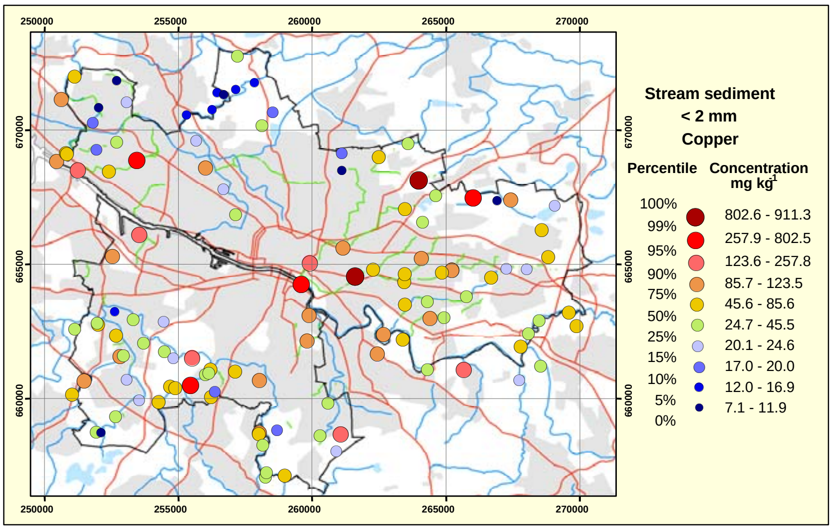
Clyde Tributaries: Report of Urban Stream Sediment and Surface Water Geochemistry for Glasgow

Urban Geoscience and Geological Hazards Programme

Commissioned Report CR/04/037



BRITISH GEOLOGICAL SURVEY

COMMISSIONED REPORT CR/04/037

Clyde Tributaries: Report of Urban Stream Sediment and Surface Water Geochemistry for Glasgow

F M Fordyce, B É Ó Dochartaigh, T R Lister, R Cooper, A Kim, I Harrison, C Vane and S E Brown.

The National Grid and other Ordnance Survey data are used with the permission of the Controller of Her Majesty's Stationery Office.
Ordnance Survey licence number 100017897/2004

Key words

Urban, stream sediment, stream water, geochemistry, contamination, organic contaminants, metals.

Front cover
Geochemical map of copper concentrations in < 2mm stream sediments in Glasgow

Bibliographical reference

FORDYCE F M, Ó DOCHARTAIGH B É, LISTER T R, COOPER R, KIM A, HARRISON I, VANE C AND BROWN S E. 2004. Clyde Tributaries: Report of Urban Stream Sediment and Surface Water Geochemistry for Glasgow. *British Geological Survey Commissioned Report*, CR/04/037. 169pp.

Contributors

Field Survey

J Harvey and S Quigley

Sample Preparation

M Allen and N Fortey

Sediment Analysis

M Ingham, C Gowing, B P Vickers and V L Moss-Hayes

Water Analysis

S Reeder, J Cook and S Chenery

Keyworth, Nottingham British Geological Survey 2004

BRITISH GEOLOGICAL SURVEY

The full range of Survey publications is available from the BGS Sales Desks at Nottingham and Edinburgh; see contact details below or shop online at www.thebgs.co.uk

The London Information Office maintains a reference collection of BGS publications including maps for consultation.

The Survey publishes an annual catalogue of its maps and other publications; this catalogue is available from any of the BGS Sales Desks.

The British Geological Survey carries out the geological survey of Great Britain and Northern Ireland (the latter as an agency service for the government of Northern Ireland), and of the surrounding continental shelf, as well as its basic research projects. It also undertakes programmes of British technical aid in geology in developing countries as arranged by the Department for International Development and other agencies.

The British Geological Survey is a component body of the Natural Environment Research Council.

Keyworth, Nottingham NG12 5GG
☎ 0115-936 3241 Fax 0115-936 3488
e-mail: sales@bgs.ac.uk
www.bgs.ac.uk
Shop online at: www.thebgs.co.uk

Murchison House, West Mains Road, Edinburgh EH9 3LA
☎ 0131-667 1000 Fax 0131-668 2683
e-mail: scotsales@bgs.ac.uk

London Information Office at the Natural History Museum (Earth Galleries), Exhibition Road, South Kensington, London SW7 2DE
☎ 020-7589 4090 Fax 020-7584 8270
☎ 020-7942 5344/45 email: bgslondon@bgs.ac.uk

Forde House, Park Five Business Centre, Harrier Way, Sowton, Exeter, Devon EX2 7HU
☎ 01392-445271 Fax 01392-445371

Geological Survey of Northern Ireland, 20 College Gardens, Belfast BT9 6BS
☎ 028-9066 6595 Fax 028-9066 2835

Maclean Building, Crowmarsh Gifford, Wallingford, Oxfordshire OX10 8BB
☎ 01491-838800 Fax 01491-692345

Parent Body

Natural Environment Research Council, Polaris House, North Star Avenue, Swindon, Wiltshire SN2 1EU
☎ 01793-411500 Fax 01793-411501
www.nerc.ac.uk

Acknowledgements

The authors are grateful to Mr Paul Mellon of the Development and Regeneration Services Department of Glasgow City Council for his support of this project and assistance with the survey design and logistics and provision of sample handling facilities in Glasgow. Mr David Robertson of the Watercourse Engineers Department of Glasgow City Council is gratefully thanked for his advice and aid with the collection of samples from culverted streams. Mr Justin Carter is thanked for permission to use his photographs of sampling on the Camlachie Burn. Dr Mike Browne of the British Geological Survey is thanked for overall project management and Dr Chris Johnson and Mr Dave Bridge of the British Geological Survey for their comments on the text.

Contents

FIGURES

TABLES

Glossary

AAS	Atomic Absorption Spectrometry
AFS	Atomic Fluorescence Spectrometry
API	American Petroleum Institute
ASE	Accelerated Solvent Extraction
ASTM	American Society for Testing and Materials
BGS	British Geological Survey
CEC	Council of the European Community
CLEA	Contaminated Land Exposure Assessment
CRM	Certified Reference Material
DR-Arc-ES	Direct Reading Arc Emission Spectrometry
DEFRA	Department of the Environment, Food and Rural Affairs
DETR	Department of Transport and the Regions
DMSO	Dimethylsulphoxide
EA	Environment Agency
EAC	Ecotoxicological Assessment Criteria
ED-XRFS	Energy Dispersive X-Ray Fluorescence Spectrometry
ESRI	Environmental Systems Research Institute
FID	Flame Ionisation Detector
DBT	Dibutyltin dichloride
DCM	Dicholormethane
DO	Dissolved Oxygen
G-BASE	Geochemical Baseline Survey of the Environment
GCC	Glasgow City Council
GC-MS	Gas Chromatography Mass Spectrometry
GIS	Geographic Information System
GPS	Global Positioning System
GSUE	Geochemical Survey of Urban Environments
HPLC	High Performance Liquid Chromatography
HMSO	Her Majesties Stationary Office
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICRCL	Interdepartmental Committee for the Redevelopment of Contaminated Land
ISE	Ion Selective Electrode
LLD	Lower Limit of Detection

LLR	Lower Limit of Reporting
MAC	Maximum Admissible Concentration
MAFF	Ministry of Agriculture, Fisheries and Food
MBT	Monobutyltin trichloride
NDIR	Non Dispersive Infra Red Gas Analysis
NGR	National Grid Reference
NOAA	National Oceanographic and Atmospheric Administration
NPOC	Non Purgeable Organic Carbon
OS	Ordnance Survey
OSPAR	Oslo And Paris Conventions For The Prevention Of Marine Pollution
PAH	Polycyclic Aromatic Hydrocarbons
PCB	Poly Chlorinated Biphenyls
PHE	Potentially Harmful Elements
PHS	Potentially Harmful Substances
PLM	Polarised Light Microscopy
RBCA	Risk-Based Corrective Action
RBSL	Risk-Based Soil-Screening Levels
SEPA	Scottish Environmental Protection Agency
SGV	Soil Guideline Value
SSTL	Site-Specific Target Levels
TBT	Tributyltin chloride
TDS	Total Dissolved Solids
THF	Tetrahydrofuran
TIC	Total Inorganic Carbon
TLIC-FID	Thin Layer Chromatography Flame Ionisation Detector
TOC	Total Organic Carbon
TPH	Total Petroleum Hydrocarbons
UKAS	United Kingdom Accreditation Service
US-EPA	United States Environmental Protection Agency
ULR	Upper Limit of Reporting
WD-XRFS	Wavelength Dispersive X-Ray Fluorescence Spectrometry
WFD	Water Framework Directive
WHO	World Health Organisation
WSR	Water Supply Regulations
XRD	X-Ray Diffraction Analysis

Summary

This report presents the results of an urban drainage geochemical survey carried out jointly by the British Geological Survey (BGS) and Glasgow City Council (GCC) during June 2003. 118 stream sediment and 122 surface water samples were collected at a sample density of 1 per 1 km^2 from all tributaries draining into the River Clyde within the GCC administrative area. The study was carried out as part of the BGS systematic Geochemical Surveys of Urban Environments (GSUE) programme.

Stream sediment and surface water samples underwent analysis for approximately 46 chemical elements including contaminants such as As, Al, Cd, Cu, Cr, Ni, Pb, Se, V and Zn according to standard GSUE procedures. In addition, parameters such as ammonium, asbestos and Hg as well as organic contaminants such as total petroleum hydrocarbons (TPH), polycyclic aromatic hydrocarbons (PAH), poly-chlorinated biphenyls (PCB) and organo-tin compounds were assessed.

The aim of the project was to provide an overview of urban drainage geochemistry in Glasgow to link to an on-going sister project, which is investigating the geochemistry of the Clyde estuary. This report presents the initial findings of the Clyde tributaries survey but it is envisaged that the data will be interpreted in more detail as part of a wider Clyde basin study once the Clyde estuary survey is completed.

This report documents the survey and analytical methods and presents the geographic distribution of parameters as a series of graduated symbol geochemical maps. These were generated by the project GIS which accompanies this report.

Comparisons between the urban drainage data and rural geochemical data collected previously by the BGS Geochemical Baseline Survey of the Environment (G-BASE) programme demonstrate that many metal elements are elevated 2-3 times in the urban versus rural environment regardless of parent material type. Two sediment size fractions were examined during the present study and the results show that the majority of contaminants are concentrated in the fine fraction material and are probably associated with clay minerals, iron and manganese oxides and organic matter. These results have implications for the mobility and transport of contaminants in the environment and it is recommended that these issues be examined further as part of a wider Clyde basin study.

Although there are no current UK guidelines for sediment quality, comparisons with soil quality guidelines and with UK water regulations revealed that many metal elements and TPH, PAH and PCB exceed the guidelines particularly in the north-west, east and south-east of the city and Clyde corridor in areas influenced by heavy engineering, iron and steelworks, railway works, coal mining, and fill materials. Levels of Cr in waters up to 903 $\mu g\ L^{-1}$ associated with Cr processing waste are of particular concern and it is recommended that relationships between land use, catchment hydrodynamics, and contaminant transport be assessed in more detail as part of future Clyde basin geo-environmental study.

1 Introduction

This report presents the results of a joint project between Glasgow City Council (GCC) and the British Geological Survey (BGS) to carry out a systematic urban stream sediment and stream water geochemical survey across the Glasgow City Council administrative area between June 2003 and March 2004. The aim of the project was to provide an overview of sediment and water quality on all tributaries draining into the River Clyde as an aid to planning and development.

The geochemical data are presented as a series of graduated symbol maps in the annexes of this report and are available digitally in the accompanying project geographic information system (GIS), which is based on the Arc8® software package. The geochemical survey and the GIS are described in this report

The project forms part of a larger joint initiative between GCC and BGS, which aims to characterise the geo-environment of the Clyde basin. In this context, this report presents the initial findings of the Clyde tributaries geochemical survey but it is anticipated that further interpretation of the data will take place in conjunction with an on-going GCC-BGS joint project to characterise the Clyde estuary (Jones et al., 2004).

1.1 GEOCHEMISTRY AND ENVIRONMENTAL CONCERNS

The 92 naturally occurring elements on Earth that form the different rocks, soils, waters and gases that are the building blocks of the planet are not distributed evenly across the globe. Concentrations at any location are often controlled by factors such as geology, vegetation, soil forming processes and climate. In addition to natural sources of these elements, environmental concentrations can be enhanced by anthropogenic activities such as mining, industrialisation, urbanisation and waste disposal. The distribution of the elements is of concern because although many are essential to life, at least 26 of the naturally occurring elements are potentially harmful to plants and animals in high doses (Table 1.1). The toxicity and mobility of these potentially harmful substances (PHS) are often controlled by the amount of other elements present so it is important to understand as fully as possible, the chemical composition of the environment.

Table 1.1 Potentially harmful elements for human, animal and plant health

Chemical Symbol	Element Name	Chemical Symbol	Element Name
Al	Aluminium	Mn	Manganese
As	Arsenic	Mo	Molybdenum
B	Boron	Ni	Nickel
Bi	Bismuth	Pb	Lead
Cd	Cadmium	Sb	Antimony
Cl	Chlorine	Se	Selenium
Co	Cobalt	Sn	Tin
Cr	Chromium	Te	Tellurium
Cu	Copper	Th	Thorium
F	Fluorine	Tl	Thallium
Fe	Iron	U	Uranium
Hg	Mercury	V	Vanadium
I	Iodine	Zn	Zinc

Although potentially harmful in excess, the majority of elements are essential to health in small doses. Elements listed in blue have no/limited biological function and are generally toxic to most organisms (From Appleton, 1995)

Also of concern are the quantities of potentially harmful organic compounds mainly of man-made origin many of which are detrimental to health. These include the polycyclic aromatic hydrocarbons (PAH), which have been linked to cancer, the polychlorinated biphenyls (PCB), and toxins such as cyanide.

Many UK city environments have a long history of urbanisation resulting in elevated concentrations of potentially harmful substances (PHS) including organic contaminants (PAH, PCB etc.), radioactive materials and potentially harmful elements (PHE) such as As, Cd, Cr, Cu, Ni, Pb, V and Zn derived from industrial and mineral processing and the atmospheric deposition of Pb and other toxins from traffic fumes. Whether or not these substances constitute a hazard depends on a variety of factors. These include their chemical form, concentration, mobility and behaviour in the environment, the extent to which they are taken up by living organisms (bioavailability), the properties of the substrate in which they occur (for example, the acidity of waters or soils and the soil texture and mineral composition), the level of exposure and the dose received. Water is unlikely to pose a risk to human health due to the high standard of public water quality in the UK and the minimal use of private wells in city areas; however, the protection of water resources is a major issue in the urban environment.

1.2 UK LEGISLATIVE FRAMEWORK

Prompted by concerns about land and water quality, national governments and international agencies are developing policies to limit the amount and impacts of PHS in the environment. Although links between long term human health effects and PHS are often difficult to prove, the majority of regulatory authorities adopt a precautionary principal approach to legislate against high environmental concentrations of PHS.

In the UK, one of the main legislative drivers relating to PHS is the Government target for sustainable development, which focuses on the re-use of brownfield sites for 60% of new residential homes. Whilst this policy protects green belts around urban environments, brownfield sites include land that may or may not be contaminated with PHS.

The Environmental Protection Act, Part IIa (1990) was implemented on 1st April 2000 in England, 14th July 2000 in Scotland and 1st July 2001 in Wales. The Act places the responsibility for the identification, assessment, remediation and monitoring of contaminated land with local authorities as follows:

Environmental Protection Act, Part IIa (1990)
Definitions:

Contaminated land is defined as:
"any land which appears to the local authority in whose area it is situated to be in such a condition by reason of substances in, on or under the land that:

Significant harm is being caused or there is a significant possibility of such harm being caused or
Pollution of controlled water is being or likely to be caused"

Harm is defined as:
"harm to the health of living organisms, or other interference with the ecological systems of which they form a part, and in the case of man, harm to his property"

The Act addresses the pollution of waters and threats to ecosystems and buildings in addition to human health risks and operates a 'polluter pays' principle in terms of remediation. However, it is important to point out that Part IIa only applies to a sub-set of land that is chemically contaminated. The identification of contaminated land relies on the concept of risk assessment, based on a pollutant linkage whereby the presence or source of contamination has the potential to impact on a receptor by means of a pathway (Figure 1.1). If the linkage does not exist then, in terms of the Act, the land is not contaminated. Thus, for example, an area of ground could contain high concentrations of As but if this is not affecting water resources, property, living organisms or ecosystems then it will not be classified as contaminated.

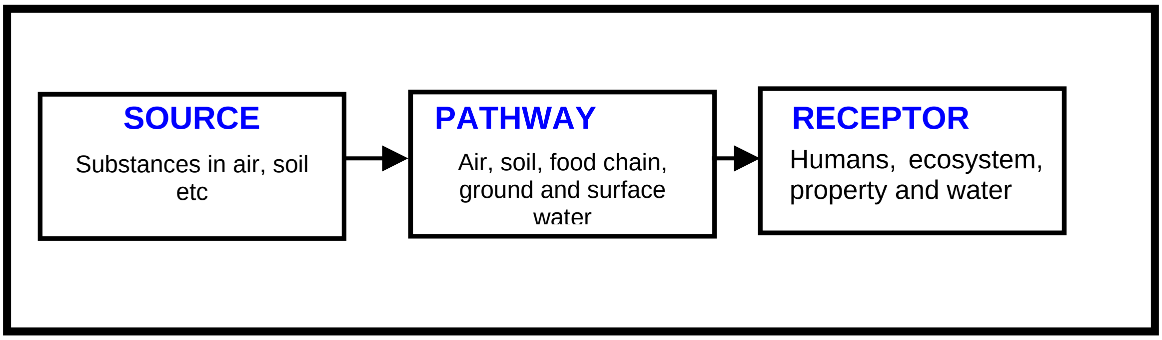


Figure 1.1 Concept of source, pathway and receptor in the assessment of contaminated land

Several guidelines exist to aid the identification, assessment and management of contaminated land. In terms of water quality, the World Health Organisation (WHO) defines maximum admissible concentrations (MAC) of PHS in drinking water (WHO, 1996). The European Union Water Quality Framework Directive (CEC, 1998) incorporates many of the WHO values and is the legislative basis for water suppliers and regulatory authorities in Scotland (WSR, 2000) (Table 1.2).

There are no current guidelines relating to freshwater sediment quality in the UK but soil guidelines can be used as an approximation for sediments. Until recently, the UK Government Interdepartmental Committee for the Redevelopment of Contaminated Land (ICRCL, 1987) guidelines provided maximum recommended thresholds or trigger values for contaminants in soil depending on the land use (Table 1.3). However, the Government is currently developing a new risk assessment tool for human exposure known as the Contaminated Land Exposure Assessment (CLEA) model. Initially conceived by Nottingham University, the model is now being developed by the Environment Agency (EA) and to date includes risk assessment information for As, Cd, Cr, cyanide, Pb, Hg, Ni, phenols, PAH and Se. In due course, the Government aims to provide information for approximately 50 PHS. On this basis 'typical' soil guideline values (SGV) for As, Cd, Cr, Pb, Hg, Ni and Se have been defined (Table 1.3). A similar risk assessment model compatible with CLEA has been developed with the Scottish Environmental Protection Agency (SEPA) (SNIFFER, 2003). The United States National Oceanographic and Atmospheric Administration (NOAA) has established screening values for freshwater sediment (Table 1.3) on the basis of ecotoxicological effects on aquatic organisms but these are not regulatory action or clean-up thresholds rather they provide a guide to sediment quality (NOAA, 1999). Similarly, the Oslo and Paris Conventions provide non-regulatory indicators of marine sediment quality for the Prevention of Marine Pollution (OSPAR, 1997).

Table 1.2 Water quality guideline values

Parameter	Units	WSR	WHO	CEC Drinking Water	CEC Aquatic Life	Canadian	Norwegian	Russian	US-EPA
Aluminium	µg L^{-1}	200	100	200	1.6		200		50-200
Ammonium	mg L^{-1}	0.5	1.5	0.5	0.04 - 1				
Antimony	µg L^{-1}	5		5			10		6
Arsenic	µg L^{-1}	10	10	10	10	50	10	50	50
Barium	mg L^{-1}		0.7	0.1		1	0.1	0.1	2
Beryllium	µg L^{-1}							0.2	4
Bismuth	µg L^{-1}							100	
Cadmium	µg L^{-1}	5	3	5	0.07	5	5	1	5
Calcium	mg L^{-1}		100 - 300	100			15-25 min		
Chloride	mg L^{-1}		250	250		250	25		4
Chromium	µg L^{-1}	50	50	50	1	50	50		100
Cobalt	µg L^{-1}							100	
Conductivity	µS cm^{-1}	1500		2500					
Copper	µg L^{-1}	2000	2000	2000	2	1000	300	1000	1300
Dissolved Oxygen	mg L^{-1}			5.0	7				
Fluoride	mg L^{-1}	1.5	1.5	1.5		1.5	1.5		
Iron	mg L^{-1}	0.2	0.3	0.2		0.3	0.2	0.3	
Lead	µg L^{-1}	25	10	10	0.1	50	20	30	15
Lithium	µg L^{-1}							30	
Magnesium	mg L^{-1}			50			20		
Manganese	mg L^{-1}	0.05	0.4	0.05		0.05	0.05	0.1	0.05
Mercury	µg L^{-1}	1	1	1	0.003	1	0.5	0.5	2
Molybdenum	µg L^{-1}		70					250	
Nickel	µg L^{-1}	20	20	20	15		50	100	40
Nitrate	mg L^{-1}	50	50	50	0.3	10	10		
PAH	µg L^{-1}	0.1		0.1					
PCB	µg L^{-1}								0.5
pH		6.5 - 10	6.5 - 9.5	6.5 - 9.5	6.5 - 9				
Phosphorus	mg L^{-1}			5	0.01		5		
Potassium	mg L^{-1}			12			12		
Selenium	µg L^{-1}	10	10	10		10	10	1	50
Silicon	mg L^{-1}							10	
Sodium	mg L^{-1}	200	200	200			150		
Strontium	mg L^{-1}							7	4
Sulphate	mg L^{-1}	250	250	250		500	100		
Sulphide	mg L^{-1}	250		250		0.05			
Thallium	µg L^{-1}							0.1	50
Total Alkalinity	mg L^{-1}		100 - 200		200				
Total Cyanide	µg L^{-1}	50	100	50					200
Total Dissolved Solids	mg L^{-1}		600	1500					
Uranium	µg L^{-1}		9			20		1700	100
Vanadium	µg L^{-1}							100	
Zinc	µg L^{-1}	5000	4000	5000	45	5000	300	1000	5000

WSR = WSR (2000) Drinking Water Supply Regulations Scotland
WHO = WHO (1996) Drinking Water Standards
CEC Drinking Water = CEC (1998) Drinking Water Standards
CEC Aquatic Life = CEC (1978) Aquatic Life Standards Class I Rivers
Canadian = Canadian Drinking Water Standards (Reimann and Caritat, 1998)
Norwegian = Norwegian Drinking Water Standards (Reimann and Caritat, 1998)
Russian = Russian Drinking Water Standards (Reimann and Caritat, 1998)
US-EPA = US-EPA (2004) Drinking Water Standards

Table 1.3 Soil and sediment quality guideline values

Parameter	Units	US-EPA Soil Cleanup	CLEA Soil Guidelines	ICRCL Soil Guidelines	German Soil Guidelines	Netherlands Soil Remediate	US-NOAA Sediment
Aluminium	wt%						2.55
Antimony	mg kg^{-1}	28			5		3
Arsenic	mg kg^{-1}	21	20	10	20	55	5.9
Barium	mg kg^{-1}					625	
Cadmium	mg kg^{-1}		1 or 2 or 8	3.0	1.5	12.0	0.58
Chromium	mg kg^{-1}		130	600	100	380	36
Cobalt	mg kg^{-1}				50	240	
Copper	mg kg^{-1}			130	100	190	28
Iron	wt%						4
Lead	mg kg^{-1}		450	500	100	530	35
Manganese	wt%						82
Mercury	mg kg^{-1}		8	1	1	10	0.17
Molybdenum	mg kg^{-1}				5	200	
Nickel	mg kg^{-1}		50	70		210	18
PAH	mg kg^{-1}			50			0.026
PCB	mg kg^{-1}			5			0.031
pH				5			
Silver	mg kg^{-1}						4.5
Selenium	mg kg^{-1}		35	3	10		
Thallium	mg kg^{-1}	1			1		
Tin	mg kg^{-1}				50		
Total Cyanide	mg kg^{-1}			25			
Uranium	mg kg^{-1}				5		
Vanadium	mg kg^{-1}				50		
Zinc	mg kg^{-1}			300	300	720	98

US-EPA = US-EPA (2004a) Soil Clean-Up Guideline
CLEA Guideline = DEFRA (2004) 'Typical' Soil Guideline Values
ICRCL Guideline = ICRCL (1987) Soil Trigger Values
Netherlands Remediation = Reimann and Caritat (1998) Soil Remediation Threshold
German Guideline = Reimann and Caritat (1998) Soil Guideline Values
US-NOAA = NOAA (1999) Freshwater Sediment Screening Values

In order to aid the assessment of environmental quality in urban environments, the BGS is providing systematic information on the concentrations of PHS across British cities as follows.

1.3 GEOCHEMICAL SURVEYS OF URBAN ENVIRONMENTS (GSUE)

The BGS is responsible for carrying out the national strategic geochemical survey of Great Britain, known as the Geochemical Baseline Survey of the Environment (G-BASE), which defines the spatial distribution of chemical element concentrations across the British surface environment. The mapping programme is based primarily on the collection of fine fraction (< 150 µm) rural stream sediments and stream waters from first and second order streams at a sampling density of 1 per 1.5 km^2. The programme began in the late 1960s in the north of Scotland and working southwards, will eventually provide information for the whole country (BGS, 2000). In more recent years, soil sampling been incorporated into the programme, hence soil data are available from Mid England southwards. Soil sampling is based on the < 2 mm fraction of rural top (5 to 0.20 m) deeper (0.35 to 0.50 m) soils collected at a density of 1 per 2 km^2. Although initially, the programme focussed on rural areas, in response to concerns about

PHS in the urban environment and the new statutory requirements on local authorities (Environmental Protection Act Part IIa, 1990), urban mapping commenced in 1992.

The Geochemical Surveys of Urban Environments (GSUE) project, developed from preliminary studies carried out in collaboration with Imperial College, London in Wolverhampton and Richmond-on-Thames (Kelly et al., 1996; Bridge et al., 1997; Kelly, 1997) and to date, 21 urban centres have been sampled (McMillan et al., 2001). Urban surveying is primarily based upon the collection of soil samples at a sampling density of 4 per km^2 and is designed to give an overview of the city geochemical signature. A systematic soil geochemical survey of the Glasgow conurbation was undertaken during 2000 – 2001 by the BGS and the results of this study will be reported later in 2004.

GCC expressed interest to the BGS in an urban drainage geochemical survey of the River Clyde tributaries to link with the work being carried out on Clyde estuary geochemistry (Jones et al., 2004). Although drainage geochemical sampling forms the basis of the BGS rural G-BASE programme and urban stream sampling was piloted during orientation studies carried out for the GSUE project in Wolverhampton and Telford, urban drainage does not form part of the routine GSUE urban survey. Although some work has been carried under the Estuarine Contamination programme in BGS to assess river catchment and estuarine relationships using the G-BASE and estuarine geochemical datasets (Ridgway et al., 2001), the Clyde Basin study is the first time that samples have been collected specifically for this purpose and the first time that these investigations have been carried out in an urban environment.

The routine methods used for rural drainage sampling were amended for the Glasgow urban survey. In addition to the 40 or so total element concentrations (including the PHS As, Cd, Cr, Cu, Ni, Pb, Se, V, Sn, U and Zn) determined in sediments and waters by the G-BASE/GSUE programmes, GCC were interested in organic and particulate contaminants therefore, PAH, PCB, organo-tin, cyanide, total petroleum hydrocarbons (TPH) and asbestos were included in the survey. The study was designed to provide an overview of urban drainage quality within the GCC area.

The concentrations of many substances are enhanced in the urban environment as a result of atmospheric and terrestrial contamination, effluent and waste discharges and the nature of urban ground, which is often disturbed and in-filled and bears little relation to the bedrock/superficial cover of the surrounding rural hinterland. Hence it is necessary to establish the overall urban geochemical signature so that areas of concern within a city can be highlighted. It should be noted that systematic urban surveys do not replace the need for site-specific investigations; rather the data provide the citywide framework and context to more detailed assessments.

1.4 URBAN GEOGRAPHIC INFORMATION SYSTEMS

The GSUE geochemical data are stored digitally allowing ready incorporation into a geographic information system (GIS). A GIS is a computer system for capturing, storing, checking, integrating, manipulating, analysing and displaying spatial data. Maps are the most common type of spatial data and show the distribution of features and the locational relationships between objects. A GIS is based upon a database that allows spatial information such as grid references or postcodes, which can only be visualised by plotting on a map, to be linked to attribute data. Attribute data provide other information about points in space such as the type of a building or road, or the height of a hill. A GIS digitally integrates databases and maps to produce a very powerful tool for environmental analysis. One of the main benefits of a GIS is the ready ability to store different information as separate data layers, which can be superimposed and interrogated simultaneously. GIS were developed to make cartography and data analysis easier and as such allow the storage of large amounts of data in a systematic format and the easy output of information as maps and reports. Due to their versatility, local authorities to aid urban planning use GIS increasingly.

The importance of geoscience information and GIS to urban planning have been outlined by Ellison et al. (1998) and Hooker et al. (2000) and the BGS is currently developing several urban GIS procedures for local authorities (Brown and Marchant, 2000). Future GIS developments involving geochemical data are likely to take place within the broader context of the urban planning and contaminated land prioritisation GIS currently under construction in the BGS. A number of GIS software packages are commercially available and the Arc8® software was selected for the present study, as it is the BGS corporate standard and is the system most commonly used by local authorities.

1.5 OBJECTIVES OF THE PRESENT STUDY

Throughout the development of the Clyde tributaries survey, the objectives of the study were to:

1. Provide an overview of urban sediment and water quality of all tributaries draining into the Clyde in the GGC area
2. Present in report and GIS format, the results of the survey with initial interpretation of the data
3. Provide information for future integrated studies with data from the Clyde estuary and GSUE urban soils projects

2 Environmental Information

This chapter provides a background to the study area outlining the data layers available for incorporation into the Glasgow tributaries GIS. Many of these layers were derived from the environmental geological mapping of the Glasgow area carried out by the BGS during the 1980s (Forsyth et al., 1984a, b, c; Forsyth et al. 1985; Browne et al., 1986 and Hall et al., 1998). A summary of the information pertinent to the present study is presented here.

2.1 THE GLASGOW CITY COUNCIL STUDY AREA

The study area comprises approximately 198 km^2 of the central urban area of Glasgow contained within the administrative boundary of GCC (Figure 2.1). The settlement of Glasgow has existed since the Bronze Age and developed on high ground close to the most reliable seaward ford of the River Clyde. The City and Burgh were decreed by Royal Charter during the 12th century, but up until the establishment of the university in 1451 the city was essentially a small ecclesiastical centre (population 4500) based around the Cathedral (Figure 2.1). By the end of the 16th century, coal was being exported in flat-bottomed barges but development of the River Clyde was necessary to allow safe passage for larger vessels. In the 19th century a dredged channel was cut to allow ocean-going ships access to the city centre. The development of the area was based largely on the combination of transport via the River Clyde and mineral extraction related to the local geology. The numerous and easily accessible coal and ironstone seams of the Coal Measures provided the fuel and raw materials to support a thriving industrial centre. From 1732 onwards the establishment of ironworks and forges increased the local demand for coal and ironstone at the expense of the export trade and by 1800 the population had grown to 84,000 reflecting the gathering momentum of the industrial revolution.

The trend of increasing population and commercial success continued through the 19th century with the advent of stream trains and iron ships which made further demands on the coal and iron resources. The mining of ironstone peaked around 1880 but declined rapidly as the ore proved unsuitable for steel production and it finally ended after the First World War (1914-1918). In contrast, the subsurface mining of coal was at its height in the early 20th century and continued until 1983. Coal-ash and mining waste materials were used as soil conditioners and fill materials across the city. Several other materials were extracted in the area including limestone, seatclay, sandstone, sand and gravel, and dolerite. Several of the quarries have been infilled and used for waste disposal such as at Greenoakhill, which was Scotland's largest recipient of liquid waste (Figure 2.1).

In addition to mining, Glasgow became the third most important port in the UK after London and Liverpool during the 18th and 19th centuries with imports of tobacco, cotton coffee, rum and sugar. In the last years of the 18th and the early years of the 19th centuries, Glasgow became the centre of a cotton spinning region; the number of cotton-mills within a radius of twenty-five miles of the city rose from 19 to a 134 between 1787 and 1834. The flourishing cotton industry stimulated the development of related industries such as bleaching, dyeing and fabric printing. Cotton spinning, weaving, calico printing and bleaching, was centred in the Gallowgate in 1779 and moved to Thornliebank in Renfrewshire, as business expanded (Figure 2.1). Paisley and the

Vale of Leven in Dumbartonshire attracted textile printworks partly because of the suitability of the water.

Heavy industry, particularly shipbuilding which was focussed at Clydebank, developed along the Clyde during the 19th and first half of the 20th centuries and Glasgow was renowned for iron and steel manufacture including the Clydebridge, Westburn, Camlachie and Cathcart Holm works. Heavy engineering was centred at complexes such as Shieldhall, Pollockshaws, Provanmill and Swinton and the railway yards at St Rollox in Royston and Cowlairs (Figure 2.1). Numerous gas works were located throughout the city including Provanmill, Maryhill and Hurlet. Glasgow was also a centre of mineral processing, the company of JJ Whites in Rutherglen (Figure 2.1), was the world's largest chrome producer during the 19th century and operated until 1967. Chromite-ore processing residues were extensively used as landfill material around southeast Glasgow and between 1960 and 1966 it is estimated that 60 – 70 tonnes of chromite waste were dumped daily.

The city, and in particular Clydebank, sustained heavy bombing during the 2nd World War (1939-1945) and large tracts of the 19th century tenement housing were cleared between the 1950s and 1970s as part of the city's post-war regeneration programme. Much of the inner city population moved out to satellite developments such as Drumchapel, Easterhouse and East Kilbride at this time. This coupled with a decline in heavy industry over the same period, left the city with a legacy of derelict land, which has subsequently been the subject of regeneration schemes, which continue to the present day. Glasgow today is a thriving business, retail cultural and tourism centre with a modern mixed economy including biosciences, optoelectronics, contact centre management, software development, creative industries, construction and communication technologies.

2.2 ENVIRONMENTAL DATA FOR GLASGOW

As background to the present study, environmental data for Glasgow were incorporated into an Arc8® GIS for the urban area. The following sections briefly describe these data and restrictions on their usage.

2.2.1 Ordnance Survey Topographic Information

All data derived from the Ordnance Survey (OS) are covered by the corporate BGS and GCC licensing agreements, which allow data to be used for internal projects. Figure 2.1 shows the main roads, railways and built-up areas derived from OS meridian data across the region.

2.2.2 Drainage Network

The drainage network over the study area is also outlined in Figure 2.1. This information was derived from OS data and from information on the location of culverted stream sections provided to the project by GGC for use with the project only.

2.2.3 Land Use Information

Detailed historical and current digital polygonised land use information is available for Glasgow and has been developed in the Environmental Services Department as part of the Council's contaminated land prioritisation strategy under Part IIa of the Environmental Protection Act (1990). This information was not included in the current project as detailed assessments including land use are likely to form part of future integrated studies of the Clyde catchment. The Council provided some information on likely sources of contamination for use with this project, which was included in the geochemical databases to aid data interpretation.

2.2.4 Solid Geology and Superficial Deposits

1: 50 000 and 1: 250 000 scale digital solid geology line work and 1: 50 000 and 1: 625 000 scale digital superficial deposit linework for the study area were incorporated into the GIS from the BGS DigMap® database. The solid geology information was rationalised into the main lithology groups for the area for comparison with the geochemical data (Figure 2.2). The main coal seams in the Glasgow area are also shown on Figure 2.3. Table 2.1 outlines how the rationalised geology key relates to BGS lexcode and 1:50 000 scale solid geology information. Comparisons were also made with the 1: 625 000 superficial deposits (Figure 2.4). The use of these data outside the BGS is covered by the standard BGS DigMap® licensing agreements.

The oldest rocks in the Glasgow area are metamorphosed Dalradian psammites, pelites and greywakes, which occur to the west of Dumbarton. These are overlain unconformably by Lower and Upper Devonian sandstones and Lower Carboniferous (Dinantian age) Inverclyde Group sediments. These sediments comprise sandstones, calcareous sandstones, carbonate cornstones, and mudstones. None of these rock types are shown on the urban area map in Figure 2.2 but are represented on the wider area map in Chapter 4.

Uplift occurred after the deposition of the Inverclyde sediments and was followed by a major period of subaerial volcanic activity. This produced the lavas and volcaniclastic rocks of the Clyde Plateau Volcanics, which form the Kilpatrick Hills to the south of Glasgow and the Campsie Hills to the north and are generally alkali basalt in composition (Figure 2.2). The Calciferous Sandstone grouping of sediments comprise sandstones, siltstones, mudstones and conglomerates derived from the upstanding volcanic terrain formed by the Clyde Plateau Volcanics and underlie areas to the west and south of Glasgow (Figure 2.2). Although coals, sandstones and marine bands are present in this sequence, they are poorly developed. The Hurlet Limestone at the base of the overlying Lower Limestone Group marks a significant change in the sequence indicating that the area was slowly subsiding at this time allowing more extensive marine transgression.

The Lower Limestone Group comprises interbedded dark grey mudstones, clayband ironstones, siltstones, sandstones and marine limestones laid down in quiet conditions with deposition occurring westwards from a large delta that is thought to have occupied most of the central Midland Valley. This is overlain by the Upper Carboniferous (Namurian age) Limestone Coal Formation which was laid down in quiet conditions similar to the Lower Limestone period but with stronger currents bearing sediment from the delta to the east preventing fully marine conditions. The land surface periodically emerged and vegetation colonised the alluvial plain leading to the development of thin coals. The sequence comprises bedded dark grey mudstones, siltstones, sandstones, clayband ironstones and coals near the top. Despite its name, the Limestone Coal Formation contains only a few argillaceous shelly limestones.

The overlying Upper Limestone Formation marks a contrast in the paleaeogeography of the area. The district was inundated by a shallow sea at least 4 times. The sequence comprises thin marine limestones, sandstones and thin coals indicating that deltaic and swampy vegetative conditions prevailed periodically but not to the same extent as in the earlier Limestone Coal Formation.

The Namurian to Westphalian age Passage Formation above, marks a change to fluvially dominated conditions and comprises sandstones, some of which are coarse-grained with large pebbles and unbedded mudstones. The depositional basin probably contracted at this time almost completely excluding the sea and subsidence was reduced so that the basin was repeatedly filled with fluvial sands minimising the opportunities for coal formation. The fluvially-dominated conditions of the Passage Formation gradually gave way to a broad flat coastal deltaic plain where coal-swamp conditions occurred frequently and persistently giving rise to the Westphalian age Coal Measures at the top of the solid geological sequence in the study area. Cyclical sequences of marine bands, mudstones, siltstones, sandstones, seatearths and coals predominate. These rocks underlie most of east and southern Glasgow (Figure 2.2) and the coals have been extensively mined across the area. The locations of the major coal seams in the Glasgow area are outlined in Figure 2.3.

Superficial (drift) deposits occur extensively throughout the area mainly comprising glacial boulder clays and morainic material (Figure 2.4). Under the current BGS classification scheme these deposits would be categorised as diamicton, however, boulder clay is referred to throughout this report to be consistent with the information provided in Hall et al., (1998) and maintain familiar terminology for non-specialists. These deposits underlie much of southern and northern Glasgow and in places can be in excess of 100 m thick. Much of this material has been moulded into drumlins but elsewhere forms a gently undulating plain and commonly rests directly on the bedrock. With the exception of the northern outskirts of the city, fluvio-glacial sand and gravel deposits normally overlie the boulder clay and have been extensively worked in south-east Glasgow. Raised beach and marine deposits comprising muds and sands dominate the centre of the city to the south and north of the River Clyde (Figure 2.4) and were formed during periglacial marine incursions into the Clyde Valley. Peat is generally the uppermost natural superficial deposit and is developed in hollows and low-lying areas to the east of the city (Figure 2.4). Recent coarse-grained sand and gravel alluvial deposits occupy the Clyde Valley in the centre of the city (Figure 2.4).

Table 2.1 Rationalised geology groupings for the present project related to BGS standard 1: 50 000 geological classifications

Rationalised Rock Unit	**BGS DigMap® Codes**	**1: 50 000 Geology Classification**
Carboniferous Rocks		
Coal Measures	UCMS-MEAS, MCMS-MEAS, LCMS-MEAS, PGP-MEAS	Coal Measures Group and Passage Formation
Limestone Coal Group	LSC-MEAS	Limestone Coal Formation
Lower and Upper Limestone Groups	LLMS-MEAS, ULGS-MEAS, BKLS-LMST, BLLS-LMST, BBLS-LMST, CAL-LMST, CAS-LMST, DYLS-LMST, HCLS-LMST, HHLS-LMST, HUR-LMST, ILS-LMST, LLS-LMST, MAHO-LMST, OLS-LMST, P2-LMST, TOHO-LMST, BGN-MDST, LLGS-MEAS	Lower Limestone Formation and Upper Limestone Formation
Calciferous Sandstone Group	LWM-MEAS, DMQ-CONG, BGN-MDST, BGN-MDSL	Strathclyde Group
Inverclyde Group	INV-SARL	Inverclyde Group
Devonian Rocks		
Lower and Upper Devonian Sandstones	KNW-SDST, SCK-SDST, THF-SDST, RON-CONG, OXF-MDST, IMC-CONG, KNW-CORN, KNW-VCSR, THF-SDSL, CXF-MDSD	Devonian Stratheden and Strathmore Groups
Dalradian Rocks		
Dalradian	DCBG-PSPE, DCDP-PELM, DCBB-PSPE	Southern Highland Group and Bullrock Greywacke Formation
Intrusives/Extrusives		
Clyde Plateau Volcanics	All other codes in the area	Clyde Plateau Volcanic Formation

2.2.5 Artificial and Made Ground

Extensive areas of man-made deposits are present in and around the urban areas of Glasgow (Figure 2.5). In many areas, the natural ground surface has been covered by redistributed geotechnically variable natural and man-made materials. Typically made ground of this nature is only a few meters thick but in areas close to former excavations, thicker deposits up to tens of meters may be expected. These deposits, where known, are indicated as fill on Figure 2.5. Examples of major ground disturbance include the motorway network, former coal pit bings, slag tips and dredged material from the River Clyde and the Clyde Road Tunnel.

2.2.6 Quarries

As indicated above, the district has been extensively quarried for minerals including sand and gravel, brick clay, hardrock aggregate fireclay, shale, sandstone and coal. The locations of known quarries derived from BGS data are outlined in Figure 2.6. Many former quarries have been infilled with variably compacted materials and built over. Furthermore, early landfill in Glasgow took place in the numerous sand, gravel and brick pits and in building stone quarries in and around the city. The existence of some of these quarries and landfills has only been revealed by drilling over the last 15 years. The Wilderness Landfill at Buchley (Figure 2.6) was formerly a sand and gravel pit and suffered leachate loss into the River Kelvin during the 1970s. The problem was subsequently rectified via engineering works. Another problematic site was at Balmuildy where sand and gravel lenses on the floodplain of the River Kelvin allowed leachate to access the river (Figure 2.6). The adjacent Blackhill Brickworks site was engineered in the early 1980s to allow leachate to access the Upper Limestone Formation via the sands and gravels. However, by the mid-1980s techniques had progressed and the nearby Summerston site was constructed for containment of the leachate using an impermeable liner. The former Greenoakhill Quarry was Scotland’s largest recipient of liquid waste whereas domestic waste has also been disposed of at Summerston, Wilderness and Mavis Valley (Figure 2.6).

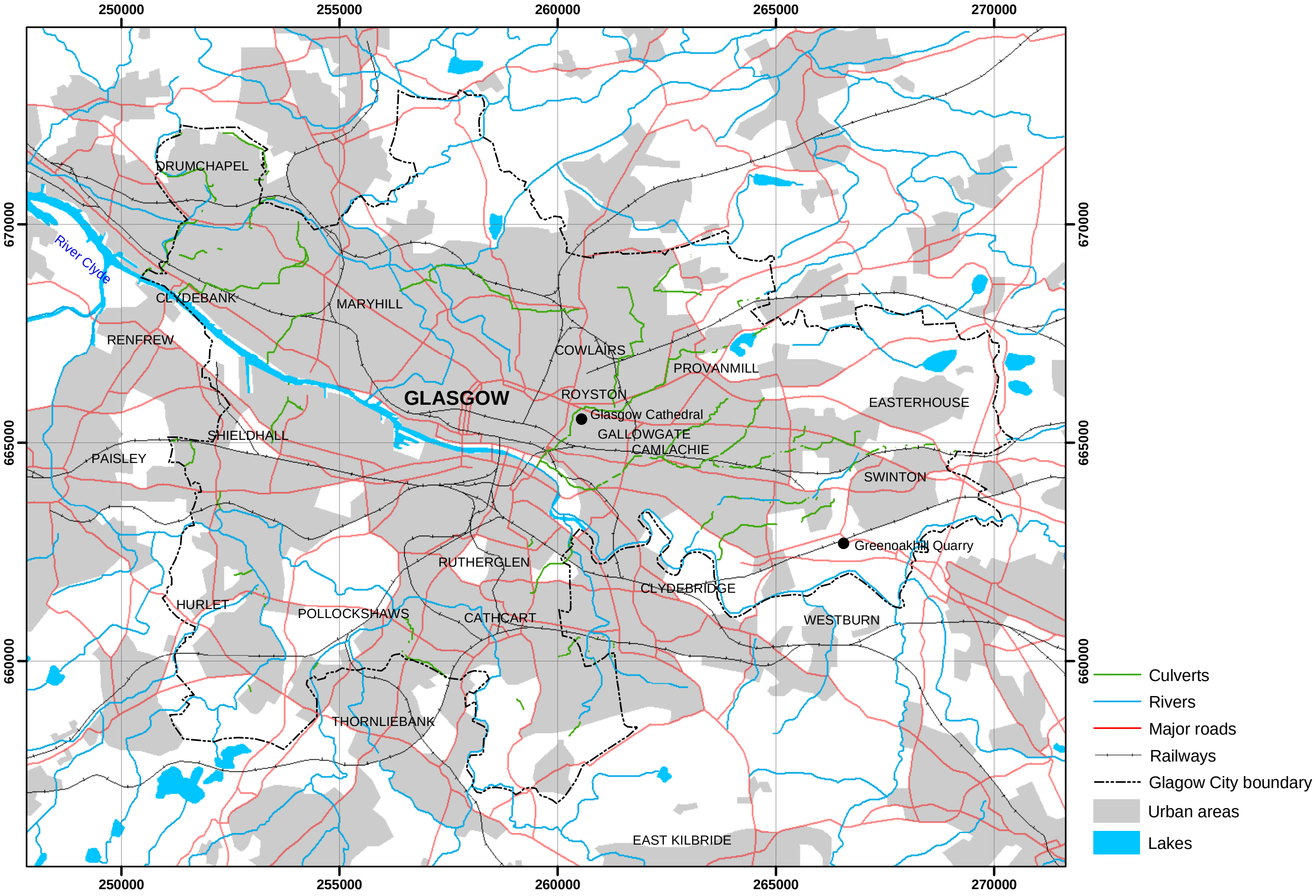


Figure 2.1 Map of the Glasgow tributaries study area showing selected areas of the city associated with former industrial activity and post-war redevelopment.

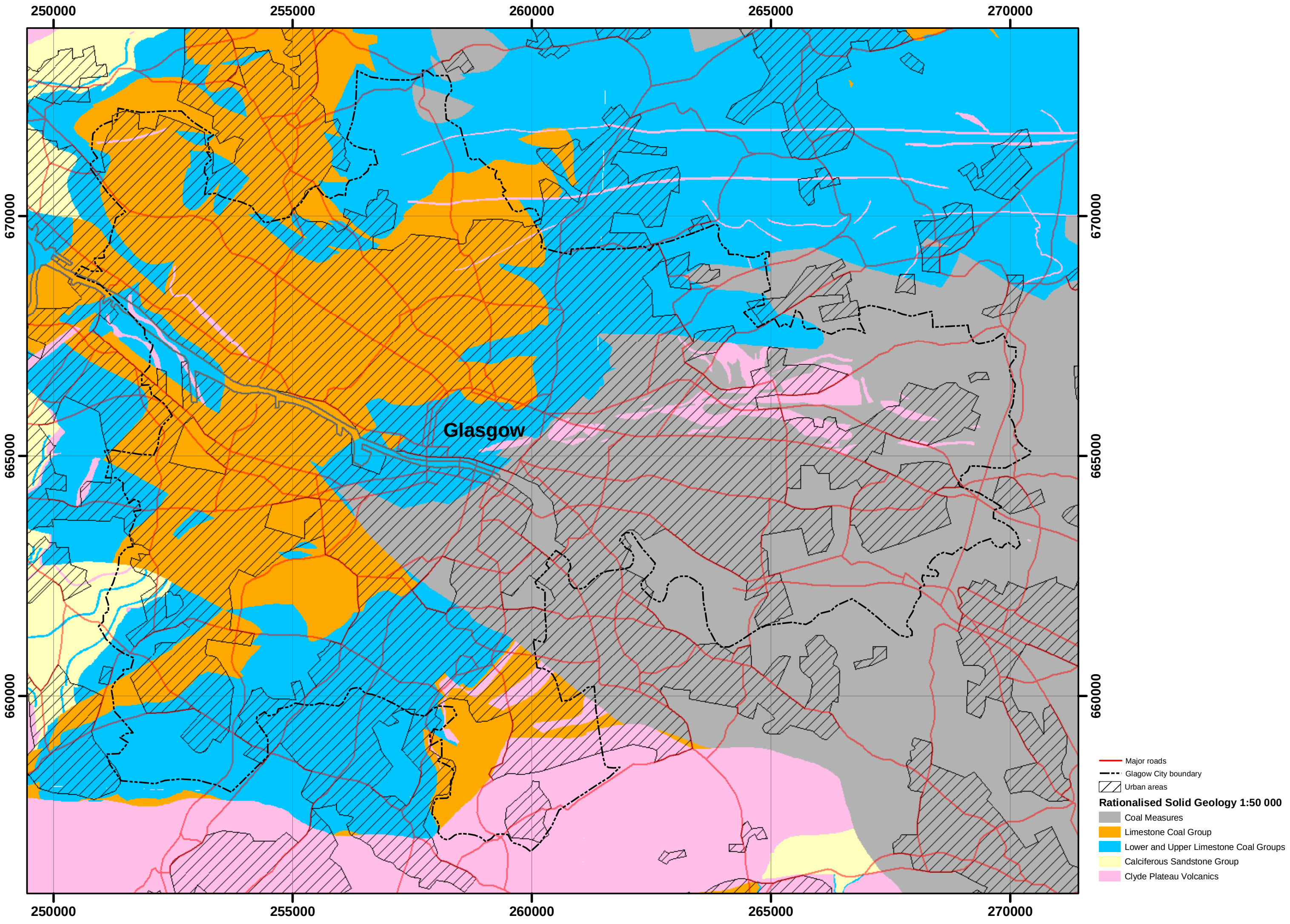


Figure 2.2 Simplified bedrock geology map (1: 50 000 scale) of the Glasgow tributaries study area derived from BGS data.

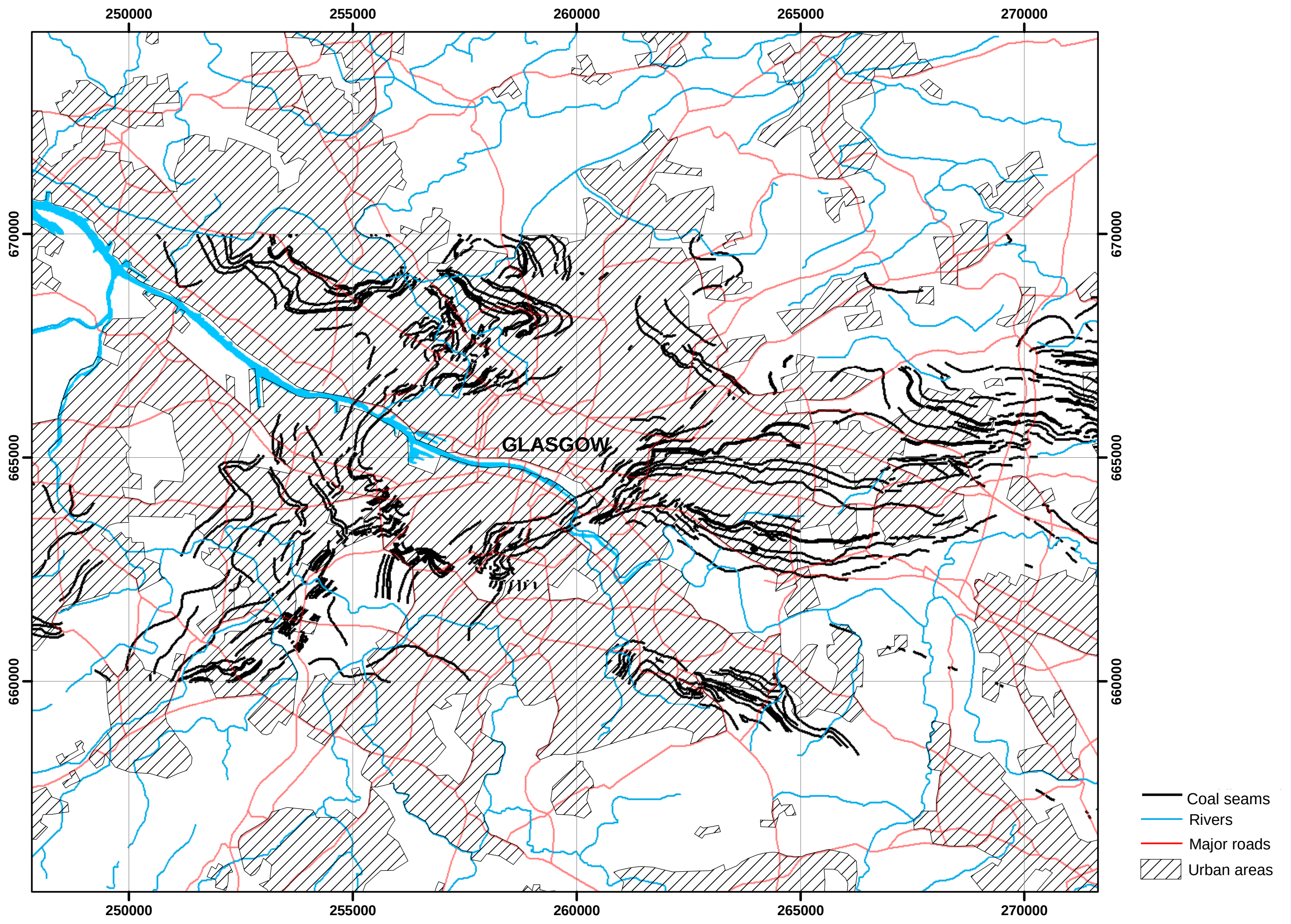


Figure 2.3 Coal seams (1: 10 000 scale) of the Glasgow tributaries study area derived from BGS data.

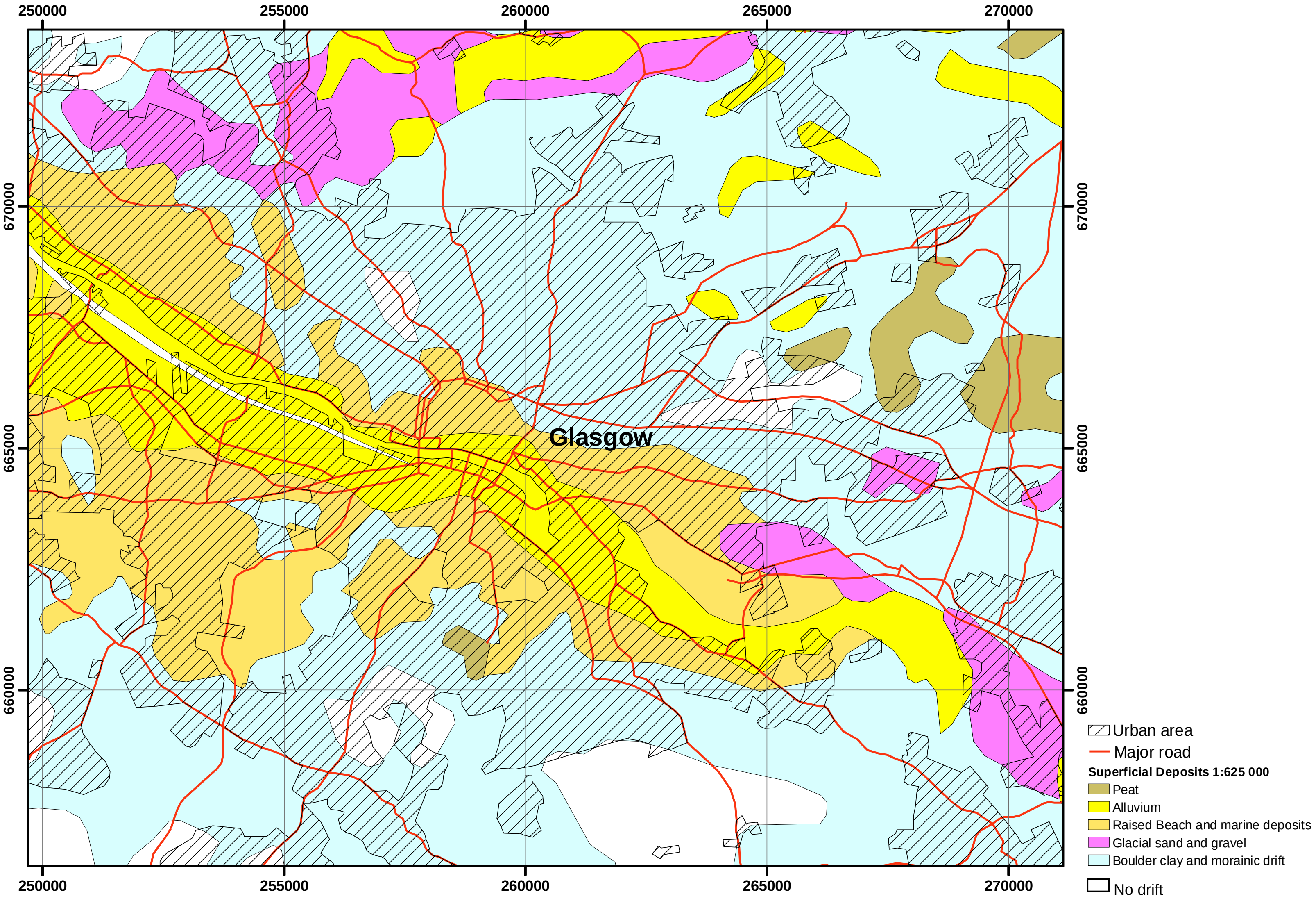


Figure 2.4 Superficial deposits (drift) map (1: 625 000 scale) of the Glasgow tributaries study area derived from BGS data.

