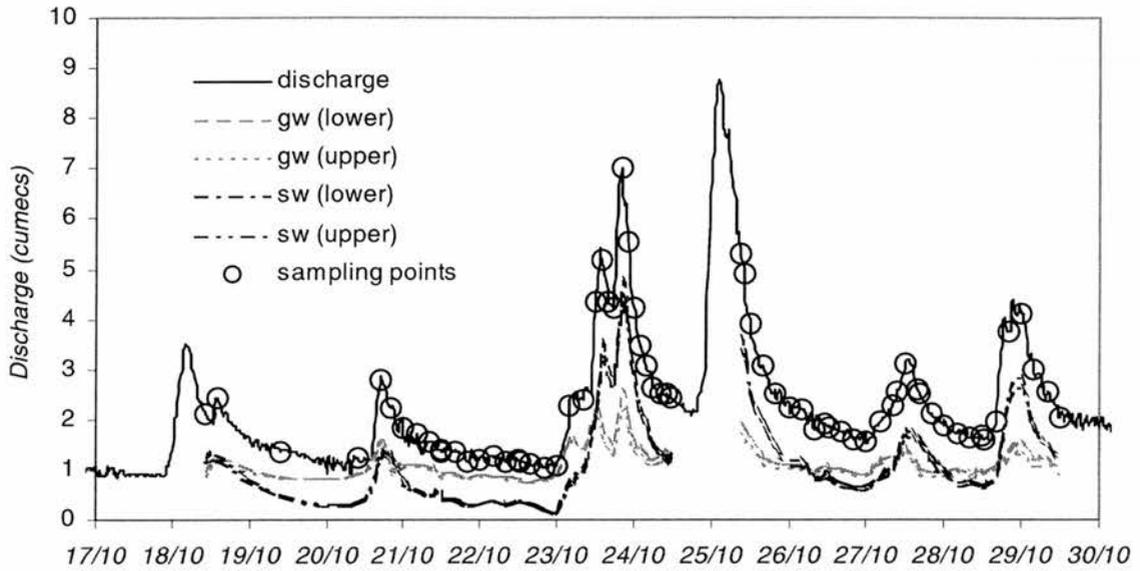


Figure 6. 18: Hydrograph split for Winterhope Burn based on event data (18 October 2000-30 October 2000)

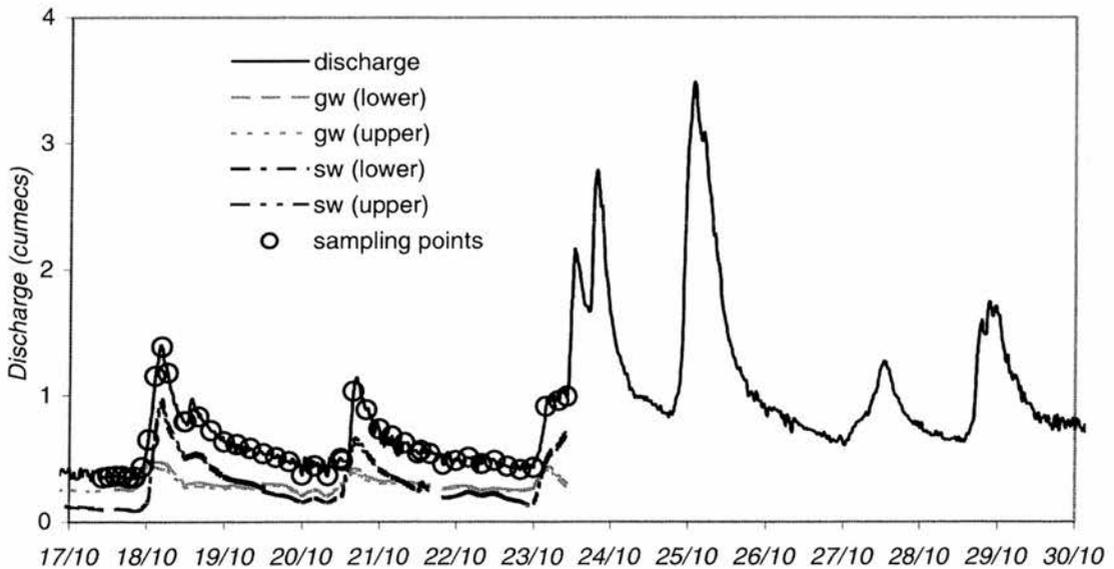


Figure 6. 19: Hydrograph split for Shielhope Burn based on event data (18 October 2000- 30 October 2000)

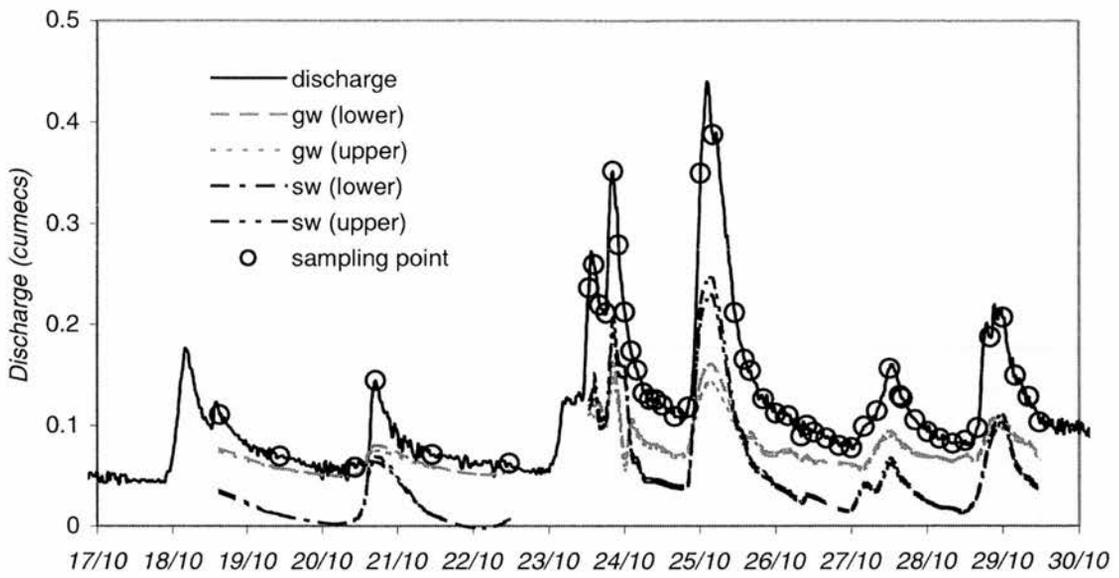


Figure 6. 20: Hydrograph split for Peaty Muckle Burn based on event data (18 October 2000- 30 October 2000)

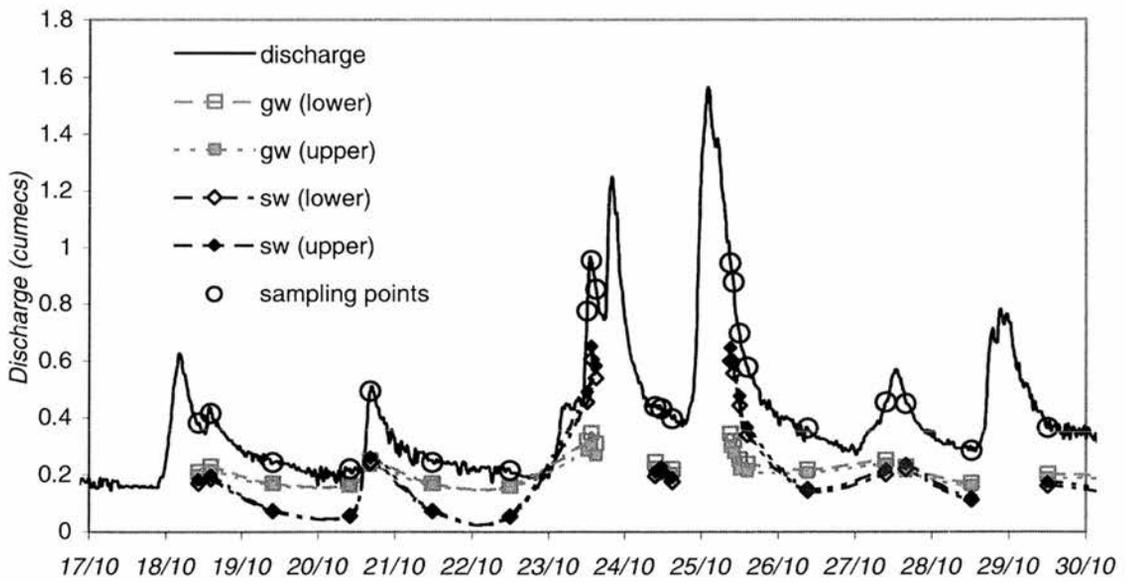


Figure 6. 21: Hydrograph split for Black Burn based on event data (18 October 2000- 30 October 2000)

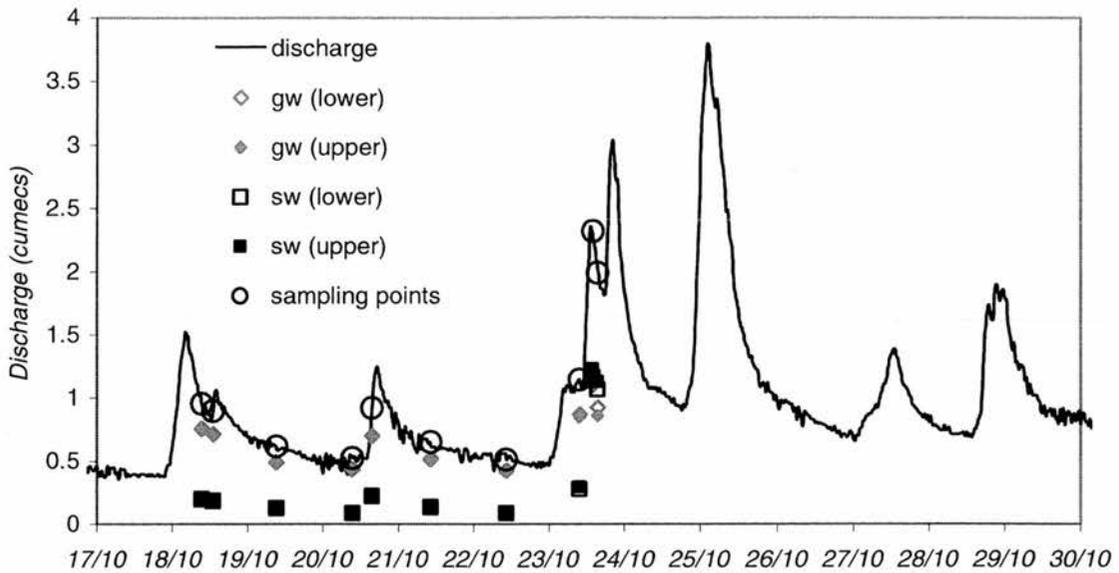


Figure 6. 22: Hydrograph split for Linghope Burn based on event data (18 October 2000 - 30 October 2000)

Notwithstanding the uncertainty over the flow estimates in the ungauged catchments, the graphs (Figure 6. 18-Figure 6. 22) clearly highlight the variations in soil- and groundwater contribution, and it is apparent that the contribution of the two components differs between individual streams. At all streams, the groundwater component dominates stream composition at lower flows. Its contribution exceeds that of soilwater inputs, although at Shielhope Burn soilwater inputs during the intensive sampling period make up 29-47 % of the flow during low flow periods indicating a high contribution of slow drainage waters from organic soils. Linghope Burn and Peaty Muckle Burn generally show the highest groundwater contributions at low flows with maximum values of 82 % and 88 % and, although surprising in the case of Peaty Muckle Burn, this suggests that drainage from the blanket peats occupying the flat-lying lower parts and the hilltops of the catchment has only a small influence on stream baseflow and the important contribution is derived from more

freely-draining peaty podzols occupying the steep slopes at the middle reaches of the stream. In Winterhope Burn and Black Burn the low flow proportion of groundwater during the intensive sampling programme averages around 70 %, but drops during the second part of the programme as will be shown later.

At high flows the soilwater contribution is generally highest, even though the groundwater volume in the stream also increases and the response of individual streams to runoff events differs depending on soil type distribution, catchment size and antecedent conditions. Stream response patterns are less defined in Linghope Burn, due to the limited data collected at this stream, but will still be considered in the following discussion since general trends can be inferred. Differences in catchment response are most clearly seen in Shielhope Burn, which shows a sharp rise in soilwater contribution during events followed by a slow decline (long recession limb), reflecting the generally more flashy soilwater response followed by the slow movement of throughflow from slow-draining organic soils, which dominate the catchment area. During the sampled events soilwater contributes up to 74 % of the flow at Shielhope Burn (*Figure 6. 19*), but higher soilwater contributions are likely to occur during large events (e.g., 25 October 2000), not sampled at this stream. A rapid increase in soilwater influence during stormflow is also seen at Winterhope Burn, Peaty Muckle Burn, Black Burn and Linghope Burn with maximum peak flow soilwater contributions of 68 %, 74 %, 68 % and 57 %, respectively, the high value at Peaty Muckle Burn being due to the higher proportion of blanket peats in its catchment area and the low values at Linghope Burn reflecting the lack of data from large events. During small events (e.g., 20 October 2000), however, soilwater contribution at these streams does not exceed that of groundwater, which also rises

rapidly during events (*Figure 6. 18* to *Figure 6. 22*) and this dynamic response is probably due to waters from lower soil horizons and near stream areas, rather than waters from deep bedrock sources, contributing to the groundwater component. At Shielhope Burn groundwater contribution during events is generally lower, but also increases rapidly. The distinct groundwater peak on the rising limb of the storm hydrograph suggests that flushing from the riparian zone is an important mechanism by which groundwater is delivered to the stream prior to peak flow and this is consistent with the results from the Factor analysis (see *section 6.5.3*). Similar processes can be inferred for Winterhope Burn (and would also be expected to occur at Linghope Burn), indicated by the early groundwater peaks, but are less distinct in Peaty Muckle Burn and Black Burn. Both of these drain smaller catchments and have less developed riparian zones, particularly true of Black Burn. Although this interpretation appears reasonable, there are a number of other factors that may also have contributed to the observed pattern, such as catchment size, which may explain the simultaneous occurrence of soilwater and groundwater peaks in Peaty Muckle Burn (*Figure 6. 20*) and Black Burn (*Figure 6. 21*), not seen in the larger catchments (*Figure 6. 18*, *Figure 6. 19*), where soilwater from upper parts of the catchment has to travel longer distances before reaching the (main) stream. Furthermore, some of the delay in soilwater response, in particular during the early events, may be due to hysteresis, although if of considerable influence, a similar delay in soilwater response would be expected in the small catchments. The graphs clearly reflect the effects of antecedent conditions, best illustrated in Shielhope Burn (*Figure 6. 19*), where soilwater contribution in-between storms increases from 29 % to 47 % following the storm events on 18 October and 20 October. Similarly, both, Winterhope Burn and Black Burn show an increase in low flow soilwater contribution from 27 % to 43 %

after events on 23/24 October 2000 and 25 October 2000 and, although less evident at Linghope Burn and Peaty Muckle Burn, this suggests that the general rise in stream level is mainly due to increased soilwater runoff.

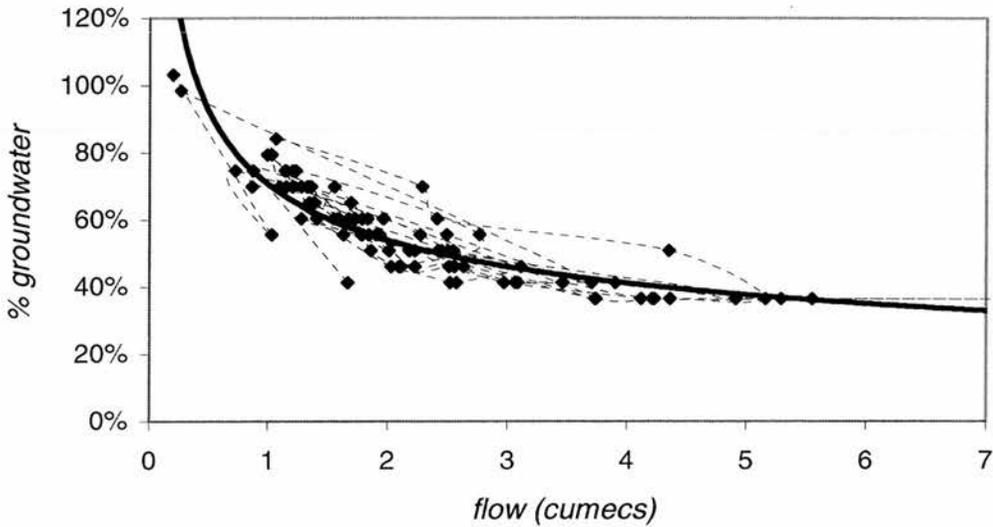


Figure 6. 23: Relationship between groundwater proportion and flow at Winterhope Burn.

In order to estimate groundwater proportion for the entire sampling period based on the time series of flow data the strong relationship between flow and percent groundwater, shown for Winterhope Burn in *Figure 6. 23* may be used, which makes it possible to reconstruct the streamwater time series without requiring continuous alkalinity data as were used in similar studies (Jarvie *et al.* 2001, Foster, 2000). An equation is fitted to the data, which takes the form of

$$\%gw = m \cdot flow^{-n}$$

(Eq 6. 6)

where %gw is the proportion of groundwater calculated from EMMA, *flow* is stream flow (*cumecs*) and *m* and *n* are the constants describing the equation. The fitted equations for all streams (using the lower soil end-member) are summarised in *Table 6. 7* together with their coefficient of determination ( $R^2$ ).

This method of fitting a single line to the data has the obvious disadvantage that effects of hysteresis and different antecedent conditions, illustrated by the loops in the sequentially joined data points in *Figure 6. 23* and by the range of alkalinities occurring at the same flows (*Figure 6. 23*), are not accounted for. Nevertheless, it is still a powerful tool for approximating the relative proportions of groundwater and soilwater contribution to stream flow over the sampling period.

<u>Stream</u>	<u>Fitted Equations</u>	<u>Coefficient of determination (<math>R^2</math>)</u>
Winterhope Burn	$\%gw = 0.7067 \cdot flow^{-0.3906}$	0.81
Peaty Muckle Burn	$\%gw = 0.2588 \cdot flow^{-0.4357}$	0.85
Black Burn	$\%gw = 0.3445 \cdot flow^{-0.5017}$	0.96
Shielhope Burn	$\%gw = 0.4093 \cdot flow^{-0.4092}$	0.74
Linghope Burn	$\%gw = 0.6779 \cdot flow^{-0.1441}$	0.57

*Table 6. 7: Equations describing relationship between %gw and flow, used for hydrograph split based on flow data time series.*

The fitted equations for the individual streams (*Table 6. 7*) were then applied to the time-series flow data and the resulting hydrograph split for the entire sampling period is displayed in *Figure 6. 24* and *Figure 6. 25*.

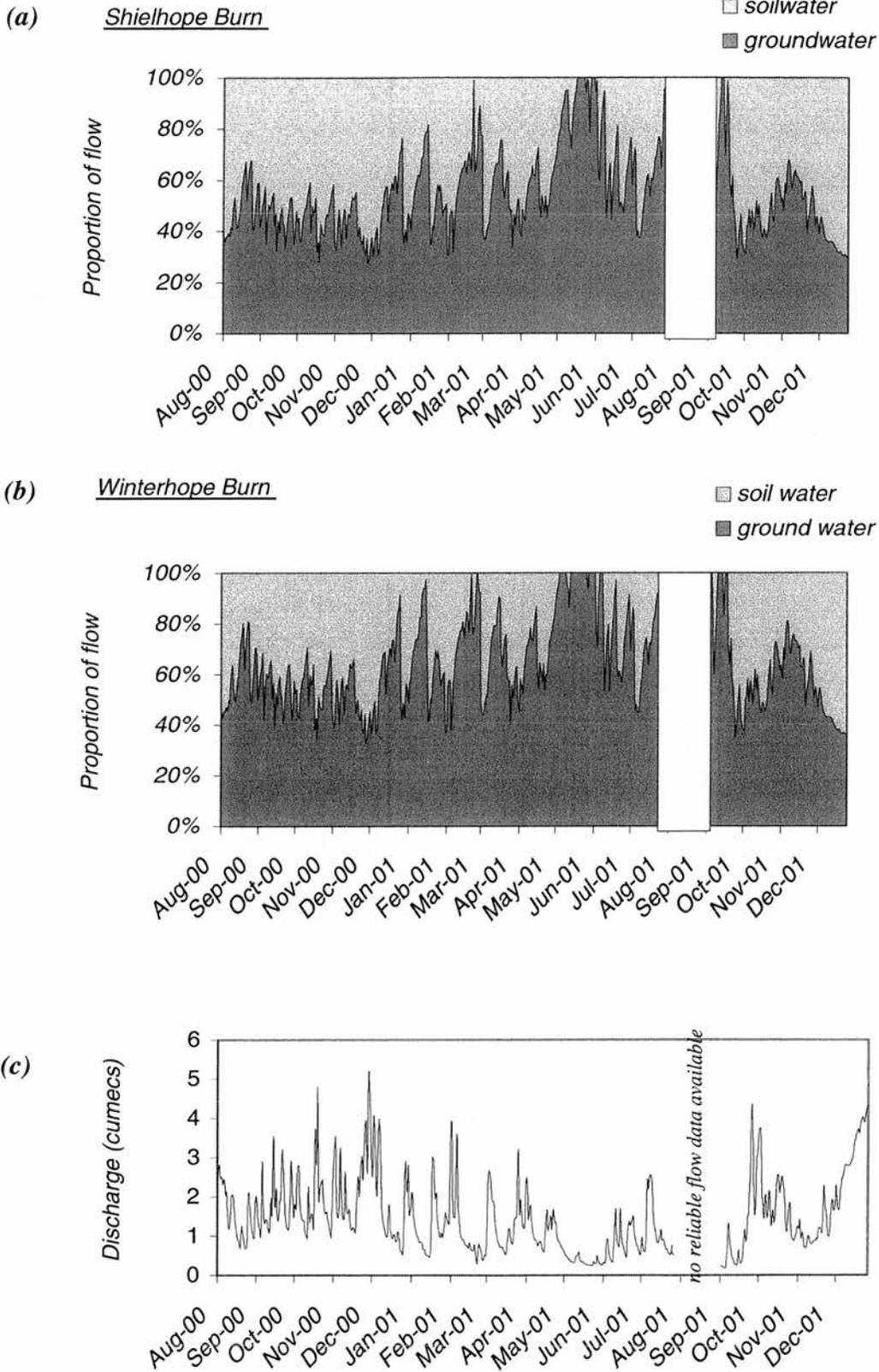


Figure 6. 24: Hydrograph split for (a) Shielhope Burn and (b) Winterhope Burn using time series flow data and (c) stream hydrograph for Winterhope Burn.

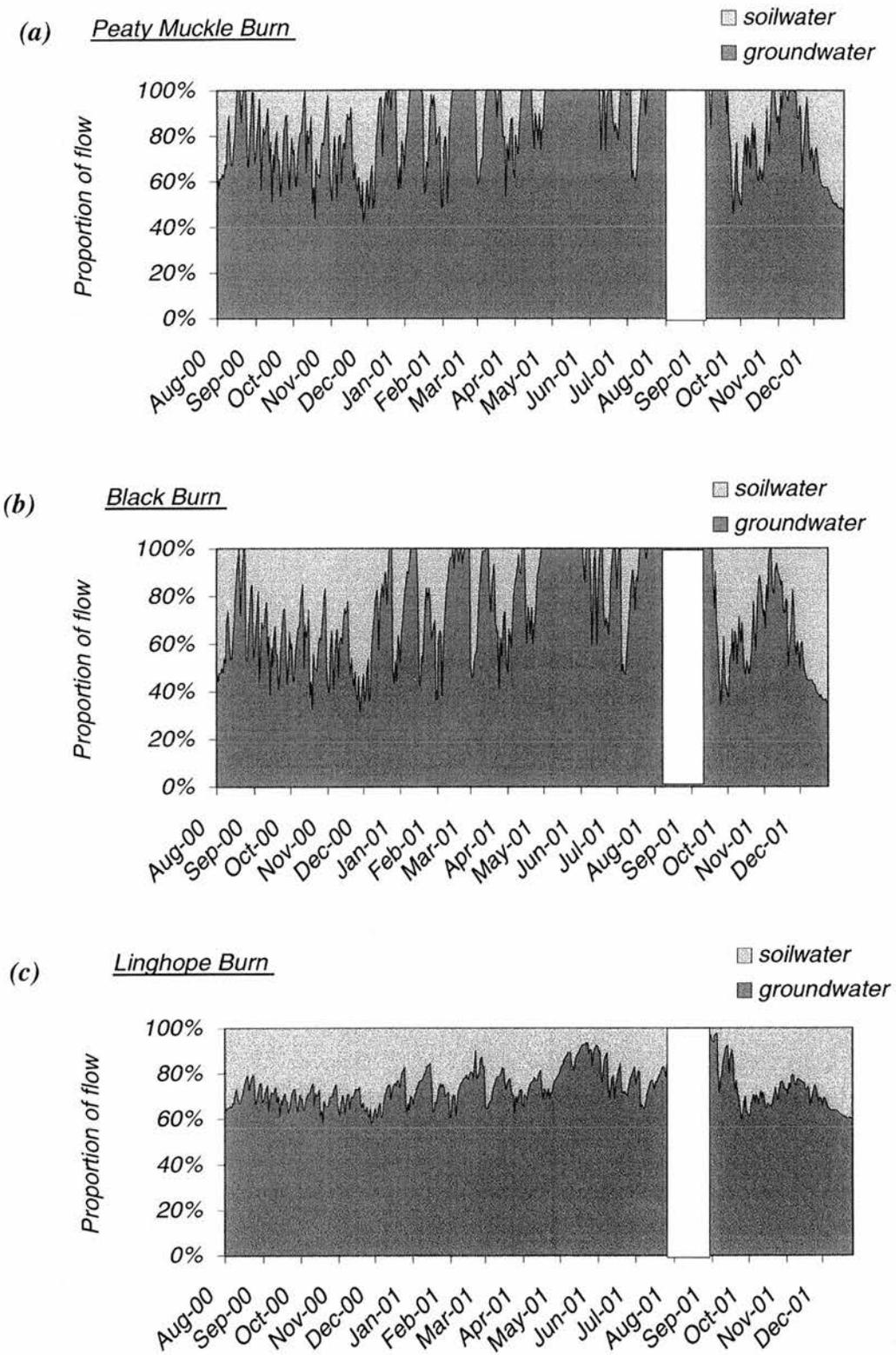


Figure 6. 25: Hydrograph split for (a) Peaty Muckle Burn, (b) Black Burn and (c) Linghope Burn using time series flow data.

The graphs clearly reflect the annual variations in the contribution of the two flow components, with high groundwater proportions dominating summer flow (May-August), diluted by soilwater inputs during the wetter autumn and winter period (September-January) and during spring storm events. The graphs also highlight periods during which high amounts of soilwater are transported by the streams, and such information is very valuable for catchment management purposes, as soilwater from organic rich peats are associated with high loadings in colour and complexed metals. With regard to the Megget Reservoir, the graphs imply that the bulk of iron and manganese is delivered to the reservoir during autumn and winter storm events rather than during the drier summer month.

Also reflected in the graphs are differences in runoff behaviour of individual streams, briefly discussed in the previous section. It is interesting to note that groundwater and deeper soilwater provides most of the runoff in Peaty Muckle Burn and Black Burn, even during periods of high rainfall intensity and this probably reflects both the smaller catchment size relative to Winterhope Burn and Shielhope Burn and the higher proportion of more freely draining soils (peaty podzols), which results in a smaller surface storage reservoir in the soils. On the contrary, the catchments of Shielhope Burn and Winterhope Burn cover larger areas of poorly draining organic soils, which generate large amounts of soilwater runoff during events and also provide constant soilwater inputs in-between events during the wet autumn and winter period. The somewhat higher soilwater contributions in Shielhope Burn possibly relate to higher proportions of organic soils and/or to the lower slope angles in the catchment, while displacement flow from the waterlogged peaty gleys of the riparian zone may further contribute to the high soilwater inputs.

The hydrograph split for Linghope Burn (*Figure 6. 25c*) suggests that stream flow is dominated by high proportions of groundwater (>58 %) throughout the year, but constant contributions from a soilwater component are also indicated, even during periods of very low flows (*Figure 6. 24c*). While the higher groundwater proportions seem realistic and are also obvious from the stream chemistry data (Chapter 5), the less dynamic stream response, seen in the graphs, and the constant soilwater contribution are difficult to explain and may be remnants of the method, resulting from a too low soilwater end-member and/or the under-representation of extreme high and low flows in the data used to carry out the hydrograph split. As a result, the derived relationship between groundwater proportions and flow, which is based on alkalinity measurements, is a poor predictor of the stream response at Linghope Burn, as is also indicated by the low  $R^2$  value in *Table 6. 7*. Using a soilwater end-member with higher alkalinity (+70  $\mu\text{Eq L}^{-1}$ ), for example, as observed by Soulsby and Dunn (2003) in mineral soils in the Allt a'Mharcaidh catchment gives a more dynamic response (*Figure 6. 26*), although the coefficient of determination ( $R^2=0.52$ ) for the fitted equation does not improve the results (see *Table 6. 7*). Alternatively, a third flow component, not accounted for in this hydrograph separation, may be required to reconstruct stream flow response at Linghope Burn, for example, a deeper soilwater source with intermediate alkalinity.

To test the ability of the EMMA model to reconstruct stream composition from flow data, the strong correlation between stream Ca concentrations and percent groundwater is used and an equation can be fitted to the data as is illustrated in *Figure 6.27* for Winterhope Burn. Using the previously derived EMMA model (*Table 6. 7*)

Ca levels are then predicted from the flow data and the results are compared with measured Ca concentrations.

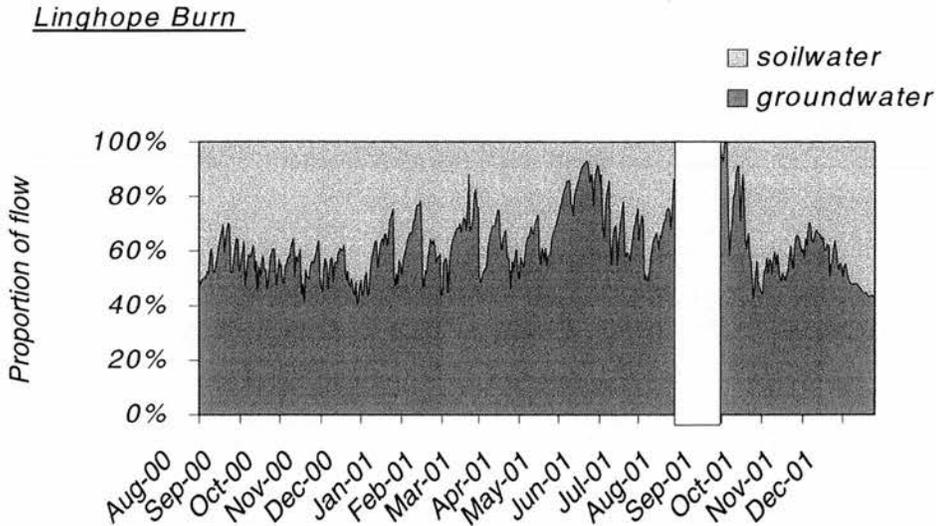


Figure 6. 26: Hydrograph split for Linghope Burn based on end-member with higher alkalinity ( $+70\mu\text{Eq L}^{-1}$ ) and using time series flow data.

The linear regression relations between predicted and measured Ca concentrations, illustrated in Figure 6. 28 and summarised in Table 6. 7, give  $R^2$  values ranging between 0.86 and 0.95 and slopes of the equations are 0.89 and 0.94 for Winterhope Burn and Black Burn, suggesting that for these streams the EMMA model is a strong, unbiased predictor. The slope values are somewhat lower at Shielhope Burn (0.64) and Peaty Muckle Burn (0.77) indicating under- and overestimation of high and low Ca concentrations, respectively, although the general trend is well captured by the predicted data as seen in the high  $R^2$  values (Table 6. 8). At Linghope Burn both, slope (0.27) and  $R^2$  (0.36) values are very low indicating that Ca concentrations are poorly predicted by the model. Using the higher soilwater end-member (alkalinity  $70\mu\text{E L}^{-1}$ ) for the prediction of stream Ca concentrations does not improve the results. Thus, the

poor performance of the model is assumed to be due to insufficient data coverage at Linghope Burn, in particular due to the lack of samples taken during periods of high flows, as such data are required to implement end-member mixing (Wade *et al.* 1999). However, the presence of a third unobserved stream flow component is also possible and a similar problem has been encountered by Chapman *et al.* (1997).

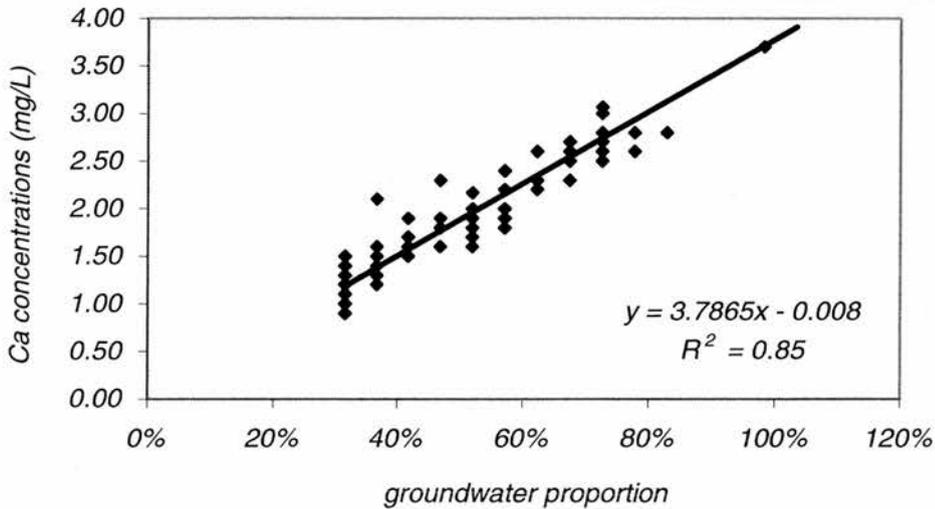


Figure 6.27: Relationship between proportion of groundwater and Ca at Winterhope Burn (5% steps seen in the groundwater proportion data are remnants of alkalinity values being reported as  $\text{mgCaCO}_3 \cdot \text{L}^{-1}$  in the original data).

<u>Streams</u>	<u>Slopes</u>	<u>Coefficient of determination (<math>R^2</math>)</u>
Shielhope Burn	0.64	0.87
Winterhope Burn	0.89	0.87
Peaty Muckle Burn	0.77	0.86
Black Burn	0.94	0.95
Linghope Burn	0.27	0.36

Table 6. 8: Slopes and coefficients of determination ( $R^2$ ) derived from the regression relations between predicted and measured Ca concentrations

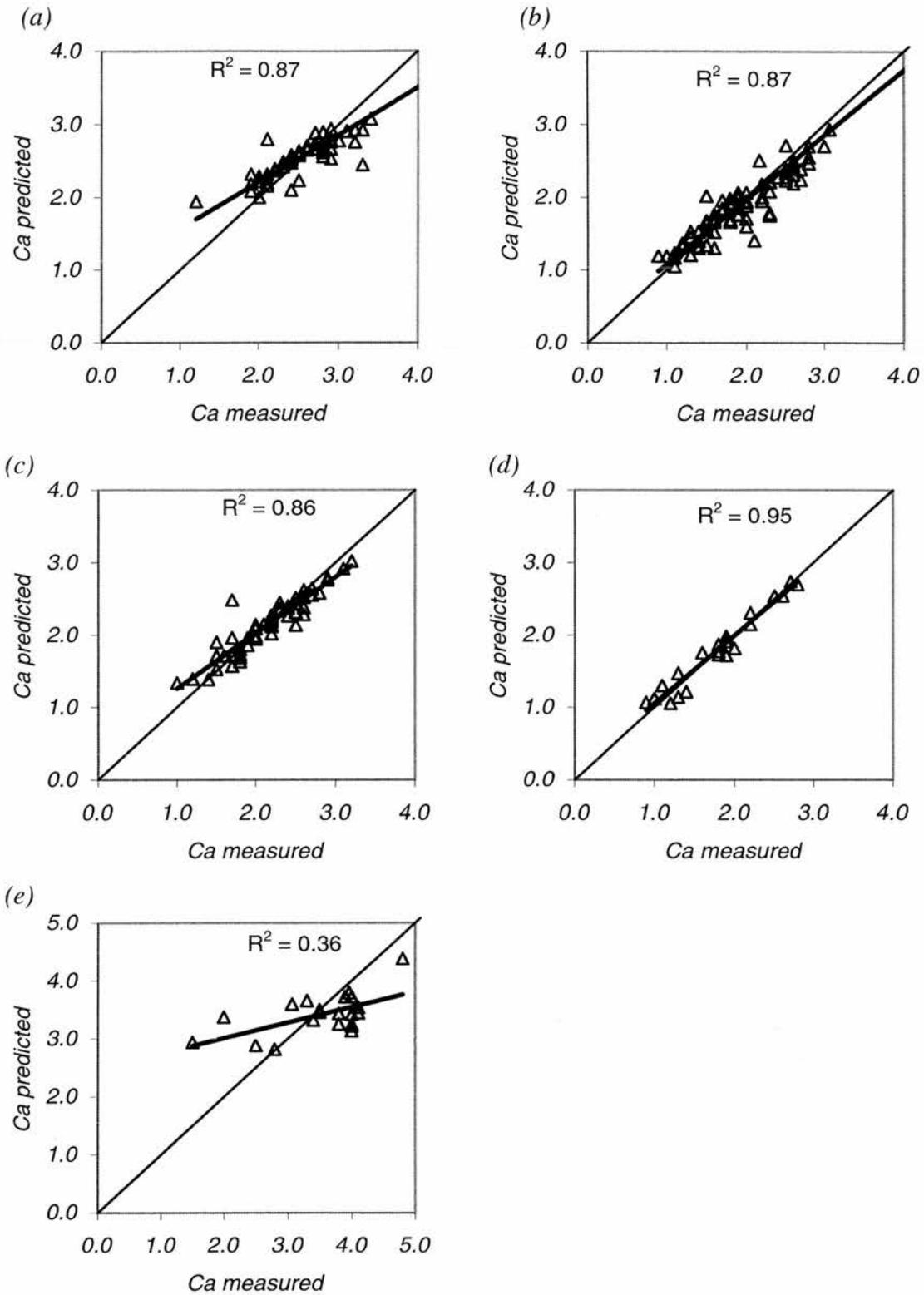


Figure 6. 28: Regression relationships between predicted and measured Ca concentrations for (a) Shielhope Burn, (b) Winterhope Burn, (c) Peaty Muckle Burn, (d) Black Burn and (e) Linghope Burn. Heavy lines are fitted trendlines; lighter lines indicate a slope of one (1:1 lines).

Despite the strong correlation between stream Ca concentrations and percent groundwater seen above, the linear regressions of stream Fe and Mn concentrations against the proportion of soilwater, calculated for all streams except Linghope Burn<sup>1</sup>, only give R<sup>2</sup>-values of < 0.30 and < 0.19 (Table 6. 9), respectively. This not only demonstrates the non-conservative behaviour of these elements, but also indicates the existence of Fe and Mn sources other than soilwater. At the same time, it demonstrates the limitations of using EMMA for predicting concentrations of these elements in the Megget streams. R<sup>2</sup> values for Al are clearly higher, indicating the more conservative behaviour of Al, which is generally less affected by redox processes.

	<i>Fe</i>	<i>Mn</i>	<i>Al</i>
<i>Winterhope Burn</i>	0.06	0.12	0.61
<i>Peaty Muckle Burn</i>	0.20	0.18	0.61
<i>Black Burn</i>	0.17	0.16	0.62
<i>Shielhope Burn</i>	0.30	0.19	0.42
<i>Linghope Burn</i>	Not calculated	Not calculated	Not calculated

Table 6. 9: Coefficient of determination (R<sup>2</sup>) for linear regression between stream metal concentrations and stream soilwater proportion

## 6.7 Discussion

The data collected during the intensive sampling programme and analyses undertaken since then clearly highlight the utility of short-term sampling during storm events for catchment studies, the importance of which is widely recognised in the hydrological community (e.g., Jenkins *et al.* 1994b; Peters, 1994a; Longabucco and Rafferty, 1998;

<sup>1</sup> Excluded from analysis due to poor performance of model for predicting Ca concentrations (see Table 6.8)

Foster, 2000; Jarvie *et al.* 2001). While substantiating the general trends observed during routine sampling, discussed in Chapter 5, event-sampling details the rapid changes in stream chemistry during events and thereby exposes the wide range of stream chemical loadings that occur at individual streams. The results not only corroborate high Fe, Mn and Al concentrations at Shielhope Burn, Winterhope Burn and Peaty Muckle Burn but also show unusually high Al loadings at Linghope Burn and Black Burn, which are fairly unexpected and when observed during routine sampling would probably be questioned. Sampling at small time-increments during storm events also demonstrates its utility for identifying processes, in particular when interpretation is coupled with results from statistical factor analysis (R- and Q-mode factor analysis) and simple modelling techniques (EMMA). In this study, it is the amalgamation of detailed hydrochemical event data with such simple analytical tools that provides an insight into the functioning of the Megget catchment and its different sub-catchments, notwithstanding the limitations imposed by differing sampling periods and intervals at individual streams.

#### Catchment runoff response

Factor analysis was successfully applied to the data and the results clearly demonstrate that flow related changes in soilwater inputs (associated with changes in flow pathways) exert a major control on stream chemistry during storm events, accounting for 67 % - 82 % of the data variability in the individual streams. One could rightfully argue that flow related changes in stream chemistry emerge as the principal factor, simply because the variables in the input data set are highly correlated to flow. However, this is not a contradiction rather it demonstrates the close link between flow pattern and stream chemistry and emphasizes the important

influence of changing hydrological pathways during storm events on stream composition in upland regions, which has long been recognised (see reviews in Church, 1997 and Soulsby, 1997) and which is also obvious from EMMA.

The results from EMMA show that soilwater has a major influence on the stream hydrochemistry during events and is large enough to dominate stream chemistry and override the groundwater signal, although a significant portion of deep water is also reaching the stream during these runoff periods and at individual streams still makes up between 26 % and 43 % of stream flow at maximum flow. Such buffering of stream water chemistry by groundwater inputs at high flows has also been reported in other Scottish upland catchments (e.g., Soulsby *et al.* 1998, Giusti and Neal, 1993), and is mainly attributed to inputs from riparian areas and from valley bottom glacial deposits fed by recharge from the upper parts of the catchment dominated by freely-draining alpine soils, although bedrock fractures may also act as flow pathways during storm events (Hill and Neal, 1997), so that inputs from a dynamic groundwater component is also possible.

In all streams the contribution of deep water dominates stream chemistry during hydrograph rise and, except for the smaller catchments of Peaty Muckle Burn and Black Burn, peaks about 1-2 hours before peak of the soilwater end-member, which typically occurs at maximum flow. This early deep-water peak is probably associated with displacement of pre-existing soilwater in deeper horizons of the riparian zone, as observed by Giusti and Neal (1993) at Dargall Lane, southwest Scotland, and this is consistent with the results from factor analysis, which indicate flushing of deep waters enriched in reduced Fe and Mn into the stream prior to soilwater peak and flow maximum. The process is most pronounced in Shielhope Burn, reflecting the high

proportion of waterlogged gley soils in the riparian area, promoting reduction of Fe and Mn, which is subsequently flushed into the stream along with displaced riparian groundwater (Reid *et al.* 1981). This underlines the importance of the riparian zone in runoff generation during storm events found in various other studies (e.g., Fiebig *et al.* 1990; Burns *et al.* 2001).

The obtained results further reflect the effects of soil type distribution on stream chemistry, in particular with respect to Fe and Mn loading and stormflow response, and also demonstrate the importance of antecedent conditions and storm intensity. High loadings in colour and organically complexed metals are generally associated with high proportions of organic rich soils in the catchment area (Aitkenhead *et al.* 1999; Dawson *et al.* 2001) which not only provide peak runoff, but can also give rise to a permanent, though small, organic rich flow component (Rees *et al.* 1989; Giusti and Neal, 1993; Stunell and Younger, 1995; Holden and Burt, 2000). Both, magnitude and exact timing of groundwater and soilwater peaks appear to be strongly dependent on antecedent conditions and storm intensity and such relationships between catchment wetness, storm magnitude and quantity of runoff from the different in-catchment stores are well-documented for a wide range of catchment settings (Giusti and Neal, 1993; Robson *et al.* 1993; Hoeg *et al.* 2000; Burns *et al.* 2001 and references within).

### Fe and Mn sources

Two Fe and Mn sources are identified in the catchments studied; (1) organic soilwater sources, associated with Fe and Mn accumulation in organic-rich soil horizons and (2) deeper soilwater source related to reductive solution of Fe and Mn oxides and

hydroxides under low redox conditions in deeper soils and near stream area. The contribution of the two sources varies between individual catchments and also depends on antecedent conditions and storm magnitude. The organic soilwater source is typically the dominant Fe and Mn source during storm events, where runoff from organic soil horizons increases, and maximum contributions from that source occurs at peak discharge. It also shows a positive relationship to storm magnitude and this is consistent with the finding that the contribution of pre-event water to runoff increases with increasing rainfall intensity and amount (Giusti and Neal, 1993; see Burns *et al.* 2001). In the peat-dominated Shielhope catchment, the high proportion of organic rich soils not only provides a suitable substrate for formation of a large store of readily soluble Fe and Mn, but the waterlogged and/or ill-draining peaty soils also contribute water to the baseflow very slowly (e.g., Rees *et al.* 1989, Giusti and Neal, 1993), thus providing constant Fe and Mn inputs into the stream, even during low flow periods. Flushing of reduced Fe and Mn from the deeper soils is most important during the rise of the hydrograph, associated with the displacement of riparian groundwater into the streams. In Winterhope Burn, Peaty Muckle Burn and Black Burn, however, it appears that leaching from the more freely draining peaty podzols provides constant, though small, inputs of reduced Fe and Mn into the streams, and this may be promoted by the steeper slopes in these catchments. During successive storm events the Fe and Mn reservoir in the soils becomes gradually depleted, and consequently the importance of this source for stream loading gradually declines during prolonged wet periods, in particular after high magnitude events (e.g., 23 October and 25 October).