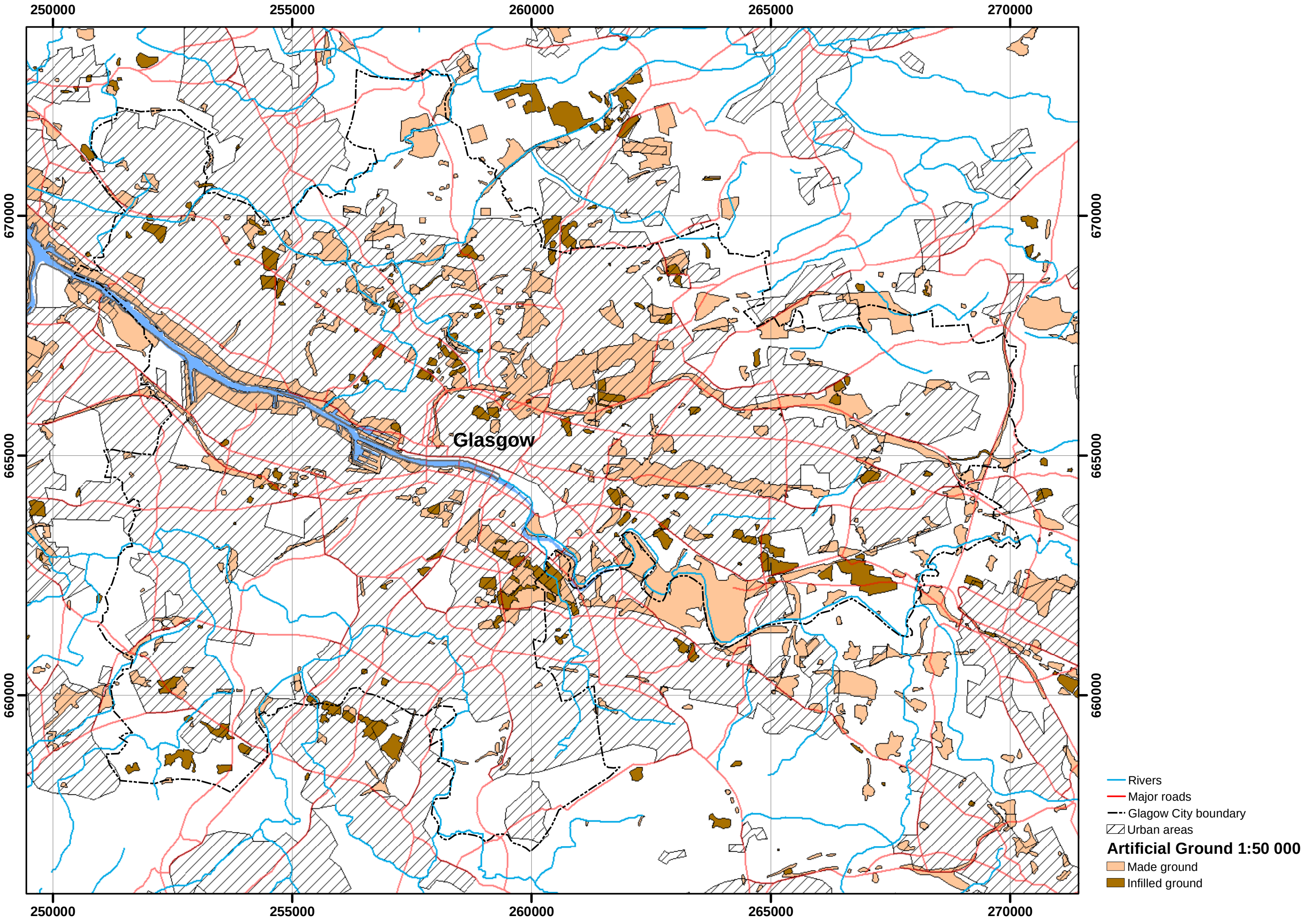


Figure 2.5 Made and infilled ground (1: 50 000) over the Glasgow tributaries study area derived from BGS data.

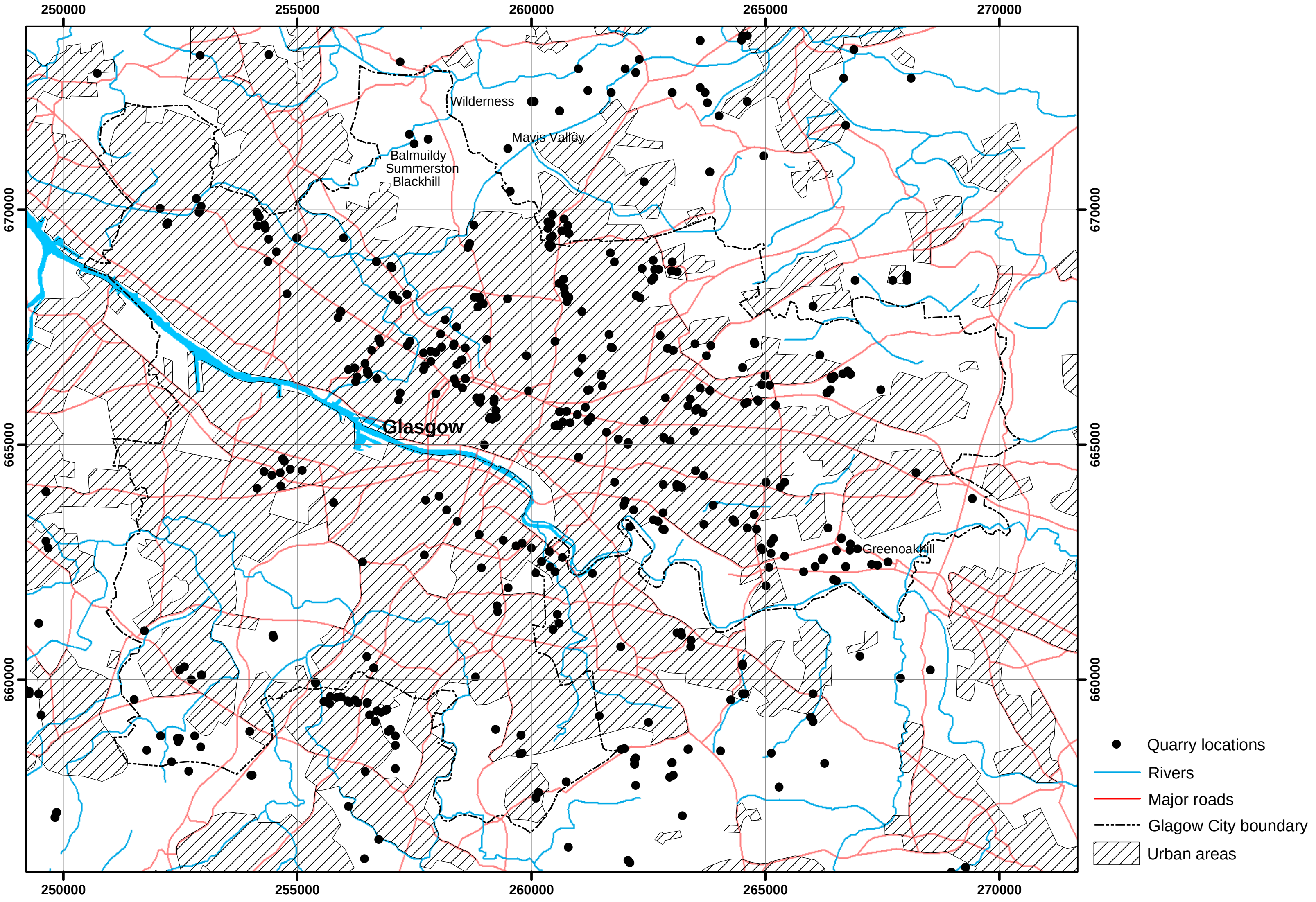


Figure 2.6 Quarry locations in the Glasgow tributaries study area derived from BGS data

3 Urban Drainage Geochemical Survey Methods

3.1 INTRODUCTION

Geochemical surveys rely on carefully devised sampling, error control, analytical standards, and protocols to ensure data quality and consistency and to provide the best possible estimate of likely element concentrations in the surface environment (McMillan et al., 2001; Johnson et al., 2003). In the urban environment, ground investigation reports frequently contain analytical data on the chemical composition of different sites. However, in order to compare data from different surveys it is important to know the sampling and analytical methods used so that the likely effects, if any, of the survey procedures on the analytical outcome can be assessed. For example, many metals are concentrated in the fine clay material in sediments; therefore if the fine fraction (< 150 μm) of the sediment is analysed, this will invariably return much higher metal concentrations than an analysis of the coarse fraction (< 2 mm) of the same sediment. This chapter outlines the standardised methods used to generate data in the geochemical drainage survey of Glasgow.

3.2 SURVEY STRATEGY

GCC identified an area of interest of approximately 18 x 11 km containing all open and culverted streams and watercourses draining into the River Clyde within the City Council boundary. Canals did not form part of the remit as the British Waterways Authority manages these.

To be consistent with the surrounding rural stream sediment and stream water information collected for the G-BASE programme, and to provide an overview of the whole area, a strategy was devised to sample all open waterways at a density of 1 sample per kilometre of stream length across the area and culverted waterways at all sites where they appeared at surface. GCC also expressed interest in sediment and water quality in culverted streams. On this basis the BGS nominated sites on culverted streams where sample collection would be desirable to enhance the sampling network. Culvert sampling was carried out in collaboration with the Watercourses Engineering section of the Council (Figure 3.1). Approximately 130 potential sampling sites were identified including 11 culverted sites and 5 sites on the south side of River Clyde in South Lanarkshire Council area (Figure 3.2).

As outlined in Chapter 1 of this report, in addition to the standard suite of chemical elements normally determined in sediments by X-ray Fluorescence Spectrometry (XRFS) for the G-BASE programme, GCC expressed interest in sediment pH, cyanide, mercury (Hg), asbestos, total organic carbon (TOC), TPH, PAH, PCB and organo-tin determinations. Cyanide, Hg and pH analyses were carried out on all the sediment samples whereas a sub-set of 51 samples was selected for asbestos determination based on an even distribution across catchments in the survey area. TOC and TPH were determined on all samples and on the basis of these results and on the locations of likely sources of contamination, sub-sets of 52 samples for PAH, 10 samples for organo-tin and 23 samples for PCB were selected for analyses.

Photographs © Justin Carter reproduced with kind permission of Justin Carter

Figure 3.1 Sampling of sediment from culverted sections of the Camlachie Burn, in Glasgow Green

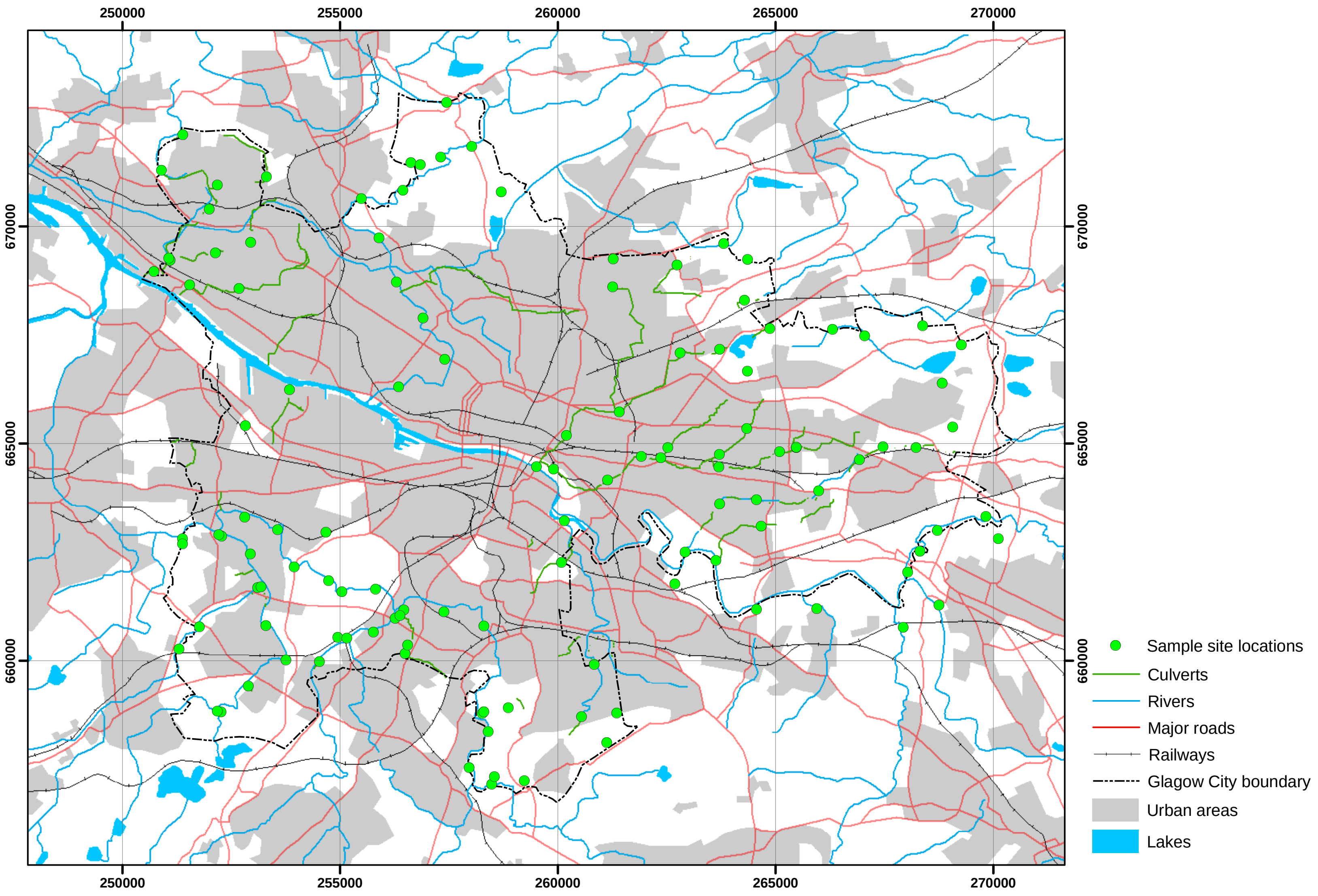


Figure 3.2 Location of geochemical sampling sites across the Clyde tributaries study area

Similarly, in addition to the standard suite of parameters normally determined in waters by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for the G-BASE programme, analyses of ultra-trace selenium (Se) and Hg, ammonium, sulphide and dissolved oxygen were incorporated into the project.

For quality assurance purposes, three field duplicate sediment and water samples were collected in the same way as the original samples a few meters away from the original samples following standard G-BASE procedures (Johnson et al., 2003).

Existing rural G-BASE stream sediment data for the Clyde catchment are based on analysis of a < 150 µm size fraction. However, the Clyde estuary sediment geochemical data are based on analysis of a < 2 mm size fraction due to the coarser nature of estuarine sediments (Jones et al., 2004). In order to determine fractionation of contaminants between coarse and fine sediments and compare the onshore – estuarine systems, the urban drainage sediment samples were sieved to both < 2 mm and < 150 µm size fractions for inorganic analysis.

3.3 SAMPLE COLLECTION

Due to increased health and safety risks in urban versus rural streams, sampling was carried out by a team of 5 BGS staff (rather than student voluntary workers commonly used by G-BASE), between 2 – 10th June 2003. Rural stream sediment samples are normally sieved at site prior to collection but again due to increased health and safety risks in urban areas, this strategy was altered to minimise contact between the samplers and the samples thus wet bulk sediment was collected. In all other respects, the samples were collected in accordance with standard G-BASE procedures whereby samplers worked in pairs that were interchanged daily to reduce the possibility of sampling bias introduced by the use of individual procedures (Johnson et al., 2003). All jewellery was removed prior to sampling to avoid possible metal contamination. In open streams, water samples were collected prior to stream sediment collection and slightly upstream of the stream sediment site to avoid contamination by disturbed sediment or pore water and great care was taken to avoid any other sources of contamination such as touching the insides of the sample bottles etc. In culverted streams, the water samples were collected first in a plastic bucket for removal to the surface where they were filtered and transferred into bottles. Where possible at each site, the following suite of samples was collected.

3.3.1 Stream Sediment

Sample for inorganic chemical analysis - sediment samples were retrieved from the active water channel using a steel trenching tool allowing as much water as possible to drain off before collection into a large self-seal plastic bag. Approximately 8 – 10 kg of material was collected following removal of any leaf and other organic matter and large stones. However, it should be noted that particularly in some of the culverted streams it was only possible to obtain amounts as little as 1 kg of material.

Sample for organic chemical analysis - sediment samples were retrieved from the active water channel using a steel trowel removing any leaf and other organic matter and large stones and allowing as much water as possible to drain off before collection into a 500 mg ultra-clean glass jar with screw caps lined with aluminium foil. To avoid volatilisation, samples were kept in cool boxes following collection and were frozen on return to the field-base.

Sample for cyanide analysis - sediment samples were retrieved from the active water channel using a steel trowel removing any leaf and other organic matter and large stones and allowing as much water as possible to drain off before collection into a 500 mg clean glass jar.

3.3.2 Surface Water

Filtered water samples were collected using a 25 ml plastic syringe and a disposable 0.45µm filter. A new filter cartridge was used for each site to avoid any possible cross-contamination between sites. Water was drawn into the syringe, which was rinsed out twice. The syringe was filled with water again and connected to the filter cartridge, which was also rinsed out twice. The syringe was refilled and the sample bottle was rinsed out twice with filtered water from the site prior to being filled.

For unfiltered water samples, the bottles were rinsed out twice in the water. Where possible, the bottles were submerged underwater whilst the caps were secured making sure that no air was trapped in the sample container. This minimises the degassing of bicarbonate (HCO_3) in the samples. Care was taken to keep all bottles and filters clean. Samples collected for major cation analysis were acidified at the end of fieldwork each day by the addition of 0.3 ml (8 drops) ARISTAR grade nitric acid (HNO_3). Addition of 1% vol/vol acid reduces the pH of the samples to approximately 1.0, thus preventing adsorption of dissolved metals to the interior walls of the storage bottle and minimising post-sampling microbial activity.

Water samples were kept in cool boxes upon collection and stored in a cool dark location until dispatched to the laboratory where they were stored at 4 °C. Samples for mercury (Hg) determination were refrigerated following collection.

The following suite of water samples was collected:

- 250ml polythene Nalgene® bottle – unfiltered water for total alkalinity and conductivity determinations
- 30ml polythene (black cap) - unfiltered water for pH determinations
- 30ml Nalgene® sterile bottle pre-dosed with sodium hydroxide (NaOH) pellet - unfiltered water for sulphide determinations
- 30ml polythene Nalgene® sterile bottle - filtered water not acidified for chloride (Cl), nitrate (NO_3), sulphate (SO_4), fluoride (F) and non-purgeable organic carbon (NPOC) determinations

- 30ml Greiner® sterile tube - filtered water acidified at the field-base with 1% HNO_3 for Inductively Coupled Plasma –Atomic Emission Spectrometry (ICP-AES) analysis for 14 elements

- 30ml polythene Nalgene® sterile bottle - filtered water acidified at the field-base with 1% HNO_3 for Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for 29 elements

- 30ml polythene Nalgene® sterile bottle – filtered water acidified at the field-base with 1% HNO_3 for Atomic Fluorescence Spectrometry (AFS) for selenium (Se) determinations

- 30 ml polythene Nalgene® sterile bottle – filtered water and acidified at the field-base with 1% sulphuric acid (H_2SO_4) for ammonium determinations

- 50ml glass sterile bottle pre-dosed with 1ml 0.1% potassium dichromate ($K_2Cr_2O_7$) in 50% v/v 1% HNO_3 - filtered water for AFS Hg determinations

- Dissolved Oxygen (DO) was also determined at each site

3.3.3 Field Observations and Data Recording

At each sample site, information on the location, contamination, land use and other features required for data interpretation was entered on a computer-compatible field data card in standard BGS format (Table 3.1) (Johnson et al., 2003). The location was determined using a Garmin-12® global positioning system unit (GPS) and noted on a field copy of the 1: 25 000 Ordnance Survey (OS) map. On completion of each days' fieldwork, the sample locations were plotted on stable-base 1: 25 000 OS maps using the data cards and the field copies of the OS 1: 25 000 maps.

The field cards were pre-numbered according to a random number system (see Section 3.5.1 of this report). The area code for the Clyde tributaries study was 61 and then each site was assigned a 4-digit code randomised on every 100 numbers. In addition to the BGS sample numbering system, GCC proposed a sample code based on the different catchments. These codes were included in the data recording as this was a convenient way to label the samples in terms of their geographic associations. An index to the BGS and GCC number systems and the sample locations is provided in Table 3.2. On the basis of conditions encountered in the field, a full sample suite was not collected at all the proposed sites as indicated in Table 3.2.

Table 3.1 Summary of field observation information recorded on G-BASE field data cards

Observation	**Description**
Ref_Map	1: 25 000 OS map sheet covering the sampling area
Collectors	Initials of the BGS staff involved in collecting the samples
Date	Date of sample collection
Drainage Type	Category of drainage channel
Drainage Condition	Qualitative assessment of amount of water flow
Weather	Indication of rainfall conditions at the time of sampling
Clast Precipitates	Qualitative assessment of the amount (light, moderate, heavy) and colour (orange, brown or black) of precipitates present on stream clasts as an indication of iron and manganese oxides present in the stream
Sediment Colour	Qualitative assessment of the sediment colour DB-BL = dark-brown-black; LB-O = light-brown-orange; GR = grey
Sediment Clay	Qualitative assessment of the sediment clay content, low, moderate or high
Sediment Organic	Qualitative assessment of the sediment organic matter content, low, moderate or high
Contamin	List of contaminants evident at the site
Land Use	Categories of land use surrounding the site according to the BGS corporate land use classification scheme
Clasts	The lithology of the stream clasts found at the site
Bedrock	Indication if bedrock is cropping out at the site or not
Drift	Indication of the type of drift deposits evident at the site
Site Geology	indication of the type of bedrock if present at the site
Water Colour	Qualitative assessment of the water colour, clear, yellow or brown
Suspended Solids	Qualitative assessment of the amount of visible suspended solids in water, low, moderate, high
Comments	Any other comments about the site

Table 3.2 Index to BGS and GCC sample codes and site locations

GCC Sample Code	Catchment	BGS Sample Code	Easting	Northing	Comments
A1	Hillington				Not present at surface, not sampled
A2	Hillington	611790	252820	665410	
AH1	Auldhouse Burn	611819	256260	660980	
AH2	Auldhouse Burn	611886	255760	660660	
AH3	Auldhouse Burn	611805	254940	660540	
AH4	Auldhouse Burn	611804	254520	659980	
AL1	Allander Water	611712	257440	672850	
AU1	Aurs Burn	611864	252170	658840	
BK1	Brock Burn	611854	253180	661700	
BK2	Brock Burn	611834	253290	660810	
BK3	Brock Burn	611870	253750	660020	
BK4	Brock Burn	611882	252890	659420	
BK5	Brock Burn	611841	252260	658820	
BLA1	Bishop Loch	611765	267050	667480	
BLA2	Bishop Loch	611737	266310	667630	
BLB1	Bishop Loch	611716	269270	667270	
BLC1	Bishop Loch	611780	268830	666390	Limited fine fraction material, no pH analysis
BLC2	Bishop Loch				Coverage not needed, too remote
BLD1	Bishop Loch	611772	267690	667520	Dry site, sediment only
BLD2	Bishop Loch				Not present at surface, not sampled
BLD3	Bishop Loch	611717	268380	667710	No sediment, water only
BT1	Battle Burn	611718	263630	662310	
BT2	Battle Burn	611732	265170	663100	Dry site, sediment only
BT1A	Battle Burn	611770	264670	663100	No cyanide sample, limited sediment
BY1	Blacksey Burn	611789	251370	662690	
CF1	Cityford Burn	611731	260830	659910	
CF2	Cityford Burn	611727	260540	658710	
CF3	Cityford Burn	611730	261120	658120	
CFA1	Cityford Burn				Not present at surface, not sampled
CFB1	Cityford Burn	611753	261350	658800	
CL1	Camlachie Burn	611751	259900	664410	
CL2	Camlachie Burn	611811	261140	664160	No sediment, water only
CL2A	Camlachie Burn	611794	261920	664700	
CL3	Camlachie Burn	611774	262370	664670	No sediment, water only
CL4	Camlachie Burn	611798	263700	664460	
CL5	Camlachie Burn	611726	265090	664810	
CL6	Camlachie Burn	611719	265480	664910	
CLA1	Camlachie Burn	611735	265480	664920	
CN1	Cleddans Burn	611713	250890	671290	
CN2	Cleddans Burn	611788	251380	672110	
CT1	Carntyne Burn	611723	262530	664910	
E1	Auchengree	611761	264360	669240	No sediment, water only
EF1	Eastfield Burn	611725	262690	661770	Limited fine fraction material, no Hg or pH analysis
GD1	Garscadden Burn	611724	251090	669220	No cyanide sample, limited sediment
GD2	Garscadden Burn	611750	252130	669390	
GD3	Garscadden Burn	611733	252940	669630	
GG1	Garngad Burn	611755	261260	668610	
GK1	Garnkirk Burn	611740	264290	668300	
GN1	Garscadden Burn North	611720	252170	670950	
GN2	Garscadden Burn North	611764	253300	671140	
GNA1	Garscadden Burn North	611766	252850	671950	Dry site, sediment only
HL0	Hole Burn	611900	256370	661040	
HL1	Hole Burn	611829	256550	660360	
KK1	Kirk Burn	611796	264560	661180	
KN1	River Kelvin	611763	256340	666310	No sediment, water only
KN2	River Kelvin	611776	257400	666940	
KN3	River Kelvin	611702	256900	667890	
KN4	River Kelvin	611743	256290	668720	
KN5	River Kelvin	611729	255890	669730	
KN6	River Kelvin	611744	255480	670640	

GCC Sample Code	Catchment	BGS Sample Code	Easting	Northing	Comments
KN7	River Kelvin	611773	256440	670830	
KN8	River Kelvin	611792	257310	671590	
KN9	River Kelvin	611706	258020	671840	
KNA1	River Kelvin	611752	256620	671470	
KNA2	River Kelvin	611758	256840	671420	
KT1	Kittoch Water	611868	258480	657160	
KTA1	Kittoch Water	611871	258540	657330	No organics sample, limited sediment
KTB1	Kittoch Water	611801	259230	657240	
LH1	Linthouse Burn	611704	253830	666240	
LH2	Linthouse Burn				Not present at surface, not sampled
LT1	Light Burn	611756	263710	664750	
LT1A	Light Burn	611715	264340	665350	
LV1	Levern Water	611783	252270	662870	
LV2	Levern Water	611708	252930	662460	
LV3	Levern Water	611839	253100	661690	
LV4	Levern Water	611822	251760	660780	
LV5	Levern Water	611847	251290	660270	
MA1	Manse Burn	611836	255150	660520	
MM1	Malls Mire Burn	611759	260080	662270	
MO1	Molendinar Burn	611797	259510	664470	No sediment, water only
MO2	Molendinar Burn	611827	260200	665190	
MO3	Molendinar Burn	611736	261410	665730	
MO4	Molendinar Burn	611771	262810	667090	No sediment, water only
MO5	Molendinar Burn	611784	263720	667170	
MO6	Molendinar Burn	611793	264870	667650	
MOA1	Molendinar Burn	611721	264360	666670	
MY1	Merry Burn	611815	256490	660170	
N1	North Glasgow	611787	258700	670790	
N2	North Glasgow	611714	258360	670260	Dry site, sediment only, limited material, no pH analysis
N3	North Glasgow				Not present at surface, not sampled
N4	North Glasgow	611782	261270	669250	
NC0	North Calder	611738	268040	662040	
NC1	North Calder	611791	268320	662520	
NC2	North Calder	611767	268720	663000	
NC3	North Calder	611769	269840	663320	No cyanide sample, limited sediment
NC4	North Calder	611701	270120	662810	
NCA1	North Calder				Not present at surface, not sampled
NT1	Newton Burn	611707	265950	661200	
PM1	Polmadie Burn	611711	260150	663220	
PW1	Pow Burn	611799	268760	661280	
RC1	Rotten Calder	611703	267940	660770	
ST1	Stand Burn	611748	263810	669610	
ST2	Stand Burn	611757	262740	669110	
ST3	Stand Burn				Not present at surface, not sampled
TC1	Tollcross Burn	611749	262920	662500	
TC2	Tollcross Burn	611746	263720	663610	
TC3	Tollcross Burn	611741	264560	663710	
TC4	Tollcross Burn	611745	265990	663910	
TC5	Tollcross Burn	611739	266930	664630	
TC6	Tollcross Burn	611728	267470	664930	
TC7	Tollcross Burn	611754	268230	664910	
TC8	Tollcross Burn	611762	269070	665380	Limited fine fraction material, no Hg and pH analysis
WC1	White Cart	611734	251370	662810	No sediment, water only
WC10	White Cart	611876	258300	660800	
WC11	White Cart	611885	258300	658830	
WC11A	White Cart	611831	258400	658370	
WC12	White Cart	611873	257960	657540	No sediment, water only
WC2	White Cart	611795	252210	662900	
WC3	White Cart	611779	252800	663310	
WC4	White Cart	611705	253560	663020	
WC5	White Cart	611760	253940	662160	
WC6	White Cart	611848	254730	661840	

GCC Sample Code	Catchment	BGS Sample Code	Easting	Northing	Comments
WC7	White Cart	611823	255810	661650	
WC8	White Cart	611806	256460	661170	
WC9	White Cart	611833	257380	661130	
WCA1	White Cart	611896	254670	662960	
WCB1	White Cart	611878	255030	661590	No organics sample, limited sediment
WCC1	White Cart	611825	258260	658790	
WCC2	White Cart	611838	258860	658920	
YK1	Yoker Burn	611777	250720	668960	
YK2	Yoker Burn	611800	251060	669270	
YK3	Yoker Burn	611742	251990	670400	
YM1	Yoker Mains Burn	611747	251540	668650	
YM2	Yoker Mains Burn	611709	252670	668570	
YM3	Yoker Mains Burn	611785	253750	669020	Dry site, sediment only. No cyanide sample, limited sediment

3.4 ANALYTICAL METHODS

3.4.1 Field Methods

Dissolved oxygen, pH, total alkalinity and conductivity determinations in water were carried out during the field survey as follows:

Dissolved oxygen (DO) was determined in water at each site using a temperature compensated Hanna Instruments® HI9143 dissolved oxygen meter. The meter was calibrated to 0 mg L^{-1} O_2 in air and 10 mg L^{-1} O_2 in a standard potassium chloride calibration solution. The DO measurement requires flowing water so in culverted streams where water was brought to the surface in a bucket, the probe was agitated to create flow.

On return to the field-base each evening, water pH was determined using a temperature compensated glass combination electrode connected to a high-performance pH meter (Radiometer® Model PHN 80) according to standard G-BASE methods (Johnson et al., 2003).

Total alkalinity and conductivity were determined the day after sample collection. Total alkalinity was measured using a Hach® digital titrator with sulphuric acid (0.8 M or 0.08 M) and bromocresol green indicator. The results were reported as mg L^{-1} bicarbonate (HCO_3). Conductivity was determined using a Hanna Instruments® conductivity meter (HI 933100) according to standard G-BASE methods (Johnson et al., 2003).

3.4.2 Sample Preparation

3.4.2.1 STREAM SEDIMENTS

The 8 kg bulk wet unsieved sediment samples collected in self seal bags, were homogenized and 250 – 300 g splits of material taken from the 51 samples selected for asbestos determination.

The remaining samples were wet sieved through nylon sieves to < 2 mm and then to < 150 µm resulting in two size fractions of material a coarser fraction of 2 mm - 150 µm and a finer fraction of < 150 µm. The amount of material in each fraction was not routinely recorded for each sample but varied depending on the size of the original bulk sample and the grain size. Approximate weights ranged from 6 kg to less than 50 g in the case of the coarser fraction and 500 to less than 50 g for the < 150 µm fraction.

The < 150 µm Clyde tributaries fraction is directly comparable with rural G-BASE stream sediment samples for the area and with three < 150 µm sediment samples collected as part of the Clyde estuary project. The remaining Clyde estuary samples were sieved to < 2 mm and therefore represent 2 to 0 mm material (Jones et al., 2004). Although this methodology is not identical to the 2 mm – 150 µm Clyde tributaries fraction, the estuarine < 2 mm and tributaries 2 mm – 150 µm material are none-the-less comparable as estuarine sediments tend to contain very little fine fraction material relative to stream sediments.

The < 2 mm and < 150 µm tributaries size fractions were oven dried at low temperature (< 30 °C) to avoid volatilisation of Hg and Se.

< 2 mm samples were homogenized, cone and quartered and a 10 g split taken for pH analysis. A further 50 g sub-sample was ground in an agate planetary ballmill until 95 % was less than 53 µm. A 5 g split of the ground material was taken for Hg by AFS and a 12 g split for XRFS analysis.

< 150 µm samples were homogenized, cone and quartered and a 50 g sub-sample was ground in an agate planetary ballmill until 95 % was less than 53µm. A 12 g split of ground material was taken for XRFS analysis.

XRFS pellets were prepared by grinding 12 g of milled sample and 3 g of binder in an agate planetary ball mill for 30 minutes. The mixture was then pressed under a 25-ton load into 40 mm diameter pellets. The binder consists of 9 parts EMU120FD styrene co-polymer (BASF plc) and one part Ceridust 3620 a micronised polyethylene wax (Hoechst), after Van Zyl (1982).

Samples colleted in ultraclean glass jars for organic analysis were freeze dried and sieved through metallic sieves to < 2mm. The samples were then milled in agate (tema and ball mill) to < 100 µm and splits taken for TPH (2 g), PAH (0.5 g), organo-tin (10 g) and PCB analysis (10 g).

Samples collected in glass jars for cyanide analysis were dispatched straight to the laboratory for analysis.

3.4.2.2 SURFACE WATERS

Following collection and storage in a cool environment, the water samples underwent no further processing before dispatch to the laboratory for chemical analysis.

3.4.3 Laboratory Analysis

3.4.3.1 SEDIMENT X-RAY FLUORESCENCE SPECTROMETRY (XRFS) ANALYSIS

Major, minor and trace element determinations in all the stream-sediment samples were carried out by wavelength-dispersive X-ray fluorescence spectrometry (WD-XRFS) (Ingham and Vrebos, 1994) and energy-dispersive X-ray fluorescence spectrometry (ED-XRFS) at the BGS. Two Philips PW2400 sequential x-ray fluorescence spectrometers fitted with rhodium-anode X-ray tubes (3 kW 60 kV) were used for Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2, MnO, Fe_2O_3, Sc, V, Cr, Co, Cs, Ba, La and Ce as one suite and Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Hf, Ta, W, Tl, Pb, Bi, Th, and U as another. The Philips spectrometers were controlled using Philips SuperQ application software package, version 3.0H, running under MicroSoft (tm) Windows2000 operating system. A PANalytical Epsilon 5 energy-dispersive, polarised, x-ray fluorescence spectrometer fitted with a gadolinium-anode X-ray tube (600W, 100kV) was used for Ag, Cd, Sn, Sb, Te and I. The PANalytical spectrometer was controlled using the E5 application software package, version 1.0, running under MicroSoft (tm) Windows2000 operating system. In the energy dispersive (E5) spectrometer, the primary X-radiation is scattered off a secondary or polarisation target, which is used to optimise the effectiveness of the exciting X-radiation and to minimise the spectral background. Two secondary/polarisation targets are used to give optimal coverage of the elements from Ag to I; all elements are deconvoluted to improve the accuracy of the corrections on the analytes of interest. Rather than being diffracted the whole of the emitted X-ray spectrum is detected simultaneously using a Ge detector.

Lower limits of detection (LLD) and upper and lower reporting limits (ULR and LLR) are shown in Table 3.3. The quoted LLDs are theoretical values for the concentration equivalent to three standard deviations above the background count rate for the analyte in a silica matrix. High instrumental stability results in practical values for these materials approaching the theoretical. Over 200 reference materials were measured for the calibration, followed by a validation exercise using stream and lake sediment reference materials and International Soil Exchange proficiency testing samples. These methods are not accredited by the United Kingdom Accreditation Service (UKAS).

3.4.3.2 SEDIMENT MERCURY ANALYSIS

Sediment Hg analysis was carried out at the BGS on all the < 2 mm sediment samples. A portion of sample (0.5 g) was weighed into a 50 ml graduated boiling tube and left overnight at room temperature in 10 ml of a 1:1 mixture of deionised water and aqua-regia (3 HCl:1 HNO_3). The mixture was then taken to boiling point and maintained at that temperature for 2 hours. After cooling, the solutions were diluted to volume with deionised water and allowed to settle. The resulting clear solution was analysed for Hg by Atomic Fluorescence Spectrometry (AFS). The solution was pumped into a vapour generator where it was mixed with tin(II) chloride to reduce Hg^{II} to Hg^{o}. The resulting Hg vapour was separated from the liquid in a gas/liquid separator and was swept by a stream of argon to the detector via a membrane separator tube to remove moisture. The atoms were excited by light from a mercury excitation source and the emitted fluorescence is measured, with the intensity being directly proportional to the concentration of Hg^{o} in solution. The instrument was calibrated using standards prepared to match the acid concentration in the samples. The reporting limit was 0.01 mg kg^{-1} (Table 3.3). The method is accredited by UKAS.

3.4.3.3 SEDIMENT PH ANALYSIS

Sediment pH was measured at the BGS by adding 10 g of each < 2 mm sample to 25 ml of 0.01M $CaCl_2.2H_2O$ calcium chloride (Rowell, 1994). The samples were magnetically stirred for one minute and then left to settle for 15 minutes. Prior to recording of the pH value, the samples were stirred to reform the suspension. The pH was measured using a glass slurry electrode and Orion 720A meter. The pH meter was calibrated to 4 and 7 or 7 and 9 depending on the pH of the slurry to be measured. This method of pH determination generally gives lower results (0.5 pH units) than water based methods. This method is the G-BASE standard but is not accredited by UKAS.

3.4.3.4 SEDIMENT CYANIDE ANALYSIS

Sediment cyanide analysis was carried out at the Alcontrol Ltd laboratories on all the samples. Solid samples were extracted with 1M sodium hydroxide prior to analysis and the extracts were filtered through #1507 filter paper before being decanted into test tubes. The method uses a Skalar Sans ++ System® Segmented Flow Analyser for automated sampling, dilution, distillation and colorimetric analysis of the samples. It can be used for solid samples in the range of 1 to 25 mg kg^{-1} without dilution. Out of range solid samples can be diluted with 1M sodium hydroxide and the detection limits are outlined in Table 3.3. The method determines thiocyanate, free cyanide (hydrogen cyanide and cyanide ion) and total cyanide (free and metal cyanide complexes) based on the following reactions.

Thiocyanate - firstly free cyanide is complexed by formaldehyde. The thiocyanate is converted to cyanogen chloride by reaction with chloramine-T. Cyanogen chloride subsequently reacts with iso-nicotinic acid and 1,3-dimethyl barbituric acid to give a violet/red coloured complex. This complex is then measured photometrically at 600 nm.

Free cyanide (easily liberatable cyanide) - Hydrogen cyanide is liberated on acidification to pH 4.0 and then distilled to separate it from the sample matrix. The cyanide then reacts with chloramine-T to form cyanogen chloride. Cyanogen chloride subsequently reacts with iso-nicotinic acid and 1,3-dimethyl barbituric acid to give a violet/red coloured complex. This complex is then measured photometrically at 600 nm.

Total cyanide (the sum of easily liberatable and complex cyanides) - In acidic solution, the complexed cyanide is converted to free cyanide by ultraviolet radiation. This liberated cyanide together with the already present easily liberatable cyanide is converted to hydrogen cyanide, which is then removed from the sample by distillation. The hydrogen cyanide then reacts with chloramine-T to form cyanogen chloride. Cyanogen chloride subsequently reacts with iso-nicotinic acid and 1,3-dimethyl barbituric acid to give a violet/red coloured complex. This complex is then measured photometrically at 600 nm.

It should be noted that the individual analyses within this method may interfere with each other if the analytical procedure is not followed closely. The pH of the distillation reagent is very critical for free cyanide. The presence of high levels of oxidising agents such as chlorine may partially oxidise cyanide to cyanate. High levels of sulphide may give a positive interference. The method is UKAS accredited.

Table 3.3 Limits of detection for determinands in Glasgow sediments

Analyte	LLD (mg kg^{-1})	LLR (%)	ULR (mg kg^{-1})	ULR (%)
Ag	0.5		1000	
Al_2O_3		0.1		60
As	1		10000	
Ba	6		600000	
Bi	1			
Br	1			
CaO		0.1		60
Cd	0.5		500	
Ce	6			
Co	2		10000	
Cr	2		250000	
Cs	1			
Cu	1		6500	
Fe_2O_3		0.01		100
Ga	0.7			
Ge	1			
Hf	1			
Hg *	0.01			
I	0.5		1000	
K_2O		0.05		15
La	6			
MgO		0.1		50.0
MnO		0.010		10.0
Mo	1		1000	
Na_2O		0.1		
Nb	1			
Ni	1		4000	
P_2O_5		0.05		1.5
Pb	1		10000	
Rb	1			
Sb	0.5		10000	
Sc	1			
Se	0.5		1000	
SiO_2		0.1		100.0
Sn	1		10000	
Sr	1			
Ta	0.5		1000	
Te	0.5		1000	
Th	0.5		1000	
TiO_2		0.020		100.0
Tl	0.5		1000	
U	0.5		650	
V	2		20000	
W	0.5		1000	
Y	1			
Zn	1		10000	
Zr	1			
Total Cyanide#	1		25	
TOC~		0.1		100
PCB`	0.0003			
Organo-Tin`	0.07/0.12			
TPH^	100			

LLD = Lower Limit of Detection
LLR = Lower Limit of Reporting
ULR = Upper Limit of Reporting
Unless otherwise stated values refer to XRFS analysis

*AFS Analysis
Colorimetric Analysis
~ Carbon/Sulphur Analyser
^ Iatroscan Analysis

` GC-MS Analysis (0.12 mg kg^{-1} = DBT)

3.4.3.5 SEDIMENT FIBROUS MINERALS ANALYSIS

Initial screening for the presence of fibrous minerals in all the samples was carried out prior to cyanide determinations at the Alcontrol Ltd laboratories. A known weight of sediment was sieved to remove the fine sediment matrix leaving behind any asbestos fibres on the sieve. The samples were coned and quartered to ensure representative subsampling of 100 g of wet sediment. This material was placed into a 125 µm Endecot® brass sieve. The samples were sieved under gently running water to ensure all large clumps were broken down, to free any fibres and wash the fine clay matrix away. Any fibres present were noted on the sample sheet.

3.4.3.6 SEDIMENT ASBESTOS ANALYSIS

The 250 – 300 g sample splits from 51 selected samples were analysed for asbestos content at the HSL laboratories. The samples were placed in an oven and dried at 100 °C. The samples were homogenised and a representative sub-sample of 20 – 50 g was taken. The sub-samples were placed in petri-dishes and examined for approximately 30 minutes using a low-power (8x – 20x magnification) steriomicroscope. Small fibres bundles or individual fibres thought to be asbestos were picked out using needle-point tweezers. The fibres were mounted in a refractive index liquid chosen to match the most likely asbestos type. The fibres were then analysed by polarised light microscopy (PLM) based on optical properties with magnification from x120 upwards.

Asbestos identification by this method is qualitative not quantitative and a lack of asbestos may be due to the heterogeneity of the samples or the sub-sample examined being too small. Fibres may also be too small (< 0.4 µm wide) to be seen hence a negative reading for asbestos in the samples does not guarantee that asbestos is not present. However, the analyst can usually make approximate estimates of the asbestos contents of the material under investigation as follows:

- If the analyst has difficulty finding asbestos fibres the sample will be categorised as having only trace amounts < 1%.
- If it is clear that the material is pure or almost pure asbestos then the sample will be categorised as having > 50% asbestos.
- By default if the amount of asbestos is between these ranges it will be categorised accordingly.

This method is recommended as a useful screen for asbestos, however, if UKAS accredited estimation of asbestos is required the material should be analysed by X-ray Diffraction Techniques (XRD).

3.4.3.7 SEDIMENT TOTAL ORGANIC CARBON (TOC) ANALYSIS

TOC was determined in all sediments by Alcontrol Ltd. laboratories, using a UKAS accredited method. Freeze dried samples (< 2 mm) were sent to Alcontrol in glass vials. Inorganic carbonate was removed as carbon dioxide from the samples by hydrochloric acid treatment, followed by rinsing with deionised water and drying. The remaining residue containing non-water soluble and non-volatile organic carbon was determined using an Eltra CS444 carbon / sulphur analyser which combusts the sample in a flow of oxygen and any carbon present is converted to carbon dioxide which is measured by an infra-red detector. The percentage carbon is then calculated with respect to the original sample weight. The range for the method is 0.10-100 % TOC (Table 3.3).

3.4.3.8 Sediment Total Petroleum Hydrocarbon (TPH) Analysis

TPH analysis was carried out on all the < 2 mm sediment samples at the BGS by Iatroscan. The Iatroscan is a thin layer chromatography - flame ionisation detector (TLC-FID) technique that separates and quantifies broad classes of non-volatile organic compounds according to their polarity (aromatic, aliphatic, and polar / NSO). The sum of aromatics and aliphatics is equal to the total petroleum hydrocarbons (TPH). It can be used as a rapid screening method for sediment pollutants, petroleum hydrocarbons and source rocks, etc.

A known amount of sediment organic extract (dissolved in a suitable solvent) is deposited on a silica-coated quartz rod, called a “Chromrod” (100 mm x 1 mm). The rods are then developed by placing in a series of suitable solvents contained in a shallow tank (15 mm of solvent). The solvent moves up the silica coating, by capillary action. The broad classes of organics (aromatics and aliphatics) are separated according to their interaction with the stationary phase (the silica) and the mobile phase (the solvent). The developed rods are then placed into the pre-calibrated Iatroscan instrument. A flame ionisation detector (FID) moves along the rods, as the organics are “burned-off” the FID measures the conductivity of the flame, this is registered as an increase in voltage (called the response). The response is directly proportional to the amount of organic material present in the rod giving a quantitative assessment.

A stock solution containing a known amount of anthracene (aromatic, 140-160 mg) and pristane (aliphatic, 140-160 mg) was made up in toluene in a 20 ml volumetric flask, giving 7-8 mg mL^{-1} (i.e. 14-16 mg mL^{-1} TPH). To assist dissolution of the standards, the flask was placed in an ultrasonic bath for 30 seconds. For the calibration standard, the stock solution was diluted with toluene to obtain a known concentration with within the range 1.2–1.5 mg mL^{-1}. The sources of the stock solutions are outlined in Table 3.4.

Table 3.4 Chemicals and reagents used in Iatroscan analysis

Description	Comments	Source
Anthracene		Sigma-Aldrich Company Ltd., Gillingham, Dorset, UK
Dichloromethane (DCM)	HPLC grade	Rathburn Chemicals, Peebleshire, UK.
Hexane (95-7% *n*-hexane)	HPLC grade	Rathburn Chemicals, Peebleshire, UK.
Hydrogen	high purity	BOC Industrial Gases Ltd., Manchester, UK.
Hydromatrix		Varian Ltd., Walton-on-Thames, Surrey, UK.
Pristane		Sigma-Aldrich Company Ltd., Gillingham, Dorset, UK
Toluene		Rathburn Chemicals, Peebleshire, UK.

The extraction efficiency standard used was made as follows: approximately 1 kg of soil was taken and air dried for 48 hours, crushed using a pestle and mortar and sieved to < 0.5 mm. All solvent extractable organics were removed from the soil using Soxhlet extraction with dichloromethane (DCM) for 24 hours. The DCM was evaporated from the soil in a fume cupboard for 12 hours and allowed to air dry for 24 hours. The resulting solvent-extracted soil was spiked with anthracene (800 mg kg^{-1}) and pristane (800 mg kg^{-1}), dissolved in DCM, which give a combined TPH of 1600 mg kg^{-1}.

Accelerated solvent extraction (ASE) was performed using a Dionex ASE 200 system. Extraction cells (33 mL) were filled with 1-10 g (usually 2 g) of freeze-dried sample mixed with an appropriate amount of hydromatrix (an inert dispersing agent). Extraction conditions were: solvent DCM:hexane (50:50), temperature 175 °C, pressure 2000 psi, heat-up time 1 minute, static time 8 minutes, flush volume 120 %, purge time 60 seconds, total solvent used 37-44 mL per sample. The resulting solvent extract was rotary evaporated to 3-5 mL, quantitatively transferred to a glass vial (10 mL), reduced to "dryness" using a stream of nitrogen gas and stored in darkness at 4°C. Immediately prior to analysis the samples were dissolved in an appropriate known volume of toluene (0.5-25 mL, normally 1 mL).

Standards and samples were applied to clean chromrods using an SES A-4100 autospotter (SES Analysesysteme, Bechenheim, Germany). The chromrods were developed sequentially in hexane (21 minutes) followed by toluene (8 minutes). The rods were analysed using an Iatroscan MK-6 (SES Analysesysteme, Bechenheim, Germany) using a scan speed of 30 seconds, data acquisition and integration was performed using ChromStar32® software. The Iatroscan was linearly calibrated from 0.6-3.0 µg per rod (i.e. 1.2-6.0 µg of TPH). Samples exceeding this range were diluted to an appropriate concentration. Analytical figures of merit were determined: limit of detection for a 2 g sample was typically 100-150 mg kg^{-1} TPH, precision for aromatics ±8 % and precision for aliphatics ±7 % (i.e. precision for TPH ± 7 %).

3.4.3.9 SEDIMENT POLYCYCLIC AROMATIC HYDROCARBON (PAH) ANALYSIS

PAH concentrations were determined in 52 selected samples at the BGS. Following solvent extraction of the PAH from the samples, high performance liquid chromatography (HPLC) was used for their separation and fluorescence detection applied for their individual quantification. Fluorescence detection is a selective and sensitive means of determining PAH, however, it will only allow 15 of the 16 PAH specified in the United States Environmental Protection Agency (US-EPA) methods to be quantified (Table 3.5). This is because one of the 16 US-EPA PAH, *viz.* acenaphthylene, is not a fluorescent compound. Nevertheless, sufficient data can be generated to gain a meaningful assessment of PAH content and distribution in samples without knowledge of acenaphthylene concentrations.

Table 3.5 Abbreviations for the 15 PAH determined in the study.

Ace.	Acenaphthene	Anth.	Anthracene	Chrys.	Chrysene
Fanth.	Fluoranthene	Fluor.	Fluorene	Phen.	Phenanthrene
Pyr.	Pyrene	Naph.	Naphthalene		
B(a)A.	Benzo(a)anthracene	B(a)P.	Benzo(a)pyrene		
B(b)F.	Benzo(b)fluoranthene	B(k)F.	Benzo(k)fluoranthene		
B(ghi)P.	Benzo(ghi)perylene	DB(ah)A.	Dibenzo(ah)anthracene		
I(123cd)P.	Indeno(1,2,3-cd)pyrene				

In order for the samples to be in a form suitable for chromatographic analysis it was necessary to leach the PAH into solution by means of solvent extraction. This was accomplished in the following manner:

For each sample, approximately 0.5 g was accurately weighed into a pre-cleaned 25 mL amber bottle. To this was added 25 mL (accurately weighed, so that the actual volume added could be calculated from the density) of an extractant that consisted of a 50/50 v/v mix of acetonitrile and tetrahydrofuran (THF), both of HPLC grade. The bottle was sealed with a screw-cap closure containing a PTFE-faced silicone rubber septum (PTFE face towards the bottle contents). After sealing the bottle was shaken vigorously to suspend the contents, which were then sonicated in a heated ultrasonic bath (Camlab, 300W) for 45 minutes at 50 °C. During this period the bottle was occasionally inverted and shaken to continually re-suspend the sample. The bottle was then stored in the dark for *ca.* 2 hours, to permit some clarification of the supernantant, before taking a 2 mL aliquot in a 2.5 mL gas-tight glass syringe, attaching a 0.45 μm in-line syringe filter (25 mm diameter - Nylon 66), and filtering the extract into an amber 4 mL vial (with PTFE-faced screw cap closure) after discarding the first few drops of filtrate. The 4 mL vials of extract were stored in a refrigerator to await analysis, which took place as soon as possible after extraction.

Quality control was achieved by subjecting a low-level PAH certified reference material (LGC 6188 – River Sediment) to the above procedure (except that a weighed 2 g was used) and analysing it by the same method as for the samples. A procedural blank prepared from 0.5 g white quartz sand (Sigma Aldrich, UK) – a material devoid of PAH - was treated in a similar fashion. A total of eight quality control (LGC 6188), ten procedural blanks and nine duplicate sample determinations were conducted at intervals throughout the analysis of the samples.

A small aliquot, *ca.* 50 μL, was taken from each vial of filtered sample extract (including those of the quality control and the procedural blank) by an HPLC syringe and used to completely rinse and fill the 5 μL sample loop installed on the HPLC (Waters 600E). This was then connected into the flow of eluent (1 mL min^{-1}) from the HPLC pump and swept through the chromatographic separation column (Hypersil®PAH 100 mm x 4.6 mm inner diameter). Baseline separation of the 15 PAH was achieved within 40 minutes by gradient programming the eluent *i.e.* increasing its eluotropic strength with time according to a defined programme. Thus, far-UV HPLC grade acetonitrile (Rathburn Ltd.) with a high eluotropic strength, and HPLC grade water (Milli-Q) with a low eluotropic strength were pumped as a 50/50 mix at the start of each chromatographic run. This condition was maintained for 5 minutes into the run. Thereafter, up to 27 minutes, the proportion of acetonitrile was continuously and linearly increased from 50 % to 100 %. From 27 minutes until the end of the run (40 minutes.) elution with 100 % acetonitrile was maintained.

As each individual PAH exited the column, with its own distinctive retention time, it was directed into the scanning fluorescence detector (Waters 474). The detector was programmed so that optimised excitation and emission wavelengths for each PAH were selected based on their retention times. The following programme was found to produce optimum chromatography (Table 3.6). The method is not UKAS accredited.

Table 3.6 Wavelength programming of the fluorescence detector

Run Time (mins)	Ex (nm)/Em(nm)	PAH Detected
00.0 – 14.2	275/325	Naphthalene, Acenaphthene, Fluorene
14.2 – 16.0	253/273	Phenanthrene
16.0 – 22.0	340/430	Anthracene, Fluoranthene, Pyrene
22.0 – 31.8	270/382	Benzo(a)anthracene, Chrysene, Benzo(b)fluoranthene, Benzo(k)flouranthene, Benzo(a)pyrene
31.8 – 40.0	300/470	Dibenzo(ah)anthracene, Benzo(ghi)perylene, Indeno(1,2,3-cd)pyrene

3.4.3.10 SEDIMENT ORGANO-TIN ANALYSIS

Monobutyltin trichloride (MBT), dibutyltin dichloride (DBT) and tributyltin chloride (TBT) were determined in 10 stream sediment samples by Gas Chromatography Mass Spectrometry (GC-MS) at the BGS laboratories. The following internal standards (dissolved in methanol) were added to the sediment samples 24 hours prior to extraction, dipropyltin dichloride (4.07 mg as Sn kg^{-1}), phenyltin dichloride (1.50 mg as Sn kg^{-1}), diphenyltin dichloride (1.22 mg as Sn kg^{-1}). The following internal standards (dissolved in methanol) were added to the certified reference materials 24 hours prior to extraction, dipropyltin dichloride (4.07 mg as Sn kg^{-1}), phenyltin dichloride (0.94 mg as Sn kg^{-1}), diphenyltin dichloride (0.76 mg as Sn kg^{-1}).

All glassware was cleaned in chromic acid (24 hours), rinsed with deionised water (4 times), dried at 100 °C for 12 hours and rinsed with HPLC grade n-hexane prior to use. Anhydrous Na_2SO_4, and quartz wool were cleaned by Soxhlet-DCM extraction for 24 hours. The reagents used in the analysis are presented in Table 3.7.

Accelerated solvent extraction (ASE) was performed using a Dionex ASE 200 system. Extraction cells (3 mL) were filled with 2-10 g (usually 10 g) of freeze-dried sample mixed with an appropriate amount of hydromatrix (an inert dispersing agent). Extraction conditions were: solvent 1M acetic acid in methanol: 1M sodium acetate in methanol (50:50), temperature 100 °C, pressure 1500 psi, heat-up time 5 minutes, static time 5 minutes, flush volume 60 %, purge time 100 seconds, total solvent used 40-45 mL per sample (Arnold et al., 1998). An extraction efficiency standard of triphenyltin chloride (8.35 µg as Sn dissolved in methanol) was added to each extract.

The derivation was based on the method by Łobiński, et al. (1992). The extract was made up to 100 mL using a saturated solution of NaCl and extracted with hexane (3 x 20 mL). The resulting hexane extract was rotary evaporated to 3-5 mL and quantitatively transferred to a glass vial (10 mL). The extract was derivatised with Grignard reagent (1 mL, 0.5M *n*-pentyl magnesium bromide) followed by gentle agitation for 2 minutes. To destroy the excess Grignard reagent deionised water (5 mL) was added to the extract and shaken with deionised hexane (3 x 2 mL). After each addition of hexane, the organic phase was dried by passing it through a glass Pasture pipette filled with anhydrous Na_2SO_4 and reduced to approximately 0.1 mL using a steam of nitrogen gas. The resulting sample was stored at < -10 °C in darkness prior to GC-MS analysis, all sample extracts were analysed within 24 hours of derivation.

Table 3.7. Reagents used for organotin, extraction and sample clean up.

Name	**Grade**	**Comments**
Acetic acid (glacial)	Glass distilled grade	Rathburn Chemical Company, Peebleshire, UK
Dibutyltin dichloride (DBT), $(C_4H_9)_2$ Sn Cl_2		QmX Laboratories Ltd., Thaxted, Essex, U.K.
Diphenyltin dichloride, $(C_6H_6)_2$ Sn Cl_2	96%	Sigma-Aldrich, Poole, Dorset, UK
Dipropyltin dichloride, $(C_3H_7)_2$ Sn Cl_2	Analytical grade	QmX Laboratories Ltd., Thaxted, Essex, U.K.
Helium	CP grade	BOC Speciality Gases Ltd., Guildford, Surrey, U.K.
n-hexane	HPLC grade	Rathburn Chemical Company, Peebleshire, UK
Methanol	HPLC grade	Rathburn Chemical Company, Peebleshire, UK
Monobutyltin trichloride (MBT), (C_4H_9) Sn Cl_3		QmX Laboratories Ltd., Thaxted, Essex, U.K.
Pentylmagnesium chloride, $(C_5H_{11})MgCl$ (2M in diethyl ether)	Analytical grade	Sigma-Aldrich, Poole, Dorset, UK
Phenyltin trichloride, (C_6H_5) Sn Cl_3	98%	Sigma-Aldrich, Poole, Dorset, UK
Sodium acetate trihydrate	AnalR	VWR International Ltd., Lutterworth, Leicestershire, UK
Sodium chloride	AnalR	VWR International Ltd., Lutterworth, Leicestershire, UK
Sodium sulphate		Sigma-Aldrich, Poole, Dorset, UK
Tributyltin chloride (TBT), $(C_4H_9)_3$ Sn Cl		QmX Laboratories Ltd., Thaxted, Essex, U.K.
Triphenyltin chloride, $(C_6H_5)_3$ Sn Cl	95%	Sigma-Aldrich, Poole, Dorset, UK

Standards containing monobutyltin trichloride (MBT), dibutyltin dichloride (DBT) and tributyltin chloride (TBT) were derivatised as above and analysed by GC-MS to establish retention times and obtain characteristic mass spectra.

The GC-MS used was a "Fisons MD 800". Mass range: full scan ion monitoring (m/z: 39-600), with electron impact and quadrupole analyser. On-column injection was onto a DB-5 column (60 m length x 0.32 mm internal diameter x 0.25 μm film thickness). Oven temperature programme: 60 °C (1 minute isothermal) to 250 °C (at 10 °C / minute), isothermal at 250 °C for 10 minutes, then to 320 °C (at 10 °C / minute) and isothermal at 320 °C for 10 minutes. Carrier gas: helium at 16 p.s.i.

In this current study the limit of detection for TBT was 0.07 mg kg^{-1} (as Sn). The TBT, DBT and MBT concentrations obtained (from 15 analyses) for the certified reference material

(CRM) (PACS-2 harbour sediment) were in agreement with the confidence limits of the certified values (Table 3.8). The method is not UKAS accredited.

Table 3.8 Results for organo-tin CRM and blank samples and extraction efficiency tests

Sample	**Comments**	**MBT mg kg $^{-1}$ Sn**	**DBT mg kg $^{-1}$ Sn**	**TBT mg kg $^{-1}$ Sn**	**Extraction Efficiency %**
Procedural Blank	Hydromatrix	<0.07	<0.12	<0.07	29%
CRM mean	PACS2 (n=11)	0.46	0.92	0.99	85%
CRM Value	PACS2	0.45 (±0.05)	1.09 (±0.15)	0.98 (±0.13)	
611704					Interference
611711					n.d.
611747					25%
611749					26%
611776					51%
611777					30%
611791					n.d.
611794					Interference
611795					33%
611827					35%

n.d = not determined Interference = could not be calculated due to high matrix interference

3.4.3.11 Sediment Poly -Chlorinated Biphenyl (PCB) Analysis

PCB were determined in 23 selected samples at the BGS laboratories using a non-UKAS accredited GC-MS method. All glassware was cleaned in chromic acid (24 hours), rinsed with deionised water (4 times), dried at 100 °C for 12 hours and rinsed with HPLC-grade n-hexane prior to use. Anhydrous Na_2SO_4, anti-bumping granules and quartz wool were cleaned by Soxhlet-DCM extraction for 24 hours.

The method used is based on that described by Ayris et al. (1997). Each sediment sample was placed on a watch glass and authentic standards of PCB dissolved in n-hexane were added to the sediment, this was allowed to evaporate away prior to transfer of the samples to sealed glass containers. The samples were shaken and subsequently stored for 24 hours at room temperature prior to extraction. Accurately weighed portions of sediment and silica procedural blank (10 g) were mixed with an equal amount of anhydrous sodium sulphate and extracted with Hexane/acetone (1:1v/v) in an accelerated solvent extraction system ASE 200 (Dionex) fitted with stainless steel 33 ml cells and 60 ml glass (amber) collection vials. The ASE was operated at 100 °C at a pressure of 14 Mpa, with an oven heat-up time of 5 minutes and static time of 5 minutes, the flush volume was 50 % of the extraction cell volume. Acetone was removed from the extracts with 2 × 50 ml of 18 MΩ de-ionised water. Elemental sulphur was removed from the acetone free extracts by the addition of nitric acid washed/solvent cleaned copper wire and the volume reduced to 4 ml using rotary evaporation as well as a stream of nitrogen gas. Humic bound PCB were released by washing with an equivalent volume of concentrated sulphuric acid. The organic layer was then removed and dried by passing through a Pasteur pipette containing pre-cleaned anhydrous sodium sulphate (1 g) the volume reduced to about 3 ml using nitrogen gas. All extracts were eluted through a Pasteur pipette containing Florosil (1 g activated at 500 °C for 6 hours, 60-100 mesh) with 10 ml of n-hexane. To remove aliphatic compounds the eluant from this column was extracted with dimethylsulphoxide (DMSO, 2 × 12 ml) in separating funnel. The DMSO extracts were combined and diluted with 18 MΩ de-ionised water (25 ml) prior to extraction with n-hexane (50 ml). The n-hexane extracts were combined and the volume reduced to 5 ml by rotary evaporation. This was then dried by passing it through a Pasteur pipette containing pre-cleaned anhydrous sodium sulphate (1 g) and the volume reduced to approximately 100 µL using a gentle stream of nitrogen gas.

Quality control was achieved by subjecting a PCB certified reference material (LGC 6113 – Soil) to the above procedure in duplicate and analysing it by the same method as for the samples. A procedural blank prepared from white quartz sand (Sigma Aldrich, UK) – a material devoid of PCB - was treated in a similar fashion. Samples, reagent blanks and CRM were prepared and run in random order. Extraction efficiency of tri and tetra-chlorinated biphenyls was determined using those recovery determination standards listed in Table 3.9. Results for CRM and efficiency determinations are given in Table 3.10.

The GCMS used was a "Fisons MD 800". Mass range: full scan ion monitoring (m/z: 39-600), with electron impact and quadrupole analyser. On-column injection was onto a fused silica VF-5ms column (60 m length x 0.32 mm i.d. x 0.25 µm film thickness). Oven temperature programme: 60 °C (1 minute isothermal) to 320°C (at 10 °C / minute) and isothermal at 320 °C for 30 minutes. Carrier gas: helium at 16 p.s.i. The concentration of PCB congeners was determined from the peak area of the main selected ion. Confirmation of the identity of every integrated PCB congener was achieved by examination of mass fragmentation pattern over the entire mass range. The limits of detection based on the minimum concentrations that gave clearly defined peaks was 0.3 ng g^{-1} (Table 3.3)

Table 3.9 PCB species by congener number

Congener Number	IUPAC Name	PCB type
19	2,2′6-trichlorobiphenyl	SES
29	2,4,5-trichlorobiphenyl	RDS
34	2,3′5- trichlorobiphenyl	IS
28	2,4,4′-trichlorobiphenyl	Analyte
52	2,2′,5,5′-tetrachlorobiphenyl	Analyte
62	2,3,4,6-tetrachlorobiphenyl	IS
101	2,2′,4,5,5′-pentachlorobiphenyl	Analyte
119	2,3′,4,4′,6-pentachlorobiphenyl	IS
147	2,2′,3,4′,5,6-hexachlorobiphenyl	SES
118	2,3′,4,4′,5-pentachlorobiphenyl	Analyte
131	2,2′,3,3′,4,6-hexachlorobiphenyl	IS
153	2,2′,4,4′,5,5′-hexachlorobiphenyl	Analyte
138	2,2′,3,4,4′,5′- hexachlorobiphenyl	Analyte
157	2,3,3′,4,4′,5′- hexachlorobiphenyl	RDS
173	2,2′,3,3′,4,5,6-heptachlorobiphenyl	IS
180	2,2′,3,4,4′,5,5′-heptachlorobiphenyl	Analyte

SES= sample extraction standard RDS= recovery determination standard IS=internal standard

Table 3.10 Results for PCB CRM and extraction efficiency tests

Sample	PCB 28 ng g^{-1}	PCB 52 ng g^{-1}	PCB 101 ng g^{-1}	PCB 118 ng g^{-1}	PCB 153 ng g^{-1}	PCB 138 ng g^{-1}	PCB 180 ng g^{-1}	Total of 7 PCB ng g^{-1}	Tri Extract. Efficiency %	Tetra Extract. Efficiency %
CRM	22.75	4.72	18.99	23.36	33.49	48.36	24.37	176.03	112%	91%
St Dev	1.03	1.04	0.21	2.66	3.05	2.75	1.86	10.55		
CRM Values	14 (±3)	11 (±3)	23 (±6)	28 (±9)	42 (±12)	43 (±13)	29 (±8)	None given		
611704									71%	60%
611707									int	int
611711									int	55%
611714									41%	36%
611725									24%	23%
611726									98%	int
611729									70%	46%
611736									104%	78%
611740									72%	34%
611743									90%	97%
611747									int	int
611754									89%	57%
611777									95%	56%
611791									89%	int
611794									124%	44%
611798									int	int
611805									86%	86%
611819									50%	41%
611822									93%	58%
611823									93%	90%
611827									95%	24%
611876									84%	56%
611785									int	int

Int= could not be calculated due to high matrix interference
CRM=certified reference material PCB in soil LGC 6113

Tri Extract. = Tri -chlorinated biphenyls extraction
Tetra Exract. = Tetra-chlorinated biphenyls extraction

3.4.3.12 WATER MAJOR AND TRACE ELEMENT ANALYSIS

ICP-AES analysis for 14 major cations and trace elements and ICP-MS analysis for 29 trace elements in water were carried out at the BGS by standard UKAS accredited G-BASE methods (BGS, 1999). The detection limits were based on five times the standard deviation of the blank (Table 3.11). The major anions (chloride, nitrate sulphate and fluoride) were determined by ion chromatography using standard G-BASE methods, which are not UKAS accredited.

Total inorganic Hg was analysed at the BGS by vapour generation AFS, which is a UKAS accredited method. The solution was pumped into a vapour generator where it was mixed with tin(II) chloride to reduce Hg^{II} to Hg^{o}. The resulting mercury vapour was separated from the liquid in a gas/liquid separator and was swept by a stream of argon to the detector via a membrane separator tube to remove moisture. The atoms were excited by light from a mercury excitation source and the emitted fluorescence was measured, with the intensity being directly proportional to the concentration of Hg^{o} in solution. The instrument was calibrated using standards prepared to match the acid concentration in the samples and the detection limit was 0.02 µg L^{-1} (Table 3.11).

Selenium was analysed at the BGS by AFS. Prior to analysis Se^{VI}, which does not react to form gaseous hydride, has to be reduced to Se^{IV} by the addition of potassium bromide and heating at 70 °C for 40 minutes. After the reduction was completed the solution was pumped into a vapour generator where it was mixed with alkaline sodium borohydride to form gaseous selenium hydride and hydrogen. The resulting vapours were separated from the liquid in a gas/liquid separator and were swept by a stream of argon to a hydrogen diffusion flame, via a membrane separator tube to remove moisture, where the selenium hydride was broken down into selenium atoms. The atoms were excited by a selenium boosted hollow cathode lamp and the emitted fluorescence was measured, with the intensity being directly proportional to the concentration of Se^{IV} in solution. The instrument was calibrated using standards prepared to match the acid concentration in the samples. The reporting limit was 0.20 µg L^{-1} (Table 3.11). This method is not UKAS accredited.

3.4.3.13 WATER ORGANIC CARBON ANALYSIS

The determination of NPOC was carried out at the BGS using a Shimadzu TOC 5000 analyser (Serial No. 28604210) with associated ASI 5000 auto-sampler (Serial No. 29D07360). Samples were automatically pre-treated by the addition of a small volume of 10% HCl and sparged with inert gas to remove any inorganic carbon in the sample. Technically, any organic species that are volatile on acidification are also removed, although such species are rare in natural waters. The remaining organic carbon in the sparged sample is then combusted in a furnace, evolving carbon dioxide which is measured using a non-dispersive infra-red (NDIR) gas analysis system. Samples are calibrated against a series of standards, and the method is subject to stringent quality control and proficiency testing regimes. The limit of detection is shown in Table 3.11. The determination of NPOC is accredited by UKAS.

3.4.3.14 WATER COLORIMETRIC ANALYSIS

Ammonium and sulphide in waters were determined by colorimetric analysis at Alcontrol Ltd. laboratories. This method is UKAS accredited for ammonium but not for sulphide.

Table 3.11 Lower limits of detection for determinands in waters

Parameter	Units	Method	Detection Limit
Al	µg L^{-1}	ICP-MS	1
As	µg L^{-1}	ICP-MS	1
Ba	µg L^{-1}	ICP-AES	0.003
Be	µg L^{-1}	ICP-MS	0.05
Bi	µg L^{-1}	ICP-MS	0.01
Ca	mg L^{-1}	ICP-AES	0.03
Cd	µg L^{-1}	ICP-MS	0.02
Ce	µg L^{-1}	ICP-MS	0.01
Cl	mg L^{-1}	IC	0.05
Co	µg L^{-1}	ICP-MS	0.05
Cr	µg L^{-1}	ICP-MS	0.5
Cs	µg L^{-1}	ICP-MS	0.02
Cu	µg L^{-1}	ICP-MS	1
F	mg L^{-1}	IC	0.01
Fe	mg L^{-1}	ICP-AES	0.01
Ho	µg L^{-1}	ICP-MS	0.01
Hg	µg L^{-1}	AFS	0.02
K	mg L^{-1}	ICP-AES	0.1
La	µg L^{-1}	ICP-MS	0.01
Li	µg L^{-1}	ICP-MS	0.1
Mg	mg L^{-1}	ICP-AES	0.06
Mn	mg L^{-1}	ICP-AES	0.003
Mo	µg L^{-1}	ICP-MS	0.05
Na	mg L^{-1}	ICP-AES	0.08
Ni	µg L^{-1}	ICP-MS	1
NH_4	mg L^{-1}	Colorimetric	0.77
NO_2	mg L^{-1}	IC	0.005
NO_3	mg L^{-1}	IC	0.02
P	mg L^{-1}	ICP-AES	0.07
Pb	µg L^{-1}	ICP-MS	0.2
Rb	µg L^{-1}	ICP-MS	0.02
Sb	µg L^{-1}	ICP-MS	0.05
Se	µg L^{-1}	AFS	0.20
Si	mg L^{-1}	ICP-AES	0.08
Sn	µg L^{-1}	ICP-MS	0.04
SO_4	mg L^{-1}	IC	0.05
S^{2-}	mg L^{-1}	Colorimetric	0.20
Sr	mg L^{-1}	ICP-AES	0.001
Th	µg L^{-1}	ICP-MS	0.02
Tl	µg L^{-1}	ICP-MS	0.01
TIC	mg L^{-1}	TOC analyser	0.5
TOC	mg L^{-1}	TOC analyser	1
U	µg L^{-1}	ICP-MS	0.02
V	µg L^{-1}	ICP-MS	0.5
Y	µg L^{-1}	ICP-MS	0.01
Zn	µg L^{-1}	ICP-MS	2
Zr	µg L^{-1}	ICP-MS	0.01

3.5 ERROR CONTROL AND DATA QUALITY

3.5.1 Field and Laboratory

Systematic error in field sampling and analysis was monitored using a method based on randomised sample site numbers (Plant, 1973). Samples were collected in random number order but analysed in sequential order so that any analytical instrument drift can be distinguished from genuine geographic variances. No analytical drift problems were evident in the samples.

Rigorous field-based control procedures at each stage of the sampling process are designed to minimise error (Johnson et al., 2003). Long-term analytical drift between batches of samples was monitored using a series of standards representing a range of concentration for each element. The standards included several bulk sediment samples collected over representative rock types, three of which were analysed in every batch of 100 samples. Time versus concentration plots for each of these reference samples were prepared. Tolerance limits arbitrarily set at the mean $\pm 2\sigma$ were used to assess data quality. Simple arithmetic correlations were applied to normalise the data for systematic drift (BGS, 2000). Variability in the sampling and analytical methods was monitored by means of field and analytical duplicate samples and analytical standards. Values below the lower limit of detection were assigned to a value of one half of the detection limit and all field duplicate sample results removed prior to statistical treatment according to standard G-BASE procedures (BGS, 2000).

3.5.2 Stream Sediments

In order to assess variability, three field duplicate sediment samples were collected. Each sample was dried and split into two portions, producing a total of four analytical replicates from each site. As a check against mis-labelling or other errors, the analyses of the replicates were plotted against each other, for selected elements of differing chemical properties, to assess whether any sample pairs were consistently out-lying. The results for the replicate pairs of samples were averaged, and the field duplicate sample pairs were examined in a similar manner. No labelling errors were found. Analytical replicate results for stream sediments are outlined in Tables 3.12 and 3.13 and Figures 3.3 and 3.4 and demonstrate excellent repeatability of the analytical methods for both < 2 mm and < 150 µm sediments (1:1 straight line relationship).

The field duplicate results in general also show excellent repeatability between samples collected at the same site. The exceptions are duplicate sample pair A and B (Figures 3.5 and 3.6). Element concentrations in < 2 mm sediment sample A are generally higher than in sediment sample B and this pattern is even more marked for the < 150 µm samples. These samples were collected from the River Kelvin in Kelvin Walk Park (National Grid Reference (NGR) 257400, 666940). At this point the river is large and swift flowing and it was difficult to obtain fine sediment from the active river channel. As a result, the A sample was collected from the lee of a sediment bar and the B sample was collected 4 m away on the same bar but further into the active channel. Therefore, the A sample is likely to contain a much greater proportion of fine material organic matter and heavy minerals which drop out of solution more readily in the low-flow conditions of the lee-side of the bar than the B sample. Location A is also more likely to act as a deposit for gross contamination in the urban environment (accumulation of glass, pottery fragments, metal fragments, tin cans etc.). Since many of the metal elements are concentrated in the fine material in sediments, these are enhanced in the A sample relative to the B sample (Tables 3.12 and 3.13 and Figures 3.5 and 3.6). Elements that tend to concentrate in heavy minerals such as zircon (Zr) in zirconium also show markedly higher values for the A sample than the B sample (Tables 3.12 and 3.13 and Figures 3.5 and 3.6). These results highlight the likely variability in sediment composition in the larger rivers draining the catchment area with deposition of fine materials, heavy materials and contaminants occurring on banks and bars and washing out of fine material in the main river channel. Experience from rural areas suggests that natural variability between sample locations is less marked in small streams than in larger rivers due to the smaller scale of the sediment transport processes in operation.

Field duplicate pairs A2-B2 and C-D show good compatibility between results (Tables 3.12 and 3.13 and Figures 3.5 and 3.6). Both these duplicate pairs were collected at different sites on the White Cart Water (NGR 258400, 658370 and 257380, 661130 respectively). Zirconium is marginally elevated in < 150 µm duplicate B2 compared to A2 (Table 3.13 and Figure 3.5) again probably reflecting variability in the presence of heavy minerals between the two samples.

The A2-B2 field duplicate pair underwent analysis for asbestos content and crysotile (< 1 %) was reported in the A2 duplicate but not in the B2 duplicate sample. This may reflect genuine variability in the sample material collected or the reliability of the analytical method as outlined in Section 3.4.3.6 above.

Field duplicate pair A-B underwent total TPH and aromatic and aliphatic hydrocarbon analysis. The results appear to show poor repeatability between the duplicate pairs (Table 3.12) However, as explained in the preceding paragraphs, the A sample contains more organic carbon than the B sample (5.05 % and 3.32 % respectively) probably reflecting a greater proportion of vegetative material such as leaves. Leaf waxes are made up of high-molecular-weight aliphatics, which explains why compatibility between the aliphatics in the two samples is lower than that for aromatics. Once the data are corrected for organic matter content, there is good analytical repeatability between the results (A-sample corrected values: aromatics 1500 mg kg^{-1}, aliphatics 874 mg kg^{-1}and TPH 2374 mg kg^{-1}).

3.5.3 Surface Waters

Two sample numbers in each batch of 100 samples were reserved for the insertion of blank waters. These were made up from a stock supply of ultrapure deionised water and inserted in the analytical batches during the field campaign for ICP-AES, ICP-MS, AFS, ion chromatography, colorimetric and TOC analysis. The blank samples were treated with preserving agents such as nitric acid etc. in the same way as the field samples as outlined in Section 3.3 of this report. Following analysis of the samples, plots of the blank water data were generated to assess any low-level contamination of the samples and none was evident.

Quality control during the ICP-AES and ICP-MS analysis was maintained by means of drift-correction standards, in-house quality-control standards and participation in the Aquacheck inter-laboratory testing scheme. Drift-correction standards were measured before each analytical run to validate the instrument calibration. The drift-correction standards were also measured throughout the run approximately every 15 samples to monitor instrument performance. The results were used to adjust the calculated concentrations for changes in instrument response during the analytical run according to standard G-BASE methods (BGS, 1999). Two in-house quality-control solutions were analysed several times in each run to check analytical accuracy. For ion chromatography, standards were analysed at the beginning and end of each analytical run and quality a control-check sample was included in the analytical batch.

Ionic balances were calculated according to procedures described in Hem (1992) as a further test of analytical accuracy and gross errors (Table 3.14). In general, the balances are exceptionally good, and virtually all are within the normally acceptable 5 % tolerance limits used by the laboratory. Samples 611711, 611716, 611743, 611752, 611761, 611780, 611825, 611838, 611870 and 611882 all have balances that exceed 5 % probably due to variances in the field alkalinity measurement. All the balances fall within 5 % if the total inorganic carbon (TIC) data are used as an estimate of alkalinity.

The blank water samples (611710, 611775, 611814 and 611862) and the other low total dissolved solids (TDS) sample 611717 all have balances exceeding 5 %, but this is considered acceptable given the low TDS content of these samples. Sample 611759 contains very little chloride (Cl), repeat analysis of major cations and anions failed to improve this balance, although the anion deficiency may arise from an anionic species of undetermined nature observed on the IC chromatogram.

A further check on the overall quality of the data was given by determining the ratio of TDS to conductivity. In general the values obtained were all in the acceptable range ~ 0.60 to 0.95 (Table 3.14).

Three field duplicate samples were collected to check sample and analytical variability. In general the results show excellent agreement between samples collected at the same site (Table 3.15 and Figure 3.7) with the exception of zinc (Zn) in sample pair A2-B2. This variability is probably due to the presence of localised site contamination in one sample and not in the other.

Table 3.12 Field duplicate and analytical replicate results in < 2 mm stream sediments

Parameter	Units	Sample	DUPA	SSA	DUPB	SSB	DUPA2	SSA2	DUPB2	SSB2	DUPC	SSC	DUPD	SSD
		Samp No	611776	611786	611781	611778	611831	611877	611837	611858	611833	611802	611883	611843
Ag	mg kg^{-1}		0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Al_2O_3	wt %		7.3	7.1	5.9	6.0	13.6	13.4	13.3	13.1	10.2	9.6	9.4	9.8
As	mg kg^{-1}		20.9	18.9	8.9	9.9	3.6	5.0	4.6	5.7	4.3	5.9	7.3	4.9
Ba	mg kg^{-1}		468	461	397	398	531	497	493	470	390	364	353	374
Bi	mg kg^{-1}		1.1	0.5	1.0	0.5	0.5	1.2	0.5	0.5	0.5	0.5	0.5	1.9
Br	mg kg^{-1}		1.7	1.7	2.3	2.5	1.4	1.6	1.8	1.7	2.2	2.2	1.8	2.2
CaO	wt%		3.64	3.95	2.44	2.49	2.43	2.41	2.10	2.05	1.37	1.37	1.24	1.24
Cd	mg kg^{-1}		0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Ce	mg kg^{-1}		43	39	29	29	83	87	80	74	61	52	54	52
Co	mg kg^{-1}		25.3	24.3	18.3	17.3	44.5	42.8	41.1	43.5	29.3	29.2	28.0	26.7
Cr	mg kg^{-1}		70	72	58	71	104	99	103	102	109	111	109	112
Cs	mg kg^{-1}		1	1	1	1	2	3	4	1	1	1	1	2
Cu	mg kg^{-1}		37.1	34.0	22.8	29.5	33.1	47.8	32.0	32.6	45.9	42.5	43.1	44.6
Fe_2O_3	wt%		7.18	6.89	5.13	5.21	10.94	10.99	10.56	10.50	8.03	7.83	7.63	7.74
Ga	mg kg^{-1}		7.0	6.6	4.9	4.9	20.4	20.4	19.8	18.0	12.2	10.8	11.2	12.1
Ge	mg kg^{-1}		0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1.1	1.1	0.5
Hf	mg kg^{-1}		7.7	6.2	4.9	4.3	7.3	8.4	6.9	6.5	6.6	3.8	5.0	3.8
Hg	mg kg^{-1}		0.06	0.08	0.07	0.05	0.02	0.02	0.03	0.02	0.05	0.04	0.04	0.05
I	mg kg^{-1}		0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.5	0.25	0.5	0.25	0.25
K_2O	wt%		0.67	0.64	0.64	0.65	1.79	1.72	1.64	1.59	1.21	1.14	1.10	1.15
La	mg kg^{-1}		24	23	17	20	57	55	56	57	37	38	35	37
MgO	wt%		1.1	1.2	0.8	0.8	2.2	2.2	2.1	2.1	1.6	1.5	1.4	1.5
MnO	wt%		0.175	0.184	0.112	0.121	0.137	0.134	0.130	0.133	0.097	0.095	0.089	0.096
Mo	mg kg^{-1}		4.0	3.8	1.6	1.9	1.9	2.1	1.0	1.4	0.8	1.6	1.9	0.7
Na_2O	wt%		1.2	1.2	0.9	0.9	1.2	1.2	1.2	1.2	1.1	1.0	1.0	1.0
Nb	mg kg^{-1}		12.7	12.7	8.9	9.3	48.2	47.5	44.6	43.7	30.3	29.5	28.5	29.4
Ni	mg kg^{-1}		29.9	29.4	19.4	21.8	86.9	83.2	82.9	81.4	57.8	54.3	51.1	54.3
P_2O_5	wt%		0.27	0.25	0.17	0.18	0.46	0.45	0.44	0.43	0.31	0.29	0.28	0.29
Pb	mg kg^{-1}		1377.8	1323.9	825.8	755.4	32.5	31.9	42.5	38.6	54.2	52.0	60.1	58.3
Rb	mg kg^{-1}		19.8	17.9	17.5	17.5	44.8	44.2	45.5	43.9	33.8	31.0	29.8	31.8
Sb	mg kg^{-1}		1.70	2.10	1.10	1.70	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Sc	mg kg^{-1}		9	8	6	6	14	13	14	13	9	9	8	10
Se	mg kg^{-1}		0.4	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
SiO_2	wt%		77.6	78.4	85.2	83.9	53.1	53.0	54.4	56.2	70.2	73.0	73.2	71.8
Sn	mg kg^{-1}		35.5	50.7	20.4	18.5	5.4	5.2	7.0	10.1	15.0	14.1	18.9	18.9
Sr	mg kg^{-1}		249.7	245.4	167.7	173.5	213.6	214.4	194.3	190.4	150.8	144.4	136.6	135.8
Ta	mg kg^{-1}		0.50	0.25	1.70	0.25	3.40	0.90	2.00	2.20	2.00	0.25	1.40	2.40
Te	mg kg^{-1}		0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Th	mg kg^{-1}		1.8	2.0	2.1	2.5	6.4	5.9	6.5	5.9	5.3	5.1	4.5	4.3
TiO_2	wt%		0.709	0.677	0.487	0.498	1.947	1.956	1.867	1.827	1.265	1.224	1.193	1.205
Tl	mg kg^{-1}		2.80	3.00	1.10	1.50	0.25	0.25	0.50	0.25	0.60	0.70	0.25	0.50
U	mg kg^{-1}		0.25	0.25	0.25	0.90	0.90	1.70	1.20	2.20	1.60	1.90	0.25	0.25
V	mg kg^{-1}		63	61	44	46	139	141	137	135	100	98	90	96
W	mg kg^{-1}		0.25	0.25	1.20	1.00	1.20	0.60	0.50	0.60	1.10	0.80	0.25	0.90
Y	mg kg^{-1}		17.6	15.4	11.1	13.0	27.5	30.4	25.2	25.4	17.8	18.6	15.6	17.9
Zn	mg kg^{-1}		204.7	236.6	137.3	133.4	212.2	210.1	202.0	195.6	190.4	177.4	168.8	181.9
Zr	mg kg^{-1}		239.8	259.4	200.4	182.0	321.5	329.9	308.8	303.5	219.4	210.4	199.2	214.0
Asbestos	%		ND	ND	ND	ND	Chrysotile (<1%)	ND	None	ND	ND	ND	ND	ND
Fibres			None	ND	None	ND	None	ND	None	ND	None	ND	None	ND
Cyanide	mg kg^{-1}		0.5	ND	0.5	ND	0.5	ND	0.5	ND	0.5	ND	0.5	ND
pH			6.02	ND	6.06	ND	6.58	ND	6.35	ND	6.40	ND	6.16	ND
TOC	%		5.04	4.78	3.32	3.09	1.04	1.04	0.78	0.79	0.72	0.71	0.71	0.70
Aromatics	mg kg^{-1}		ND	1557	1000	ND	ND	ND	ND	ND	ND	ND	ND	ND
Aliphatics	mg kg^{-1}		ND	1121	583	ND	ND	ND	ND	ND	ND	ND	ND	ND
TPH	mg kg^{-1}		ND	2678	1583	ND	ND	ND	ND	ND	ND	ND	ND	ND

Dup = Field Duplicate
SS = Analytical Replicate
ND = Not determined

Table 3.13 Field duplicate and analytical replicate results in < 150 µm stream sediments

Parameter	Units	Sample	DUPA	SSA	DUPB	SSB	DUPA2	SSA2	DUPB2	SSB2	DUPC	SSC	DUPD	SSD
		Samp No	611776	611786	611781	611778	611831	611877	611837	611858	611833	611802	611883	611843
Ag	mg kg^{-1}		0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Al_2O_3	wt %		13.1	13.0	11.5	12.1	17.2	17.0	16.2	15.9	12.2	12.1	12.2	12.2
As	mg kg^{-1}		16.9	17.1	12.3	12.0	6.3	5.3	4.5	5.1	4.9	3.6	5.7	5.5
Ba	mg kg^{-1}		923	938	633	662	604	593	543	542	513	501	507	522
Bi	mg kg^{-1}		0.5	0.5	1.1	1.1	0.5	1.3	0.5	0.5	1.2	0.5	1.2	1.1
Br	mg kg^{-1}		21.1	21.6	17.7	17.9	18.9	18.6	12.6	12.1	16.0	14.9	14.5	16.5
CaO	wt%		5.26	5.23	3.46	3.39	2.36	2.28	1.80	1.79	1.49	1.45	1.43	1.46
Cd	mg kg^{-1}		1.00	0.60	0.50	0.50	0.25	0.70	0.50	0.25	0.60	0.50	0.25	0.25
Ce	mg kg^{-1}		87	82	59	66	109	110	100	102	77	80	76	82
Co	mg kg^{-1}		38.7	39.7	30.9	30.5	45.7	46.5	41.8	40.5	29.2	30.7	29.8	29.1
Cr	mg kg^{-1}		142	140	105	106	169	164	164	165	192	185	188	188
Cs	mg kg^{-1}		0.5	0.5	1.0	1.0	1.0	1.0	6.0	3.0	2.0	1.0	1.0	2.0
Cu	mg kg^{-1}		167.2	171.8	65.2	65.7	58.9	60.9	52.7	53.1	109.1	92.7	92.9	108.2
Fe_2O_3	wt%		8.39	8.36	7.54	7.56	10.48	10.47	10.05	9.99	8.24	8.29	8.33	8.22
Ga	mg kg^{-1}		12.6	12.1	11.6	12.3	22.9	21.8	20.9	20.4	14.6	14.3	14.9	14.3
Ge	mg kg^{-1}		2.3	1.7	1.1	1.7	1.1	1.1	1.1	1.3	2.0	1.3	2.0	1.7
Hf	mg kg^{-1}		35.2	34.7	13.2	13.5	11.6	11.8	13.6	13.0	16.3	16.5	16.5	18.5
I	mg kg^{-1}		9.5	9.2	6.8	7.0	5.6	5.5	4.1	4.1	4.8	4.2	4.0	4.3
K_2O	wt%		1.17	1.17	1.13	1.18	1.58	1.57	1.47	1.46	1.27	1.25	1.25	1.26
La	mg kg^{-1}		47	44	41	40	70	68	62	64	48	48	51	51
MgO	wt%		1.5	1.5	1.4	1.4	1.9	1.9	1.7	1.7	1.5	1.5	1.5	1.5
MnO	wt%		0.354	0.356	0.215	0.213	0.194	0.196	0.173	0.171	0.160	0.157	0.156	0.158
Mo	mg kg^{-1}		4.2	3.5	1.9	2.4	3.2	3.3	2.5	2.4	1.9	2.0	1.8	1.6
Na_2O	wt%		0.8	0.9	0.8	0.8	0.5	0.5	0.6	0.6	0.7	0.7	0.7	0.7
Nb	mg kg^{-1}		22.4	22.6	18.4	17.7	49.7	49.3	48.1	48.9	38.2	37.9	37.7	37.0
Ni	mg kg^{-1}		61.4	61.8	38.8	41.7	105.2	104.3	87.1	89.8	59.4	58.6	58.2	58.3
P_2O_5	wt%		0.48	0.48	0.50	0.57	0.58	0.57	0.49	0.48	0.46	0.44	0.44	0.45
Pb	mg kg^{-1}		3536.9	3544.4	836.1	825.1	85.5	83.2	79.0	77.2	124.9	119.4	119.4	126.1
Rb	mg kg^{-1}		42.5	41.9	35.3	36.8	52.7	53.3	51.6	49.8	40.0	39.2	38.2	38.9
Sb	mg kg^{-1}		5.7	5.5	2.6	2.7	0.8	1.2	0.9	1.2	1.0	1.0	1.2	1.3
Sc	mg kg^{-1}		13	14	11	14	16	17	15	15	11	13	12	12
Se	mg kg^{-1}		1.8	1.4	1.1	1.2	1.1	0.9	0.7	0.9	0.7	0.8	0.7	0.8
SiO_2	wt%		57.6	57.1	62.0	54.7	47.8	47.8	52.0	51.4	63.2	63.3	64.2	63.2
Sn	mg kg^{-1}		76.4	77.3	18.7	17.3	16.5	16.6	13.5	12.6	27.4	26.4	26.8	26.7
Sr	mg kg^{-1}		308.2	310.0	213.9	211.7	157.1	154.5	144.7	143.0	132.9	129.3	130.8	130.2
Ta	mg kg^{-1}		0.7	0.25	1.7	0.25	1.3	2.4	1.3	0.7	1.4	1.6	2.3	1.7
Te	mg kg^{-1}		0.25	0.6	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Th	mg kg^{-1}		7.3	5.6	5.0	4.7	8.2	7.5	8.0	8.5	7.3	7.0	7.0	6.9
TiO_2	wt%		1.219	1.221	1.148	1.172	2.299	2.310	2.204	2.200	1.747	1.749	1.755	1.742
Tl	mg kg^{-1}		5.4	5.9	1.0	1.7	0.25	0.7	0.9	0.25	0.5	0.8	0.7	0.6
U	mg kg^{-1}		0.3	0.3	0.3	0.3	1.6	0.8	1.0	1.8	1.3	1.4	1.1	1.0
V	mg kg^{-1}		108	109	100	103	172	173	163	163	132	130	130	131
W	mg kg^{-1}		0.25	0.25	0.50	0.25	0.25	0.25	0.60	0.25	0.25	0.25	0.25	0.90
Y	mg kg^{-1}		32.5	33.2	23.4	22.4	29.8	30.2	29.2	28.0	24.4	23.9	24.7	24.9
Zn	mg kg^{-1}		673.9	672.2	359.8	363.1	380.0	381.7	311.6	309.5	279.8	271.9	268.8	277.5
Zr	mg kg^{-1}		1445.6	1366.0	621.4	563.6	487.4	502.3	571.5	578.2	745.8	748.2	757.3	752.7

Dup = Field Duplicate SS = Analytical Replicate

Table 3.14 Ionic balance results for surface water samples

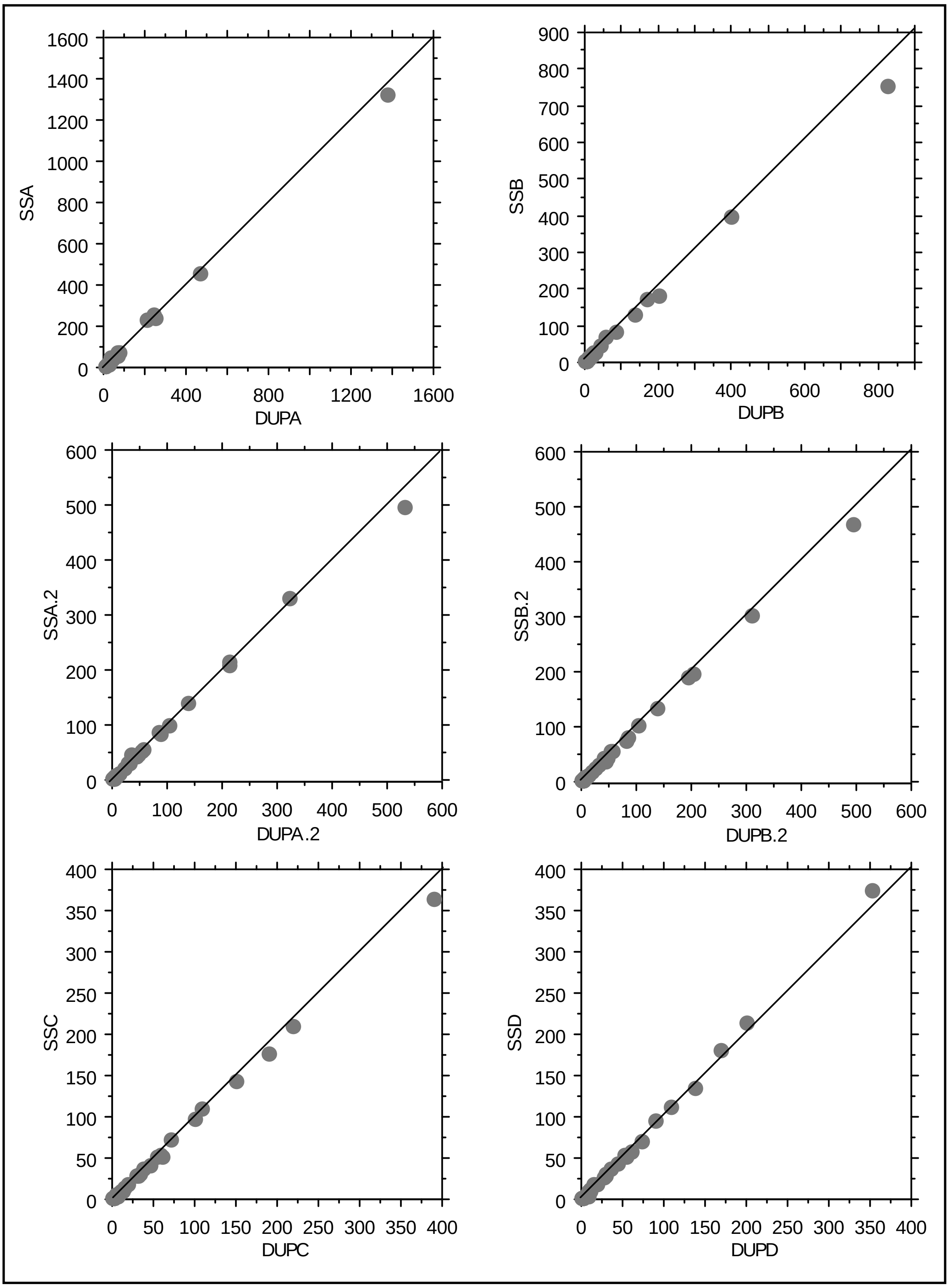
Sample Number	Comments	Cation Total	Anion Total	Balance	Conductivity	TIC Balance	TDS/Cond
		meq L^{-1}	meq L^{-1}	%	µS cm^{-1}	%	
611701		6.76	6.83	-0.53	668	-1	0.69
611702		2.86	2.73	2.38	291	2	0.68
611703		5.62	5.65	-0.29	515	0	0.78
611704		2.55	2.54	0.32	231	0	0.76
611705		3.64	3.62	0.18	360	0	0.72
611706		3.30	3.20	1.56	328	2	0.70
611707		8.55	8.35	1.17	741	1	0.80
611708		2.98	2.91	1.14	292	1	0.72
611709		4.69	4.59	1.08	438	1	0.77
611710	Blank Water	0.01	0.00	66.40	n/a	0	n/a
611711		2.34	2.06	6.21	251	6	0.62
611712		1.98	1.92	1.68	197	2	0.71
611713		4.74	4.66	0.83	456	1	0.76
611715		9.23	8.96	1.49	857	1	0.73
611716		3.98	3.35	8.54	348	9	0.68
611717		0.48	0.17	48.06	50	48	0.27
611718		10.14	9.81	1.63	888	2	0.79
611719		5.93	5.85	0.67	614	1	0.64
611720		5.34	5.34	0.01	517	0	0.72
611721		6.03	5.80	1.95	556	2	0.73
611723		7.84	8.17	-2.09	742	-2	0.74
611724		3.06	2.94	2.13	291	2	0.74
611725		3.48	3.55	-0.91	343	-1	0.73
611726		5.69	5.83	-1.17	608	-1	0.63
611727		1.11	1.08	1.23	133	1	0.59
611728		11.65	10.86	3.49	917	3	0.89
611729		2.99	2.80	3.36	304	3	0.67
611730		3.03	2.93	1.72	320	2	0.64
611731		2.38	2.30	1.83	247	2	0.67
611733		4.30	4.13	2.02	403	2	0.74
611734		3.37	3.29	1.19	333	1	0.72
611735		9.61	9.55	0.30	903	0	0.71
611736		12.03	12.05	-0.07	990	0	0.84
611737		8.14	7.52	3.99	650	4	0.88
611738		7.80	7.53	1.81	627	2	0.87
611739		11.60	11.14	2.04	923	2	0.90
611740		8.25	8.10	0.93	680	1	0.92
611741		9.96	9.54	2.17	813	2	0.88
611742		4.93	4.79	1.45	464	1	0.75
611743		2.98	2.54	8.07	308	0	0.37
611744		3.03	2.89	2.39	310	2	0.68
611745		10.35	9.79	2.75	890	3	0.82
611746		9.91	9.28	3.32	839	3	0.83
611747		3.85	3.77	1.01	363	1	0.78
611748		11.30	10.99	1.41	926	1	0.86
611749		9.52	9.03	2.60	818	3	0.83
611750		3.82	3.71	1.53	361	2	0.75
611751		8.46	8.26	1.16	725	1	0.83

Sample Number	Comments	Cation Total	Anion Total	Balance	Conductivity	TIC Balance	TDS/Cond
		meq L^{-1}	meq L^{-1}	%	µS cm^{-1}	%	
611752		3.70	3.24	6.51	382	7	0.61
611753		6.42	6.28	1.08	611	1	0.75
611754		8.52	8.06	2.79	632	3	0.94
611755		3.37	3.14	3.48	331	3	0.67
611756		5.31	5.78	-4.22	516	-4	0.77
611757		14.47	13.20	4.60	1064	5	0.92
611758		3.22	3.09	2.04	328	2	0.68
611759		8.92	6.53	15.42	774	15	0.71
611760		3.69	3.43	3.57	362	4	0.69
611761		2.45	2.11	7.67	231	8	0.71
611762		5.66	5.28	3.47	505	3	0.79
611763		3.08	2.83	4.20	318	4	0.66
611764		4.95	4.87	0.78	525	1	0.64
611765		7.65	7.00	4.44	634	4	0.85
611767		7.85	7.56	1.89	663	2	0.83
611769		11.90	11.40	2.17	1007	2	0.80
611770		5.37	5.05	3.08	503	3	0.71
611771		5.56	5.36	1.85	504	2	0.78
611773		3.34	3.36	-0.33	333	0	0.73
611774		7.71	7.59	0.78	694	1	0.76
611775	Blank Water	0.00	0.00	100.00	n/a	0	n/a
611776		4.17	3.91	3.25	407	3	0.70
611776	Duplicate	4.12	3.89	2.89	407	3	0.69
611777		4.47	4.50	-0.29	429	0	0.75
611779		3.60	3.46	1.96	347	2	0.72
611780		3.01	2.49	9.59	279	10	0.68
611781		4.15	3.91	3.03	402	3	0.70
611781	Duplicate	4.12	3.88	3.03	402	3	0.70
611782		4.77	4.68	0.95	501	1	0.65
611783		2.93	2.85	1.39	288	1	0.71
611784		3.38	3.08	4.71	292	5	0.83
611787		9.84	9.56	1.43	881	1	0.80
611788		5.91	5.71	1.75	567	2	0.75
611789		3.59	3.46	1.74	337	2	0.76
611790		0.75	0.73	1.04	79	1	0.65
611791		7.84	7.55	1.90	676	2	0.82
611792		3.82	3.58	3.36	370	3	0.72
611793		9.64	8.73	4.95	1013	5	0.68
611794		4.12	3.90	2.74	407	3	0.67
611795		3.72	3.55	2.32	360	2	0.72
611796		12.04	11.70	1.46	990	1	0.84
611797		8.47	8.33	0.85	744	1	0.80
611798		2.55	2.36	3.83	261	4	0.64
611799		11.15	10.61	2.48	958	2	0.77
611800		4.62	4.45	1.92	438	2	0.74
611801		5.13	5.04	0.87	485	1	0.74
611804		3.29	3.14	2.33	321	2	0.72
611805		3.27	2.96	4.87	319	5	0.68
611806		2.64	2.56	1.65	260	2	0.72

Sample Number	Comments	Cation Total	Anion Total	Balance	Conductivity	TIC Balance	TDS/Cond
		meq L^{-1}	meq L^{-1}	%	µS cm^{-1}	%	
611811		6.20	6.20	0.07	574	0	0.76
611814	Blank Water	0.00	0.00	100.00	n/a	0	n/a
611815		5.30	5.13	1.60	465	2	0.81
611817		4.27	4.15	1.48	405	1	0.74
611819		3.50	3.35	2.27	340	2	0.72
611822		2.53	2.35	3.65	247	4	0.71
611823		2.64	2.45	3.61	259	4	0.70
611825		1.13	0.97	7.71	119	8	0.62
611827		9.14	9.03	0.59	815	1	0.78
611829		5.23	5.07	1.58	475	2	0.78
611831		3.79	3.73	0.91	370	1	0.71
611831	Duplicate	3.77	3.74	0.39	370	0	0.71
611833		3.78	3.75	0.37	379	0	0.69
611833	Duplicate	3.73	3.76	-0.38	379	0	0.69
611834		2.30	2.22	1.71	226	2	0.72
611836		5.03	4.82	2.09	463	2	0.76
611837		3.82	3.81	0.16	368	0	0.72
611837	Duplicate	3.78	3.81	-0.35	368	0	0.72
611838		1.91	1.63	8.02	197	8	0.62
611839		2.62	2.45	3.27	252	3	0.72
611841		1.84	1.69	4.30	185	4	0.67
611847		2.49	2.29	4.20	242	4	0.70
611848		2.48	2.28	4.16	246	4	0.69
611854		2.29	2.16	3.03	226	3	0.70
611862	Blank Water	0.01	0.00	100.00	n/a	0	n/a
611864		2.69	2.55	2.58	258	3	0.74
611868		5.53	5.45	0.73	544	1	0.70
611870		2.28	1.95	7.80	227	8	0.64
611871		2.71	2.63	1.66	253	2	0.79
611872		4.30	4.12	2.04	431	2	0.69
611873		4.19	4.11	0.92	431	1	0.67
611876		2.73	2.70	0.54	274	1	0.70
611878		2.87	2.68	3.39	267	3	0.74
611882		2.12	1.78	8.83	218	9	0.61
611883		3.99	3.79	2.58	413	3	0.65
611883	Duplicate	3.99	3.78	2.62	413	3	0.65
611885		3.27	3.01	4.08	277	4	0.77
611886		3.40	3.23	2.57	332	3	0.71
611888		4.35	4.15	2.40	431	2	0.70
611896		4.52	4.41	1.30	423	1	0.76
611900		5.00	4.91	0.93	453	1	0.79

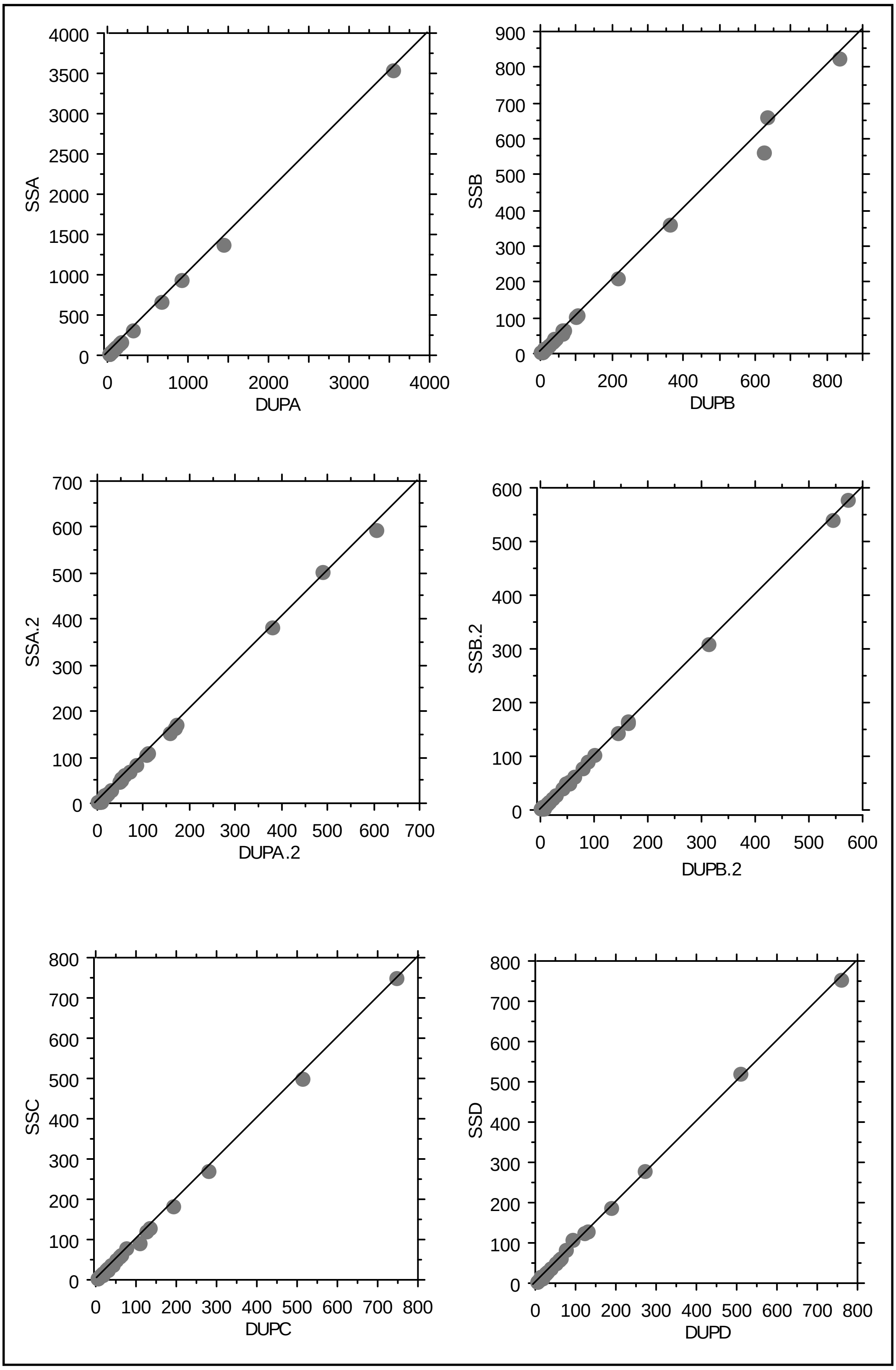
Table 3.15 Field duplicate results in surface water samples

Parameter	Units	Sample	Dup A	Dup B	Dup A2	Dup B2	Dup C	Dup D
		Samp No	611776	611781	611831	611837	611833	611883
Al	µg L^{-1}		9	9	23	20	18	18
As	µg L^{-1}		0.5	0.5	0.5	0.5	0.5	0.5
Ba	mg L^{-1}		0.100	0.093	0.041	0.046	0.051	0.071
Be	µg L^{-1}		0.025	0.025	0.025	0.025	0.025	0.025
Bi	µg L^{-1}		0.005	0.005	0.005	0.005	0.005	0.005
Ca	mg L^{-1}		43.0	42.8	33.0	33.4	32.1	33.3
Cd	µg L^{-1}		0.01	0.01	0.01	0.01	0.01	0.01
Ce	µg L^{-1}		0.05	0.05	0.07	0.04	0.04	0.04
Cl	mg L^{-1}		36.5	36.1	45.7	46.3	44.3	45.6
Co	µg L^{-1}		0.43	0.44	0.30	0.31	0.30	0.28
Conductivity	µS cm^{-1}		407	402	370	368	379	413
Cr	µg L^{-1}		1.8	1.8	0.6	0.6	0.5	0.25
Cs	µg L^{-1}		0.05	0.05	0.01	0.01	0.01	0.02
Cu	µg L^{-1}		2	2	3	2	2	2
DO	mg L^{-1}		9.4	9.4	5.2	5.7	5.2	5.2
F	mg L^{-1}		0.116	0.118	0.129	0.138	0.123	0.123
Fe	mg L^{-1}		0.28	0.28	0.08	0.11	0.07	0.09
$HC0_3^-$	mg L^{-1}		117	118	104	107	102	100
Hg	µg L^{-1}		0.01	0.01	0.01	0.01	0.01	0.01
Ho	µg L^{-1}		0.005	0.005	0.005	0.005	0.005	0.005
K	mg L^{-1}		4.4	4.4	3.8	3.8	4.0	4.2
La	µg L^{-1}		0.03	0.03	0.03	0.03	0.02	0.02
Li	µg L^{-1}		4.0	4.2	1.9	2.0	1.8	1.8
Mg	mg L^{-1}		9.74	9.69	4.81	4.86	4.89	5.16
Mn	mg L^{-1}		0.047	0.049	0.032	0.031	0.026	0.028
Mo	µg L^{-1}		0.69	0.66	2.13	2.15	2.68	3.10
Na	mg L^{-1}		25.0	24.8	33.5	33.5	33.5	35.7
NH_4	mg L^{-1}		0.385	0.385	3.45	3.46	3.73	4.17
Ni	µg L^{-1}		3	3	2	2	2	2
NO_3	mg L^{-1}		9.40	8.58	6.61	6.84	9.54	9.59
P	mg L^{-1}		0.035	0.035	0.32	0.35	0.35	0.34
Pb	µg L^{-1}		0.4	0.3	0.6	0.5	0.5	0.4
pH			7.75	7.90	7.58	7.61	7.51	7.55
Rb	µg L^{-1}		5.01	5.07	3.68	3.76	3.95	4.05
S^{2-}	mg L^{-1}		0.10	0.10	0.10	0.10	0.10	0.10
Sb	µg L^{-1}		0.25	0.25	0.65	0.66	0.56	0.42
Se	µg L^{-1}		0.125	0.125	0.125	0.125	0.125	0.125
Si	mg L^{-1}		1.87	1.76	2.38	2.41	2.41	2.67
Sn	µg L^{-1}		0.30	0.29	0.22	0.19	0.22	0.21
SO_4	mg L^{-1}		38.6	38.7	30.1	30.0	31.8	33.8
Sr	mg L^{-1}		0.277	0.276	0.166	0.168	0.166	0.173
TDS	mg L^{-1}		284	283	261	266	263	267
Th	µg L^{-1}		0.01	0.01	0.01	0.01	0.01	0.01
TIC	mg L^{-1}		26.1	26.0	22.0	22.1	22.1	20.9
Tl	µg L^{-1}		0.005	0.005	0.005	0.005	0.005	0.005
TOC	mg L^{-1}		4.99	5.01	6.07	6.36	6.70	6.67
U	µg L^{-1}		0.14	0.13	0.12	0.12	0.11	0.11
V	µg L^{-1}		0.25	0.5	1.4	1.5	1.3	1.1
Y	µg L^{-1}		0.05	0.05	0.05	0.04	0.04	0.04
Zn	µg L^{-1}		2	2	43	16	6	7
Zr	µg L^{-1}		0.10	0.09	0.06	0.06	0.05	0.05



Dup = Field duplicate
SS = Analytical duplicate
Includes all data except, asbestos, fibres, aromatics, aliphatics and TPH
Line = 1:1 correlation

Figure 3.3 Plots of analytical replicate results for < 2 mm sediment samples



Dup = Field duplicate
SS = Analytical duplicate
Includes all data
Line = 1:1 correlation

Figure 3.4 Plots of analytical replicate results for < 150 µm stream sediments

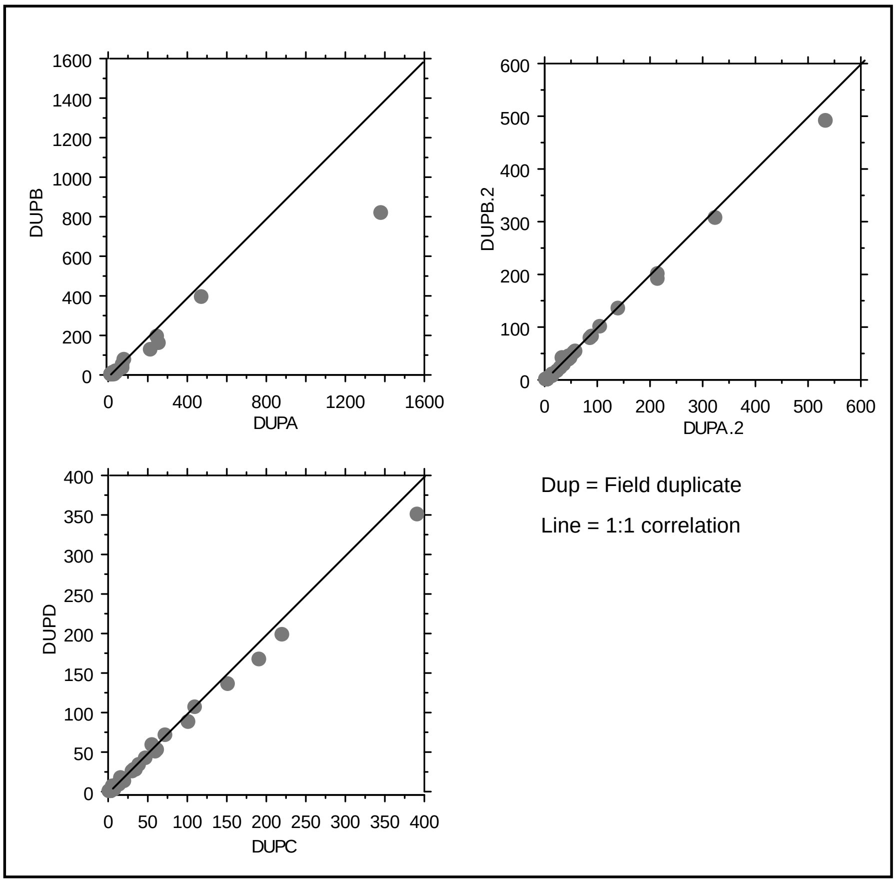


Figure 3.5 Plots of field duplicate results for < 2 mm stream sediments

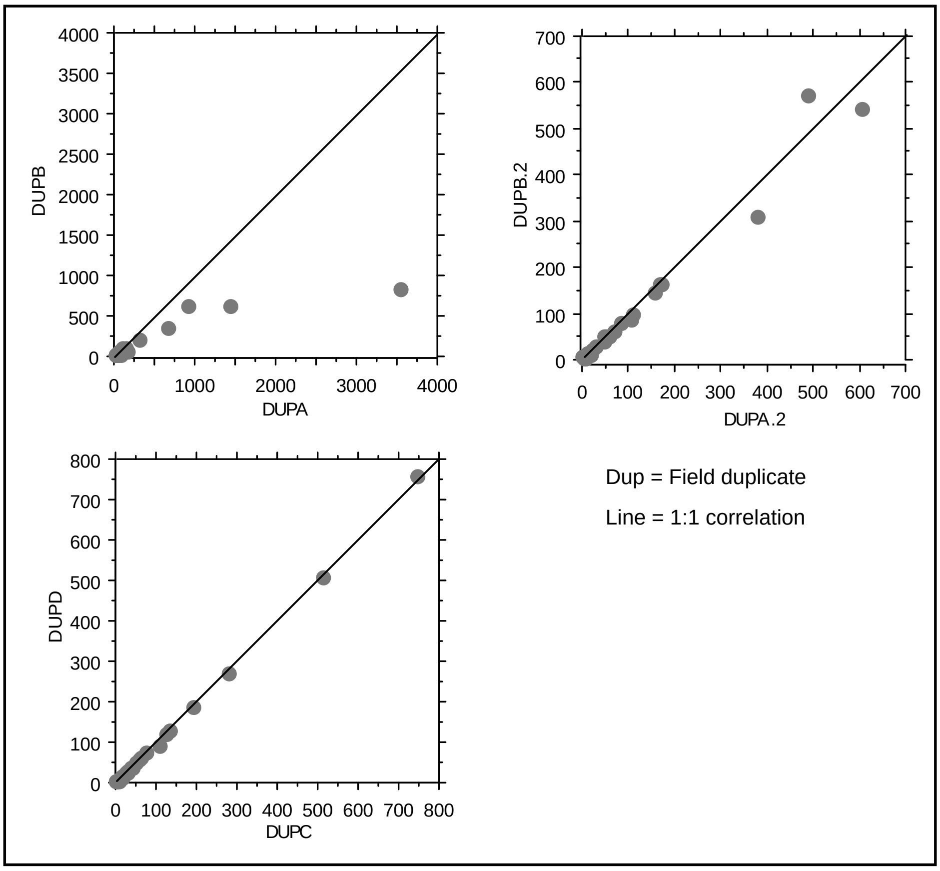


Figure 3.6 Plots of field duplicate results for < 150 µm stream sediments

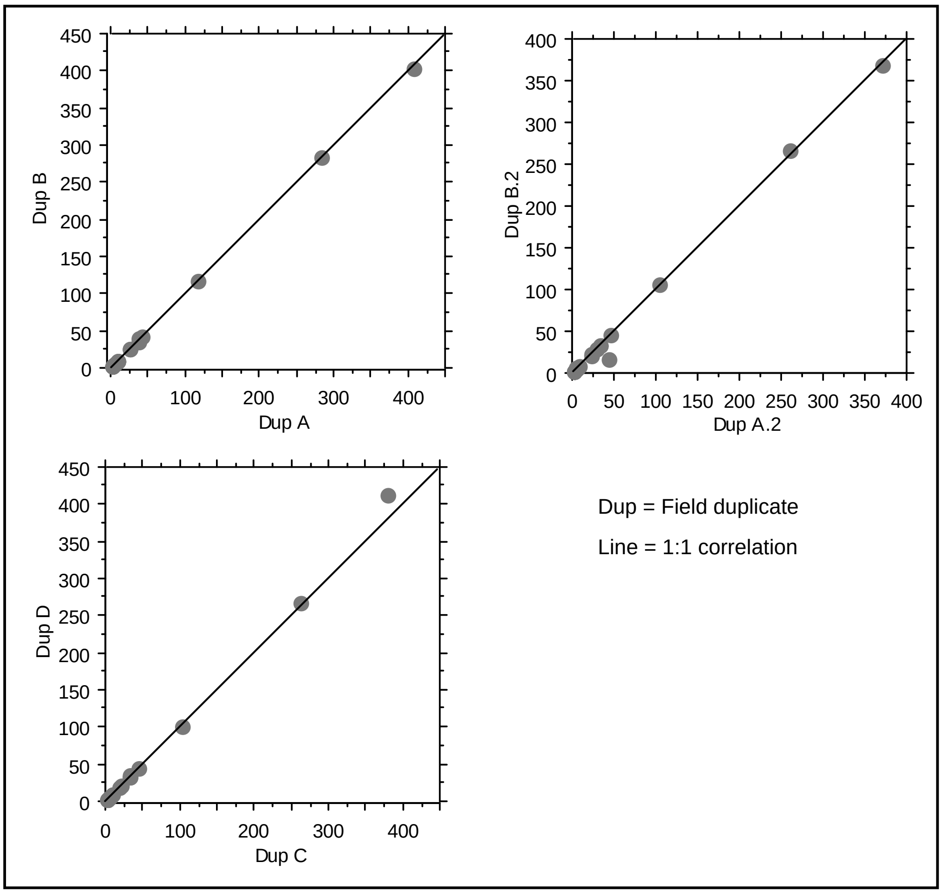


Figure 3.7 Plots of field duplicate results for surface waters

3.6 DATA PRESENTATION AND CLYDE TRIBUTARIES GIS

Once full error control and data quality procedures were completed, the Glasgow tributaries geochemical results were merged with locational and field-observation data into datasets for sediment, water and organic determinands in Excel® spreadsheet format. These datasets were reported to GCC to accompany the project report and GIS. A summary of the data held in the datasets, once field duplicate results etc. were removed, is given in Table 3.16. The datasets contain both BGS and GCC sample codes as outlined in Table 3.2 and samples sites are referred to throughout this report using the GCC sample codes. On completion of the project, the data will be formally loaded onto the BGS Corporate Oracle® Geochemistry Database (Harris and Coats, 1992) where they may be retrieved by means of a database front-end.