### EMMA and Factor analysis

EMMA is clearly a simple, but powerful tool for assessing the contribution of the different runoff sources to the stream hydrograph. The hydrograph separation presented here gives a first approximation of the changing soilwater and groundwater influence at the different catchments during the sampling period. The technique includes some degree of uncertainty arising from the somewhat arbitrary end-member definition. However, if, for example, different alkalinity values were used in the model calculations the proportion of total flow from groundwater sources would indeed be altered, but the general patterns would not change (Giusti and Neal, 1993); hence, the fundamental processes can be expected to be well represented by the technique, even if the end-members may not be defined accurately.

Factor analysis is used as an additional tool for identifying the controls on Fe and Mn concentrations in the Megget streams. It has the advantages that (1) (more or less) all solutes can be considered in the analysis, not only those displaying conservative behaviour, and (2) while EMMA infers flow pathways and runoff sources from one or two parameters (out of all the data), factor analysis explores the multivariate relationships inherent in all data and thus, provides a better basis for 'speculations' about processes that underlie the stream chemical composition. Similar factor approaches have been carried out in a variety of hydrochemical studies (e.g., Reid *et al.* 1981; Heal *et al.* 1997, in press) and in End-Member Mixing Analysis (EMMA) principle component analysis (PCA) is used to determine the number of potential end-members (Christophersen and Hooper, 1992; Brown *et al.* 1999), whereby these analyses only include solutes that mix conservatively within the system.

Although results from such factor analyses cannot be directly compared to each other and/or to the results obtained in this study due to the differences in catchment characteristics and sampling design, it is still surprising that the factor patterns in the current study are very similar to those observed by Reid *et al.* (1981) in the Glendye catchment, NE Scotland, suggesting that similar hydrochemical controls may prevail in both catchments.

The combination of the two methods, R- and Q-mode factor analysis and EMMA, has proved a practical tool in identifying factors and processes controlling stream chemistry and runoff generation in the Megget catchment. The strength of EMMA lies in its simplicity as a modelling tool, and when combined with factor analysis can provide insight into basic catchment functioning. The latter has shown great potential in aiding the end-members identification and in elucidating processes by which runoff from the different sources (end-members) is delivered to the streams, although it has yet to be clarified what exactly the identified end-member represents.

While the applied method was successful in predicting the timing of high Fe and Mn loadings in the streams, there are serious difficulties in correctly representing stream chemistry quantitatively, in particular with regards to non-conservative elements. As such the technique has limitations and cannot be used reliably for predicting the concentrations of Fe and Mn in the Megget streams. If, however, it is possible to separate the Fe and Mn rich riparian waters as an individual end-member then a better estimate of stream Fe and Mn loadings may be achieved. Future applications in which Fe and Mn concentrations are to be predicted quantitatively should therefore aim to improve the end-member definition and incorporation of a third end-member, representing the Fe- and Mn-rich waters in the riparian zone, should unquestionably

be considered. Where resources are sufficient, hydrometric measurements within the catchment would be desirable, the benefits of which have been demonstrated in a variety of studies (e.g., Hensel and Elsenbeer, 1997; Hooper, 2001) and are discussed in detail in Bonell and Fritsch (1997). The definition of a third end-member may also be helped by using a combination of both isotope and hydrochemical tracers, provided that a distinct isotopic signature can be observed, although such combinations of different tracers in itself may lead to inconsistent results (Hoeg *et al.* 2000).

### Management implications

The timing of maximum annual Fe and Mn concentrations in runoff has important implications for water supply management in upland catchments. In this study, the critical periods for high Fe and Mn concentrations in stream runoff are identified as autumn and winter storm events, during which the bulk of Fe and Mn is delivered to the reservoir. These results are consistent with Reid *et al.* (1981) and Giusti and Neal (1993), but should not be generalised, as in some upland catchments high levels in Mn and Fe are reported during summer baseflows (Heal *et al.* 1997; in press; Stunell and Younger, 1995). In the Megget catchment, loadings may be markedly higher during the first autumn storms, particularly after a dry summer period, due to accumulation of Fe and Mn in the soils (Neal *et al.* 1997a), but then probably decrease with successive storm events as the (deeper) soil reservoirs become gradually depleted. However, a better knowledge and understanding of the nature of the different sources, in particular the deeper source, is necessary to better predict when and where undesirable Fe and Mn concentrations will occur.

## **6.8 Summary**

In this chapter, results from intensive short-term storm sampling (16 October 2000 to 30 October 2000) undertaken at Shielhope Burn, Linghope Burn, Winterhope Burn, Black Burn and Peaty Muckle Burn are presented and data are analysed using simple analytical techniques, namely combined R- and Q-mode factor analysis and End-Member Mixing Analysis.

The results concur with measurements of Fe and Mn in runoff from other upland catchments and the frequent sampling programme employed here highlights the importance of stormflow in transporting Fe and Mn. Episodic chemical and hydrological response of the streams in the Megget catchment are outlined and the importance of hydrological pathways is discussed. The observed differences in stream chemistry between individual streams suggest variations in the importance of different pathways in the sub-catchments and also demonstrate the effects of catchment characteristics, above all soil type, on stream chemical composition.

Using EMMA it was possible to discriminate between different source waters and their pathways contributing to stream flow and in conjunction with factor analysis techniques this provided a better understanding of the processes controlling streamwater chemical variations in the individual catchments. Two different mechanisms were identified by which Fe and Mn are released into the streams: runoff of complexed Fe and Mn from shallow organic soils and flushing of reduced Fe and Mn from soils in near-stream areas.

Hydrograph separation based on EMMA further produced a simple model by which the contributions from the different runoff sources to stream hydrograph over the sampling period can be reproduced. While this simple conceptualisation of the system behaviour shows considerable utility as a management tool for predicting the hydrochemical stream response to runoff events and to identify critical periods of high Fe and Mn loadings, it has limitation in quantitatively predicting Fe and Mn concentrations in the streams, and as such requires further refinement.

# 7

## **Sediment Studies**

---

In this study a sediment survey was carried out to investigate the physical and chemical characteristics of the bottom sediments in the Megget Reservoir and their spatial distribution in order to (1) gain insight in sediment transport and deposition processes within the reservoir and (2) identify areas of metal accumulation and potential sites for increased metal release. The following chapter describes the methods applied during sample collection and details the different laboratory techniques used for the physical and chemical characterisation of the samples.

### **7.1 Introduction**

Sediment may be regarded as a mixture of inorganic and organic material both of which are derived from sources outside (allochthonous) or within (autochthonous) the water body. The sediment particles arrive at the site of deposition as a solid particle or are incorporated into the sediment from solution in a variety of ways. Alteration processes (diagenesis) occurring in the sediment may produce new components (authigenic) and also alters the composition of the pore fluid. As the transport of sediments is strongly dependent on particle size and density, the physical characteristics of the sediment are of major importance for sedimentological studies and studies of transport regimes. Moreover, sediment particles, such as clay minerals and organic material also provide effective adsorption surfaces to which elements such as nutrients and metals can be

bound and are transported by the host sediment. Besides transporting these elements, sediments also mediate their uptake, storage, release and transfer at the sediment-water interface. Consequently, they also affect the composition and processes of the superimposed water body and sediment characteristics need to be considered when dealing with water quality issues. Furthermore, the physical and chemical characteristics of the surficial bottom sediments hold valuable information about reservoir dynamics and chemical inputs (Thomas and Meybeck, 1996) and thus, may reveal some of the processes that have occurred during the draw down event.

## 7.2 Sampling design and methods

Sediments often show a heterogeneous distribution of physical and chemical characteristics. Since samples collected at given sampling sites within a water body are meant to represent the sediment characteristics at these locations as well as the surrounding area, the selection of appropriate locations and positions of sample collection are of key importance. Further consideration has to be given to the number of samples that are required in order to give a satisfactory statistical validity of the final sediment data. Different approaches are presented in the literature (see Golterman *et al.* 1983) to estimate the sampling intensities that sufficiently represent the water body under investigation. For example, Håkanson and Jansson (1983) proposed a 'pilot sampling formula' in which the bottom roughness of a given water body is calculated from its area and shoreline development to provide an indirect measure of topographical irregularities onto which the estimation of the required sample numbers can be based. A more general 'rule of thumb' is given by Golterman *et al.* (1983) who suggested the collection of a minimum of 10 samples from each sediment type in each region of the water body. These sample numbers, however, can be decreased if preliminary

information, such as acoustic survey data is available for designing appropriate sampling grids. In that case, sample numbers and complexity of bottom sediment distribution can be estimated with reference to the bathymetric chart since the sediment to water depth relationships tend to be fairly constant within each water body (Golterman *et al.* 1983).

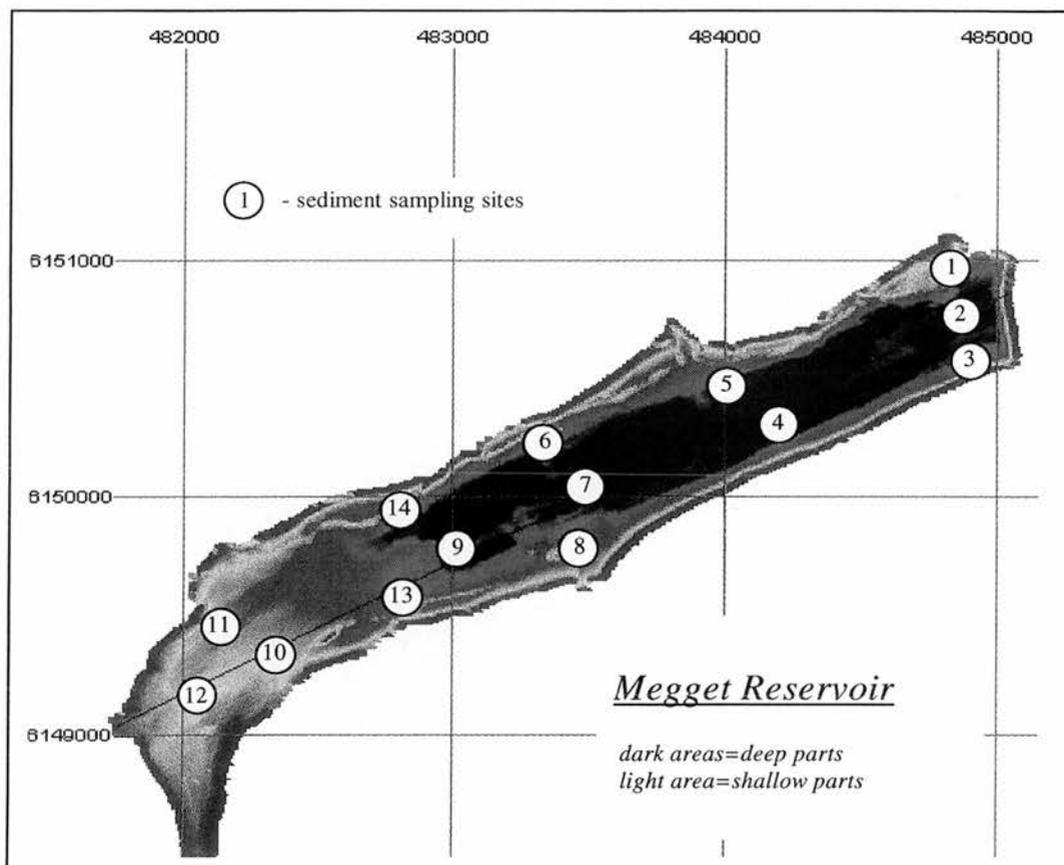


Figure 7. 1: Location of sampling sites during sediment survey

In this study, the sampling sites for the sediment survey were chosen on the basis of the available information, including bathymetric survey data, and under consideration of existing water sampling stations. The sediment survey was carried out on 27 August 2000 and sediment samples were collected at five transverse sections perpendicular to the longitudinal axes of the reservoir. Three of these transects intersected with the regular water sampling stations (A, C, E), which were chosen to represent the different

sedimentary environments within the reservoir as distinguished by Thornton (1990a): riverine zone, transitional zone and lacustrine zone.

Problems encountered during sample collection (e.g., strong winds, difficulties with sample recovery) required some modifications of the original sample set-up, resulting in the final sampling grid presented in *Figure 7. 1*.

### 7.2.1 Sample collection

A variety of manuals, protocols and recommendations for sampling and analysis of soils and sediments (Poppe *et al.* 2000, Mudroch and Macknight, 1991, Buurman, 1996, Elliott and Mickelson, 2001) are available and together with general textbooks (Håkanson and Jansson, 1983; Förstner and Wittmann, 1981) and review papers (Loring and Rantala, 1992) form the basis on which the protocols and sampling procedures for this study were developed, as described in the following sections.

Surface sediment samples were successfully collected at 11 of the 14 locations chosen throughout the reservoir (*Figure 7. 1*). Sampling stations were located using a geographic positioning system (GPS) and the sampling grid which had been prepared prior to the survey. Samples were collected using a stainless steel 0.1m<sup>2</sup> Paterson Type Grab sampler (*Figure 7. 2*). Before and between sample collection the grab sampler and all equipment used during sample collection was thoroughly rinsed with reservoir water in order to remove excess sediment and avoid cross-contamination. For sample collection the sampler was carefully lowered through the water column. On reaching the bottom sediment an extra meter or so of rope was given out to allow the sampler to settle into the sediment. Care was taken when lifting the sampler from the bottom to ensure that the sampler had closed properly. On retrieval the sampler was examined to

ensure that it had been properly closed with no loss of entrapped sediment, especially fine-grained material. Overlying water was carefully decanted through de-watering holes in the lid of the sampler so that no fine material was lost. The sampler was then secured on board and its content emptied into a plastic bowl, where the sample was visually inspected for acceptability (*Figure 7. 2*). Ideally, 4-5 cm of sediment should be collected to obtain an acceptable sample. Where the amount of sediment was less the sample was discarded and a new sample was collected. If sample acceptability was met, a representative sub-sample of 4-5cm was collected using a plastic shovel and spatula. The sample was immediately transferred into a plastic bag, which was then sealed and labelled appropriately, according to sample location and event. Where the water content of the sample was very high the entire sample material (including the water) was collected in order to avoid the loss of fine material suspended in the water. For each sample a brief description, including colour, texture, special features and amount of collected sample material, were recorded together with water depth, GPS co-ordinates, sampling time, weather conditions and deviations from the standard sampling procedure.

Replicate samples were collected at six sampling stations for the determination of reproducibility. At each of these sites a total of three replicates were collected using identical equipment and sampling techniques. Results obtained from the physical and chemical analysis of these samples provide a measure of the variability due to sampling and analytical techniques and also indicate the sediment heterogeneity at individual sampling sites. After collection all samples were kept dark in a cooling box and transported to the laboratory in St Andrews. On arrival the samples were transferred to the cold store where they were stored at a temperature of 4°C until being further processed the next morning.

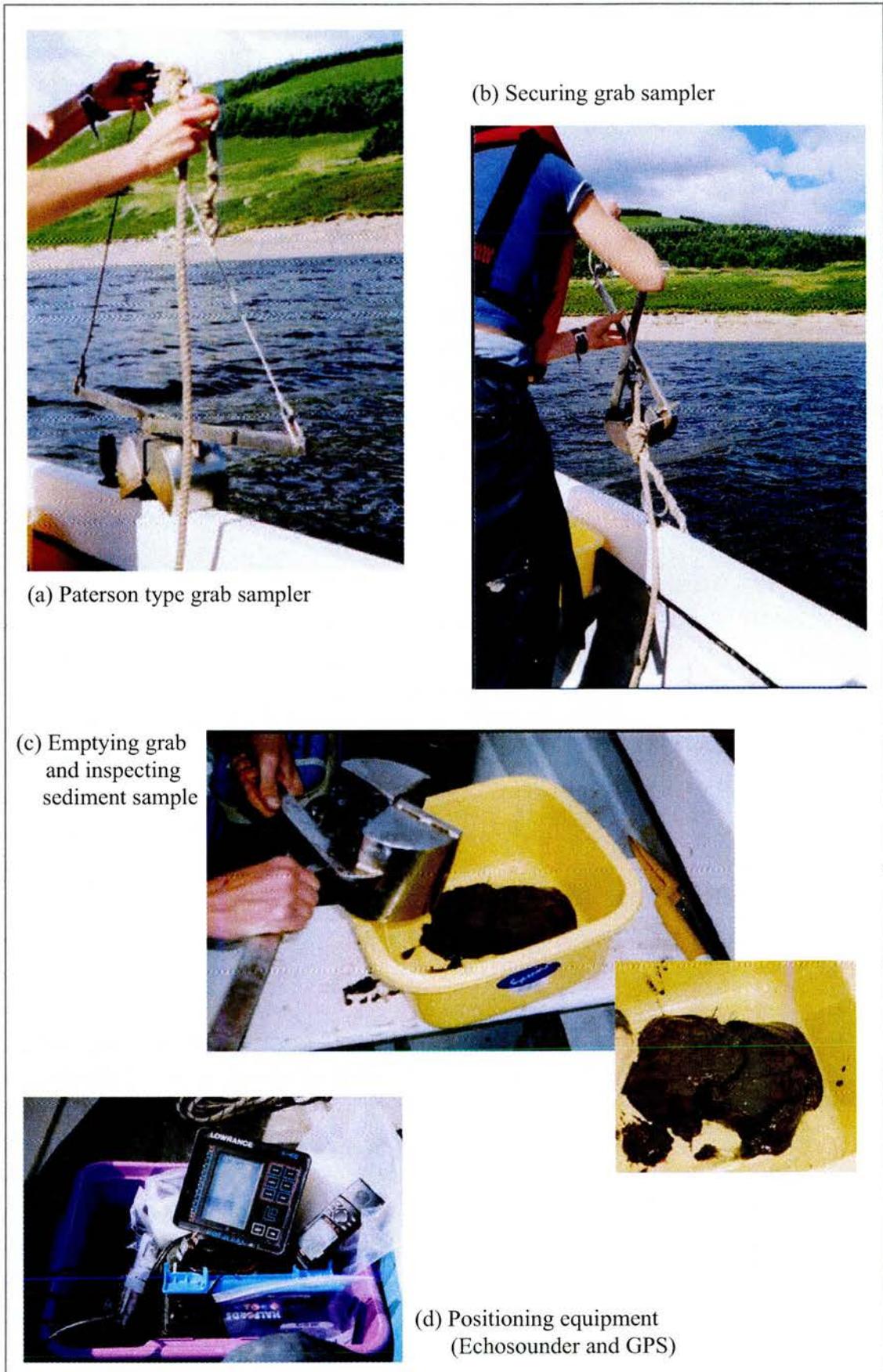


Figure 7.2: Sediment sample collection

Difficulties encountered during sample collecting mainly resulted from two factors: (1) strong winds, which made it difficult to anchor securely, and (2) incomplete closure of the grab sampler due to the mechanism being obstructed by boulders and plant material. The latter only occurred in two areas of the reservoir: near the shore, where boulders and hill scree have accumulated at the bottom of the steep slopes and at the shallow end of the reservoir, where the original valley vegetation (mainly heather) still predominates the bottom of the reservoir. At three locations, no sample was recovered after three trials, the sites were found to be unsuitable for sediment collection due to the encountered problems described above.

### **7.3 Sediment analysis**

#### **7.3.1 Physical analysis**

##### *Sample homogenisation and sub-sampling*

A variety of analyses were performed on each sample, which means that each sample had to be divided into a set of sub-samples. In sub-sampling it is important to ensure homogeneity of the sample. This is especially important where only small sample sizes are required for the analysis, for example in laser diffraction (grain size), XRF analysis. According to Mudroch and MacKnight (1991), homogenisation of wet sample can be achieved by shaking the sample or by intensive manual mixing of the wet sediment. It is further suggested that samples collected by grab sampler should be homogenised in the field by manually mixing in sufficiently large containers and subsequently divided into sub-samples for different analysis.

In this study, the samples collected during the sediment survey were homogenised in the laboratory by intensive manual mixing of the sample until textural and colour

homogeneity was achieved. The samples were then divided into three sub-samples for the analysis of:

- Grain size
- XRF and Sediment digestion
- Water content and loss on ignition

The sub-samples were then transferred to a ventilated oven and dried at 105°C until constant weight was reached. The remaining sediment was frozen to provide backup samples.

#### Water content

The water content ( $w$ ) of sediment is defined as the weight of water in relation to the total wet weight of the sample. Based on the assumption that the lake sediment is saturated with water and that therefore the mass and volume of gases can be neglected it can be expressed as:

$$w = \frac{w_t - w_s}{w_t} \times 100 \quad (\text{Eq 7. 1})$$

where  $w_t$  = total wet weight of the sample and  $w_s$  = dry weight of solids (Håkanson and Jansson, 1981). This simple measurement can be useful in characterising changes in sediment composition with depths in lake sediment cores. Generally, the proportion of solids in the sediment tends to increase gradually with depth beneath the sediment surface. Also, organic matter content decreases with depth owing to compaction and decomposition processes, respectively. However, there are often variations in sedimentation rates and in biotic productivity of a given systems and the resulting

differences in inorganic and organic sediment content can modulate this trend (Maher, 1998).

In this study, the water content of the samples was derived following the method suggested by Kuijper (1996). For each sample 3-5g wet sediment were transferred into clean, pre-labelled crucibles, weighted and transferred into a ventilated oven where they were dried at 105°C overnight. The samples were then removed from the oven and placed in a desiccator for cooling. When they had reached room temperature the samples were re-weighted and further used for determination of the loss on ignition (LOI).

#### Loss on ignition

Loss on ignition (LOI) is widely used as a measure of the organic content of sediments and is prerequisite where sediment metal release pattern are of concern because of the vital role of organic matter in metal binding and complexation processes, as discussed in Chapter 2. LOI is based upon measuring the weight loss from a dry soil sample when exposed to high temperatures. The weight loss that occurs at this temperature is then correlated to oxidisable organic carbon. The LOI is given by:

$$LOI = \frac{w_s - w_r}{w_s} \times 100 \quad (\text{Eq 7. 2})$$

with  $w_s$  = dry weight of solids and  $w_r$  = weight of inorganic residue (Håkanson and Jansson, 1981).

When determining the LOI of a sediment sample, the temperature for the combustion of organic matter is important as too low a temperature can lead to incomplete combustion

of the organic material while too high temperatures cause combustion of carbonates, both of which lead to incorrect results. A variety of temperatures are proposed in the literature for the complete combustion of organic matter, most of which lie between 450°C and 550°C (e.g., Håkanson and Jansson, 1981; Mudroch and MacKnight, 1991; Maher, 1998; Kelts *et al.* 1997). Temperatures in that range destroy most of the organic substances, but may also evaporate some chemically bound water and void compounds (Håkanson and Jansson, 1981). Higher temperatures (950-1050°C) are usually applied when carbonate content of the sample (e.g., Maher, 1998) is of interest or when preparing samples for XRF analysis (e.g., Kuijper, 1996; Dietrich and Schwadner, 2000).

For the determination of the LOI the previously dried and weighed samples were placed in a muffle furnace and allowed to warm up to 450°C. When the temperature was reached the samples were ignited for four hours. The samples were then removed from the furnace and transferred to a desiccator to cool before being weighed again. Weight measurements collected from wet (raw), dried (105°C) and ignited (450°C) samples allowed the calculation of water content and LOI of the sediment according the formulas given above.

### Grain size analysis

Grain size of sediments is an indispensable parameter for geochemical studies dealing with water quality. It not only influences processes related to re-suspension, transportation and deposition of sediments but is also strongly associated with the capacity of the material to bind metals. Grain size, therefore, exercises a determining influence on the metal concentration in sediments (Förstner and Wittmann, 1981). In the

context of lake sedimentology, the objective of grain size analysis is to accurately measure the individual grain size of the sample, determine their frequency distribution and calculate a statistical description that characterises the sample adequately. A wide variety of analytical methods are available for the grain size determination of a sediment sample (see Poppe *et al.* 2000, Håkanson and Jansson, 1983, Golterman *et al.* 1983), but as with most types of sedimentological analysis there is no ultimate technique or procedure that will produce the most reliable grain size results. Generally, the choice is between manual techniques like sieve analysis (dry and wet sieving) or sedimentation methods (Pipette method, Hydrometer method) and automated methods using Electro-resistance or Laser Diffraction analysers. In this study, the grain size distribution of the sediment samples is determined using a laser diffraction method which is integrated in a complete computerised grain size analysis system. The system, Coulter LS230 Grain Size Machine (PSM), automatically determines grain size distributions of a sediment sample in the range of 0.04  $\mu\text{m}$  to 2000  $\mu\text{m}$  using the diffraction of a laser beam, in combination with the Polarisation Intensity of Scattered light (PIDS) of three different wavelength. The results are then analysed and evaluated by the internal data-acquisition and processing software integrated in the system. Generally, the accuracy of the grain size measurements not only depends on analytical methods and equipment but is also sensitive to factors related to sample collection, storage, preparation and processing. Ideally the sediment samples should be analysed as soon as possible after collection (Mudroch and MacKnight, 1991), although in many cases an immediate analysis of the collected material is not possible and adequate sample storage and preparation techniques need to be used. Various authors (Poppe *et al.* 2000; Loring and Rantala, 1992) suggest drying of the sediment samples at temperatures between 100°C-105°C, respectively, as these temperatures only remove the interstitial water from the sediment

and should not affect the grain size (Poppe *et al.* 2000). In this study, sediment samples collected for the grain size analysis were dried overnight at 105°C in a ventilated oven and stored in labelled plastic bags until required for grain size analysis. The samples were then prepared for the analysis at the Coulter Counter as described in the following section.

### *Sample pre-treatment*

Grain size analysis on fine sediments requires that all aggregates in the sample have been disintegrated and the individual grains are detached and that all grains are well dispersed. This can be achieved through pre-treatment of the sample, which usually includes the removal of strongly cementing material like carbonates and the destruction of organic matter. The choice to remove iron oxides (iron coating), although often applied generally depends on the sample material itself and on the aim of the study (Buurman, 1996). Destruction of organic matter is especially important in sediments with an elevated organic content (>3%), not only to achieve complete dispersion of the clay but also to prevent the organics from being counted as part of the sample, which would bias the grain size distribution (Poppe *et al.* 2000).

In this study, prior to assigning pre-treatment procedures and using the above method, a selection of sediment samples from the Megget Reservoir was tested with 1N hydrochloric acid (HCl) for carbonate content. There was no effervescence observed in any of them, leading to the conclusion that the carbonate content in the sediment is minimal (as expected for acidic upland catchments) and removal of carbonate is not necessary. It is assumed that iron oxides present in the sediment consist of both iron coated sediment grains delivered by the tributaries as well as coatings on sediment grain

surface precipitated in-situ as a consequence of changing redox conditions. Since it is not clear which of the processes predominates and if iron oxides are of autochthonous or allochthonous nature it was decided that removal of iron oxides would not be carried out. Consequently, with the aims of the investigation in mind and in view of the low carbonate content, only the destruction of organic material was necessary to prepare the sample for the particle size analysis.

#### *Removal of organic matter*

Organic matter is readily sorbed onto inorganic mineral grains and tends to bind and cement grains into aggregates (Gibbs, 1977). It is therefore necessary to destroy all adhering organic material prior to any form of grain size analysis (Thornton, 1990c).

Generally, there are two methods that are commonly used for the removal of organic matter from sediments; destruction by ignition at high temperatures and oxidation by a strong oxidising agent. Unfortunately, heating of the sediment during ignition results in aggregation of the fine sediment (Mudroch and MacKnight, 1991) and alteration of the structural properties of the clay minerals (Thornton, 1990c). Due to the high amount of fine material in the samples from the Megget Reservoir the application of this technique was considered inappropriate as pre-treatment for grain size analysis. However, loss on ignition was employed for comparative quantitative assessment of organic matter content of the samples collected during the sediment survey (see *Loss on ignition*).

Oxidising agents are widely applied for the destruction of organic matter, one of the most commonly used ones being hydrogen peroxide ( $H_2O_2$ ). It selectively removes organic material from sediment samples by oxidation of the organic material, but may also oxidise sulphides to sulphates (Rauret, 1998). Still, this method is more preferable

than thermal destruction (Thornton, 1990c) and has achieved wide use among many researchers (Buurman, 1996; Poppe *et al.* 2000; Thornton, 1990c) working in marine and freshwater systems.

The peroxide oxidation reaction is temperature and pH sensitive and the amount of material removed is strongly dependent on reaction conditions, peroxide concentration and duration of treatment. For example, the effectiveness of  $H_2O_2$  can be greatly enhanced under slightly acidic conditions and many workers recommend removal of carbonates (Buurman, 1996; Poppe *et al.* 2000) or oxide extraction (Rauret, 1998) using HCl prior to peroxide treatment. However, the addition of acid will cause a very low pH, which causes the destruction of small clay particles (Buurman, 1996) and can itself lead to flocculation and poor dispersion (Thornton, 1990c), thus, defeating the object of the procedure. As the buffer capacity of the sediments analysed in this study can be assumed to be very low (lack of carbonates), the pre-treatment with HCl (to enhance the effectiveness of the procedure) was found unnecessary. Moreover, degradation of the organic compounds during the oxidation reaction itself and their conversion into organic acids causes the extraction suspension to become slightly acidic (Thornton, 1990c), and thereby automatically enhances the effectiveness of the  $H_2O_2$  as the destruction process progresses. Besides the complete breakdown of the aggregates into their particles, as achieved by removal of organic matter, it is important that these particles are de-flocculated, forming a dispersed suspension that is maintained during the analysis. This can be achieved by applying dispersing agents to the sample, the most popular of which is sodium hexametaphosphate. Various other chemicals have been used as peptising agents and were discussed in detail by Thornton (1990c). However, sodium hexametaphosphate has been found the most effective deflocculant (see

Thornton, 1990c) and in this study was applied in the final stage of sample pre-treatment to disperse the sediment particles.

#### *Procedure adopted*

The treatment of the sediment samples closely followed the methods suggested by Evans (2001, personal communication) and Nørgaard-Pedersen (2001, personal communication). The untreated dried samples were carefully crushed (not grinded), weighed to 1g and transferred into labelled glass beakers. These were then mixed with 5 mL de-ionised water and left to soak for 30-40 minutes. The samples were heated on a sand bath at 60-70°C and 10mL of 30 %-vv H<sub>2</sub>O<sub>2</sub> were added. Once the strong effervescence had ceased, the beakers were covered with lids to slow evaporation down and the suspension was maintained on the sand bath at about 70°C to accelerate the reaction. A volume of 10 mL 30%-vv H<sub>2</sub>O<sub>2</sub> was added to the beakers after 1.5-2 hours when effervescence had stopped or drastically slowed down. Reactions that became too vigorous were controlled by removing the lid from the beaker or removing the sample from the sand bath until the reaction had eased off. The procedure of adding 10 mL of H<sub>2</sub>O<sub>2</sub> was repeated 4 times and after approximately 7-8 hours of heating the samples were removed from the sand bath and left to stand at room temperature until all activity had ceased. After the treatment the sediment had a light ochre-brown colour contrasting with the dark grey appearance of the untreated material and indicating that the organic components had been removed. The sediment samples were then thoroughly washed with de-ionised water and the clear supernatant was decanted together with the fragments of incompletely digested fibrous material (mainly small root fragments), which cannot be removed with H<sub>2</sub>O<sub>2</sub> and thus, had remained as a pale brown litter floating on the liquid surface. As a last step, 2 mL of 4% sodium hexametaphosphate

solution was added to the sample to disaggregate (deflocculate) the sample components (mainly clay particles) and obtain a stable, dispersed sediment suspension. The mixture was thoroughly shaken on a rattle shaker, mixed with de-ionised water and stored in the refrigerator for at least 24 hours in order to let the dispersing agent take effect (non-flocculation of clay minerals). Finally, the supernatant was decanted leaving the disaggregated and dispersed sediment residue available for grain size analysis in the Coulter Counter.

### *Grain size analysis*

After pre-treatment the sample was transferred to the Coulter granulometer. Before the analysis the Coulter Counter was set up and automatically calibrated. Each sample measurement was repeated three times before the sample was discarded. Calibration curves of the instrument were re-calculated at regular intervals throughout the analysis. Before entering the measuring vessel, the sediment samples were passed through a 2 mm sieve. The instrument then measured the obscuration, which for consistent analysis was required to be between 8-12 %. When outside these limits, the obscuration was corrected by adding sample material to the measuring vessel or by diluting the suspension with de-ionised water, respectively. On completion of the measurements the sample was discarded and the vessel was automatically rinsed repeatedly and prepared for the next sample. Quality control replicates were performed with each sampling set. The replicates were prepared and analysed identically, using the same reagents, equipment and methods. A replicate number of 5% minimum or 1 replicate per 20 samples was applied for quality control samples as proposed by Elliott and Mickelson (2001).

### 7.3.2 Chemical analysis

A number of different sediment chemical analyses were carried out on the sediment samples in order to (1) characterise the chemical composition of the sediments and their spatial distribution and (2) to estimate the proportion of loosely bound metals in the sediment, which are readily available for re-mobilisation (related to changing condition at the sediment-water interface). The applied sediment analysis techniques are detailed below, and identical methods were utilised during the sediment core study discussed in Chapter 8.

#### Sediment digestion / HOAc extraction

##### *Introduction*

Metals along with other elements are introduced in the aquatic environment mainly via streams and rivers. In most water columns they appear in low concentrations where they exist in a variety of forms, not all of which are equally toxic, mobile or bioavailable.

However, in most natural systems metals are found primarily as part of or associated with solid surfaces, such as suspended organic or inorganic particles or aggregates of different origin and chemical character (Håkanson and Jansson, 1983). The metal load can be associated with these so called 'carrier particles' in different ways; they can be loosely bound to the particles or locked up physically and/or chemically in detrital particles and minerals. The form of association will determine the dynamics of these metals in water and sediments and also determines their ecological effects on the aquatic system. Thus, when assessing the influence of metals in sediments on the water environment or when investigating the effects of remobilisation the particular physical

and chemical forms in which particulate metals occur (speciation) may be more important than the total metal concentration (Förstner and Wittmann, 1981).

Several experimental procedures varying in manipulative complexity have been developed to determine the speciation of particulate metals (see Rauret, 1998). These methods are strictly operationally defined, partitioning the solid material into specific, conceptually defined fractions. The individually defined fractions may vary significantly between the different methods and care must be taken when comparing results from different extraction schemes. *Single extraction methods* using acetic acid (HOAc/CH<sub>3</sub>COOH) (Loring, 1978) or weak hydrochloric acid (HCl) solutions (Doherty *et al.* 2000; Kim, 2000), nitric acid (HNO<sub>3</sub>) (Baveye *et al.* 1999; Kim, 2000) or aqua regia (HNO<sub>3</sub> and HCl) are designed to partition the total metal concentration into loosely bound (non-detrital, non-residual) and residual (detrital) phases and to estimate the maximum content of reactive and available elements in the sediment. Data obtained from such determinations also aid better definition of the contrast between anomalous and background concentrations (Tessier *et al.* 1979; Adami *et al.* 1999) and allow deductions of the carriers, transport mode and potential bioavailability of the metals (Loring and Rantala, 1992). Moreover, single extraction procedures are often chosen to evaluate a particular release controlling mechanism such as complexation by competing organic agents (Rauret, 1998). Therefore, the applied digestion method has to be carefully chosen as each method can suffer from the difficulty of finding a single reagent, that is effective in dissolving quantitatively the non residual forms of metals without attacking the residual detrital forms (Tessier *et al.* 1979). Generally, exchangeable and weakly adsorbed metals in sediments are selectively displaced by soft extractants, such as acetic acid or weak hydrochloric acid. Other extractants are often

less selective and beside the exchangeable fraction also extract metals bound to other sediment phases (Rauret, 1998). Thus, for single extraction of the exchangeable metal fraction weak acid digestion methods using hydrochloric acid (Kim, 2000) or acetic acid (Loring and Rantala, 1992) are more suitable than strong acid digestion using nitric acid or aqua regia. The latter were found to yield incomplete, inaccurate and unverifiable determinations of metals and the results strongly depend on sample type, matrix and determined elements (Loring and Rantala, 1992, Baveye *et al.* 1999).

More elaborate methods make use of *sequential extraction methods*, partitioning the solid material into specific fractions according to metal association and predominant bonding processes. No standard method has yet been established for determining metal fractionation, although increasing efforts are directed towards a standardisation and harmonisation of these extraction procedures (Förstner and Wittmann, 1981; Rauret, 1998). However, at present many different sequential extraction schemes are in use (Bryant *et al.* 1997, Calmano *et al.* 1993, Golterman *et al.* 1983, Håkanson and Jansson, 1983, Rauret, 1998) out of which the most widely used one is that proposed by Tessier *et al.* (1979). The procedure differentiates between (1) exchangeable, (2) carbonate, (3) iron and manganese oxide, (4) organic matter and sulphide, and (5) a residual silicate phase fraction, but has been modified by several authors (see references in Rauret, 1998).

Although sequential extraction can provide more detailed information about origin, biological and physiochemical availability, mobilisation and transport of metals (Tessier *et al.* 1979), these methods are often of limited value as they fail to provide actual particulate speciation (Nirel and Morel, 1990). Moreover, different analytical problems and loss of certain elements (e.g., organic matter, sediment-bound manganese) during the analysis have been associated with sequential sediment extraction (Bendell-Young

and Harvey, 1992b). Finally, sequential extractions are much more time consuming when compared to single extraction procedures, taking up to 3 days to complete all five extraction steps for one sample (Bendell-Young and Harvey, 1992b). It has been suggested that simultaneous single extractions on individual aliquots, rather than sequential extraction procedures are a valid approach (Gavin *et al.* 2001; Bendell-Young and Harvey, 1992b), because partial values obtained from single extractions are comparable with values obtained by sequential extraction (Vanni *et al.* 1997).

The choice of method and the detail of the metal fractionation usually depend on the objective of the conducted study. The general aim of many environmental studies involving chemical extraction is the determination of element distribution among different phases of sediment. Tack and Verloo (1999) pointed out that the use of single extraction rather than sequential extraction is justified for practical purposes. For example, where the environmental influence of metals in sediments on the aquatic environment is assessed, the most mobile phase of these elements should be considered (Förstner and Wittmann, 1983). These fractions are represented by elements that are loosely bound to sediment particles in sorbed, precipitated or complexed form, but are potentially available for (diagenetic) remobilisation. Consequently, sediments that usually act as sinks for these elements may become a potential source when physico-chemical conditions in the aquatic system change causing release of these elements from their sorption sites. Since chemical extraction of sediments was shown to be adequate for determining the metals associated with the source constituents in sediments (Rauret, 1998), a single extraction method, as suggested by Loring and Rantala (1992), is used in this study to estimate the potential of the bottom sediments for metal remobilisation in the Megget Reservoir.

*Procedure adopted*

The operationally defined method chosen for this study closely follows the procedure suggested by Loring and Rantala (1992) for marine sediments and will be detailed in the next section. It is based on the use of acetic acid to release the proportion of weakly bound metals from such sites as ion-exchange positions, easily soluble amorphous compounds of iron and manganese, carbonates and those metals weakly held in organic matter. The extracted fractions should then represent the proportion of Fe and Mn potentially available for (diagenetic) remobilisation.

Before extraction the dried samples were placed in an agate mortar and lumps that had formed during drying were gently crushed. Following, two grams of the sample were transferred in a pre-labelled centrifuge tube and both, tube and sample were weighed. For the extraction of the samples 25 mL of 25%-vv acetic acid (HOAc) were added to the centrifuge tube, which was then tightly capped. After shaking the tube thoroughly by hand and on a rattle shaker to ensure complete initial mixing of acetic acid with the sediment, the tubes were transferred to an orbital shaker, where they were slowly shaken at 200rpm for 6 hours. The red-coloured supernatant was then separated from the sediment by centrifugation for 10 minutes and transferred in a pre-labelled 50-mL centrifuge tube. To remove remaining extracts from the sediment, the sediment was washed by adding 10 mL deionised water to the sample and placing it briefly on a rattle shaker. The wash water was separated by centrifugation, added to the previously abstracted supernatant and then made up to a volume of 50 mL by adding deionised water. The extracted supernatant samples were stored at 4°C in a temperature-controlled room until analysis. Acidification of the samples was not necessary as the sample

extract had an acidity of 10-12%-vv and the pH was sufficiently low (pH ~2.5) to prevent re-adsorption of the metals to the walls of the storage tubes. All samples were analysed at CEH Wallingford as described in Chapter 4

### X-Ray Fluorescence (XRF) analysis

This chapter documents the application of x-ray analytical techniques, principally X-Ray Fluorescence (XRF) spectrometry, for the chemical characterisation of the sedimentary material examined in this study. The principles behind XRF analysis are briefly discussed and the sample preparation techniques are explained. For a more detailed discussion of these topics the reader is referred to Williams (1987), Hagopian-Babikian *et al.* (1998), Ferek and Jenkins (1998) and Kuijper (1996).

### *Introduction*

X-ray fluorescence spectrometry is a non-destructive technique, which is widely used to measure the elemental composition of materials. It is based on the analysis of an x-ray spectrum generated from the sample under controlled conditions. X-radiation arises when matter is irradiated with a beam of high-energy electrons or x-rays. For example, when a primary x-ray excitation source strikes a sample the x-rays can either be absorbed by the atom or scattered through the material. During absorption the energy of the primary x-ray is transferred to the innermost electron shells, from which, if the primary energy is sufficient (above the critical excitation potential), electrons are ejected or excited to higher energy orbitals of the atom, creating vacancies. These vacancies present an unstable condition for the atom. As the atom reverses to its stable ground state, electrons from the high-energy outer-orbitals are transferred to the temporally unfilled inner (lower energy) shells. In the process a characteristic,

secondary x-ray is emitted whose energy is the difference between the two binding energies of the corresponding shells. This process produces a characteristic line spectrum and is referred to as X-Ray Fluorescence (XRF). As each element has a unique set of energy levels, the actual excitation potentials and wavelengths of these characteristic lines are unique for each element. Thus, determination of wavelengths for various lines in an emitted x-ray spectrum allows the identification of elements present in the sample. The intensity with which a particular characteristic line is emitted is a function of the concentration of the emitting element. Thus, concentrations of the elements present in the sample can be obtained by comparing the measured radiation with that emitted by standards of known composition.

#### *Sample preparation*

The chemical analysis of sediment samples by XRF requires special sample preparation procedures in order to eliminate errors caused by matrix adsorption effects, arising from mineral size and compositional heterogeneity from the results. Sample preparation should result in specimens which are reproducible and which, for a certain calibration range, have similar physical properties, including attenuation coefficients, density, particle size and particle homogeneity (Ferek and Jenkins, 1998).

The most common method of preparing sediment samples is to prepare pressed powder pellets. For that, the samples are first ground and then pelletised at high pressure. This method is quick and effective and also has the advantage of minimising inhomogeneities and particle size effects. However, as pointed out by Ferek and Jenkins (1998), there is a potential problem of contaminating the sample during the grinding process. To reduce the risk of contamination, an agate mortar was used, which, between

samples, was thoroughly cleaned with acetone. Errors may also occur in very inhomogeneous samples where harder compounds present in the matrix cannot be completely broken down during grinding. The resulting particle size or microabsorption (= mineralogy) effect will generally be found to be most severe when analysing light elements such as Na and Mg.

Sediment samples collected for the analysis by XRF were dried overnight at 105°C in a ventilated oven to remove absorbed water, which could interfere with the analysis, from the sediment. The dried samples were stored in airtight bags until required for the preparation of the pressed pellets. The samples were then prepared by grinding the dry bulk material in an agate mortar to a fine powder with a particle size of approximately 100 µm to achieve particle size equalisation. Following, the samples were made into 32 mm pressed pellets by compressing approximately 8 g of the sediment powder under 8 tons pressure on 1 1/4" die in a pressing cylinder. The addition of binder was not required due to the good self-bonding properties of the samples caused by the relatively high organic content.

## **7.4 General results and spatial pattern**

### **7.4.1 Physical sediment properties**

The data produced by the particle size analysis were analysed using graphical and statistical methods. The results are given in *Table 7.1* and *Table 7.2* as well as in *Figure 7.3* to *Figure 7.5*, and will be presented in the following sections beginning with the graphical analysis.

Sample ID	Sampling Position		Depth (m)	Water content (%)		L.O.I. (%)	
	Coordinates N	Coordinates W		S.D. [%]	S.D. [%]	S.D. [%]	S.D. [%]
MS1	55° 29' 41.6"	3° 15' 16.9"	20.4	80.9	15.4	14.4	7.2
MS2	55° 29' 40.0"	3° 15' 13.5"	39.0	74.4	2.1	11.3	10.4
MS3	55° 29' 33.8"	3° 15' 13.4"	43.9	-	-	10.5	-
MS4	55° 29' 18.2"	3° 15' 57.4"	33.2	no sample recovered after 3 trials			
MS5	55° 29' 24.3"	3° 16' 08.8"	40.8	75.9	-	11.1	-
MS6	55° 29' 19.0"	3° 16' 46.9"	29.6	67.0	-	17.1	-
MS7	55° 29' 13.2"	3° 16' 44.7"	36.6	76.1	8.6	12.0	22.0
MS8	55° 29' 04.5"	3° 16' 38.0"	19.2	79.9	-	15.8	-
MS9	55° 29' 04.4"	3° 17' 06.7"	30.9	79.2	6.0	12.4	9.6
MS10	55° 28' 46.6"	3° 17' 46.4"	9.3	no sample recovered after 3 trials			
MS11	55° 28' 50.3"	3° 17' 51.6"	13.8	92.5	2.2	24.2	1.7
MS12	55° 28' 44.0"	3° 17' 55.4"	12.1	no sample recovered after 3 trials			
MS13	55° 28' 57.9"	3° 17' 09.3"	22.5	78.7	2.4	20.2	28.7
MS14	55° 29' 07.5"	3° 17' 16.5"	33.2	81.2	-	11.8	-

Table 7. 1: Physical sediment characteristics (SD=Standard deviation)

Cumulative frequency distribution curves for selected samples from each of the sampling sites are summarised in *Figure 7. 3*. It is interesting to note the similarities between these curves with regard to their size range and general gradient, which indicates relatively small variability in particle size distributions between the different sites throughout the reservoir. The graphs show that at all locations, except for MS3 and MS6, the sediment material is relatively well sorted and the silt size particles make up the bulk of the sediment, which is otherwise devoid of any material coarser than fine sands. At MS3 and MS6, however, range and gradient of the curves are different.