It is standard procedure in the field of geochemistry to present the data as a series of single-element maps showing the geographic distribution of the results. Rural geochemical data are commonly presented as continuous interpolated surface maps as these aid the identification of regional geochemical patterns (see for example BGS 1993). However, interpolated maps do not provide a suitable method for presenting urban data. At the close scale of interrogation necessary in urban areas, interpolations can give misleading results, as the spatial extent of high element values can be over-emphasised. As a result, methods of presenting urban geochemical data as graduated symbol maps have been developed by the GSUE project (for example O'Donnell 2004). Graduated symbol maps avoid uncertain extrapolation between sampling points (as portrayed in interpolated-surface maps) and display the data in a form that more truly indicates the spatial representation of urban samples.

Maps of element concentrations in stream sediment and surface water for Glasgow were generated using the Arc8® GIS graduated symbol function and are presented in the Annexes of this report. The standard way to plot geochemical maps is using a full range of percentiles to describe the data distribution. Elements were classified according to the 5th, 10th, 25th, 50th, 75th, 90th, 95th and 99th percentiles of the real data whereby circle-symbol size and colour correspond to the data percentile class. Whilst this method of data presentation is the international standard in the field of geochemistry and allows ready interpretation of the data, it should be noted that the element value for each percentile class will vary depending on the dataset.

Hence, the percentile distributions for the combined rural-urban stream sediment datasets presented in Annex 1 are different from those of the urban dataset only presented in Annex 3. This is important because data above the 95th percentile in a distribution are commonly considered to represent anomalous or high values but this has to be viewed in the context of the dataset under examination. For example, the 95th percentile value for As in rural-urban < 150 μm stream sediments is 20 mg kg^{-1} whereas the 95th percentile for the urban data only is 72 mg kg^{-1} (Annex 1 and Annex 3 respectively). Whilst these concepts are well understood in the field of geochemistry, they can be misleading for the non-specialist. Hence in addition to percentile-class plots, the Clyde tributaries geochemical data are presented as a series of maps relating to regulatory guideline values to highlight areas of potential concern within the urban environment (Annexes 5 and 8).

The percentile and regulatory guideline maps were incorporated into the Clyde tributaries urban geochemistry GIS where they can be interpreted and assessed in the context of other environmental information for contaminated land and urban planning purposes.

It should be noted that for data close to the analytical detection limit, the results are rounded up to the nearest integer and this may lead to several percentile classes in the data distribution with the same element concentration. Whilst this is a true reflection of the data and prevents "over-interpretation" of the data to decimal points, which are not significant, it leads to the absence of several percentile classes on the graduated symbol maps for some elements such as Cd, Sb and Bi.

The GIS allows the user to view the urban geochemistry datasets spatially. The ESRI Arc8® GIS project file (CLTR.mxd) runs from the CD-ROM or can be copied across to a local or network drive. For further information on the use of Arc8® consult the ESRI user guide. Each dataset is held in the GIS as a layer and these are listed in Table 3.17. All the data are stored as feature classes in a personal geodatabase (CLTR.mdb).

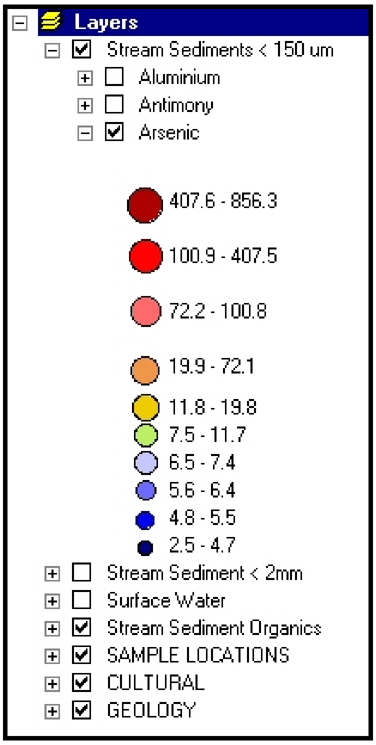
The sample sites are presented against a backdrop of topographic information and the underlying geology. Each theme has associated attributes, for example, the user can query one of the sample site locations to find out its unique ID and the values for the elements sampled. In Arc8® it is possible to group similar data layers to form a collapsible group layer. The visibility of individual layers contained within the group is controlled by the top check box (see Figure 3.8). These layer files were used to save the graduated symbol legends manually generated for each element (see folder \GIS\Layers).

Table 3.16 Summary of data available from the Clyde tributaries survey

Sample Type	Number of Samples	Determinands	Analytical Method
Sediment < 2 mm	118	46 elements	XRFS
	116	Hg	AFS
	114	pH	Electrode
	114	Total cyanide	Colorimetric
	114	Fibrous minerals	Sieving
	48	Asbestos	PML
	116	TOC	Carbon/Sulphur analyser
	115	TPH	Iatroscan
	52	PAH	HPLC-Fluorescence
	10	Organo-tin	GC-MS
	23	PCB	GC-MS
Sediment < 150 µm	118	46 elements	XRFS
Water	122	14 elements	ICP-AES
	122	29 elements	ICP-MS
	122	Hg, Se	AFS
	122	Cl, NO_3, SO_4, F	IC
	122	NPOC	TOC analyser
	122	S^{2-}, NH_4	Colorimetric

Table 3.17 List of environmental datasets incorporated to the Clyde tributaries urban geochemistry GIS

GROUP LAYER NAME **Layer Name**	**Description**	**Source**
CULTURAL DATA		
Culverts		Glasgow City Council
Rivers		OS Meridian
Glasgow city boundary		OS Meridian
Major roads		OS Meridian
Coastline		OS Meridian
Lakes		OS Meridian
Railways		OS Meridian
Urban areas		OS Meridian
Quarry locations		BGS
Project extent		BGS
GEOLOGY		
Rationalised DigMap 50k	Simplified bedrock geology	BGS
Coal lines 10k	1:10000 coal lines	BGS
Glasgow faults	1:10000 faults	BGS
Bedrock 50k	1:50000 bedrock geology	BGS
Artificial 50k	1:50000 artificial deposits	BGS
Superficial 50k	1:50000 superficial deposits	BGS
Mass movement 50k	1:50000 mass movement	BGS
Bedrock 250k	1:250000 bedrock geology	BGS
Bedrock 625k	1:625000 bedrock geology	BGS
Superficial 625k	1:625000 superficial deposits	BGS
SAMPLE LOCATIONS		
Stream sediments <150um		BGS
Stream sediments < 2mm		BGS
Surface water		BGS
Stream sediment organics		BGS
Sample annotation	Glasgow City Council Sample Codes	GCC



Layers
☑ Stream Sediments < 150 um
  ☐ Aluminium
  ☐ Antimony
  ☑ Arsenic
    ● 407.6 - 856.3
    ● 100.9 - 407.5
    ● 72.2 - 100.8
    ● 19.9 - 72.1
    ● 11.8 - 19.8
    ● 7.5 - 11.7
    ● 6.5 - 7.4
    ● 5.6 - 6.4
    ● 4.8 - 5.5
    ● 2.5 - 4.7
☐ Stream Sediment < 2mm
☐ Surface Water
☑ Stream Sediment Organics
☑ SAMPLE LOCATIONS
☑ CULTURAL
☑ GEOLOGY

Figure 3.8 Example of data presentation within the Clyde tributaries urban geochemistry GIS.

4 Rural-Urban Drainage Geochemistry Comparisons

4.1 INTRODUCTION

In order to place the urban stream sediment and stream water data in the context of the surrounding environment, overview comparisons were made between the Clyde tributaries dataset and rural G-BASE drainage samples collected from the Southern Scotland Atlas area during the 1980s as part of the routine survey programme (BGS, 1993). These data were not included in the Clyde tributaries GIS but are presented in this report for information. Analytes common to both the rural and urban geochemical datasets are outlined in Table 4.1. The rural stream sediment and water samples were collected from first and second order streams at an approximate sample density of 1 per 1.5 km^2 for stream sediments and 1 per 2.5 km^2 for waters. Stream sediment samples were wet sieved to < 150 µm at site and analysed by a combination of Direct-Reading-Arc-Emission-Spectrometry (DR-Arc-ES), XRFS and Atomic Absorption Spectroscopy (AAS) (BGS, 1993). Rural-urban comparisons were made using the < 150-µm urban stream sediment data to maintain size-fraction compatibility with the rural dataset. Rural stream water samples were collected for pH, conductivity, bicarbonate and fluoride determinations. Fluoride was determined by ion selective electrode (ISE) according to standard procedures (BGS, 1993) and the other parameters by the methods outlined in Chapter 3 of this report. Comparisons between the two datasets have to be treated with caution for some elements due to differences in the limits of detection between various analytical methods; however, the data provide an interesting overview of the rural versus urban environment.

Table 4.1 Parameters analysed in both rural and urban drainage geochemical datasets

Sediments	Waters
Al_2O_3	HCO_3
As	Conductivity
Ba	F
CaO	pH
Cd	
Co	
Cr	
Cu	
Fe_2O_3	
Ga	
K_2O	
La	
MgO	
MnO	
Nb	
Ni	
P_2O_5	
Pb	
Rb	
Sb	
SiO_2	
Sn	
Sr	
TiO_2	
U	
V	
Y	
Zn	
Zr	

Approximately 1900 rural stream sediment and 1500 stream water results were selected for the comparison from the G-BASE database around Glasgow covering the six 1: 50 000 solid geology map sheets of the area (rural-urban area extends from NGR 217600, 628200 to 279900, 688300). This area comprises similar superficial and solid geology to the Glasgow urban centre allowing comparison between the built versus non-built environment over similar natural conditions. The rationalised 1: 50 000 solid geology and 1: 625 000 superficial deposit maps for the wider rural-urban study are show in Figures 4.1 and 4.2 respectively.

Summary statistics for the combined rural-urban data set are shown in Tables 4.2 and 4.3 and graduated symbol maps of the distributions of elements in the rural-urban environment are presented in Annexes 1 and 2 of this report. Using the spatial query functionality of the GIS, it is possible to categorise the data according to solid and superficial geology and urban versus rural environment. The data are presented in these categories in the box and whisker plots in Figures 4.3 to 4.8.

4.2 STREAM SEDIMENTS

The stream sediment data show that the majority of metal elements As, Cd, Cr, Cu, Ni, Pb, Sb, Sn, V and Zn are elevated in the urban environment relative to the rural background (Annex 1 and Figure 4.3). Based on median values, concentrations in urban streams are As, Cd, Pb (x2), Cr and Ni (x1.5), Cu (x3.5), Sn (x9) and Zn (x2.5) greater than that of the rural stream sediments probably as a result of contamination (Table 4.2).

In contrast, many of the major elements (Al, Mg, Mn, K, Ti, Fe, Si and Ba) are present in lower concentrations in the urban centre than in the surrounding rural environment reflecting the diverse geological sources of these elements in the area (Annex 1 and Figure 4.3).

These trends are apparent even taking the sediment geological parent material into consideration. Regardless of parent material type, many metal elements are elevated and many major elements depleted in the urban environment relative to the surrounding rural area (Figure 4.4).

A full description of the rural geochemical data and natural distribution of the elements in the area is provided in the regional geochemical atlas for Southern Scotland (BGS, 1993). A brief summary of the distributions for the main elements of environmental interest is provided in this report in the context of rural–urban comparisons.

Aluminium, (Al) and titanium (Ti) are some of the main constituents of clay minerals in sediments therefore are often useful indicators of clay content. Similarly gallium (Ga) can substitute into the clay matrix and can also indicate argillaceous or pelitic source rocks. As expected these three elements are generally low in concentration over the arenaceous quartz-rich rocks of the Coal Measures, the Devonian sandstones and the Silurian sandstones present in the area but are higher over the acid igneous rocks of the Clyde Plateau Volcanics and in low-lying boggy locations were the low flow conditions probably lead to an increased clay content of the sediment (Annex 1). High Ga values in the Misty Law area west-south-west of Paisley reflect hydrothermal alteration associated with mineralisation (Annex 1).

The results for antimony (Sb) should be treated with caution due to differing detection limits between the analytical methods used for the rural and urban datasets. None-the-less, the results show a striking anthropogenic control on the distribution of the element in the urban environment. Isolated rural anomalies in the very south of the area are associated with localised mineralisation around the Distinkhorn granodioritic pluton (Annex1).

The results for arsenic (As) should also be treated with caution due to differing detection limits between the analytical methods used for the rural and urban datasets. However, some interesting associations are evident. Contamination in the urban environment exerts a fundamental control on the distribution of the element, however, in the rural environment naturally high values are associated with the Distinkhorn granodioritic pluton in the south of the study area and with localised mineralisation in the Dalradian in the far north-west of the study area. The association with acid lavas in the Clyde Plateau Volcanics in the Misty Law area west-south-west of Paisley may reflect precipitation of iron and manganese oxides, which scavenge many heavy metals including arsenic as well as the presence of localised mineralisation.

Barium (Ba) concentrations are generally low over the Clyde Plateau Volcanics with the exception of barium mineralisation in the Misty Law area west-south-west of Paisley. High values in the south of the area are due to localised mineralisation in Silurian sandstones whereas elevated values on the north-eastern edge of Glasgow city may relate to fault controlled barium mineralisation in the underlying Carboniferous Limestone Group (Annex 1).

The results for cadmium (Cd) should also be treated with caution due to differing detection limits between the analytical methods used for the rural and urban datasets. None-the-less, the results show that localised contamination in the urban environment is a dominant control on the element distribution with the exception of naturally high values associated with the mineralisation in the Clyde Plateau Volcanics at Misty Law west-south-west of Paisley (Annex 1).

Calcium (Ca) concentrations are generally low over metamorphosed psammitic rocks of the Dalradian in the far north-west of the study area and the Silurian in the south-east of the area but are elevated in the urban environment of Glasgow probably reflecting greater disturbance of the underlying calcareous Carboniferous bed-rock and the presence of calcareous fill materials. Moderate to high values are present over much of the Carboniferous and Clyde Plateau Volcanics consistent with bedrock composition (Annex 1).

Chromium (Cr) levels are higher over the Devonian sandstones to the north-west of Glasgow and the Ayrshire coast and Silurian sandstones in the south of the area than over the Carboniferous rocks that underlie much of the centre of the area. Concentrations over the northern extension of the Clyde Plateau Volcanics are much lower than those over the southern lavas reflecting compositional changes and lava evolution. High Cr values in the urban environment of Glasgow are probably related to contamination. (Annex 1).

High cobalt (Co) concentrations in the urban environment probably reflect contamination but naturally high values are associated with mineralisation in the north-west of the study area, Misty Law to the west-south-west of Paisley and at other minor localities in the Clyde

Plateau Volcanics Formation. As with arsenic, Co may also be associated with secondary iron and manganese oxides in these sediments (Annex 1).

Copper (Cu) shows very marked elevation in the urban environment as a result of contamination relative to the rural background. Isolated naturally high values are associated with mineralisation in the north-west of the study area and over the Devonian rocks of the Ayrshire coast. Concentrations over the Lower Carboniferous sequence are lower than over the Upper Carboniferous Coal Measures reflecting bedrock composition and the presence of coals (Annex 1).

High iron (Fe) concentrations in the area are associated with the Clyde Plateau Volcanic rocks whereas levels over Silurian and Devonian sandstones are generally low. Concentrations are elevated at Misty Law west-south-west of Paisley reflecting mineralisation and the presence of iron and manganese oxides in the stream sediments of this area. Iron concentrations over the Coal Measures are generally elevated relative to the Lower Carboniferous rocks reflecting the presence of coals (Annex 1). Localised high-iron concentrations associated with coal-mine drainage are common throughout the Midland Valley of Scotland.

Lead (Pb) shows marked enrichment in urban sediments versus the rural background reflecting contamination. Localised mineral enrichment does occur over the Clyde Plateau Volcanics near Strathaven to the south of East Kilbride and to the west of Paisley and the element is enriched over the Misty Law Clyde Plateau Volcanics relative to the other lavas of the formation (Annex 1).

Magnesium (Mg) is enriched over the Clyde Plateau Volcanics relative to other rock types in the area and is associated in particular with basic lavas. Concentrations over the Devonian and Upper Carboniferous rocks of the area are low in contrast. Values over the Lower and Upper Limestone Groups are higher than over the Coal Measures due to the greater dominance of limestone lithologies. Elevated values in the urban environment are likely to reflect calcareous fill materials (Annex 1).

Manganese (Mn) is associated with the basic rocks of the Clyde Plateau Volcanics whereas concentrations over Carboniferous rocks are generally low. High values at Misty Law west-south-west of Paisley probably indicate the presence of secondary Mn-oxides in the sediments. High values in the urban dataset are likely to reflect contamination or the presence of secondary oxides (Annex 1).

High nickel (Ni) values are associated with the basic rocks of the Clyde Plateau Volcanics whereas low values characterise sediments over the acid Misty Law lavas of to the west-south-west of Paisley. Concentrations over Lower Carboniferous rocks are generally lower than in the Upper Carboniferous Coal Measures reflecting the presence of coals. Local anomalies are associated with coal mining whereas high values in the urban environment are likely to reflect contamination (Annex 1).

Phosphorus (P) concentrations are higher over the Carboniferous rocks of the area than the other rock types and sporadic high values may be related to phosphatic deposits in the sedimentary sequence. High values may also indicate agricultural contamination and the use of fertilisers as well as ground disturbance due to coal mining and sewage disposal (Annex 1).

Silicon (Si) tends to be concentrated in quartz-rich sandy sediments hence can be used as an indicator of sand content. As expected, values are high over the Devonian, Silurian and Upper Carboniferous sandstones of the area and low over the Clyde Plateau Volcanics (Annex 1).

The concentrations of tin (Sn) in most non-mineralised environments are generally very low, hence the element can be used as an indicator of anthropogenic contamination. Results for the area show that the element is enhanced in the urban versus rural environment and sporadic high values in the rural environment probably also reflect contamination (Annex 1).

Uranium (U) concentrations are highest over the Devonian and Upper Carboniferous rocks of the area reflecting the presence of organic materials such as coal in these sequences which restrict the mobility of U under anoxic conditions (Annex 1).

Vanadium (V) is associated with the basic rocks of the Clyde Plateau Volcanics but lower concentrations characterise the more evolved lavas of the Misty Law complex west-south-west of Paisley and the Eaglesham area south of East Kilbride. As is the case with Cu, values over the Upper Carboniferous Coal Measures are enhanced relative to the Lower Carboniferous rocks reflecting the presence of coals. Sporadic high values in the rural environment may reflect disturbance by coal mining (Annex 1).

Zinc (Zn) is naturally elevated over the Misty Law volcanic complex to the west-south-west of Paisley reflecting mineralisation and the presence of secondary iron and manganese oxides. However, the dominant control on Zn concentrations in the area is anthropogenic, as values are noticeably elevated in the urban versus the rural environment around Glasgow (Annex 1).

Hence in the area around Glasgow, several elements show strong spatial associations with the underlying solid geology but relationships with superficial deposits are harder to discern. Element concentrations in sediments sampled over different drift types are broadly similar (Figure 4.5) and the relationships between superficial deposits and element associations are generally less important than differences between the rural and urban environments. As indicated above, many of the major elements (see for example Si and Al) are depleted in the urban environment relative to rural areas regardless of superficial deposit type whereas many of the metal elements are elevated over superficial deposits in the urban area relative to the rural environment due to contamination (Figure 4.5). However, it is interesting to note that phosphorus (P) concentrations over rural raised beach and alluvial deposits are higher than other drift types which may be a result of natural sources of the element in these recent sediments or could indicate the fact that these superficial deposits act as a sink for contamination from fertiliser use in the area. Higher Fe, Mn, As and Ga concentrations reported over rural peat relative to the other drift types probably indicate the presence of secondary iron and manganese oxides in the sediments in the acid organic-rich environment often associated with peat deposits. It is also interesting to note that Cr, Ni, Zn, Cu, As, Pb, Cd and Sb in the urban environment show greatest enrichment over the alluvial and raised beach deposits, this may indicate the fact that the major river basins in the urban area act as sinks for these contaminants but may also reflect the close spatial association between heavy industry and the River Clyde.

4.3 SURFACE WATERS

Although only 4 parameters are common to both the urban and rural surface water datasets, some interesting associations are evident. In general surface water pH is neutral to alkaline across the area reflecting the calcareous nature of the Carboniferous bedrock that underlies most of the region. In contrast, low pH values are associated with the peaty upland areas developed over acid volcanic rocks of Misty Law west-south-west of Paisley and in the Kilpatrick Hills south of East Kilbride. Low values to the north-east of Glasgow may be associated with peat deposits or indicate acid waters related to coal mining (Annex 2 and Figures 4.6 and 4.7). Unfortunately the total alkalinity data for the rural area surrounding Glasgow are rather limited, none the less the relationships with geology are evident. Low alkalinities are associated with the Clyde Plateau Volcanics whereas values over the calcareous Carboniferous rocks of the area are higher as expected. High values in the east of Glasgow may be associated with disturbed ground in the Coal Measures due to mining and the presence of calcareous fill materials and other contaminants (Annex 2 and Figures 4.6 and 4.7). Conductivity determinations in surface waters show a strong geological relationship, low values are associated with the Clyde Plateau Volcanics and higher values with the Carboniferous rocks that underlie most of the area. High values in eastern Glasgow are associated with Coal Measure rocks but levels may also be enhanced as a result of ground disturbance related to coal mining, calcareous fill materials and contamination (Annex 2 and Figures 4.6 and 4.7). Fluoride shows a similar pattern and is associated with the coal bearing strata of the Upper Carboniferous whereas values are generally low over the Clyde Plateau Volcanics. The relatively high concentrations in the east of Glasgow probably reflect Coal Measure geology and ground disturbance related to coal mining, fill materials and contamination (Annex 2 and Figures 4.6 and 4.7).

Although the parameters show strong spatial relationships with the underlying solid geology, relationships with superficial deposits are harder to ascertain. Parameter concentrations in waters sampled over different drift types are broadly similar (Figure 4.8) and the relationships between superficial deposits and parameter associations are generally less important than differences between the rural and urban environments. However it is evident that pH and total alkalinity are lower over peat than the other deposit types as expected (Figure 4.8).

Table 4.2 Summary statistics for parameters in rural and urban stream sediment datasets

	Rural					**Urban**					**Rural + Urban**				
	Count	**Min**	**Max**	**Mean**	**Median**	**Count**	**Min**	**Max**	**Mean**	**Median**	**Count**	**Min**	**Max**	**Mean**	**Median**
Al_2O_3 wt%	1895	3.80	41.90	17.98	17.30	118	1.60	26.70	13.35	13.55	2013	3.80	41.90	17.71	17.00
As mg kg^{-1}	1011	0.00	210.00	10.28	5.00	118	2.50	856.30	35.62	11.70	1129	0.00	856.30	12.92	5.00
Ba mg kg^{-1}	1895	183.28	11564.78	749.53	577.53	118	191.00	1701.00	677.50	650.50	2013	183.28	11564.78	745.30	585.27
CaO wt%	1895	0.24	8.75	1.43	1.37	118	0.54	83.37	4.36	2.19	2013	0.24	83.37	1.61	1.39
Cd mg kg^{-1}	1705	0.00	29.80	0.84	0.50	118	0.25	25.30	1.45	0.90	1823	0.00	29.80	0.88	0.50
Co mg kg^{-1}	1894	17.10	172.38	38.13	36.09	118	16.80	90.80	35.25	32.05	2012	17.10	172.38	37.96	35.67
Cr mg kg^{-1}	1894	0.00	1568.37	121.37	112.05	118	80.00	3561.00	273.44	162.00	2012	0.00	3561.00	130.29	115.59
Cu mg kg^{-1}	1895	5.53	695.67	33.80	27.79	118	18.20	2984.60	201.83	95.45	2013	5.53	2984.60	43.65	28.68
Fe_2O_3 wt%	1895	1.72	32.18	10.66	10.58	118	3.57	27.23	8.56	8.27	2013	1.72	32.18	10.54	10.21
Ga mg kg^{-1}	1895	0.00	37.26	16.87	16.92	118	1.40	42.40	15.44	15.35	2013	0.00	42.40	16.78	16.71
K_2O wt%	1895	0.90	6.09	2.32	2.18	118	0.25	2.16	1.33	1.33	2013	0.90	6.09	2.26	2.14
La mg kg^{-1}	1895	0.00	164.09	45.96	45.33	118	9.00	83.00	50.66	52.00	2013	0.00	164.09	46.23	45.94
MgO wt%	1895	0.51	10.80	2.28	2.02	118	0.50	5.60	1.70	1.60	2013	0.50	10.80	2.25	1.99
MnO wt%	1895	0.02	22.01	0.54	0.34	118	0.05	2.65	0.30	0.18	2013	0.02	22.01	0.53	0.32
Nb mg kg^{-1}	1744	0.00	222.00	29.09	23.00	118	3.20	49.70	19.15	17.20	1862	0.00	222.00	28.46	22.00
Ni mg kg^{-1}	1895	4.43	284.77	43.24	39.56	118	16.30	466.60	71.81	63.65	2013	4.43	466.60	44.91	40.25
P_2O_5 wt%	1731	0.00	2.28	0.58	0.56	118	0.12	1.41	0.54	0.53	1849	0.00	2.28	0.57	0.56
Pb mg kg^{-1}	1895	0.00	2001.31	66.68	45.06	118	23.60	5001.00	365.77	212.25	2013	0.00	5001.00	84.21	47.65
Rb mg kg^{-1}	1895	26.39	197.57	60.91	55.24	118	5.80	89.00	45.64	45.45	2013	26.39	197.57	60.01	54.70
Sb mg kg^{-1}	827	0.00	16.50	0.67	0.50	118	0.25	61.30	6.15	4.00	945	0.00	61.30	1.35	0.50
SiO_2 wt%	1895	32.90	90.00	65.76	65.90	118	9.00	67.40	51.62	53.60	2013	32.90	90.00	64.93	65.20
Sn mg kg^{-1}	1885	0.00	574.00	5.34	2.00	118	3.30	1148.80	45.70	18.65	2003	0.00	1148.80	7.72	2.00
Sr mg kg^{-1}	1895	41.06	1238.75	166.76	157.38	118	90.60	672.00	168.31	148.20	2013	41.06	1238.75	166.85	155.85
TiO_2 wt%	1895	0.51	6.63	1.80	1.64	118	0.09	2.53	1.19	1.15	2013	0.51	6.63	1.76	1.60
U mg kg^{-1}	1879	0.30	14.80	2.40	2.40	118	0.25	12.40	1.35	1.15	1997	0.30	14.80	2.33	2.30
V mg kg^{-1}	1891	34.58	631.85	147.09	138.00	118	11.00	361.00	150.46	144.50	2009	34.58	631.85	147.28	138.00
Y mg kg^{-1}	1895	9.38	96.33	30.29	29.58	118	3.40	37.10	25.03	25.50	2013	9.38	96.33	29.98	29.58
Zn mg kg^{-1}	1895	31.41	3489.84	226.53	173.63	118	75.40	2001.00	569.56	480.25	2013	31.41	3489.84	246.63	180.98
Zr mg kg^{-1}	1895	98.49	4425.93	463.29	363.46	118	25.20	1868.90	467.26	448.05	2013	98.49	4425.93	463.52	368.45

Table 4.3 Summary statistics for parameters in rural and urban stream water datasets

	Rural					Urban					Rural + Urban				
	Count	Min	Max	Mean	Median	Count	Min	Max	Mean	Median	Count	Min	Max	Mean	Median
F mg L^{-1}	493	0.02	1.05	0.09	0.07	122	0.01	0.68	0.18	0.15	615	0.01	1.05	0.10	0.08
pH	1101	3.60	9.30	7.01	7.10	122	4.50	9.28	7.65	7.66	1223	3.60	9.30	7.08	7.20
Conductivity µS cm^{-1}	1106	5	2700	256	206	122	50	1064	474	404	1228	5	2700	278	221
HCO^{3-} mg L^{-1}	105	3.0	268.0	60.1	48.0	122	0.012	451.1	161.3	121.3	227	0.012	451.1	114.5	95.1

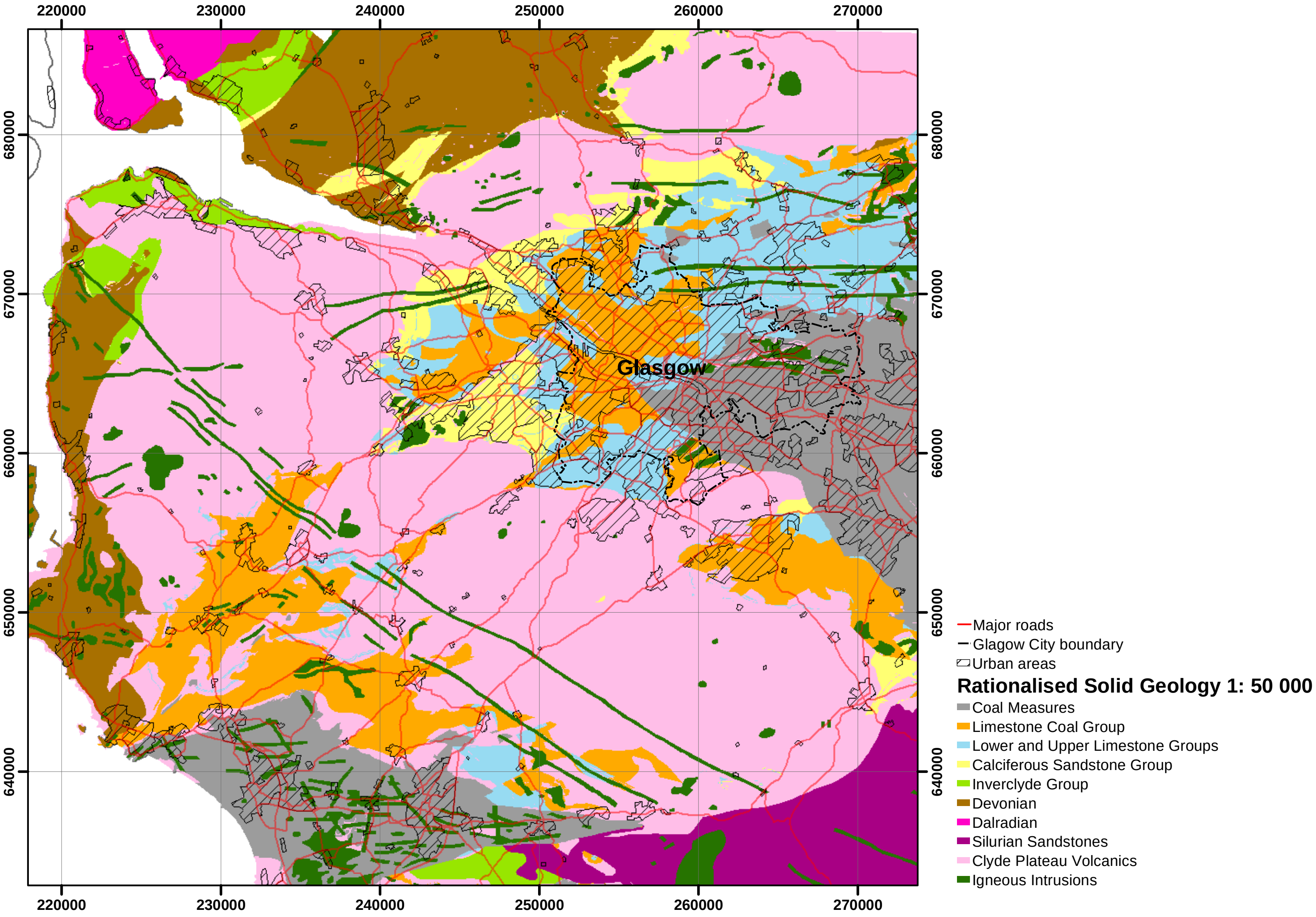


Figure 4.1 Simplified bedrock geology map (1: 50 000 scale) of the Glasgow rural-urban study area derived from BGS data.

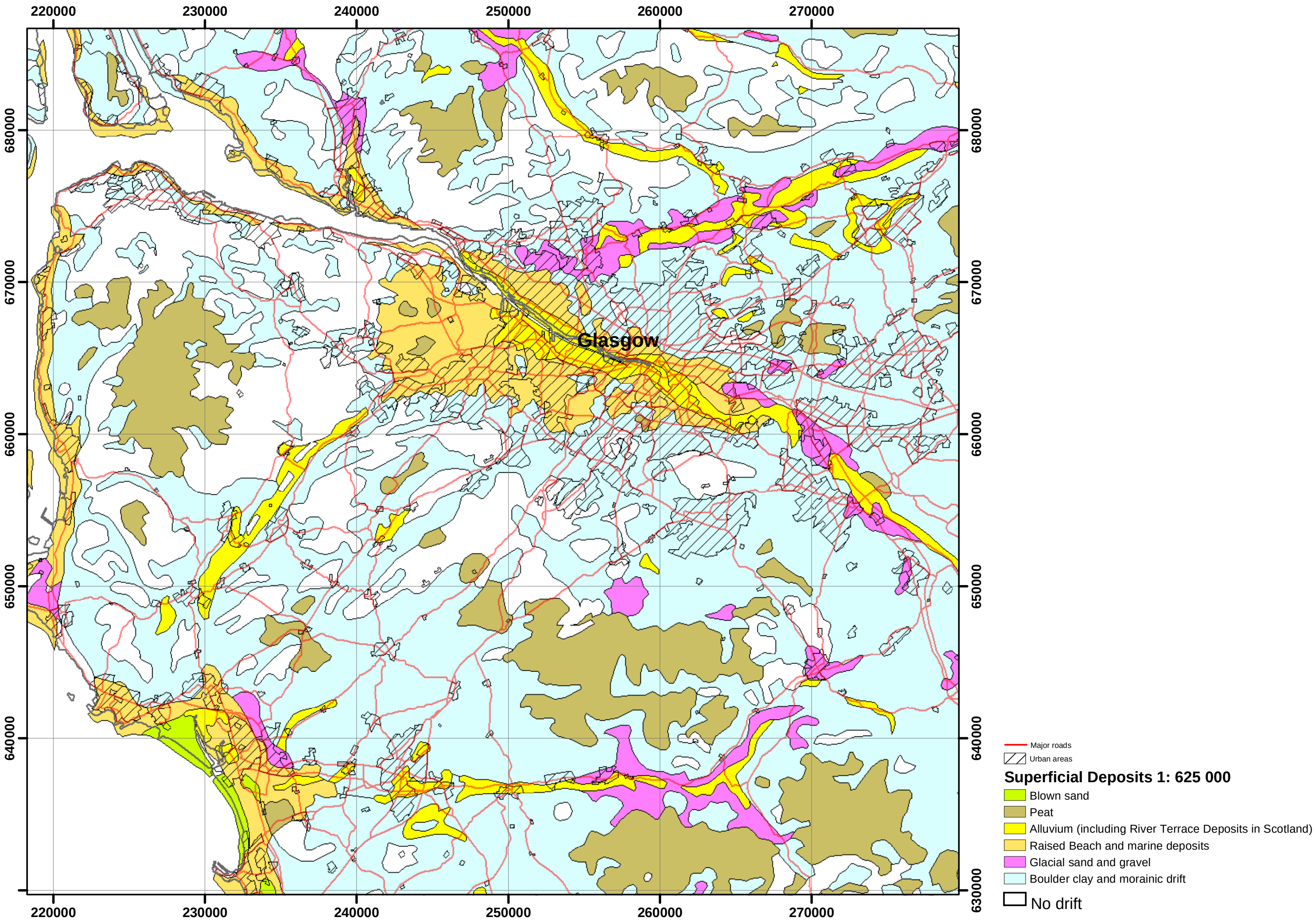


Figure 4.2 Superficial deposits (drift) map (1: 625 000 scale) of the Glasgow rural-urban study area derived from BGS data.

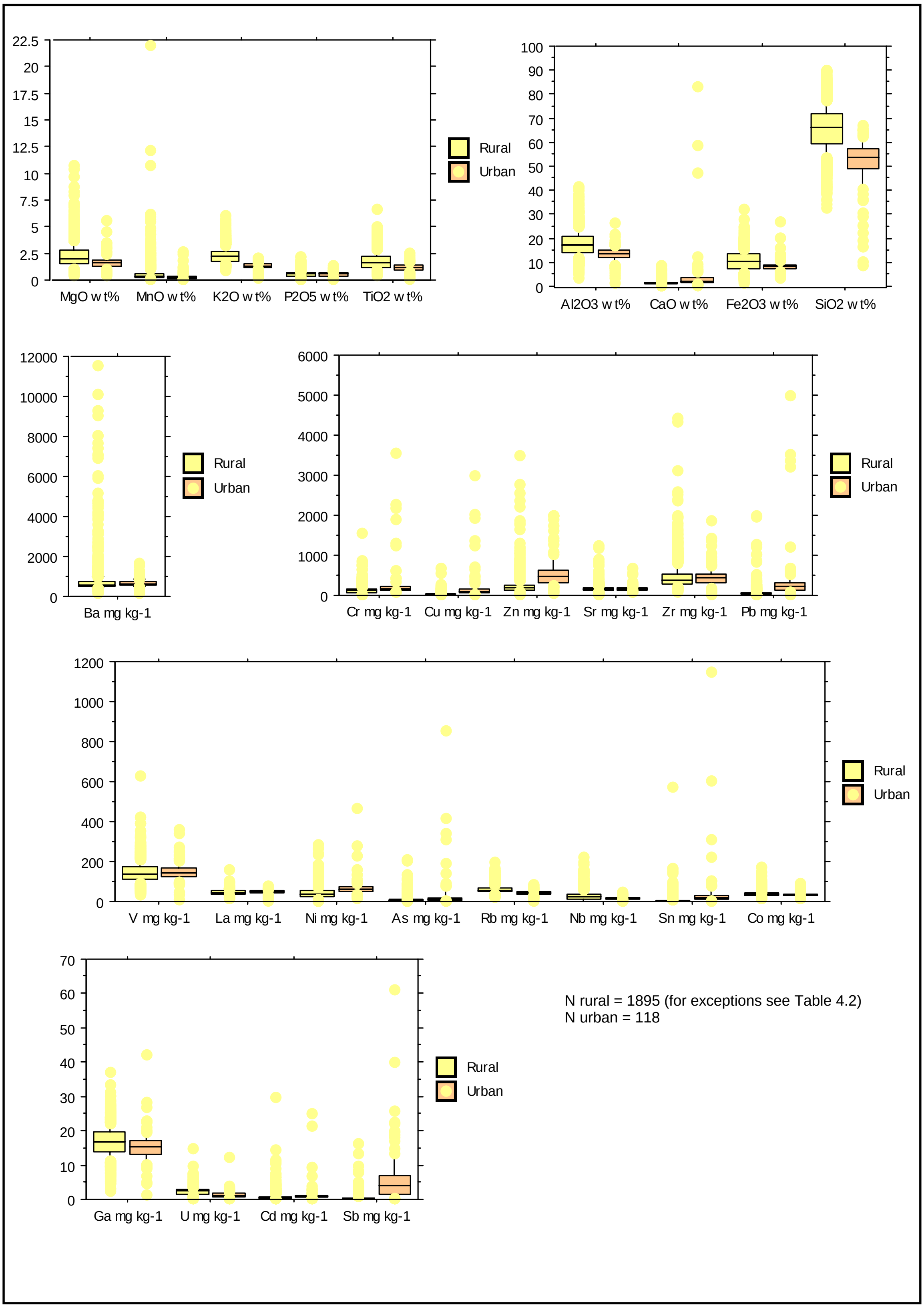


Figure 4.3 Box and whisker plots showing the 10th, 25th, 50th, 75th and 90th percentiles of element distributions in < 150 µm stream sediments in the Glasgow rural and urban datasets

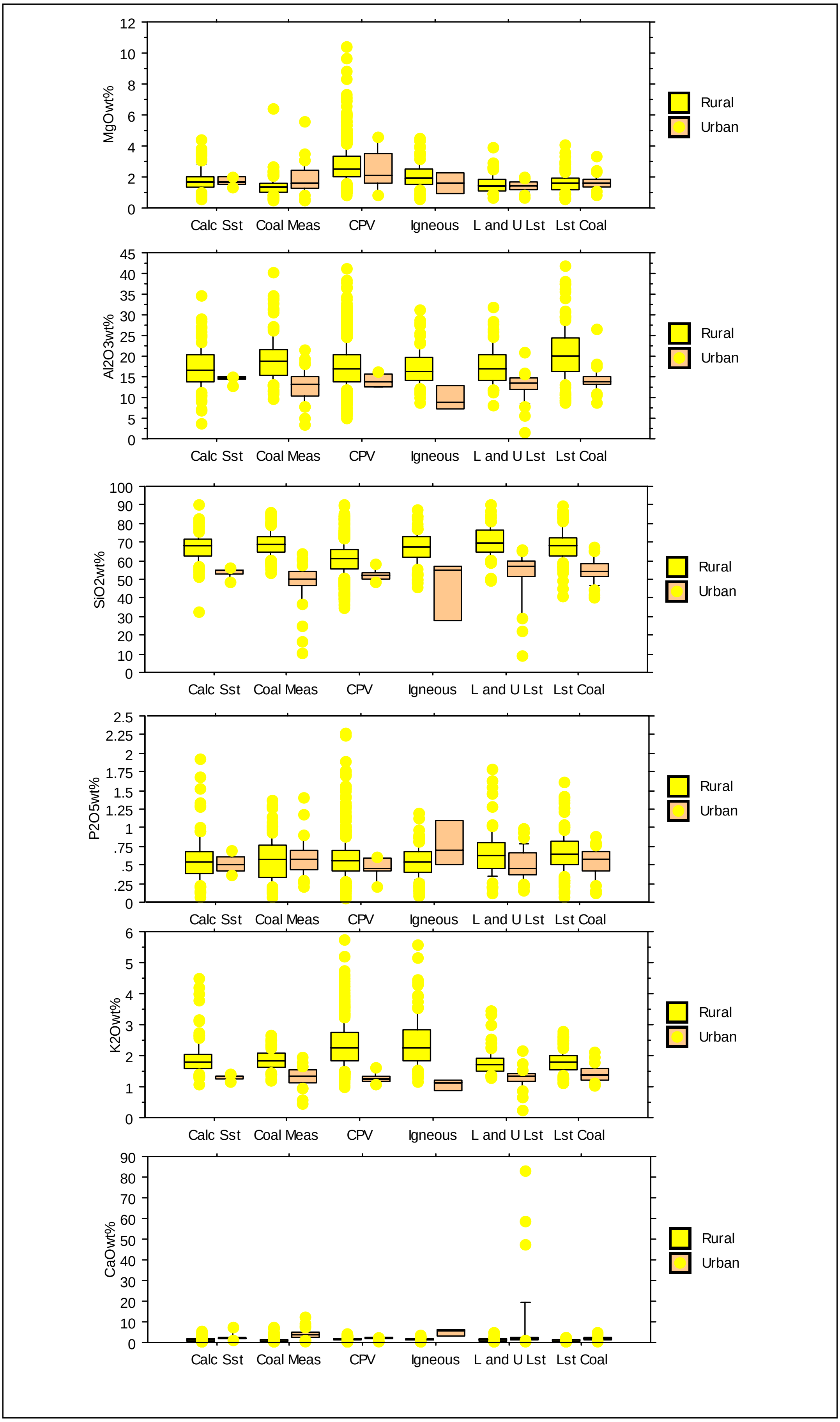
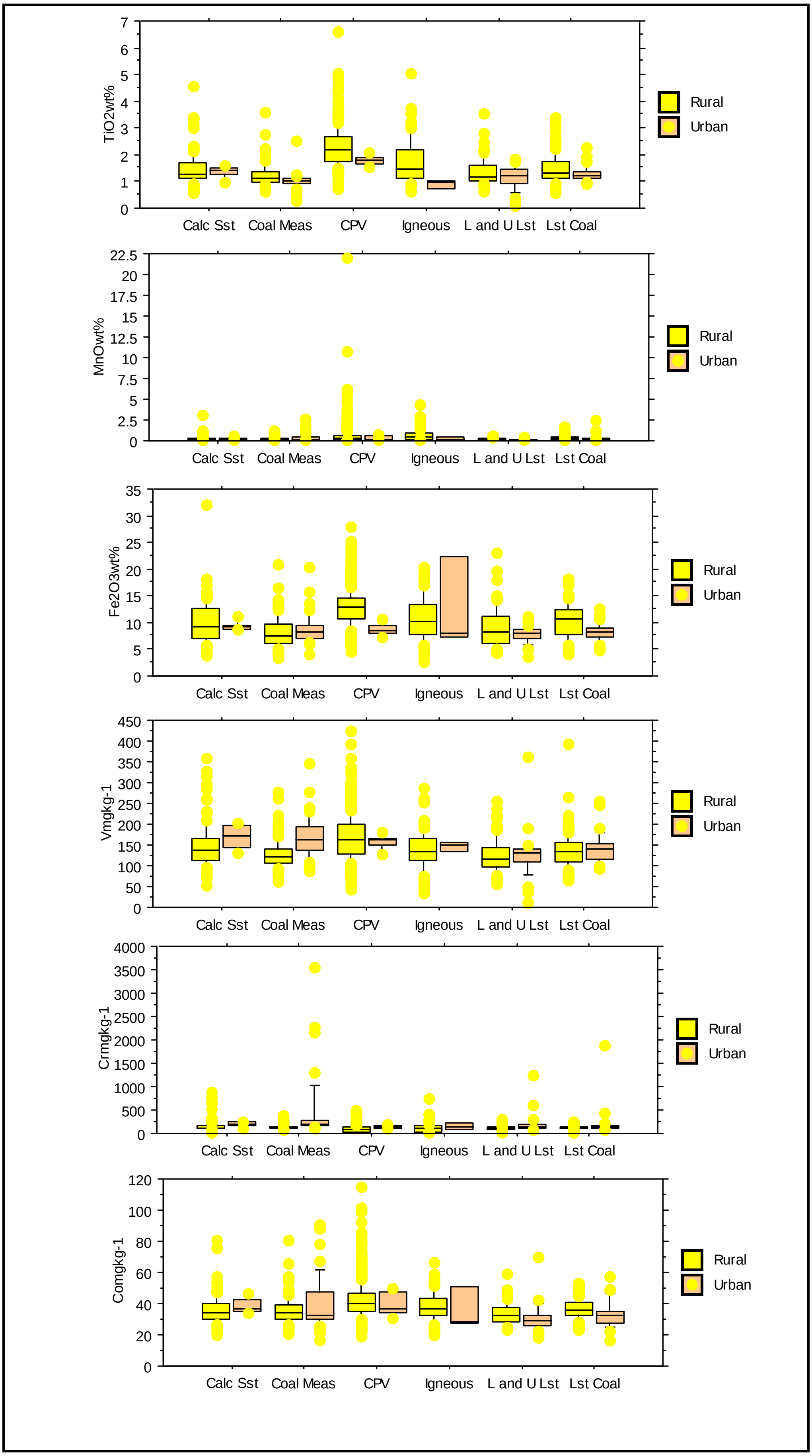
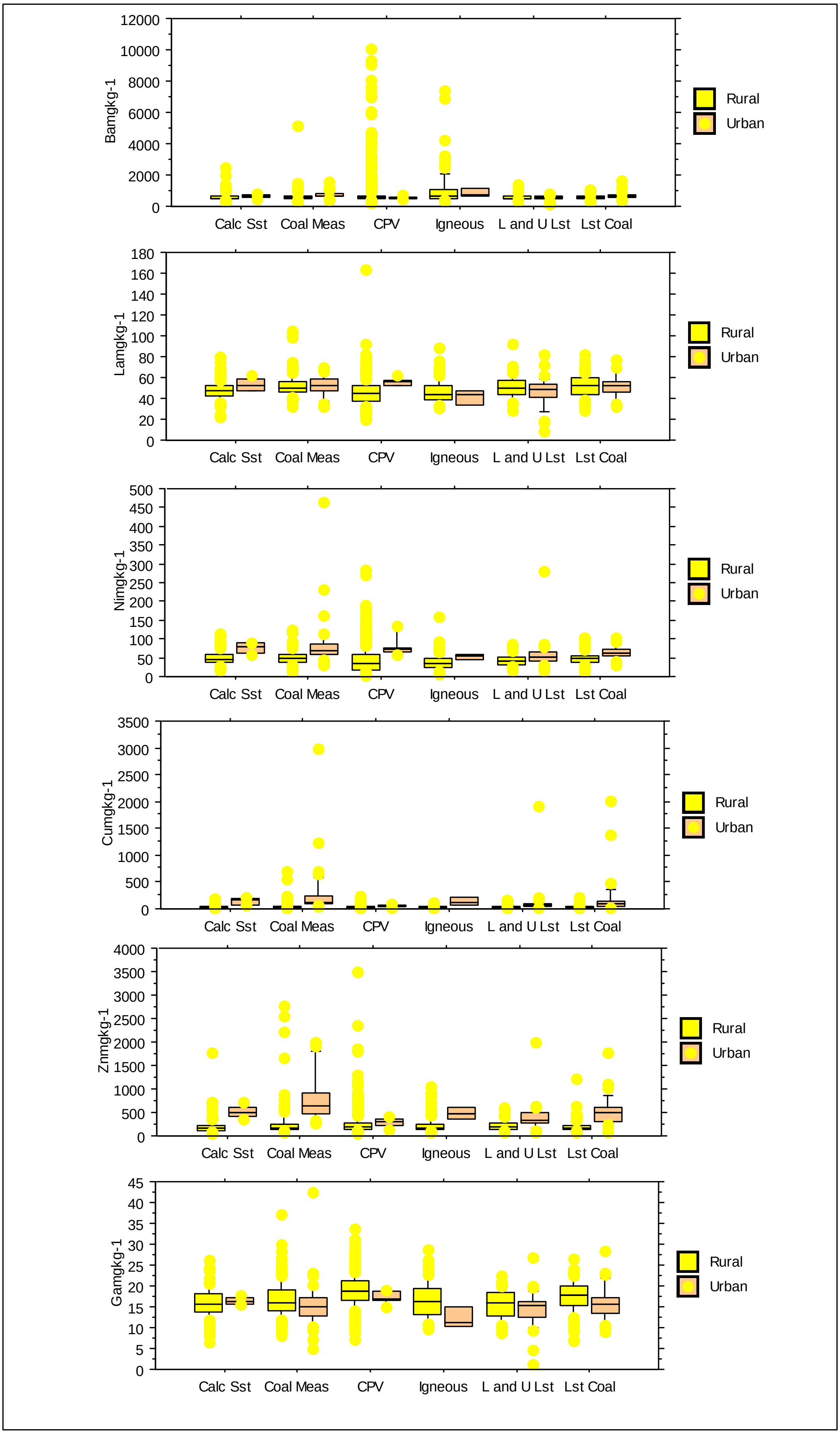
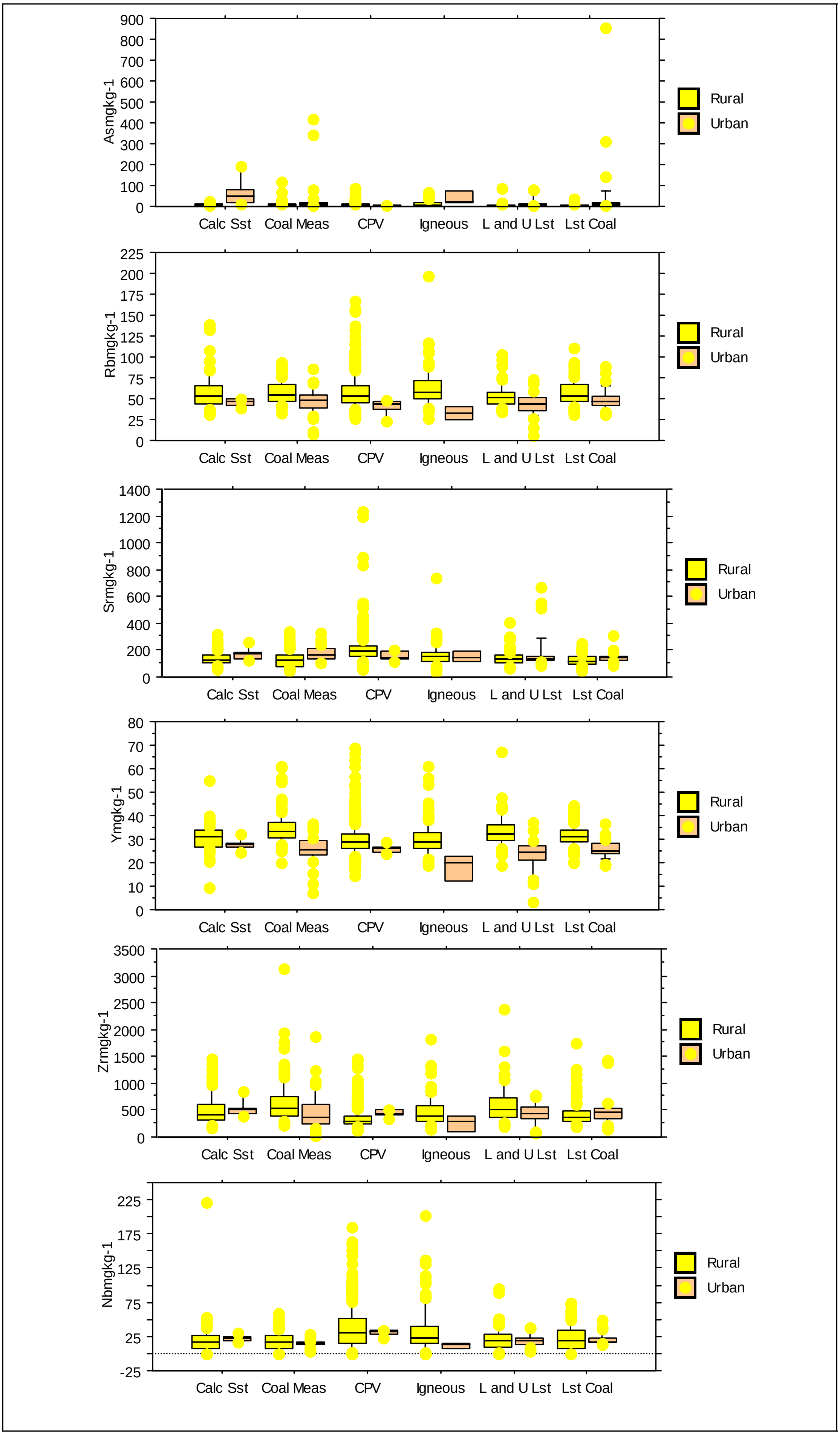
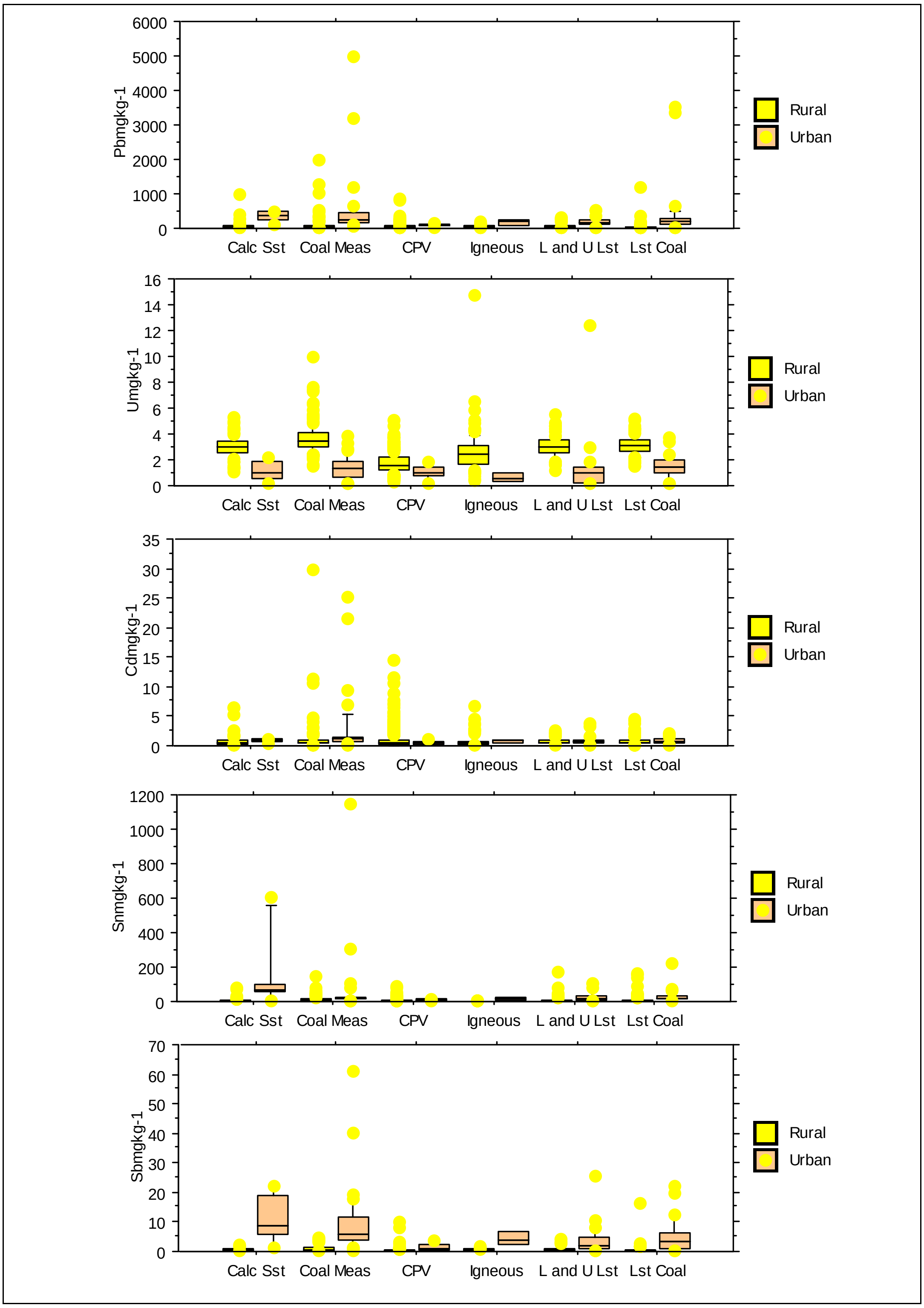


Figure 4.4 Box and whisker plots showing the 10th, 25th, 50th, 75th and 90th percentiles of element distributions in rural and urban < 150 µm stream sediments over different solid geology parent materials for the Glasgow rural-urban study area.


TiO2wt%
0
1
2
3
4
5
6
7
Calc Sst
Coal Meas
CPV
Igneous
L and U Lst
Lst Coal
Rural
Urban
MnOwt%
0
2.5
5
7.5
10
12.5
15
17.5
20
22.5
Calc Sst
Coal Meas
CPV
Igneous
L and U Lst
Lst Coal
Rural
Urban
Fe2O3wt%
0
5
10
15
20
25
30
35
Calc Sst
Coal Meas
CPV
Igneous
L and U Lst
Lst Coal
Rural
Urban
Vmgkg-1
0
50
100
150
200
250
300
350
400
450
Calc Sst
Coal Meas
CPV
Igneous
L and U Lst
Lst Coal
Rural
Urban
Crmgkg-1
0
500
1000
1500
2000
2500
3000
3500
4000
Calc Sst
Coal Meas
CPV
Igneous
L and U Lst
Lst Coal
Rural
Urban
Comgkg-1
0
20
40
60
80
100
120
Calc Sst
Coal Meas
CPV
Igneous
L and U Lst
Lst Coal
Rural
Urban


Bamgkg-1
12000
10000
8000
6000
4000
2000
0
Rural
Urban
Lamgkg-1
180
160
140
120
100
80
60
40
20
0
Nimgkg-1
500
450
400
350
300
250
200
150
100
50
Cumgkg-1
3500
3000
2500
2000
1500
1000
500
Znmgkg-1
4000
Gamgkg-1
45
40
35
30
25
20
15
10
5
Calc Sst
Coal Meas
CPV
Igneous
L and U Lst
Lst Coal


Asmgkg-1
900
800
700
600
500
400
300
200
100
0
Calc Sst
Coal Meas
CPV
Igneous
L and U Lst
Lst Coal
Rural
Urban
Rbmgkg-1
225
200
175
150
125
100
75
50
25
0
Calc Sst
Coal Meas
CPV
Igneous
L and U Lst
Lst Coal
Rural
Urban
Srmgkg-1
1400
1200
1000
800
600
400
200
0
Calc Sst
Coal Meas
CPV
Igneous
L and U Lst
Lst Coal
Rural
Urban
Ymgkg-1
80
70
60
50
40
30
20
10
0
Calc Sst
Coal Meas
CPV
Igneous
L and U Lst
Lst Coal
Rural
Urban
Zrmgkg-1
3500
3000
2500
2000
1500
1000
500
0
Calc Sst
Coal Meas
CPV
Igneous
L and U Lst
Lst Coal
Rural
Urban
Nbmgkg-1
225
175
125
75
25
-25
Calc Sst
Coal Meas
CPV
Igneous
L and U Lst
Lst Coal
Rural
Urban



	Rural	Urban
N Calc Sst =	102	6
N Coal Meas =	132	39
N CPV =	899	6
Igneous =	103	3
N L and U Lst =	72	32
N Lst Coal =	131	32

Calc Sst = Calciferous Sandstone Group
Coal Meas = Coal Measures
CPV = Clyde Plateau Volcanics
Igneous = Igneous Intrusions
L and U Lst = Lower and Upper Limestone Groups
Lst Coal = Limestone Coal Group

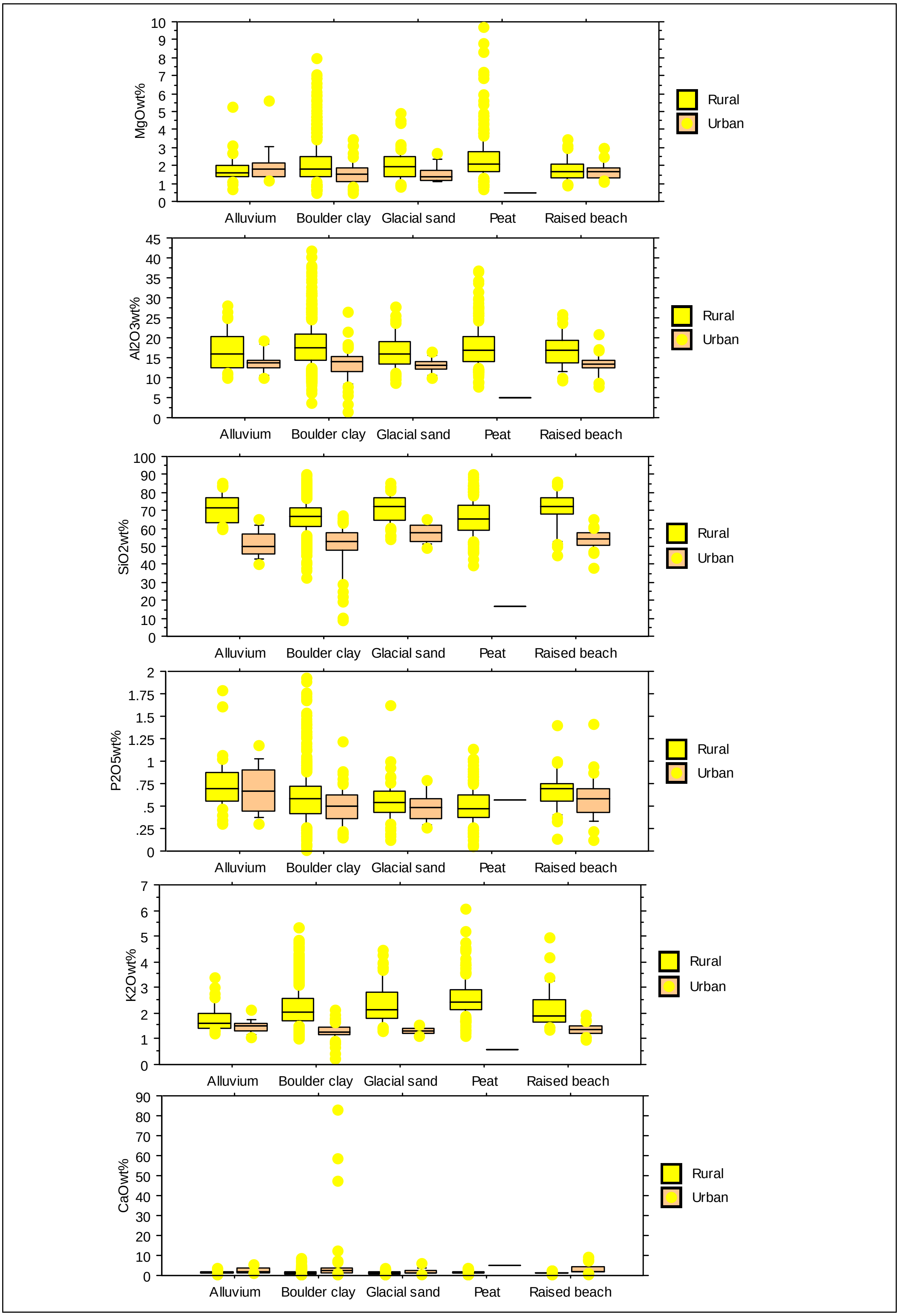
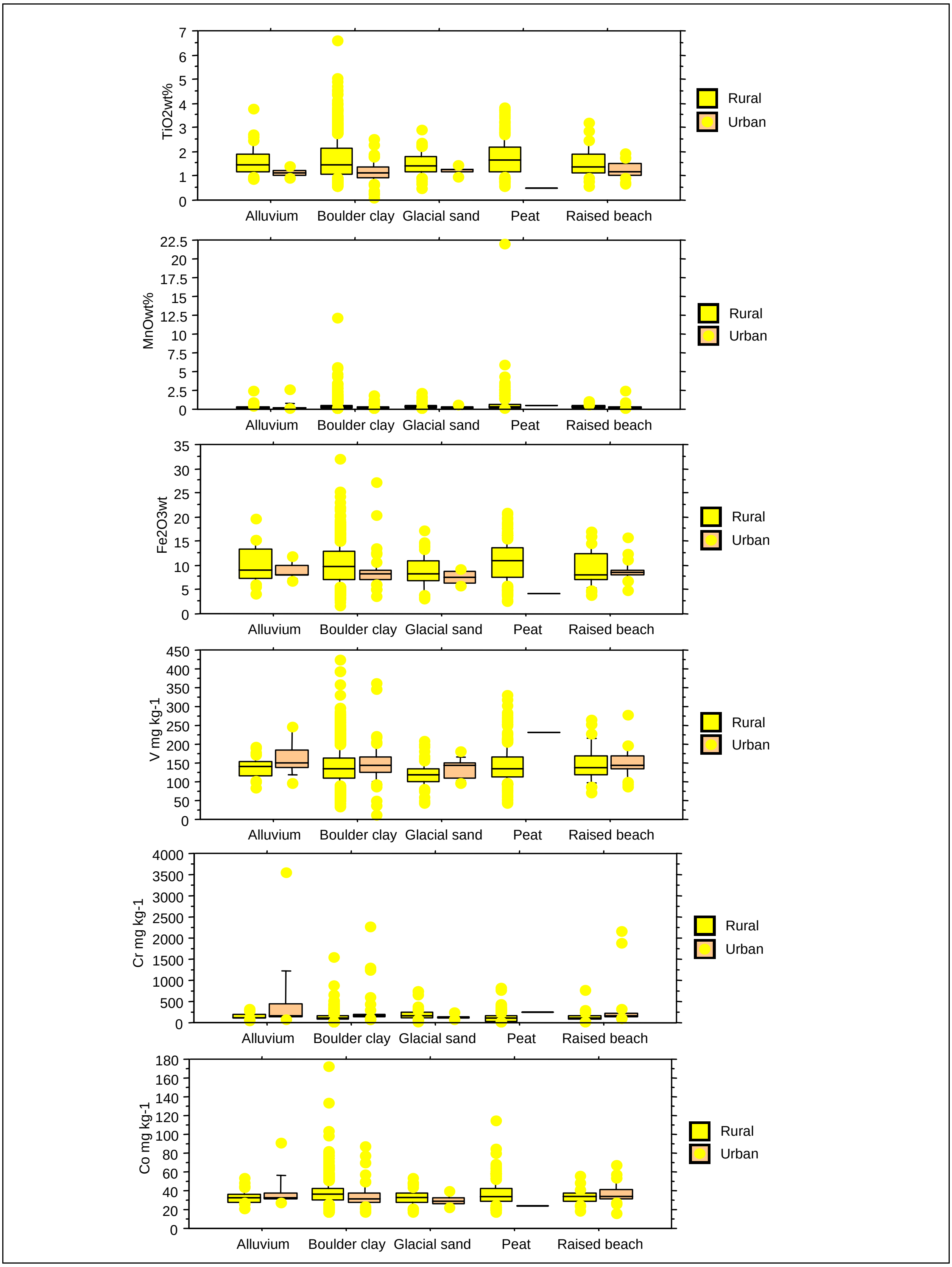
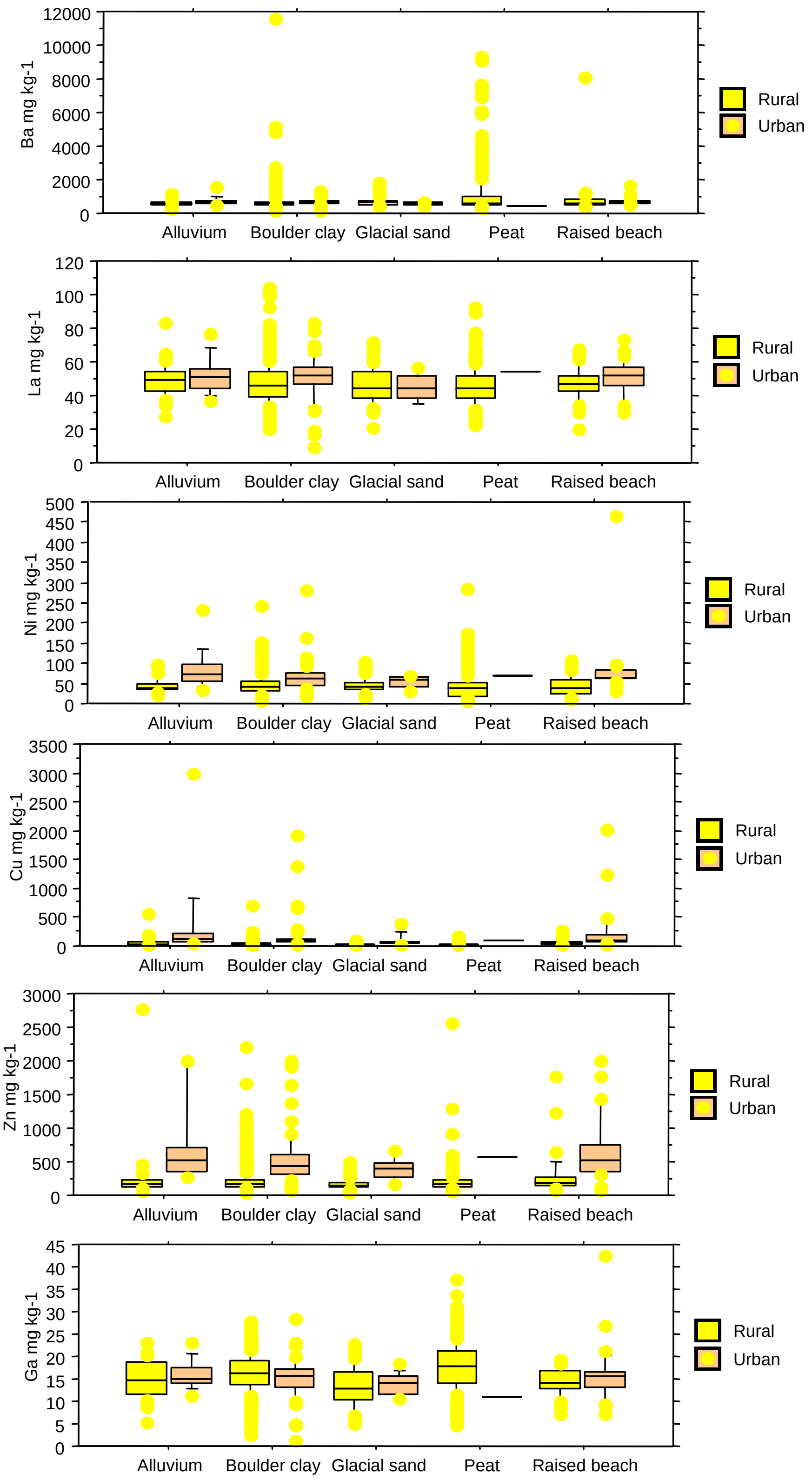
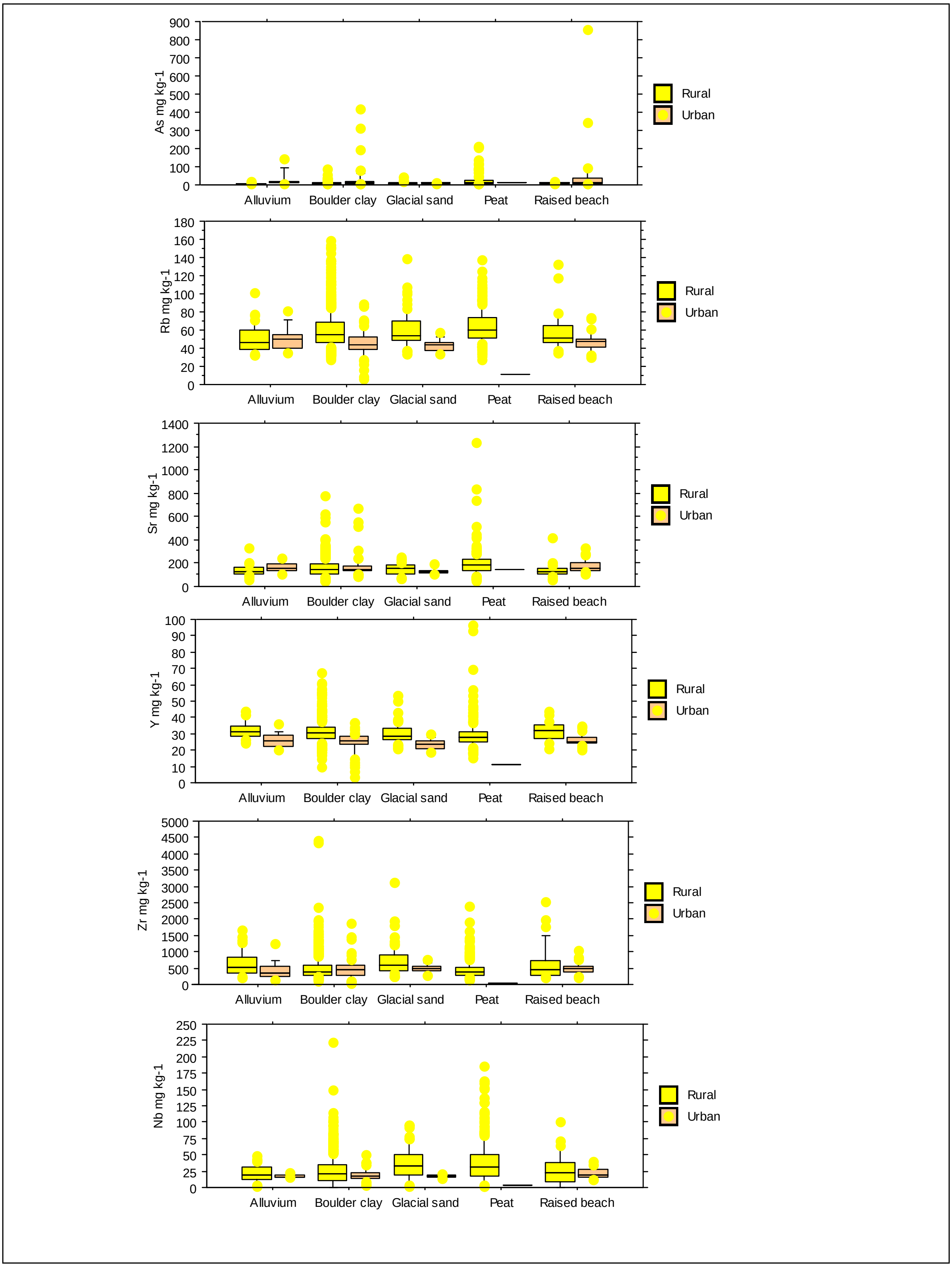


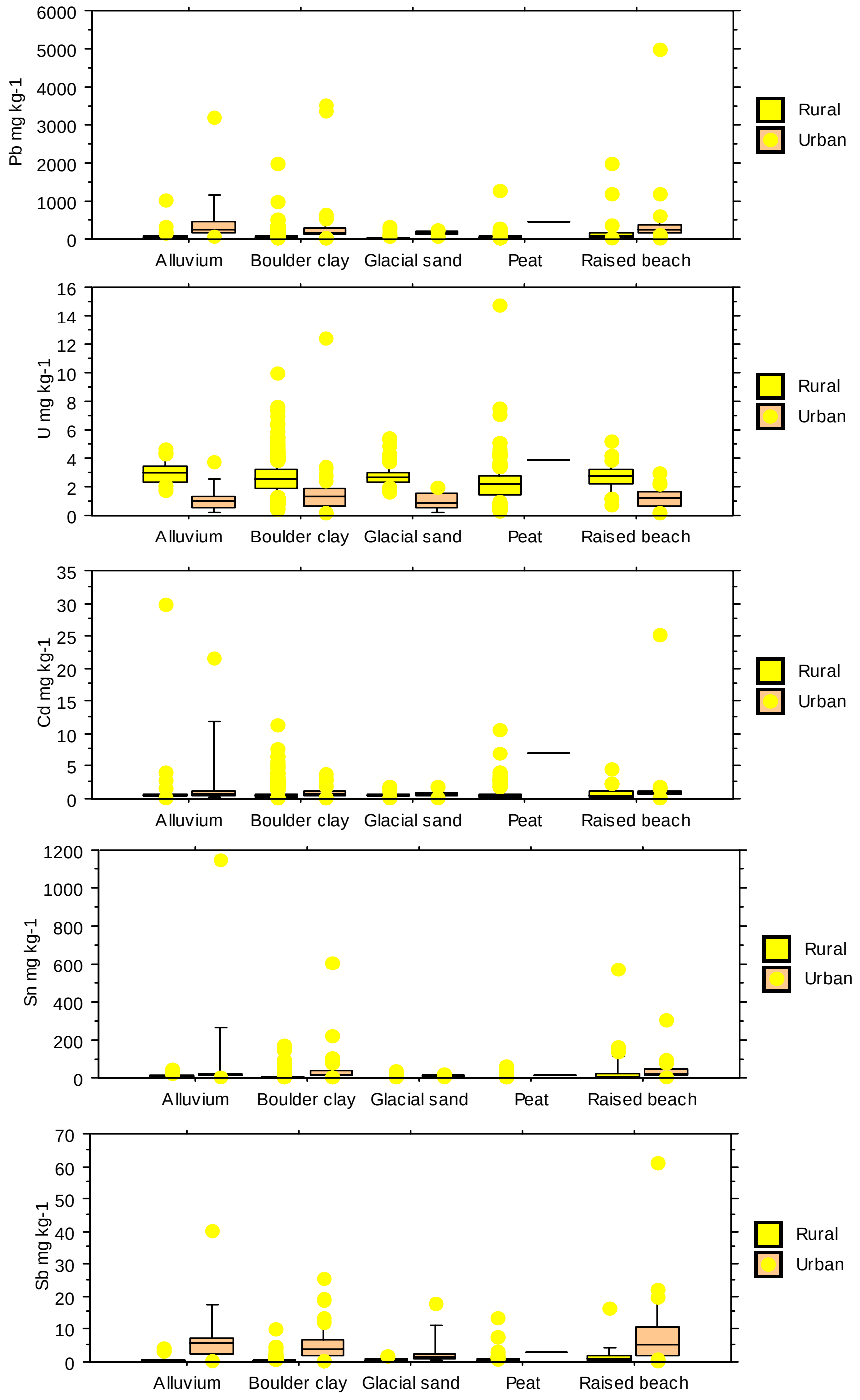
Figure 4.5 Box and whisker plots showing the 10th, 25th, 50th, 75th and 90th percentiles of element distributions in rural and urban < 150 µm stream sediments over different superficial parent materials for the Glasgow rural-urban study area.


TiO2wt%
0
1
2
3
4
5
6
7
Alluvium
Boulder clay
Glacial sand
Peat
Raised beach
Rural
Urban
MnOwt%
0
2.5
5
7.5
10
12.5
15
17.5
20
22.5
Alluvium
Boulder clay
Glacial sand
Peat
Raised beach
Rural
Urban
Fe2O3wt
0
5
10
15
20
25
30
35
Alluvium
Boulder clay
Glacial sand
Peat
Raised beach
Rural
Urban
V mg kg-1
0
50
100
150
200
250
300
350
400
450
Alluvium
Boulder clay
Glacial sand
Peat
Raised beach
Rural
Urban
Cr mg kg-1
0
500
1000
1500
2000
2500
3000
3500
4000
Alluvium
Boulder clay
Glacial sand
Peat
Raised beach
Rural
Urban
Co mg kg-1
0
20
40
60
80
100
120
140
160
180
Alluvium
Boulder clay
Glacial sand
Peat
Raised beach
Rural
Urban

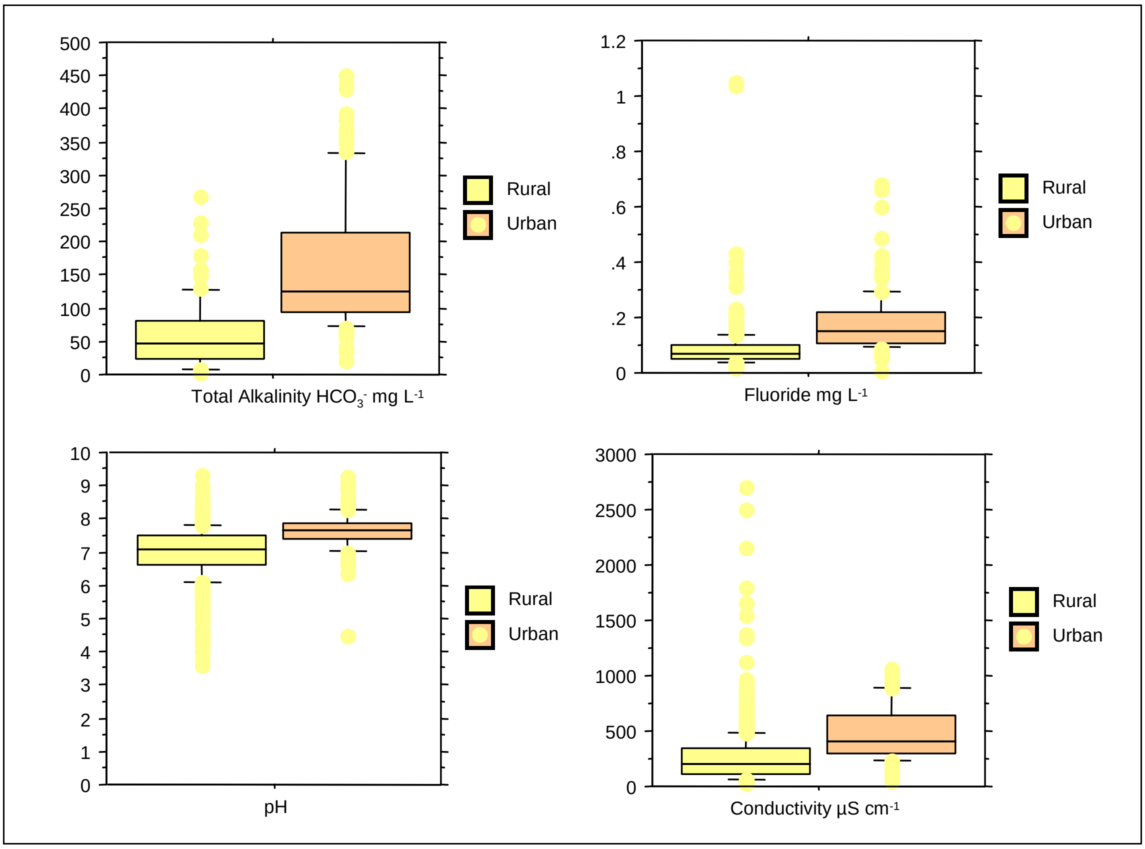


Ba mg kg-1
12000
10000
8000
6000
4000
2000
0
Alluvium
Boulder clay
Glacial sand
Peat
Raised beach
Rural
Urban
La mg kg-1
120
100
80
60
40
20
0
Alluvium
Boulder clay
Glacial sand
Peat
Raised beach
Rural
Urban
Ni mg kg-1
500
450
400
350
300
250
200
150
100
50
0
Alluvium
Boulder clay
Glacial sand
Peat
Raised beach
Rural
Urban
Cu mg kg-1
3500
3000
2500
2000
1500
1000
500
0
Alluvium
Boulder clay
Glacial sand
Peat
Raised beach
Rural
Urban
Zn mg kg-1
3000
2500
2000
1500
1000
500
0
Alluvium
Boulder clay
Glacial sand
Peat
Raised beach
Rural
Urban
Ga mg kg-1
45
40
35
30
25
20
15
10
5
0
Alluvium
Boulder clay
Glacial sand
Peat
Raised beach
Rural
Urban


As mg kg-1
0
100
200
300
400
500
600
700
800
900
Alluvium
Boulder clay
Glacial sand
Peat
Raised beach
Rural
Urban
Rb mg kg-1
0
20
40
60
80
100
120
140
160
180
Alluvium
Boulder clay
Glacial sand
Peat
Raised beach
Rural
Urban
Sr mg kg-1
0
200
400
600
800
1000
1200
1400
Alluvium
Boulder clay
Glacial sand
Peat
Raised beach
Rural
Urban
Y mg kg-1
0
10
20
30
40
50
60
70
80
90
100
Alluvium
Boulder clay
Glacial sand
Peat
Raised beach
Rural
Urban
Zr mg kg-1
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
Alluvium
Boulder clay
Glacial sand
Peat
Raised beach
Rural
Urban
Nb mg kg-1
0
25
50
75
100
125
150
175
200
225
250
Alluvium
Boulder clay
Glacial sand
Peat
Raised beach
Rural
Urban

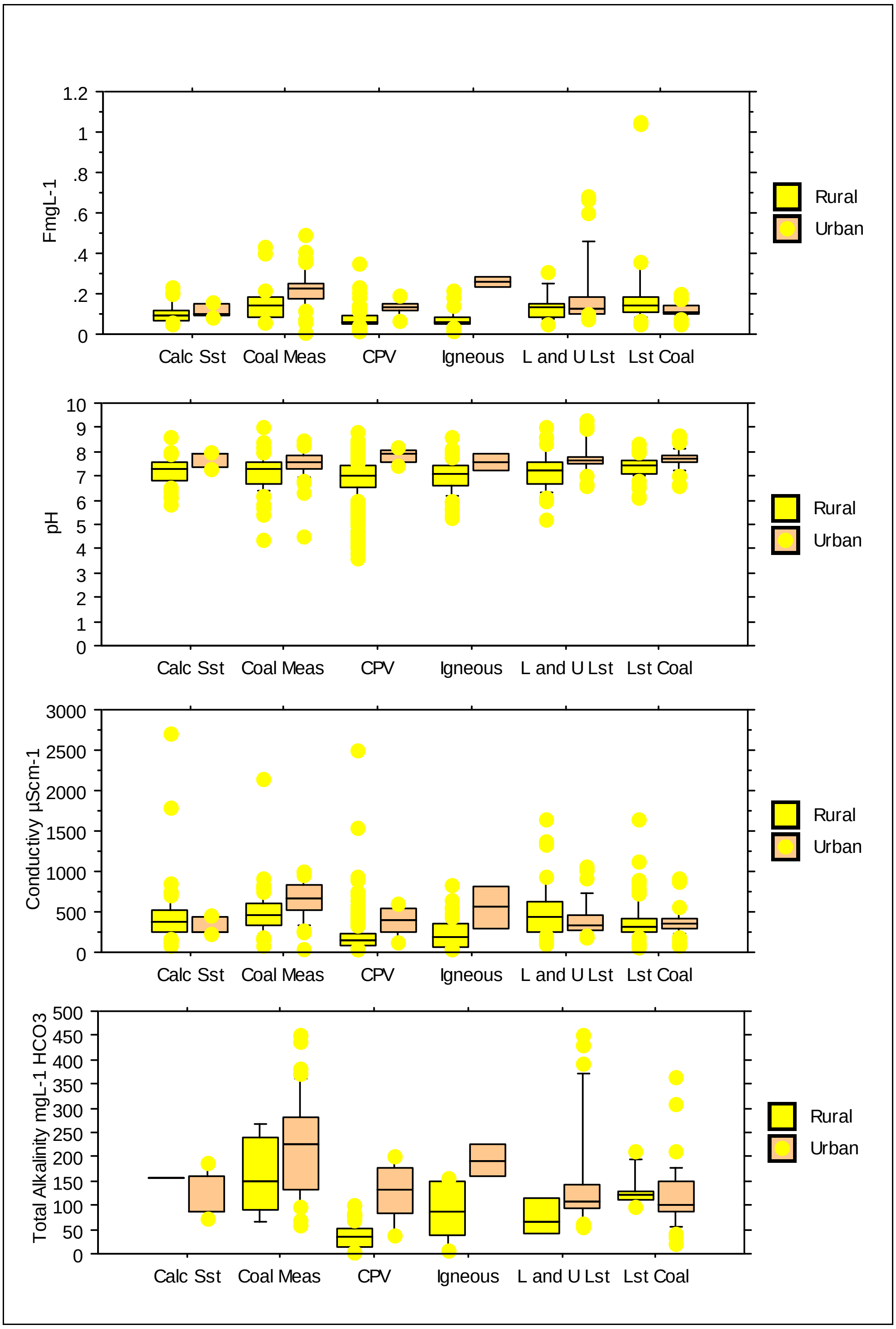


	Rural	Urban
N Alluvium =	38	13
N Boulder clay =	1028	62
N Glacial sand =	70	11
N Peat =	297	1
N Raised beach =	31	28



N Rural = 1106 (for exceptions see Table 4.3)
N Urban = 122

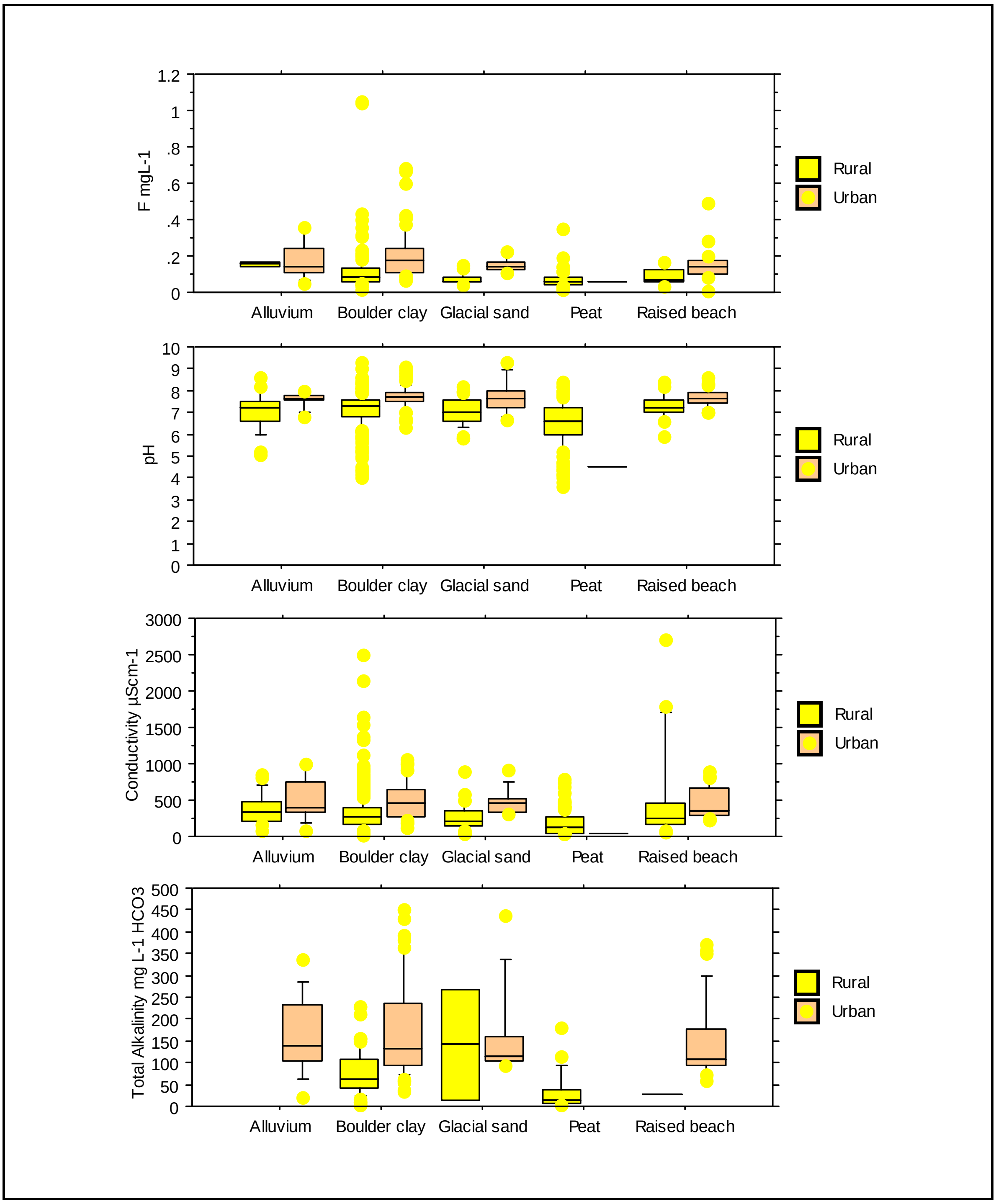
Figure 4.6 Box and whisker plots showing the 10th, 25th, 50th, 75th and 90th percentiles of parameter distributions in stream waters in the Glasgow rural and urban datasets



	Rural	Urban
N Calc Sst =	74	6
N Coal Meas =	103	42
N CPV =	756	6
Igneous =	81	2
N L and U Lst =	51	33
N Lst Coal =	95	33

Calc Sst = Calciferous Sandstone Group
Coal Meas = Coal Measures
CPV = Clyde Plateau Volcanics
Igneous = Igneous Intrusions
L and U Lst = Lower and Upper Limestone Groups
Lst Coal = Limestone Coal Group

Figure 4.7 Box and whisker plots showing the 10th, 25th, 50th, 75th and 90th percentiles of element distributions in rural and urban surface waters over different solid geology parent materials for the Glasgow rural-urban study area.



	Rural	Urban	
N Alluvium =	32	14	(Note there are no rural alluvium total alkalinity data)
N Boulder clay =	831	64	
N Glacial sand =	52	9	
N Peat =	248	1	
N Raised beach =	27	31	

Figure 4.8 Box and whisker plots showing the 10th, 25th, 50th, 75th and 90th percentiles of element distributions in rural and urban stream waters over different superficial parent materials for the Glasgow rural-urban study area.

5 Urban Drainage Geochemistry

5.1 INTRODUCTION

The locations of the 118 stream sediment and 122 surface water sampling sites collected across the GCC area from all tributaries draining into the River Clyde are shown in Figure 5.1 identified with the GCC catchment labelling codes. The spatial distributions of the geochemical parameters determined during the study are shown in graduated symbol maps in Annexes 3 to 8 of this report. This chapter considers the results of the geochemical survey with particular reference to contaminants in the urban drainage system.

5.2 POTENTIAL SOURCES OF CONTAMINATION IN THE URBAN ENVIRONMENT

A huge variety of contaminants including metals, inorganic elements and compounds, nutrients, organic compounds and radionuclides are present in urban fluvial and estuarine systems. Contaminants enter these systems from a number of natural and anthropogenic sources such as bedrock mineralisation, mines, industry, waste disposal, transport and agriculture. The contaminants are derived either from point discharges such as tailing effluent, industrial outflows, sewage discharges and spillages or from diffuse sources such as the remobilisation of historically contaminated alluvium and agricultural run-off. Many factors influence the contaminant concentration of fluvial and estuarine systems including the nature of input sources, sediment grain size and organic matter content. River floodplains and channels act as sinks for contaminant deposition and many studies have demonstrated that significant quantities of contaminants can be stored in sediment these environments (Hudson-Edwards, 2003). The magnitude and spatial and temporal variation of deposition is primarily controlled by the contaminant content of the sediment. This in turn reflects the sources of sediment and contamination, and the amounts of sediment deposited on the floodplains and channel beds, which is a function of the local hydrological and geomorphological conditions.

The likely sources of contaminants in urban environments have been well documented in the literature and useful synopses are provided by Fergusson (1990); Bridge et al. (1997); Appleton (1995), Hooker et al., (2000) and D'Arcy et al. (2001). Possible sources include building, waste disposal, transport, industrial and manufacturing activities and the use of fossil fuels. The types of contaminants commonly associated with these activities are summarised as follows.

5.2.1 Buildings, Households and Waste Disposal

Metal accumulation in the environment is well documented and is often associated with the disposal of fossil fuel residues (ash and soot), household refuse, bonfires and the application of phosphate fertilizers (P_2O_5 and Cd). Soils, sediments and waters are also affected by atmospheric contamination from the burning of fossil fuels, vehicle emissions and industrial processes. Although the majority of building materials are relatively inert, the demolition of properties, particularly older buildings may lead to contamination with metals such as Pb from paint and substances such as asbestos. Metal contaminants are often present in variable concentrations in domestic and industrial wastes. Over 90 % of refuse in the UK is now deposited in landfill sites from which there is usually little dispersion of metals into the neighbouring environment, however, the disposal of waste materials was often undocumented and uncontrolled in the past. In addition to solid refuse, waste-waters from a host of urban activities such as food processing, laundries and breweries often contain high concentrations of metal and metalloid elements; arsenic is present in household detergents, for example. Urban drainage systems often receive high organic matter and nutrient (nitrogen and phosphorus) inputs from sewage works and combined storm flows. For example, Dodd et al. (2003) have shown that a major source of sediment-bound phosphorus is organic matter.

5.2.2 Urban Surface Run-off and Transport

Urban surface run-off waters often contain high concentrations of Pb, Zn, Cu, TPH and other organic compounds derived from road traffic and industrial sources. Until recently, traffic fumes have also been a major source of Pb in the surface environment and, for example, Kelly et al. (1996), Davies (1995) and Ward (1990) have demonstrated the effects of proximity to roads on urban geochemistry. Although there is evidence to suggest that Pb levels in urban environments are falling due to removal of this element from petrol, studies have shown a coincident increase in Pt concentrations as a result of usage in catalytic converters (Farago et al., 1996). Elements such as Zn (used in tyres) are also enhanced in the urban environment as a result of road vehicle usage. Robertson et al. (2003) have shown that Fe, Cu and Pb derived from road surface run-off are associated with the reductable fraction of urban sediments therefore may be remobilised as a result of changes in pH or redox conditions. Zinc is enriched in the exchangeable fraction suggesting it is vulnerable to mobilisation during run-off. In addition to road transport, areas of railway land often contain scrap metal, oil and debris from rolling stock in the soil whereas canal sediments are commonly contaminated with spillage from cargo, motor fuel and paint. Organo-tin compounds are commonly associated with coastal sediments due to their use as anti-fouling agents on the hulls of vessels by the shipping industry.

5.2.3 Metal Smelting

Metal smelting activities can result in the contamination of land and drainage via stack and fugitive emissions, liquid effluent and the dumping and erosion of slag materials and the transport and spillage of metal concentrates. Historically, atmospheric emissions were large but today depend on the technology employed in the plant, the composition of the raw materials and the pollution control system. Elevated levels of Ni, Cu, Zn, Cd, As, Sb Ag, Se, Hg and Pb are often recorded in the vicinity of smelters and other elements such as F, Mo, Tl, Sn, W, Au and Bi may also be enhanced in the local environment depending on the type of smelter.

5.2.4 Extraction and Combustion of Fossil Fuels

Coal mining and the waste products derived from it (ash and slag) can contain elevated concentrations of PHS. Drainage waters from old coal mines and leachates and run-off from coal and waste piles may be extremely acid due to the oxidation of sulphides. These fluids can contain high levels of Fe, Mn, Cu, Ni and Zn and appreciable amounts of other elements such as As and Pb which can contaminate the surface environment. Sites of disused and demolished power stations often contain soluble salts such as B, residues of coal and pulverised fuel ash (which is highly alkaline pH 11 – 12). Atmospheric contaminants associated with power stations include Cu, Zn, Ag, Cd, Sb, Se, Hg and Pb and environments around coal power stations can be enhanced in Ti, Fe, Co, Cr, Ni, Cu, Zn, Cd and Hg. Fly ash from power stations, which was often used historically to condition land, contains concentrated levels of B, Be, V, Ni, Mn, Cu, Zn, Cd, Mo, As, Se, Sb and Te and may result in contamination if application was not regulated correctly. In addition fuel combustion is a major source of PAH and TPH in the environment.

5.2.5 Manufacturing Industries

Many industrial processes can give rise to contamination, as a general rule, the older the industry, the more likely it is to have produced substantial contamination of nearby drainage systems. Chemical works, gas works and oil refineries give rise to a wide range of contaminants in air, soil, sediment and waters. Potential pollutants from chemical works include Cr, Cu, Zn, Cd, Sn, Hg and Pb. Agricultural-chemical and fertiliser industries may be associated with a wide range of contaminants (trace metals, metalloid elements, phosphorus and nitrogen) whilst explosive works residues may contain Cu, As, Hg and Pb. Oil refineries and the manufacture of oil- based products are potential sources of TPH, PAH, Cr, Ni, V, Co, Cu, Zn, Cd, Mo, As and Pb whereas petroleum cracking catalysts have been traced as the source of light rare-earth element anomalies. Old gas works may be contaminated with coal and coal residues, spent iron oxides, cyanides, sulphates and a range of organic compounds.

Many metals may be present in high concentrations around steelworks, foundries, electroplating and finishing works. The cleaning and etching of bare metal surfaces in metal finishing and plating processes are major sources of Cr, Ni, Cu, Zn and Cd in drainage systems. Battery manufacture may generate waste rich in Ni, Cd, Zn, Sb, Hg and Pb. The processing of scrap metals results in site contamination with metal and metalloid elements in addition to organic substances. Waste-waters derived from paint and dye-stuff producers often contain elevated levels of Cr, Cu, Cd, Se, Hg and Pb from the pigments and raw materials of these industries. Electrical and electronic industry waste can contain Cd, Zn, Se, Cu and Pb whereas Zn, Sn, Pb and Cd are used in the manufacture of synthetic rubber and plastics as stabilisers and pigments. The leather and textile industries use chromates and dichromates to condition cloth, which can be sources of Cr enhancement in drainage systems. The glass and ceramic industries use Cr, Pb, Co, Se, Cu, Mo, Ti and Fe among other elements as pigments, glazes and conditioning agents. Finally, new technologies such as mobile phones and integrated circuits are adding new trace element contaminants to the environment such as tantalum (Ta). For example a mobile phone contains 39 mined and processed inorganic chemical elements.

In summary, an extensive array of activities in urban environments form potential sources of contamination and urban drainage systems often act as sinks for these pollutants. Some of these pollutants are considered in more detail in the following section of this report.

5.3 SEDIMENT SIZE FRACTION RELATIONSHIPS

As indicated in the previous section of this report, sediment grain size often has a fundamental control on levels of contaminants in urban drainage systems. Contaminants are often associated with the fine fraction rather than coarser material. During the present study, two sediment size fractions were analysed, a coarse < 2 mm fraction to be compatible with Clyde estuary sediments and a fine < 150 µm fraction for comparison with rural G-BASE stream sediment data. Summary statistics for the two sediment size fractions are presented in Table 5.1 and comparisons between the two fractions in Figure 5.2. In general, the X-Y plots in Figure 5.2 show a positive correlation between element contents in the < 2 mm and < 150 µm size fractions. However, the results demonstrate that elements such as Si, Na and Sr are partitioned into the coarser < 2 mm fraction probably reflecting the dominance of quartz and feldspar mineral grains in this size fraction. In contrast, elements such as Al and Ga, which are typical clay constituents, are predominantly found in the fine < 150 µm fraction as expected (Figure 5.2). Iron (Fe) and Mn are also partitioned in the fine fraction reflecting the association of these elements with clay minerals and fine-grained iron and manganese oxides and heavy minerals. Zirconium (Zr) and Hf are also preferentially enhanced in the fine fraction due to the presence of fine-grained heavy minerals such as zirconium and sphene. Many of the metal elements such as Cu, Cr, Co, Ba, Ni, Cu, As, Se, Mo, Pb and Sb also show strong enhancement in the fine fraction as expected reflecting their association with organic matter, clay minerals and iron and manganese oxides. Elements such as Zn, Cd and Sn show an interesting distribution, with high concentrations found in both size fractions indicating partitioning into the fine fraction but the presence of coarse-grained gross contaminants in the sediments also. The presence of gross contaminants such as metal fragments causes greater inhomogeneity in coarse relative to fine sediments.

These findings have implications for contaminant transport from the tributaries network to the Clyde estuary as coarser and heavy minerals are likely to drop out of suspension more readily than lighter fine clay particles. For example, investigations into the Mersey catchment have shown that fine-grained sediments are often scoured from the inner estuary environment and deposited in the outer estuary (Ridgway et al., 2003). Examining the dynamics of the Clyde tributary and estuary system were beyond the scope of the present study but it is recommended that further investigations be carried once the Clyde estuary geochemical survey is completed (Jones et al., 2004).

5.4 SEDIMENT AND WATER RELATIONSHIPS

As indicated above, in fluvial and estuarine systems, sediments often act as sinks for contaminants that are remobilised into the water column during sediment disturbance. The relationships between < 2 mm and < 150 µm urban stream sediment and surface water samples are shown in the X-Y plots in Figure 5.3 and 5.4 respectively. In general many elements show poor associations between the concentrations in sediments and waters as the dissolution of elements from minerals in the sediments depends not only on the sediment composition but also on physio-chemical controls such as the pH and redox conditions of the environment and presence of clay minerals and organic matter. Interestingly, TOC and pH in sediments and waters show broad correlation (Figure 5.3). Some of the disparity between the water and sediment results may also be due to aquatic contamination. Values that do not fit the general trends shown on the graphs presented in Figures 5.3 and 5.4 were examined in more detail as follows.

Samples BLB1, and BLC1 contain > 100 mg L^{-1} Al and > 4 mg L^{-1} Fe in water but the levels in corresponding sediments are not abnormally high (Figures 5.3 and 5.4). However, these samples lie in peaty and marshy areas with low pH acid conditions (< pH 7) hence Al and Fe will be more readily mobilised into waters in these environments. Samples LT1A and KNA2 also contain high Al in waters relative to the trend with sediments. At KNA2 this possibly relates to marshy peaty conditions although the pH recorded is alkaline. In the case of LT1A the high Al content in waters probably reflects contamination as this site is influenced by industrial processing, including chromite waste (Figures 5.3 and 5.4).

High P in water (> 4 mg L^{-1}) at site PM1 does not correspond to high concentrations in sediments and may indicate sewage or other contamination as this site has a number of possible contaminant sources (Figures 5.3 and 5.4).

Samples HL0, HL1 and MY1 all in the south-west of Glasgow contain Ca contents in fine sediments > 40 wt% that do not correspond to high values in waters, the higher Ca in sediments may indicate the presence of calcareous fill materials in the area or may be natural (Figure 5.4).

Vanadium (V) concentrations anomalous to the general trend in sediments and waters exceeding 8 µg L^{-1} in waters are associated with chromite waste, steelworks, ironworks and gas works sites at PM1, EF1, MO2 and MO3 indicating mobilisation of this contaminant into the water column. In contrast, although there are high V, U and Se concentrations (> 350 mg kg^{-1}, > 10 mg kg^{-1} and > 20 mg kg^{-1} respectively) in sediments at GK1 probably associated with railway sidings contamination and acid peaty conditions, levels in water are moderate to low (Figures 5.3 and 5.4).

Chromium (Cr) concentrations in general show a positive correlation between sediment and water with the exception of sites PM1, and CL2A, which have very high Cr concentrations in sediment (> 2000 mg kg^{-1}) but do not have highest concentrations in water. These are known industrial sites with Cr contamination. Highest Cr concentrations in water (903 µg L^{-1}) are recorded at LT1A. The association of the high Cr with elevated sulphate and Ca in water confirm this site is influenced by chromite waste and the mobilisation of Cr into the water system is of concern in terms of contaminated land risk assessments. In all cases, highest Cr values in sediments are associated with the fine fraction sediment (Figures 5.3 and 5.4).

Nickel (Ni), Zn and Cu concentrations also show a broad correlation between sediments and waters but values in sediments at the ironworks and railway sidings sites CL2A and GK1 are high (> 100 mg kg^{-1} Ni and > 800 in mg kg^{-1} Cu respectively) in < 2 mm sediments relative to the trend with waters. In both cases, sediment pH conditions are acid and at GK1 the presence of peaty conditions probably also enhance the levels of metals present. Ni (> 7 µg L^{-1}) and Zn (> 120 µg L^{-1}) concentrations in water are high at site N1 where there are no contamination sources noted but low flow and marshy conditions predominate. Water Ni is also high at ST2, which is proximal to an area of infill and has elevated concentrations of Ca in water and Ba, Fe and Zn in sediments, which may indicate foundry waste. This site may also be affected by iron and manganese oxide precipitates enhancing the levels of metals present. Concentrations of Cu (> 9 µg L^{-1}) in water are highest at LH1, which lies in heavy engineering area, this site also has elevated Zn (> 120 µg L^{-1}) in waters and low pH, hence metals are likely to be more mobile.