Sample ID	Sampling Position		Particle Size Parameters ( $\mu\text{m}$ )								Sampling error: S.D. (%)						
	Coordinates N	Coordinates W	Depth (m)	d10	d50	d90	Mean	Mode	Sorting ( $\sigma$ ) S.D.	Specific Surface area	d10	d50	d90	Mean	Mode	Sorting ( $\sigma$ ) S.D.	Specific Surface area
MS1	55° 29' 41.6"	3° 15' 16.9"	20.4	1.237	8.75	42.1	16.48	9.9	21.04	16956	5.5	9.9	9.3	8.2	5.08	4.8	6.5
MS2	55° 29' 40.0"	3° 15' 13.5"	39.0	1.404	9.54	41.8	16.76	10.7	20.45	15380	6.7	12.1	15.7	13.5	5.12	11.0	7.4
MS3	55° 29' 33.8"	3° 15' 13.4"	43.9	1.587	12.96	91.6	33.20	11.3	55.07	13085	-	-	-	-	-	-	-
MS4	55° 29' 18.2"	3° 15' 57.4"	33.2						<i>no sample recovered after 3 trials</i>								
MS5	55° 29' 24.3"	3° 16' 08.8"	40.8	1.386	9.82	44.2	18.05	11.3	23.81	15280	-	-	-	-	-	-	-
MS6	55° 29' 19.0"	3° 16' 46.9"	29.6	1.562	15.03	112.4	47.76	10.3	91.87	12925	-	-	-	-	-	-	-
MS7	55° 29' 13.2"	3° 16' 44.7"	36.6	1.307	8.48	33.9	13.94	10.8	16.46	16734	12.3	15.2	7.2	9.4	12.03	4.4	11.5
MS8	55° 29' 04.5"	3° 16' 38.0"	19.2	1.356	8.74	36.0	14.84	10.3	18.48	15967	-	-	-	-	-	-	-
MS9	55° 29' 04.4"	3° 17' 06.7"	30.9	1.442	10.08	45.4	18.47	11.3	24.32	14968	10.7	15.0	22.5	17.6	7.62	19.8	10.5
MS10	55° 28' 46.6"	3° 17' 46.4"	9.3						<i>no sample recovered after 3 trials</i>								
MS11	55° 28' 50.3"	3° 17' 51.6"	13.8	1.302	7.95	30.1	12.78	9.8	15.28	16990	9.9	13.0	10.2	9.4	6.62	2.0	9.8
MS12	55° 28' 44.0"	3° 17' 55.4"	12.1						<i>no sample recovered after 3 trials</i>								
MS13	55° 28' 57.9"	3° 17' 09.3"	22.5	1.424	9.76	46.7	18.47	11.0	24.37	15088	4.4	3.1	13.4	12.7	4.53	24.9	3.6
MS14	55° 29' 07.5"	3° 17' 16.5"	33.2	1.505	11.02	46.5	20.63	12.4	31.34	14113	-	-	-	-	-	-	-

Table 7. 2: Statistical grain size parameters and estimated sampling error

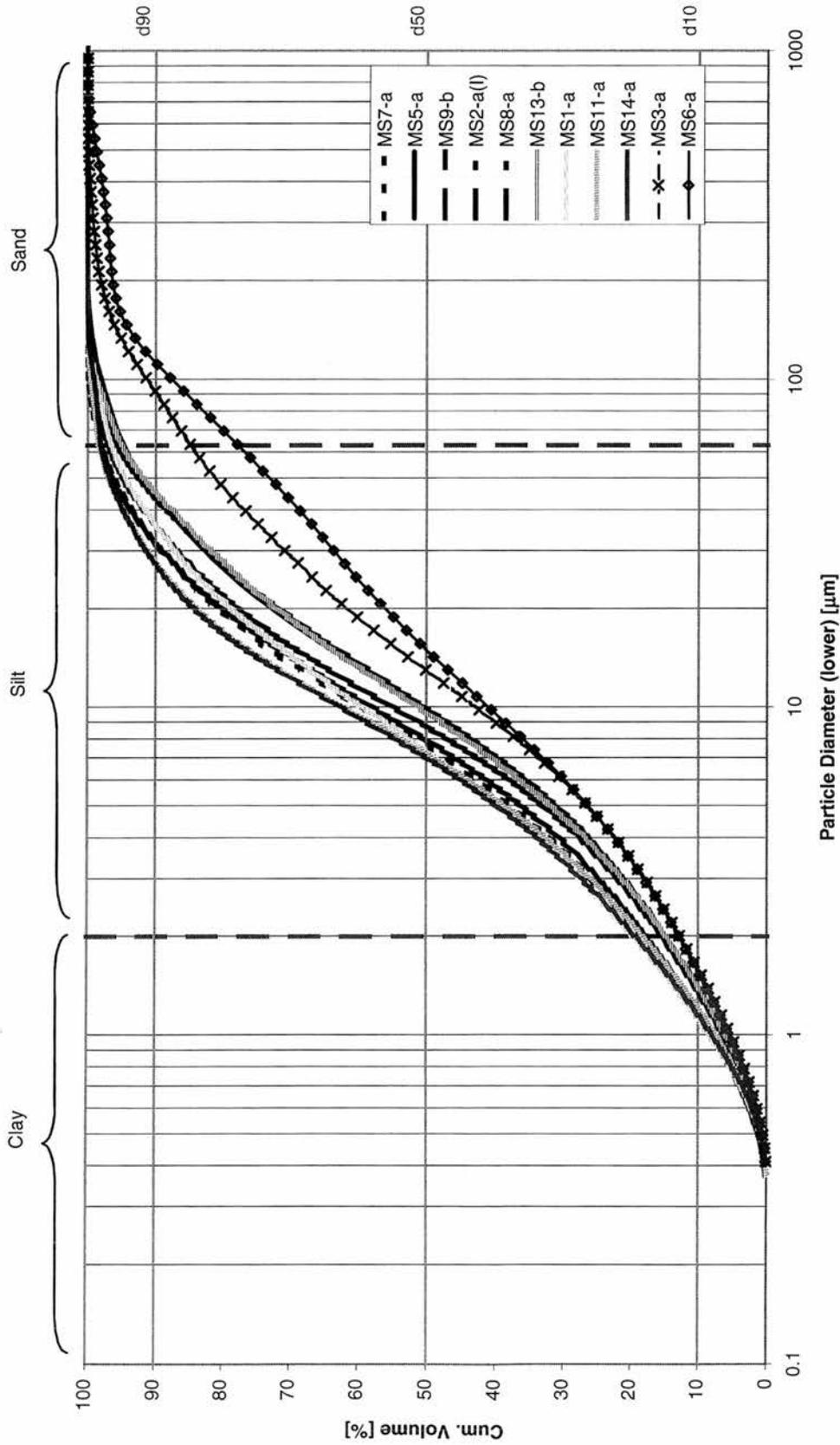


Figure 7. 3: Cumulative frequency distribution curves (all locations).

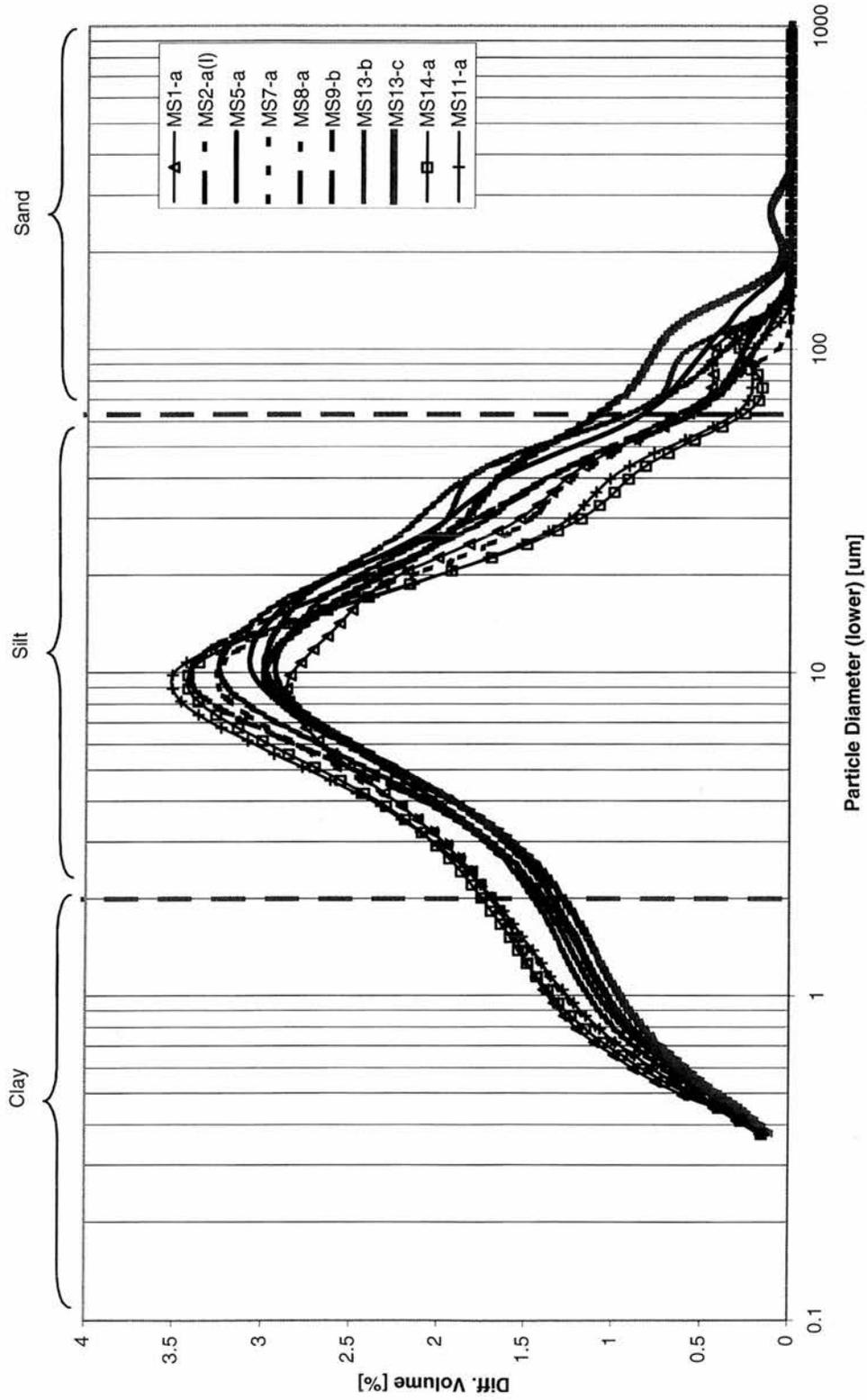


Figure 7. 4: Frequency distribution curves (Locations MS1, MS2, MS5, MS7,MS8, MS9, MS11, MS13, MS14).

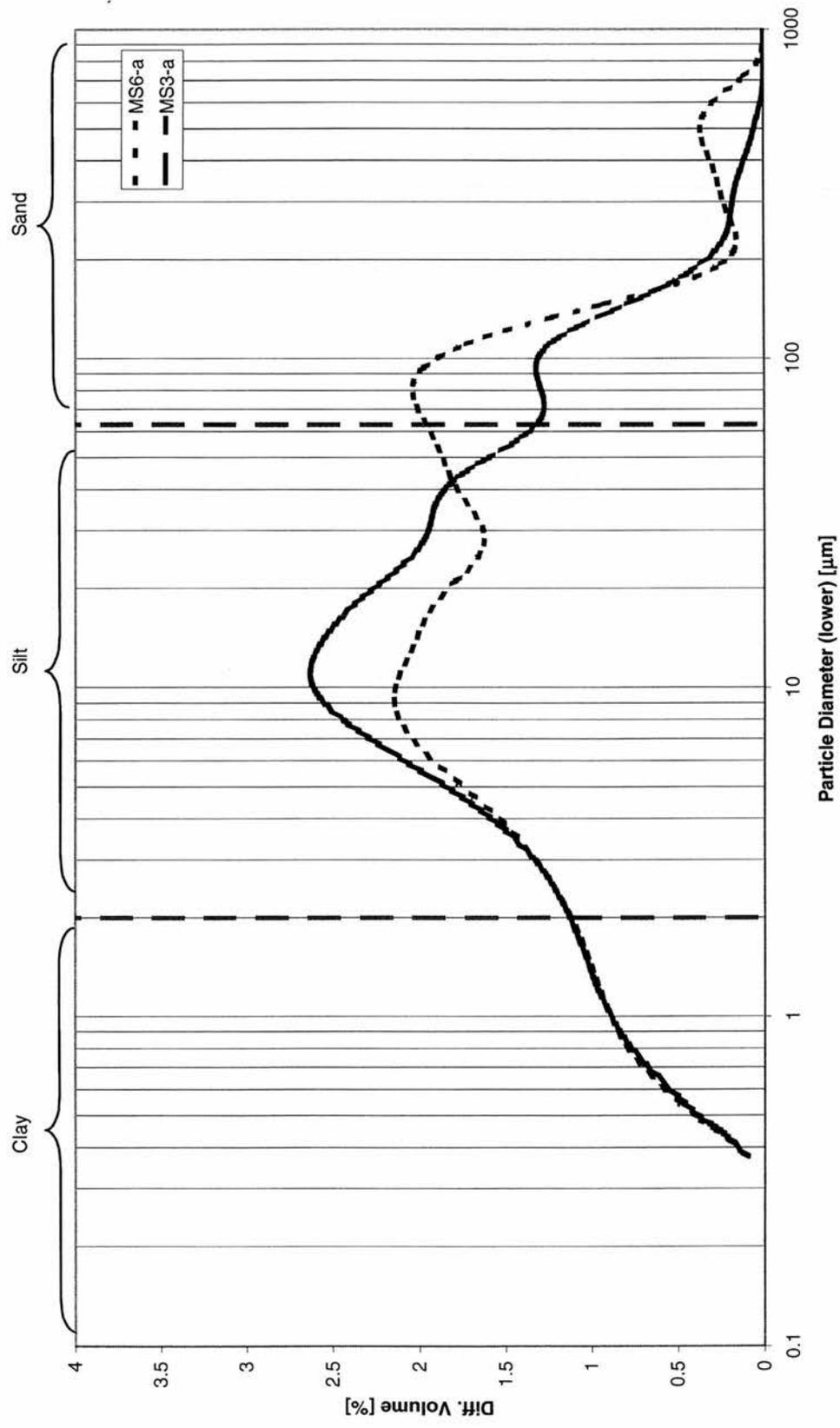


Figure 7. 5: Frequency distribution curves (Locations MS3, MS6).

Sediment deposits at these sites appear to be less well sorted and contain a higher proportion of fine to medium sand.

To analyse the differences in particle size distributions and the constituent particle population simple frequency curves were produced for each of these samples. The resulting graphs show separation of the samples into two main groups (*Figure 7. 4, Figure 7. 5*).

*Figure 7. 4* displays samples collected at sites MS2, MS5, MS7, MS8 and MS9, which are uni-modal in nature and clearly dominated by a medium silt mode between 10  $\mu\text{m}$  and 11  $\mu\text{m}$ . The samples display very similar grain size distributions though some variations occur in the coarser grain fractions according to sampling locality. Two samples collected at MS13 (*Figure 7. 4*) illustrate the somewhat different sediment characteristics observed at this sampling point. As can be seen from the graph the general grain size distribution at MS13 is very similar to the other samples with the exceptions that:

- ❖ the slope gradient on the falling limb of the curve changes (undulates)
- ❖ a secondary mode is developed in the fine to medium sand fraction.

The latter is only observed in sample MS13-c, but not in 13-b, which demonstrates the degree of variation found in sediments at individual locations (as will be discussed later in this chapter). Bi-modal distributions are also found in the samples collected at MS1, MS11 and MS14 (*Figure 7. 4*). These sites are characterised by a slightly higher clay component but display the same primary medium silt mode. In all samples a secondary but much smaller mode is developed in the fine sand fraction at around 100  $\mu\text{m}$ . The secondary mode in the fine sand fraction can also be found in the frequency curves of

sediments collected at MS3 and MS6 (*Figure 7. 5*), which, in general, differ distinctively from any of the other curves. As for all other samples the most abundant grain size lies in the medium silt fraction, but a secondary fine sand mode is well established between 80  $\mu\text{m}$  and 100  $\mu\text{m}$  and at MS6 assumes almost equal importance to the medium silt mode. A further mode is established in the medium sand fraction of the MS6 curve at about 500  $\mu\text{m}$ .

Statistical analysis was carried out on the data as this, besides defining the position of the frequency curves, enables numerical comparisons to be made between the samples. Basic statistical parameters for all samples were derived from moment statistics calculated by the analysis software of the LS230. For better comparison, mean values of statistical parameters were derived from the samples collected at individual sampling sites and are summarised in *Table 7. 2*. Generally, it can be seen that the statistical data are in good agreement with the findings from the graphical interpretation of the data: variability between individual sampling sites is comparatively small (with the exception of MS3 and MS6) and samples are dominated by sediments in the medium silt fraction between 10  $\mu\text{m}$  and 12  $\mu\text{m}$ . It is also interesting to note that the specific surface area of the sediments does not differ significantly between individual sampling sites, which is particularly important when considering sediment sorption capacity for iron, manganese and nutrients.

Some differences between the tabulated statistical values and those displayed in the graphs occur, resulting from averaging between the replicate samples collected at individual sampling sites. To account for this variability, the standard deviation was estimated from the replicates (where available) and is also given in *Table 7. 2*. It not

only provides a measure of the degree of variability introduced by sampling and analytical techniques but also gives an indication of the heterogeneity of the bottom sediment at the individual sampling sites and in the following sections will be referred to as 'sampling error'. It is important to note that the standard deviation for some parameters was found to take values greater than 20%, which needs to be considered when interpreting the data, particularly when comparing different sampling sites and/or assigning spatial distribution trends.

Presented in *Table 7. 1* are data for the total organic matter content of the samples, estimated by weight percent loss on ignition (LOI) of all samples examined. Values range between 10.5% and 24.2% and increase directly with decreasing main grain size (mode) and increasing percentage of fine material (median/d50), reflecting the general dependence of sedimentary organic matter concentrations on these parameters. It is also interesting to note that highest amount of organic matter is found in samples MS11 and MS13, and this may represent the influences of decomposing, former valley bottom vegetation at these sampling sites.

The water content of the surface sediments is similar throughout the reservoir, indicating low degree of compaction. The water content is somewhat higher in samples collected at the shallow end of the reservoir, and this agrees with the increased organic matter content observed at these sites (*Table 7. 1*). However, relatively high standard deviations are calculated for both, LOI and water content, reflecting the inhomogeneous nature of the bottom sediments, although for the latter, incomplete decanting of overlying water during sample collection (*Section 7.2.1*) may, at least in part, have contributed to the high sampling error.

### 7.4.2 Sediment chemistry

Sediment compositional data were derived from XRF analysis of the sediment and results are given in *Table 7.4*. The data show clear variations in sediment chemistry between individual sites indicating changes in relative contribution of individual mineral phases and/or biogenic components. When displayed as scatter plots (*Figure 7.7*), the data reveal several interesting relationships. Most importantly, all sediment samples collected throughout the reservoir can be separated into two groups represented by different proportions of Al, Si, K, Na, P, Ti and Cr. The groups will be referred to as sediment type 1 and sediment type 2, where type 1 sediment is characterised by relative enrichment in Al and Cr (MS10-MS14) compared to type 2 sediment, which has higher proportions of Si, K, Na, P and Ti (MS1-MS9). Considering the spatial distribution of the sediment, it is interesting to note that the two sediment types occupy different areas of the reservoir.

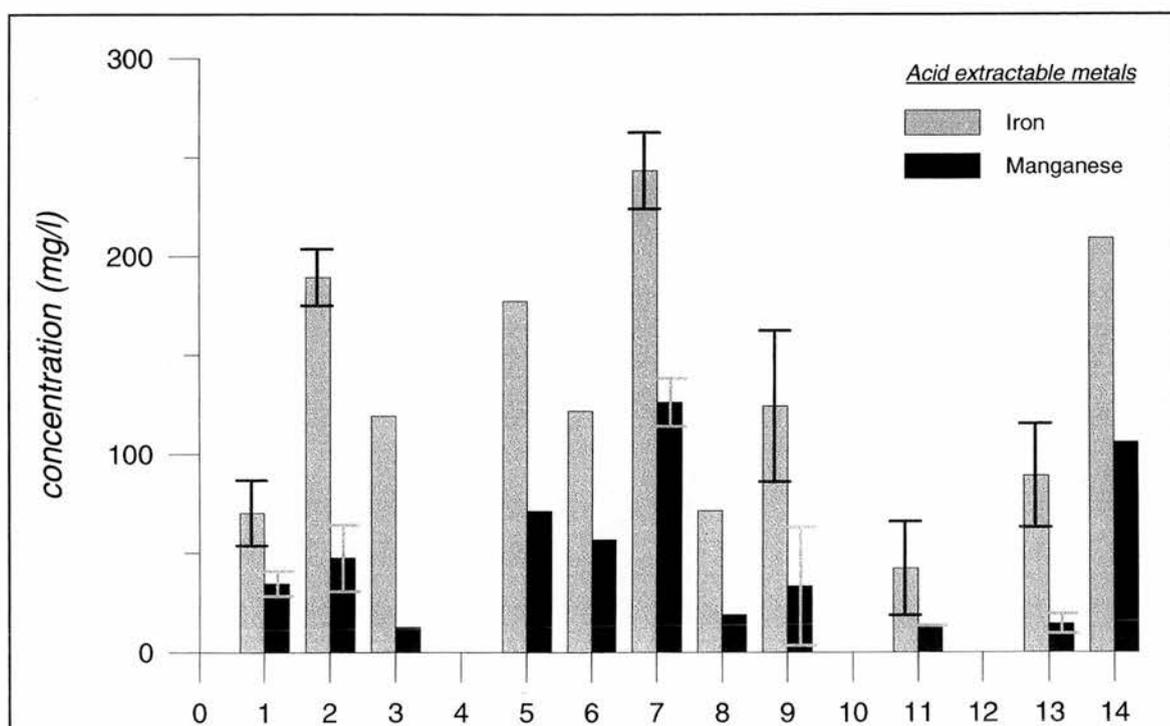


Figure 7. 6: Concentrations of acid-extractable (weakly bound) iron and manganese extracted from the sediments (HOAc extraction).



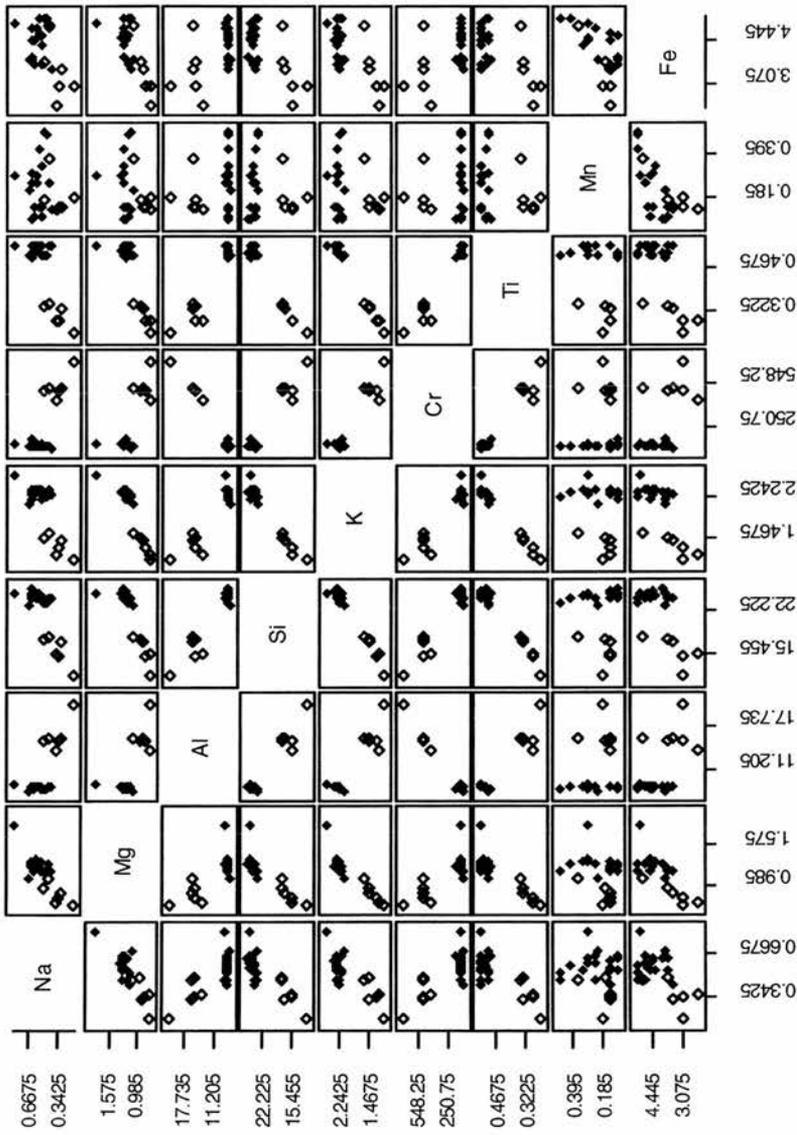


Figure 7. 7: Relationships between total concentrations (determined by XRF) of selected metals in the sediment samples collected at sites MSI-MS9 (full diamonds) and MSI0-MS14 (open diamonds).

Type 1 sediments dominate the shallow end of the reservoir (MS10-MS14) while those of type 2 are found in the middle section of the water body and towards the dam. While this is likely to be the result of sediment transport and deposition processes it may also reflect the presence of compositionally different source material in these areas.

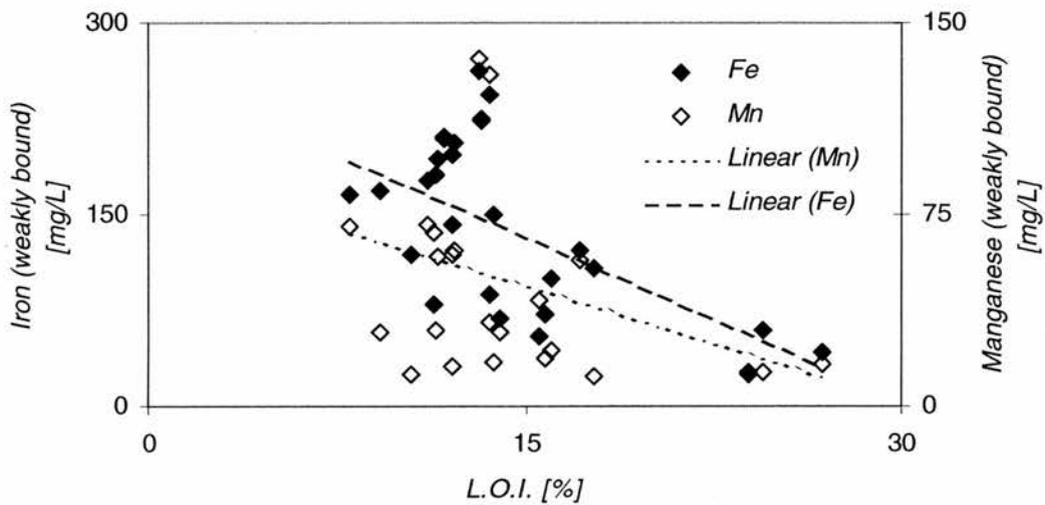
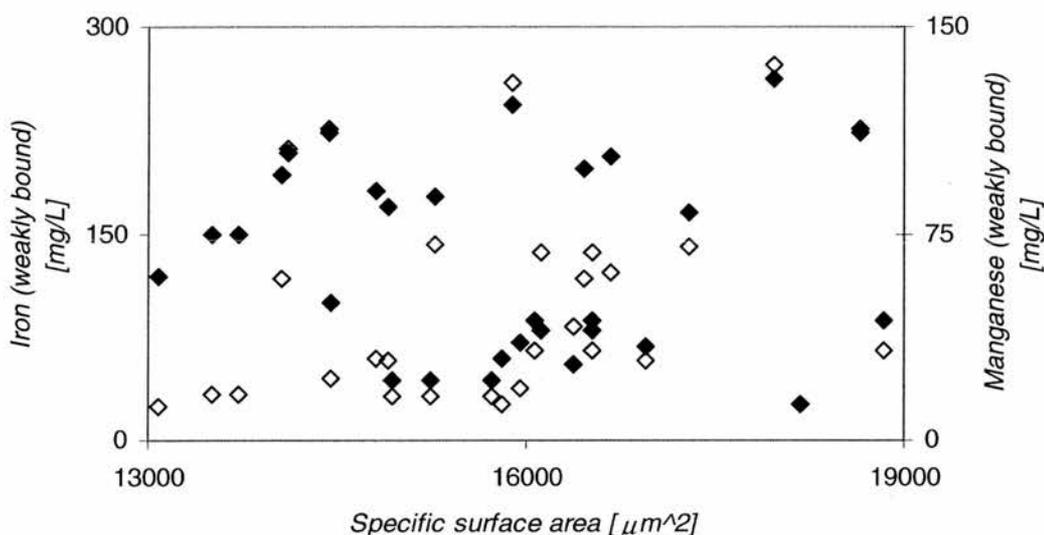


Figure 7. 8: Relationship between weakly bound iron and manganese (derived from HOAc extraction) and loss on ignition (~organic content) of the sediment samples.

Proportions of Fe and Mn weakly bound in ion-exchange positions, amorphous compounds of Fe and Mn or carbonates and those weakly held in organic matter were derived using sediment digestion. The results are displayed in *Figure 7. 6* and show no clear pattern in the spatial distribution of weakly bound metals, although somewhat higher Fe concentrations in samples collected in the central, deeper parts (>30 m) of the reservoir may be inferred. The graph also illustrates the high standard deviations obtained from analysis of field and laboratory replicates (see *sections 7.2.1* and *7.3.2*), demonstrating the relatively high degree of uncertainty inherent in the data. This poor reproducibility is probably related to the heterogeneous distribution of chemical

characteristics in the sediment deposits, which is closely linked to small-scale variations in redox conditions and organic content in the sediments. Including LOI and physical sediment parameters into the analysis (*Figure 7. 8, Figure 7. 9*) shows that concentrations of HOAc-extractable Fe and Mn in the samples are negatively correlated with the organic matter (LOI) content, while no clear relationship exists between concentrations of weakly bound metals and grain size parameters (e.g., specific surface area).



*Figure 7. 9: Relationship between weakly bound iron and manganese (derived from HOAc extraction) and specific surface area of the sediment samples.*

## 7.5 Discussion

The results highlight the variations in sediment grain size distribution across the reservoir and also show the relatively high degree of sediment heterogeneity encountered at individual sampling sites, introducing sampling errors of up to 22%. However, despite this limitation, valuable information about sedimentation pattern in

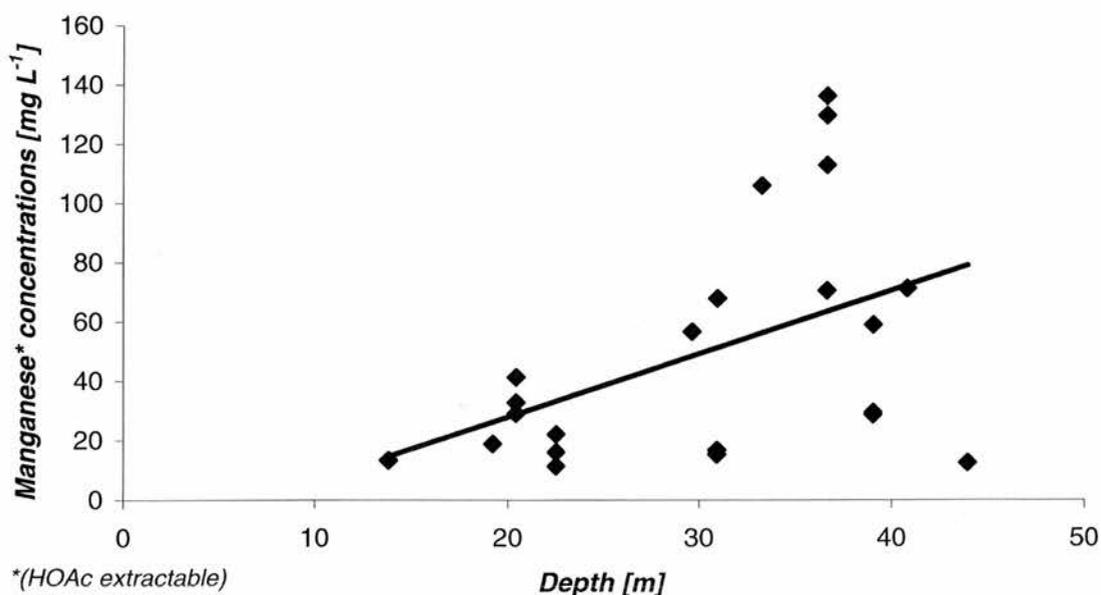
the reservoir could be extracted from the data. It is shown that the dominating size fraction at all sampling sites lies in the medium silt fraction between 10  $\mu\text{m}$  and 12  $\mu\text{m}$ . The presence of a further, more coarse-grained sediment population is observed in samples from MS1, MS11, MS14, MS6, MS3 and MS13, which are characterised by bimodal distribution curves with a secondary mode in the fine sand fraction between 80  $\mu\text{m}$  and 100  $\mu\text{m}$ . As these sampling sites are located near the sides of the reservoir (*Figure 7. 1*), this may reflect inputs from inflowing streams and/or the influence of turbidity currents and debris flows originating from the steep slopes of the reservoir. The latter is particularly evident in samples collected at sites MS3 and MS6, which are located at the steep slopes of the reservoirs and show two and three distinct sediment populations, respectively. It can be assumed that there is also a considerable amount of scree and rock debris deposited at these sites as was indicated by sampling at MS4, where sediment recovery was impossible due to the high amount of boulders present at this site. Considering the grain size range of the secondary mode, the low sediment load of the streams (TSS <8 mg L<sup>-1</sup> to 17 mg L<sup>-1</sup>) as well as the spatial distribution of the sampling sites in relation to stream inflow areas it appears that mass flows from the steep slopes of the reservoir is the dominating mechanism responsible for the deposition of the fine (and medium) sand populations, rather than sediment input from the streams.

No distinct longitudinal patterns in grain size distribution are observed at the Megget Reservoir, although longitudinal sorting of particle matter from the main river inflow to the dam would be expected (Thornton, 1990b). However, establishment of classical reservoir zonation into riverine, transition and lacustrine zones, as suggested by Thornton *et al.* (1981), is not apparent from the particle size data and may be due to the relatively equitable distribution of inflows around the perimeter of the reservoir or low

sediment input into the reservoir. Even though the main inflow (Megget Water) to the reservoir is located at a considerable distance from the dam, runoff from smaller streams provides some sediment input along the sides of the reservoir (up to the dam), preventing differential sedimentation to occur. In addition, the lack of clear sedimentation pattern may also be attributed to the draw down of the reservoir in 1997/98 as such water control measures may significantly alter sedimentation pattern in the reservoir through redistribution, re-suspension and erosion of previously deposited sediment (Thornton, 1990b).

Sediment composition data from untreated samples as analysed by XRF show distinct differences in sediment chemistry between sediments at the shallow end of the reservoir and those from the deeper parts (in the middle and dam area) indicating variations in the proportions of feldspar, clay minerals, quartz and biogenic components in these sediments. Surprisingly enough, geological maps of the area provide no evidence of significant changes in underlying bedrock geology which could explain the observed compositional variations, although Chapman *et al.* (2000) suggest the presence of a mineralisation centre in the area, probably associated with the convergence zone northeast of the Megget dam (see *Figure 3. 11*). Moreover, the distribution of drift deposits (see *Figure 3. 11*) suggest differences in the glacial history of individual catchment parts, and the moraine deposits west of the reservoir may have contributed to the observed variations in sediment chemical composition. However, as most of the elements determined by XRF are partitioned between different mineral and/or biogenic phases, XRF data are insufficient to detect such variations in sample mineralogy. Thus, mineral composition data, as determined by X-Ray Diffraction (XRD) analysis, would be required for a conclusive interpretation of the sediment data collected in this study.

There appears to be no distinct trend in the distribution of Fe and Mn potentially available for (diagenetic) remobilisation, although the inverse relationship between the HOAc extractable metal fraction with LOI suggests that Fe and Mn held in more labile exchangeable and specifically sorbed fractions are preferentially associated with organic rich sediments, probably due to enhanced cycling and mobility promoted by the lower redox conditions usually present in such sediments (see Chapter 2). This preferential association with organic matter may also explain the indistinct relationship between specific surface area of the sediment and its exchangeable/specially sorbed Fe and Mn content, which is somewhat surprising as sediment sorption capacity for these elements is expected to increase with decreasing grain size. However, given the high standard errors observed for both, the sediment digestion technique (*Figure 7. 6*) and the grain size analysis (*Figure 7. 2*), this may, at least partly, be attributed to the high degree of uncertainty (scatter) inherent in the data.



*Figure 7. 10: Relationship between depths of overlying water column and (acid available) Mn concentrations*

The average (acid available) Fe to Mn ratio in the Megget sediments is around 25:1 and this is somewhat smaller than the ratios suggested for sediments of shallow waters (Davison, 1993). Since most samples were collected at deeper sites (>20 m) the higher Mn retention in the sediments would be expected. A positive relationship between depths of overlying water column and Mn concentrations in the sediments is indicated in *Figure 7. 10* and similar observations were made in other systems (references in Davison, 1993). However, the relatively high degree of scatter seen in the graph suggests that factors other than depths (e.g., organic matter content, sub-surface currents, re-suspension and focusing) may also be important in controlling pattern of Mn retention in the sediments.

The limitations of the presented sediment data with respect to their interpretability are indicated by the estimated errors derived from replicates and given in *Figure 7. 2*, *Table 7. 3* and *Figure 7. 6* for the particle size, XRF and sediment extraction data, respectively. For most analyses laboratory error and instrument error are comparatively small (0-8 %), with the exception of grain size analysis, where a maximum analysis error of 22.3 % was observed. This is likely to result from sediment digestion, which when compared to undigested samples was found to increase standard deviation of replicates (Bergen and Tsukada, 2002). However, the high sampling errors estimated from field replicates reveal that some of the results, in particular sediment chemistry data, presented here may not be representative for the sediment characteristics at the sampling site. This applies in particular to sediment chemistry data where errors > 50 % occur. Highest variability in sediment chemistry at individual sampling sites was found for redox elements (e.g., Mn, Fe) and hence is likely to be due to local

enrichment/depletion of these elements in the sediment resulting from variations in redox conditions.

Small analysis errors (laboratory and instrument errors) and the fact that sediment collection and analysis strictly followed the described procedures suggest that the degree of variability present in the field replicates is due to the heterogeneous nature of the sediment deposits at individual sampling sites, rather than due to sampling and analysis techniques. However, to overcome these limitations it is suggested that in future studies the number of samples collected at individual sampling sites is increased, in particular when a more detailed interpretation of spatially varying sediment characteristics is required.

## **7.6 Summary**

A sediment survey including 14 sampling sites across the reservoir has provided insight in the spatial variability in (bottom) sediment characteristics in the Megget Reservoir. Physical and chemical sediment parameters have been derived and their spatial distribution investigated.

The results have shown that sediment deposits in the Megget Reservoir are dominated by the medium silt fraction, while near-shore areas are also affected by inputs of coarser sediments from the steep reservoir slopes, which promote the generation of turbidity currents and debris flows. Although the grain size data did not show a longitudinal zonation in riverine, transitional and lacustrine zone, results from XRF analysis indicate differences in sediment composition between the deeper, eastern part of the reservoir and the shallower part in the west, which are probably related to varying proportions of feldspar, clay minerals, quartz and biogenic components in these sediments. However, a

conclusive interpretation of the observed patterns is not possible from the available data, and the application of other analysis techniques, such as XRD, would be beneficial.

The analysis of field replicates has indicated the difficulties associated with the collection of 'representative' samples from individual sampling sites and the results have demonstrated the high spatial heterogeneity in bottom sediment characteristics. Most severe limitations occurred in the interpretation of the results derived from chemical sediment (HOAc) extraction, and the high variability in the data is attributed to small-scale variations in redox conditions in the sediments.

# 8

## Process Studies

---

In this study, an experimental approach was chosen to evaluate the processes, which may have contributed to the high Fe and Mn levels experienced during draw down of the Megget Reservoir in 1997/98. Two main factors were identified:

- (I) Wind-induced re-suspension of the bottom sediment caused by exposure of deep-water regions to higher energy regimes.
- (II) Disturbance of a stratified bottom layer that develops during summer temperature stratification and is enriched in Fe and Mn.

This chapter details the laboratory-based investigation of these processes, including design and realisation of the experiments and the results.

### 8.1 Experimental design

#### 8.1.1 Introduction

Sediment plays an important role in the cycling of Fe and Mn in the aquatic environment. It is not only responsible for transporting significant proportions of these elements, but also mediates their uptake, storage, release and transfer at the sediment-water interface. Thus, it also affects the composition and processes of the superimposed water body. A variety of processes including sediment release (Mortimer, 1941, 1942;

Bonanni *et al.* 1992; Gomez *et al.* 1998; Linnik and Zubenko, 2000; Warnken *et al.* 2001) and sediment re-suspension (Hulscher *et al.* 1992; Brassard *et al.* 1994; Evans, 1994; Pierson and Weyhenmeyer, 1994; Gálvez and Niell, 1992) have been identified as potential control mechanisms influencing water quality of the overlying water body. Still, the different mechanisms involved in the Fe and Mn cycle, and responsible for the remobilisation and release of Fe and Mn into the water column, are often too complex to separate in natural systems. Thus, an experimental approach in the laboratory can help to better understand the controls and behaviour of Fe and Mn under changing environmental conditions. The basic problem, however, remains the extrapolation of the experimental results to the *in-situ* conditions in the actual water body; thus, laboratory studies can only provide a first indication of the potential processes that are occurring. Nevertheless, compared to field measurements laboratory studies have the advantage that the phenomena can be investigated under controlled conditions, which can help to separate different mechanisms and controls. As a first approach they can help to identify important internal processes related to re-suspension and sediment release and their effects on the water quality of the reservoir. In conjunction with field measurements, this can contribute to a more integrated interpretation of their qualitative and quantitative significance.

A set of laboratory experiments was designed such that the conditions simulate reservoir stratification and significant water level draw down. Undisturbed sediment cores, collected at the Megget Reservoir on 4 October 2001 were installed in the laboratory and subjected to various treatments simulating different internal and external forcing conditions (e.g., oxygen depletion and wind induced shear stress).