Arsenic (As) and Sb concentrations in the Molendinar Burn (MO2 and MO3) waters are high (> 40 µg L^{-1} and > 5 µg L^{-1} respectively) relative to the trends with sediments at other sites and probably relate to the heavily industrialised nature of the surrounding environment in both locations (Figures 5.3 and 5.4).

Lead (Pb) concentrations in fine sediments are high (> 2000 mg kg^{-1}) relative to the trend with waters at CL1, CL2A, and on the River Kelvin at KN4 and KN2. The first three sites are proximal to heavy industry and chemical works whereas values at KN2 probably relate to general Pb accumulation in the River Kelvin basin due to urban surface run-off etc.

Cd concentrations in sediments are high (> 20 mg kg^{-1}) compared to the trend in waters at the steel and ironworks locations of NT1 and CL2A (Figures 5.3 and 5.4).

Tin (Sn) tends to be relatively immobile in the environment and this is reflected in the comparisons between stream sediments and surface waters shown in Figures 5.3 and 5.4. Concentrations in water are moderate even at the highest concentrations found in sediments.

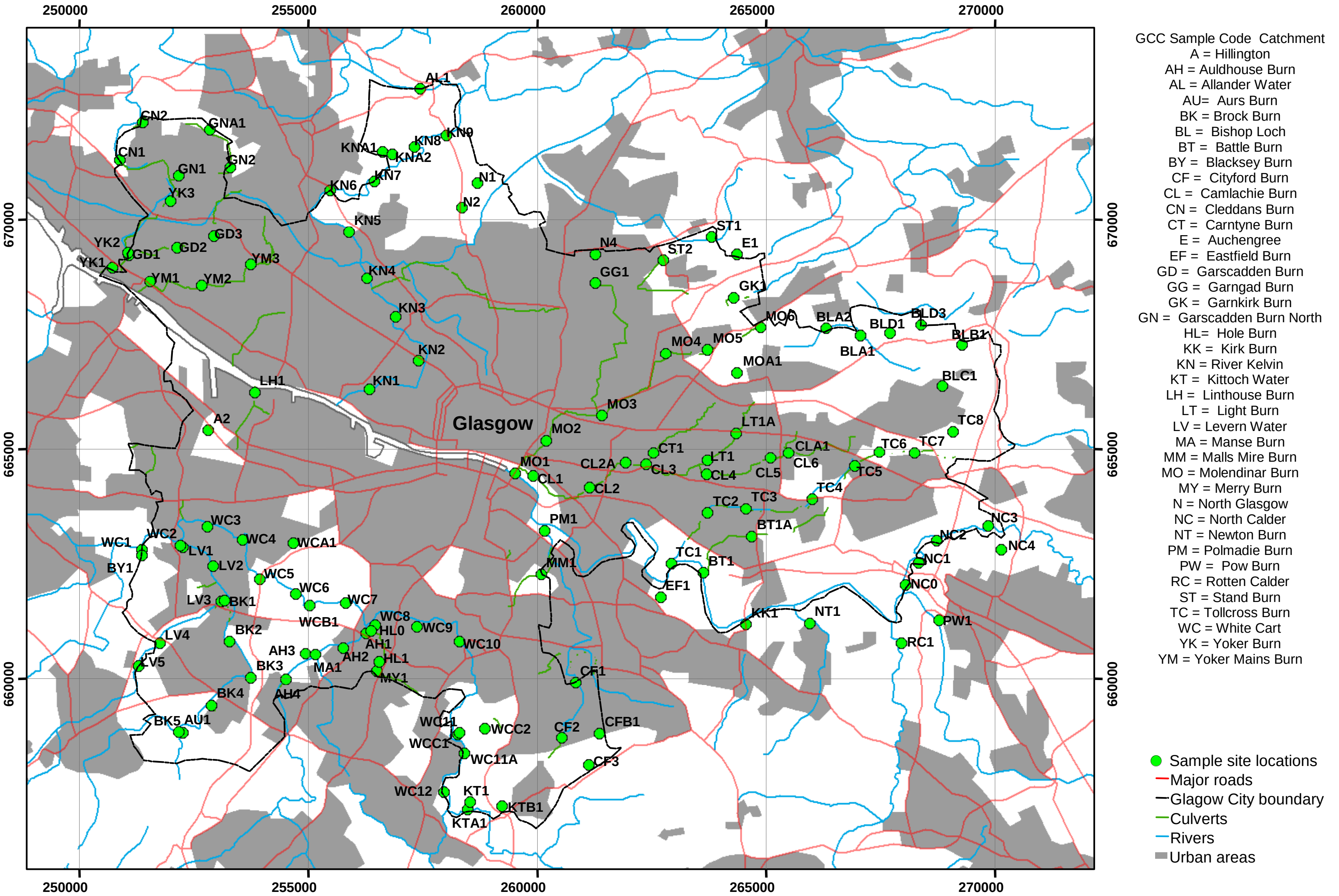
It is not possible to make reasonable comparisons between levels of Hg in waters and sediments as all determinations in water were below the limit of detection, the graph is presented in Figure 5.3 for information only.

It is recommended that the relationships between sediment and water and controls on contaminant mobility be examined in more detail as part of the proposed follow-on Clyde estuary-Clyde basin study.

Table 5.1 Summary statistics for determinands in < 2 mm and < 150 µm urban stream sediments

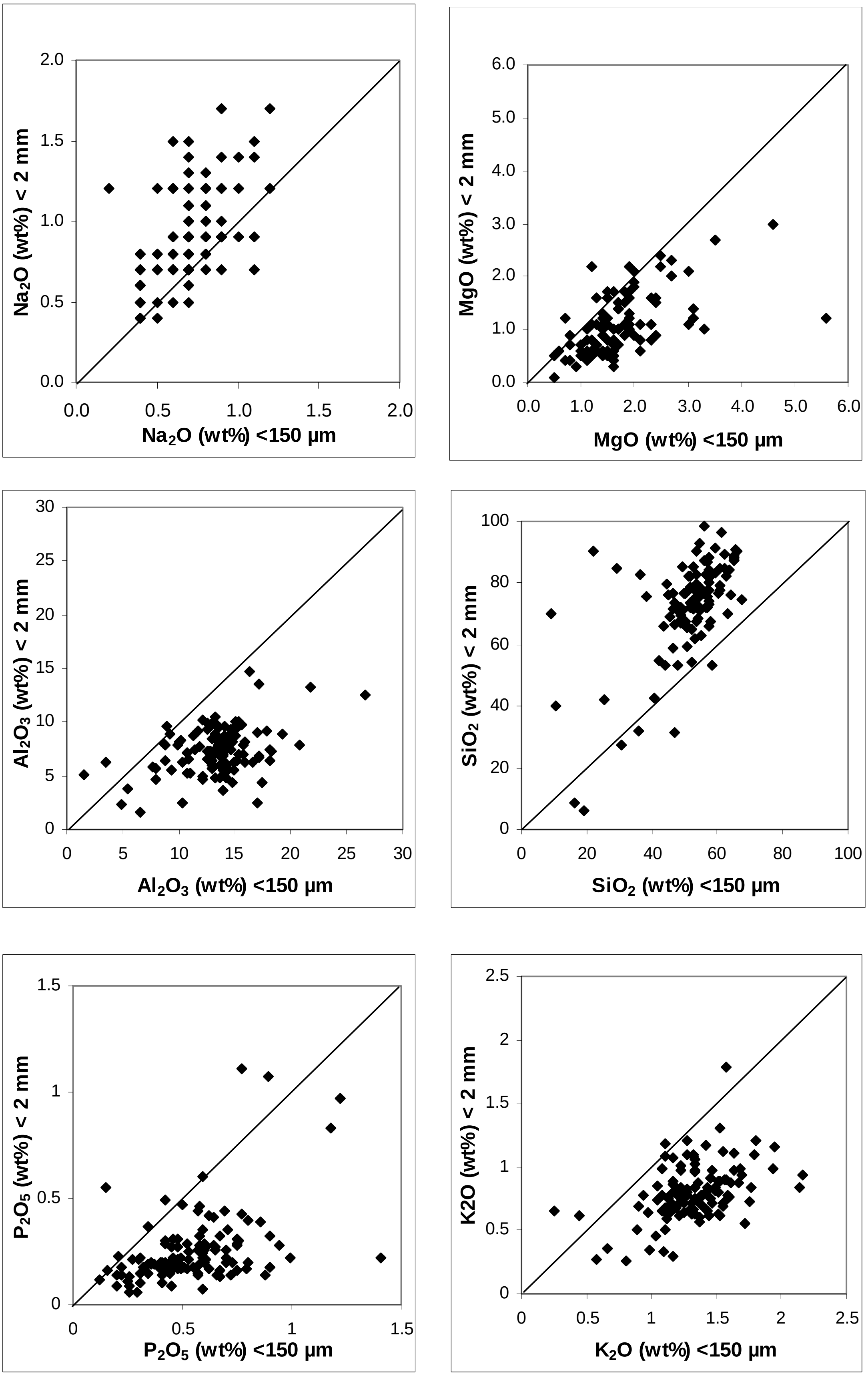
Parameter	< 2mm Stream Sediment					< 150 µm Stream Sediment				
	Count	Min	Max	Mean	Median	Count	Min	Max	Mean	Median
Ag mg kg^{-1}	118	0.25	16.00	0.53	0.25	118	0.25	124.10	2.12	0.25
Al_2O_3 wt%	118	1.60	14.70	7.37	7.30	118	1.60	26.70	13.35	13.55
As mg kg^{-1}	118	1.80	243.30	13.68	6.25	118	2.50	856.30	35.62	11.70
Ba mg kg^{-1}	118	141.00	1257.00	374.83	366.50	118	191.00	1701.00	677.50	650.50
Bi mg kg^{-1}	118	0.50	2.20	0.62	0.50	118	0.50	12.70	1.00	0.50
Br mg kg^{-1}	118	0.80	83.10	5.04	2.30	118	4.60	115.50	22.60	20.10
CaO wt%	118	0.10	16.97	2.69	1.64	118	0.54	83.37	4.36	2.19
Cd mg kg^{-1}	118	0.25	9.50	0.63	0.25	118	0.25	25.30	1.45	0.90
Ce mg kg^{-1}	118	7.00	170.00	40.33	39.00	118	9.00	119.00	77.00	79.00
Co mg kg^{-1}	118	12.00	54.00	24.70	23.65	118	16.80	90.80	35.25	32.05
Cr mg kg^{-1}	118	30.00	2345.00	121.12	82.50	118	80.00	3561.00	273.44	162.00
Cs mg kg^{-1}	118	1.00	6.00	1.07	1.00	118	1.00	5.00	1.00	1.00
Cu mg kg^{-1}	118	7.10	911.30	80.20	45.50	118	18.20	2984.60	201.83	95.45
Fe_2O_3 wt%	118	3.61	12.46	6.43	6.04	118	3.57	27.23	8.56	8.27
Ga mg kg^{-1}	118	1.40	20.40	7.77	7.60	118	1.40	42.40	15.44	15.35
Ge mg kg^{-1}	118	0.50	48.50	2.54	1.55	118	0.50	37.10	3.50	2.60
Hf mg kg^{-1}	118	0.50	7.70	2.77	2.50	118	0.50	48.10	11.10	10.20
Hg mg kg^{-1}	116	0.01	2.90	0.20	0.07	Nd	Nd	Nd	Nd	Nd
I mg kg^{-1}	118	0.25	12.30	1.06	0.50	118	0.70	73.30	8.09	5.55
K_2O wt%	118	0.26	1.79	0.80	0.78	118	0.25	2.16	1.33	1.33
La mg kg^{-1}	118	10.00	108.00	28.41	26.00	118	9.00	83.00	50.66	52.00
Na wt%	118	0.10	3.00	1.08	1.00	118	0.20	1.20	0.70	0.70
MgO wt%	118	0.02	0.49	0.12	0.09	118	0.50	5.60	1.70	1.60
MnO wt%	118	0.15	7.30	1.88	1.50	118	0.05	2.65	0.30	0.18
Mo mg kg^{-1}	118	0.40	1.70	0.90	0.90	118	0.90	111.80	4.40	2.60
Nb mg kg^{-1}	118	1.70	48.20	10.93	8.90	118	3.20	49.70	19.15	17.20
Ni mg kg^{-1}	118	7.30	173.40	41.98	38.80	118	16.30	466.60	71.81	63.65
P_2O_5 wt%	118	0.06	1.11	0.26	0.21	118	0.12	1.41	0.54	0.53
Pb mg kg^{-1}	118	9.00	1377.80	136.72	87.05	118	23.60	5001.00	365.77	212.25
Rb mg kg^{-1}	118	4.40	45.20	23.49	22.50	118	5.80	89.00	45.64	45.45
Sc mg kg^{-1}	118	0.25	14.60	2.14	0.95	118	1.00	23.00	15.00	15.00
Sb mg kg^{-1}	118	2.00	23.00	9.04	9.00	118	0.25	61.30	6.15	4.00
Se mg kg^{-}	118	0.20	27.70	0.84	0.20	118	0.20	59.40	2.5	1.7
SiO_2 wt%	118	6.00	98.40	72.99	75.95	118	9.00	67.40	51.62	53.60
Sn mg kg^{-1}	118	1.00	472.30	29.44	10.25	118	3.30	1148.80	45.70	18.65
Sr mg kg^{-1}	118	29.00	404.30	145.45	133.60	118	90.60	672.00	168.31	148.20
Ta mg kg^{-1}	118	0.25	3.40	0.62	0.25	118	0.25	3.80	0.81	0.60
Te mg kg^{-1}	118	0.25	0.25	0.25	0.25	118	0.25	0.60	0.26	0.25
Th mg kg^{-1}	118	0.20	7.10	3.38	3.30	118	0.20	14.50	6.70	6.80
TiO_2 wt%	118	0.14	2.21	0.63	0.52	118	0.09	2.53	1.19	1.15
Tl mg kg^{-1}	118	0.25	3.50	0.62	0.50	118	0.25	10.60	1.04	0.80
U mg kg^{-1}	118	0.25	9.60	1.26	1.00	118	0.25	12.40	1.35	1.15
V mg kg^{-1}	118	19.00	442.00	95.74	88.00	118	11.00	361.00	150.46	144.50
W mg kg^{-1}	118	0.25	7.10	1.39	1.20	118	0.25	12.00	1.29	0.90
Y mg kg^{-1}	118	4.20	40.40	14.60	14.20	118	3.40	37.10	25.03	25.50
Zn mg kg^{-1}	118	20.00	2001.00	250.80	175.75	118	75.40	2001.00	569.56	480.25
Zr mg kg^{-1}	118	12.60	375.00	109.42	99.80	118	25.20	1868.90	467.26	448.05
pH	114	4.75	7.23	6.14	6.14	Nd	Nd	Nd	Nd	Nd
TOC %	116	0.14	35.00	4.64	3.04	Nd	Nd	Nd	Nd	Nd
Cyanide mg kg^{-1}	114	0.50	2.35	0.56	0.50	Nd	Nd	Nd	Nd	Nd
TPH mg kg^{-1}	115	72.07	37879.22	2778.88	1082.25	Nd	Nd	Nd	Nd	Nd
PAH mg kg^{-1}	52	2.31	4225.61	123.69	21.99	Nd	Nd	Nd	Nd	Nd
TBT mg kg^{-1} Sn	10	0.04	0.35	0.08	0.04	Nd	Nd	Nd	Nd	Nd
Total PCB ng g^{-1}	23	2.16	808.99	137.17	45.98	Nd	Nd	Nd	Nd	Nd

Nd = Not determined



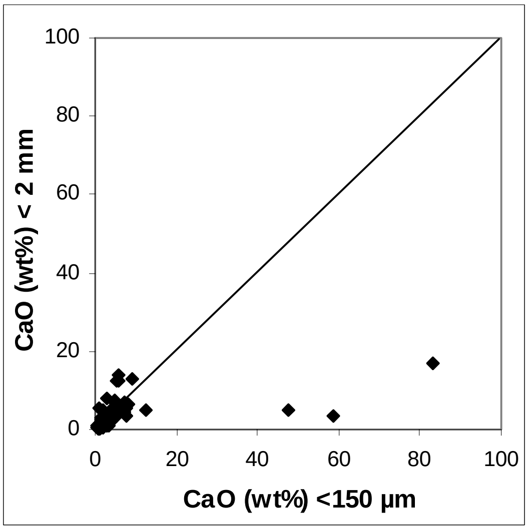
GCC Sample Code Catchment
A = Hillington
AH = Auldhouse Burn
AL = Allander Water
AU= Aurs Burn
BK = Brock Burn
BL = Bishop Loch
BT = Battle Burn
BY = Blacksey Burn
CF = Cityford Burn
CL = Camlachie Burn
CN = Cleddans Burn
CT = Carntyne Burn
E = Auchengree
EF = Eastfield Burn
GD = Garscadden Burn
GG = Garngad Burn
GK = Garnkirk Burn
GN = Garscadden Burn North
HL= Hole Burn
KK = Kirk Burn
KN = River Kelvin
KT = Kittoch Water
LH = Linthouse Burn
LT = Light Burn
LV = Levern Water
MA = Manse Burn
MM = Malls Mire Burn
MO = Molendinar Burn
MY = Merry Burn
N = North Glasgow
NC = North Calder
NT = Newton Burn
PM = Polmadie Burn
PW = Pow Burn
RC = Rotten Calder
ST = Stand Burn
TC = Tollcross Burn
WC = White Cart
YK = Yoker Burn
YM = Yoker Mains Burn

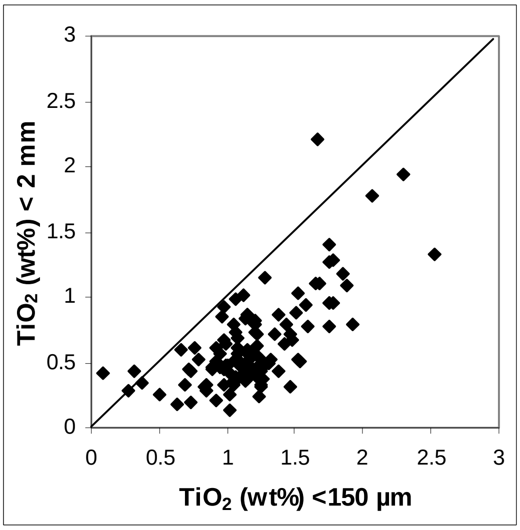
Figure 5.1 Urban drainage sample locations and catchment codes for the Glasgow study area

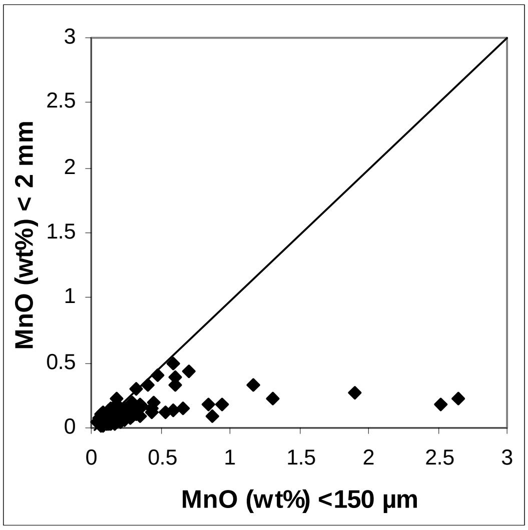


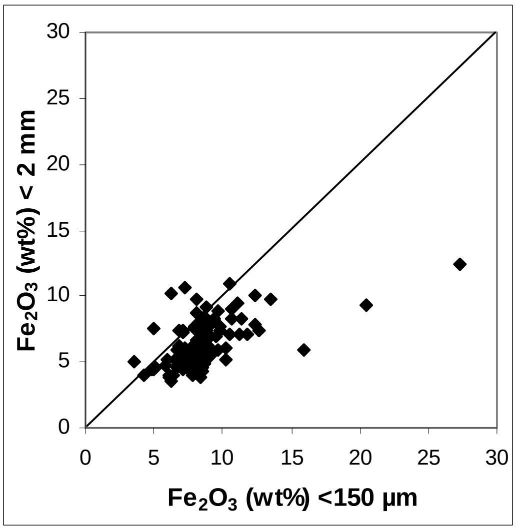
Line = 1:1 correlation N = 118

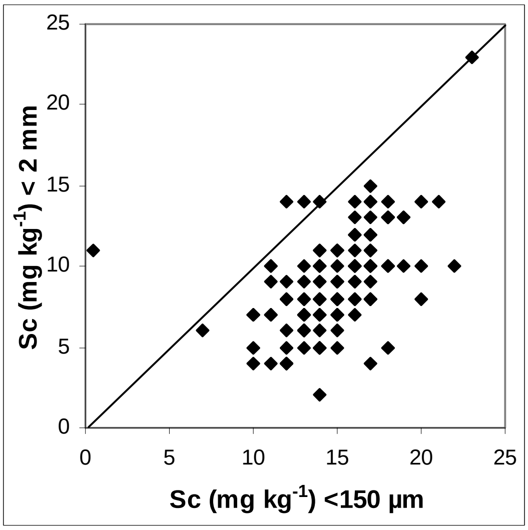
Figure 5.2 Plots of parameter distributions in < 2 mm and < 150 µm urban stream sediments

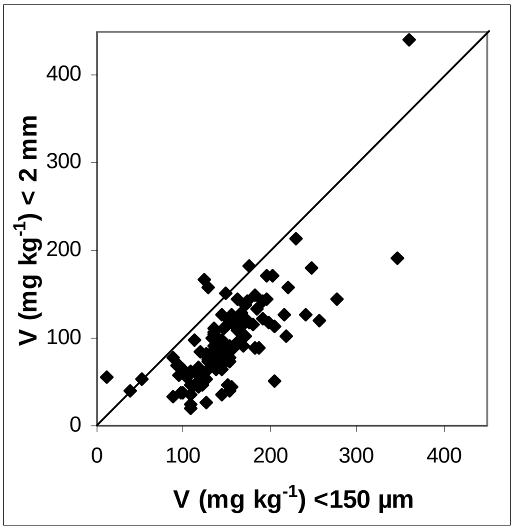

CaO (wt%) < 2 mm
CaO (wt%) <150 µm
0
20
40
60
80
100

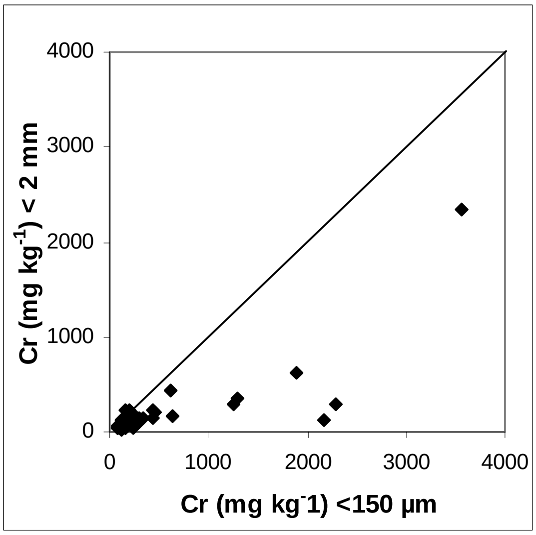

TiO_2 (wt%) < 2 mm
TiO_2 (wt%) <150 µm
0
0.5
1
1.5
2
2.5
3

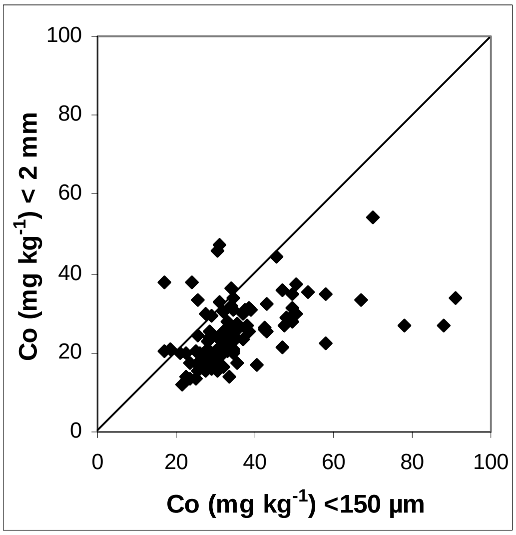

MnO (wt%) < 2 mm
MnO (wt%) <150 µm
0
0.5
1
1.5
2
2.5
3

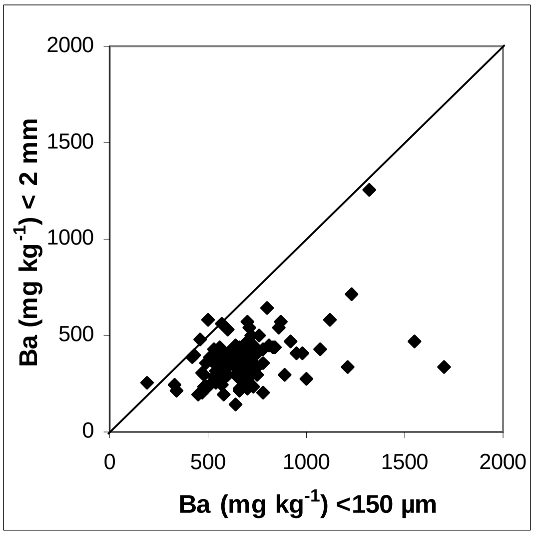

Fe_2O_3 (wt%) < 2 mm
Fe_2O_3 (wt%) <150 µm
0
5
10
15
20
25
30

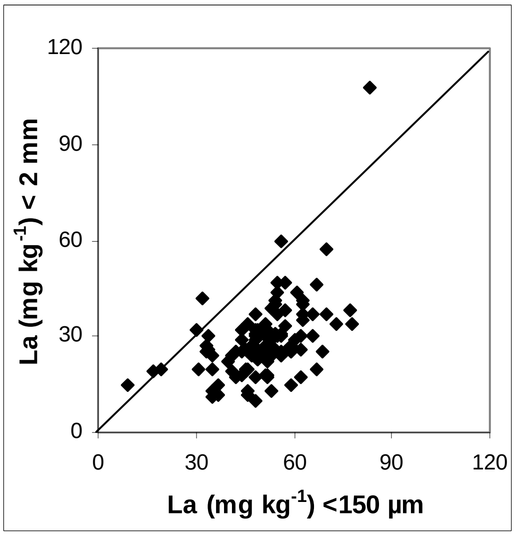

Sc (mg kg^{-1}) < 2 mm
Sc (mg kg^{-1}) <150 µm
0
5
10
15
20
25

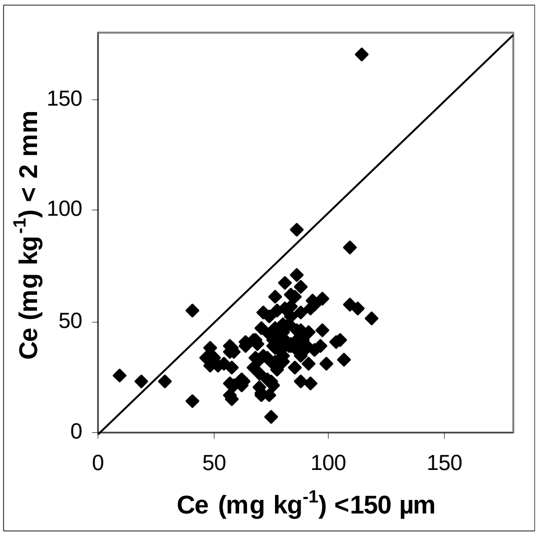

V (mg kg^{-1}) < 2 mm
V (mg kg^{-1}) <150 µm
0
100
200
300
400

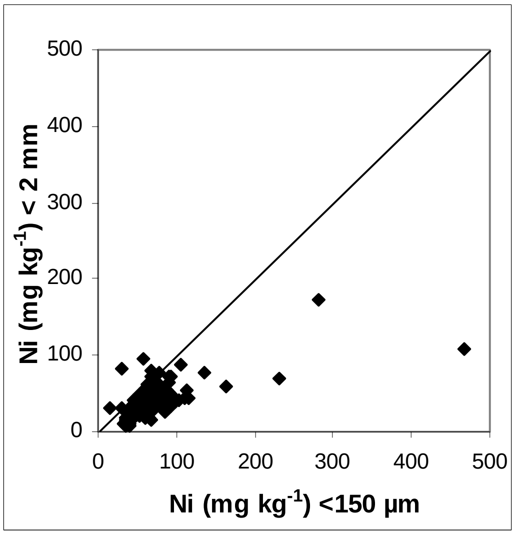

Cr (mg kg-1) < 2 mm
4000
3000
2000
1000
0
0
1000
2000
3000
4000
Cr (mg kg-1) <150 µm

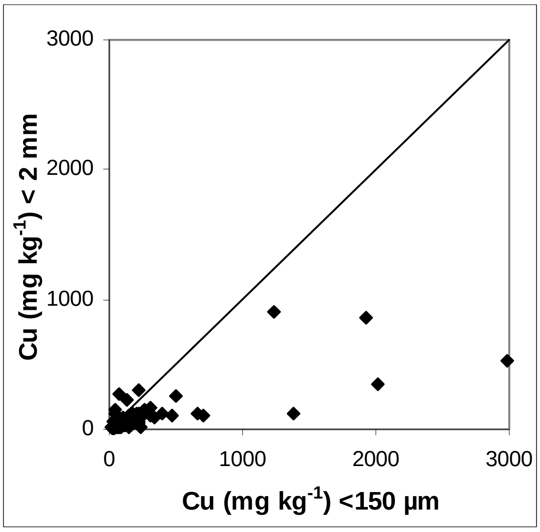

Co (mg kg-1) < 2 mm
100
80
60
40
20
0
0
20
40
60
80
100
Co (mg kg-1) <150 µm

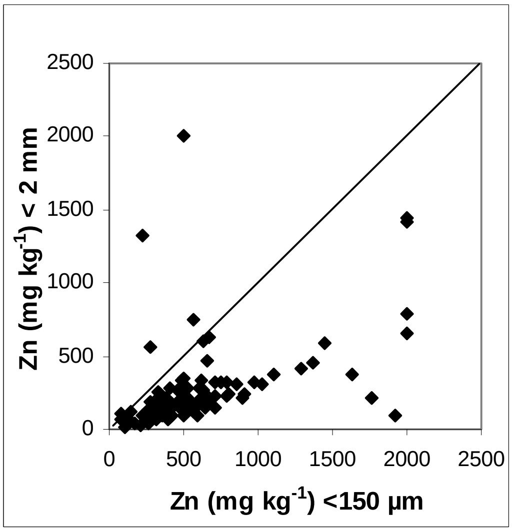

Ba (mg kg-1) < 2 mm
2000
1500
1000
500
0
0
500
1000
1500
2000
Ba (mg kg-1) <150 µm

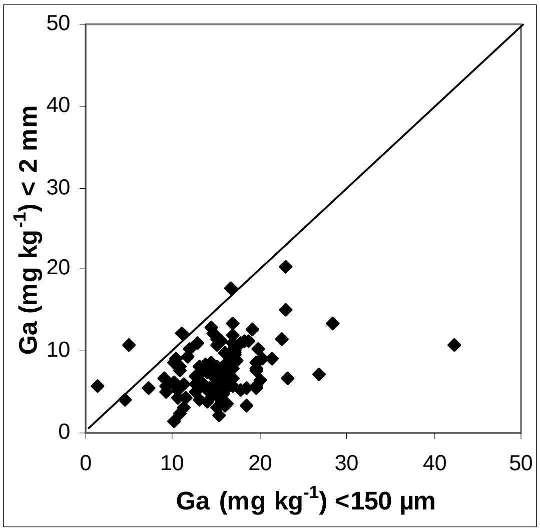

La (mg kg-1) < 2 mm
120
90
60
30
0
0
30
60
90
120
La (mg kg-1) <150 µm

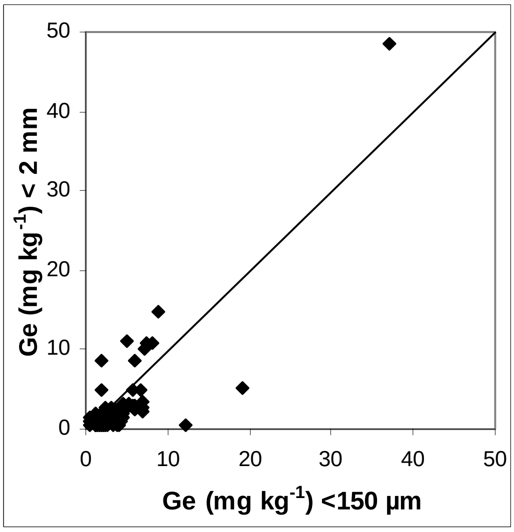

Ce (mg kg-1) < 2 mm
150
100
50
0
0
50
100
150
Ce (mg kg-1) <150 µm

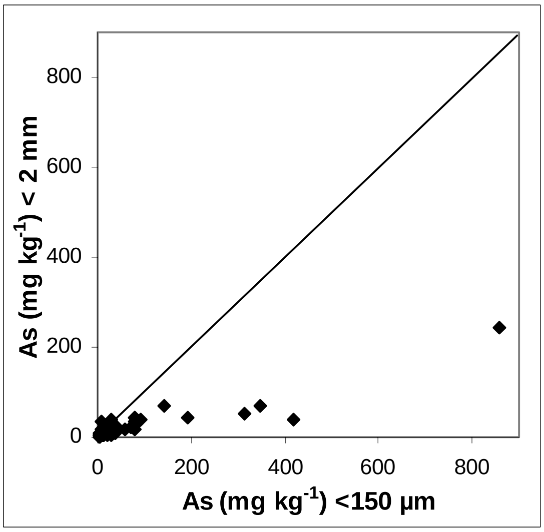

Ni (mg kg-1) < 2 mm
500
400
300
200
100
0
0
100
200
300
400
500
Ni (mg kg-1) <150 µm

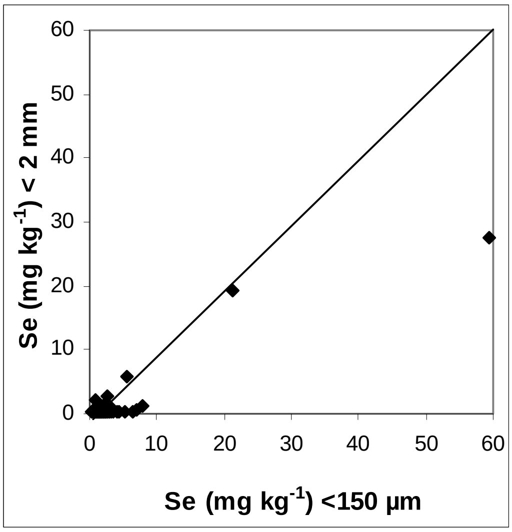

3000
2000
1000
0
Cu (mg kg-1) < 2 mm
0
1000
2000
3000
Cu (mg kg-1) <150 µm

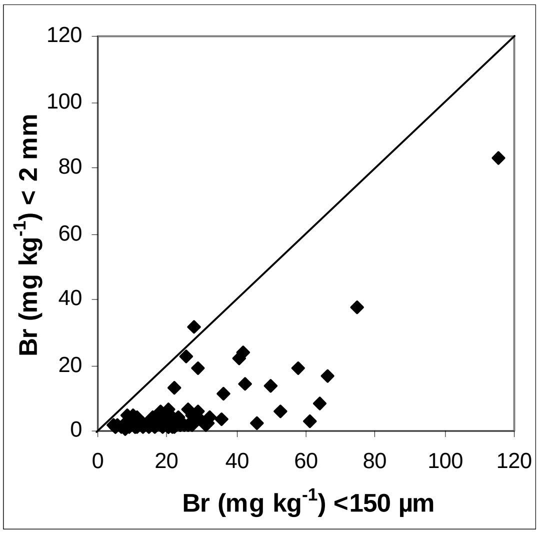

2500
2000
1500
1000
500
0
Zn (mg kg-1) < 2 mm
0
500
1000
1500
2000
2500
Zn (mg kg-1) <150 µm

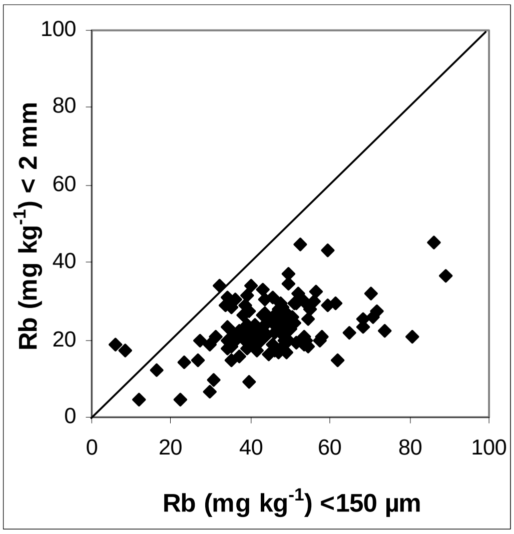

50
40
30
20
10
0
Ga (mg kg-1) < 2 mm
0
10
20
30
40
50
Ga (mg kg-1) <150 µm

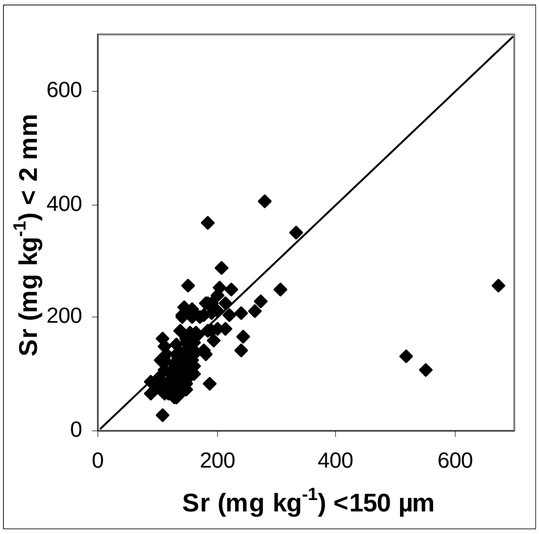

50
40
30
20
10
0
Ge (mg kg-1) < 2 mm
0
10
20
30
40
50
Ge (mg kg-1) <150 µm

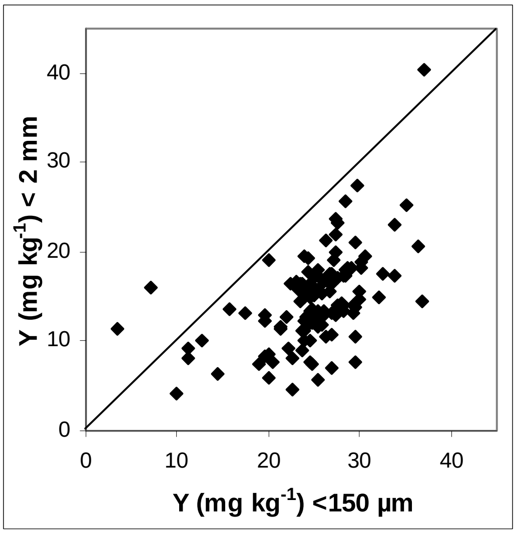

800
600
400
200
0
As (mg kg-1) < 2 mm
0
200
400
600
800
As (mg kg-1) <150 µm

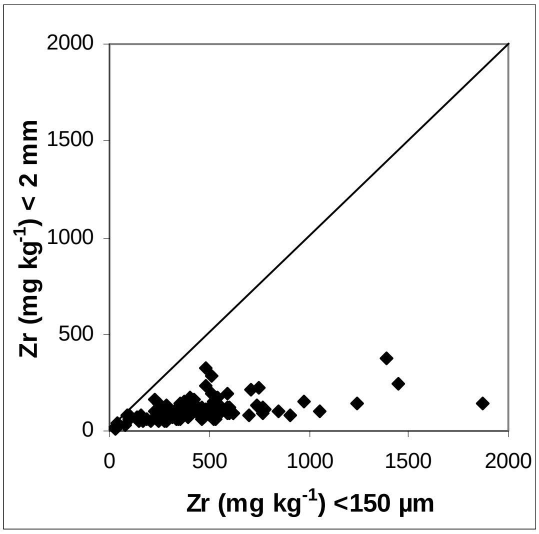

60
50
40
30
20
10
0
Se (mg kg-1) < 2 mm
0
10
20
30
40
50
60
Se (mg kg-1) <150 µm

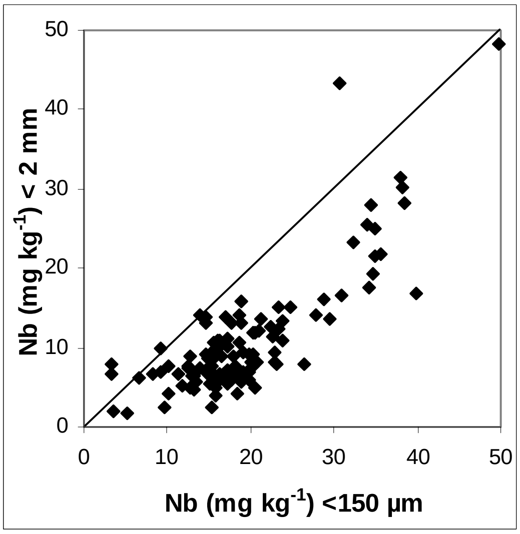

Br (mg kg^{-1}) < 2 mm
0
20
40
60
80
100
120
0
20
40
60
80
100
120
Br (mg kg^{-1}) <150 µm

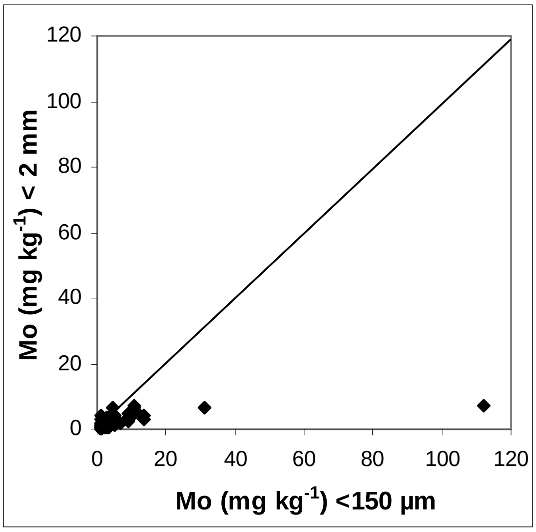

Rb (mg kg^{-1}) < 2 mm
0
20
40
60
80
100
0
20
40
60
80
100
Rb (mg kg^{-1}) <150 µm

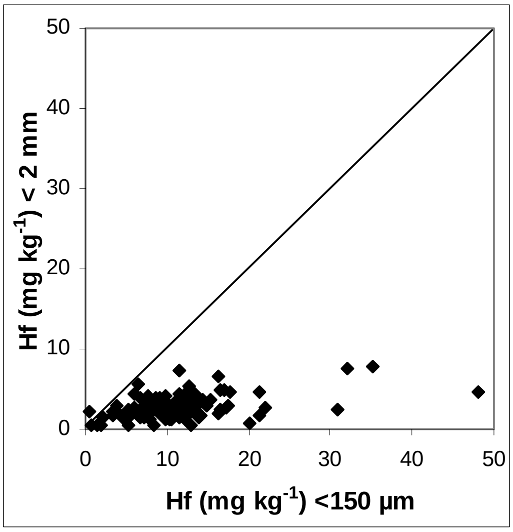

Sr (mg kg^{-1}) < 2 mm
0
200
400
600
0
200
400
600
Sr (mg kg^{-1}) <150 µm

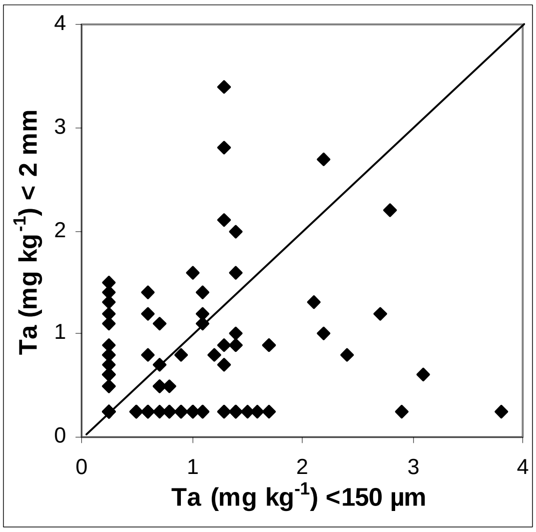

Y (mg kg^{-1}) < 2 mm
0
10
20
30
40
0
10
20
30
40
Y (mg kg^{-1}) <150 µm

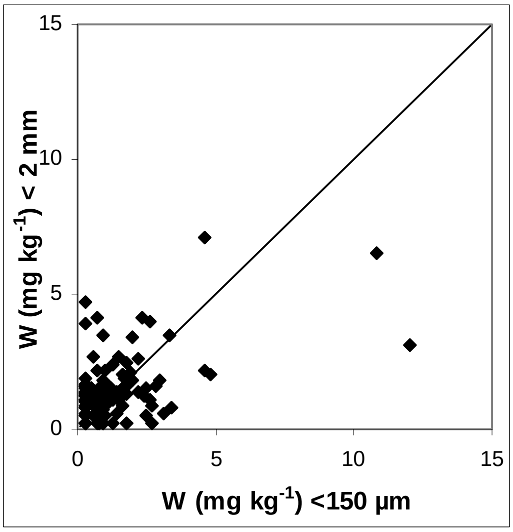

Zr (mg kg^{-1}) < 2 mm
0
500
1000
1500
2000
0
500
1000
1500
2000
Zr (mg kg^{-1}) <150 µm

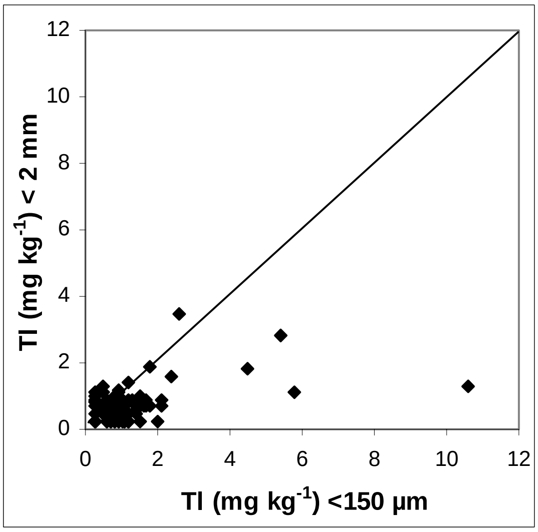

Nb (mg kg^{-1}) < 2 mm
0
10
20
30
40
50
0
10
20
30
40
50
Nb (mg kg^{-1}) <150 µm

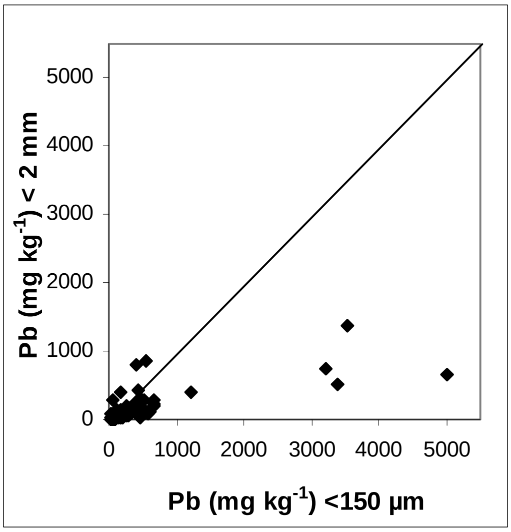

Mo (mg kg^{-1}) < 2 mm
Mo (mg kg^{-1}) <150 µm
0
20
40
60
80
100
120

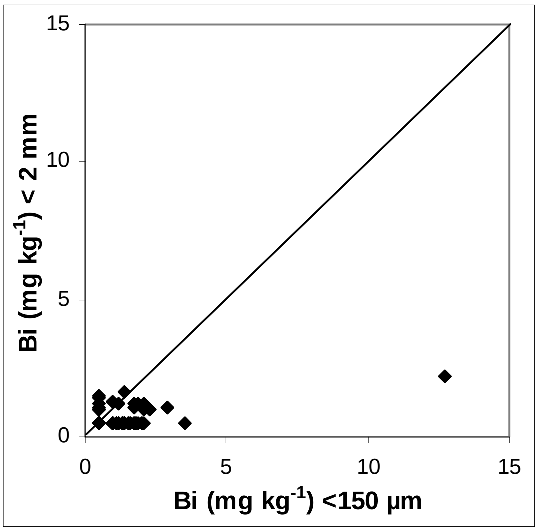

Hf (mg kg^{-1}) < 2 mm
Hf (mg kg^{-1}) <150 µm
0
10
20
30
40
50

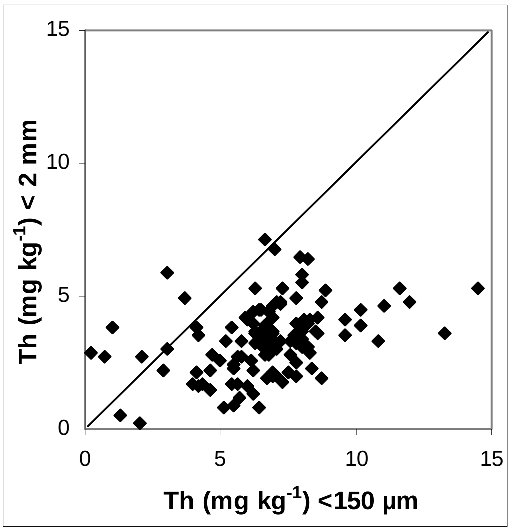

Ta (mg kg^{-1}) < 2 mm
Ta (mg kg^{-1}) <150 µm
0
1
2
3
4

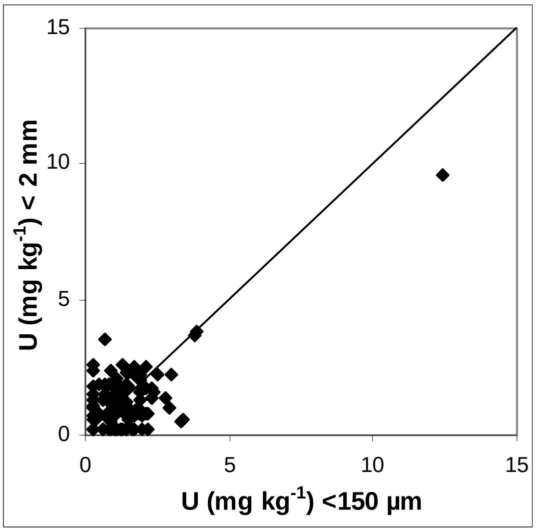

W (mg kg^{-1}) < 2 mm
W (mg kg^{-1}) <150 µm
0
5
10
15

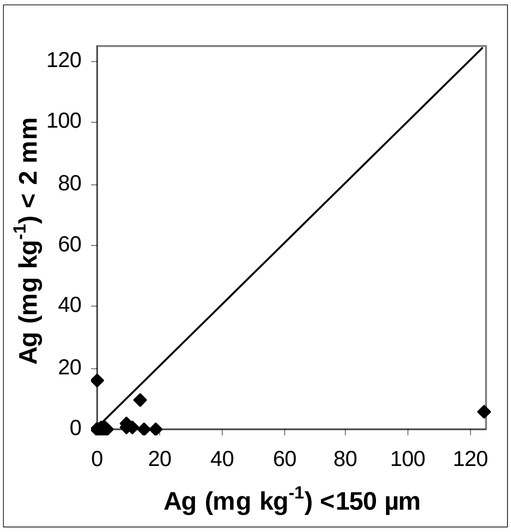

Tl (mg kg^{-1}) < 2 mm
Tl (mg kg^{-1}) <150 µm
0
2
4
6
8
10
12

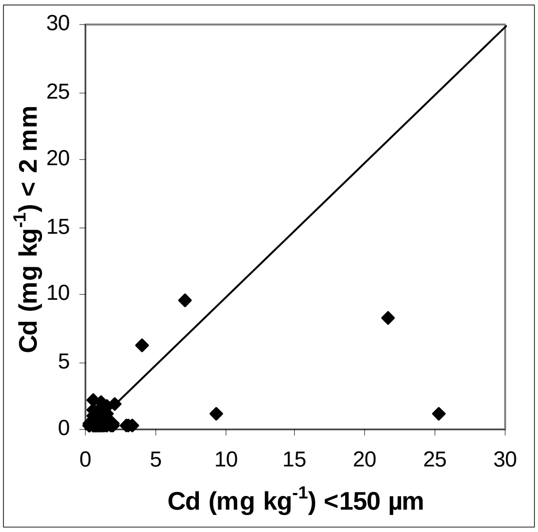

Pb (mg kg^{-1}) < 2 mm
Pb (mg kg^{-1}) <150 µm
0
1000
2000
3000
4000
5000

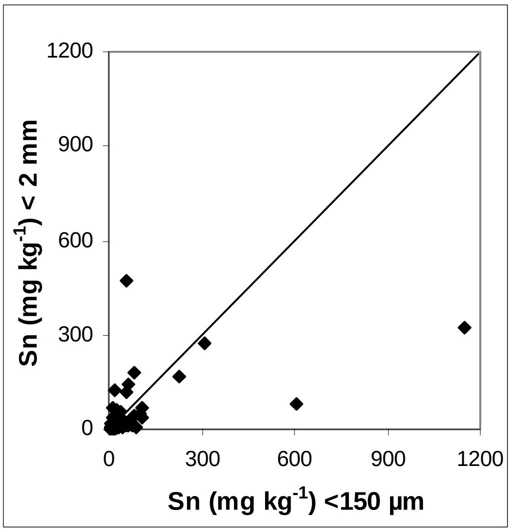

Bi (mg kg-1) < 2 mm
15
10
5
0
0
5
10
15
Bi (mg kg-1) <150 µm

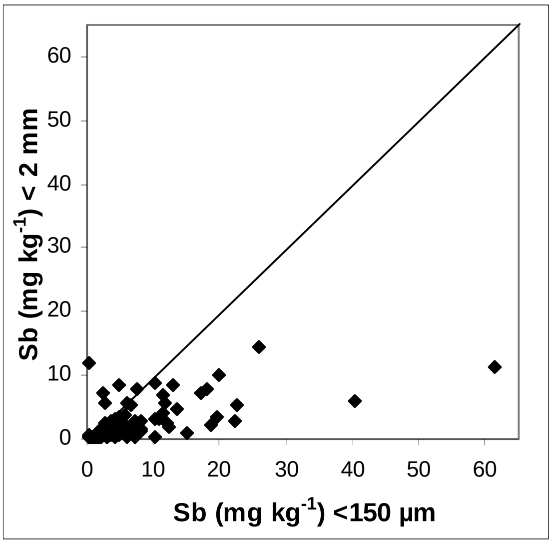

Th (mg kg-1) < 2 mm
15
10
5
0
0
5
10
15
Th (mg kg-1) <150 µm

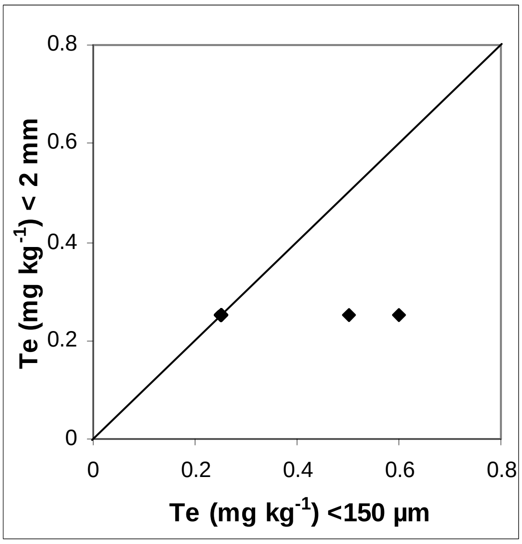

U (mg kg-1) < 2 mm
15
10
5
0
0
5
10
15
U (mg kg-1) <150 µm

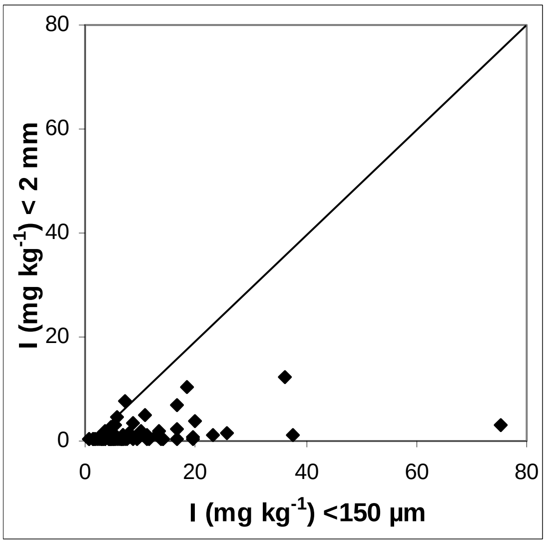

Ag (mg kg-1) < 2 mm
120
100
80
60
40
20
0
0
20
40
60
80
100
120
Ag (mg kg-1) <150 µm

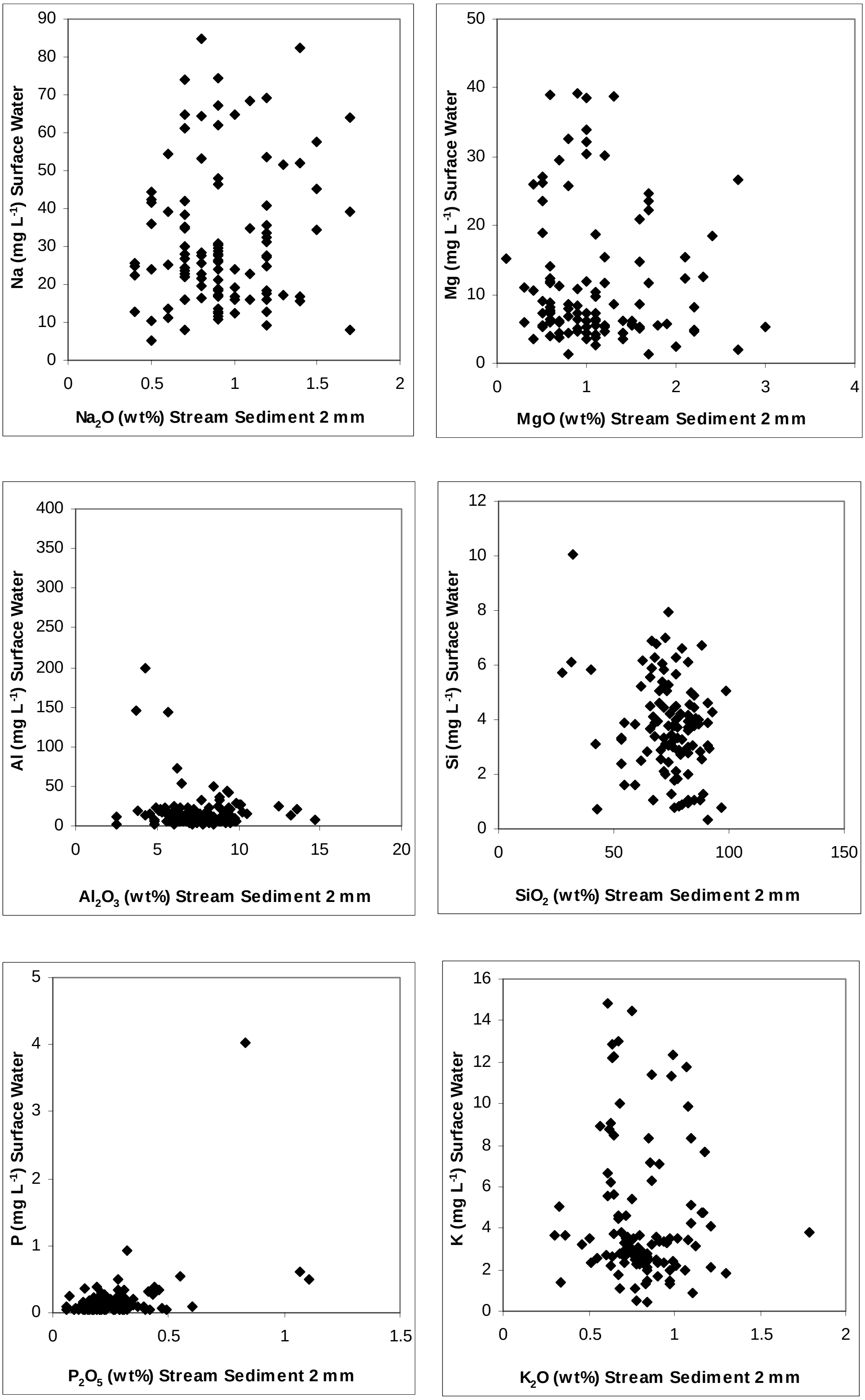

Cd (mg kg-1) < 2 mm
30
25
20
15
10
5
0
0
5
10
15
20
25
30
Cd (mg kg-1) <150 µm


Sn (mg kg-1) < 2 mm
1200
900
600
300
0
0
300
600
900
1200
Sn (mg kg-1) <150 µm


60
50
40
30
20
10
0
0
10
20
30
40
50
60
Sb (mg kg-1) < 2 mm
Sb (mg kg-1) <150 µm

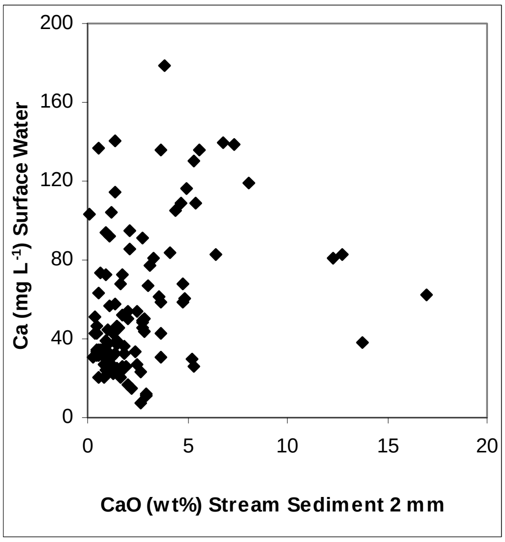

0.8
0.6
0.4
0.2
0
0
0.2
0.4
0.6
0.8
Te (mg kg-1) < 2 mm
Te (mg kg-1) <150 µm

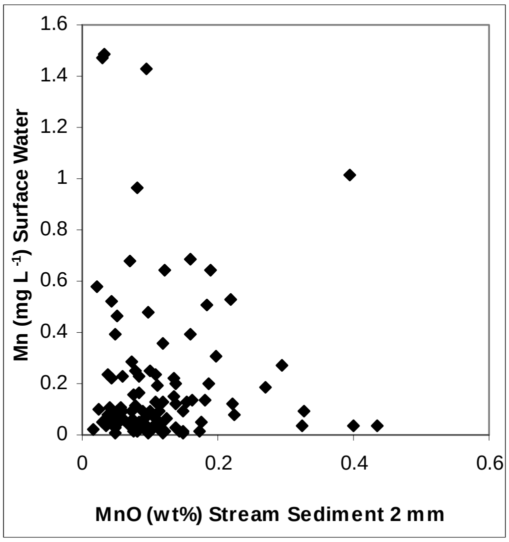

80
60
40
20
0
0
20
40
60
80
I (mg kg-1) < 2 mm
I (mg kg-1) <150 µm

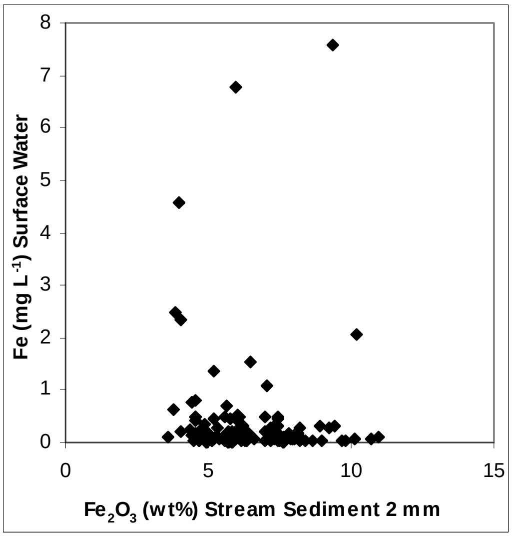


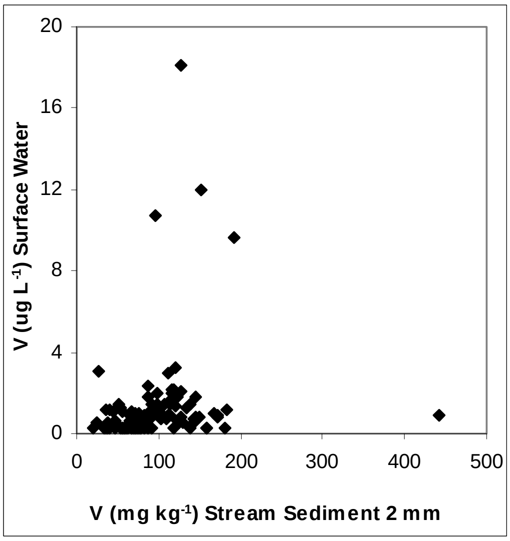
N = 113

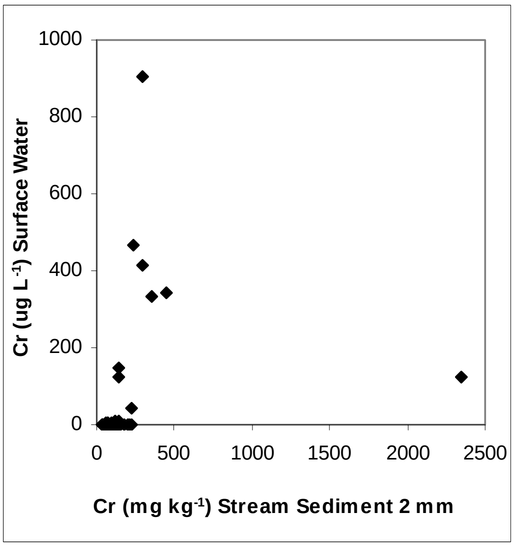
Figure 5.3 Plots of parameter distributions in urban < 2 mm stream sediments and surface waters

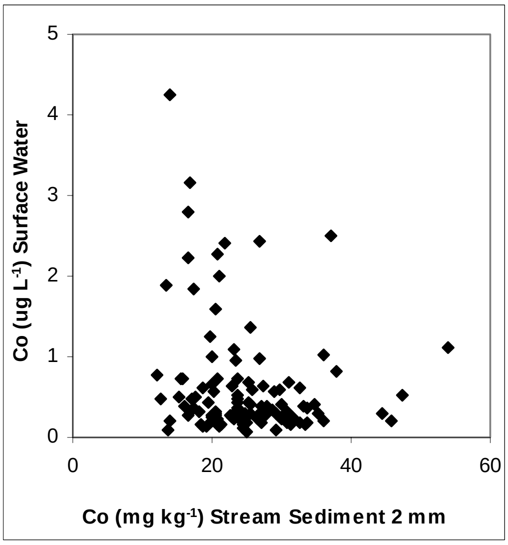

Ca (mg L^{-1}) Surface Water
0
40
80
120
160
200
0
5
10
15
20
CaO (wt%) Stream Sediment 2 mm

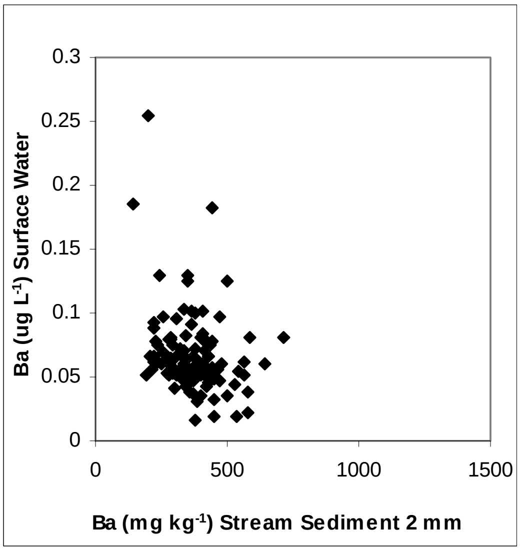

Mn (mg L^{-1}) Surface Water
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
0
0.2
0.4
0.6
MnO (wt%) Stream Sediment 2 mm

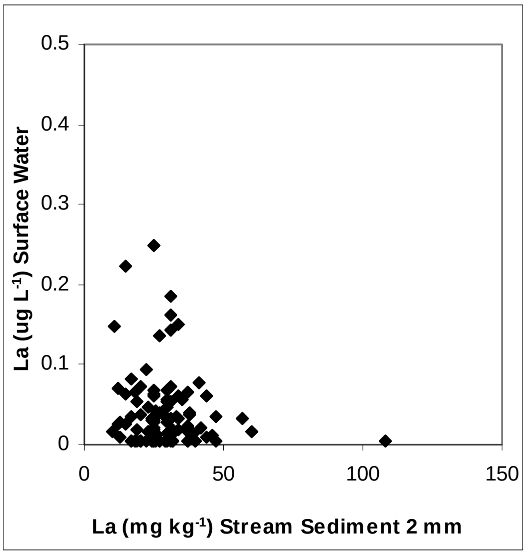

Fe (mg L^{-1}) Surface Water
0
1
2
3
4
5
6
7
8
0
5
10
15
Fe_2O_3 (wt%) Stream Sediment 2 mm

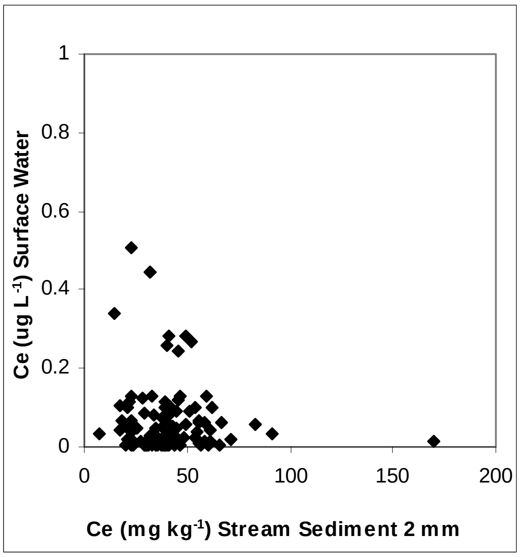

V (ug L^{-1}) Surface Water
0
4
8
12
16
20
0
100
200
300
400
500
V (mg kg^{-1}) Stream Sediment 2 mm

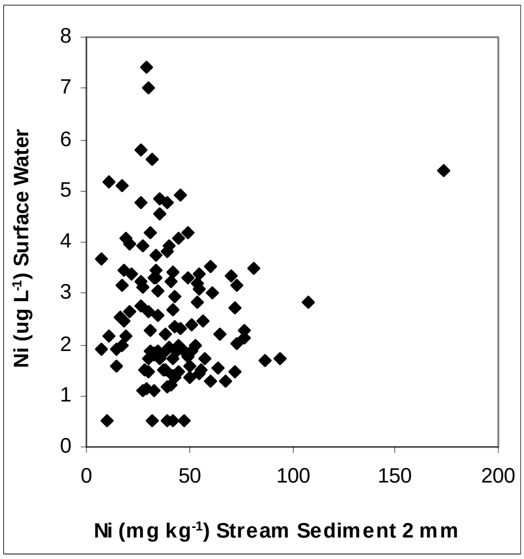

Cr (ug L^{-1}) Surface Water
0
200
400
600
800
1000
0
500
1000
1500
2000
2500
Cr (mg kg^{-1}) Stream Sediment 2 mm

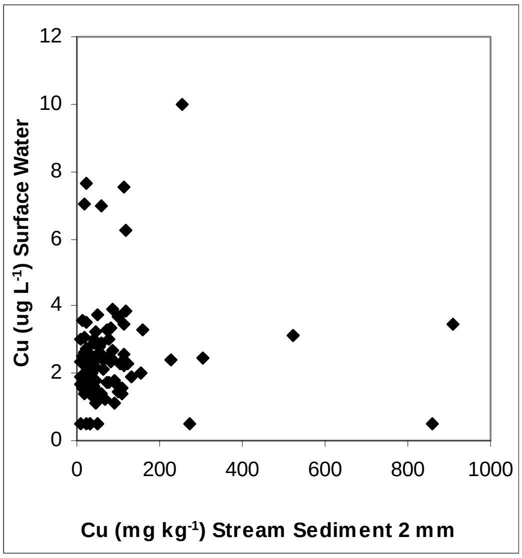

Co (ug L^{-1}) Surface Water
0
1
2
3
4
5
0
20
40
60
Co (mg kg^{-1}) Stream Sediment 2 mm

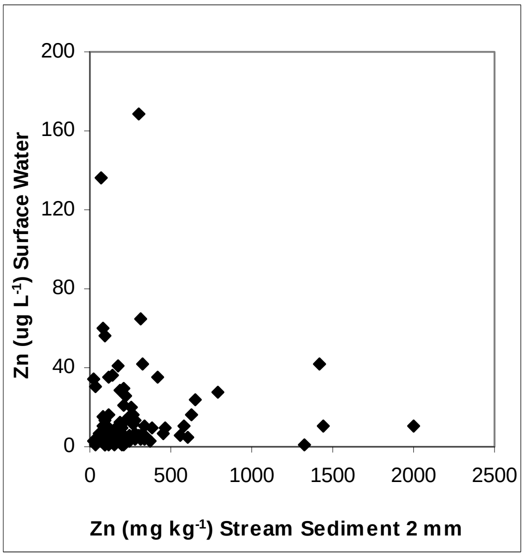

Ba (ug L^{-1}) Surface Water
0.3
0.25
0.2
0.15
0.1
0.05
0
0
500
1000
1500
Ba (mg kg^{-1}) Stream Sediment 2 mm

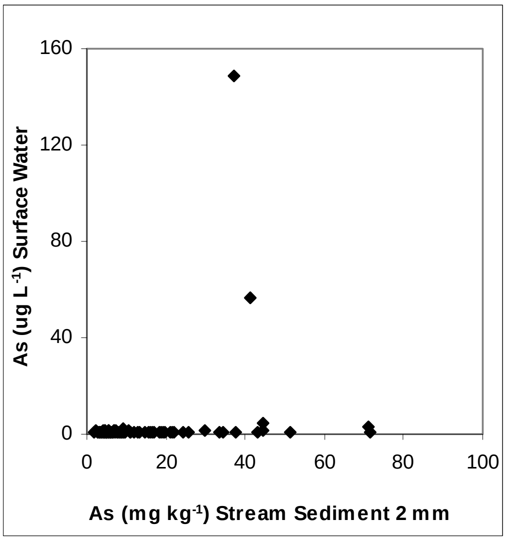

La (ug L^{-1}) Surface Water
0.5
0.4
0.3
0.2
0.1
0
0
50
100
150
La (mg kg^{-1}) Stream Sediment 2 mm

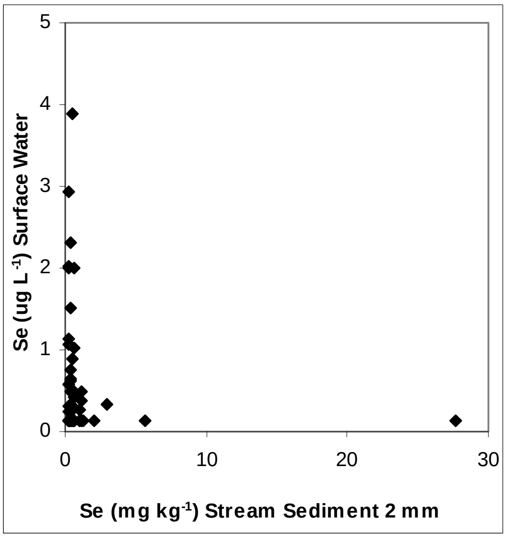

Ce (ug L^{-1}) Surface Water
1
0.8
0.6
0.4
0.2
0
0
50
100
150
200
Ce (mg kg^{-1}) Stream Sediment 2 mm

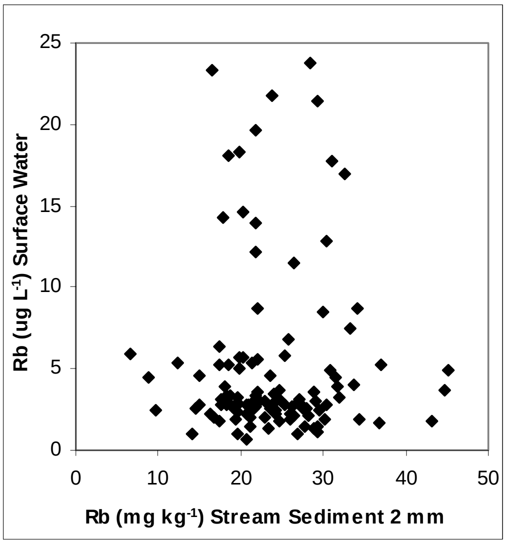

Ni (ug L^{-1}) Surface Water
8
7
6
5
4
3
2
1
0
0
50
100
150
200
Ni (mg kg^{-1}) Stream Sediment 2 mm

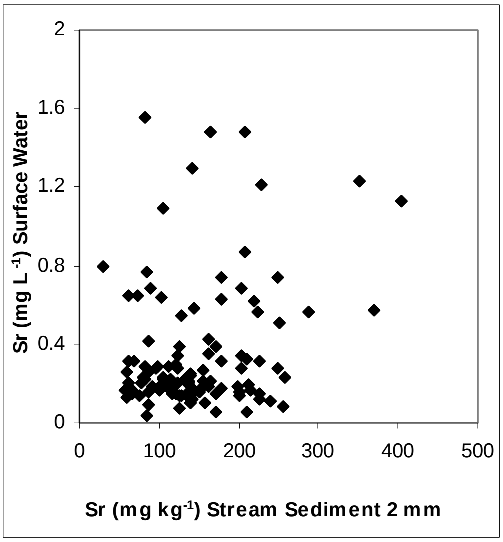

Cu (ug L^{-1}) Surface Water
12
10
8
6
4
2
0
0
200
400
600
800
1000
Cu (mg kg^{-1}) Stream Sediment 2 mm

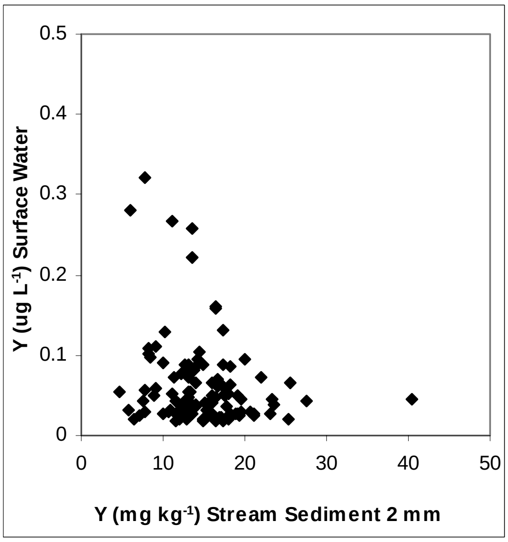

Zn (ug L^{-1}) Surface Water
200
160
120
80
40
0
0
500
1000
1500
2000
2500
Zn (mg kg^{-1}) Stream Sediment 2 mm

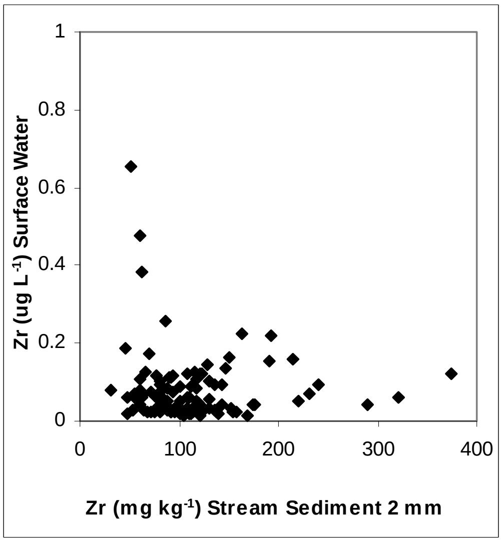

As (ug L-1) Surface Water
160
120
80
40
0
0
20
40
60
80
100
As (mg kg-1) Stream Sediment 2 mm

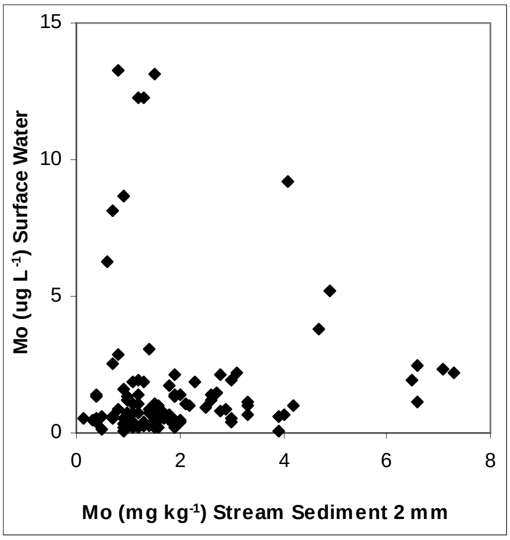

Se (ug L-1) Surface Water
5
4
3
2
1
0
0
10
20
30
Se (mg kg-1) Stream Sediment 2 mm

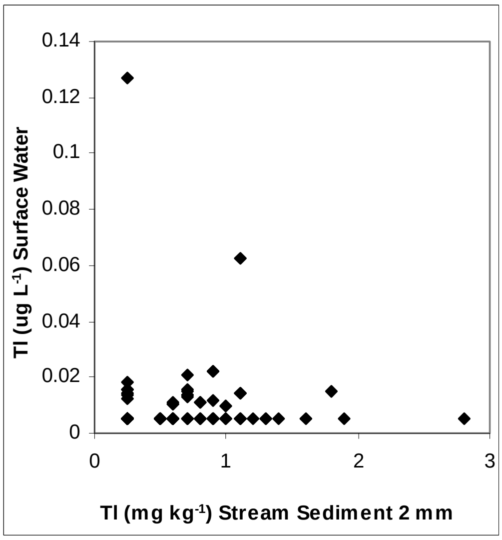

Rb (ug L-1) Surface Water
25
20
15
10
5
0
0
10
20
30
40
50
Rb (mg kg-1) Stream Sediment 2 mm

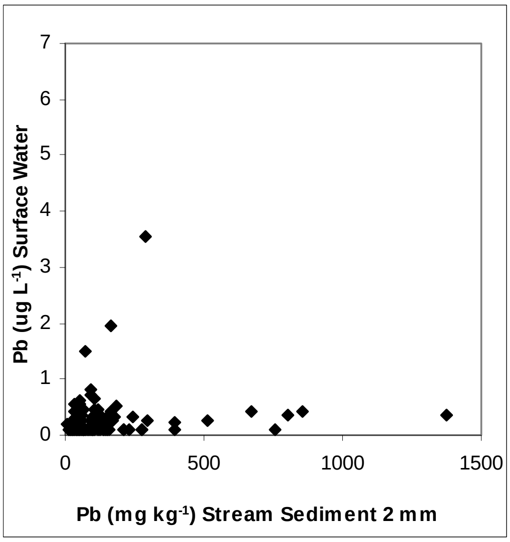

Sr (mg L-1) Surface Water
2
1.6
1.2
0.8
0.4
0
0
100
200
300
400
500
Sr (mg kg-1) Stream Sediment 2 mm

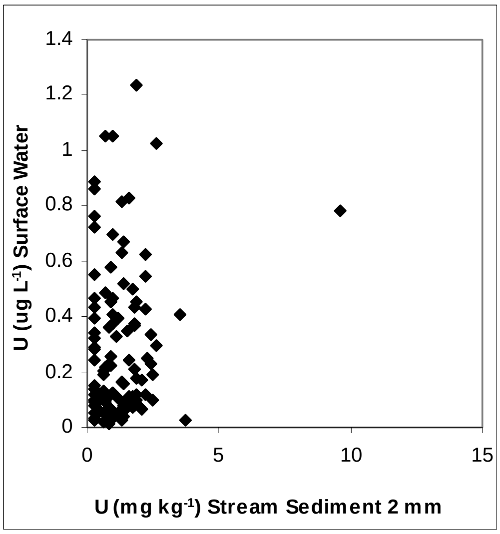

Y (ug L-1) Surface Water
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
Y (mg kg-1) Stream Sediment 2 mm

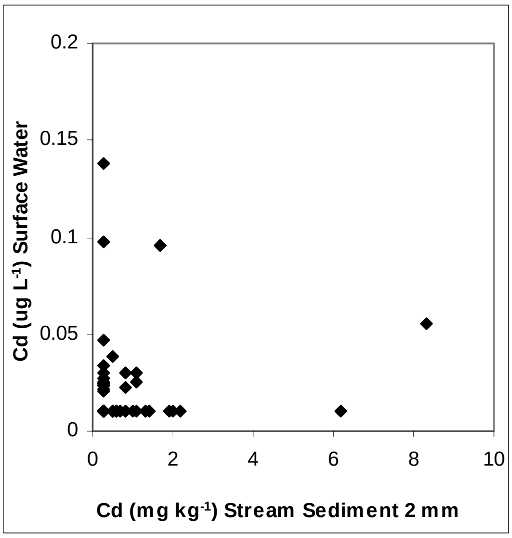

Zr (ug L-1) Surface Water
1
0.8
0.6
0.4
0.2
0
0
100
200
300
400
Zr (mg kg-1) Stream Sediment 2 mm

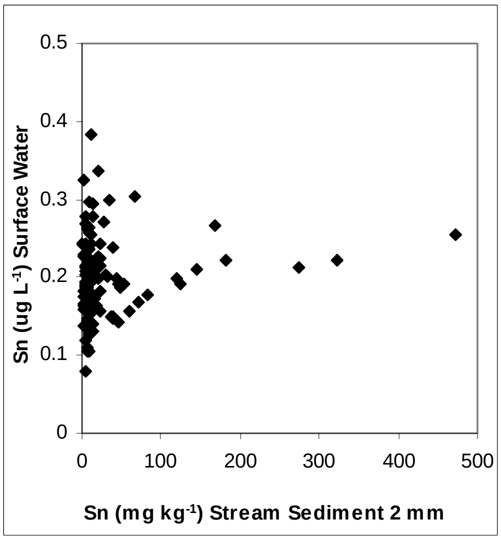

Mo (ug L^{-1}) Surface Water
Mo (mg kg^{-1}) Stream Sediment 2 mm
15
10
5
0
0
2
4
6
8

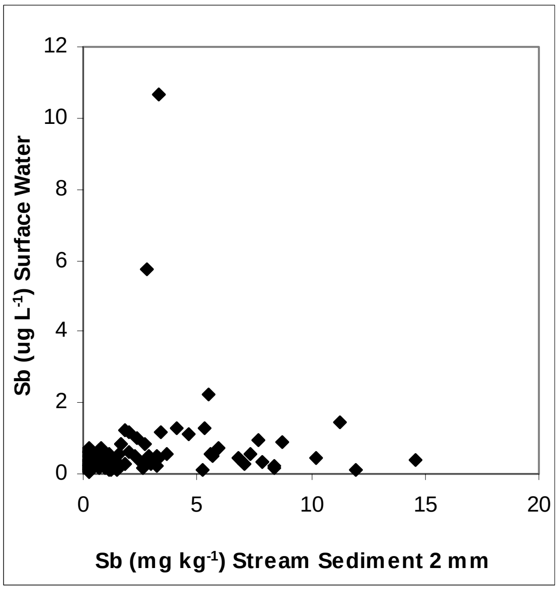

Tl (ug L^{-1}) Surface Water
Tl (mg kg^{-1}) Stream Sediment 2 mm
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0
1
2
3

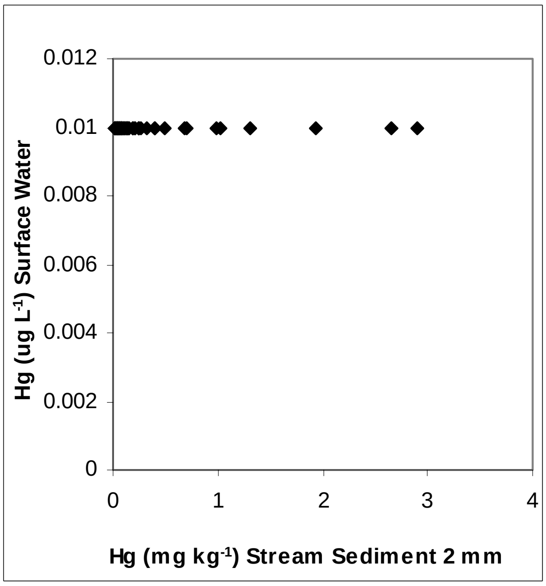

Pb (ug L^{-1}) Surface Water
Pb (mg kg^{-1}) Stream Sediment 2 mm
7
6
5
4
3
2
1
0
0
500
1000
1500

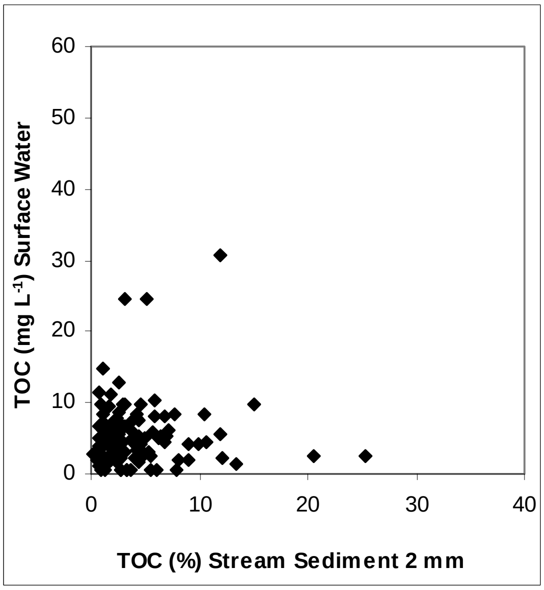

U (ug L^{-1}) Surface Water
U (mg kg^{-1}) Stream Sediment 2 mm
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
5
10
15

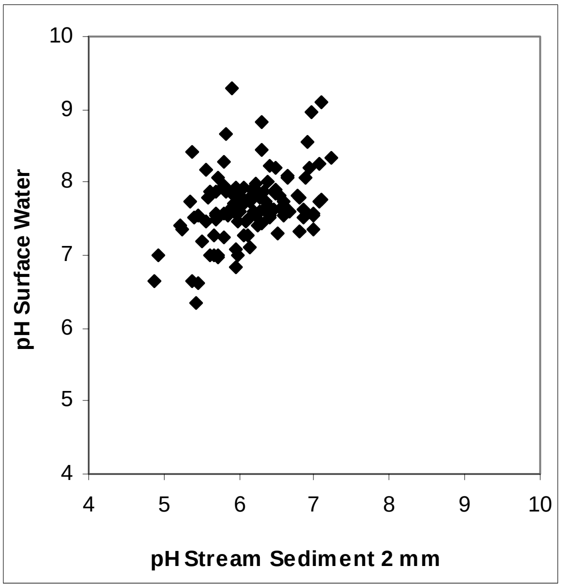

Cd (ug L^{-1}) Surface Water
Cd (mg kg^{-1}) Stream Sediment 2 mm
0.2
0.15
0.1
0.05
0
0
2
4
6
8
10

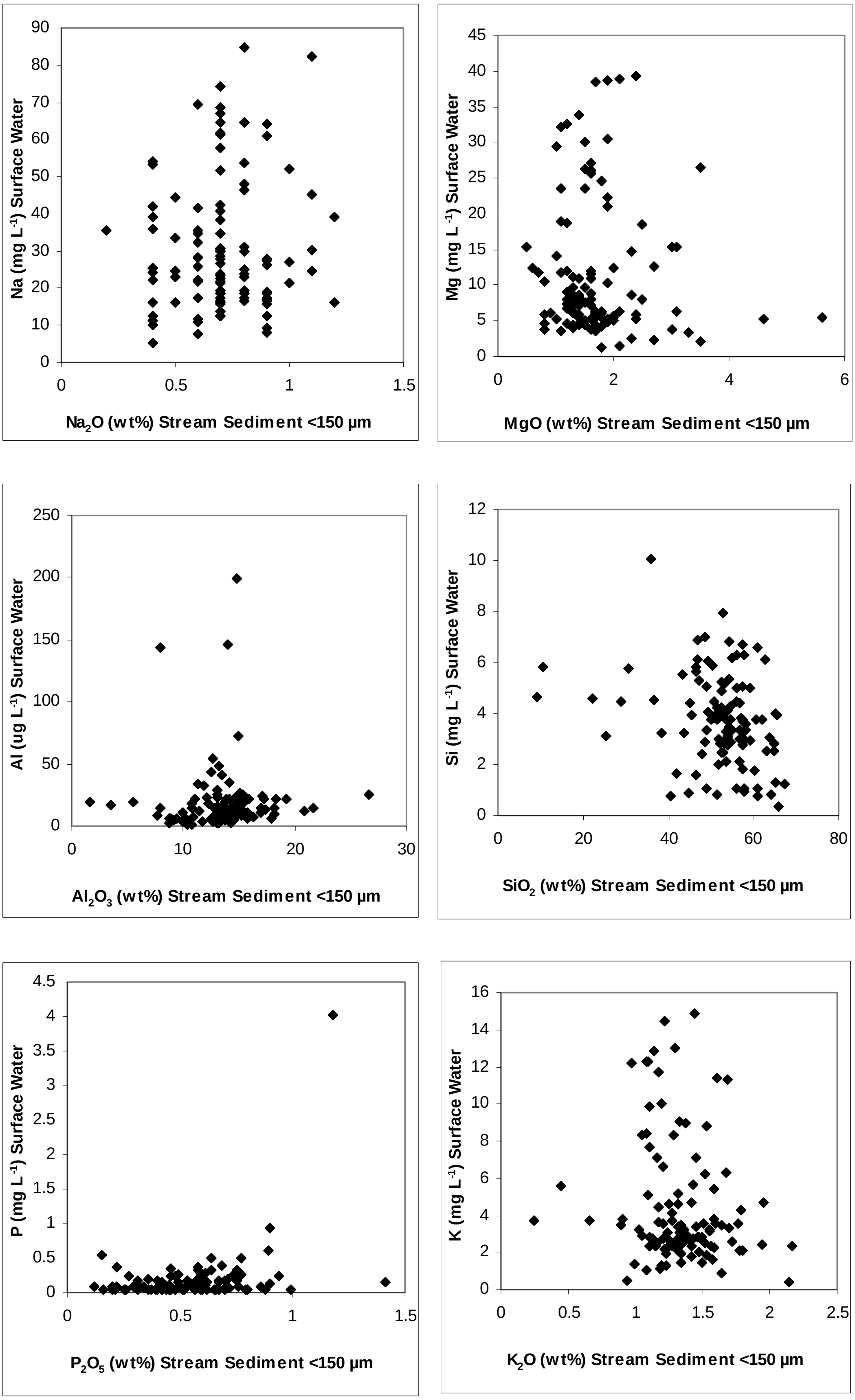

Sn (ug L^{-1}) Surface Water
Sn (mg kg^{-1}) Stream Sediment 2 mm
0.5
0.4
0.3
0.2
0.1
0
0
100
200
300
400
500


Sb (ug L^{-1}) Surface Water
12
10
8
6
4
2
0
0
5
10
15
20
Sb (mg kg^{-1}) Stream Sediment 2 mm


Hg (ug L^{-1}) Surface Water
0.012
0.01
0.008
0.006
0.004
0.002
0
0
1
2
3
4
Hg (mg kg^{-1}) Stream Sediment 2 mm

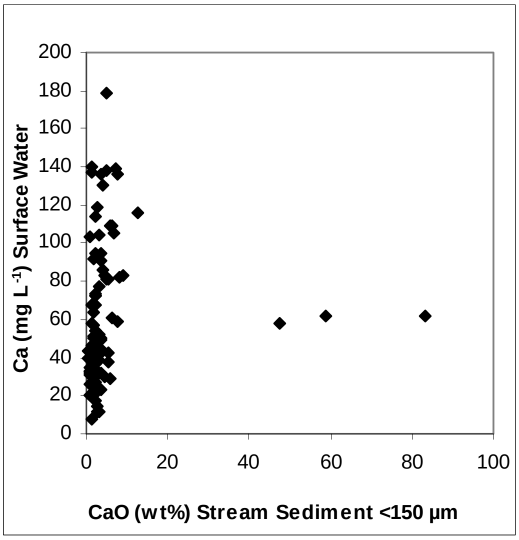

TOC (mg L^{-1}) Surface Water
60
50
40
30
20
10
0
0
10
20
30
40
TOC (%) Stream Sediment 2 mm

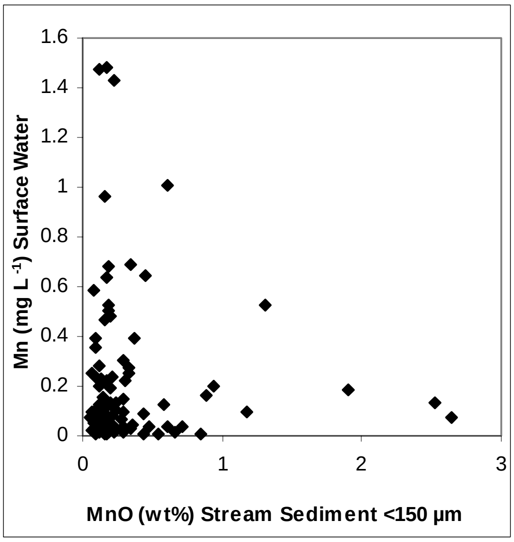

pH Surface Water
10
9
8
7
6
5
4
4
5
6
7
8
9
10
pH Stream Sediment 2 mm

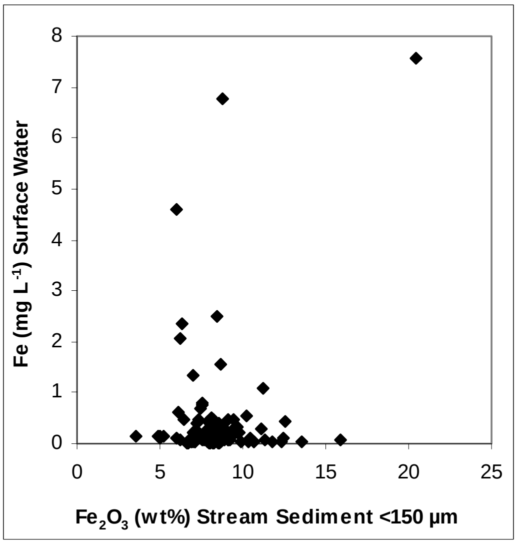


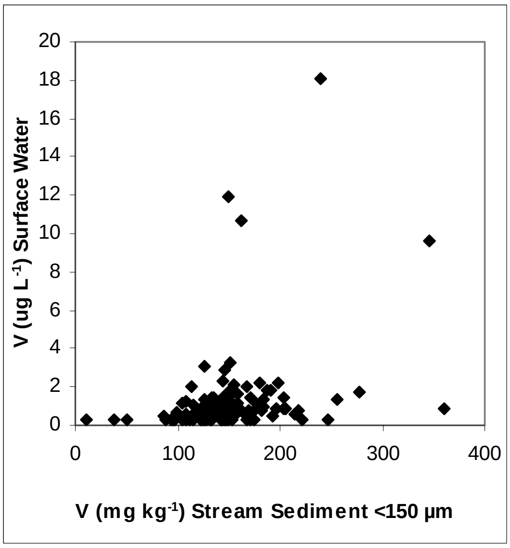
N = 113

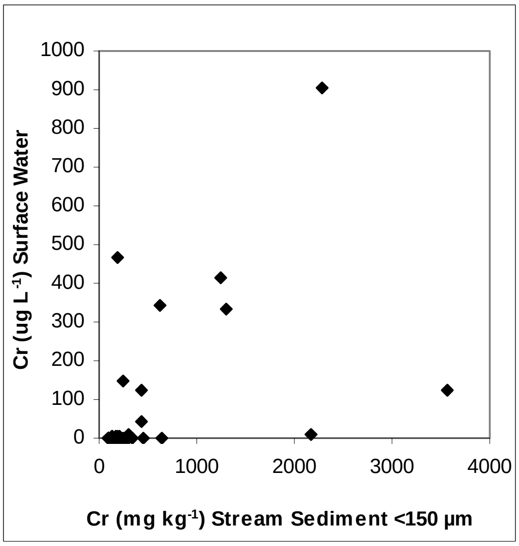
Figure 5.4 Plots of parameter distributions in urban < 150 µm stream sediments and surface waters

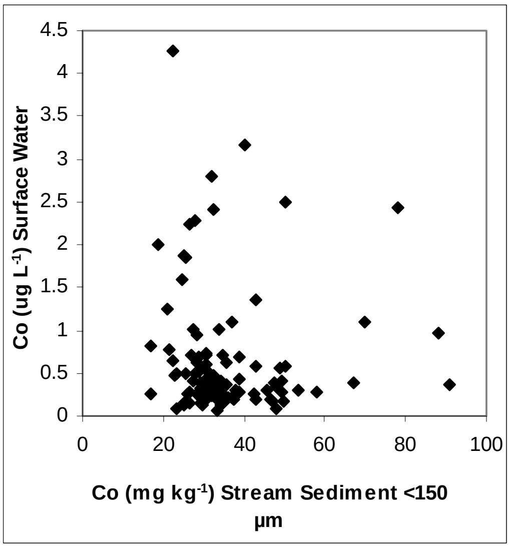

Ca (mg L-1) Surface Water
0
20
40
60
80
100
120
140
160
180
200
0
20
40
60
80
100
CaO (wt%) Stream Sediment <150 µm

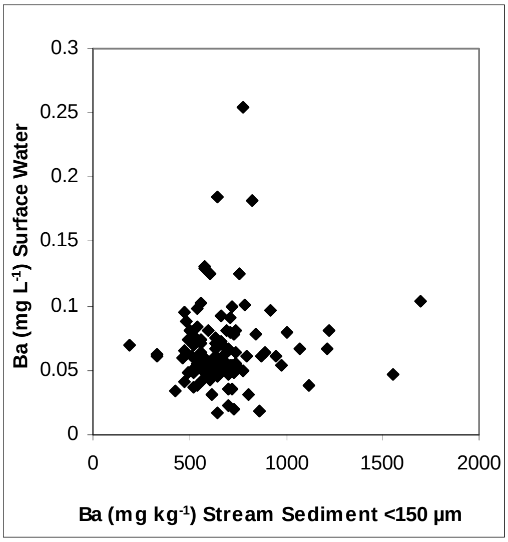

Mn (mg L-1) Surface Water
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
0
1
2
3
MnO (wt%) Stream Sediment <150 µm

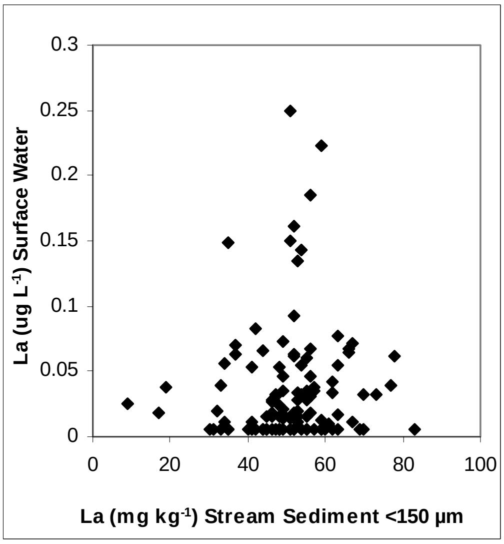

Fe (mg L-1) Surface Water
0
1
2
3
4
5
6
7
8
0
5
10
15
20
25
Fe2O3 (wt%) Stream Sediment <150 µm

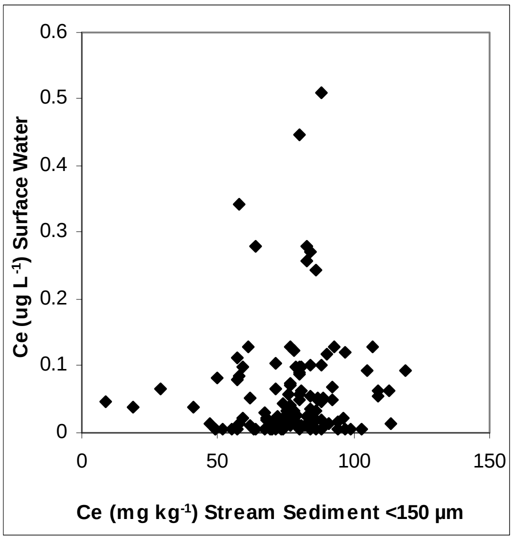

V (ug L-1) Surface Water
0
2
4
6
8
10
12
14
16
18
20
0
100
200
300
400
V (mg kg-1) Stream Sediment <150 µm

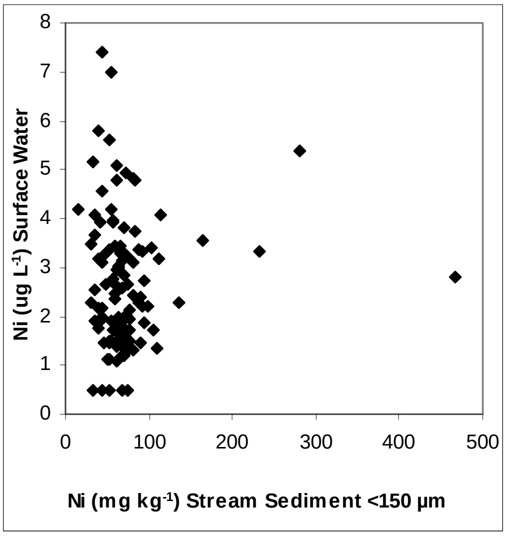

Cr (ug L-1) Surface Water
0
100
200
300
400
500
600
700
800
900
1000
0
1000
2000
3000
4000
Cr (mg kg-1) Stream Sediment <150 µm

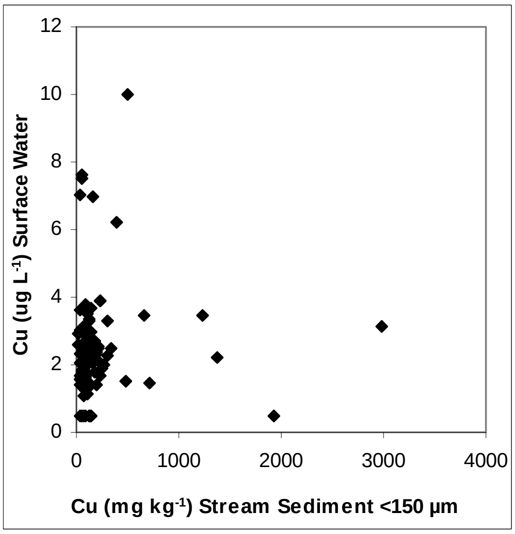

Co (ug L-1) Surface Water
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
0
20
40
60
80
100
Co (mg kg-1) Stream Sediment <150 µm

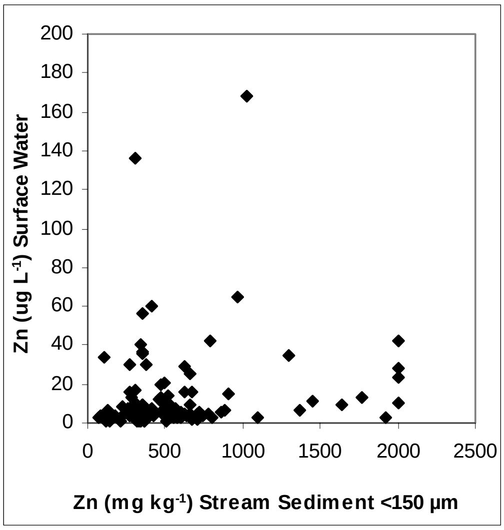

Ba (mg L-1) Surface Water
Ba (mg kg-1) Stream Sediment <150 µm
0
0.05
0.1
0.15
0.2
0.25
0.3
0
500
1000
1500
2000

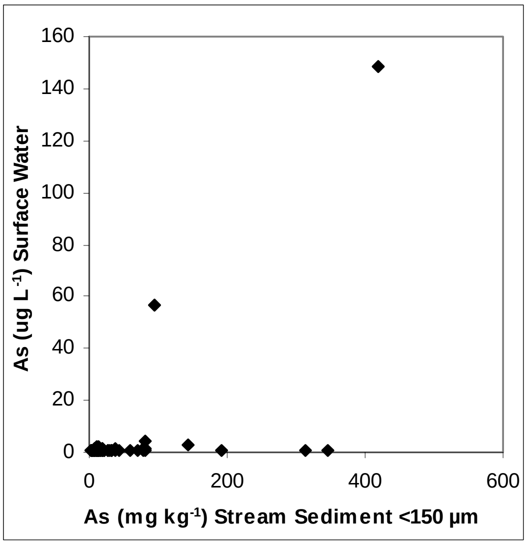

La (ug L-1) Surface Water
La (mg kg-1) Stream Sediment <150 µm
0
0.05
0.1
0.15
0.2
0.25
0.3
0
20
40
60
80
100

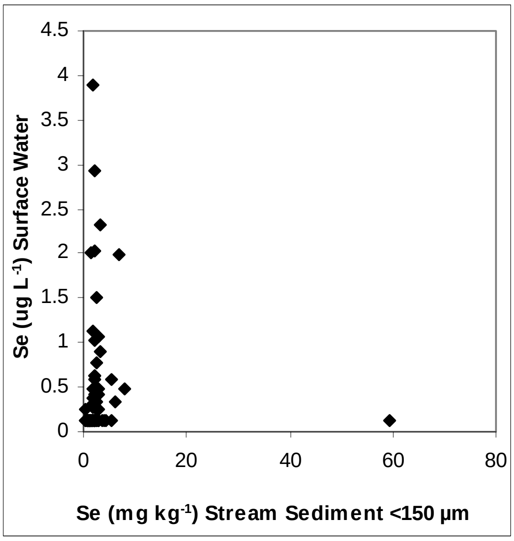

Ce (ug L-1) Surface Water
Ce (mg kg-1) Stream Sediment <150 µm
0
0.1
0.2
0.3
0.4
0.5
0.6
0
50
100
150

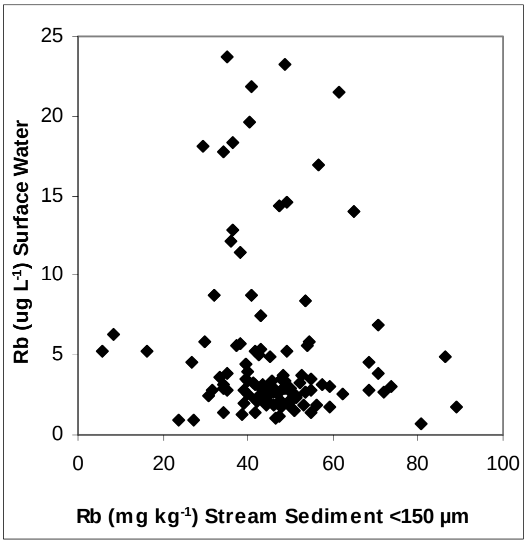

Ni (ug L-1) Surface Water
Ni (mg kg-1) Stream Sediment <150 µm
0
1
2
3
4
5
6
7
8
0
100
200
300
400
500

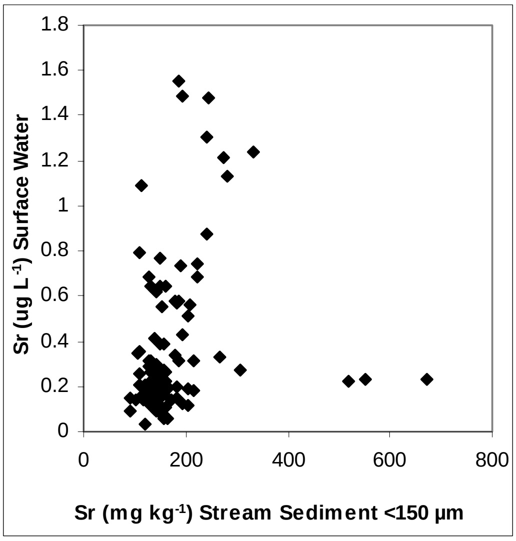

Cu (ug L-1) Surface Water
Cu (mg kg-1) Stream Sediment <150 µm
0
2
4
6
8
10
12
0
1000
2000
3000
4000

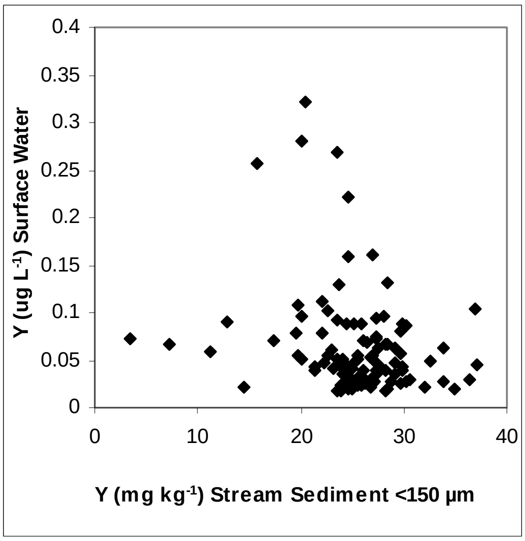

Zn (ug L-1) Surface Water
Zn (mg kg-1) Stream Sediment <150 µm
0
20
40
60
80
100
120
140
160
180
200
0
500
1000
1500
2000
2500

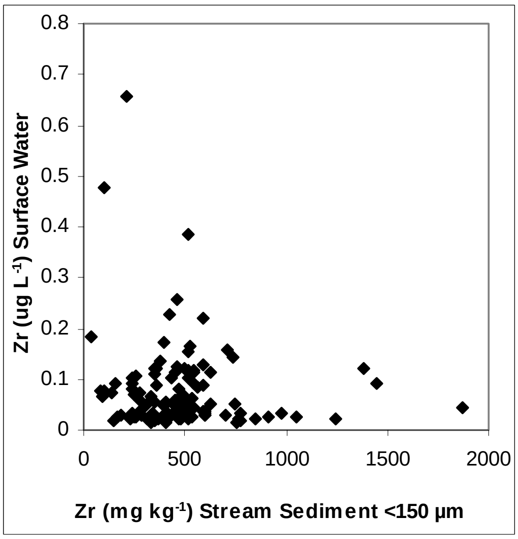

As (ug L-1) Surface Water
160
140
120
100
80
60
40
20
0
0
200
400
600
As (mg kg-1) Stream Sediment <150 µm

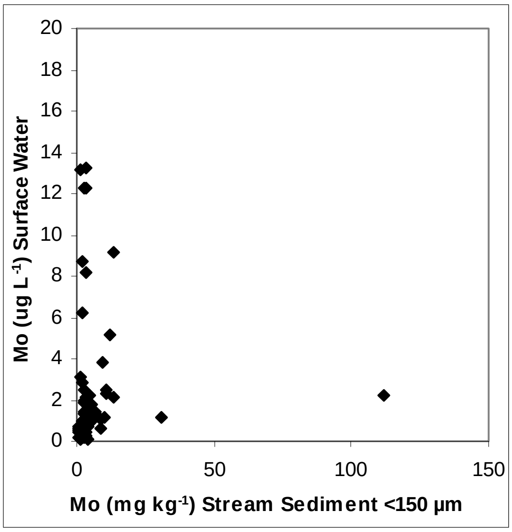

Se (ug L-1) Surface Water
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
20
40
60
80
Se (mg kg-1) Stream Sediment <150 µm

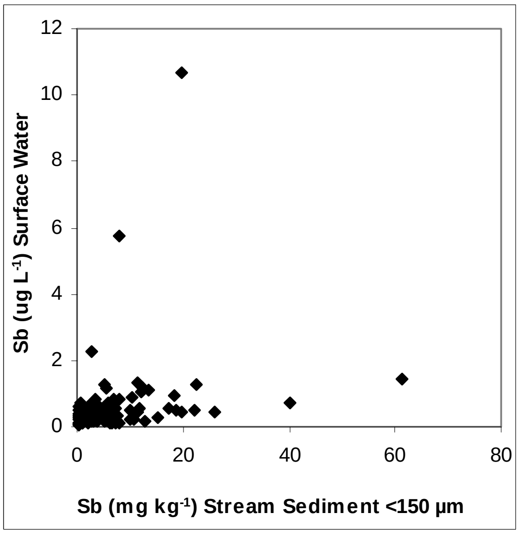

Rb (ug L-1) Surface Water
25
20
15
10
5
0
0
20
40
60
80
100
Rb (mg kg-1) Stream Sediment <150 µm

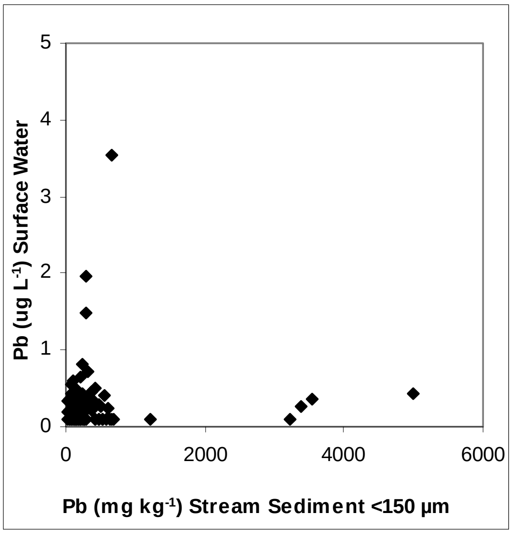

Sr (ug L-1) Surface Water
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
200
400
600
800
Sr (mg kg-1) Stream Sediment <150 µm

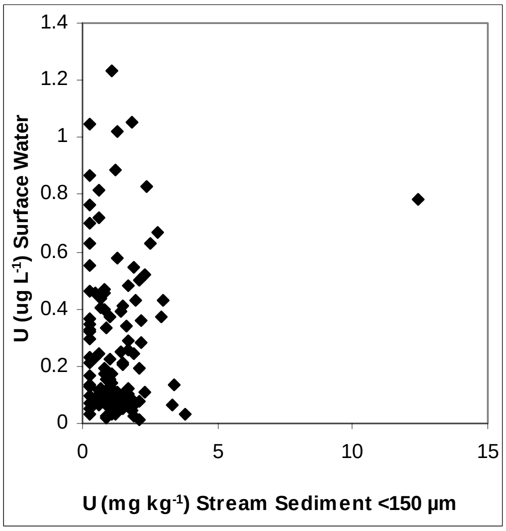

Y (ug L-1) Surface Water
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
10
20
30
40
Y (mg kg-1) Stream Sediment <150 µm

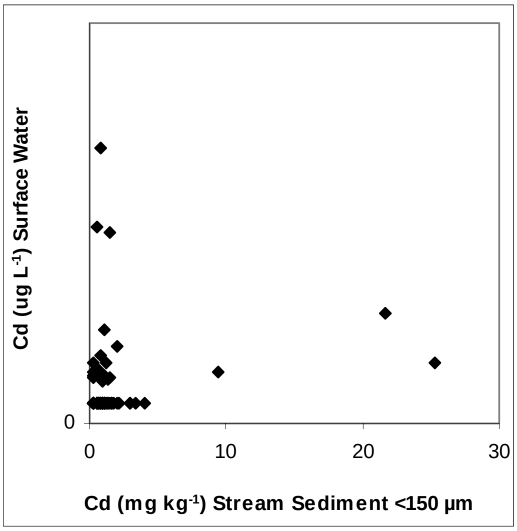

Zr (ug L-1) Surface Water
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
500
1000
1500
2000
Zr (mg kg-1) Stream Sediment <150 µm

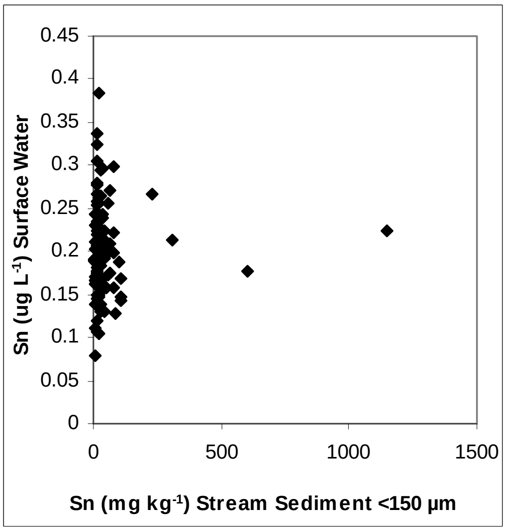

Mo (ug L-1) Surface Water
0
2
4
6
8
10
12
14
16
18
20
0
50
100
150
Mo (mg kg-1) Stream Sediment <150 µm


Sb (ug L-1) Surface Water
0
2
4
6
8
10
12
0
20
40
60
80
Sb (mg kg-1) Stream Sediment <150 µm


Pb (ug L-1) Surface Water
0
1
2
3
4
5
0
2000
4000
6000
Pb (mg kg-1) Stream Sediment <150 µm


U (ug L-1) Surface Water
0
0.2
0.4
0.6
0.8
1
1.2
1.4
0
5
10
15
U (mg kg-1) Stream Sediment <150 µm


Cd (ug L-1) Surface Water
0
0
10
20
30
Cd (mg kg-1) Stream Sediment <150 µm


Sn (ug L-1) Surface Water
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0
500
1000
1500
Sn (mg kg-1) Stream Sediment <150 µm

5.5 INORGANIC DETERMINANDS IN < 2 MM SEDIMENTS

Parameter distributions in < 150 µm sediments are presented in Annex 3 for information but are not considered further as many of the guideline values which give an indication of contamination refer to < 2 mm material, however, the guideline values are shown in Annex 3 for comparison. Maps showing the distribution of inorganic determinands in < 2mm stream sediments are presented in Annex 4 of this report. Soil guideline values and mean concentrations of parameters in stream sediments from rural areas are included on the maps for comparison. However, it should be noted that many of the guidelines refer to soils and do not necessarily imply risk in sediments rather highlight areas that should perhaps be investigated in more detail to establish risk. Comparisons with land use and potential contaminant sources are not examined in detail as part of this report but it is recommended that these issues be investigated further as part of the proposed follow-on Clyde estuary-Clyde basin study.