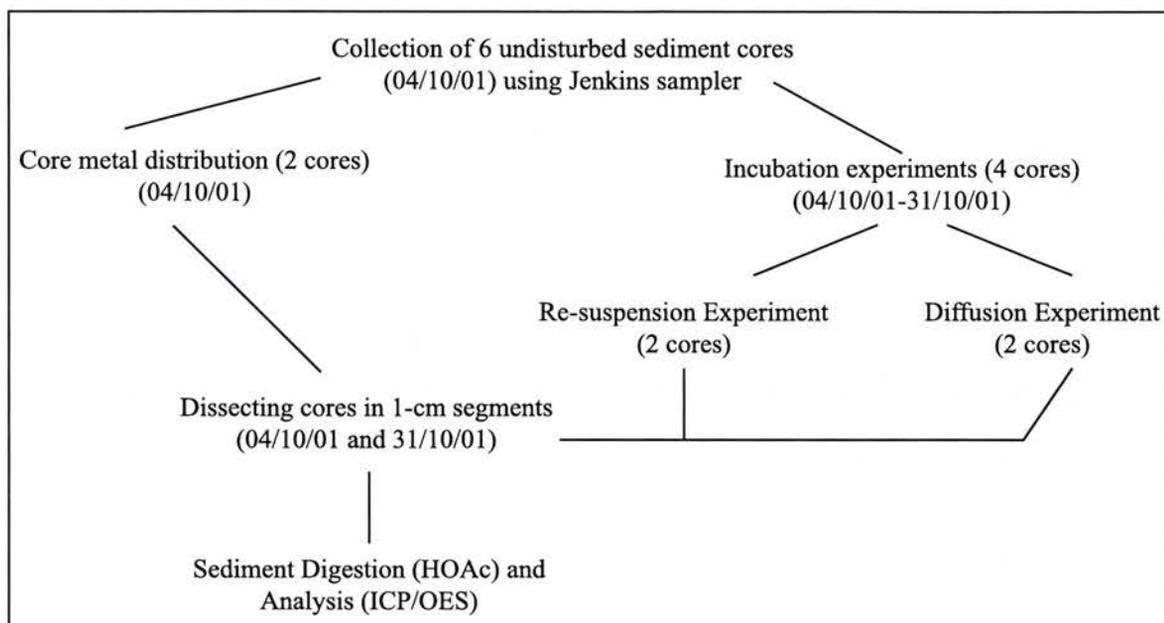


Figure 8.1 : Experimental Design

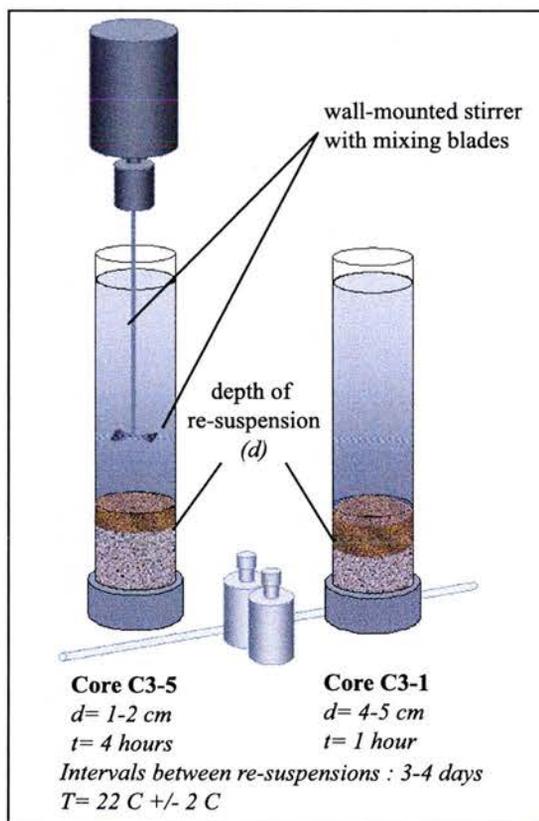


Figure 8.2 :  
Experimental set-up: Re-suspension

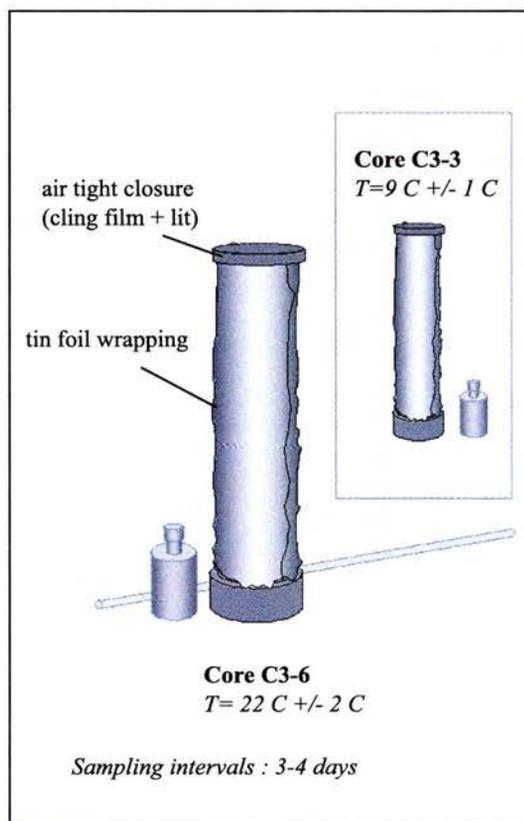


Figure 8.3 :  
Experimental set-up: Diffusion

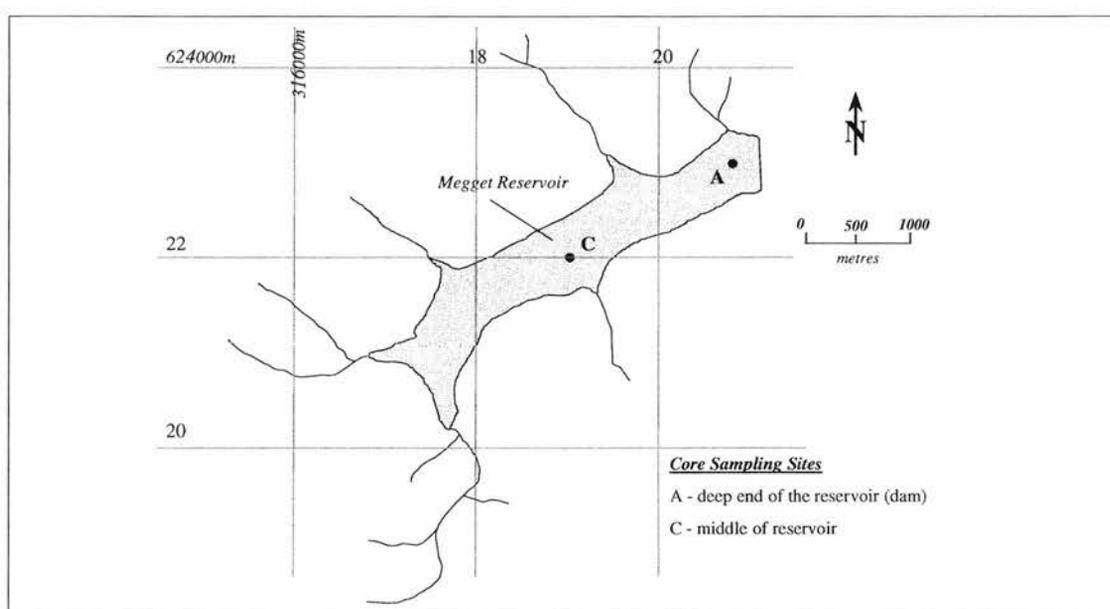
The design of the experiment is summarised in *Figure 8. 1* and details of set up and sampling frequencies are given in *Figure 8. 2* and *Figure 8. 3*.

### 8.1.2 Core collection

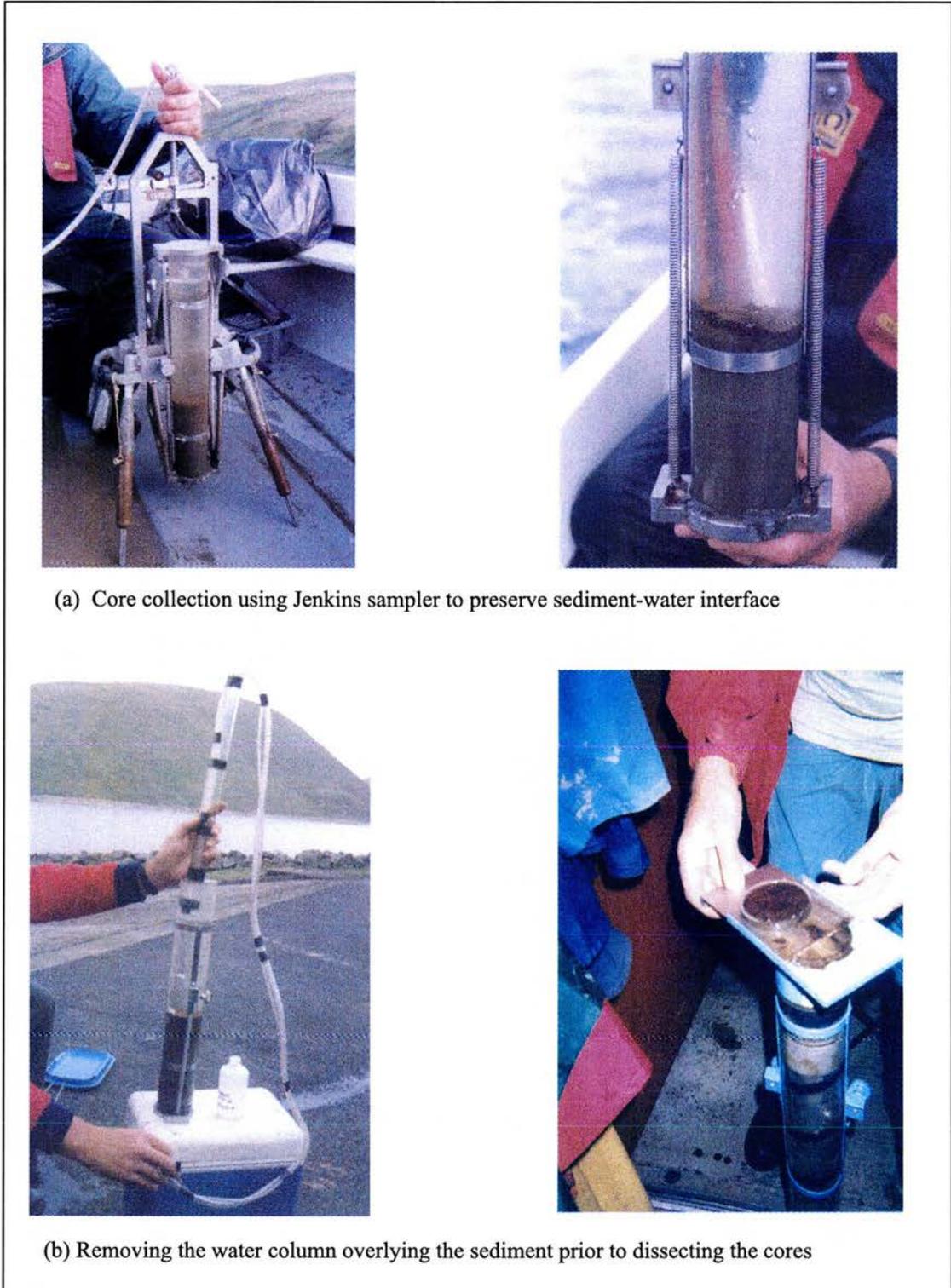
The sampling sites for sediment core collection were chosen on the basis of a bathymetric survey conducted at the reservoir in 1999, the results from the initial sediment grab sampling survey, and on-site Echo-sounder readings, and sites that were flat and as deep as possible were chosen. Previous coring attempts have shown that the best sites for core collection using the Jenkins samplers (*Figure 8. 5a*) are deep and flat areas in the middle of the reservoir. Recovery of sediment cores was more difficult at sites near the shore because of the steep slopes, which prevented the corer from settling into the sediment properly. Problems with core collection and sediment grab sampling were also encountered at the shallow end of the reservoir (site E), where former valley floor vegetation is still dominating the bottom of the reservoir. Strong heather roots and other plant material made grab sample collection at these sites very difficult and the recovery of sediment cores using the Jenkins corer was impossible. As a consequence core collection was limited to sites A and C (*Figure 8. 4*), and a total number of six sediment cores were collected.

The undisturbed sediment cores were collected using a Jenkins core sampler (see *Figure 8. 5a*) in order to preserve the sediment water interface. The Jenkins corer is designed to capture the upper 20-30 cm or so of the sediment and a corresponding column of overlying water without disturbing the core or the sediment interface (Mortimer, 1971) (*Figure 8. 5a*). Measurements of temperature and conductivity were made prior to core collection and water samples were collected according to the reservoir sampling

protocols (Appendix I). All samples were stored in a cool box until arrival at the laboratory. A volume of 10 litres of reservoir water was collected for the experiments. The cores were inspected carefully on the shore after collection and arranged according to their future use. Cores collected for chemical sediment analysis were prepared for dissection. Water overlying the sediment was removed from the core tube by a siphon (*Figure 8. 5b*) and the final 5 cm of the water column above the sediment were collected into clean sample-rinsed polyethylene bottles for metal analysis. Cores collected for laboratory experiments remained sealed and were transported to St Andrews and stored in the cold room at 9°C until required for the experimental set-up. All sediment cores collected for the experiments are shown in *Table 8. 1* together with descriptions of the individual cores.



*Figure 8. 4: Location of core collection sites at the Megget Reservoir*



*Figure 8.5: Collection and preparation of sediment cores for laboratory experiments and for the analysis of metal distribution in the sediments (04/10/01).*

Table 8. 1: Description of collected cores



Collection Date	: 04/10/01	Sampling site:	: MC3
Location	: Megget	GPS coordinates	: 55°29'12.5" / 03°16'43.9"
		Water depth	: 38 m

Core No	C3-5	C3-1	C3-3	C3-6																												
Core length	11.5 cm	13.5 cm	20.0 cm	18.0 cm																												
Use	Re-suspension (1-2cm)	Re-suspension (4-5 cm)	Diffusion (9°C)	Diffusion (22°C)																												
<b>Core characteristics</b>																																
Depth	(* loose accumulation of small particles of decomposing organic matter)																															
0-2					Dark brown layer of unconsolidated 'fluff', high water content																											
2-4									Grey mud with seams of brown organic material																							
4-6													Grey mud, fine grained, compact																			
6-8																	Layer of brown unconsolidated 'fluff' * gradually mixing with grey mud															
8-10																					Grey mud, fine grained, compact											
10-12																									Layer of brown unconsolidated 'fluff' * gradually mixing with grey mud							
12-14																													Grey mud, fine grained, compact			
14-16																																
16-18	Grey mud, fine grained, compact, Slightly darker towards the bottom of the core																															
18-20					Layer of brown unconsolidated 'fluff' * gradually mixing with grey mud																											
cm below sediment-water interface																																

## 8.2 Sediment re-suspension

Sediment re-suspension and particulate matter exchange along the sediment-water interface has been thoroughly studied and a broad variety of direct and indirect approaches are now available for investigating the phenomenon; a comprehensive review is given in Blösch (1994, 1995). Direct measurements of re-suspension can be made using beam transmission meters (Pierson and Weyhenmeyer, 1994; Gloor *et al.* 1994, Effler *et al.* 1998a), isotopes (Cornett *et al.* 1994), radionuclide techniques (see references in Blösch, 1995), sediment trap measurements (James and Barko, 1993; Gálvez and Niell, 1992; Effler *et al.* 1998a, Hicks *et al.* 1994) or sediment cores (James and Barko, 1993). Indirect methods include modelling approaches, such as mass balance (input-export) calculations for total suspended solids (TSS) (Effler *et al.* 1998a; Hulscher *et al.* 1992) based on regular water sample collection. Relatively little work has been done in the laboratory. Experimental approaches mostly utilise flumes and chambers into which shear stress can be induced through water oscillations (Brassard *et al.* 1994; McAuliffe *et al.* 1998; references in Blösch 1995). The results provide insight into physical processes related to re-suspension and also allow an evaluation of the effects on nutrient release (McAuliffe *et al.* 1998) and metal exchange (Brassard *et al.* 1994).

In this study, laboratory experiments were designed to investigate the effects of sediment re-suspension, and related metal release from sediments, on the water quality in the Megget Reservoir. The experiments were not only carried out 'reproducing' the conditions arising during significant water level draw down of the reservoir, but also to investigate the rates of Fe and Mn release into the water column under various temperature and disturbance conditions. Undisturbed sediment cores were subjected to

different re-suspension conditions with the aim to simulate storm events of different intensities and duration.

### 8.2.1 Methods and materials

The two cores collected for the re-suspension experiment were fitted with a wall-mounted motor to which a 20 cm stainless steel stirrer was attached (*Figure 8. 2*). The stirrer was adjusted to sit 12-14 cm above the sediment surface. Depth of re-suspension was controlled by adjusting the speed of the stirrer and uniformity was achieved by constant revolution. The cores were left uncovered and exposed to light as these conditions were thought to resemble the conditions in the shallow areas of the reservoir which are exposed to wind-induced turbulence and prone to re-suspension.

Prior to re-suspension, in situ measurements of temperature and redox potential were recorded for each core and column-integrated water samples were withdrawn for determination of pH and metal content. Water samples were collected by slowly lowering a glass tube into the core tubes to just above the sediment surface such that the sediment water interface was not disturbed. The glass tube was then capped and an integral sample of the water column was withdrawn. The sample was emptied into a clean vial. This was repeated until the required volume of water, usually about 70 mL, had been collected. Separate samples for the analysis of total and dissolved metal concentrations, as well as pH measurements, were collected and the amount of water removed from the core was recorded along with the measurements taken. The pH of the core water was then measured on the collected sub-sample using a red-rod pH probe system. Samples collected for the analysis of dissolved metals were filtered through a 0.45- $\mu\text{m}$  pore size filter (Whatman) and all samples were acidified to 1 %-vv with concentrated AristaR grade nitric acid. The water in the core tube was replenished with

reservoir water collected on the day of core collection and stored in the cold store at a constant temperature of  $9^{\circ}\text{C} \pm 1^{\circ}\text{C}$ . Re-suspension of the cores was then started. In core C3-5, the top 1-2 cm was suspended for 4 hours whereas core C3-1 was re-suspended for 1 hour to a depth of 3-5 cm. Re-suspension of the cores was repeated at 3-4 day intervals over a period of 21 days (26 including collection and dissection). The relevant details of the experiments are summarised in *Figure 8. 2*.

After termination of the experiments, the experimental cores were prepared for dissection (see Section 8.1.2). The water column overlying the sediment was collected as two separate samples; (1) water column >5cm above the sediment, and (2) water column between 0-5cm above the sediment. All water samples were stored in the dark at  $4^{\circ}\text{C}$  until transferred to the laboratory at CEH Wallingford for analysis (Chapter 4).

### 8.2.2 Results

The effect of re-suspension on the properties of the water column above the incubated cores C3-1 and C3-5 is illustrated in *Figure 8. 6* and *Figure 8. 7*. A dramatic increase in Fe and Mn in the water column is seen associated with the initial re-suspension of the sediment. Subsequently, the metal concentrations remain fairly constant, with the exception of core C3-1, where a Fe peak develops after 12 days of incubation. The peak is also reflected in the Mn concentrations, but is much less distinct. The amount of total Fe present in the water column is generally higher than that of Mn, with maximum Fe concentrations of  $79.5 \text{ mg L}^{-1}$  in C3-1 and  $29.4 \text{ mg L}^{-1}$  in C3-5, compared to  $16.3 \text{ mg L}^{-1}$  and  $12.6 \text{ mg L}^{-1}$  Mn. Fe is mostly present in particulate form while soluble-colloidal forms account for 4 % to 7 % (C3-5) and 3 % to 4 % (C3-1) of the total concentrations. In comparison, the proportion of the filterable species is much higher for Mn lying between 67% and 76% of the total concentration in C3-5 and between 39 % and 51 % in

C3-1. It is interesting to note that the proportions of soluble-colloidal species of both Fe and Mn are lower in core C3-1, where a higher amount of sediment is suspended in the water column. Comparison between the two cores indicates that total metal concentrations in the water column increase in proportion to the amount of sediment introduced into the water. However, while Fe concentrations in core C3-1 almost triple in relation to C3-5, the increase in Mn is less than 30 %, suggesting that most Mn is accumulated in the uppermost centimetres of the sediment column.

*Figure 8. 6* and *Figure 8. 7* present the results for water column samples collected at the end of the experiments prior to core segmentation above the sediment (bottom 0-5cm (■) and (□)) and in the overlying water column (>5cm (◆) and (◇)). The data indicate a fairly homogeneous distribution of Fe and Mn in the water column of the cores, except for C3-1 which shows increased Fe levels near the sediment reflecting the incomplete sediment settling in the lower part of the water column at the time of water collection.

Redox values measured prior to core re-suspension are displayed in *Figure 8. 9*. Redox is generally higher in core C3-5, where only the top 1-2 cm of the sediment was re-suspended and conditions in the water column remain well oxygenated (>200 mV), as would be expected given the free oxygen exchange at the air-water interface. The low value observed on day 9 of incubation cannot be easily explained, but is likely to result from a variation in measurement depth; as the sediment had not completely settled out, lower redox conditions at depth can be expected due to the high amounts of suspended particles still present in the water column. A dramatic drop in redox potential is observed in core C3-1, where anoxic conditions develop following the initial re-suspension of the core. Lowest redox values of -143 mV are observed after 9-12 days of incubation and indicate that oxygen demand in the water column exceeds oxygen

input to the water column supplied by diffusion at the air-water interface. These low redox values are probably related to an increased amount of reducing substances, such as organic matter, in the water column. After 12 days of incubation the redox potential in core C3-5 begins to rise again, as most reducing substances, repeatedly re-suspended in the water column, are gradually oxidised.

The pH measured before each re-suspension interval is given in *Figure 8. 8* and shows slightly acidic conditions in the water column of both cores. Values are somewhat lower in core C3-1 and decline from pH 6.66 to pH 6.39 during the experiments. At the end of the experiments, lower pH values are observed in the upper part of the water column (>5cm: pH 6.29/6.57) compared to those near the sediment (0-5cm: pH 6.53/6.68), which suggests that pH is controlled by processes in the water column, such as decomposition of organic matter rather than by release from the sediments. The constant pH decrease in core C3-1 is likely to be related to higher rates of microbial (decompositional) respiration encouraged by high concentrations of organic matter in the water column, while variations in core C3-5 seem to be partially controlled by temperature variations in the water column.

Associated with sediment re-suspension was a significant increase in watercolour, which changed from colourless to orange-brown (*Figure 8. 10*) during initial re-suspension of the cores. This discolouration of the water persisted throughout the duration of the experiments and was also present during periods where sediment had (more or less completely) settled out, suggesting that colour is due to small organic matter particles suspended in the water column. Filtration of the samples using 0.45  $\mu\text{m}$  Whatman filter disks removed colouration of the water together with most (more than 90%) of the Fe and 30% to 60% of the Mn present in the sample.

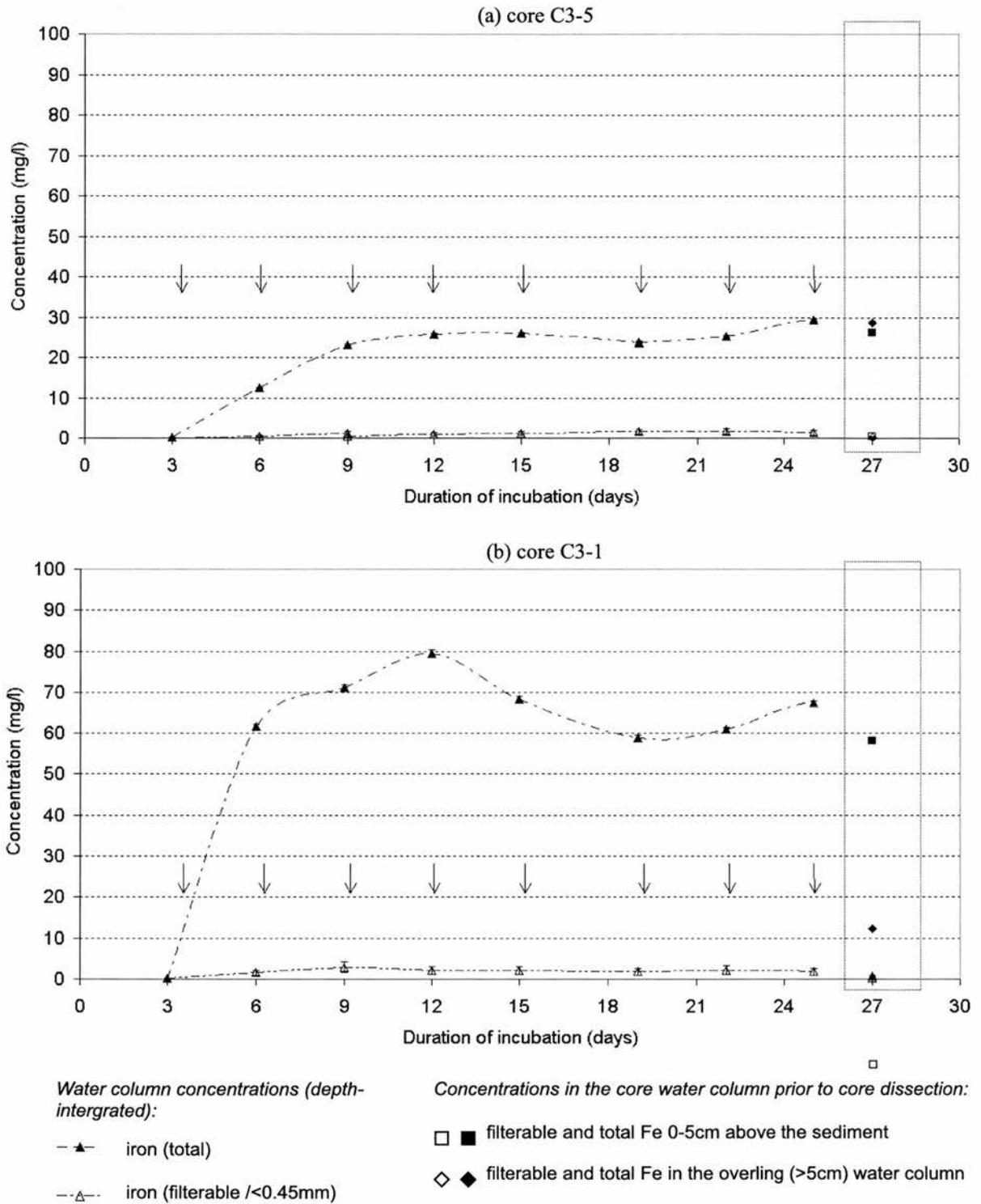


Figure 8.6: Iron concentrations in water column overlying re-suspended cores (a) C3-5, re-suspended to 1-2cm depth for 4 hours and (b) C3-1, re-suspended to 4-5cm depth for 1 hour. Arrows mark intervals of core re-suspension.

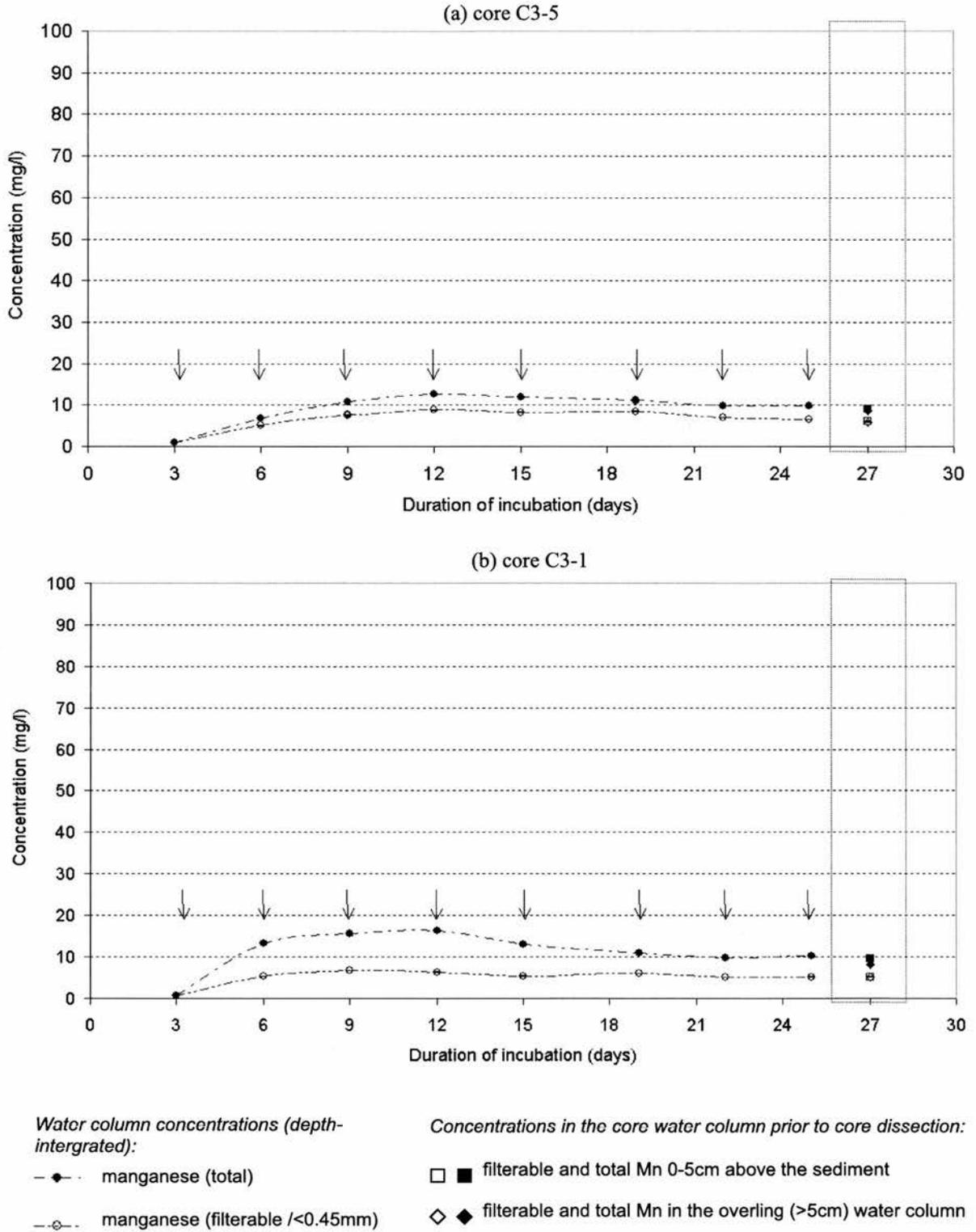


Figure 8.7: Manganese concentrations in water column overlying re-suspended cores (a) C3-5, re-suspended to 1-2cm depth for 4 hours and (b) C3-1, re-suspended to 4-5cm depth for 1hour. Arrows mark intervals of core re-suspension.

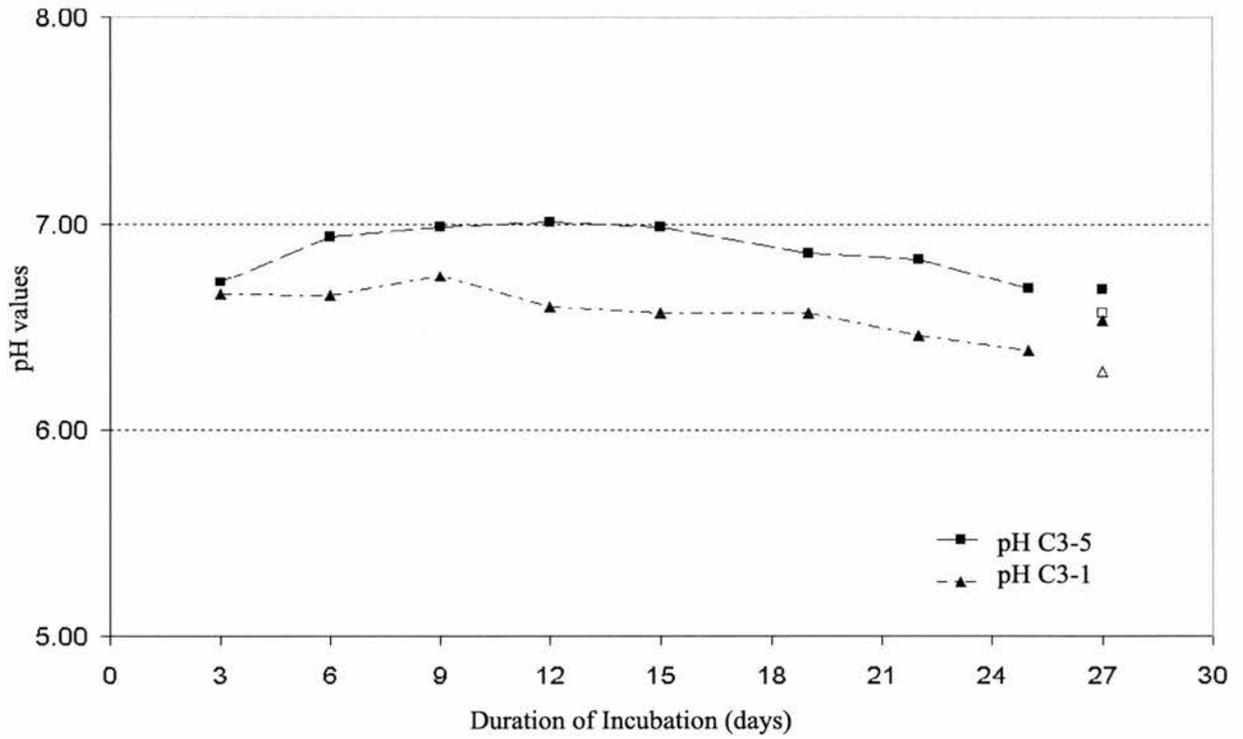


Figure 8.8: Temporal variations in pH values in the incubated cores during re-suspension experiments.

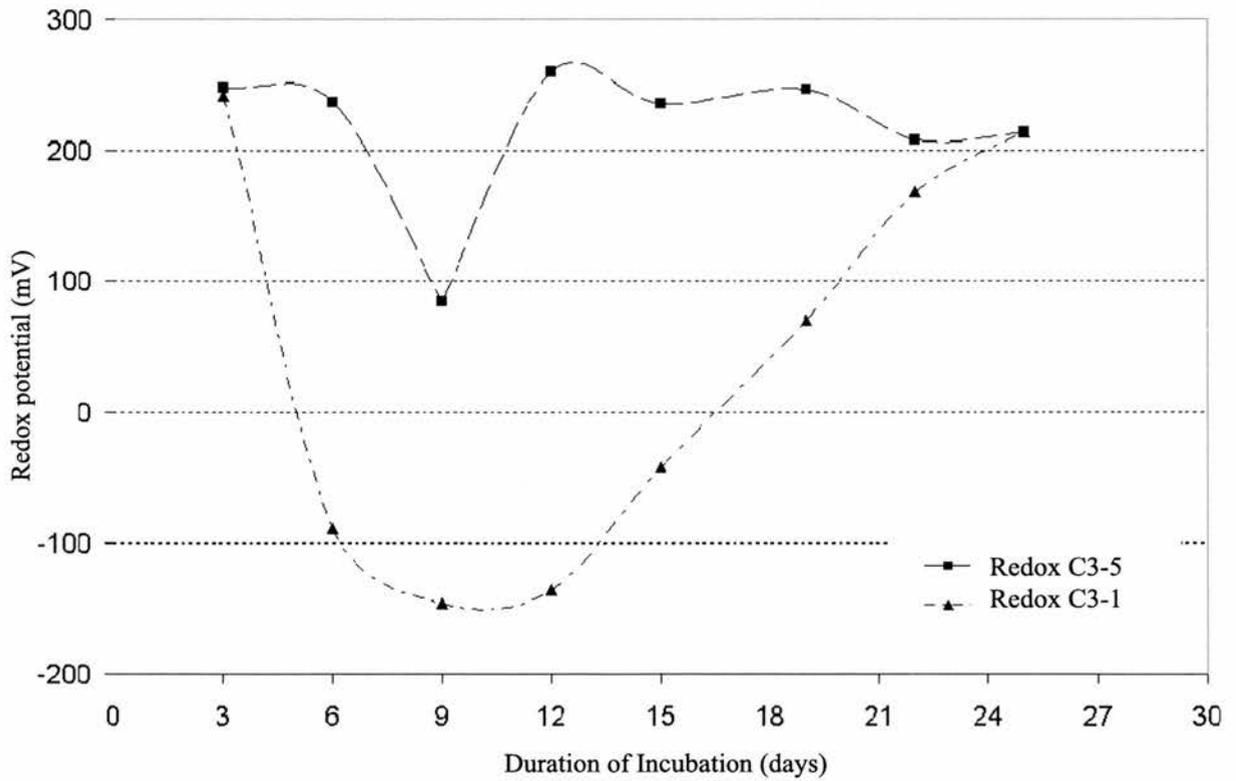


Figure 8.9: Temporal variations in redox potential in the incubated cores during re-suspension experiments.

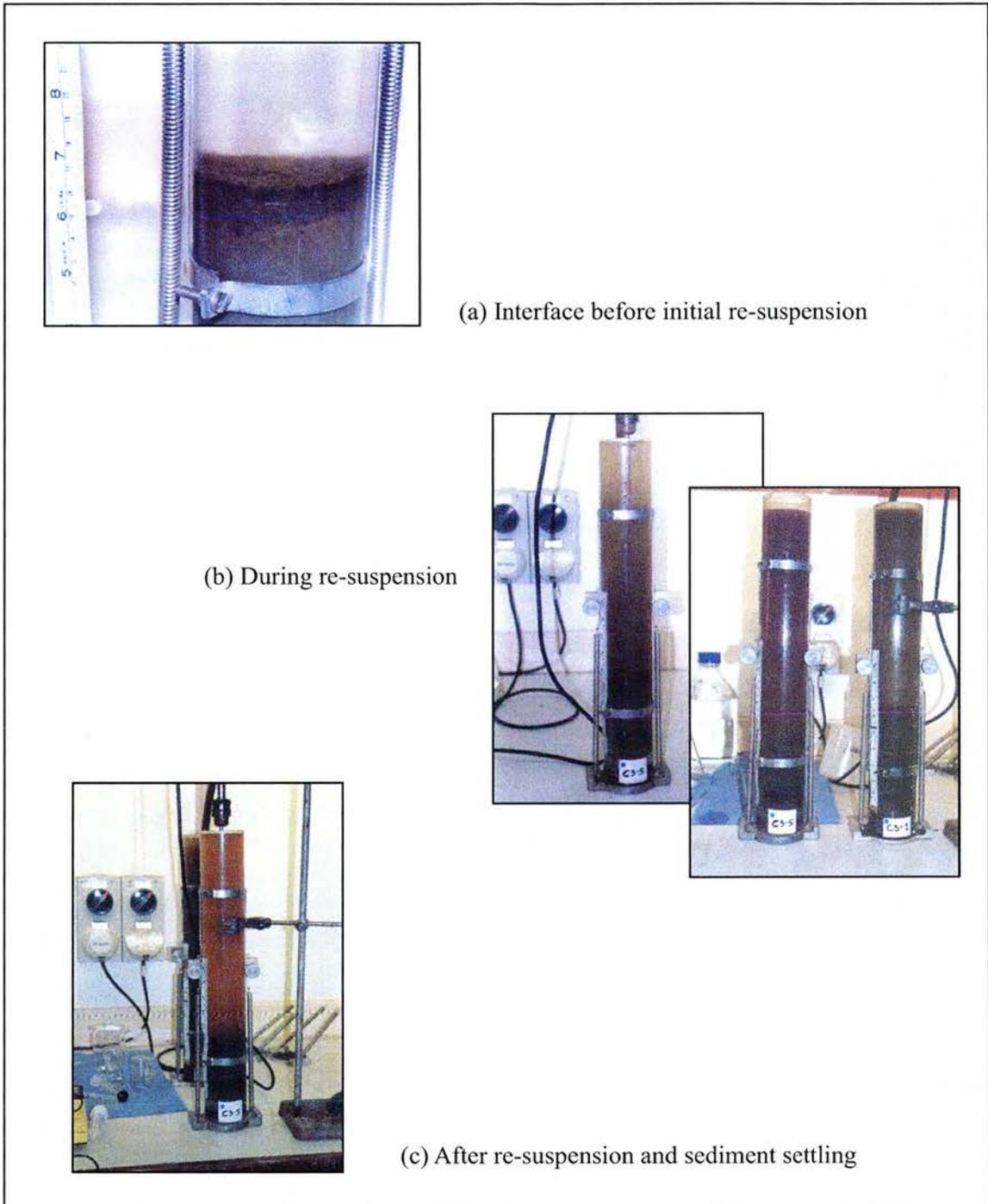


Figure 8.10: Documentation of the re-suspension experiments

### 8.3 Sediment release

Processes of Fe and Mn release are not straightforward (Davison, 1993) and may be influenced by various system parameters such as bathymetry, climatic conditions, biological productivity and sediment type (Sholkovitz, 1985). A variety of field studies have been conducted to obtain information on the dynamics of Fe, Mn and other elements in the aquatic system and diffusive fluxes between water and sediments using traditional water sampling techniques (e.g., Zaw and Chiswell, 1999; Mortimer, 1941, 1942), sediment traps (e.g., Davison *et al.*, 1982) and/or benthic chambers installed in the sediments (e.g., Bonanni *et al.* 1992; Kelly, 1992). Laboratory studies and experiments were carried out to better understand processes related to oxidation and reduction of Fe and Mn in natural waters and sediments (e.g., Tipping, 1984; Tipping *et al.* 1984; Nealson *et al.* 1989; Stumm and Sulzberger, 1992), as well as to evaluate processes involved in diffusive fluxes of nutrients (Schröder *et al.* 1992; Erickson and Auer, 1998; Gomez *et al.* 1999; McAuliffe *et al.* 1998; Mortimer, 1971) and metals (Mortimer, 1971; Hsiung and Tissue, 1994; Warnken *et al.* 2001) across the sediment-water interface and their correlation to changing conditions in the water column.

In this study, incubation experiments were carried out to simulate *in situ* conditions and to investigate the effect of oxygen depletion in the water column on Fe and Mn mobilisation and their release from the sediment. It is hypothesised that a combination of both reduced-upwards dispersion due to limited circulation, as well as redox-related Fe and Mn release due to oxygen depletion in the bottom waters, may be responsible for increased Fe and Mn concentrations below the thermocline. The experiments utilised undisturbed sediment cores, collected at the Megget Reservoir (Section 8.1.2), and experimental conditions were chosen to resemble the conditions that are expected during summer stratification in the hypolimnion of the reservoir.

### 8.3.1 Methods and materials

For the study of sediment release, two sediment cores were wrapped in tin foil to minimise photosynthesis in the water column and sealed off with a plastic film to avoid oxygen exchange at the water-air interface. Core C3-3 was maintained at  $9^{\circ}\text{C} \pm 1^{\circ}\text{C}$  in a temperature controlled room. The temperature setting was chosen to simulate conditions similar to those present at the bottom of the reservoir during thermal stratification in summer (*Figure 4. 4*) when the oxygen supply to the bottom layers is interrupted. It was expected that continuous microbial activity, benthic respiration, decomposition of organic material at the sediment water interface and limited oxygen circulation would cause depletion of oxygen in the water column and changes in redox potential to occur. As a consequence increasing amounts of Mn and Fe should be released and enter the water column via the sediment-water interface. However, to accelerate processes of oxygen consumption in the core water column and thereby accelerate oxygen depletion and sediment release, the second core C3-6 was kept in the main laboratory at a temperature of  $22^{\circ}\text{C} \pm 2^{\circ}\text{C}$  (see *Figure 8. 3*). At regular intervals (3-4 days) *in-situ* measurements were made of temperature and redox potential, and water samples were taken for the analysis of total and dissolved metals and pH. Sample collection followed the same procedure outlined in the re-suspension experiment in *Section 8.2.1*. The employed sampling method had the advantage that the sediment water interface was not disturbed by currents induced by pumping or siphoning of water, and that an integrated sample of the entire water column was obtained, as opposed to a single point sample. After sample collection the water column was replenished with reservoir water and the core tube was sealed off with plastic film and covered with aluminium foil. The pH of the samples was measured and preservation, storage and analysis of the samples followed the procedure described in *Section 8.2.1*. Experimental set-up and details are

given in *Figure 8. 3*. After completion of the experiments, the experimental cores were dissected and water column samples were collected as previously described in *Section 8.2.1*.

### 8.3.2 Results

*Figure 8. 11* and *Figure 8. 12* show that Fe concentrations in the incubated cores increase constantly during the course of the experiment. The rate of increase is higher in core C3-6, maintained at  $22^{\circ}\text{C} \pm 2^{\circ}\text{C}$  where concentrations increase from 0.8 to 4.1 mg L<sup>-1</sup> compared to 0.5 to 2.0 mg L<sup>-1</sup> in core C3-3 stored at  $9^{\circ}\text{C} \pm 1^{\circ}\text{C}$ , indicating the increased rate of microbial decomposition (and oxygen consumption) at higher temperatures and demonstrating the important role of micro-organisms in the mobilisation of Fe and Mn from sediments (Nealson *et al.* 1989; Tipping, 1984; Davison, 1993). The majority of Fe is present in particulate form, but colloidal-soluble species make up 14% to 36% of the total concentration in core C3-6 and 13% to 43% in core C3-3. Different behaviour is observed for Mn, which in contrast to Fe, is present almost exclusively (94-100%) in its filterable (colloidal-soluble) form, illustrating the differences in the redox chemistry of Fe and Mn and the appreciably slower rate of Mn(II) oxidation compared to Fe(II) oxidation (Davison, 1993). Mn concentrations in the water column of the two cores are very similar ranging from 2.2 mg L<sup>-1</sup> to 3.9 mg L<sup>-1</sup> in core C3-3 and 1.3 mg L<sup>-1</sup> to 2.7 mg L<sup>-1</sup> in core C3-6 and show a constant increase during the first stage of the experiment. However, this trend comes to a halt after 12-18 days of incubation, after which the Mn concentrations in the water column remain constant (C3-3) or decline (C3-6), indicating depletion of the Mn reservoir in the

sediment (Davison, 1993) and/or the presence of an effective removal mechanism, such as microbially mediated oxidation (Tipping *et al.* 1984; Nealson *et al.* 1989).

Water samples collected prior to core segmentation at 0-5 cm above the sediment and at >5cm are also shown in *Figure 8. 11* and *Figure 8. 12*, displayed as ((■), (□)) and ((◆), (◇)), respectively. It can be seen that Fe concentrations near the sediment-water interface are significantly higher than those detected in the overlying water column, indicating Fe accumulation near the sediment-water interface. For Mn, however, no concentration gradient is observed, suggesting equal distribution throughout the water column.

Variations in redox potential of the core water measured during the incubation period are shown in *Figure 8. 14*. Values range between 178 mV and 357 mV in core C3-3 and (-8.7 mV) 101 mV and 239 mV in core C3-6, indicating a dominance of oxic to sub-oxic conditions in the water column. Similar conditions were observed in the reservoir water samples collected from the hypolimnion at the day of core collection, where redox values around 200 mV indicate relative depletion of oxygen in the hypolimnion compared to well-oxygenated surface waters, which at 25°C and neutral pH display redox potentials between 400 mV and 500 mV (Hutchinson, 1957; Horne and Goldman, 1994). It would be expected that redox potentials in the core water column decline during the course of the experiment as oxygen is depleted by microbial respiration and decomposition processes at the sediment-water interface. However, the opposite trend is observed and the increase in redox potential in the water column can only be explained by oxygen exchange across the air-water interface of the incubated cores. This may be due to inadequate sealing of the core water surface, but more likely occurred during

short intervals of sample collection, when foil covering and the plastic seal were temporarily removed from the core water surface. The initial depression in redox in C3-6 may be attributed to high initial oxygen consumption caused by microbial activity accelerated by the sudden increase in water temperature (from 16°C in the reservoir to 22°C in the laboratory). Increase in redox potential in the experimental water column may also be caused by CO<sub>2</sub> consumption within the water column as a result of photosynthetic activity. However, this is thought to be unlikely, as cores were wrapped in tin foil and photosynthetic activity in core C3-3 is further repressed by the low temperatures.

*Figure 8. 15* shows that pH and redox ranges encountered in the core water columns during the experiments lie at the solid solution boundary between Fe<sup>2+</sup> and ferrihydrite. Provided that ferrihydrite is the ferric oxide phase in most aquatic systems, as is suggested by Davison (1993), lower potential during the early stages of the experiment indicate favourable conditions for Fe<sup>2+</sup> stability, and could explain the initially higher proportions of soluble-colloidal Fe in the water column (29-34%). During the incubation period, however, as redox potentials in the water column increase, ferrihydrite becomes more stable, causing the soluble-colloidal Fe levels to decline to 12-14%. Still, the diagram strictly shows equilibrium relationships and is based on the assumption that the redox measurements respond to a single redox pair, and since departure from these conditions is common in natural waters these diagrams only give an indication of processes that should take place.

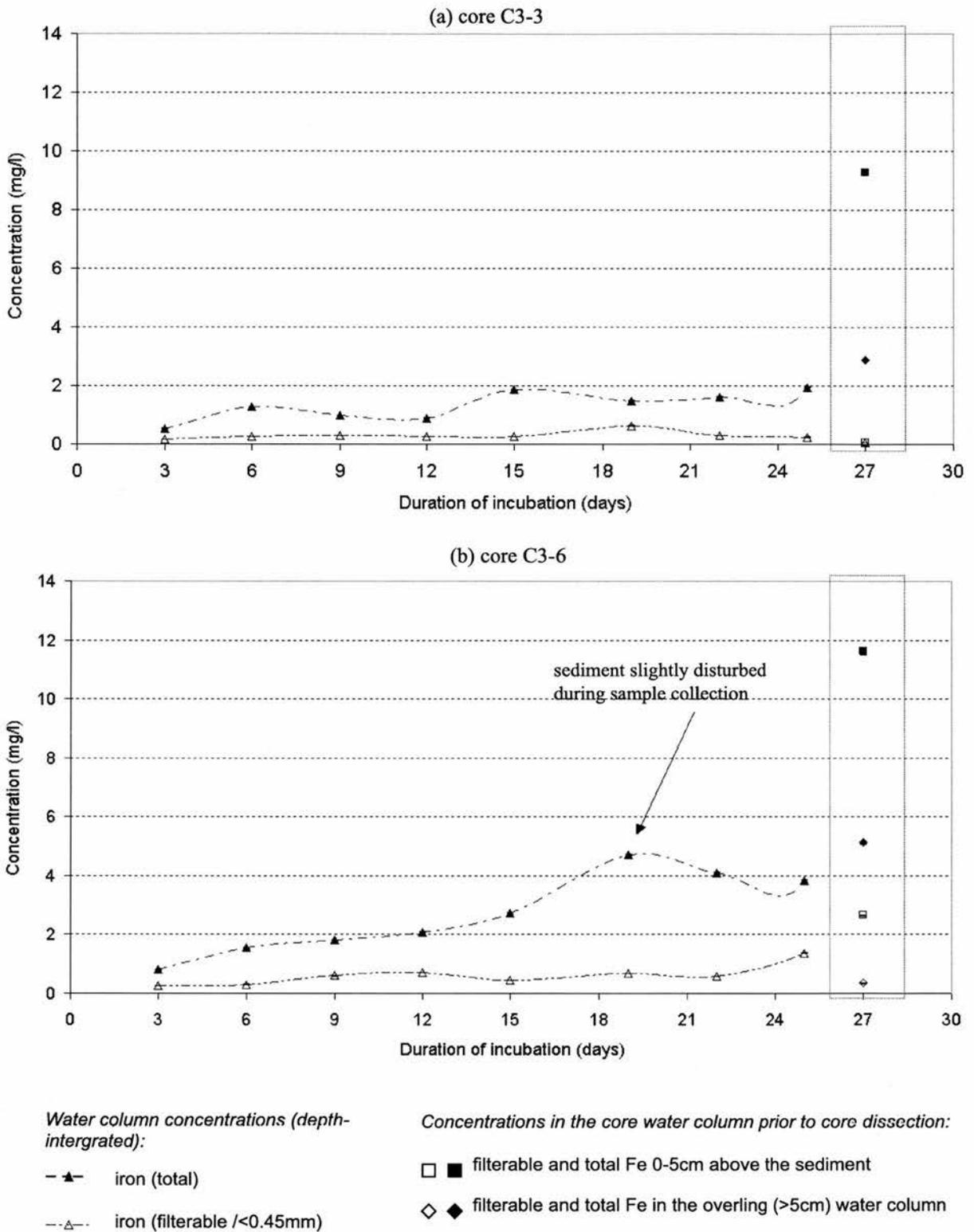


Figure 8.11: Iron concentrations in water column overlying incubated cores (a) C3-3, incubated at 9°C (± 1°C) and (b) C3-6, incubated at 22°C (± 2°C).

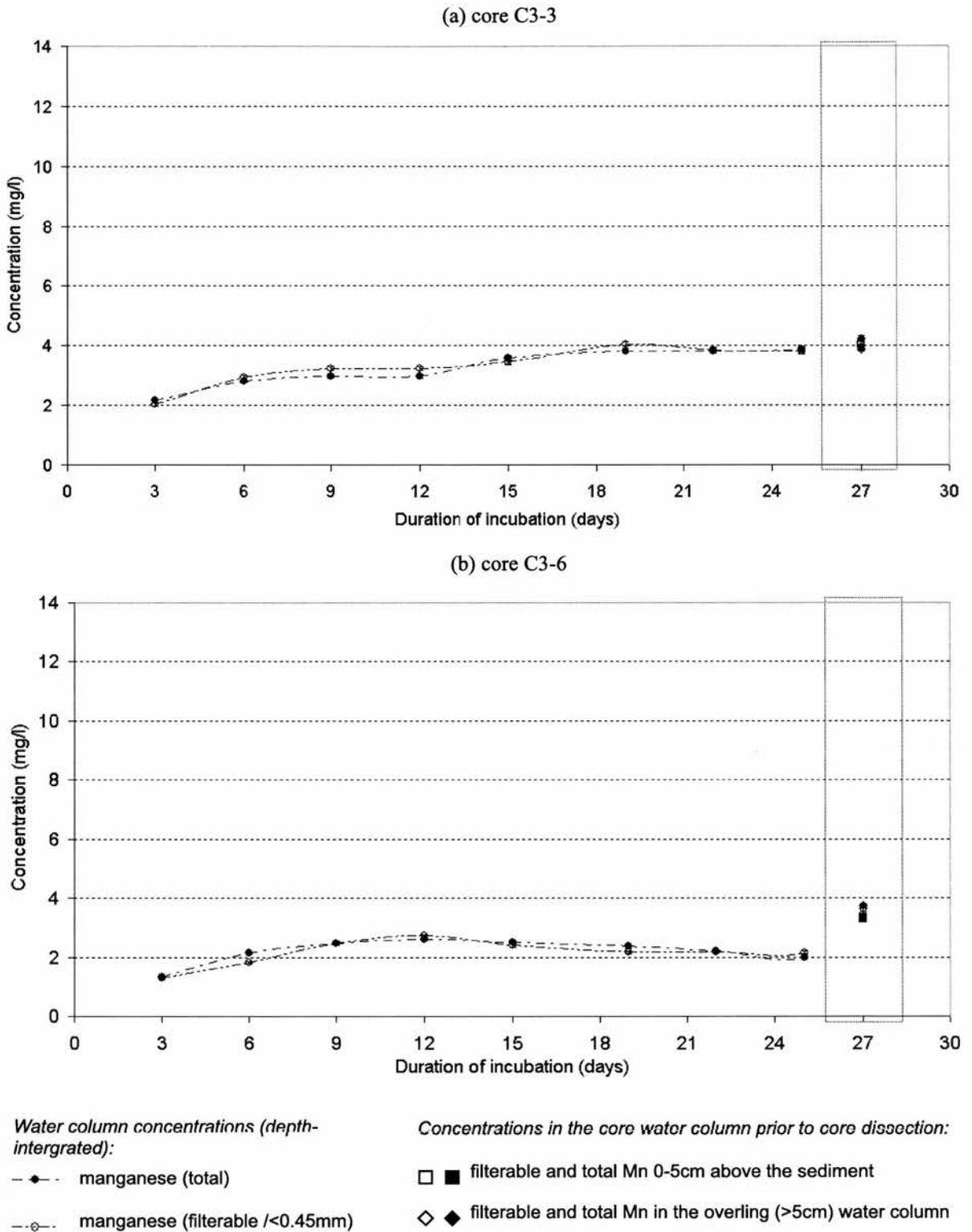


Figure 8.12: Manganese concentrations in water column overlying incubated cores (a) C3-3, incubated at  $9^{\circ}\text{C}$  ( $\pm 1^{\circ}\text{C}$ ) and (b) C3-6 incubated at  $22^{\circ}\text{C}$  ( $\pm 2^{\circ}\text{C}$ ).

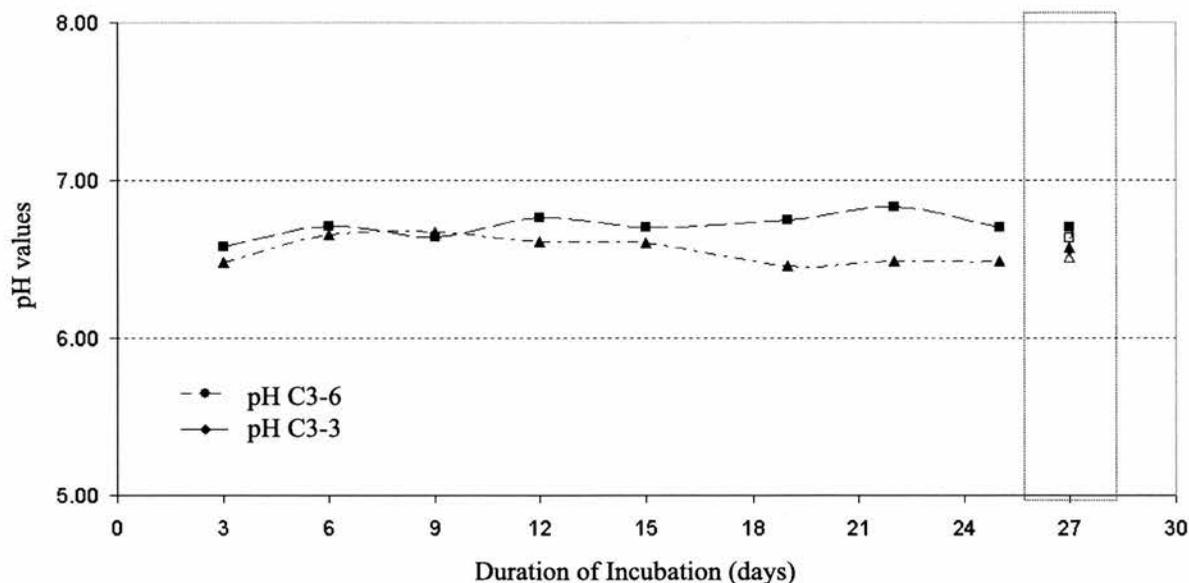


Figure 8.13: Temporal variations in pH values in the incubated cores during sediment release (diffusion) experiments.

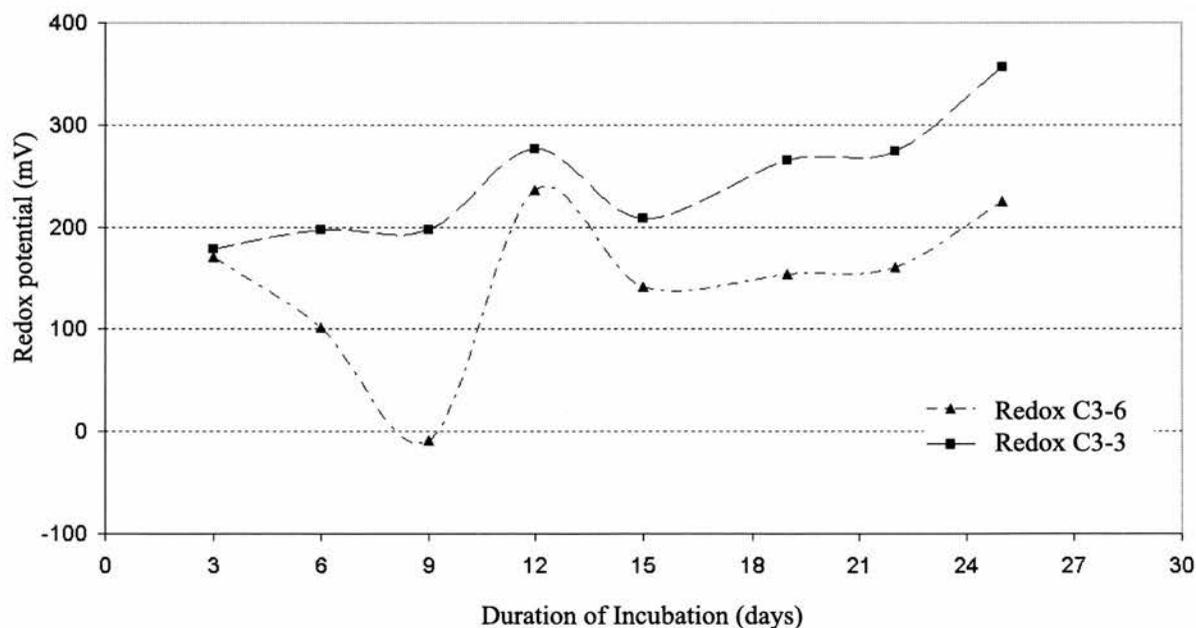


Figure 8.14: Temporal variations in redox potential in the incubated cores during sediment release (diffusion) experiments.

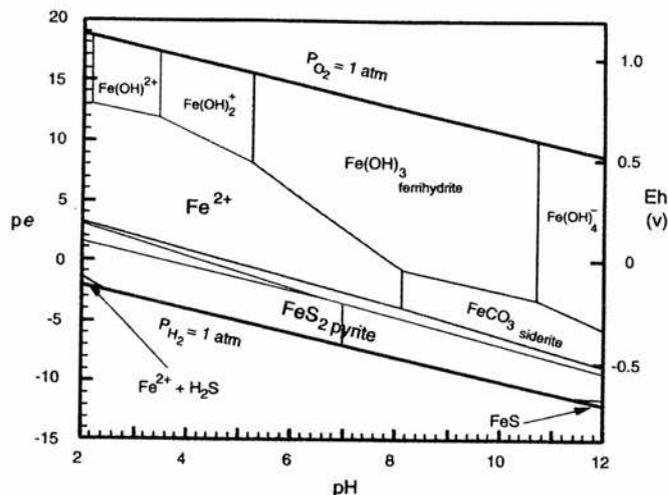


Figure 8. 15: Stability relation in the system  $Fe-O-H_2O-S-CO_2$  at  $25^\circ C$ , assuming ferrihydrite as the ferric oxide phase,  $\Sigma S=10^{-2}m$  and  $P_{CO_2}=10^{-3}atm$ . Solid-solution boundaries are drawn for an activity of dissolved Fe species of  $10^{-6}$  (after Drever, 1997).

Scatter plots displaying the interrelationship between different metals detected in the water column are shown in Figure 8. 16. The plots demonstrate the close relationship between Fe and Mn and different alkali (Na, K), alkaline-earth (Mg, Ca, Ba) and trace elements (B, Sr). Strong correlations are seen for Mn-Ba and Fe-B-Sr-Ca and a variety of processes may be responsible for the observed correlations including dissolution of oxides and carbonates, mineralisation of organic matter, desorption processes and others (Sholkovitz, 1985). Based on the available data it is not possible to define the underlying processes, but oxide dissolution and release of associated trace elements is believed to be the dominant control on metal release in these experimental sediment-water systems.

Variations in pH of the water column in both cores are relatively small ( $<0.25$  pH units) as seen in Figure 8. 13. A gradual decline in pH is observed in C3-6 indicating input of  $CO_2$  from respiration and decomposition processes (Davison, 1993) related to the oxidative degradation of organic material (Hsiung and Tissue, 1994).



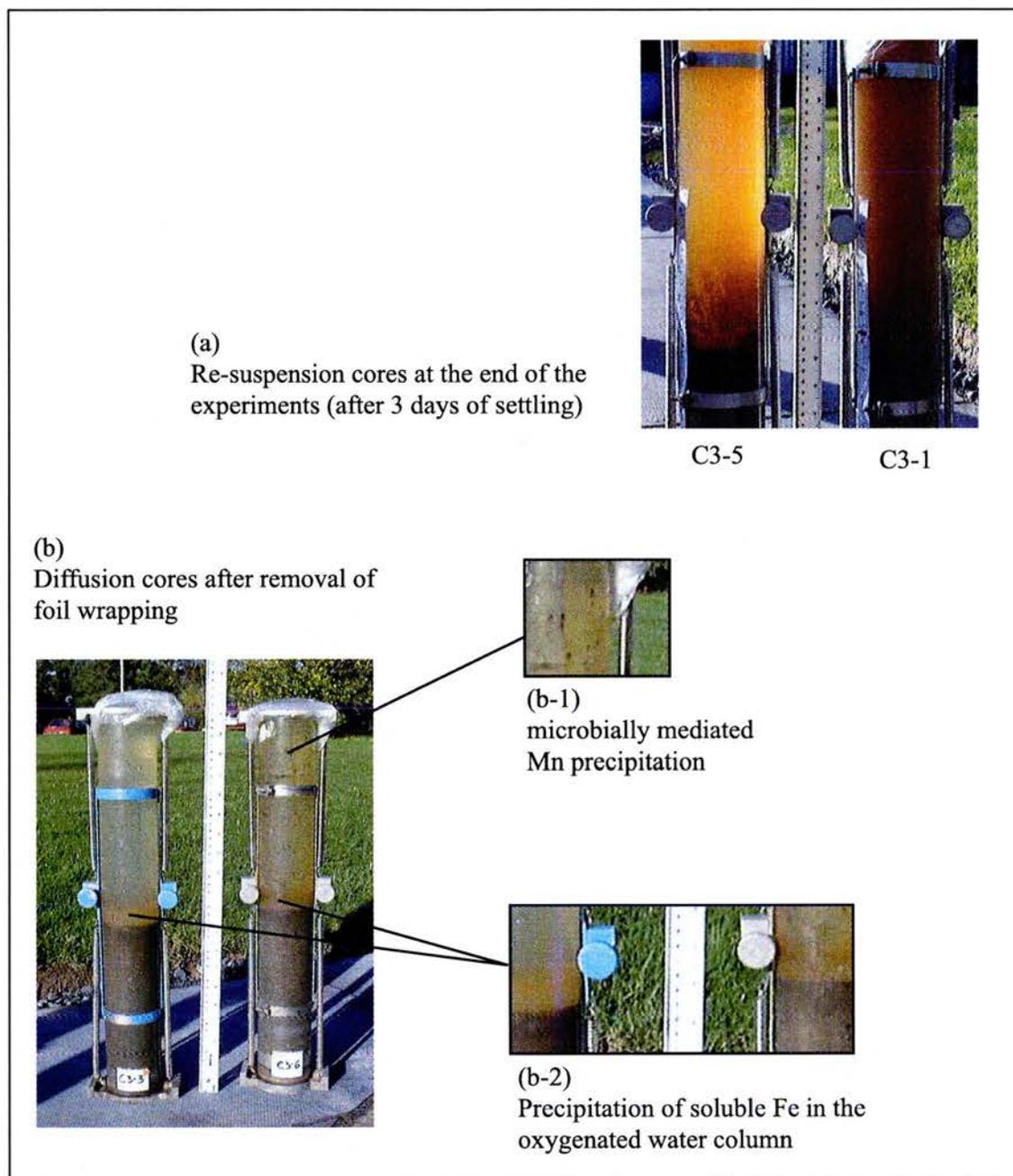


Figure 8.17 : Experimental cores at the end of the experiments prior to core segmentation.

*Figure 8. 17* shows the incubated cores after foil wrapping has been removed. Most noticeable is the red precipitation rim found in both cores, C3-3 and C3-6, at about 1-2 cm above the sediment surface, which indicate the release of soluble Fe(II) at the sediment-water interface (also seen in the increasing water column concentrations) and subsequently, the rapid oxidation to Fe(III) in the oxygenated water column. Removal of the tin foil wrapping also exposed black stains on the inside of the core tube of core C3-6 as seen in *Figure 8. 17*, which are interpreted as Mn precipitates. Such precipitates are not found in core C3-3, which was stored at lower temperatures around 9°C.

#### **8.4 Core metal distribution**

In many environmental studies sediment cores provide a useful tool for studying vertical distributions of particular elements within the sediment. Cores can be used to evaluate historical changes in metal loading and/or sedimentation rates, to assess the potential effects of sediment contamination or to study processes related to early diagenesis of the sediment, such as the post-depositional mobilisation of metals and nutrients. The latter is of particular interest in many lake studies as release of elements, such as As, Cd, Mn, P, N from the sediments can affect the overlying water column and may cause serious water quality problems.

In many studies sediment core studies are combined with investigations of pore water concentration, which also contain information about post-depositional reactions and diagenesis. Such investigations are often seen as being 'essential for studies of the exchange of elements or compounds across the sediment-water interface' (Håkanson and Jansson, 1983). However, in this study collection of interstitial water from the

sediment cores was not attempted because the collection of interstitial water is time consuming and difficult as minimal changes in the environmental conditions can lead to significant changes in pore water composition. This is especially important in anoxic sediments, where exposure to oxygen causes reduced species such as ferrous iron (Fe(II)) to be rapidly oxidised (Golterman *et al.* 1983). Moreover, it has been shown that temperature and pressure also exert a strong influence on the composition of the interstitial waters (Förstner, 1981 cited in Förstner and Wittmann, 1981). Although employed successfully in a variety of studies (e.g., Bendell-Young and Harvey, 1992a,b; Farmer *et al.* 1994; Bryant *et al.* 1997; Gavin *et al.* 2001), Håkanson and Jansson (1983) emphasise that results of pore water studies are strongly influenced by the applied sampling techniques and, in terms of chemical composition, can be quite variable. As pointed out by Farmer (2001, personal communication), the benefits gained from analysing interstitial water do not always ‘justify’ the difficulties incorporated with its collection. Thus, it was decided not to include pore water collection in this study. Instead, sediment extraction was carried out on the dried sediments (including the pore water residue) and information on the distribution of weakly bound metals (including the freshly precipitated amorphous particles) was inferred.

Segmentation and sediment extraction using acetic acid (HOAc) was carried out on two cores collected at the Megget Reservoir on 4 October 2001 (segmented within 4 hours after collection), as well as on the cores used for the laboratory experiments, to allow comparison of vertical metal distribution prior to, and after, the experiments.

### 8.4.1 Methods and materials

Following the removal of the overlying water (see methods in Section 8.1.2) the cores were prepared for dissection using the appropriate equipment provided by the manufacturers of the Jenkins corer (see *Figure 8. 5b*). Cores were dissected into 1-cm segments. Individual segments were then transferred into pre-labelled plastic bags and stored in a cool box until they were transferred to the cold store. The sediment was then prepared for the analysis of acid extractable metal content using a sediment extraction method suggested by Loring and Rantala (1992) and detailed in Chapter 6.

### 8.4.2 Results

The results obtained from chemical extraction of the core sediment (*Figure 8. 18*) illustrate the distribution of weakly bound Fe and Mn in the sediment cores analysed (*a*) prior to and (*b, c*) after the experiments. Concentrations of Al are also included in the graphs to provide a 'conservative' reference and a basis for evaluating and visualising the relative changes in Fe and Mn concentrations in the cores. *Figure 8. 18 (a)* shows enrichment of weakly bound Mn and Fe in the surface 0-3 cm and 0-1 cm of the pre-experiment cores, indicating accumulation of Mn and Fe in the form of easily soluble amorphous compounds, ion exchange positions or bound to organic matter in the surface sediments. It is possible that at least part of the weakly bound Fe and Mn represents freshly precipitated material, formed during drying of the sediment segments and resulting from the oxidation of soluble species present in the pore waters of the cores. Thus, high concentration in the surface sediments may also indicate concentration maxima in the pore waters, but this can only be hypothesised since pore water data from the sediment cores are not available. The presence of a redox boundary near the

sediment water interface can be inferred from the profile shapes of the pre-experimental cores where the soluble species, Fe(II) and Mn(II), diffuse downwards into the sediment and upwards into the overlying water column. The graphs in *Figure 8. 18a* also show that the Mn peak in core A and core C3-4 is generally better established than that of Fe and encompasses higher concentrations, demonstrating that Mn supplied to the sediments is more readily reduced than Fe. Below 2 cm in the sediment cores concentrations of acid-extractable Fe constantly increase with depth, reaching a maxima at around 7 cm in core C3-4, after which concentrations decline towards the bottom of the core. A similar increase in weakly bound Fe with depth is seen in core A, although a peak is not apparent. The peak may suggest the presence of a deeper redox boundary in core C3-4. No such pattern is detected in the Mn profiles, in which concentrations below 4 cm remain more or less constant. The graphs also show that the deeper redoxcline in the cores is not very sharp (with respect to Mn), indicating that redox conditions in the sediment change gradually so that differences in the redox potentials of Fe and Mn and the rates for reactions become apparent (Davison, 1985).

A very different picture emerges when comparing the pre-experimental metal distributions in cores A and C3-4 (*Figure 8. 18a*) with those observed in the re-suspended (*Figure 8. 18c*) and incubated (*Figure 8. 18b*) cores after the experiments. Most noticeable are the extremely low concentrations of weakly bound Mn in the post-experimental cores with concentrations ranging between 7-30 mg L<sup>-1</sup> (C3-6) and 13-47 mg L<sup>-1</sup> (C3-3) compared to 86-281 mg L<sup>-1</sup> (A) and 79-406 mg L<sup>-1</sup> (C3-4) in the pre-experimental cores. As the soluble reduced forms of the metals play the dominant role in transport processes within the sediment (Davison, 1985) this must indicate that most Mn was solubilised and released into the water column during the incubation period

leaving the sediments almost completely depleted of Mn. Changes also occur in the distribution of weakly bound Fe in the core sediments and are most clearly seen in core C3-6 which was incubated at 22°C. The profile shows the relative enrichment of weakly bound Fe in the upper 3-4 cm of the core, followed by gradual decline down-core and low concentrations at depth below 10cm. Assuming a pre-experimental Fe distribution similar to core A and core C3-4 and provided that molecular diffusion is the dominant mode of transport in the sediment, this suggests that changing redox conditions in the sediment column allowed the deeper redox boundary to progress upwards, towards the sediment-water interface. Consequently, Fe, solubilised in the deeper part of the sediment column, was released into the overlying water column as oxygen depletion in the sediments and water column progressed. The difference here is that Fe(II) forms at depths within the sediment and diffuses into the overlying bottom water column, as opposed to being formed at the sediment-water interface by rapid reduction of oxyhydroxide particles supplied by the water column.

A somewhat different Fe profile is seen in core C3-3, incubated at 9°C, where concentrations in the sediment remain fairly constant throughout all depth and then decline below 14 cm. It appears that a distinct redox boundary, as seen in the other cores, is not established in this core, although a small peak is seen at around 5 cm. However, the redox conditions in the core sediment appear to be favourable for solubilisation of Fe, as seen by re-distribution of the weakly bound Fe fraction and also by the reduced concentrations in the lower parts of the core, which indicate upwards diffusion of Fe. It is also interesting to note that there is no indication of an accumulation of weakly bound Fe near the sediment-water interface; in fact, concentrations are slightly lower in the upper centimetres of the core. This may suggest that most of the oxyhydroxides have been released from the interface, while redox

conditions in the upper core are not yet favourable for the release of Fe solubilised at depth within the sediments as seen in core C3-6. This hypothesis can be supported by considering the comparatively slower rate of oxygen consumption in this core, relative to that in C3-6, resulting from the low incubation temperatures (9°C), which slow down metabolism and microbial activity (Horne and Goldman, 1994). Based on these observations, it is hypothesised that the profile observed in C3-3 can be regarded as a transitional distribution between the pre-experimental distributions and that observed at core C3-6. The peak at around 5-cm depth may indicate the position of the redoxcline (region of large gradient of redox intensity with depth), although sub-millimetre information would be required to further test this assumption. Nonetheless, this interpretation is in good agreement with the water column observations previously discussed in Chapter 8.3.2.

Metal profiles observed for the re-suspended core C3-5, given in *Figure 8. 18b*, show distributions similar to that observed in the pre-experimental cores. This would be expected as the water column remained well oxygenated and re-suspension of the first 1-2 cm promoted the oxygen exchange across the sediment-water interface, such that redox distribution in the core did not change significantly. Similar processes would be expected to occur in core C3-1, where the upper 4-5cm were re-suspended. Conversely, distribution profiles of C3-1 show that the core generally appears to be depleted in Fe and Mn, which at first seems surprising as oxygen exchange across the air-water interface was maintained throughout the entire experiments. The observed pattern can only be explained by the development of low redox conditions in the water column and sediments, seen in *Figure 8. 9*, resulting in the mobilisation and release of Fe and Mn from the sediments. This explanation seems plausible considering the high amount of

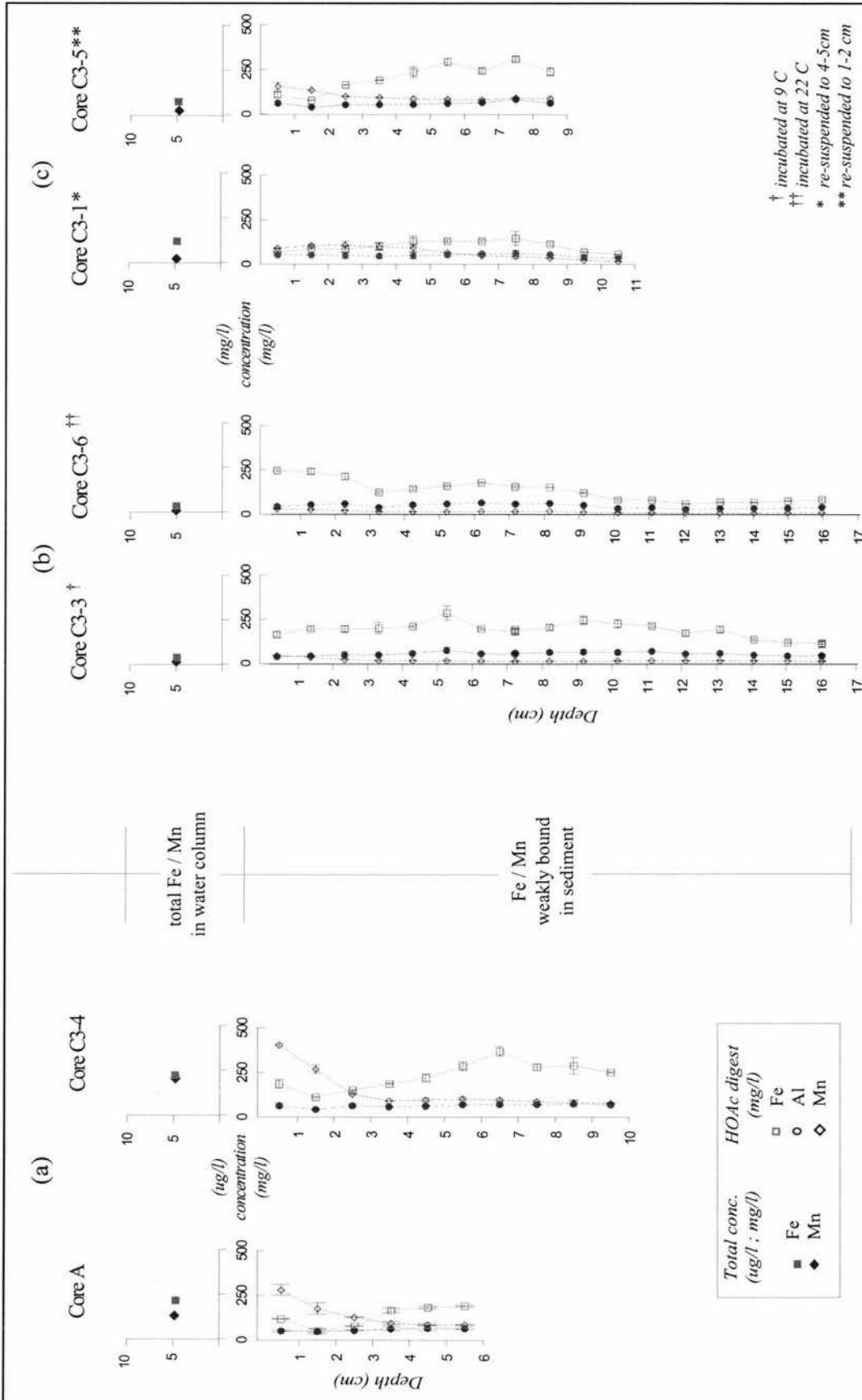


Figure 8.18: Vertical distribution of weakly bound iron and manganese in the sediments (open symbols) and concentrations of (total) iron and manganese in the overlying water column (full symbols) of the Megget cores analysed (a) immediately after collection, (b) after incubation and (c) after re-suspension experiments [note the differences in units in water column concentrations in (a)].

organic matter and reduced metals species, which have accumulated in the sediments (see LOI values given in Chapter 6 and *Figure 8. 18a*), and are introduced into a relatively small-volume water column during re-suspension.

## 8.5 Discussion

Re-suspension of the core sediment introduced high levels of Fe and Mn into the overlying water column. The higher amount of Fe found in the water column of the two re-suspended cores relative to that of Mn reflects the differences in Fe and Mn retention in the sediments caused by the form in which these elements are predominantly present in the aquatic environment. Generally, high proportions of Fe entering the aquatic system are incorporated into the lattice of clay minerals and accumulate within the sediment without reaction. Tessier *et al.* (1980), for example studied suspended matter in two Canadian rivers draining mixed catchments and found that only about one third of the Fe was present as reactive, presumably amorphous oxyhydroxides. The remaining two thirds were incorporated in the crystal lattice of clay minerals and silicates or present as refractory Fe oxide; thus can be incorporated into the sediment. In contrast, most of the Mn entering a lake or reservoir comprises reactive oxyhydroxides (Davison, 1993; Zaw and Chiswell, 1999), which are rapidly reduced to  $Mn^{2+}$  when encountering the sediment. Thus most Mn rapidly returns to the water column in form of Mn(II) and only a small proportion is permanently accumulated in the sediment. The relatively small increase in Mn concentrations with depth of re-suspension in the water column of the re-suspended cores is attributed to rapid dissolution of Mn at the sediment-water interface, which is also seen in the surficial enrichment of acid-extractable Mn in the pre-experimental cores, and to the low concentration of Mn at depth within the

sediment. Low retention of Mn in the sediments of the Megget Reservoir was also reflected in the results from the sediment survey (Chapter 7), where total Fe concentrations exceed those of Mn by up to 50 times.

The results from core re-suspension further indicate that concentrations of dissolved metals decrease with increasing amount of sediment re-suspended in the water column. Although somewhat surprising (the rate of removal of dissolved metals through processes like oxidation and adsorption is expected to be higher at lower particle content in the water column and at higher pH, respectively), this is in good agreement with observations from similar experiments (see Brassard *et al.* 1994 and Tessier, 1992). Brassard *et al.* (1994) suggest that the decrease in dissolved metal species is caused by increased inter-particle collision due to higher particle concentrations, which leads to enhanced disaggregation and the sorption of dissolved metals onto the newly formed particle surfaces. However, given the high amount of organic material present in the sediments of the Megget Reservoir it can be assumed that the organic matter introduced into the water column also provides abundant sorption sites for dissolved metals, whereby processes of sorption and chelation with organic acids are generally more important for Fe than for Mn (Chiswell and Mokhtar, 1986; LaZerte and Burling, 1990).

Sediment re-suspension caused serious discolouration of the water, due to the presence of humic substances, characterised by the yellow water colour (Warren and Haack, 2001). These accumulate in the sediment and at the sediment water interface noted by the unconsolidated interfacial layer of orange-brown material ('fluff') overlying the sediment. Beside discolouration of the water, these humic substances provide a range of

possible metal binding sites (Livens, 1991); thus humic matter plays an important role as a chelating agent, forming low-molecular-weight-complexes and higher weight colloidal material with many transition metals (Curtis, 1993; Drever, 1997). Such complexes and colloids are relatively stable in the water column and have slow coagulation rates (Tipping *et al.* 1981; Pizarro *et al.* 1995) due to the adsorbed humic substances. Theis and Singer (1973), for example, showed that humic material reduces any Fe(III) in the water column and can maintain enhanced concentrations of Fe in solution as Fe(II) complexes even when the water column is well aerated. It is therefore assumed that these humic substances may stabilise Fe and Mn in the reservoir water column by delaying oxidation and/or aggregation of the particles, thus preventing settling and prolonging their presence in the water after re-suspension. This hypothesis may be supported by the fact that filtration removed the colouration of the water together with more than 90% of the Fe, which prior to re-suspension was mainly present in dissolved-(colloidal) form (>50%). However, this correlation does not prove the association of Fe with humic substances (as very fine silt and Fe particles would also be retained by the filter) but does provide an indication that humic substances may play a role in retaining Fe particles in the water column. Based on the available data it is not possible to distinguish between Fe associated with organic acids and that present in the form of oxyhydroxide particles, thus the contribution of organic particles in the stabilisation of Fe remains unresolved in this study, although the above references show that its influence cannot be ignored.

Organic matter, originating from the pedogenic horizons of the catchment or produced by degradation of plant tissue, is believed to have contributed to the low redox values encountered in core C3-1. It is hypothesised that the dramatic decrease in redox

potential is caused by high amounts of reducing substances, such as organic matter, introduced into the relatively small-volume water column during re-suspension. A link between lower redox potential in the water column and organic reducing substances has been previously suggested by Hutchinson (1957). Introduction of organic matter from the overlying water column and interflow of storm events was found to contribute to oxygen depletion in the metalimnion of DeGray Reservoir in Arkansas (Nix, 1981). In view of the high organic matter content found in the surface sediments of the reservoir (see Chapter 7), this explanation seems plausible, in particular since re-suspension is likely to enhance the reducing character of the accumulated organic matter. This is due to the higher rate of surface contact between organic matter particles in suspension and oxygen compared to static condition, where oxygen movement is limited by the rate of molecular diffusion. However, the presence of other reducing substances, in particular Fe(II) and Mn(II), accumulated in the surface sediments of the cores (*Figure 8. 18*) and pore waters may also have contributed to the low redox potentials. The strong reducing character of solute and solid Fe(II) complexes has been demonstrated in laboratory studies by Stumm and Sulzberger (1992) and Fe(II) and Mn(II) were also suggested to have contributed to low redox conditions near the sediment-water interface of small lakes (Hutchinson, 1957) and in the metalimnion of the DeGray Reservoir (Nix, 1981). Redox conditions in core C3-5 remained high throughout the experiment, indicating sufficient oxygen supply to counterbalance the effects of reducing substances introduced into the water column by re-suspension. Moreover, frequent re-suspension of the cores and increased mixing at the air-water interface may have enhanced the oxidation of metals and organic compounds in the core water column (McAuliffe *et al.* 1998) by increasing oxygen diffusion into the water and expediting the re-oxygenation of the water column.

The constant increase in Fe and initially Mn in the water column of the incubated cores indicates release of dissolved species of these elements from the sediments into the overlying water column (*Figure 8. 11, Figure 8. 12*). The release occurs despite oxygenated conditions in the water column, and mobilisation and release of Fe and Mn into well-oxygenated water columns has been reported by a variety of authors (e.g., Davison, 1993, Hsiung and Tissue, 1994). Direct evidence for the release of Fe and Mn from sediments overlain by oxygenated water comes from a study by Davison *et al.* (1982) who employed sediment traps near the bottom of Esthwaite Water. The authors generally agreed that Fe diffusion into oxygenated waters occurs where the redoxcline is close enough to the sediment-water interface for Fe to diffuse out of the sediment into well-oxygenated water before being re-oxidized. Given a half time of 4 hours for Fe (II) in well-oxygenated environments (pH 7, 10°C) (Davison and Seed, 1983), Fe(II) can be expected to travel about 0.5 cm (if only molecular diffusion operates) in a plentiful supply of oxidants before being re-oxidised (Hamilton-Taylor and Davison, 1995).

Mn and Fe profiles in the core sediments prior to core incubation are characterised by near-surface enhancement in acid-extractable Mn and Fe overlying uniform concentrations. Such elevated concentrations of non-refractory Fe and Mn in surface sediments are characteristic of post-depositional diagenetic cycling of Mn and Fe under reducing conditions within the sediments (Davison, 1985) and have been reported by many authors (e.g., Farmer and Lowell, 1986; Hsiung and Tissue, 1994; Bryant *et al.* 1997; Zaw and Chiswell, 1999; Warnken *et al.* 2001). From the profile shapes a redoxcline near the sediment-water interface can be inferred, which is a common feature in many freshwater systems (Warnken *et al.* 2001; Hsiung and Tissue, 1994; references

in Davison, 1985), where rapid oxygen consumption at the sediment surface (related to the decomposition of organic material) coupled with slow molecular rates of oxygen transport into the sediment cause reducing conditions to be established. The proximity of the peak to the sediment-water interface, however, makes it difficult to determine whether the solubilisation of the metals occurs within the sediments or at the sediment-water interface, as the peak in the sediment may be so sharp that a sampling interval of 1cm is insufficiently detailed to pick it up. Often millimetre or sub-millimetre sampling is required to adequately present gradients in sediments (Sundby *et al.* 1981) and pore waters (Zhang *et al.* 1995; Warnken *et al.* 2001). Yet, a constant increase in Fe and Mn concentrations in the water column is observed during the incubation period; thus, the overall net flux during the experiments is directed upwards, from the sediment into the overlying water column, and the metal distributions in the core sediments prior to and after the experiments (*Figure 8. 18*) also suggest mobilisation and release of Fe and Mn from within-sediment sources.

Nonetheless, while diagenetic mobilisation within the sediment undoubtedly occurs, it could be argued that the surficial enrichment observed prior to incubation of the cores (*Figure 8. 18a*) is initially related to the rapid reduction of oxyhydroxides by organic matter at the sediment water interface and consecutive diffusion into the sediments. Davison (1985, 1993) suggests that these processes provide the main supply of reduced Fe and Mn for the overlying water column of aquatic systems and often are more dominant than upwards diffusion and release of Fe(II) and Mn(II) formed at depth within the sediment. One may hypothesise that during the incubation period a shift in the pre-dominance of these two processes occurred, whereby the former appears to be dominating the early stages of stagnation where supply of oxyhydroxide at the sediment-water interface is plentiful and solubilisation within the sediment is limited to

a deeper redoxcline. However, as oxyhydroxides at the sediment-water interface are gradually depleted (due to solubilisation and because supply from overlying water is unavailable) and redox conditions within the sediment decline, reduction of Fe and Mn oxyhydroxides within the sediment and upwards diffusion of dissolved species become more important and release from the within-sediment sources appears to be dominating Fe and Mn release during later stages of the experiments. Similar processes have been suggested by Bonanni *et al.* (1992) for the release of nutrients from benthic chambers, where sediment diffusion was found to govern fluxes in the anoxic system while release from organic degradation at the sediment-water interface appeared important under oxic conditions.

Core metal profiles and water column concentrations have also shown that the Mn reservoir within the sediment becomes depleted during the course of the experiments, which is a common phenomenon in natural systems, where supply of less abundant Mn oxides often becomes exhausted while the supply of readily reducible Fe oxides is usually plentiful (Hamilton-Taylor and Davison, 1995). Mn is generally available in more easily reducible forms compared to Fe, which is often incorporated in the lattice of clay minerals and/or stable oxides and thus is not available for solubilisation processes (Davison and DeVitre, 1992; Davison, 1993). This has been demonstrated in several studies (e.g., Bryant *et al.* 1997; Warnken *et al.* 2001) where selective chemical extraction revealed that Mn is mostly present in forms other than refractory. Farmer and Lowell (1986), for example, extracted a maximum of 90 % of the total Mn from the sediment (using 1 M hydroxylammonium chloride and 25 % acetic acid), while only 36 % of the total Fe was removed by the extraction. This results in only a small proportion of Mn being permanently accumulated in the sediment in contrast to Fe, a high

proportion of which accumulates within the sediment without reaction and/or is buried until it reaches more reducing conditions where it is remobilised (Nembrini *et al.* 1982). Build up of high levels of Mn in the bottom waters of the Megget Reservoir during summer stratification are, therefore, unlikely to result from sediment diffusion alone, and may be supported by the reduction of settling Mn-oxide particles in the suboxic water column. The contribution of settling material to inventories of Fe and Mn in the water column was not tested in this study and can only be estimated where information about type, amount and settling velocities of particles are known. However, Balistrieri *et al.* (1992) found that the reduction of settling Mn oxide particles provides the dominant source of dissolved Mn in the suboxic to anoxic bottom water of Lake Sammamish during stratification, whereas dissolved Fe was mostly supplied by Fe(II) diffusion from the sediments, and similar observations were made in the anoxic water column of Esthwaite Water (Davison, 1981).

In oxygenated waters at circumneutral pH, Fe(II) rapidly oxidises to Fe(III), while most Mn(II) is effectively stable. Rapid oxidation of Fe(II) to Fe(III) in the water column of the experimental cores is well documented in the low concentrations of soluble Fe as well as by the distinct zone of Fe precipitation, which has developed on the insides of the tube up to 3 cm above the sediment (see *Figure 8. 17*). Diffusion of Fe(II) and oxidation to Fe(III) is probably also responsible for the elevated levels of particulate Fe near the sediment (*Figure 8. 11*), as often observed in natural systems during summer stratification (Davison and DeVitre, 1992, Davison, 1993). It remains unclear when precipitation of Fe occurred and consideration of pH-redox stability plots (*Figure 8. 15*) suggests that Fe<sup>2+</sup> may have been stable during the first days of the experiment. The abundance of dissolved Mn species in the core water column demonstrates that most

released  $\text{Mn}^{2+}$  was effectively stable in the core water column for considerable time throughout the experiments. However, declining concentrations in the water column of C3-6 suggest the presence of an effective removal mechanism, probably Mn oxidations, as indicated by the black stains at the inside of the core tube (*Figure 8. 17*), which are interpreted as Mn precipitates. In natural waters Mn oxidation is assumed to be microbially mediated (Tipping, 1984; Tipping *et al.* 1984; Nealson *et al.* 1989; Emerson, 2000) displaying temperature optima between  $\sim 15^{\circ}\text{C}$  to  $\sim 30^{\circ}\text{C}$  (Tipping, 1984) depending on the type of Mn-oxidising organism involved. This temperature dependence also explains the absence of Mn precipitates in core C3-3, where unfavourable low temperatures inhibited microbial activity in the water column. Besides Mn removal from the water column, microbial activity associated with degradation of organic matter is also found to facilitate Fe and Mn release under oxic and suboxic conditions (Davison *et al.* 1982, Sigg *et al.* 1987, Hsiung and Tissue, 1994) and microbial involvement is apparent from the different rates of elemental release, which is higher in core C3-6 where degradation of organic matter is promoted by temperatures favourable for microbial activity.

Reverse diffusion from overlying water into the interstitial water of the sediment has also been suggested to remove Mn from the water column (Davison, 1993), and mainly occurs where anoxic conditions exist in the water column, and where external inputs of Fe and Mn oxyhydroxide particles and their *in situ* dissolution are high. Given the low Mn concentrations in the sediments and considering the absence of external inputs, this seems an unlikely mechanism for the decline of Mn in the water column of the experimental cores.

The mobility of trace elements and nutrients has often been found to be indirectly involved in redox cycling of Fe and Mn oxides in lakes (see references in Sholkovitz, 1985; Hamilton-Taylor and Davison, 1995) and strong correlations between Mn and Fe and (trace) elements like Ba, B, Sr and Ca were observed in the core water column of the incubated cores. Although the exact mechanism responsible for the fluxes is not known, several authors (Stumm and Sulzberger, 1992; Hamilton-Taylor and Davison, 1995) have suggested that Fe and Mn oxyhydroxides could play an important role in controlling the concentrations of these elements in aquatic environments as they provide highly reactive surfaces for trace metal scavenging and together with organic matter are regarded as the most important carrier phases for trace element fractions under oxic conditions in aquatic sediments (Tessier *et al.* 1979; Tessier, 1992).

With regard to re-suspension and sediment release, the experiments clearly emphasise the varying importance of these processes for concentrations and fluxes in the water column. If it is assumed that clay mineral particles, introduced into the water column by re-suspension, sink more quickly than dissolved metal species and amorphous oxides, resulting from sediment release and rapid oxidation, it becomes apparent that re-suspension contributes more significantly to the fluxes at the sediment-water interface, while processes of sediment release and diffusion dominate the concentrations in the water column.

However, from the above discussion it is apparent that there are some serious limitations associated with such an experimental approach, mainly because of a number of processes, e.g., *in situ* dissolution of settling particulate material, which cannot be accounted for in these artificially enclosed sediment-water systems used here. Thus,

care must be taken when extrapolating the results from these experimental systems to the reservoir.

## 8.6 Summary

The experiments have demonstrated that re-suspension can introduce significant amounts of particulate Fe and Mn into the overlying water column, while solubilisation within, and diffusion from the sediment, is responsible for the releases of soluble Fe and Mn. Re-suspension appears to be more important for mobilising Fe due to its abundance in clay minerals and as relatively unreactive oxides, while redox-driven mobilisation and transport in solubilised form is generally more important for Mn, which is more readily soluble and in circumneutral waters has a lower oxidation rate.

Serious and prolonged discolouration of the water has occurred as a result of re-suspension due to the presence of organic matter and humic substances in the water column. Low settling velocities of these particles and water turbulences may cause persistent discolouration of the water, and organic complexation processes may also promote the prolonged presence of Fe and Mn in the water.

It was further shown that two different release mechanisms are important for the release of soluble Fe and Mn from the sediment cores during the experiments; (I) rapid reduction of oxy-hydroxide particles by organic matter decomposition at the sediment water interface and (II) release of soluble Fe and Mn species formed under reducing conditions within the sediment. The former appeared to be more important during the early stages of stagnation, where supply of oxyhydroxide at the sediment-water

interface is plentiful, whereas the latter became important during later stages of the experiments when oxyhydroxides at the sediment-water interface were depleted and redox potentials in the sediment had declined sufficiently for upwards diffusion into the overlying water column to occur. However, the Mn pool in the sediments was soon depleted where conditions were favourable for Mn mobilisation, and other *in situ* sources may contribute to the build up of high Mn levels in the bottom waters of the reservoir, such as dissolution of sedimenting oxyhydroxide particles supplied by the overlying water column. Such processes were accounted for in the experimental systems studied here, and care must be taken in extrapolating the results to the reservoir.

# 9

## Summary and Conclusions

---

This final chapter summarises the main research findings and discusses the implications for understanding the controls on , and maintaining, water quality. Both, practical and theoretical limitations associated with the applied methods are discussed and further research is proposed. The holistic approach adopted in this study has proved beneficial for understanding the water quality functioning in the Megget catchment and the reservoir system; the study has implications for the hydrochemical and biogeochemical processes in the catchment area and the reservoir, and offers recommendations on how reservoir operation and management should be modified in the light of the current findings. The results are generally applicable to similar upland catchments elsewhere.

### 9.1 Summary

This study has attempted to assess the controls on Fe and Mn cycling in the Megget Reservoir and catchment in order to understand how water chemistry and quality is influenced throughout the catchment-reservoir system. Although the study was motivated by the water quality problems experienced in 1997/98, the completed research has defined the sources and sinks of Fe and Mn, the temporal fluctuations in water chemistry both seasonally as well as during individual storm events, the spatial variations in stream chemistry with soil type and geology and has provided significant

insight into metal behaviour under changing physical and chemical conditions in the reservoir system. More specifically, these objectives have been achieved by means of comprehensive water quality monitoring at the reservoir and within the catchment area, including routine stream sampling, intensive stream sampling during storm events, sedimentological reservoir surveys and laboratory experiments and incorporates a diverse suite of analytical procedures. Field data analyses have been used to determine how reservoir and catchment characteristics influence the variability observed in water chemistry, while laboratory experiments and intensive stream sampling have provided results that allow to delineate system processes and their impact on water quality. Based on the episodic event data, a conceptual model was applied for predicting periods of high Fe and Mn loading into the reservoir.

### 9.1.1 Main research findings

In this thesis, the Megget Reservoir system has been assessed as an entity of interrelated processes. The reservoir system has been studied within the framework of its catchment area and the variability in catchment processes has also been assessed temporally as well as spatially. The spatial and temporal variability in physical and biochemical characteristics have been analysed alongside the dynamic internal processes and interactions of the reservoir sediments. As such this holistic approach differs from studies undertaken in other upland environments, most of which have treated the reservoir and catchment in isolation. However, the tight coupling of reservoir processes with those of the catchment area is known to be of fundamental importance when the management of water quality is of concern. As Straškraba *et al.* (1993) point out, a combination of approaches, including field observations, experimental tests and use of

simulation modelling, is likely to be the most valuable approach for management strategies aimed at water quality protection.

Moreover, evaluation of the temporal and spatial stream water chemistry variability within the Megget catchment area and application of EMMA modelling provide valuable information on processes and water quality functioning in unforested upland catchments, which compared to forested catchments are generally underrepresented in the bulk of (upland) mixing model studies (Burns *et al.* 2001; Bonell and Fritsch, 1997). Such knowledge, however, is becoming increasingly important for effective water quality and catchment management, particularly in the light of acidification problems increasingly encountered in pristine upland environments.

The current study offers insight in the water quality functioning of the Megget Reservoir and highlights the importance of reservoir internal processes under different operational rules. It furthermore contributes significantly to the understanding of runoff processes in unforested upland catchments in general and emphasises their role in influencing the water quality of upland reservoirs. To date, the current study presents the only holistic approach of such kind undertaken in Scotland, combining reservoir and catchment field observation, laboratory investigations and simple modelling to tackle water quality problems in a Scottish Upland reservoir, and represents one of the few examples of this approach in any upland area. The main findings of the study comprise the following points:

- I Regular sampling at the reservoir has established that the trophic state of the Megget Reservoir is oligotrophic according to the classification systems suggested by Vollenweider (1982), which means the system is characterised by low nutrient and

chlorophyll-*a* concentrations in the water column. Most distinct changes in the reservoir water chemistry occur during thermal stratification, where oxygen is progressively depleted from the hypolimnion of the reservoir. Establishment of anoxic condition in the bottom waters of the reservoir has not been observed, but substantive vertical gradients in the distribution of elements, like Fe, Mn, chlorophyll-*a* and pH develop during thermal stratification. While the Fe and Mn content in the well-mixed water column is generally low, concentrations in the hypolimnion of the reservoir during stratification were notably higher, occasionally exceeding the drinking water requirement set out for these elements by the World Health Organisation (WHO, 1993). These high concentrations have been linked to the mobilisation of soluble Fe and Mn at the sediment-water interface and/ or from within the sediment.

- II Stream chemistry data from regular sampling and episodic events have been analysed and show that temporal variations in stream chemistry are, for the most part, governed by hydrological factors. The data exhibit the characteristic variations conceptualised as being the result of changing hydrological pathways during events, which are illustrated by a number of chemical determinants. Concentrations of Fe, Mn and Al tend to be higher during periods of high runoff, since stream chemistry is dominated by more acidic 'soilwater' from metal bearing upper soil horizons, while the inputs of base-rich 'groundwater' from lower soil horizons and bedrock, which dominates baseflows, is diluted during such events. Besides hydrology, soil type differences have also been found to affect the stream chemistry, with different responses seen between catchments dominated by ill-draining blanket peats and peaty gleys and catchments with higher proportions of better-drained peaty podzols

and mineral soils. The resulting differences in stream chemistry have been attributed to the varying flow pathways, with higher proportions of soilwater contributing to stream runoff in the peat-dominated catchments. The simple two-component EMMA conceptual model applied to the data has proved a simple but powerful tool for representing how different runoff sources vary in their contribution to stream discharge through time.

III Episodic event data have been assessed and the frequent sampling programme employed here highlights the importance of stormflow in transporting Fe and Mn and also underlines the reduced ability of the routine sampling programmes to detect the full range of inter-annual variability in loading pattern. The simple conceptualisation of the system behaviour produced by EMMA has shown considerable utility as a management tool for predicting the hydrochemical stream response to runoff events and to identify critical periods of high Fe and Mn loadings in stream runoff. Here, autumn and winter storm events have been identified as such critical periods, during which the bulk of Fe and Mn is delivered to the reservoir. Using Q- and R-mode factor analysis technique, two different mechanisms were identified by which Fe and Mn are released into the streams: flushing of reduced Fe and Mn from soils in near-stream areas and runoff of complexed Fe and Mn from shallow organic-rich soil horizons. The importance of these two processes varies temporally as well as spatially, depending on factors like storm intensity, antecedent catchment conditions, dominating soil types and their distribution in the catchment as a whole and in the near-stream areas in particular. Clearly, any variability in storm frequency and magnitude, a predicted outcome of current climate change

scenarios (Werritty *et al.* 2001), will affect the rate and total amount of metals entering the reservoir.

IV Spatial variability in sediment characteristics of the Megget Reservoir has been investigated and the results from the surficial reservoir sediment survey have shown that the medium silt fraction dominates the sediment deposits throughout the reservoir. Such fine-grained particles generally provide effective adsorption sites for Fe and Mn due to their large specific surface area and may also be easily re-suspended. The absence of distinct longitudinal patterns in grain size distribution in the reservoir has been attributed to two factors: (1) the relatively equitable distribution of inflows around the perimeter of the reservoir, and (2) alteration of the sedimentation pattern during the draw down of the reservoir through re-suspension, erosion and redistribution of previously deposited bottom sediment. The application of X-ray fluorescence analysis and sediment digestion techniques has allowed the chemistry of the sediment samples to be established. Although the XRF results have indicated some variations in sediment composition between the shallow end of the reservoir and those from deeper parts (in the middle and dam area), it has not been possible to identify potential sites of increased sediment metal release as will be discussed in Section 9.1.2.

V Laboratory experiments on undisturbed reservoir sediment cores have clearly demonstrated the potential of sediment re-suspension and diffusion processes to introduce significant amounts of Fe and Mn into the overlying water column. Complementary to the experiments, core segmentation and analysis has been undertaken in order to relate the water column observations to processes within the

sediments. It has been seen that re-suspension is by far the more effective mobilisation mechanism and generally appears more important for the mobilisation of Fe which, in comparison to Mn, is present in large quantities within the sediments. Serious and prolonged discolouration of the water has occurred as a result of re-suspension and has been linked to the presence of organic matter and humic substances in the water column. Inherent in the low settling velocities of these particles is the potential to cause persistent discolouration of the water, and thus to prolong the time required for the recovery of the system's original water quality. In the absence of turbulence and physical disturbance, however, processes of sediment diffusion and release of Fe and Mn in solubilised form have been found to be important, despite the oxygenating conditions in the water column. Two different release mechanisms have been identified; rapid reduction of oxy-hydroxide particles by organic matter at the sediment water interface and upwards diffusion and release of soluble Fe and Mn formed at depth within the sediment. *In situ*, the former probably provides the main supply of reduced Fe and Mn to the water column, whereas the latter may only be important during prolonged stagnation periods when oxyhydroxides at the sediment-water interface become depleted and redox potentials in the sediment decline. It has further been demonstrated that sediment diffusion and transport in solubilised form are more important for the cycling of Mn than for Fe, as Mn is more readily soluble and is also retained in the water column for longer due to its low oxidation rate in circumneutral waters. However, the Mn pool in the sediments can soon be depleted where conditions are favourable for Mn mobilisation, although the build up of high Mn levels in the bottom water of the reservoir only seems possible where large quantities of Mn oxyhydroxides are supplied by the overlying water column.

### 9.1.2 Limitations

Some practical and theoretical limitations arise from the different methods applied in this study; either associated with the applied modelling and data analysis methods or related to laboratory studies and sample analysis techniques.

The limitations in the use of the conceptual EMMA model for predicting the hydrochemical stream response to runoff events mainly lie within the assumptions made by the method, which have been discussed in detail in Chapter 6. The main limitations are associated with the application of the two-component conceptual mixing model to the complex catchment environment and with the uncertainty in the definition of the end-member chemistry, both of which have a direct effect on the outcome of the modelling exercise. The two-component model may be too simplistic to reliably represent the flow pathways in the Megget catchment, and in other studies three components were necessary to model the system response (e.g., Hooper *et al.* 1990; Jenkins *et al.* 1994a; Burns *et al.* 2001, Soulsby and Dunn, 2003). However, even though the influence of a potential third end-member, characterised by high Fe and Mn loadings, may be inferred from the factor analysis, it has not been possible to sufficiently characterise and separate such an additional component on the basis of the available conservative measures. It seems plausible that these Fe- and Mn-rich inputs simply reflect the longer residence times of the groundwater/ deeper soilwater in the riparian zone, which inevitably leads to the question: what do the selected end-members actually represent? By definition, the distinction in this application has been drawn between 'geographic sources', namely soilwater and groundwater, rather than between 'time sources', i.e. 'new' and 'old' water, and as such the two-component approach is consistent with the chemical signature seen in the streams, despite the implicit

oversimplification of the natural system in which temporal and spatial component *per se* are inseparable.

The definition of the high-flow and low-flow end-members itself is somewhat arbitrary. For the former, the error depends on the appropriateness of the approach of using literature soil data to estimate the chemistry of the high-flow end-member, while the uncertainty for the latter lies within the method of inferring the end-member chemistry from low flow stream water composition. Yet, even if different end-member values were used in the model calculations the general patterns would not change, so that the fundamental processes can be expected to be well presented by the technique, even if the end-members may not be defined accurately. As Foster (2000) has pointed out, much may be gained from looking at the system in such a simplistic way, as long as an estimate of an integrated 'end-member' chemistry can be obtained and can successfully be used for modelling purposes, even if end-members themselves are rather hypothetical and not directly measurable.

While this simple conceptualisation of the system behaviour shows considerable utility as a management tool for predicting the hydrochemical stream response to runoff events, and to identify critical periods of high Fe and Mn loadings, it has limitations in quantitatively predicting Fe and Mn concentrations in the streams, and as such requires further refinement.

Practical limitations have been encountered during the surficial sediment survey. Attempts were made to investigate the distribution of the geochemical sediment characteristics throughout the reservoir, but this was extremely difficult due to the high sampling error derived from replicates. The variability was highest in elements

influenced by changing redox conditions, particularly Mn and has been linked to the high degree of heterogeneity in the bottom sediments, as well as to local variations in sediment redox conditions. While the heterogeneity shows little effect on the XRF results, where proportions of Mn are very small (<1%), it greatly influences the results from the chemical sediment extraction. As a consequence of the uncertainty inherent in the data, no suggestions were made regarding the spatial distribution of potential metal release sites in the reservoir. The relatively high errors in the grain size analysis are likely to result from similar causes, but may also be affected by the sediment digestion techniques, which have been shown to increase the standard deviation of replicates compared to undigested samples (Bergen and Tsukada, 1994).

Finally, further limitations arise when extrapolating the results from the laboratory experiments to the reservoir because several factors are excluded from such artificially enclosed sediment-water systems, including water column fluxes and inputs of Fe and Mn from reductive dissolution of settling particles in the water column or bioturbation and local re-suspension at the sediment-water interface. As these processes can significantly enhance the exchange across the sediment-water interface caution should be exercised in using the data in quantifying fluxes from, and to, the sediment. The experiments have further illustrated the importance of distinguishing between concentrations and fluxes. Comparing both re-suspension and diffusion processes, and assuming that clay mineral particles (introduced into the water column by re-suspension) sink more quickly than amorphous oxides (resulting from release and rapid oxidation), it becomes apparent that the former process contributes more significantly to the fluxes between water and sediment, while the latter dominates concentrations in the water column.

### 9.1.3 Future research

The study has highlighted several aspects that merit further research and there is also potential for extending and improving the work undertaken here.

- (1) It has been suggested that re-suspension is exacerbated by greater draw down of the reservoir surface and that re-suspended particles become the regulating constituents of turbidity, colour and Fe and Mn content in the water column as reservoir draw down progresses, thereby linking the aspects of water quality to operation of the reservoir. This conclusion should be further tested through appropriate monitoring for a range of reservoir operating conditions. Such investigations are not only beneficial with regards to the re-suspension phenomena, but increased draw down has also been associated with shorter stratification periods (Effler and Bader, 1998) which in itself may cause problems, e.g., mixing of Fe and Mn rich bottom waters into a reduced volume water column. One outcome of such a monitoring effort, for example, could be the establishment of a draw down threshold value, beyond which re-suspension becomes a critical factor in determining the reservoir water quality and which provides a guideline when assigning abstraction quantities. This would, at the same time, provide a step towards implementing the EC Water Framework Directive, which states that: 'control of quantity is an ancillary element in securing good water quality and therefore, measures of quantity, serving the objection of ensuring good quality, should also be established'. In addition, a modelling study investigating different wind speeds and water depths could provide estimates of when the mean grain size on the reservoir bottom would be disturbed. The practicalities and limitations of assigning a general draw down

limit need to be assessed in the context of varying natural meteorological and hydrological forcing conditions, which greatly control lake/reservoir internal processes throughout the year as well as between years.

- (2) If any future monitoring was to be undertaken in the Megget catchment, this should include all streams that supply the reservoir, but in particular Craigierig Burn, in order to investigate the nature of the unusually high nutrient loadings observed during this sampling programme. The current sampling has identified distinct differences in the baseflow chemistry of streams draining the northern part of the catchment, compared to those in the south, and the nature of these differences as well as the role of the underlying geology may also be illuminated by more detailed sampling efforts. An integral part of future sampling initiatives should be dedicated to the collection of high-flow chemistry data from all streams as such information are required to quantify the disproportionate amount of metals and nutrients delivered during relatively few events and also to establish loading estimates mass balance calculations, useful for efficient water quality management of the reservoir. Moreover, including more sites in the event-based sampling is essential to better characterise the end-member distribution in the catchment and improve the reliability of the conceptual EMMA model. This would also provide an indication of how many samples are required to reliably estimate the high-flow end-member composition when the method is applied to other catchments. Such efforts could be supported by detailed catchment studies on soilwater chemistry and distribution and further improve the characterisation of the highflow end-member.

- (3) Reliable tools in the form of predictive models are widely desired by lake and reservoir managers to guide the management decisions and to improve or maintain the water quality of a particular water body, which in the light of the EC Water Framework Directive has become an even more pressing need. Thus, future attempts, in which Fe and Mn concentrations are to be predicted, require refinement of the applied conceptual catchment model and improvement of its ability to quantitatively predict loading for these components. This objective may be approached by improving the end-member definition, and, if possible, incorporating a third end-member, which represents the Fe and Mn rich waters in the riparian zone.
- (4) Results from this study also provide the scientific background information for quantifying the major fluxes of Fe and Mn into, within and out off the reservoir. Using the acquired knowledge about the dominant sink and source terms identified in this study, a simple Fe and Mn mass balance for the reservoir can be established. However, care must be taken when incorporating the results from the laboratory experiments and more detailed knowledge of the high-flow loading patterns of all streams would also be of advantage for more reliable mass balance estimations.

#### 9.1.4 Management perspectives and wider implications

This study suggests that processes of re-suspension and diffusion have significantly contributed to the water quality problems encountered at the Megget Reservoir in 1997/98, exacerbated by the draw down of the reservoir to 13% of its capacity (28m below maximum WSE). There are other factors that may have added to the problem,

such as slumping of sediments into the reservoir from the destabilised slopes or input of reduced, metal enriched soilwater draining from the de-watering sites of the reservoir, but these were not considered here. Although the relative contribution of the two main processes, re-suspension and diffusion, has not been quantified within this study, the overall findings suggest that re-suspension is far more important in regulating colour, Fe and Mn content in the water column of the Megget Reservoir during such dramatic draw down events. It has further been shown that during autumn and winter storm events high loadings of colour, Fe and Mn are delivered to the reservoir via runoff from the catchment area. While usually diluted by a large volume water column, the impact of such high loadings on the water quality increases as the water volume of the receiving water body declines. Managers need to be cognisant of the occurrence and scale of these event processes so that related impacts on common measures of water quality can be foreseen for future draw-down events and appropriate measures, e.g., re-direction of supply route via other reservoirs to guarantee the water supply during artificial draw down, can be taken well in advance. There exists a direct link between the water quantity in the reservoir and the quality of the water, and severe water quality costs may arise when catchment runoff cannot match the amount of abstracted water that is required to (1) guarantee the required water supply for the communities and (2) to provide the seasonally varying compensation releases which during the summer period average around 41 ML day<sup>-1</sup> (Fox and Johnston, 1997). This realisation is particularly important in the light of the uncertainties of climate change outcomes, i.e., possible longer periods of drought followed by heavy storms may considerably shift this water quantity-quality balance.

Release of Fe and Mn from the sediments becomes important during stratification of the Megget Reservoir when the dilution effect of the high-volume surface water is reduced and Fe and Mn accumulate in the bottom waters (hypolimnion) of the reservoir. Where multiple abstraction structures are installed, as at the Megget Reservoir, selective withdrawal from the epilimnion or the metalimnion of the reservoir body during this period is advisable, since this, firstly, prevents high concentrations of remobilised species in the abstracted water and secondly, also minimises the potential of hypolimnic re-suspension caused by abstraction induced currents.

In many systems artificial aeration of the water column has been suggested as a management tool, to either de-stratify the entire water column or to re-oxygenate anoxic bottom waters in order to control the release of metals or nutrients from the sediments and also to reduce their concentration in the water column. The success of such measures strongly depends on system specific characteristics and may not necessarily lead to the desired results (Zaw and Chiswell, 1999); on the contrary it may even cause further problems (see Straškraba *et al.* 1993). The results from this study have indicated that increased metal concentrations in the Megget Reservoir currently only occur when the reservoir is stratified and are limited to the bottom waters (hypolimnion) of the system. Thus, under normal reservoir operation (reservoir content: ~70-100% full), stratification does not pose a problem for the quality of the water given that abstraction from the hypolimnion can and should be avoided. Artificial de-stratification and complete mixing of the system, if applied, would only provide relatively little benefit, namely dispersing the enriched bottom layers and diluting the high Fe and Mn concentration by the high volume of the meta- and epilimnic water body. On the contrary, the operation of the de-stratification/aeration facility installed at the bottom of

the Megget Reservoir may even have the opposite effect, as it is expected to introduce a high degree of turbulence into the system, promoting the re-suspension of large quantities of fine sediments from the bottom of the reservoir, and thereby re-introducing Fe and Mn into the water column together with inorganic tripton and humic substances. If necessary in the future, artificial aeration of the Megget water column should be within the hypolimnion but well above the sediment-water interface.

It has further been shown that peak Fe and Mn inputs into the reservoir occur during storm events at the end of the summer period, where the reservoir level is naturally drawn down due to increased water supply demands and reduced catchment inputs during the dry season. The high loading events also coincide with the autumn turnover of the reservoir, which is associated with the dispersion of Fe- and Mn-rich hypolimnic waters into the mixed water column and with local re-suspension of bottom sediment. This natural increase in external and internal Fe and Mn loading during autumn should be considered when planning maintenance work on the reservoir structure, as any further artificial draw down of the reservoir should be avoided at that time of year. Again, future predicted climate change outcomes, such as prolonged drought during summer followed by heavy storms, may result in concentrated fluxes of Fe and Mn into an already depleted reservoir volume and management strategies for maintaining consistent water quality need to be assessed and possibly altered.

The study has shown that event sampling is essential to reliably assess contributions and input from the catchment area, while long-term monitoring under different runoff condition is necessary to observe variability in loadings and determines the expected ranges. These findings are particularly relevant for the implementation of the EC Water

Framework Directive, as the inter-annual variability in catchment inputs and subsequent effects on lakes and reservoir must be considered when assigning load limits and/or load reduction goals for the purpose of improving or maintaining water quality.

The conceptual catchment model developed in this study has shown great utility as a management tool for predicting the hydrochemical stream response to runoff events and also to identify critical periods of high Fe and Mn loadings. Many managers will find such predictions attractive, as a representation of the inter-annual variability in stream loadings, and as a basis to evaluate the impacts of natural variations in ambient forcing conditions and resulting stream loading patterns on reservoir water quality. It additionally serves as a baseline from which future climate change scenarios and possible water quality impacts can be evaluated.

## 9.2 Conclusions

The study has identified a variety of internal and external processes that affect the water quality of the Megget Reservoir, the most important of which are summarised in *Figure 9. 1*. Furthermore, the study has demonstrated the high degree of complexity and interconnectivity between these processes, and also indicated the important influence of reservoir operational rules on water quality. Processes in the catchment area displayed a high degree of spatial and temporal variability and have highlighted the need for event-based sampling. A conceptual model has been developed by which stream hydrochemical changes through time can be represented. This conceptualisation of the system behaviour shows considerable utility as a management tool for identifying critical periods of high Fe and Mn loadings, but at present has limitations in

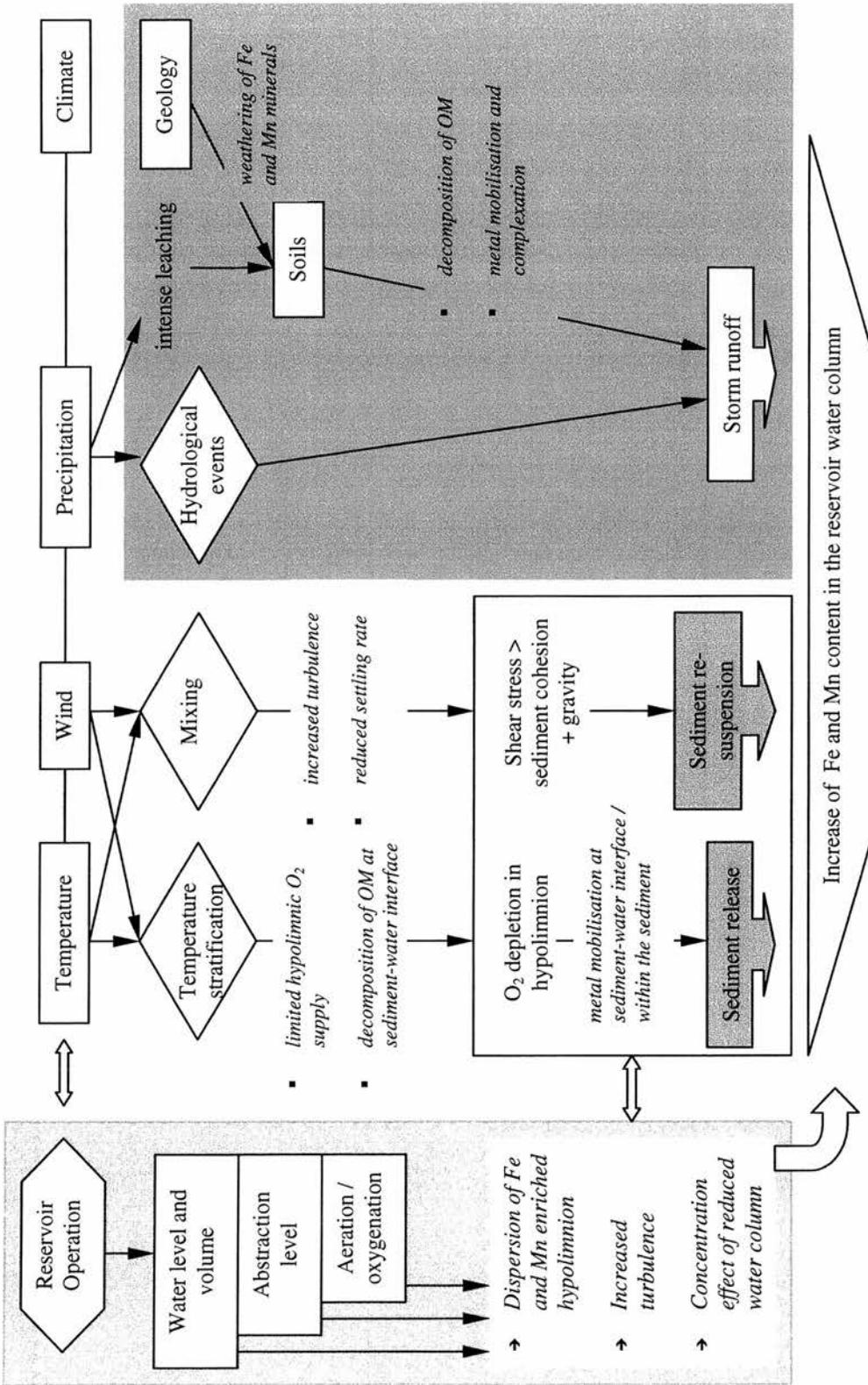


Figure 9. 1: Internal and external factors and processes influencing the iron and manganese concentrations in the water column of the Megget Reservoir (O<sub>2</sub>=oxygen; OM=organic matter)

quantitatively predicting Fe and Mn concentrations in the streams, and as such requires further refinement.

Results such as presented here may be of considerable value in supporting the development of suitable monitoring schemes and management strategies used for the protection and improvement of water quality in drinking water supplies and their catchment areas. As such, the information gained from this study may assist water authorities and controlling bodies in implementing targets under the EC Water Framework Directive. Moreover, the effective integration of the results into reservoir management strategies serves to enhance the credibility of and utility of future management protocols.

# 10

## References

---

- Adami, G, Barbieri, P and Reisenhofer, E, 1999. A comparison of five sediment decomposition procedures for determining anthropogenic trace metal pollution. *International Journal of Environmental Analytical Chemistry*, 75(3): 251-260.
- Aitkenhead, J A, Hope, D and Billett, M F, 1999. The relationship between dissolved organic carbon in stream water and soil organic pools at different spatial scales. *Hydrological Processes*, 13: 1289-1302.
- APHA, 1998. Standard Methods for the Examination of Water and Wastewater. American Public Health Association, Washington DC.
- Atkinson, S, 1619. The Discoverie and Historie of Gold Mines in Scotland. Republished by the Bannatyne Club, Edinburgh 1825.
- AWWA, 1987. Research needs for the treatment of iron and manganese. Report of the AWWA Trace Inorganic Substances Committee. *Journal of the American Water Works Association*, 79: 119-122.
- Bacchini, P, 1985. Phosphate interactions at the sediment-water interface. In: Stumm, W (Editor), *Chemical processes in lakes*. John Wiley & Sons, pp. 189-205.
- Balistrieri, L S, Murray, J W and Paul, B, 1992. The cycling of iron and manganese in the water column of Lake Sammamish, Washington. *Limnology and Oceanography*, 37(3): 510-528.
- Baveye, P, McBride, M B, Bouldin, D, Hinesly, T D, Dahdoh, M S A and Abdel-Sabour, M F, 1999. Mass balance and distribution of sludge-born trace elements in a silt loam soil following long-term applications of sewage sludge. *The Science of the Total Environment*, 227(1): 13-28.
- Becker, A and McDonnell, J J, 1998. Topographical and ecological controls of runoff generation and lateral flows in mountain catchments. In: Kovar, K, Tappeiner, U, Peters, N E and Craig, R G (Editors), *Hydrology, Water Resources and Ecology in Headwaters (Proceedings of the HeadWater'98 Conference, Meran/Merano, Italy, April 1998)*. IAHS Publications. IAHS, Wallingford, pp. 199-206.

- Bendell-Young, L and Harvey, H H, 1992a. The relative importance of manganese and iron oxides and organic matter in the sorption of trace metals by surficial lake sediment. *Geochimica et Cosmochimica Acta*, 45: 1175-1186.
- Bendell-Young, L and Harvey, H H, 1992b. Geochemistry of Mn and Fe in lake sediments in relation to lake acidity. *Limnology and Oceanography*, 37(3): 603-613.
- Bergen, M and Tsukada, D, 1994. 1993-94 SCCWRP Annual Report: Sediment Grain Size: Results of an Interlaboratory Intercalibration Experiment. SCCWRP. 23-06-2002, <http://www.sccwrp.org/pubs/annrpt/93-94/contents.htm>.
- Beven, K J and Germann, P F, 1982. Macropores and water flow in soils. *Water Resources Research*, 18: 1311-1325.
- BGS British Geological Survey, 1993. Regional geochemistry of southern Scotland and part of northern England. British Geological Survey, Keyworth, Nottingham.
- Billett, M F and Cresser, M S, 1992. Predicting stream-water quality using catchment and soil chemical characteristics. *Environmental Pollution*, 77(2-3): 263-268.
- Billett, M F and Cresser, M S, 1996. Evaluation of the use of soil ion exchange properties for predicting streamwater chemistry in upland catchments. *Journal of Hydrology*, 186: 375-394.
- Billett, M F, Lowe, J A H, Black, K E and Cresser, M S, 1996. The influence of parent material on small-scale spatial changes in streamwater chemistry in Scottish upland catchments. *Journal of Hydrology*, 187: 311-331.
- Blösch, J, 1994. A review of methods used to measure sediment resuspension. *Hydrobiologia*, 284: 13-18.
- Blösch, J, 1995. Mechanisms, measurements and importance of sediment resuspension in lakes. *Marine and Freshwater Research*, 46: 295-304.
- Bonanni, P, Caprioli, R, Ghiara, E, Mignuzzi, C, Orlandi, C, Paganin, G and Monti, A, 1992. Sediment and interstitial water chemistry of Orbetello lagoon (Grosseto, Italy); nutrient diffusion across the water-sediment interface. *Hydrobiologia*, 235/236: 553-568.
- Bonell, M and Fritsch, J M, 1997. Combining hydrometric-hydrochemistry methods: a challenge for advancing runoff generation process research. *Hydrochemistry*, 244: 165-184.
- Bown, C J and Shipley, B M, 1982. Soil Survey of Scotland: South-East Scotland (sheet 7). The Macaulay Institute of Soil Research, Aberdeen.
- Bragg, O M, 2002. Hydrology of peat-forming wetlands in Scotland. *The Science of the Total Environment*, 294(1-3): 111-130.

- Brassard, P, Kramer, R J, McAndrews, A and Mueller, E, 1994. Metal-sediment interaction during resuspension. *Hydrobiologia*, 284: 101-112.
- Brown, M P, Longabucco, P, Rafferty, M R, Robillard, P D, Walter, M F and Haith, D A, 1989. Effects of Animal Waste control practices on non-point source phosphorous loading in the West Branch of the Delaware River watershed. *Journal of Soil and Water Conservation*, 44(1): 67-70.
- Brown, V A, McDonnell, J J, Burns, D A and Kendall, C, 1999. The role of event water, a rapid shallow flow component, and catchment size in summer stormflow. *Journal of Hydrology*, 217: 171-190.
- Bryant, C L, Farmer, J G, MacKenzie, A B, Bailey-Watt, A E and Kirika, A, 1997. Manganese behaviour in sediments of diverse Scottish freshwater lochs. *Limnology and Oceanography*, 42(5): 918-929.
- Burns, D A, J.J., M, Hooper, R P, Peters, N E, Freer, J E, Kendall, C and Beven, K, 2001. Quantifying contributions to storm runoff through end-member mixing analysis and hydrologic measurements at the Panola Mountain Research Watershed (Georgia, USA). *Hydrological Processes*, 15: 1903-1924.
- Buttle, J M, 1994. Isotope hydrograph separations and rapid delivery of pre-event water from drainage basins. *Progress in Physical Geography*, 18(1): 16-41.
- Buurman, P, 1996. Particle Size Analysis and mineralogical analysis. In: Buurman, P, van Lagen, B and E.J., V (Editors), *Manual for soil and water analysis*. Backhuys Publishers, Leiden, pp. 251-278.
- Caetano, M, Madueira, M J and Vale, C, 2003. Metal Remobilisation during resuspension of anoxic contaminated sediment: short-term laboratory study. *Water, Air and Soil Pollution*, 143(1-4): 23-40.
- Calmano, W, Hong, J and Förstner, U, 1993. Binding and mobilisation of heavy metals in contaminated sediments affected by pH and redox potential. *Water Science Technology*, 28(8-9): 223-235.
- Cameron, A J and Liss, P S, 1984. The stabilisation of dissolved iron in freshwaters. *Water Research*, 18: 179-185.
- Campbell, P G C and Torgersen, T, 1980. Maintenance of iron meromixis by iron redeposition in a rapidly flushed monolimnion. *Canadian Journal of Fishery and Aquatic Sciences*, 8: 1303-1313.
- Carling, P A, Irvine, B J, Hill, A and Wood, M, 2001. Reducing sediment inputs to Scottish streams: a review of the efficacy of soil conservation practices in upland forestry. *The Science of the Total Environment*, 265(1): 209-229.
- CEC Commission of European Communities, 1980. Council Directive 80/778/EEC relating to the quality of water intended for human consumption. *Official Journal*, L/229: 1-23.

- CEC Commission of European Communities, 2000. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. *Official Journal*, L/327: 1-73.
- Chapman, P J, Reynolds, B and Wheater, H S, 1997. Sources and controls of calcium and magnesium in storm runoff: the role of groundwater and ion exchange reactions along water flow path. *Hydrology and Earth System Sciences*(3): 671-985.
- Chapman, R J, Leake, R C and Floyd, J D, 2000. Regional variation in gold mineralization in the vicinity of the Glengaber Burn, Scottish Borders. *Scottish Journal of geology*, 36(2): 165-176.
- Chapman, D, Edwards, A C and Cresser, M S, 2001. The nitrogen composition of streams in upland Scotland: Some regional and seasonal differences. *The Science of the Total Environment*, 265: 65-83.
- Chiswell, B and Mokhtar, M B, 1986. The speciation of manganese in freshwaters. *Talanta*, 33: 669-677.
- Christophersen, N, Neal, C, Hooper, R P, Vogt, R D and Andersen, S, 1990. Modelling streamwater chemistry as a mixture of soilwater end-members- A step towards second-generation acidification models. *Journal of Hydrology*, 116: 307-320.
- Christophersen, N and Hooper, R P, 1992. Multivariate analysis of stream water chemical data: The use of Principal Component Analysis for the End-Member Mixing problem. *Water Resources Research*, 28(1): 99-108.
- Christophersen, N, Clair, T A, Driscoll, C T, Jeffries, D S, Neal, C and Semkin, R G, 1994. Hydrochemical studies. In: Moldan, B and Cerny, J (Editors), *Biogeochemistry of small catchments: A tool for environmental research*. John Wiley & Sons, New York, pp. 286-297.
- Church, M R, 1997. Hydrochemistry of forested catchments. *Annual Review of Earth Planet Sciences*, 25: 23-59.
- Ciceri, G, Maran, S, Martinotti, W and Queirazza, G, 1992. Geochemical cycling of heavy metals in a marine coastal area: benthic flux determination from pore water profiles and in situ measurements using benthic chambers. *Hydrobiologia*, 235/236: 501-517.
- Colby, C J, 2000. Megget reservoir - first year report, University of St Andrews, St Andrews.
- Collienne, R H, 1983. Photoreduction of iron in the epilimnion of acidic lakes. *Limnology and Oceanography*, 28(1): 83-100.
- Cornett, R J, Chant, L A, Risto, B A and Bonvin, E, 1994. Identifying resuspended

- particles using isotope ratios. *Hydrobiologia*, 284: 69-77.
- Creig, D C, 1969. Report on the geology of the Megget Valley, Selkirkshire. 66/1/EIA, Institute of Geological Sciences.
- Cresser, M S, Killham, K and Edwards, T, 1993. Soil chemistry and its applications. *Cambridge Environmental Chemistry Series*. Cambridge University Press, Cambridge.
- Cresser, M S, Smart, R, Billett, M F, Soulsby, C, Neal, C, Wade, A, Langan, S and Edwards, A C, 2000. Modelling water chemistry for a major Scottish river from catchment attributes. *Journal of Applied Ecology*, 37(1): 171-184.
- Curtis, P J, 1993. Effect of dissolved organic carbon on  $^{59}\text{Fe}$  scavenging. *Limnology and Oceanography*, 38(7): 1554-1561.
- Cuthbertson and Partners, 1977. Megget Scheme, Megget Reservoir - Report for the Lothian Regional Council, Water Supply Services. Contract No.301.3/C.7, Edinburgh.
- Davis, J C, 1986. Statistics and data analysis in geology. John Wiley & Sons, New York.
- Davison, W, 1981. Supply of iron and manganese to anoxic lake basin. *Nature*, 290: 242-243.
- Davison, W, Woof, C and Rigg, E, 1982. The dynamics of iron and manganese in a seasonally anoxic lake; direct measurement of fluxes using sediment traps. *Limnology and Oceanography*, 27(6): 987-1003.
- Davison, W and Seed, G, 1983. The kinetics of the oxidation of ferrous iron in synthetic and natural waters. *Geochimica et Cosmochimica Acta*, 47(67-79).
- Davison, W, 1985. Conceptual models for transport at a redox boundary. In: Stumm, W (Editor), *Chemical processes in lakes*. John Wiley & Sons, London, pp. 31-53.
- Davison, W and De Vitre, R R, 1992. Iron particles in freshwater. In: Buffle, J and Van Leuwen, H P (Editors), *Environmental particles*. Lewis, Boca Raton, pp. 315-355.
- Davison, W, 1993. Iron and manganese in lakes. *Earth-Sciences Reviews*, 34: 119-163.
- Dawson, J J C, Bakewell, C and Billett, M F, 2001. Is in-stream processing an important control on spatial changes in carbon fluxes in headwater catchments? *The Science of the Total Environment*, 265: 153-167.
- De Vitre, R R, Buffle, J, Perret, D and Baudat, R, 1988. A study of iron and manganese transformations at a  $\text{O}_2/\text{S}(-\text{II})$  transition layer in a eutrophic lake (Lake Bret, Switzerland): A multimethod approach. *Geochimica et Cosmochimica Acta*, 52: 1601-1613.

- Dietrich, V and Schwadner, F, 2000. Preparation of glass beads and powder pills for XRF analysis of silicic and calcareous rocks. Institut fuer Mineralogie und Petrographie, Eidgenössische Technische Universität Zürich (ETHZ). 05-Feb-02, [http://www.xrf.ethz.ch/forms/xrf\\_instr\\_manual\\_en.pdf](http://www.xrf.ethz.ch/forms/xrf_instr_manual_en.pdf).
- Doherty, G B, Brunskill, G J and Ridd, M J, 2000. Natural and enhanced concentrations of trace metals in sediments of Cleveland Bay, Great Barrier Reef Lagoon, Australia. *Marine Pollution Bulletin*, 41(7-12): 337-344.
- Drever, J I, 1997. The geochemistry of natural waters. Prentice Hall, Upper Saddle River.
- Effler, S W and Bader, A P, 1998. A limnological analysis of Cannonsville Reservoir, NY. *Journal of Lake and Reservoir Management*, 14(2-3): 125-139.
- Effler, S W, Gelda, R K, Johnson, D L and Owens, E M, 1998a. Sediment resuspension in the Cannonsville Reservoir. *Journal of Lake and Reservoir Management*, 14(2-3): 225-237.
- Effler, S W, Perkins, M G and Johnson, D L, 1998b. The optical water quality of Cannonsville Reservoir: Spatial and temporal patterns, and the relative roles of phytoplankton and inorganic tripton. *Journal of Lake and Reservoir Management*, 14(2-3): 238-253.
- Elliott, C and Mickelson, S, 2001. Quality Assurance Project Plan for the Duwamish Estuary Water Quality Assessment. King County Department of Natural Resources, Water and Land Resources Division. 01-08-2001, [http://dnr.metrokc.gov/wlr/envlab/Lab\\_docs/CustomDocs.htm](http://dnr.metrokc.gov/wlr/envlab/Lab_docs/CustomDocs.htm).
- Emerson, D, 2000. Microbial oxidation of Fe(II) and Mn(II). In: Lovley, D R (Editor), *Environmental Microbe-Metal Interactions*. ASM Press, Washington, pp. 31-52.
- Erickson, M J and Auer, T, 1998. Chemical exchange at the sediment water interface of Cannonsville Reservoir. *Journal of Lake and Reservoir Management*, 14(2-3): 266-277.
- Evans, R D, 1994. Empirical evidence of the importance of sediment resuspension in lakes. *Hydrobiologia*, 284: 5-12.
- Farmer, J G and Lowell, M A, 1986. Natural enrichment of arsenic in Loch Lomond sediments. *Geochimica et Cosmochimica Acta*, 50: 2059-2067.
- Farmer, J G, Bailey-Watts, A E, Kirika, A and Scott, C, 1994. Phosphorous fractionation and mobility in Loch Leven sediments. *Aquatic conservation: marine and freshwater ecosystems*, 4: 45-56.
- Ferek, F and Jenkins, R, 1998. Specimen preparation procedures in x-ray fluorescence analysis. In: Buhrke, V E, Jenkins, R and Smith, D K (Editors), *A practical guide for the preparation of specimen for x-ray fluorescence and x-ray*

- diffraction analysis*. John Wiley & Sons, New York.
- Ferrier, R C, Jenkins, A, Miller, J D, Walker, T A B and Anderson, H A, 1990a. Assessment of wet deposition mechanism in an upland Scottish catchment. *Journal of Hydrology*, 113: 285-296.
- Ferrier, R C, Walker, T A B, Harriman, R, Miller, J D and Anderson, H A, 1990b. Hydrological and hydrochemical fluxes through vegetation and soil in the Allt a' Mharcaidh, western Cairngorms, Scotland: their effect on stream water quality. *Journal of Hydrology*, 116: 251-266.
- Fiebig, D M, Lock, M A and Neal, C, 1990. Soil water in the riparian zone as a source of carbon for a headwater stream. *Journal of Hydrology*, 116: 217-237.
- Fölster, J, 2001. Significance of processes in the near-stream zone on stream water acidity in a small acidified forested catchment. *Hydrological Processes*, 15(2): 201-217.
- Ford, D E, 1990. Reservoir Transport Processes. In: Thornton, K W, Kimmel, B L and Payne, F E (Editors), *Reservoir Limnology: Ecological Perspectives*. John Wiley & Sons, New York, pp. 15-42.
- Förstner, U, 1981. Metal Pollution Assessment from Sediment Analysis. In: Förstner, U and Wittmann, G T W (Editors), *Metal Pollution in the Aquatic Environment*. Springer-Verlag, Berlin, pp. 110-194.
- Förstner, U and Wittmann, G T W, 1981. *Metal Pollution in the Aquatic Environment*. Springer Verlag, Berlin.
- Foster, H L, Alexander, S, Locks, T, Wheater, H S, Lees, M J and Reynolds, B, 1997. Scale dependence of the episodic hydrochemical response of nested catchments at Plynlimon. *Hydrology and Earth System Sciences*, 1(3): 639-651.
- Foster, H L, 2000. Assessment and Modelling of Spatio-temporal Variability in Upland Stream Chemistry. PhD dissertation, Imperial College of Science, Technology and Medicine, London.
- Fox, I A and Johnson, R C, 1997. The hydrology of the River Tweed. *The Science of the Total Environment*, 194/195: 163-172.
- Gálvez, J A and Niell, F X, 1992. Sediment resuspension in a monomictic eutrophic reservoir. *Hydrobiologia*, 235/236: 133-141.
- Gavin, K G, Farmer, J G, Graham, M C, Kirika, A and Britton, A, 2001. Manganese-humic interactions in the catchment, water and sediment of Loch Bradan, S.W. Scotland. In: Swift, R S and Spark, K M (Editors), *Understanding and managing Organic Matter in Soils, Sediments and Waters*. IHSS.
- Gibbs, R J, 1977. Clay mineral segregation in the marine environment, *Journal of Sedimentology and Petrology*, pp. 237-243.

- Giusti, L and Neal, C, 1993. Hydrological pathways and solute chemistry of storm runoff at Dargall Lane, southwest Scotland. *Journal of Hydrology*, 142: 1-27.
- Gloor, M, Wüest, A and Münnich, M, 1994. Benthic boundary mixing and resuspension induced by internal seiches. *Hydrobiologia*, 284: 59-68.
- Golterman, H L, Sly, P G and Thomas, R L, 1983. Study of the relationship between water quality and sediment transport: A guide for the Collection and Interpretation of Sediment Quality Data. United Nations Educational Scientific and Cultural Organisation (UNESCO), Paris.
- Gomez, E, Durillon, C, Rofes, G and Picot, B, 1999. Phosphate adsorption and release from sediments of brackish lagoons; pH, O<sub>2</sub> and loading influence. *Water Research*, 33(10): 2437-2447.
- Gorham, E and Swaine, D J, 1965. The influence of oxidising and reducing conditions upon the distribution of some elements in lake sediments. *Limnology and Oceanography*, 10: 268-279.
- Graham, M C, Gavin, K G, Farmer, J G, Kirika, A and Britton, A, 2002. Processes controlling the retention and release of manganese in the organic-rich catchment of Loch Bradan, SW Scotland. *Applied Geochemistry*, 17: 1061-1067.
- Grieve, I C, 1984a. Concentrations and annual loading of dissolved organic matter in a small moorland catchment. *Freshwater Biology*, 14: 533-537.
- Grieve, I C, 1984b. Relationships among dissolved organic matter, iron and discharge in a moorland stream. *Earth Surfaces Processes and Landforms*, 9: 35-41.
- Grieve, I C and Marsden, R L, 2001. Effects of forest cover and topographic factors on TOC and associated metals at various scales in western Scotland. *The Science of the Total Environment*, 265(1-3): 143-151.
- Grzybowski, D S, 2001. A study of catchment discharge from tributaries that supply the Megget Reservoir in the Southern Uplands of Scotland. Undergraduate dissertation, University of St Andrews, St Andrews.
- Hagopian-Babikian, S, Hamilton, R F, Iyengar, S S, Jenkin, R and Renault, J, 1998. General Introduction. In: Buhrke, V E, Jenkins, R and Smith, D K (Editors), *A practical guide for the preparation of specimen for X-Ray Fluorescence and X-Ray Diffraction Analysis*. John Wiley & Sons, New York.
- Håkanson, L and Jansson, M, 1983. Principles of Lake Sedimentology. Springer Verlag, Berlin.
- Hamilton-Taylor, J and Davison, W, 1995. Redox-driven cycling of trace elements in lakes. In: Lerman, A, Imboden, D M and Gat, J R (Editors), *Physics and Chemistry of Lakes*. Springer-Verlag, Berlin, pp. 217-263.
- Hangen, E, Lindenlaub, M, Leibundgut, C and Wilpert, v K, 2001. Investigating the mechanism of stormflow generation by natural tracers and hydrometric data:

- A small catchment study in the Black Forest, Germany. *Hydrological Processes*, 15(2): 183-199.
- Haria, A H, Shand, P and Soulsby, C, 2002. Bedrock groundwater processes during streamflow generation in the riparian zone of an upland catchment in Wales, UK. In: Cunnane, C and Barrins, J (Editors), *The Third Inter-Celtic Colloquium on Hydrology and Management of Water Resources*. National University of Ireland, Galway, Ireland.
- Harriman, R, Likens, G E, Hultberg, H and Neal, C, 1994. Influence of management practices in catchments on freshwater acidification: Afforestation in the United Kingdom and North America. In: Steinberg, C E W and Wright, R F (Editors), *Acidification of freshwater ecosystems*. John Wileys & Sons, New York, pp. 83-101.
- Heal, K V, Kneale, P E and McDonald, A T, 1995. Manganese mobilisation and runoff processes in upland catchments, BHS 5th National Hydrology Symposium, Edinburgh, pp. 9.11-9.18.
- Heal, K V, Kneale, P E and McDonald, A T, 1997. A hydrochemical basis for managing manganese in water supplies from upland basins. In: Webb, B (Editor), *Freshwater Contamination (Proceedings of the Rabat Symposium, April-May, 1997)*. IAHS Publications. IAHS, Wallingford, pp. 367-374.
- Heal, K V, 2001. Manganese and land-use in upland catchments in Scotland. *The Science of the Total Environment*, 265: 169-179.
- Heal, K V, Kneale, P E and McDonald, A T, in press. Manganese in runoff from upland catchments: temporal patterns and control on mobilisation. *Hydrological Sciences Journal*.
- Hem, J D, 1985. Study and interpretation of the chemical characteristics of natural waters. *USGS Water-Supply Paper 2254*. USGS, Seattle, Washington.
- Hensel, D and Elsenbeer, H, 1997. Stormflow generation in tropical rainforest: a hydrochemical approach, *Hydrochemistry (Proceedings of the Rabat Symposium, April 1997)*. IAHS Publications. IAHS, Wallingford, pp. 227-234.
- Hering, J G and Stumm, W, 1990. Oxidative and reductive dissolution of minerals. In: Hochella, M F and White, A F (Editors), *Mineral-water interface geochemistry*. Reviews in Mineralogy. Mineralogical Society of America, pp. 427-465.
- Hewlett, J D and Hibbert, A R, 1967. Factor affecting the response of small watersheds to precipitation in humid areas, *International Symposium on Forestry and Hydrology*. Pergamon, New York, pp. 275-290.
- Hicks, R E, Owen, C J and Aas, P, 1994. Deposition, resuspension, and decomposition of particulate organic matter in sediments of Lake Itasca, Minnesota, USA. *Hydrobiologia*, 284: 79-91.
- Hill, T and Neal, C, 1997. Spatial and temporal variations in pH, alkalinity and

- conductivity in surface runoff and groundwater for the Upper River Severn catchment. *Hydrology and Earth System Sciences*, 1(3): 697-715.
- Hoeg, S, Uhlenbrook, S and Leibundgut, C, 2000. Hydrograph separation in a mountainous catchment - combining hydrochemical and isotopic tracers. *Hydrological Processes*, 14: 1199-1216.
- Holden, J and Burt, T P, 2000. Spatial and temporal distribution of runoff generation in upland blanket peat; implications of plot, hillslope, and catchment scale monitoring, BHS 7th National Hydrology Symposium. British Hydrological Society, Newcastle-upon-Tyne, pp. 2.89-2.96.
- Holden, J, Burt, T P and Cox, N J, 2001. Macroporosity and infiltration in blanket peat: The implications of tension disc infiltrometer measurements. *Hydrological Processes*.
- Hongve, D, 1997. Cycling of iron, manganese and phosphate in a meromictic lake. *Limnology and Oceanography*, 42(4): 635-647.
- Hooper, R P, Christophersen, N and Peters, N E, 1990. Modelling streamwater chemistry as a mixture of soilwater end-members - An application to the Panola Mountain catchment, Georgia, U.S.A. *Journal of Hydrology*, 116: 321-343.
- Hooper, R P, Aulenbach, B T, Burns, D A, McDonnell, J J, Freer, J E, Kendall, C and Beven, K, 1998. Riparian control of stream chemistry: implications for hydrological basin models., *Hydrology, Water Resources and Ecology in Headwaters (proceedings of the HeadWater '98 conference, Merano, Italy)*. IAHS Publ. No 248, pp. 451-458.
- Hooper, R P, 2001. Applying the scientific method to small catchment studies: a review of the Panola Mountain experience. *Hydrological Processes*, 15: 2039-2050.
- Horne, A J and Goldman, C R, 1994. *Limnology*. McGraw-Hill, Inc., New York.
- Hsiung, T M and Tissue, T, 1994. Manganese dynamics in Lake Richard B. Russell. In: Baker, L A (Editor), *Environmental Chemistry of Lakes and Reservoirs*. Advances in Chemistry Series. American Chemical Society, Washington, DC, pp. 499-524.
- Hughes, S, Reynolds, B and Roberts, J D, 1990. The influence of land management on concentrations of dissolved organic carbon and its effects on the mobilisation of aluminium and iron in podzol soils in Mid-Wales. *Soil Use Management*, 6: 137-145.
- Hughes, S, Reynolds, B, Hudson, J A and Freeman, C, 1997. Effects of summer drought on peat soil solution chemistry in an acid gully mire. *Hydrology and Earth System Sciences*, 1(3): 661-669.

- Hulscher ten, T E M, Mol, G A J and Lüers, F, 1992. Release of metals from polluted sediments in a shallow lake: quantifying re-suspension. *Hydrobiologia*, 235/236: 97-105.
- Hutchinson, G E, 1957. A treatise on Limnology: Chemistry of Lakes, I, Part 2. John Wiley & Sons, New York.
- Imboden, D M and Wüest, A, 1995. Mixing mechanisms in lakes. In: Lerman, A, Imboden, D M and Gat, J R (Editors), *Physics and chemistry of lakes*. Springer Verlag, Berlin, pp. 83-138.
- James, W F and Barko, J W, 1993. Sediment resuspension, redeposition, and focusing in a small dimictic reservoir. *Canadian Journal of Fishery and Aquatic Sciences*, 50: 1023-1028.
- Jarvie, H P, Neal, C, Leach, D V, Ryland, G P, House, W A and Robson, A J, 1997. Major ion concentrations in the inorganic carbon chemistry of the Humber rivers. *The Science of the Total Environment*, 194/195: 285-302.
- Jarvie, H P, Neal, C, Smart, R, Owen, R, Fraser, D, Forbes, I and Wade, A, 2001. Use of continuous water quality records for hydrograph separation and to assess short term variability and extremes in acidity and dissolved carbon dioxide for the River Dee, Scotland. *The Science of the Total Environment*, 265: 85-98.
- Jenkins, A, Ferrier, R C, Harriman, R and Ogunkoya, Y O, 1994a. A case study in catchment hydrochemistry: conflicting interpretations from hydrological and chemical observations. *Hydrological Processes*, 8: 335-349.
- Jenkins, A, Peters, N E and Rodhe, A, 1994b. Hydrology. In: Moldan, B and Cerny, J (Editors), *Biogeochemistry of small catchments: A tool for environmental research*. John Wiley & Sons, New York, pp. 31-54.
- Jones, J A A, 2002. Natural soil piping, water quality and catchment management in the British Uplands. In: Cunnane, C and Barrins, J (Editors), *The Third Inter-Celtic Colloquium on Hydrology and Management of Water Resources*. National University of Ireland, Galway, Ireland, pp. 98-106.
- Jöreskog, K G, Klován, J E and Reymont, R A, 1976. Geological Factor Analysis. Elsevier Scientific Publishing Company, Amsterdam.
- Jowitt, P W and Hay-Smith, D, 2002. Reservoir yield assessment in a changing Scottish environment. *The Science of the Total Environment*, 294(1-3): 185-199.
- Katsuyama, M, Ohte, N and Kobashi, S, 2001. A three-component end-member analysis of stream water hydrochemistry in a small Japanese headwater forested catchment. *Hydrological Processes*, 15(2): 249-260.
- Kelly, L A, 1992. Dissolved reactive phosphorous release from sediments beneath a freshwater cage aquaculture development in West Scotland. *Hydrobiologia*, 235/236: 569-572.

- Kelts, K R, Schnurrenberger, D, Russell, J, Graber, D and Gregoret, A, 1997. Loss-on-Ignition. Limnological Research Center, University of Minnesota, LRC Core Facility Handbook.
- Kim, K H, 2000. The analysis of soil-metal concentrations and selection of extraction methods. *International Journal of Environmental Health Research*, 10(1): 27-33.
- Kirnbauer, R and Haas, P, 1998. Observations on runoff generation mechanisms in small Alpine catchments. In: Kovar, K, Tappeiner, U, Peters, N E and Craig, R G (Editors), *Hydrology, Water Resources and Ecology in Headwaters (Proceedings of the HeadWater'98 Conference, Meran/Merano, Italy, April 1998)*. IAHS, Wallingford, pp. 239-247.
- Klován, J E, 1975. R- and Q-mode factor analysis. In: McCammon, R B (Editor), *Concepts in Geostatistics*. Springer Verlag, Berlin, pp. 21-69.
- Kondakis, X G, Makris, N, Leotsinidis, M, Prinou, M and Papapetropoulos, T, 1989. Possible health effects of high manganese concentrations in drinking water. *Archive of Environmental Health*, 44: 175-178.
- Kovach, W L, 1995. Multivariate data analysis. In: Maddy, D and Brew, J S (Editors), *Statistical Modelling of Quarternary Science Data*. Quarternary Research Association, Cambridge, pp. 1-36.
- Kuijper, A J, 1996. Sample preparation for x-ray fluorescence analysis. In: Buurman, P, van Lagen, B and Velthorst, E J (Editors), *Manual for soil and water analysis*. Backhuys Publishers, Leiden, pp. 279-286.
- Langan, S J, 1985. Atmospheric deposition, afforestation and water quality at Loch Dee, SW Scotland. PhD dissertation, University of St Andrews, St Andrews.
- Langan, S J, Wade, A, Smart, R, Edwards, A C, Soulsby, C, Billett, M F, Jarvie, H P, Cresser, M S, Owen, R and Ferrier, R C, 1997. The prediction of water quality in a relatively unpolluted major Scottish catchment: current issues and experimental approaches. *The Science of the Total Environment*, 194/195: 419-435.
- Lau, S S S and Chu, L M, 1999. Contaminant release from sediments in a coastal wetland. *Water Research*, 33(4): 909-918.
- Lawrie, T R M and MacGregor, A G, 1946. Water supply from underground sources of South-west Scotland. Wartime Pamphlet No. 29, Geological Survey of Great Britain, South Kensington.
- Laxen, D P H and Harrison, R M, 1981. A scheme for the physiochemical speciation of trace metals in freshwater samples. *The Science of the Total Environment*, 19: 59-82.
- LaZerte, B D and Burling, K, 1990. Manganese speciation in dilute waters of the Precambrian Shield, Canada. *Water Research*, 24: 1097-1101.

- Lick, W and Lick, J, 1988. Aggregation and disaggregation of fine grained sediments. *Journal of Great Lake Research*, 14: 514-523.
- Linnik, P M and Zubenko, I B, 2000. Role of bottom sediments in the secondary Pollution of aquatic environments by heavy metal compounds. *Lakes & Reservoirs: Research and Management*, 5: 11-21.
- Little, D I and McFadzean, C J, 1991. Bradan water treatment works extensions and upgrading. In: Haigh, M D F and James, C P (Editors), *Water and environmental management*. Ellis Horwood, pp. 178-188.
- Livens, F R, 1991. Chemical reactions of metals with humic material. *Environmental Pollution*, 70: 183-208.
- Longabucco, P and Rafferty, M R, 1998. Analysis of material loading to Cannonsville Reservoir: Advantages of event-based sampling. *Lake and Reservoir Management*, 14(2-3): 197-212.
- Loring, D H, 1978. Geochemistry of zinc, copper and lead in the sediments of estuary and Gulf of St Lawrence. *Canadian Journal of Earth Sciences*, 15: 757-772.
- Loring, D H and Rantala, R T T, 1992. Manual for the geochemical analysis of marine sediments and suspended particulate matter. *Earth Sciences Reviews*, 32: 235-283.
- Luetlich, R A, Harleman, D R F and Somlyódy, L, 1990. Dynamic behaviour do suspended sediment concentrations in a shallow lake perturbed by episodic wind events. *Limnology and Oceanography*, 35(5): 1050-1067.
- MacDonald, T D, 1994. Water supply. In: Maitland, P S, Boon, P J and McLusky, D S (Editors), *The fresh waters of Scotland: a national resource of international significance*. Wiley, Chichester, pp. 279-296.
- Maher, L J, 1998. Automating the dreary measurements for loss on ignition. INQUA Sub-Commission on Data-Handling Methods, Newsletter.
- Marsden, M W and Mackay, D W, 2001. Water quality in Scotland: the view of the regulator. *The Science of the Total Environment*, 265: 369-386.
- McAuliffe, T F, Lukatelich, R J, McComb, A J and Qiu, S, 1998. Nitrate applications to control phosphorous release from sediments of a shallow eutrophic estuary: An experimental approach. *Marine and Freshwater Research*, 49(6): 463-475.
- McKnight, D M and Bencala, K E, 1990. The chemistry of iron, aluminium, and dissolved organic material in three acidic, metal-enriched, mountain streams, as controlled by watershed and in-stream processes. *Water Resources Research*, 26(12): 3087-3100.
- Miller, J D, Adamson, J K and Hirst, D, 2001. Trends in stream water quality in Environmental Change Network upland catchments: the first 5 years. *The Science of the Total Environment*, 265: 27-38.

- Mitchell, G and McDonald, A T, 1995. Catchment characterisation as a tool for upland water quality management. *Journal of Environmental Management*, 44(1): 83-95.
- Mortimer, C H, 1941. The exchange of dissolved substances between mud and water in lakes; Part I and II. *Journal of Ecology*, 29: 280-329.
- Mortimer, C H, 1942. The exchange of dissolved substances between mud and water in lakes. *Journal of Ecology*, 30: 147-201.
- Mortimer, C H, 1971. Chemical exchanges between sediments and water in the Great Lakes - Speculations on probable regulatory mechanism. *Limnology and Oceanography*, 16(2): 387-404.
- Mudroch, A and MacKnight, S D (Editors), 1991. Handbook of Techniques for Aquatic sediment sampling. CRC Press, Boca Raton.
- Mulder, J, Pijpers, M and Christophersen, N, 1991. Water flow paths and the spatial distribution of soils and exchangeable cations in an acid rain-impacted and a pristine catchment in Norway. *Water Resources Research*, 27: 2919-2928.
- Mulder, J and Cresser, M S, 1994. Soil and soil solution chemistry. In: Moldan, B and Cerny, J (Editors), *Biogeochemistry of small catchments: A tool for environmental research*. John Wiley & Sons, New York, pp. 107-131.
- Muscutt, A D, Wheater, H S and Reynolds, B, 1990. Stormflow hydrochemistry of a small welsh upland catchment. *Journal of Hydrology*, 116: 239-249.
- Neal, C and Christophersen, N, 1989. Inorganic aluminium-hydrogen relationships for acidified streams: the role of water mixing processes. *The Science of the Total Environment*, 80: 195-203.
- Neal, C, Reynolds, B, Stevens, P and Hornung, M, 1989a. Hydrogeochemical controls for inorganic aluminium in acidic stream and soil waters at two upland catchments in Wales. *Journal of Hydrology*, 106(1-2): 155-175.
- Neal, C, Musgrove, T and Whitehead, P G, 1989b. Predicting the Long-Term Variations in Stream and Lake Inorganic Aluminium Concentrations for Acidic and Acid Sensitive Catchments. *The Science of the Total Environment*, 80(2-3): 205-211.
- Neal, C and Hill, S, 1994. Dissolved inorganic and organic carbon in moorland and forest streams: Plynlimon, Mid-Wales. *Journal of Hydrology*, 153: 231-243.
- Neal, C, Smith, C J, Jeffery, H A, Jarvie, H P and Robson, A J, 1996. Trace element concentrations in the major rivers entering the Humber estuary, NE England. *Journal of Hydrology*, 182: 37-64.
- Neal, C, Wilkinson, J, Neal, M, Harrow, M, Wickham, H, Hill, L and Morfitt, C, 1997a. The hydrogeochemistry of the headwaters of the River Severn, Plynlimon. *Hydrology and Earth System Sciences*, 1(3): 583-617.

- Neal, C, Robson, A J and Christophersen, N, 1997b. Towards coupling hydrological, soil and weathering processes. In: Saether, O M and de, C P (Editors), *Geochemical processes, weathering and groundwater recharge in catchments*. Balkena, pp. 329-380.
- Neal, C, Robson, A J, Jeffery, H A, Harrow, M, Neal, M, Smith, C J and Jarvie, H P, 1997c. Trace element inter-relationships for the Humber rivers: inferences for hydrological and chemical controls. *The Science of the Total Environment*, 194/195: 321-343.
- Neal, C, Hill, T, Hill, S and Reynolds, B, 1997d. Acid neutralisation capacity measurements in surface and groundwaters in the Upper River Severn, Plynlimon: from hydrograph splitting to water flow pathways. *Hydrology and Earth System Sciences*, 3: 687-696.
- Neal, C, Reynolds, B, Adamson, J K, Stevens, P A, Neal, M, Harrow, M and Hill, S, 1998. Analysis of the impacts of major anion variations on surface water acidity particularly to conifer harvesting: case studies from Wales and Northern England. *Hydrology and Earth System Sciences*, 2(2-3): 303-322.
- Neal, C, Reynolds, B and Robson, A J, 1999. Acid neutralisation capacity measurements within natural waters; towards a standardised approach. *The Science of the Total Environment*, 243/244: 233-241.
- Neal, C, Jarvie, H P, Whitton, B A and Gemmill, J, 2000. The water quality of the River Wear, north-east England. *The Science of the Total Environment*, 251/252: 153-172.
- Neal, C, 2001. Alkalinity measurements within natural waters: towards a standardised approach. *The Science of the Total Environment*, 265: 99-113.
- Nealson, K H, Rosson, R A and Myers, C R, 1989. Mechanism of oxidation and reduction of manganese. In: Beveridge, T J and Doyle, R J (Editors), *Metal ions and bacteria*. John Wiley & Sons, New York, pp. 383-411.
- Nembrini, G, Capobianco, J A, Garcia, J and Jaquet, J M, 1982. Interaction between interstitial water and sediment in two cores of Lac Léman, Switzerland. *Hydrobiologia*, 92: 363-375.
- Nirel, P V M and Morel, F M M, 1990. Pitfalls of sequential extractions. *Water Research*, 24: 1055-1056.
- Nix, J, 1981. Contribution of hypolimnetic water on the metalimnic dissolved oxygen minima in a reservoir. *Water Resources Research*, 17(2): 329-332.
- Nürnberg, G K and Dillon, P J, 1993. Iron budgets in temperate lakes. *Canadian Journal of Fishery and Aquatic Sciences*, 50: 1728-1737.
- Nyberg, P, Andersson, P, Degerman, E, Borg, H and Olofson, E, 1995. Labile inorganic manganese-an overlooked reason for fish mortality? *Water, Air and Soil Pollution*, 85: 333-340.

- Owens, E M, 1998. Thermal and heat transfer characteristics of Cannonsville Reservoir. *Journal of Lake and Reservoir Management*, 14(2-3): 152-161.
- Peach, B N and Horne, J, 1899. The Silurian rocks of Britain: Scotland. *Memoirs of the Geological Survey of the United Kingdom*, 1. Geological Survey of the United Kingdom, Glasgow.
- Peart, M R and Fung, L K, 1997. Hydrologic pathways and runoff sources in an upland basin in Hong Kong, *Hydrochemistry (Proceedings of the Rabat Symposium, April 1997)*. IAHS, Wallingford, pp. 267-273.
- Perkin-Elmer-Corporation, 1997. ICP Emission Spectrometry, Optima 3000 Family, Hardware Guide, U.S.A.
- Perkin-Elmer-Corporation, 1997. ICP Emission Spectrometry, ICP Winlab, Software Guide, USA.
- Peters, N E, 1994a. Variations in stream water quality in a forested Piedmont catchment, Georgia, USA: relevance of sampling frequency and design. In: Peters, N E, Allan, R J and Tsirkunov, V V (Editors), *Hydrological, Chemical and Biological Processes of Transport of Contaminants in Aquatic Environments (Proceedings of the Hydrochemistry'93 Symposium, Rostov-on Don, Russia, May 1993)*. IAHS Publications. IAHS, Wallingford, pp. 399-408.
- Peters, N E, 1994b. Hydrologic studies. In: Moldan, B and Cerny, J (Editors), *Biogeochemistry of small catchments: A tool for environmental research*. John Wiley & Sons, New York, pp. 207-228.
- Peters, N E and Ratcliffe, E B, 1997. Tracing hydrologic pathways at the Panola Mountain Research Watershed, Georgia, USA, *Hydrochemistry (Proceedings of the Rabat Symposium, April 1997)*. IAHS Publications. IAHS, Wallingford, pp. 275-289.
- Peters, N E, Ratcliffe, E B and Tranter, M, 1998. Tracing solute mobility at the Panola Mountain Research Watershed, Georgia, USA: variations in Na<sup>+</sup>, Cl<sup>-</sup> and H<sub>4</sub>SO<sub>4</sub> concentrations. In: Kovar, K, Tappeiner, U, Peters, N E and Craig, R G (Editors), *Hydrology, Water Resources and Ecology in Headwaters (Proceedings of the HeadWater'98 Conference, Meran/Merano, Italy, April 1998)*. IAHS Publications. IAHS, Wallingford, pp. 483-490.
- Petry, J, Soulsby, C, Malcolm, I A and Youngston, A F, 2002. Hydrological controls on nutrient concentrations and fluxes in agricultural catchments. *The Science of the Total Environment*, 294: 95-110.
- Pharo, C H and Carmack, E C, 1978. Sedimentation processes in a short residence time lake, Kamloops Lake, British Columbia. *Sedimentology*, 26: 523-541.
- Pierson, D C and Weyhenmeyer, G A, 1994. High resolution measurements of sediment re-suspension above an accumulation bottom in a stratified lake. *Hydrobiologia*, 284: 43-57.

- Pizarro, J, Belzille, N, Filella, M, Leppard, G G, Negre, J, Perret, D and Buffle, J, 1995. Coagulation/sedimentation of submicron particles in a eutrophic lake. *Water Research*, 29(2): 617-632.
- Poppe, L J, Eliason, A H, Fredericks, J J, Rendigs, R R, Blackwood, D and Polloni, C F, 2000. Grain Size Analysis of Marine Sediments: Methodology and Data Processing. Open-File Report 00-358., USGS.
- Pringle, J, 1948. British Regional Geology: The South of Scotland. British Geological Survey.
- Rauret, G, 1998. Extraction Procedures for the determination of heavy metals in contaminated soil and sediment. *Talanta*, 46: 449-455.
- Rees, R M, Parker-Jarvis, F and Cresser, M S, 1989. Soil effects on water chemistry in three adjacent upland streams at Glen Dye in northeast Scotland. *Water Research*, 23: 511-517.
- Reid, J M, MacLeod, D A and Cresser, M S, 1981. Factors affecting the chemistry of precipitation and river water in an upland catchment. *Journal of Hydrology*, 50: 129-145.
- Reynolds, B, Neal, C, Hornung, M and Stevens, P A, 1986. Baseflow buffering of streamwater acidity in five mid-Wales catchments. *Journal of Hydrology*, 87: 167-185.
- Reynolds, B, Renshaw, M, Sparks, T H, Crane, S, Hughes, S, Brittain, S S and Kennedy, V H, 1997. Trends and seasonality in stream water chemistry in two moorland catchments of the Upper River Wye, Plynlimon. *Hydrology and Earth System Sciences*, 1(3): 571-581.
- Robins, N S, 1990. Hydrogeology of Scotland. HMSO, London.
- Robins, N S, 2002. Groundwater quality in Scotland: major ion chemistry of the key groundwater bodies. *The Science of the Total Environment*, 294(1-3): 41-56.
- Robinson, M, Moore, R E, Nisbet, T R and Blackie, J R, 1998. From moorland to forest: the Coalburn catchment experiment. 133, Institute of Hydrology, Wallingford.
- Robson, A J and Neal, C, 1990. Hydrograph separation using chemical techniques: an application to catchments in mid-Wales. *Journal of Hydrology*, 116: 345-363.
- Robson, A J, Neal, C, Smith, C J and Hill, S, 1992. Short term variations in rain and stream water conductivity at a forested site in mid-Wales - implications for water movement. *The Science of the Total Environment*, 119: 1-18.
- Robson, A J, 1993. The use of continuous measurement in understanding and modelling the hydrogeochemistry of uplands. PhD dissertation, University of Lancaster, Lancaster.

- Robson, A J, Neal, C, Hill, S and Smith, C J, 1993. Linking variations in short- and medium-term stream chemistry to rainfall inputs - some observations at Plynlimon, Mid-Wales. *Journal of Hydrology*, 144: 291-310.
- Robson, A J and Neal, C, 1996. Water quality trends at an upland site in Wales, UK, 1983-1993. *Hydrological Processes*, 10: 183-203.
- Rogerson, P A, 2001. Statistical methods for geography. Sage Publications, London.
- Salomons, W and Förstner, U, 1984. Metals in the Hydrosphere. Springer Verlag, Berlin.
- Schofield, T, Perkins, R and Simms, J S, 1991. Frankley water-treatment works development: pilot studies. *JIWEM*, 5: 370-380.
- Schröder, F, Klages, D, Blöcker, G, Vajen-Finnern, H and Knauth, H-D, 1992. The application of a laboratory apparatus for the study of nutrient fluxes between sediment and water. *Hydrobiologia*, 235/236: 545-552.
- Seip, H M, Christophersen, N, Mulder, J and Taugbol, G, 1995. Integrating field work and modelling. In: Trudgill, S (Editor), *Solute modelling in catchment systems*. John Wiley & Sons.
- Sholkovitz, E R, 1985. Redox-related geochemistry in lakes: alkali metals, alkaline-earth elements, and  $^{137}\text{Cs}$ . In: Stumm, W (Editor), *Chemical Processes in Lakes*. John Wiley & Sons, New York, pp. 119-139.
- Shotyk, W and Steinmann, P, 1994. Pore-water indicators of rainwater-dominated versus groundwater-dominated peat bog profiles (Jura Mountains, Switzerland). *Chemical Geology*, 116: 137-146.
- Sigg, L, 1985. Metal transfer mechanism in lakes; the role of settling particles. In: Stumm, W (Editor), *Chemical processes in lakes*. John Wiley & Sons, London, pp. 283-310.
- Sigg, L, Sturm, M and Kistler, D, 1987. Vertical transport of heavy metals by settling particles in Lake Zürich. *Limnology and Oceanography*, 32: 112-130.
- Sklash, M G and Farvolden, R N, 1979. The role of groundwater in storm runoff. *Journal of Hydrology*, 43: 45-65.
- Smart, R, Soulsby, C, Neal, C, Wade, A, Cresser, M S, Billett, M F, Langan, S J, Edwards, A C, Jarvie, H P and Owen, R, 1998. Factors regulating the spatial and temporal distribution of solute concentrations in a major river system in NE Scotland. *The Science of the Total Environment*, 221: 93-110.
- Smart, R, Soulsby, C, Cresser, M S, Wade, A, Townend, J, Billett, M F and Langan, S J, 2001. Riparian zone influence on stream water chemistry at different spatial scales: a GIS-based modelling approach, an example for the Dee, NE Scotland. *The Science of the Total Environment*, 280: 173-193.

- Soulsby, C, 1997. Hydrochemical Processes. In: Wilby, R L (Editor), *Contemporary Hydrology*. John Wiley & Sons, Chichester, pp. 59-106.
- Soulsby, C, Chen, M, Helliwell, R C, Ferrier, R C, Jenkins, A and Harriman, R, 1997. Groundwater influence on the hydrology and hydrochemistry of upland streams in Scotland, BHS 6th National Hydrology Symposium, Salford, pp. 2.9-2.16.
- Soulsby, C, Chen, M, Ferrier, R C, Helliwell, R C, Jenkins, A and Harriman, R, 1998. Hydrogeochemistry of shallow groundwater in an upland Scottish catchment. *Hydrological Processes*, 12: 1111-1127.
- Soulsby, C, Gibbins, C, Wade, A J, Smart, R and Helliwell, R C, 2002a. Water quality in the Scottish Uplands: a hydrological perspective on catchment hydrochemistry. *The Science of the Total Environment*, 294(1-3): 73-94.
- Soulsby, C, Rodgers, P, Smart, R, Dawson, J and Dunn, S, 2002b. A tracer based assessment of hydrological pathways at different spatial scales in a mesoscale Scottish catchment. *Hydrological Processes*.
- Soulsby, C and Dunn, S, 2003. Towards integrating tracer studies with a conceptual rainfall-runoff model: recent insights from a sub-arctic catchment in the Cairngorm Mountains, Scotland. *Hydrological Processes*, 17: 403-416.
- Sposito, G, 1984. The surface chemistry of soils. Oxford Press, Oxford.
- Stigliani, W M, 2001. Environmental impact assessment with respect to potential long-term impacts of heavy metal accumulated in soils and sediments. Environmental Research and Teaching at the University of Toronto Publications. 11-Oct-01, <<http://www.utoronto.ca/env/papers/munn/munn1cp9.htm>>.
- Straškraba, M, Tundisi, J G and Duncan, A, 1993. State-of-the-art reservoir limnology and water quality management. In: Straškraba, M, Tundisi, J G and Duncan, A (Editors), *Comparative reservoir limnology and water quality management*. Kluwer Academic Press, Netherlands, pp. 213-288.
- Stumm, W and Morgan, J J, 1981. Aquatic Chemistry: An introduction emphasizing chemical equilibria in natural waters. John Wiley & Sons, New York.
- Stumm, W and Sulzberger, B, 1992. The cycling of iron in natural environments: Considerations based on laboratory studies of heterogeneous redox processes. *Geochimica et Cosmochimica Acta*, 56: 3233-3257.
- Stunell, J M and Younger, P L, 1995. Hydrogeology of upland peat: hydrological and chemical processes in Redesdale, N.England, 5th National Hydrology Symposium. BHS, Edinburgh, pp. 5.9-5.15.
- Sullivan, A B and Drever, J I, 2001. Spatiotemporal variability in stream chemistry in high-elevation catchment affected by mine drainage. *Journal of Hydrology*, 252: 237-250.

- Sundby, G, Siverberg, N and Chesselet, R, 1981. Pathways of manganese in an open estuarine system. *Geochimica et Cosmochimica Acta*, 45: 293-307.
- Swan, A R H and Sandilands, M, 1995. Introduction to geological data analysis. Blackwell Science, Oxford.
- Tack, F M G and Verloo, M G, 1999. Single extraction versus sequential extraction for the estimation of heavy metal fractions in reduced and oxidised dredged sediments. *Chemical Speciation and Bioavailability*, 11(2): 43-50.
- Tessier, A, Campbell, P G C and Bisson, M, 1979. Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. *Analytical Chemistry*, 51(7): 844-851.
- Tessier, A, Campbell, P G C and Bisson, M, 1980. Trace metal speciation in the Yamaska and St Francois River (Quebec). *Canadian Journal of Earth Sciences*, 17: 90-105.
- Tessier, A, 1992. Sorption of trace elements on natural particles in oxic environments. In: Buffle, J and Van Leuwen, H P (Editors), *Environmental Particles*. Lewis, Boca Raton, pp. 425-453.
- Theis, T L and Singer, P C, 1973. The stabilisation of ferrous iron by organic compounds in natural waters. In: Singer, P C (Editor), *Trace metals and metal-organic interactions in natural waters*. Ann Arbor, Woburn, pp. 303-320.
- Thomas, R L and Meybeck, M, 1996. The use of particulate material. In: Chapman, D (Editor), *Water quality assessment*. E & FN Spon, London, pp. 127-174.
- Thornton, K W, Kennedy, R H, Carrol, J H, Walker, W W, Gunkel, R C and Ashby, S, 1981. Reservoir sedimentation and water quality- A heuristic model. In: Stefen, H G (Editor), *Symposium on surface water impoundments*. American Society of Civil Engineers, New York, pp. 654-661.
- Thornton, K W, 1990a. Perspectives on Reservoir Limnology. In: Thornton, K W, Kimmel, B L and Payne, F E (Editors), *Reservoir Limnology: Ecological Perspectives*. John Wiley & Sons, New York, pp. 1-14.
- Thornton, K W, 1990b. Sedimentary Processes. In: Thornton, K W, Kimmel, B L and Payne, F E (Editors), *Reservoir Limnology: Ecological Perspectives*. John Wiley & Sons, New York, pp. 43-70.
- Thornton, S F, 1990c. The clay mineralogy, sedimentology and geochemistry of the sediments of the Tay estuary. PhD dissertation, University of Dundee, Dundee.
- Thornton, G J P and Dise, N B, 1997. Major-ion chemistry of streams draining the English Lake District (Cumbria), 6th National Hydrology Symposium. BHS, Salford.

- Tipping, E, 1981. The adsorption of aquatic humic substances by iron oxides. *Geochimica et Cosmochimica Acta*, 45: 191-199.
- Tipping, E, Woof, C and Cooke, D, 1981. Iron oxide from a seasonally anoxic lake. *Geochimica et Cosmochimica Acta*, 45: 1411-1419.
- Tipping, E, 1984. Temperature dependence of Mn(II) oxidation in lake waters: a test of biological involvement. *Geochimica et Cosmochimica Acta*, 48: 1353-1356.
- Tipping, E and Ohnstad, M, 1984. Colloid stability of iron oxide particles from a freshwater lake. *Nature*, 308: 266-268.
- Tipping, E, Thompson, D W and Davison, W, 1984. Oxidation products of Mn(II) in lake waters. *Chemical Geology*, 44: 359-383.
- Tipping, E, Backes, C A and Hurley, M A, 1989. Modelling the interactions of Al species, protons and  $\text{Ca}^{2+}$  with humic substances in acid waters and soils. In: Lewis, T E (Editor), *Environmental chemistry and toxicology of aluminium*. Chelsea, Michigan, pp. 83-105.
- Tipping, E, Rey-Castro, C, Bryan, S E and Hamilton-Taylor, J, 2002. Al(III) and Fe(III) binding by humic substances in freshwaters, an implication for trace metal speciation. *Geochimica et Cosmochimica Acta*, 66(18): 3211-3224.
- van Loon, G W and Duffy, S J, 2000. *Environmental Chemistry - a global perspective*. Oxford University Press, New York.
- Vanni, A, Gennaro, M C, Cignetti, A, Petronino, B M, Petruzzelli, G and Liberatori, A, 1997. Heavy metal speciation in anaerobic municipal sludge-Comparison between single and sequential extraction. *Journal of Environmental Science*, 32(5): 1467-1489.
- Vollenweider, R A, 1982. *Eutrophication of waters: Monitoring, assessment and control*. OECD (Organisation for economic co-operation and development), Paris.
- Wade, A, Neal, C, Soulsby, C, Smart, R, Langan, S J and Cresser, M S, 1999. Modelling streamwater quality under varying hydrological conditions at different scales. *Journal of Hydrology*, 217: 266-283.
- Walden, J, Smith, J P and Dackombe, R V, 1992. The use of simultaneous R- and Q-mode factor analysis as a tool for assisting interpretation of mineral magnetic data. *Mathematical Geology*, 24(3): 227-247.
- Walden, J and Smith, J P, 1995. Factor Analysis: A practical application. In: Maddy, D and Brew, J S (Editors), *Statistical modelling of quaternary science data*. Quaternary Research Association, Cambridge, pp. 39-63.
- Walton, E K and Weir, J A, 1974. The upper Glenkiln-Hartfell cherts and mudstones of Broadlaw and their stratigraphical significance. *Scottish Journal of Geology*, 9: 320-321.

- 
- Warnken, K W, Gill, G A, Griffin, L L and Santschi, P H, 2001. Sediment-water exchange of Mn, Fe, Ni and Zn in Galveston Bay, Texas. *Marine Chemistry*, 73: 215-231.
- Warren, L A and Haack, E A, 2001. Biogeochemical controls on metal behaviour in freshwater environments. *Earth Sciences Reviews*, 53(4): 261-320.
- Werritty, A, Black, A and Duck, R, 2001. Climate Change: Flooding occurrence review. Scottish Executive. 01-May-03,  
<http://www.scotland.gov.uk/cru/kd01/lightgreen/ccfo-06.asp>.
- Wetzel, R G, 1975. Limnology. W.B. Saunders Company, Philadelphia.
- WHO World Health Organisation, 1993. Guidelines for drinking-water quality, 1. World Health Organisation, Geneva.
- Williams, A L, 1987. Introduction to x-ray spectrometry. Allan & Unwin, London.
- Younger, P L, 2001. Mine water pollution in Scotland: nature, extend and preservative strategies. *The Science of the Total Environment*, 265: 309-326.
- Zaw, M and Chiswell, B, 1999. Iron and manganese dynamics in lake water. *Water Research*, 33(8): 1900-1910.
- Zhang, H, Davison, W, Miller, S and Tych, W, 1995. *In situ* high resolution measurements of fluxes of Ni, Cu, Fe and Mn and concentrations of Zn and Cd in porewaters by DGT. *Geochimica et Cosmochimica Acta*, 59(20): 4181-4192.
- Zhou, d, Chang, T and Davis, J C, 1983. Dual extraction of R-mode and Q-mode factor solutions. *Journal of International Association for Mathematical Geology*, 15: 581-606.

# Appendix I – Sampling Protocols

---

Field and laboratory protocols

Megget Reservoir Regular Sampling Programme

*Author:* C. Abesser

*Last updated:* February 2001

---

## Content

- a. Stream Water Sampling
- b. Reservoir Water Sampling
- c. Sample Storage and Preservation

## Stream Water Sampling

---

**SUMMARY:** The primary objective is to assess variability in iron and manganese fluxes in the streams draining into the Megget Reservoir. The sampling programme at each stream sampling site is therefore designed to monitor parameters relevant to geochemical cycling in this environment. Discrete grab samples are collected at each stream-sampling site representing a snapshot in space and time of the chemical composition of the stream water. The discrete grab samples collected at a biweekly/monthly interval can provide background information about seasonal pattern in stream geochemical cycling.

---

### *Equipment and Supplies*

250 mL bottles for metal samples (polyethylene)  
 1 L bottles for general chemistry water samples (polyethylene)  
 Temperature probe & meter  
 Conductivity probe & meter

### *Sampling Location*

Stream water samples are taken fortnightly at Shielhope Burn, Winterhope Burn and Linghope Burn, and monthly at Meggethead, Craigierig Burn and Cramalt Burn.

1. Collection sites at these streams are located in relatively straight channel reaches, closed to the inflow mouth into to reservoir but upstream of the stream sections that are affected by fluctuations of the reservoir water level.
2. Where possible samples are taken midstream.
3. At gauged streams sampling locations are near the gauging stations.

#### 4. Shielhope Burn

- Sampling site: directly at stream gauging station
- ca. 5 m behind fence
- ca. 15 m upstream of reservoir inflow bay
- Sampling from east shore, mid stream

#### Winterhope Burn

- Sampling site: 10 m downstream of small bridge
- 25 m upstream of stream gauging station
- Sampling from west shore, mid stream at low and medium flows, side stream at high flows

#### Meggethead

- Sampling site: opposite stream gauging station
  - 25 m upstream of inflow into reservoir
  - Sampling from south shore, side stream
- Linghope Burn
- Sampling site: ca 3-4 m behind fence
  - 10 m upstream of former stream gauging station
  - 2 m downstream of little pool in stream bed
  - Sampling from east shore, mid stream at low and medium flows, side stream at high flows
- Cramalt Burn
- Sampling site: directly upstream of wooden fence
  - Opposite inflow of stream coming from Clockmore
  - Sampling from west shore, side stream
- Craigierig Burn
- Sampling site: 10 m downstream of bridge/concrete channel
  - 20 m upstream of inflow into reservoir
  - Sampling from west shore, midstream

### *Sampling Set*

A stream sampling set includes:

- ⇒ 250 mL-sample bottle for metal analysis (ESW) → no preservation
- ⇒ 1 L-sample bottle for the analysis of general chemistry (ESW) → no preservation

### *Sampling Procedure*

1. Water samples for the analysis of general chemistry and metals are collected into clean 1 L and 250 mL sampling bottles (provided by ESW), respectively.
2. Before taking a water sample the sampling bottle is thoroughly rinsed twice with water from the stream.
3. The sample is taken as midstream as possible by immersing the hand-held bottle in the flow, 5-10 cm below the stream surface with the mouth of the bottle directed towards the current.
4. Sample bottles are filled and tightly capped. In the 1 L sample bottles the air space is kept to a minimum in order to minimise CO<sub>2</sub> exchange with the headspace, as it would affect the pH of the sample. 250 mL bottles are filled to the bottleneck leaving space for mixing and for addition of preservatives.
5. After sampling the bottles are labelled including location, time and date of sample collection and information pertinent to the sampling are recorded in the field logbook (see documentation).

### *Field measurements*

#### Temperature

1. The temperature meter is switched on and the probe is placed properly so that air temperature (and not temperature of a surface) can be measured. Air temperature reading is taken when value at meter is settled and does not change anymore.
2. Temperature probe is immersed into flowing section of the stream and water temperature reading is taken after value at the meter settled.

#### Conductivity

1. Conductivity meter is switched on with temperature compensation switch set on 'In' position. Readings are taken after the probe is immersed into flowing section of the stream and the appropriate effective range for the measurements is chosen.
2. All measurements and information pertinent to the sampling are recorded in the field log book (see documentation)

### *Documentation*

1. After sampling the bottles are labelled including location, date and time of sampling.
2. Documentation at each sampling site includes:
  1. Name of sample collector
  2. Sampling location
  3. Date and Time of sampling
  4. Location of sampling in the stream (cross section: mid stream / side stream)
  5. Type and number of samples collected (metal, general chemistry, biology)
  6. In-stream measurements taken (conductivity, temperature) and instruments used and effective range of measurements (conductivity)
  7. Site information: weather conditions, air temperature (measured in shadow/sun), stream flow (low/high), and additional information and observations (ice on the stream etc.), catchment conditions (very wet, snow etc.)
  8. Sample information: e.g., colour
  9. Time of sample preservation (if applied)

### *Quality Control Samples*

#### Replicates

Sample replicates are taken at each sampling day to estimate the precision of concentration values determined from the combined sample-processing and analytical scheme.

Replicates are taken at one of the sampling sites interchangeably for the analysis of either metal (250 mL bottles) concentrations or general chemistry (1 L bottle). The samples are collected, preserved, transported and processed in the same way as the other (native) samples.

*Sample Storage and Transport*

Samples are stored in an insulated cooling box and delivered to the ESW lab on the day of collection where they are filtered, preserved and analysed as soon as possible, according to the ESW standards and regulations.

*Sample Preservation*

No preservation applied

*References*

- APHA (1998) Collection and Preservation of Samples, In: APHA, *Standard methods for the Examination of Water and WasteWater*, 20<sup>th</sup> edition, American Public Health Association, Washington.
- Karl, D.M; Winn, C.D.; Hebel, D.V.W. and Letelier, R.: Hawaii Ocean Times Series Program: Field and Laboratory Protocols, September 1990, <<http://hahana.soest.hawaii.edu/hot/protocols/protocols.html>>
- Shelton, L.R. (1994): Field guide for collecting and processing stream water samples for the National Water Quality Assessment Program, USGS, Open-File Report 94-455, Sacramento, CA.

## Reservoir Water Sampling

---

**SUMMARY:** The primary objective is to assess variability in iron and manganese concentrations and fluxes in the Megget Reservoir. Depth integrated grab samples are collected at three stations along the longitudinal axes of the reservoir on a monthly basis. Due to safety reasons and because of the reduced dynamics of the reservoir system during winter and the relatively constant water composition (as observed in winter 1999/2000) the sampling programme is not conducted between December 2000 and March 2001. The sampling programme at each station is designed to monitor physical and chemical parameters relevant to geochemical cycling of iron and manganese in the reservoir environment.

---

### *Equipment and Supplies*

250 mL bottles for metal samples (polyethylene)

1 L bottles for general chemistry water samples (polyethylene)

Pump

12V car battery

Filter capsule

Whatman GFC-4.25Ø filter papers for Chlorophyll samples

Kitchen foil

Liquid nitrogen/frozen CO<sub>2</sub>

Reel with 60m sampling hose, conductivity probe & temperature probe

Temperature meter

Conductivity meter

### *Sampling Locations*

Sampling locations are aligned along the length of the reservoir:

- at the deep end of reservoir at the dam (lacustrine zone)
- at the middle of the reservoir (transitional zone)
- at the shallow end of the reservoir (riverine zone)

Location A

⇒ Dam, close to the tower, deep end of the reservoir

⇒ GPS location: ~ 55°29'40"/ 03°15'10"

**Location C**

- ⇒ Middle of the reservoir, opposite Shielhope Burn inflow
- ⇒ GPS location: ~55°29'10"/ 03°16'40"

**Location E**

- ⇒ Shallow end of the reservoir, between Winterhope and Meggethead Bay
- ⇒ GPS location: ~ 55°28'50"/ 03°17'50"

*Sampling Set*

A reservoir sampling set includes:

- ⇒ 250ml-sample bottle for metal analysis (ESW) → no preservation
- ⇒ 1l-sample bottle for the analysis of general chemistry (ESW) → no preservation
- ⇒ Chlorophyll sample → frozen in CO<sub>2</sub>

*Sampling strategy*

1. Depth integrated water grab samples are taken at three locations along the length of the reservoir.
2. Parallel to the water sampling, temperature and conductivity readings are taken at the surface and at regularly spaced intervals, 2 m or 1 m (close to thermocline), throughout the profile. Secchi disk transparency is measured using a 30 cm diameter weighted Secchi disk.
3. During sampling collection the boat is anchored at the appropriate sampling position and the engine is switched off to avoid contamination of the samples.
4. Samples are taken from the surface to the bottom at two or three depths depending on the reservoir depths at the sampling site and according to position and extend (depth) of the thermocline.
5. At the deep sampling sites (locations A, C) a minimum of three samples is collected consisting of sampling
  - 0.2 m below water surface
  - above the thermocline
  - below the thermocline
  - and if possible above bottom sediment at depth that can be achieved without disturbing the sediment

At the shallow end of the reservoir (location E) a minimum of two samples is taken, including samples collected

- 0.2 m below water surface (= above the thermocline)
- below the thermocline (= above bottom sediment at depth that can be achieved without disturbing the sediment)

*Sampling procedure*

1. At each station GPS co-ordinates, time of arrival at the sampling station and air temperature are recorded in the field log book along with observations about weather conditions and general features of interest (reservoir level, catchment conditions (e.g., snow), etc.).
2. The hose is placed in the water and lowered to the first sampling depth (measured from water surface to end of sampling tube) and cleared of previously sampled water by pumping a defined volume of 2 litres of water.
3. Before taking a water sample the sampling bottle is thoroughly rinsed twice with water from the sampling depth.
4. Water samples for the analysis of general chemistry and metals are collected into clean 1L and 250 mL sampling bottles, respectively.
5. Sample bottles are filled and tightly capped. In the 1 L sample bottles the air space is kept to a minimum in order to minimise CO<sub>2</sub> exchange with the headspace, as it would affect the pH of the sample. 250 mL bottles are filled to the bottleneck leaving space for mixing and for addition of preservatives.
6. At each depths a sample for the analysis of chlorophyll-*a* is taken by filtering a volume of 1 litre of water through an in-line Whatman GFC-filter. The filter paper with the chlorophyll is then folded, enclosing the sample, wrapped in tin foil and labelled accordingly.
7. After sampling the bottles are labelled including location, time and date of sample collection and information pertinent to the sampling are recorded in the field logbook (see documentation).
8. Then hose is lowered to the next sampling depth, cleaned and prepared for collecting the next sample.
9. Surface water samples (0.2 m depth) are taken per hand ca. 20 cm below the water surface of the reservoir.

*Field measurements*

## Temperature and Conductivity

1. Temperature and conductivity are measured parallel to the water sampling.
2. Before starting the sampling programme the hose is placed in the water, conductivity meter and temperature meters are switched on and the appropriate effective range for the measurements is chosen.
3. Readings are taken at 2 m intervals throughout the profile and at 1 m intervals where significant changes in conductivity or temperature (thermocline) of the water occur.
4. Depth readings are recorded in the field logbook, along with depth and samples taken etc. (see documentation).

## Secchi depth transparency

1. Secchi depth transparency is measured at the lee site of the boat and where light reflections are least affecting the measurement.

2. The Secchi disk is lowered into the reservoir until the disk disappears from sight and the depths is read of the marked line.
3. The measurements are repeated three times.
4. Readings are noted down in the field book along with name of the person measuring, time of measurement, weather and light conditions, conditions of water surface (still, wind ripples etc.)

### *Quality Control Samples*

#### Replicates

Sample replicates are taken at each day of sampling to estimate the precision of concentration values determined from the combined sample-processing and analytical scheme.

Replicates are taken at one of the sampling sites interchangeably for the analysis of either metal (250 mL bottles) concentrations or general chemistry (1 L bottle). The samples are collected, preserved, transported and processed in the same way as the other (native) samples.

#### *Documentation*

1. After sampling the bottles are labelled including sampling location and depths, date and time of sampling.
2. Documentation at each sampling site includes
  - i. Name(s) of sample collector(s)
  - ii. Sampling location
  - iii. Time of Arrival at the station
  - iv. Time of Leaving the station
  - v. Sampling depth, type and number of samples collected (metal, general chemistry, biology)
  - vi. Date and Time of sample collection
  - vii. Field measurements:
    - Temperature-conductivity-depth profiles
    - Secchi disk transparency (including time of measurement, light and weather conditions (cloud cover, wind and water surface conditions))
  - viii. Site information: weather conditions (e.g., wind, cloud cover, rain), Air temperature, reservoir water level and additional information and observations (ice on the stream etc.), catchment conditions (snow etc.)
  - ix. Sampling information (e.g., probe hit the bottom, boat drift)
  - x. Sample information: e.g., colour, sediment in sample
  - xi. Time of sample preservation

*Sample Storage and Transport*

Samples are stored in an insulated cooling box and delivered to the ESW lab on the day of collection where they are filtered, preserved and analysed as soon as possible, according to the ESW standards and regulations.

During sample collection chlorophyll-*a* samples are kept in an insulated cooling box, but on arrival on-shore are immediately transferred into a storage container with liquid nitrogen.

*Sample Preservation*

No preservation applied

*References*

- APHA (1998) Collection and Preservation of Samples, In: APHA, *Standard methods for the Examination of Water and WasteWater*, 20<sup>th</sup> edition, American Public Health Association, Washington.
- Bartram, J. & Balance, R. (eds.) *Water Quality Monitoring*, Chapman & Hall, Padstow, 1996.
- Karl, D.M; Winn, C.D.; Hebel, D.V.W. and Letelier, R.: Hawaii Ocean Times Series Program: Field and Laboratory Protocols, September 1990, <<http://hahana.soest.hawaii.edu/hot/protocols/protocols.html>>
- Thornton, J., Steel, A. & Rast, W. (1996) Reservoirs, In: Chapman, D., *Water Quality Assessment*, E&FN Spon, University Press, Cambridge, p. 369-412.

## Sample storage and preservation

---

**SUMMARY:** Samples for (trace) metal analysis are filtered to separate the filterable fraction from the particulate fraction in order to differentiate between total and 'dissolved' metals present in the matrix. These fractions are operationally defined and the term 'filterable' is used to indicate components that pass through a filter with a pore size of 0.45  $\mu\text{m}$  and which may be classed as 'dissolved' for some practical purposes, but will often include colloidal species.

---

### *Equipment and Supplies*

Disposable 30 mL PVC syringes

Disposable filter disks (Puradisk 25 AS 0.45 $\mu\text{m}$ , Filter media: Polyethersulfone)

Vials

De-ionised water

Disposable gloves

### *Filtration*

1. Vials for all sub-sample filtrates are pre-labelled and placed on the lab bench along with the associated sample bottle.
2. The syringe is rinsed with de-ionised water.
3. A filter is attached to the syringe and volume of 20 mL of the sample is poured into the syringe and filtered into the appropriate vial. Vial and Sample bottle are closed.
4. The filter is removed from the syringe and disposed and the syringe is cleaned with de-ionised water before the next sub-sample is filtered.
5. A new filter disk is used for each sub-sample.
6. After all sub-samples are filtered, all used filter disks and syringes are disposed

## Appendix II: Water analysis methods – ESW laboratory

---

The following paragraphs are intended to summarise the methods used for the analysis of the water samples and, where not stated differently, the given information are derived directly from members of staff at the ESW laboratory or withdrawn from the *Organic and Inorganic Procedure Manual for the Analysis of Raw and Portable Water*. The later provides detailed description of all methods and procedures applied during sample processing and analysis and should be referred to where more methodical details are required.

---

### Determination of Colour, Conductivity, pH and Turbidity

Colour, conductivity, pH and turbidity measurements of the water samples are determined using an automated analytical system – the *Anachem Aqualyser System*- and are based on the following principles:

The colour of water is the result of different wavelengths that are not absorbed by the water itself and are reflected and refracted by substances present in the water. Hence, the colour of a sample gives a first indication of the presence of dissolved and particulate matter in the water. Generally, it is distinguished between true colour and apparent colour. The true colour is the colour of the water and its contents. It originates from natural minerals such as ferric hydroxide or organic substances (humic acids) and can only be obtained after turbidity of the sample has been removed by filtration or centrifugation. Apparent colour is the colour as seen by the observer and is caused by the reflection and scattering of light on coloured particles in the water. Thus, it includes not only colour due to substance in the water, but also that due to suspended matter such as sediment or phytoplankton.

The method used by ESW determines the ‘true colour’ of a sample, defined as ‘the colour due to dissolved matter in a sample that is measurable at an absorbance of 400 nm’. The water sample is filtered through a cellulose acetate membrane of 0.45- $\mu\text{m}$  pore size and its absorbance is measured at 400 nm. The absorbance is then related to that of a series of standard Pt/Co solutions, and the results are expressed as  $^{\circ}\text{Hazen}$  ( $1\text{mg L}^{-1}\text{ Pt/Co} \equiv 1^{\circ}\text{Hazen}$ ).

Limit of Detection: 1.3  $^{\circ}\text{Hazen}$   
Reporting Limit: 2  $^{\circ}\text{Hazen}$

### Precision Data ( $^{\circ}\text{Hazen}$ ):

<u>Colour</u>	<u>Mean</u>	<u>StDev</u>
Treated water (plus Spike)	2.677 (60.718)	0.324 (1.364)
Untreated water (plus Spike)	25.036 (74.745)	0.848 (1.733)

Low Standard (10 Hazen)	90.455	0.322
High Standard (90 Hazen)		2.029

Conductivity (*specific conductance*) is a measure of the ability of an aqueous solution to conduct an electric current and can be defined as the reciprocal of the resistance measured between two electrodes 1-cm apart with a cross sectional area of 1cm<sup>2</sup>. It therefore depends on the content of dissolved solids, mostly mineral salts, in the solution and the degree to which those salts dissociate into ions. Moreover, the conductivity is also influenced by the temperature of the measured solution and thus, in most cases, measurements are referred to a temperature of 25°C so that differences in conductance are only a function of the type and the concentration of the dissociated ions.

The method used by ESW for the determination of conductivity values is a non-specific test to detect the presence of ionised substances in a sample. Using a conductivity cell and balancing with a headstone bridge, the electrical resistance of a sample  $R_s$  and a standard solution  $R_{KCL}$  of Potassium Chloride of known conductivity  $C_{KCL}$  are measured at the same temperature. The sample conductivity  $C_s$  can then be calculated using the following equation  $C_s = (C_{KCL} \times R_{KCL})/R_s$ .

Limit of Detection:	1.9 $\mu\text{S cm}^{-1}$
Reporting Limit:	2 $\mu\text{S cm}^{-1}$

Precision Data ( $\mu\text{S cm}^{-1}$ ):

<u>Conductivity</u>	<u>Mean</u>	<u>StDev</u>
Treated water (plus Spike)	112.636 (741.374)	1.051 (1.664)
Untreated (plus Spike)	73.000 (709.455)	1.206 (2.240)
Low Standard (266 $\mu\text{S/cm}$ )	267.591	0.735
High Standard (1156 $\mu\text{S/cm}$ )	1157.682	2.515

pH is a measure of the intensity of the acidic or basic character of a solution and is controlled by the dissolved chemical compounds and biochemical processes in the solution.

It can be defined as the logarithm to base 10 of the reciprocal of the hydrogen ion activity,

i.e.

$$pH = -\log a_H$$

where  $a_H$  is the activity of hydrogen ions in the solution expressed in mol L<sup>-1</sup>.

In the ESW laboratory, pH is determined using an electrode system in which the potential difference measured is a function of the concentration of the hydrogen ion. The  $pH_{(x)}$  of a sample is determined by measuring the electromotive force (e.m.f.)  $E_x$ , of a cell containing the sample and comparing it with the e.m.f. of a similar cell,  $E_s$  in which the sample is replaced by a standard buffer solution. pH is then calculated using the equation:

$$pH_{(x)} - pH_{(s)} = \frac{(E_s - E_x) \times F}{2.3026 \times R \times T}$$

where  $pH_{(s)}$  is the pH of the standard buffer solution,  $R$  is the gas constant,  $T$  is the absolute temperature and  $F$  is the Faraday constant. As the equation illustrates, pH is a function of temperature and though the electrode response is adjusted for temperature effects the sample must be measured at the same temperature as the buffer solution.

Limit of Detection: N/A

Reporting Limit: N/A

Precision Data (pH units):

<u>pH</u>	<u>Mean</u>	<u>StDev</u>
treated water	7.8036	0.0347
untreated water	7.520	0.1064
4.00 pH	4.0023	0.0147
6.88 pH	6.8616	0.0089
9.23 pH	9.1909	0.0157

Turbidity is an expression of the optical property of a liquid and results from suspended and colloidal matter, which is present in the water causing the incident light to be scattered and adsorbed rather than transmitted straight through the solution. It is controlled by the concentration of the suspended matter and also by its type. Suspended matter is defined as the fraction that will not pass through a 0.45 $\mu$ m pore filter and consist of clay, silt, fine particles of organic and inorganic matter, soluble organic compounds, phytoplankton and other microscopic organism (APHA,1998; Chapman and Kimstach, 1996).

At the ESW laboratory turbidity of the water samples is measured using an Anachem Aqualyser, which determines the turbidity of a water samples, by nephelometry. The method is based on comparison of the intensity of light scattered by a sample under defined conditions with the intensity of light scattered by a standard suspension under the same conditions.

For that, light from a tungsten source is scattered by the suspended and/or colloidal material present in the sample and is measured at 90° relevant to the incident beam. The intensity of the light scattered is compared with that measured for standard formalin suspensions and expressed as nephelometric turbidity units (NTU).

Limit of Detection: 0.3 NTU  
Reporting Limit: 0.3 NTU

Precision Data (NTU):

<u>Turbidity</u>	<u>Mean</u>	<u>StDev</u>
Treated Water (plus Spike)	0.267 (3.719)	0.125 (0.183)
Untreated water (plus Spike)	0.655 (4.137)	0.053 (0.189)
Low Standard	0.558	0.103
High Standard	4.552	0.210

#### Determination of Alkalinity

Alkalinity of water is as an indication of the buffering capacity of the water system and the susceptibility to alterations in pH and is controlled by the sum of titratable bases.

At the ESW laboratory alkalinity is derived by using a *Radiometer Auto Titrator*, which, using 0.02N hydrochloric acid, automatically titrates the sample to an end-point of pH 4.5, which is measured using the pH electrode. It is, as determined in the procedure, a measure of the carbonate alkalinity, which derives from the analysis of carbonate and bicarbonate ions dissolved in water. It can be expressed as:

$$\text{alkalinity} = [\text{HCO}_3^-] + 2 \times [\text{CO}_3^{2-}] + [\text{OH}^-] + [\text{H}^+]$$

where the terms in brackets are the respective ionic activities in mol L<sup>-1</sup>.

Limit of Detection: 0.62 mg L<sup>-1</sup> HCO<sub>3</sub><sup>-</sup>  
Reporting Limit: 1 mg L<sup>-1</sup> HCO<sub>3</sub><sup>-</sup>

Precision Data (mg L<sup>-1</sup>):

<u>Alkalinity</u>	<u>StDev</u>
Tap water	1.32
Low Standard	0.26
High Standard	1.47

Determination of Chloride, Nitrite, Nitrate, Total Organic Nitrogen (TON), Ammonia, Phosphate (SR) and Sulphate

Concentrations of dissolved Chloride, Nitrate (by calculation), Nitrite, Total Oxidised Nitrogen, Ammonia, Phosphate (soluble reactive) and Sulphate are determined using *Kone Auto Analyser Systems: Kone Lab 60* and *Kone Delta*. These are automated analytical systems designed for the measurement of these parameters based on the following principles:

For determining Chloride concentrations the sample is reacted with mercuric thiocyanate to form a mercuric chloride complex. Released thiocyanate is then reacted with Fe(III) to form a red, ferric thiocyanate complex. The absorbance of the complex is measured at 510 nm and is then related to the chloride concentration using a standard calibration graph.

Limit of Detection: 0.85 mg L<sup>-1</sup> Cl  
Reporting Limit: <2.0 mg L<sup>-1</sup> Cl

Precision Data (mg L<sup>-1</sup>):

<u>Chloride</u>	<u>Mean</u>	<u>StDev</u>
Treated water (plus spike)	10.6318 (30.1364)	0.1459 (0.5166)
Untreated water (plus spike)	9.8318 (29.463)	0.1545 (0.4063)

Nitrite concentrations are determined by reacting the sample with sulphanilamide and N-I-naphtyl ethylene di-amine in dilute phosphoric acid. As part of the reaction an azo-dye is formed. The absorbance of the complex is measured at 540 nm and the absorbance is related to the nitrite concentration using a calibration graph.

Limit of Detection: N/A  
Reporting Limit: N/A

Precision Data (mg L<sup>-1</sup>)

<u>Nitrite</u>	<u>Mean</u>	<u>StDev</u>
Treated water (plus spike)	38.6818 (160.7727)	0.8457 (3.6109)
Untreated water (plus spike)	51.0091 (170.9045)	2.1011 (3.9609)

TON is measured by reacting the sample with hydrazine-copper reagent to reduce any Nitrate present in to Nitrite. The Nitrite is then reacted with Sulphanilamide and N-I-naphtyl ethylene di-amine in dilute phosphoric acid. As part of the reaction an azo-dye is formed. The absorbance of the complex is measured at 540 nm and the absorbance is related to the nitrite concentration using a calibration graph.

Limit of Detection:  $650.53 \mu\text{g L}^{-1}$   
 Reporting Limit:  $<1.0 \text{ mg L}^{-1}$

Precision Data ( $\mu\text{g L}^{-1}$ ):

<u>T.O.N.</u>	<u>Mean</u>	<u>StDev</u>
Treated water (plus spike)	1165.1360 (5245.0640)	115.1770 (196.4687)
Untreated water (plus spike)	1228.6320 (5350.4770)	89.1027 (225.4870)

Nitrate is empirically calculated for a sample by subtracting the analytically derived  $\text{NO}_2$  value from the analytically derived value of TON.

For the determination of Ammonia concentrations the sample is reacted with phenol and hypochlorite in the presence of sodium nitroprusside. This leads to the formation of blue indophenol compounds. The absorbance of the complex is measured at 660nm and the absorbance is related to the absorbance concentration using a calibration graph.

Limit of Detection:  $16.32 \mu\text{g L}^{-1}$   
 Reporting Limit:  $<0.030 \text{ mg L}^{-1}$

Precision Data ( $\text{mg L}^{-1}$ ):

	<u>Mean</u>	<u>StDev</u>
Treated water (plus spike)	0.9091 (101.6318)	1.0190 (7.4491)
Untreated water (plus spike)	8.0136 (106.6273)	1.5437 (3.8591)

Phosphate concentrations are measured by reacting the sample with molybdic acid and ascorbic acid. Any ortho-Phosphate ions present react to form a 12-molybdophosphoric acid. This is then reduced to phosphomolybdenum blue (in which antimony is incorporated). The absorbance of the complex is measured at 880nm and the absorbance is related to the phosphate concentration using a calibration graph.

Limit of Detection:  $33.36 \mu\text{g L}^{-1}$   
 Reporting Limit:  $<50.0 \mu\text{g L}^{-1}$

Precision Data ( $\mu\text{g L}^{-1}$ ):

	<i>Mean</i>	<i>StDev</i>
Treated water (plus spike)	2.9818 (399.9227)	1.9964 (6.0415)
Untreated water (plus spike)	4.2045 (399.4318)	1.6860 (11.5249)

Determination of *Sulphate* concentrations is achieved by allowing the sample to react with barium chloride. This precipitates out the sulphate – the resultant turbidity is measured at 405 nm and is related to the sulphate concentration using a calibration graph.

*Summary of detection ranges*

	<u>Concentration range</u> (Konelab 60)	<u>Limit of detection</u>	<u>Reporting limit</u>
Chloride	0-100 mg L <sup>-1</sup>	0.85 mg L <sup>-1</sup> Cl	<2.0 mg L <sup>-1</sup> Cl
Nitrite (as N)	0-200 $\mu\text{g L}^{-1}$	N/A	<0.005 mg L <sup>-1</sup> NO <sub>2</sub>
Nitrate (as N)	0-20,000 $\mu\text{g L}^{-1}$	1.37 $\mu\text{g L}^{-1}$ N	<4.5 mg L <sup>-1</sup> NO <sub>3</sub>
TON (as N)	0-20,200 $\mu\text{g L}^{-1}$	650.53 $\mu\text{g L}^{-1}$ N	<1.0 mg L <sup>-1</sup> TON
Ammonia (as N)	0-500 $\mu\text{g L}^{-1}$	16.32 $\mu\text{g L}^{-1}$ N	<0.030 mg L <sup>-1</sup> NH <sub>4</sub>
Phosphate (SR)	0-2000 $\mu\text{g L}^{-1}$	33.36 $\mu\text{g L}^{-1}$ P	<50.0 $\mu\text{g L}^{-1}$ P
Sulphate	0-200 mg L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>

## Determination of non-purgeable organic carbon in waters

The *Total Organic Carbon (TOC)* is defined as that carbon in organic compounds which is converted to carbon dioxide by oxidation after inorganic carbon has been removed or subtracted. Although TOC in water samples should ideally include carbon in volatile material it is widely accepted that the proportion of volatile organics present in these matrices is negligible. Consequently, it is established practice to report non-purgeable organic carbon as TOC.

In this method persulphate oxidation is used by acidification and purging to remove inorganic carbon (TIC) before oxidation of organics. Phosphoric acid is added to the sample in the digestion vessel, where a gas stream purges out any carbon dioxide formed from inorganic carbon in the sample. The carbon dioxide is carried to a molecular sieve trap where it is trapped and concentrated before further transported to a non-dispersive infrared detector.

Sodium persulphate is added to the remaining sample, which then reacts with the organic carbon in the sample to produce carbon dioxide. Purge gas flow to the digestion vessel is shut off at this time. After a pre-set time any carbon dioxide produced by the persulphate oxidation, which has accumulated in the digestion vessel is carried to the

trap where, as previously for the TIC, it is trapped and concentrated before being transported to the detector.

The detector is calibrated to directly display the mass of carbon dioxide detected. This mass is equivalent to the mass of TOC (or TIC) in the sample. The system automatically calculates the concentration of TOC by dividing the mass found by the sample volume. The non-purgeable organic carbon (NPOC) is defined as that organic carbon, which remains in solution after the sample has been purged by a stream of gas under a specific set of purging conditions. As indicated above, this is reported as TOC and is considered valid for all samples containing negligible volatile or purgeable organic compounds.

Limit of Detection: 0.2429 mg L<sup>-1</sup>  
 Range: up to 20 mg L<sup>-1</sup>

Precision Data (mg L<sup>-1</sup>):

<u>TOC</u>	<u>Mean</u>	<u>StDev</u>
Tap water (plus Spike)	1.2315 (15.1820)	0.0985 (0.4295)
Raw water (plus Spike)	2.1864 (15.9861)	0.0883 (0.3949)
Low Standard (2.0mg/l)	2.2071	0.0826
High Standard (18mg/l)	18.1474	0.5232

Determination of major and minor metallic elements and silica in waters and calculation of total hardness

The analysis of metals (Al, Cu, Fe, Mn, Zn, Ca, Mg, Na, K) and silica (SiO<sub>2</sub>) present in the water is carried out by *Inductively Coupled Plasma Optical Emission Spectrometry (I.C.P.O.E.S.)*. The method uses a high energy and temperature (8000k) Argon Plasma as an excitation source to atomise and ionise elements in a solution, which is introduced through the plasma by means of an aerosol. Electronic Transition occurs between energy levels due to energy adsorption. The electrons de-excite by the emission of photons of light. The photons of light emitted are at characteristic wavelength for each element with the emission intensity being proportional to the concentration of the analyte.

The concentrations of the elements are calculated directly by the spectrometer software and are reported by the software as  $\mu\text{g L}^{-1}$  for Al, Cu, Fe, Mn and Zn and as  $\text{mg L}^{-1}$  for Ca, Mg, Na and K.

Concentrations determined for calcium and magnesium are further used for the calculation of Total hardness using the following formula:

$$\text{Total Hardness (as Ca) mgL}^{-1} = [22.497 \times (\text{Ca mgL}^{-1}) + 4.114 \times (\text{Mg mgL}^{-1})] \times 0.4005.$$

Range and Precision (% *rsd* of the three replicate measurements)

	<u>Range <math>\mu\text{g L}^{-1}</math></u>	<u>Max % <i>rsd</i></u>	<u>Range <math>\mu\text{g L}^{-1}</math></u>	<u>Max % <i>rsd</i></u>
Al	7-20	10	20-2000	5
Cu	4.3-20	10	20-1000	5
Fe	4-20	10	20-2000	5
Mn	0.2-10	10	10-1000	5
Zn	1.8-20	10	10-1000	5
Pb	3.5-10	25	10-100	5
	<u><math>\text{mg L}^{-1}</math></u>		<u><math>\text{mg L}^{-1}</math></u>	
Ca	0.1-0.5	15	0.5-0.8	5
Mg	0.1-0.5	15	0.5-20	5
Na	0.8-2.0	15	2.00-40	5
K	0.3-2.0	5	0.5-0.8	5
SiO <sub>2</sub>	0.018-32.08			

Limit of Detection: 6.064  $\mu\text{g L}^{-1}$ Precision Data ( $\mu\text{g L}^{-1}$ ):

<u>Aluminium</u>	<u>Mean</u>	<u>StDev</u>
Low Standard	190.200	4.4620
High Standard	1799.8360	30.6004
Tap water	23.9318	1.5558
Raw water	18.1773	2.9308

Limit of Detection: 0.1083  $\text{mg L}^{-1}$ Precision Data ( $\text{mg L}^{-1}$ ):

<u>Calcium</u>	<u>Mean</u>	<u>StDev</u>
Low Standard	8.1091	0.2851
High Standard	72.9091	1.3747
Tap water	8.3773	0.1523
Raw water	11.9091	0.2329

Limit of Detection: 4.2694  $\mu\text{g L}^{-1}$ Precision Data ( $\mu\text{g L}^{-1}$ ):

<u>Copper</u>	<u>Mean</u>	<u>StDev</u>
Low Standard	98.6227	3.1119
High Standard	892.4272	14.4264
Tap water	31.9773	1.3618
Raw water	1.7091	0.9742

Limit of Detection: 3.3956  $\mu\text{g L}^{-1}$   
 Precision Data ( $\mu\text{g L}^{-1}$ ):

<u>Iron</u>	<u>Mean</u>	<u>StDev</u>
Low Standard	209.036	0.6684
High Standard	1817.95	27.8095
Tap water	46.559	1.3032
Raw water	15.9864	4.8404

Limit of Detection: 0.287  $\text{mg L}^{-1}$   
 Precision Data ( $\text{mg L}^{-1}$ ):

<u>Potassium</u>	<u>Mean</u>	<u>StDev</u>
Low Standard	0.700	0.0989
High Standard	7.2273	0.1815
Tap water	0.3182	0.1014
Raw water	0.8545	0.1455

Limit of Detection: 0.1083  $\text{mg L}^{-1}$   
 Precision Data ( $\text{mg L}^{-1}$ ):

<u>Magnesium</u>	<u>Mean</u>	<u>StDev</u>
Low Standard	2.0227	0.0977
High Standard	17.9591	0.1824
Tap water	1.4364	0.0500
Raw water	5.491	0.0599

Limit of Detection: 3.387  $\mu\text{g L}^{-1}$   
 Precision Data ( $\mu\text{g L}^{-1}$ ):

<u>Lead</u>	<u>Mean</u>	<u>StDev</u>
Low Standard	10.059	0.8834
High Standard	88.7636	1.5582
Tap water	1.7045	0.6308
Raw water	1.823	0.9191

Limit of Detection: 0.810  $\text{mg L}^{-1}$   
 Precision Data ( $\text{mg L}^{-1}$ ):

<u>Sodium</u>	<u>Mean</u>	<u>StDev</u>
Low Standard	3.9273	0.3352
High Standard	36.1955	0.6465
Tap water	3.6091	0.3046
Raw water	5.5773	0.3440

Limit of Detection: 1.7497  $\mu\text{g L}^{-1}$

Precision Data ( $\mu\text{g L}^{-1}$ ):

<u>Zinc</u>	<u>Mean</u>	<u>StDev</u>
Low Standard	103.5864	2.5651
High Standard	85.6636	11.8202
Tap water	9.8909	1.6135
Raw water	6.6955	2.9471

Limit of Detection: 0.5080  $\mu\text{g L}^{-1}$

Precision Data ( $\mu\text{g L}^{-1}$ ):

<u>Manganese</u>	<u>Mean</u>	<u>StDev</u>
Low Standard	19.5955	0.6310
High Standard	217.5545	5.1452
Tap water	1.8545	0.0633
Raw water	0.2591	0.1567

Limit of Detection: 0.0018  $\text{mg L}^{-1}$

Precision Data ( $\text{mg L}^{-1}$ ):

<u>Silica</u>	<u>Mean</u>	<u>StDev</u>
Low Standard	0.213	0.012
High Standard	28.78	0.806
Tap water	3.393	0.131
Raw water (spike)	0.592 (23.176)	0.047 (0.6596)

#### Determination of suspended solids (TSS)

For determining the amount of Total suspended solids (TSS) the sample is filtered under reduced pressure through a pre-weight glass fibre paper. The weight of the recovered material is then determined by drying at  $105\text{ }^{\circ}\text{C} \pm 5^{\circ}\text{C}$ .

Limit of Detection: 7.682  $\text{mg L}^{-1}$

Range: 8-2000  $\text{mg L}^{-1}$

Precision Data ( $\text{mg L}^{-1}$ ):

<u>TSS</u>	<u>Mean</u>	<u>StDev</u>
Low Standard (25mg/l)	24.000	1.290
Mid Standard (1000mg/l)	957.818	8.368
Waste water	402.682	7.713

## Determination of Total Nitrogen and Total Phosphorous

Concentrations of Total Nitrogen (TN) and Total Phosphorous (TP) are measured using a *Skalar San System Auto Analyser*. This method determines the TN and TP concentrations of a solution taking account of both, free and bound nitrogen and phosphorous molecules.

For the determination of *Total Nitrogen* the sample is mixed with borax buffer and, after mixing, an excess of potassium persulphate solution is added. The mixture is then transferred into a UV digester. Hereafter the nitrate is determined by the *Griess reaction* after reduction of nitrate to nitrite by a cadmium copper reductor. The colour is measured at 540 nm.

For measuring *Total Phosphorous* the sample is hydrolysed at 97°C and hereafter transferred into an UV digester. The ammonium molybdate catalysed by potassium antimony tartrate reacts in an acidic medium with diluted solutions of phosphate to form a phospho-molybdic acid complex. This complex is reduced to an intensely blue coloured complex by reaction with ascorbic acid, the colour of which is then measured at 880 nm.

The concentrations of TN and TP are calculated directly by the Skalar San System.

Limit of Detection:	0.5897 mg L <sup>-1</sup>
Reporting Limit:	1.0 mg L <sup>-1</sup>
Concentration range:	0 to 50 mg L <sup>-1</sup>

Precision Data (mg L<sup>-1</sup>):

<u>Total Nitrogen</u>	<u>Mean</u>	<u>StDev</u>
Low Standard	4.9445	0.171
High Standard	45.4723	0.854

Limit of Detection:	0.0342 mg L <sup>-1</sup>
Reporting Limit:	0.2 mg L <sup>-1</sup>
Concentration range:	0 to 10 mg L <sup>-1</sup>

Precision Data (mg L<sup>-1</sup>):

<u>Total Phosphorous</u>	<u>Mean</u>	<u>StDev</u>
Low Standard	0.9523	0.033
High Standard	9.0973	0.114

## Appendix III – ICP-OES Standards

Element	Units	STD1	STD2	STD3	STD4	STD5	STD6	STD7	STD8	STD9
Na	mg/l	2.5	5	10	12.5	25	50	12.5	25	50
K	mg/l	0.625	1.25	2.5	3.125	6.25	12.5	3.125	6.25	12.5
Ca	mg/l	1.25	2.5	5	56.25	112.5	225	56.25	112.5	225
Mg	mg/l	0.625	1.25	2.5	3.125	6.25	12.5	3.125	6.25	12.5
B	µg/l	25	50	100	250	500	1000	25	50	100
Li	µg/l	25	50	100	25	50	100	25	50	100

Table 1: Composition of standard solutions STD1 to STD9 used for the calibration of the OPTIMA 3300 (DV) ICP-OES system

Element	Unit	STD11	STD12	STD13
Al	µg/l	200	1000	2000
Sr	µg/l	100	500	1000
Be	µg/l	100	500	1000
Ba	µg/l	100	500	1000
Mn	µg/l	100	500	1000
Co	µg/l	100	500	1000
Fe	µg/l	100	500	1000
Zn	µg/l	100	500	1000
V	µg/l	100	500	1000
Cd	µg/l	100	500	1000
Cr	µg/l	100	500	1000
Ni	µg/l	100	500	1000
Mo	µg/l	100	500	1000
Pb	µg/l	100	500	1000

Table 2: Composition of the standard solutions STD11 to STD12 used for the calibration of the OPTIMA 3300 (DV) ICP-OES system

Element	Units	MN4	MN6	MN8	Deviation equation
Ca	µg/l	4000	6000	8000	$y = 0.9396x + 471.88$
Mg	µg/l	4000	6000	8000	$y = 0.9698x + 269.82$
Sr	µg/l	4000	6000	8000	$y = 0.9504x + 199.68$
Be	µg/l	4000	6000	8000	$y = 0.8726x + 385.39$
Mn	µg/l	4000	6000	8000	$y = 0.8973x + 280.76$
Fe	µg/l	4000	6000	8000	$y = 0.9329x + 268.68$
Cr	µg/l	4000	6000	8000	$y = 0.9201x + 336.9$

Table 3: Composition of high concentration standard solutions and deviation equations for elements to which correction was applied

## Appendix IV – Chlorophyll-*a* analysis using High Performance Liquid Chromatography (HPLC)

(after Colby, 2000)

### Sample collection and preparation

The samples were collected by filtering an appropriate volume of water through a 'Whatman' GFC 4.25 $\emptyset$  filter as described in Chapter 4 and stored in deep cold storage at -81°C. Prior to analysis, the glass fibre filters onto which the particulate matter from the reservoir water was collected were extracted in a solution of HPLC grade methanol (100%). For that, the filters were transferred into dark test tubes to which the Methanol was added. The test tubes were then simmered in a water bath (60°C) for about one hour before being transferred into a sonication bath, where the samples were left for another 90 minutes. Finally, the extracts had to be centrifuged to remove suspended matter or sediments from the samples.

### Sample analysis

For the analysis, a reverse-phase-three-solvent technique was applied, using a linear gradient to aid separation of the pigments. The three solvents used were:

- A 2000ml methanol, 500ml water, 3.75g Tetrabutylammonium Acetate, 19.25g Ammonium Acetate
- B 2250ml methanol, 250ml acetone
- C 435ml propanol, 565ml methanol (or a ratio of that effect).

To ready the samples for the analysis they had to be filtered into an 'Eppendorff' using 0.2 $\mu$ m NYL 4mm  $\emptyset$  filters before being loaded into the HPLC. The samples were then introduced into a photo diode array (PDA) detector in which polychromatic light was directed through the sample flow cell. The absorbance spectrum was separated on a diffraction grating down beam from the flow cell and projected onto an array of up to 400 photodiodes, each of which monitors a discrete wavelength. After completion of the analysis, the pigment signatures were compared against absorption spectra and time off the column. The chlorophyll-*a* signature was then identified and the peak area calculated using a linear regression formula derived from the standards. This had to be done separately for each successive run since correlation coefficients and regression formulas will alter (Colby, 2000).

### Appendix V - Discharge: calculated versus measured values

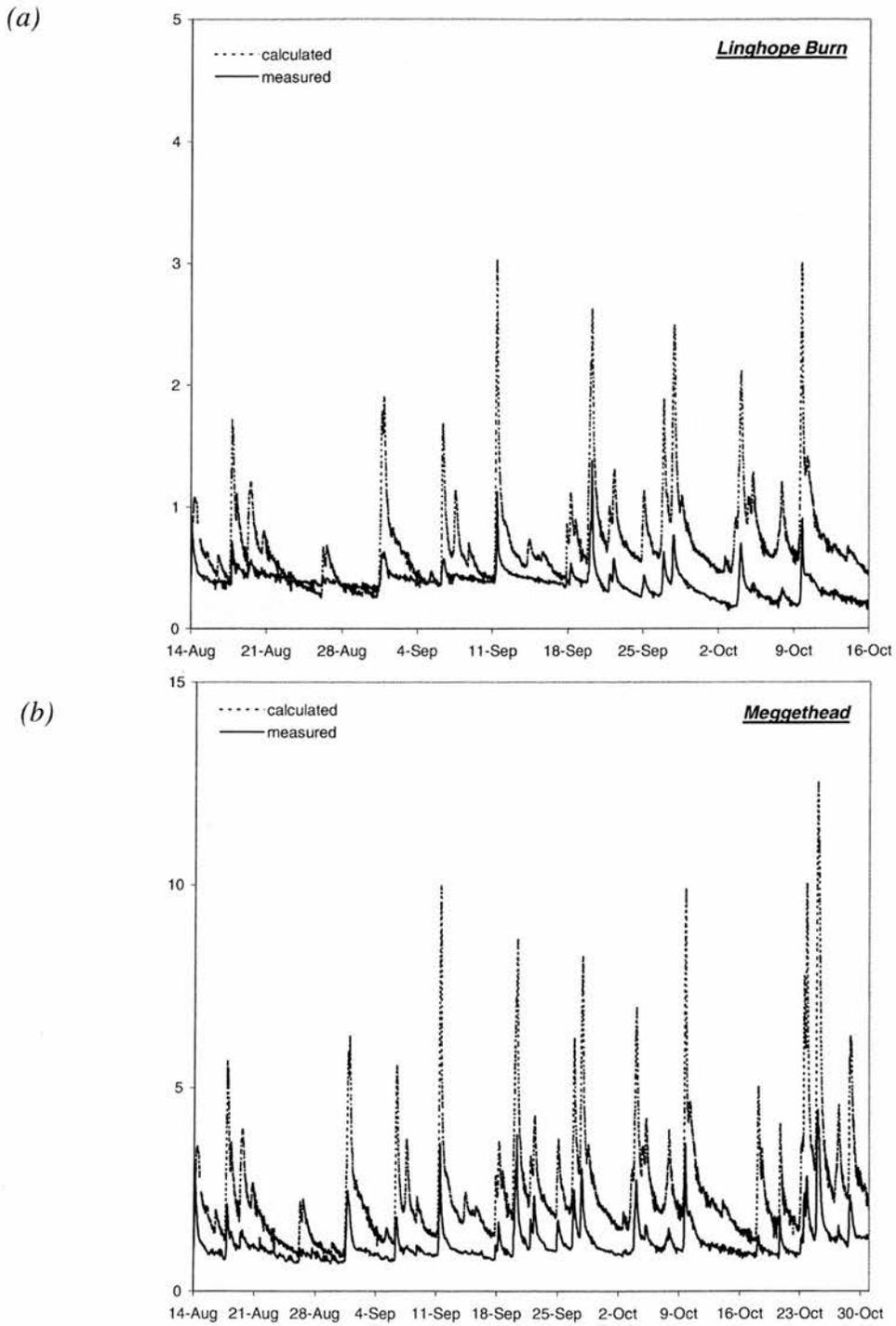


Figure 1: Comparison between measured (solid line) and calculated (dashed line) discharge values at (a) Linghope Burn and (b) Megget Water (Meggethead)