5.5.1 Inter-Parameter Relationships

The TOC content and pH of sediments can exert significant controls on the amount and mobility of elements present. The results of this study show that the metal elements V, Co, Ba, Ni, Cu, As, Se, Pb, U, Cd and Sb are significantly correlated (95% confidence level) with TOC in < 2 mm sediments as expected (Table 5.2). Of the metal elements, only Cd and Se show significant (95% confidence level) negative relationships with pH, the lack of significant correlations between pH and many of the other metal elements probably reflects the circum neutral nature of sediments in the Glasgow area. Many of the metal elements (Fe, V, Co, Ba, Ni, Cu, Zn, Sn and Pb) are significantly positively correlated (95% confidence level) with Al and Ga and negatively correlated with Si indicating their association with clay minerals rather than coarser fraction quartz-rich materials. Similarly, the majority of metal elements are correlated with Fe and Mn and are probably associated with iron and manganese oxides as well as gross metal contamination related to industrial sources.

5.5.2 Relationships With Artificial Ground

In general, there is little difference in concentration range between parameters collected on sites underlain by artificial ground as defined in Figure 2.5 and those that are not (Figure 5.5). TOC, U, Cd, Mo, Sn, V, Cu, W, Sn, Pb, Ba, Ca, K and P all show marginal elevation over artificial ground and probably reflect the use of coal mining and other waste as fill materials.

5.5.3 Inorganic Determinands

5.5.3.1 ASBESTOS

Interestingly the basic fibres screening carried out by the Alcontrol laboratories during cyanide analysis found no fibres in any of the samples and yet trace amounts of asbestos were reported in 26 samples following more detailed microscopic investigations by the HSL laboratories. It is probable that the basic fibres screening technique is only likely to flag up major asbestos contamination and not the small amounts present in the Glasgow tributaries sediments samples. Trace amounts (< 1%) of chrysotile (white asbestos) and amosite (brown asbestos) were found in samples from the Garscadden, Yoker Mains, Auldhouse,, Brock, White Cart, Molendinar, Camlachie, Battle, Polmadie, Kirk, Newton, Linthouse, Pow, Tollcross and North Calder catchments (Annex 4). Although chrysotile, which is a serpentine mineral and amosite, which is as an amphibole mineral do occur naturally in association with ultrabasic and basic igneous and metamorphic rocks, the most likely source of these trace amounts of fibres in the Glasgow area is anthropogenic. There are no current guidelines for the amount of asbestos in sediments or soils in the UK, however, the US-EPA suggest amounts greater than 1% fibres present should be investigated further (US-EPA, 2004a).

5.5.3.2 TOTAL CYANIDE

Total cyanide above the limit of detection was determined in 7 samples from the Yoker, Linthouse, Camlachie, Carntyne and Kirk catchments (Annex 4). There are currently no UK guideline values for cyanide in sediments or soil but the values reported for the present study (0.5 – 2.35 mg kg^{-1}) are below the former ICRCL soil guideline of 25 mg kg^{-1} (ICRCL, 1987).

5.5.3.3 NON-CLEA SUBSTANCES

For several contaminants there are no current UK soil guidelines therefore distributions are compared to the former ICRCL guidelines or limits from other countries as follows. The results are also compared to the NOAA sediment screening values outlined in Table 1.3 but it should be noted that these are not regulatory guidelines (NOAA, 1999). References to the guideline values used in this section and on the maps in Annex 4 are given in the key to the Annexes of this report.

Low pH values < 5 in sediments are recorded in the peaty area around Bishop Loch and in the Hillington area (site A2) (Annex 4) and have an influence on the concentrations of several of the metal elements in these locations as follows. The range of Sb in sediments (0.25 – 14.6 mg kg^{-1}) is lower than the US-EPA clean-up standard of 28 mg kg^{-1}, highest concentrations of the element are associated with the marshy railway sidings site at GK1 and peaty site at CFB1 (Annex 4).

Barium (Ba) concentrations in excess of the Netherlands soil remediation guideline (625 mg kg^{-1}) occur at N2, TC8 and BLA2 and may relate to coal mining in the case of the first site as well as low pH peaty conditions at all three sites (Annex 4).

Cobalt (Co) and U exceed the German soil guideline values of 50 and 5 mg kg^{-1} respectively only at the marshy railway sidings site GK1 (Annex 4). Concentrations of Cu above the former ICRCL soil guideline of 130 mg kg^{-1} are found in the Linthouse, Newton, Camlachie, White Cart, Auldhouse and Yoker Mains catchments as well as site GK1 and probably relate to industrial contamination. High concentrations at sites GK1, ST1, CFB1 and around Bishop Loch probably also reflect the acid peaty conditions present in these areas. Approximately 75 % of the sites exceed the NOAA sediment screening value of 28 mg kg^{-1} (Annex 4).

Molybdenum (Mo) concentrations above the German soil guideline value of 5 mg kg^{-1} are found in the Molendinar, Light, and Camlachie catchments and may reflect the presence of coals in the east of Glasgow or industrial contamination (Annex 4). More than half the dataset exceeds the German soil guideline value of 50 mg kg^{-1} for V probably as a result of the widespread presence of coals in the Glasgow area and heavy industrial contamination. The peaty acid environments of the railway sidings site GK1 (442 mg kg^{-1}) and samples around Bishop Loch (213 mg kg^{-1}) contain high concentrations of the element.

Zinc (Zn) concentrations greater than the former ICRCL soil guideline of 300 mg kg^{-1} are reported in the Kelvin, North Calder, Auldhouse, Molendinar, Light, Linthouse, Levern, Malls Mire, Carntyne, Camlachie, White Cart, and Eastfield catchments and probably relate to industrial contamination. High values, which may be associated with acid peaty areas, are found around Bishop Loch, TC8 and CFB1. Values in excess of 1000 mg kg^{-1} are reported at the peaty railway sidings site GK1 and at WC11 on the River White Cart. Approximately 75 % of the sites exceed the NOAA sediment screening value of 98 mg kg^{-1} (Annex 4).

Almost all the sites in the case of Al and Fe and 75 % of sites for Mn exceed the NOAA sediment screening values of 2.55, 4 and 4.5 mg kg^{-1} respectively (Annex 4).

5.5.3.4 CLEA SUBSTANCES

As outlined in Chapter 1 of this report, the CLEA model defines soil guideline values (SGVs) for 7 parameters, As, Cd, Cr, Hg, Ni, Pb and Se. Maps of the distributions of these parameters in Glasgow < 2 mm sediments are presented in Annex 4 of this report. Locations where these guideline values are exceeded in sediments are presented in Annex 5.

High (> 20 mg kg^{-1}) As concentrations at sites MO6 and CFB1 probably relate to the presence of peaty acid conditions and precipitates of iron and manganese oxides, which tend to adsorb metals such as As. In contrast, elevated values in the catchments of the River Kelvin, Levern Water and Yoker Mains, Hillington, Molendinar, Camlachie, and Brock burns, probably relate to industrial and effluent contamination (Annexes 4 and 5). Approximately 50 % of the sites sampled exceed the NOAA sediment screening value of 5.9 mg kg^{-1} (Annex 4).

Cadmium (Cd) concentrations exceeding the lowest 1 mg kg^{-1} CLEA soil guideline value are associated with peaty, acid iron and manganese oxide rich environments at CFB1, KTA1, NC4, TC8 and Bishop Loch. However, concentrations above the guideline value in the Kelvin, Linthouse, Hillington, Polmadie, Eastfield, Newton, Molendinar and Camlachie catchments are likely to relate to contamination. High values at the coal miming (N2) and railway sidings (GK1) sites probably reflect a combination of contamination and marshy peaty conditions (Annexes 4 and 5). Approximately 50 % of the sites are above the NOAA sediment screening value of 0.58 mg kg^{-1} (Annex 4).

Concentrations of Cr above the SGV (130 mg kg^{-1}) at Bishop Loch, Kittoch Water, Cleddans and North Calder probably reflect peaty conditions and the presence of iron and manganese oxides in these streams whereas the high values in the Yoker, White Cart, Hole, Merry, Malls Mire, Polmadie, Eastfield, Battle, Molendinar and Camlachie/Light catchments are likely to result from contamination and may be related to the extensive use of chromite processing waste as fill materials over east and southern Glasgow (Annexes 4 and 5). Approximately 95 % of the sites sampled exceed the NOAA sediment screening value of 36 mg kg^{-1} (Annex 4). The dispersal of chromite waste is one of the key contaminated land concerns affecting southeast Glasgow and more detailed examinations of the relationships between tributary inputs and sediment quality in the River Clyde are recommended as part of the proposed follow-up Clyde estuary–Clyde basin study. There is evidence from previous investigations that chromite waste is impacting upon sediment quality of the River Clyde. For example, Whalley et al. (1999) investigated Cr concentrations in sediments from 13 sites from the upper reaches of the Clyde catchment to the Inner Estuary and noted high concentrations in sediments in the Polmadie Burn (3600 mg kg^{-1})

and 6600 mg kg^{-1} in River Clyde sediments immediately downstream of the Polmadie Burn. High concentrations of Cr in sediment were evident up to 1 km downstream of this input. The mobility of Cr in sediments from the Inner Clyde Estuary has also been examined by Hursthouse et al. (2003) who found that variations in concentration could not be explained by grain size and organic matter content alone, but were related to historical industrial contamination.

Lead (Pb) concentrations in sediments exceed the 450 mg kg^{-1} SGV in the Kelvin, Camlachie, White Cart and Auldhouse catchments and probably relate to industrial and surface run-off contamination (Annexes 4 and 5). Approximately 80 % of the sites exceed the NOAA sediment screening value of 35 mg kg^{-1} (Annex 4).

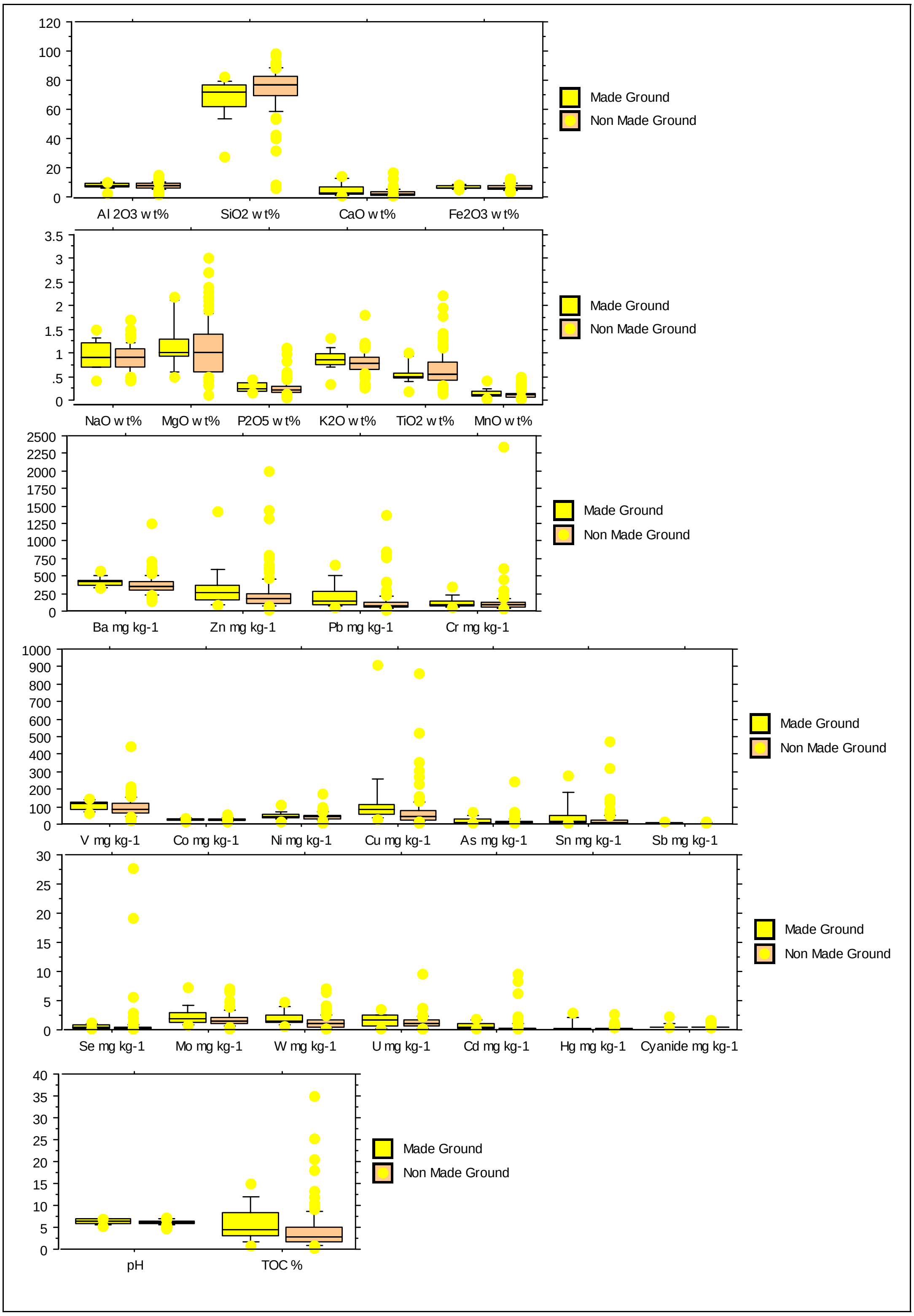
Concentrations of Ni above the SGV of 50 mg kg^{-1} around Bishop Loch, the North Calder, Cityford Burn, Kittoch Water, Cleddans Burn and site TC8 probably reflect the presence of iron and manganese oxides in peaty acid conditions. High concentrations at the railway sidings site GK1 and in the Molendinar, Camlachie, Battle, Kirk, White Cart, Levern, Manse, Auldhouse and Yoker catchments probably relate to industrial contamination (Annexes 4 and 5). Approximately 85 % of the sites exceed the NOAA sediment screening value of 18 mg kg^{-1} (Annex 4).

None of the sediments contain Hg or Se concentrations above the SGVs of 8 and 35 mg kg^{-1} respectively. Highest Hg values are associated with the contaminated catchments of the Polmadie, Malls Mire, Battle and Camlachie Burns and the North Calder. Selenium values approaching the guideline (27.7 mg kg^{-1}) are reported at the marshy railway sidings side GK1 (Annex 4). Approximately 10 % of the data for Hg and 1 % of the data for Ag exceed the NOAA sediment screening values of 0.17 and 4.5 mg kg^{-1} respectively (Annex 4).

Table 5.2 Pearson correlation matrix of parameters in < 2 mm urban stream sediments

	TOC	pH	Na	Mg	Al	Si	P	K	Ca	Ti	Mn	Fe	V	Cr	Co	Ba	Ni	Cu	Zn	Ga	As	Se	Zr	W	Pb	U	Cd	Sn	Sb
pH	**-0.282**																												
Na	**-0.308**	**0.454**																											
Mg	-0.150	**0.496**	**0.836**																										
Al	**-0.179**	**0.363**	**0.498**	**0.658**																									
Si	**-0.601**	0.087	0.074	**-0.252**	**-0.192**																								
P	**0.367**	**-0.177**	-0.128	0.142	**0.211**	**-0.643**																							
K	**-0.231**	**0.358**	**0.589**	**0.629**	**0.776**	-0.094	**0.169**																						
Ca	0.158	**0.464**	0.071	**0.287**	0.035	**-0.481**	0.120	0.038																					
Ti	**-0.190**	**0.261**	**0.650**	**0.777**	**0.728**	**-0.241**	**0.194**	**0.642**	0.013																				
Mn	0.151	**0.429**	0.103	**0.272**	0.146	**-0.416**	0.118	0.035	**0.609**	0.101																			
Fe	-0.031	**0.355**	**0.545**	**0.734**	**0.705**	**-0.384**	**0.344**	**0.518**	0.135	**0.763**	**0.301**																		
V	**0.469**	0.085	0.157	**0.404**	**0.443**	**-0.719**	**0.377**	**0.220**	**0.291**	**0.386**	**0.275**	**0.549**																	
Cr	0.144	0.085	-0.014	0.116	0.008	**-0.166**	**0.396**	0.052	0.114	0.040	0.022	0.035	0.086																
Co	**0.318**	**0.264**	**0.209**	**0.470**	**0.625**	**-0.644**	**0.358**	**0.310**	**0.327**	**0.551**	**0.462**	**0.707**	**0.835**	0.030															
Ba	**0.368**	0.134	0.146	**0.379**	**0.499**	**-0.666**	**0.626**	**0.401**	**0.266**	**0.355**	**0.291**	**0.592**	**0.670**	**0.242**	**0.669**														
Ni	**0.406**	0.141	0.075	**0.335**	**0.557**	**-0.607**	**0.294**	**0.245**	**0.247**	**0.434**	**0.283**	**0.543**	**0.877**	0.079	**0.915**	**0.671**													
Cu	**0.411**	0.007	-0.087	0.034	**0.170**	**-0.339**	0.101	0.017	0.143	0.042	0.056	0.155	**0.599**	0.111	**0.487**	**0.509**	**0.673**												
Zn	**0.409**	0.095	0.015	**0.234**	**0.321**	**-0.455**	**0.313**	**0.122**	**0.224**	0.106	**0.182**	**0.322**	**0.595**	0.050	**0.588**	**0.495**	**0.629**	**0.685**											
Ga	0.030	**0.367**	**0.524**	**0.753**	**0.886**	**-0.432**	**0.291**	**0.733**	**0.188**	**0.813**	**0.264**	**0.820**	**0.593**	0.016	**0.764**	**0.585**	**0.658**	**0.209**	**0.400**										
As	0.141	0.031	0.034	0.079	0.050	-0.131	0.092	0.042	0.096	-0.007	-0.009	0.062	0.122	**0.187**	0.081	**0.231**	0.112	**0.375**	**0.146**	0.025									
Se	**0.634**	**-0.208**	-0.257	-0.132	-0.097	**-0.592**	**0.187**	**-0.175**	**0.189**	-0.088	0.126	-0.057	**0.702**	0.018	**0.463**	**0.265**	**0.574**	**0.498**	**0.456**	0.076	0.036								
Zr	**-0.315**	**0.259**	**0.482**	**0.483**	**0.614**	0.010	0.007	**0.536**	-0.075	**0.757**	0.020	**0.574**	0.124	-0.038	**0.384**	**0.199**	**0.251**	0.001	0.049	**0.614**	0.032	**-0.175**							
W	0.153	-0.131	-0.005	0.074	-0.036	**-0.312**	0.113	-0.021	0.135	0.024	0.078	0.074	**0.370**	0.110	0.158	**0.179**	**0.198**	**0.188**	0.111	0.071	0.038	**0.303**	-0.085						
Pb	**0.264**	0.006	0.061	0.057	0.051	**-0.195**	0.125	-0.071	**0.109**	0.066	0.147	**0.223**	**0.227**	0.055	**0.307**	**0.414**	**0.308**	**0.507**	**0.401**	0.115	**0.180**	0.149	**0.247**	0.007					
U	**0.422**	-0.138	**-0.381**	**-0.191**	0.072	**-0.487**	**0.208**	-0.102	**0.212**	-0.092	0.158	-0.013	**0.645**	-0.018	**0.473**	**0.335**	**0.594**	**0.481**	**0.338**	0.105	0.153	**0.742**	-0.137	**0.385**	0.005				
Cd	**0.666**	**-0.252**	**-0.266**	-0.155	-0.145	**-0.568**	**0.243**	**-0.209**	0.146	-0.137	**0.164**	-0.011	**0.473**	0.019	**0.355**	**0.182**	**0.441**	**0.370**	**0.450**	0.037	0.021	**0.737**	**-0.166**	**0.165**	**0.235**	**0.426**			
Sn	0.109	0.143	0.097	0.123	**0.179**	-0.079	0.011	0.106	0.057	0.101	0.061	**0.220**	**0.217**	0.011	**0.299**	**0.305**	**0.343**	**0.516**	**0.369**	**0.220**	**0.184**	0.045	**0.180**	-0.012	**0.509**	-0.016	0.116		
Sb	**0.381**	0.028	-0.012	0.132	**0.189**	**-0.386**	**0.246**	0.029	0.128	0.059	0.049	**0.322**	**0.609**	0.098	**0.497**	**0.575**	**0.607**	**0.697**	**0.619**	**0.282**	**0.247**	**0.399**	0.058	**0.190**	**0.536**	**0.345**	**0.339**	**0.549**	
Hg	0.059	**0.169**	0.074	**0.167**	0.040	-0.125	0.107	0.048	**0.211**	0.055	0.131	0.125	0.132	**0.286**	0.079	0.152	0.088	0.107	0.116	0.060	0.134	0.020	0.006	0.116	0.107	0.045	0.049	0.124	0.113

R95% = 0.161, n = 112 (Koch and Link, 1970)



N Made Ground = 16
N Non-made Ground = 103
Made ground = artificial ground as defined in Figure 2.5

Figure 5.5 Box and whisker plots showing the 10th, 25th, 50th, 75th and 90th percentiles of element distributions in urban < 2 mm stream sediments categorised according to location on artificial ground.

5.6 ORGANIC COMPOUNDS IN < 2 MM SEDIMENTS

5.6.1 Total Organic Carbon (TOC)

Summary statistics for TOC data are presented in Table 5.1 and the distribution of TOC in sediments in the maps in Annex 6 of this report. Values range from 0.14 – 35 % with high organic contents associated with peaty locations around Bishop Loch, N2 and GK1. High concentrations in the Molendinar and Linthouse catchments are likely to reflect contamination.

5.6.2 Total Petroleum Hydrocarbons (TPH)

Since the Industrial Revolution vast quantities of hydrocarbons have been, and are still contaminating the environment. Past and present land on which fossil fuels were utilised include power generation, transport, oil refineries, gasworks, mining, chemical industries, landfill sites and vehicle scrap yards. Over time these activities have resulted in varying levels of contamination by direct spillage and fall out. With the expansion of conurbations and changes of land use these installations can commonly be located within residential areas at the present day. With the dereliction of industrial sites and inner city areas, fossil fuel installations, motor vehicle maintenance and breaking sites, often represent past and current potential sources of TPH pollution.

The chemical complexity of petroleum releases to the environment arises, in part, from the chemical complexity of petroleum itself. Commercial fractions of petroleum (e.g. naphtha, gasoline, kerosene, gas oil, fuel oils, asphalt etc.), which are defined in terms of their boiling point range, each contain many hundreds of individual chemicals amassed together as a 'spectrum' of closely related compounds. The fractions produced from distillation, each of which is a characteristic subset of the crude oil from which it is distilled, overlap in their composition because there is never a perfect 'cut' or separation during distillation (API, 2001).

Once released to the environment, petroleum constituents partition, to differing extents, between the oil phase and the air, soil, sediment and water phases of the environment (Zemanek et al., 1997). Physical, chemical and biological processes 'weather' or age the spilled product, resulting in additional changes in composition and complexity (Westlake et al., 1974; Morgan and Watkinson, 1989; Pollard et al., 1999).

Decision-makers (e.g. site owners, developers, occupiers and regulators) charged with making informed and scientifically sound decisions about how to manage risks at petroleum-contaminated sites must take into account the complexity of the situation, within a practical decision framework. Among the factors they must take into account are:

- the chemical and physical complexity of the source of contamination and the changes in composition of the contaminating material that have taken place since spillage

- how to measure the extent and nature of contamination in a way that is meaningful and relevant to the risks it may pose

- how to establish toxicological criteria for petroleum contamination in the environment

Different groups or types of organic pollutants have different toxic properties. For example, aromatic compounds such as polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) are more toxic compared to aliphatic compound such as *n*-alkanes. However, there is very little literature on organic pollutants in stream sediments, specifically: environmental legislation, and guideline values and risk-based approaches have not been established in the UK. Therefore, the TPH data presented in this report are compared to information for soils.

Measurements such as "total petroleum hydrocarbons (TPH)" have been used as surrogates for estimating the petroleum load of soils. This parameter, as with all analytical methods, is defined by the method used for analysis. Unless the spillage is well defined, reliance on a single parameter for petroleum hydrocarbons is unlikely to provide a sound basis for risk management (EA, 2003). Surrogate measures, such as TPH analysis, indicate little about the risks posed by contamination (Gustafson, 2002). For example, TPH can be measured in material that is not derived from petroleum: grass has been found to contain 14 000 mg kg^{-1} and dried oak leaves have been found to contain 18 000 mg kg^{-1} (API, 2001).

The Environment Agency (EA, 2003) has highlighted a number of approaches to assessing the health risks from petroleum hydrocarbons in soil. A number of national organisations have proposed methods for setting soil assessment criteria for petroleum hydrocarbon mixtures, using reviews of petroleum toxicology and existing regulatory approaches as a starting point. The approaches used fall broadly into two groups:

- The use of generic assessment criteria for TPH or whole products (diesel fuel, fuel oil etc.). These are usually developed following a review of international values for petroleum hydrocarbons in soil, and are levels above which action is required. Such criteria may or may not be risk based, and the toxicological basis for the criteria may be unclear.

- The use of generic assessment criteria for indicator compounds and/or petroleum fractions together with the use of exposure models. These criteria are toxicologically driven and developed from risk-based approaches. Here the emphasis is on identifying the key indicator compounds and/or petroleum fractions presenting risks at a site, by reference to their toxicology and/or environmental behaviour. These approaches usually start with simple initial assessments and build in complexity, as required, into a 'tiered' approach, similar to that adopted for environmental risk assessment in England and Wales (DETR, 2000). Screening criteria act as an initial check for site assessors; more detailed assessments are undertaken in later tiers if screening criteria are exceeded.

An example of a risk-based indicator compound approach is that developed by the American Society for Testing and Materials (ASTM). ASTM standards E1739-95 and E2081-00 represent three-tier approaches to risk-based corrective action (RBCA) at petroleum- and chemically-contaminated sites (ASTM, 1995 and 2000) and are in wide use in North America and Europe. They rely on reviews of toxicology and environmental fate and exposure, which are used as the basis for the development of risk-based soil screening levels (RBSLs) and site-specific target levels (SSTLs) for assessing risks from contaminated soil. As site assessors move down the three tiers of the assessment, the tiers become less generic and less conservative, although each tier has the objective of compliance with an acceptable level of risk. The RBCA approach assumes a significant proportion of the total impact on human health from all chemicals in soil is due to specific compounds, termed ‘chemicals of concern’, of significant toxicological potency. Other compounds or petroleum fractions are not considered. The most commonly selected chemicals of concern for sites contaminated by gasolines, kerosene and jet fuels are benzene, toluene, ethylbenzene and xylene (BTEX). Depending on the nature of the spill, it may also be necessary to test for lead and other fuel additives. For kerosene and fuel oils, polycyclic (or polynuclear) aromatic hydrocarbons (PAH) are important, and twelve PAH, including benzo[a]pyrene, are evaluated.

Summary statistics for concentrations of aromatic, aliphatic and TPH for the present study are presented in Table 5.3 and maps of TPH and aromatic compound distributions in Annex 6.

Table 5.3 Summary statistics for TPH determinations in sediments

	Concentration (mg kg^{-1})		
	Aromatic	**Aliphatic**	**TPH**
Minimum	46	26	72
Maximum	14041	26043	37879
Mean	1403	1400	2779
Median	564	510	1082
Count*	111	113	113

* N = 115 but no TPH compounds were detected in samples GD2 and WC3 and no aromatic compounds were detected in samples BLA2 and N2

The majority of the sites with the greatest aromatic, aliphatic and TPH concentrations are those associated with the field observations which list gross fuel / oil contamination, strong diesel smells, oily sheens, bus garages, construction sites, domestic rubbish and sanitary waste. Highest concentrations occur at sites PM1, LH1, EF1 CL4 and YM3.

Similar concentrations have been found by other workers, Balba et al. (1991) studied the bioremediation of contaminated soils from railway maintenance yards, where contamination consisted of diesel and heavy motor oil and varied between 5000-60000 mg kg^{-1} dry weight soil of TPH, these were mainly found to be linear branched alkanes of C_{22} and above. At a former gasworks site (Colchester, UK) contaminant levels of 150,000 mg kg^{-1} TPH and 30-40,000 mg kg^{-1} PAH have been recorded (ReMaDe, 2004).

As explained above, reliance on a single parameter (such as TPH) for petroleum hydrocarbons is unlikely to provide a sound basis for risk management and TPH alone indicates little about the risks posed by contamination. The aromatic concentration is useful in that it can provide a more informed assessment for a tiered approach to risk-based screening levels (RBSLs) and site-specific target levels (SSTLs) for assessing risks from contamination. This is because the aromatic fraction mainly consists of PAH and their alkylated derivatives, the minor components being PCB and some pesticide compounds.

Although the high concentration sites were sometimes associated with higher %TOC, there is little or no distinct correlation between %TOC and TPH concentrations. Examples of sample sites with high TOC and relatively low TPH were GK1 (TOC 20.55 %, TPH 2916 mg kg^{-1}) and BLC1 (TOC 11.89 %, TPH 1818 mg kg^{-1}), this is likely to be attributed to high loading of natural plant material in these peaty environments.

5.6.3 Polycyclic Aromatic Hydrocarbons (PAH)

Polycyclic aromatic hydrocarbons (PAH), a class of organic compounds comprising two or more fused aromatic rings, are present in the environment as a result of numerous anthropogenic and biogenic inputs. Concern over PAH arises because certain of their number exhibit toxic, mutagenic and carcinogenic activity (Lehr and Jerina, 1977). In general, low molecular weight two- and three-ringed PAH have significant acute toxicity, whereas four- to six-ringed PAH display higher carcinogenicity. Incomplete combustion and pyrolysis of fossil fuels represent the main source of environmental PAH (McCready et al., 2000). But in addition a petrogenic input of PAH from crude oil, coal or various refinery products can occur. This can be natural, as in oil seepage from depth, or more commonly it is anthropogenic arising as a result of runoff, industrial and sewage discharges, shipping activities, spillage etc.

Summary statistics for the concentrations of the 15 PAH determined in 52 samples appear in Table 5.4. The PAH concentrations for each sample have been summed to give the total PAH content. It should be borne in mind that this ‘total’, though useful for facilitating comparisons, is likely to underestimate the actual total concentration of PAH as it comprises only parental (i.e. non-alkylated) PAH in the two- to seven-ringed range. Also the focus on these non-alkylated species can detract from the recognition of petrogenic PAH where lower molecular weight alkylated homologues and sulphur heterocyclics abound (Bouloubassi and Saliot, 1993). That said, most sediment PAH studies are based on the determination of a limited number of individual PAH - typically between 9 and 28 (Readman et al., 2002) and the use of the 15 or 16 US-EPA PAH has been universally adopted for contaminated land assessment. Maps of the distributions of the key contaminant benzo(a) pyrene and of total PAH are presented in Annex 6.

One exceptional sample had a total PAH concentration of 4225.6 mg kg^{-1}, the remainder falling in the range 2.3 to 295.9 mg kg^{-1}. This high concentration sample (YM3) was full of oil and was taken from the vicinity of a bus garage. The high PAH content is probably largely explicable in terms of the high oil content.

Table 5.4 Summary statistics for PAH determinations in sediments

	Naph thalene	Ace naph thene	Fluor ene	Phenan threne	Anthra cene	Fluor anthene	Pyrene	Benzo (a) anthrax cene	Chry sene	Benzo (b) fluor anthene	Benzo (k) fluor anthene	Benzo (a) pyrene	Dibenzo (ah) anthrax cene	Benzo (ghi) perylene	Indeno (123-cd) pyrene	Total PAH
	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Minimum	0.04	0.02	0.06	0.22	0.02	0.34	0.27	0.11	0.10	0.08	0.08	0.08	0.01	0.03	0.05	2.31
Maximum	88.33	70.70	273.14	1258.89	708.64	844.87	525.95	157.73	109.71	42.63	56.01	61.18	4.02	16.44	8.89	4225.61
Mean	3.70	2.89	8.23	31.88	15.37	22.26	15.00	6.04	4.59	3.29	2.65	3.94	0.65	1.67	1.54	123.69
Median	0.34	0.20	0.48	2.35	0.54	3.18	2.59	1.48	1.49	1.19	0.81	1.52	0.37	0.79	0.76	21.99
Count	52	52	52	52	52	52	52	52	52	52	52	52	52	52	52	52

To set the range of the PAH concentrations for the remaining samples in context, some sediments taken from the Clyde estuary were, in a recent study of UK estuarine PAH, found to be in the range 0.5 to 41.8 mg kg^{-1} for the summed concentrations of 22 PAH and 0.23 to 28.8 mg kg^{-1} for the 4-6 ring members (Rogers, 2002). In other UK estuaries, whose environments are highly industrialised and where similar activities to those in the Clyde region occur, the following ranges were found, River Tyne (0.3 to 43.5 mg kg^{-1}); River Wear (0.2 to

31.7 mg kg^{-1}); River Tees (0.6 to 26.6 mg kg^{-1}) for the summed concentrations of 15 US-EPA PAH (Woodhead et al., 1999). These may be contrasted with the total for the 15 US-EPA PAH in the Solway estuary, a non-industrialised area, where the range is much lower, i.e. 0.1 to 1.5 mg kg^{-1} (Harrison, 2002).

Comparable ranges for PAH to those reported in this study can occur in the highly contaminated sediments found in proximity to urbanized areas, for example, Boston Harbour, Massachusetts, USA, 0.5 to 718.4 mg kg^{-1} (Shiaris & Jambard-Sweet, 1986) and 7.3 to 358.0 mg kg^{-1} (Wang et al., 2001); Milford Haven, UK, 102.5 mg kg^{-1} (Woodhead et al., 1999).

There was little or no correlation between the TOC and the total PAH concentration of the sediments as shown graphically in Figure 5.6. This is probably attributable to the highly PAH contaminated nature of the samples where in addition to the usual global pyrolitic contribution (Yunker et al., 1996), which frequently displays a somewhat loose though significant correlation with TOC (see for example Harrison, 2002), there are a variety of other industrial petrogenic inputs. This is typical for a region characterised by a large conurbation, (contributing combustion and run-off PAH from traffic, coal burning etc.) and a high density of riverside industry (contributing both combustion-related and industry-specific PAH).

In the main, the relative proportions of PAH are similar in many of the samples regardless of sampling location and total concentration. The pattern corresponds with one that is typical globally and epitomises PAH assemblages that result from high temperature combustion processes (McCready et al., 2000). It is characterised by an abundance of the high molecular weight PAH, (i.e. the 4-, 5-, 6- and 7-ringed members), eight of which tend to predominate. These are benzo(b+k)fluoranthenes, pyrene, fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, benzo(a)- anthracene, chrysene, and indeno(1,2,3-cd) pyrene. Phenanthrene, the most thermodynamically stable of the 3-ringed PAH, may be prominent also, although if it is present in large amounts, i.e. so that the phenanthrene:anthracene ratio is greater than 10, then this may be indicative of a petrogenic origin (Budzinski et al., 1997). The relative abundance of the PAH in the sediments were ranked and tabulated (Table 5.5). The eight high molecular weight pyrolitic PAH together with phenanthrene were ranked in order of their prevalence. It was observed that there were some divergences from the nine pyrolitic PAH being exclusively the predominant species, usually where significant amounts of low molecular weight PAH were present. This is indicative of a petrogenic contribution to the overall PAH content, possibly from petrol, diesel, fuel oils, lubricating oils etc.

Another approach for the ascription of petrogenic/pyrolitic PAH origin is the use of molecular indices criteria based on isomeric ratios (Readman et al., 2002). The criteria arise from thermodynamic considerations of the behaviour of pairs of PAH isomers. For instance phenanthrene is more thermodynamically stable than its isomer anthracene. Accordingly, the phenanthrene: anthracene ratio is found to be temperature dependent. At low temperature, (for example, the slow thermal maturation of organic matter in petroleum), the phen/anth ratio is high (50 at 100 °C) but at higher temperatures, (for example the combustion of fossil fuels), it is much lower (4 to 10). The criteria of phen/anth >10 for petrogenic and <10 for pyrolitic inputs emerges. It must be borne in mind that this is not rigorous and borderline values need to be treated with caution. For example, phen/anth ratios <15 usually relate to incomplete combustion of organic matter, yet the analysis of some petroleum products, can produce ratios as low as 4 to 10 for gas-oils and approximately 14 for crude oils before combustion (Budzinski et al., 1997). Similar logic may be applied to the fanth/pyr ratio, where values >1 are classically related to pyrolitic origins, but again there are exceptions. A combination of these two ratios graphically, as illustrated by Figure 5.7, provides a more reliable estimate of PAH source (Baumard et al., 1998). The ratio of the pair of isomers, benz(a)anth/chrys has yielded the criteria: >0.9 (pyrolitic) and ≤ 0.4 (petrogenic) with the same caveat of caution, particularly in the intermediate zone (Gschwend and Hites, 1981). Whilst another pair of isomers have been used in the form of the ratio of indeno(1,2,3-cd)pyrene to indeno(1,2,3-cd) pyrene plus benzo(ghi)perylene. The criteria that emerge here are that if this ratio is <0.2 a petroleum source is indicated, 0.2 to 0.5 implies liquid fossil fuel (vehicle and crude oil) combustion, and ratios >0.5 betoken coal, grass or wood combustion (Yunker et al., 2002).

Table 5.6 presents the molecular indices for the sediments. Apart from the phen/anth ratios the other isomeric pair ratios would seem to indicate that pyrolitic processes are primarily responsible for the PAH content of the samples. Only samples PM1 and LV4 show some indications of petrogenicity based on fanth/pyr ratios (approximately 0.7). Again the benz(a)anth/chrys ratio of 0.41 hints at some PAH of petrogenic origin in LV4. PM1 has gross fuel/oil contamination and LV4 is in proximity to a gasworks.

Examining the phen/anth ratios it becomes apparent that samples PM1, N2, CF2, BT2, KN4, CFB1, N4, and LV4 all exhibit some degree of petrogenic character and this is more readily discernible on the graphical plot (Figure 5.7) where all these samples plot well outside the boundaries of the pyrolitic quadrant. Interestingly, all these samples belong to those that diverge from the pyrolitic pattern when ranked in order of PAH prevalence (Table 5.5).

Although the suite of 15 or 16 US-EPA PAH are commonly encountered in contaminated land assessment they do not usually provide sufficiently detailed information on PAH distributions to permit definitive links to be made between specific sources of PAH contamination and observed sediment loads. Their principle value is in providing an estimate of total and individual PAH concentrations. Even when greater detail is obtained by increasing the number of PAH analysed, specific source identity is still invariably hindered by the complexity and diversity of inputs.

Overall, there would appear to be diverse PAH inputs and the distributions are indicative of a mainly pyrolitic input, augmented with a variety of industrial and commercial petrogenic inputs. Many of the samples have total PAH concentrations above the threshold trigger concentration (50 mg kg^{-1}) for use of land as domestic gardens, allotments and play areas (ICRCL, 1987). But none, except YM3 (Total PAH 4225.6 mg kg^{-1}), were above the action level of 500 mg kg^{-1}. The ICRCL guidelines were withdrawn by DEFRA in December 2002 because, although they had previously proved a useful guidance tool, it was considered that they did not suitably assess the 'significant possibility of significant harm to human health' and that the approach was not in line with current statutory policy. They will be replaced by the SGVs (Soil Guidance Values) that will emerge from the EA's CLEA model. Total PAH will be superseded by SGVs for a number of individual PAH that pose the most significant risk to human health such as benzo(a)pyrene. Although this SGV information is still in preparation the benzo(a)pyrene concentration values have for convenience been highlighted separately in Table 5.6 together with what is referred to as the B(a)P equivalent (Mastral et al., 2003) and the maps in Annex 6. The B(a)P equivalent takes into account the health risk arising from benzo(a)pyrene and additionally that due to other carcinogenic PAH in proportion to their carcinogenicity:

$$\text{B(a)P equiv.} = \text{B(a)P} + 0.6\ \text{DB(ah)A} + 0.06\ \text{B(a)A} + 0.07\ \text{B(b+k)F} + 0.08\ \text{I(123cd)P}$$

This equivalence approach may be helpful given that a document prepared to advise and aid in the formulation of appropriate SGVs noted that because soils contain not just benzo(a)pyrene but an array of PAH it is important that the toxicological significance of the whole PAH mixture is taken into account (EA, 2002).

A key objective of the WFD (Water Framework Directive - 2000/60/EC) is the establishment of an integrated framework for the protection of inland water systems, groundwater and coastal waters based on the principle of minimum anthropogenic impact (CEC, 2000). Since the WFD also proposes that 32 priority substances, which includes all PAH classed as a single substance, be phased out so that releases to the aquatic environment will cease within 20 years, these data should be of use in identifying and monitoring PAH sources that will impact the quality of water in the River Clyde corridor.

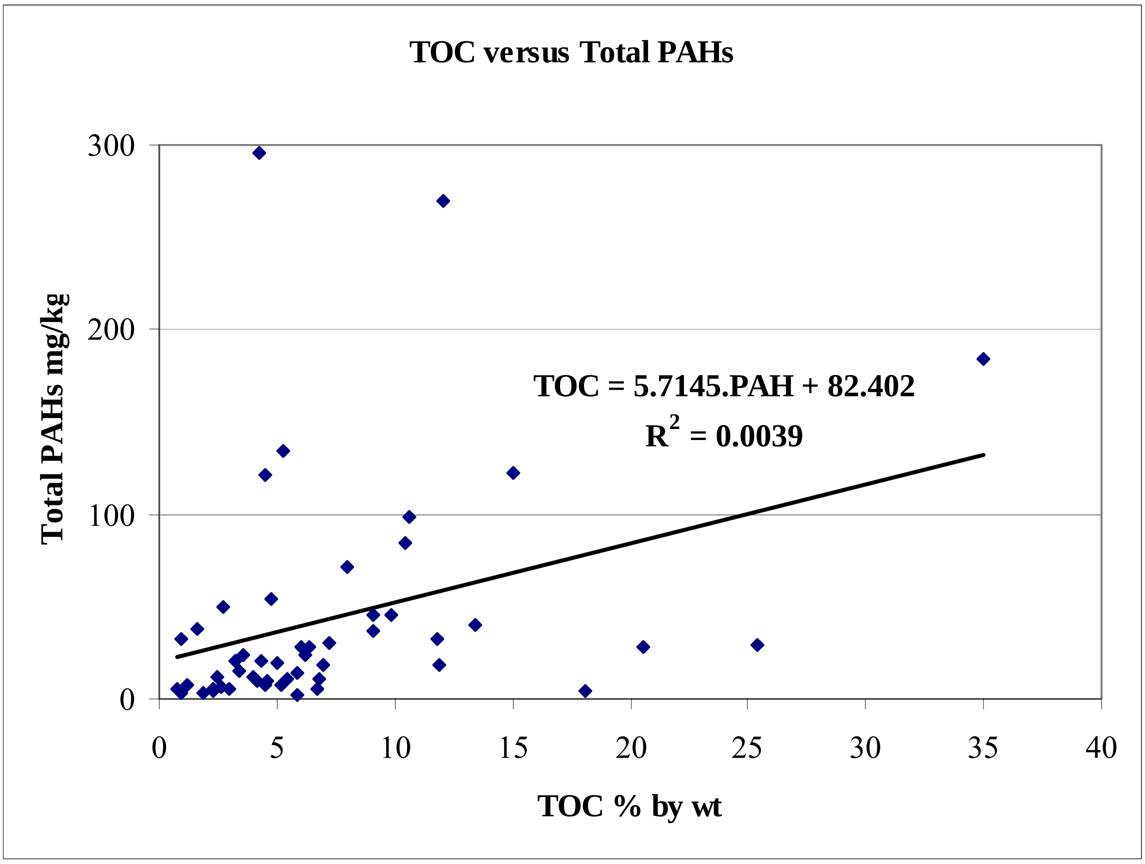


Figure 5.6 Correlation between total PAH concentrations and TOC %

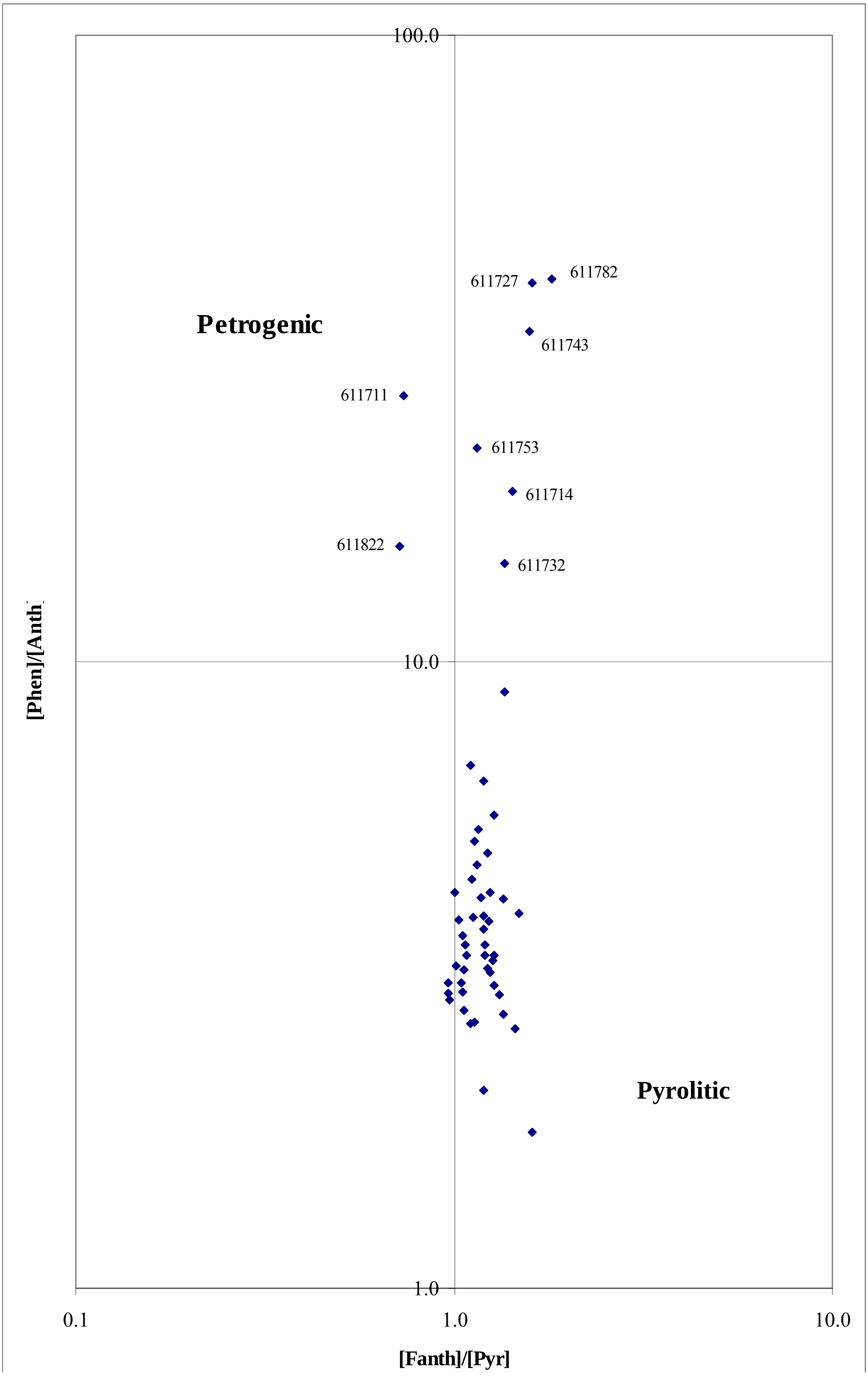


Figure 5.7 Isomeric ratios plot for PAH origin assessment

Table 5.5 PAH abundance-order and summed PAH

BGS Code	GCC Code	Naph	Ace	Fluor	Phen	Anth	Fanth	Pyr	B(a) A	Chrys	B(b+k) F	B(a) P	DB (ah)A	B(ghi) P	I(123cd) P	Total PAH
																mg kg^{-1}
Typ. PS					9		3	2	6	7	1	4		5	8	
611704	LH1				5		1	2	8	6	3	4		7	9	122.7
611707	NT1				9		2	3	5	6	1	4		7	8	45.3
611711	PM1			5	2		6	4	1	7	3	8		10	9	84.5
611714	N2	6		4	1		2	3	9	8	5	7		10	11	4.0
611718	BT1				3	9	1	2	6	5	4	7		10	8	20.4
611720	GN1				9		1	2	6	5	3	4		8	7	3.7
611721	MOA1				7		1	2	6	5	3	4		8	9	5.3
611725	EF1				9		2	1	6	5	3	4		7	8	45.7
611726	CL5				4		1	2	7	6	3	5		8	9	36.9
611727	CF2	2	4	3	1	11	5	6	9	8	7	10		12	13	134.8
611729	KN5	6	11	4	1	10	2	3	8	9	5	7	12	14	13	2.3
611732	BT2	3	5	2	1	11	4	6	10	9	7	8		12	13	54.4
611733	GD3				4		1	2	7	6	3	5		9	8	11.5
611736	MO3				3		1	2	7	6	4	5		8	9	5.2
611737	BLA2			10	2	8	1	3	7	6	5	4		9	11	29.7
611740	GK1				4		1	3	6	7	2	5		8	9	28.0
611742	YK3				9		1	2	6	5	3	4		7	8	37.4
611743	KN4	2	4	3	1	11	5	6	10	9	7	8	13	12	14	33.0
611747	YM1	8	9	4	1		2	3	5	7	6	10		11	12	295.9
611749	TC1				7		1	3	5	6	2	4		9	8	24.3
611752	KNA1				7		1	2	6	5	3	4		9	8	4.9
611753	CFB1	2	4	3	1	11	6	7	10	9	5	8		12	13	32.6
611754	TC7				9		1	3	6	5	2	4		8	7	23.6
611757	ST2	7			1		2	3	6	10	4	5		8	9	15.4
611758	KNA2				9		2	3	6	5	1	4		7	8	5.6
611759	MM1			9	2		1	3	6	4	7	5		8	10	28.0
611764	GN2				8		2	2	6	5	1	4		9	7	7.6
611767	NC2				4		2	1	6	7	3	5		8	9	9.6
611772	BLD1	5	3	2	1	4	7	8	5	9	6	10		11	12	184.3
611773	KN7	5			1		2	3	7	8	4	6		10	9	13.7
611776	KN2				3		1	4	6	7	2	5		10	9	19.1
611777	YK1				4		1	2	7	6	3	5		8	9	10.6
611780	BLC1	10	9	8	1	12	2	3	6	7	4	5		13	11	18.0
611782	N4	2	11	3	1		4	6	8	7	5	9		10	12	8.1
611784	MO5				9		1	3	6	5	2	4		7	8	49.8
611785	YM3	9	10	5	1	3	2	4	6	7	8	11		12	13	4225.6
611790	A2	9			1		2	4	6	7	3	5		8	10	9.7
611791	NC1	11		10	4	9	3	2	6	7	1	5		8	12	11.0
611794	CL2A				2	8	1	3	6	7	4	5		9	10	98.1
611795	WC2				4		2	3	7	6	1	5		8	9	17.9
611796	KK1				4		1	2	6	7	3	5		9	8	121.8
611798	CL4			9	2	7	1	3	5	8	4	6		11	10	269.2
611801	KTB1				4		1	3	6	7	2	5		9	8	71.1
611805	AH3				5		1	2	7	6	3	4		8	9	29.9
611819	AH1				5		1	2	6	7	3	4		9	8	20.1
611822	LV4	11		10	5		3	2	6	4	1	9	8	7	12	3.2
611823	WC7				4		1	3	7	6	2	5		9	8	6.3
611827	MO2				2	9	1	3	7	6	4	5		8	10	39.8
611834	BK2	8			3		2	4	7	6	1	5	9	11	10	4.3
611838	WCC2	10		8	1		2	4	7	6	3	5		11	9	7.4
611876	WC10				5		1	2	6	7	3	4		9	8	12.0
611896	WCA1				9		1	3	6	5	2	4		8	7	28.5

Typ PS = Typical Pyrolitic Source (McCready et al., 2000)

Table 5.6 Isomeric Ratios and Benzo(a)pyrene Factors

BGS	GCC	Isomeric Ratios				Benzo(a)pyrene	
Code	Code	Phen/Anth	Fanth/Pyr	B(a)A/Chrys	I(123-cd) / I(123-cd)+B(ghi)P	B(a)P mg kg^{-1}	B(a)P Equivalent mg kg^{-1}
611704	LH1	3.26	1.01	0.87	0.50	13.7	17.8
611707	NT1	2.65	1.11	1.12	0.50	4.6	6.3
611711	PM1	26.56	0.73	3.76	0.53	3.1	5.5
611714	N2	18.74	1.42	0.85	0.49	0.1	0.2
611718	BT1	3.54	1.21	1.00	0.51	1.6	2.2
611720	GN1	3.22	1.06	0.95	0.53	0.4	0.5
611721	MOA1	2.97	1.05	0.97	0.47	0.5	0.7
611725	EF1	2.95	0.96	0.85	0.48	5.2	6.8
611726	CL5	3.53	1.07	0.93	0.50	3.4	4.5
611727	CF2	40.33	1.60	1.00	0.49	1.4	1.9
611729	KN5	5.69	1.28	1.08	0.63	0.1	0.2
611732	BT2	14.36	1.36	0.94	0.48	1.5	2.0
611733	GD3	4.73	1.15	0.96	0.51	1.0	1.4
611736	MO3	3.65	1.05	0.83	0.43	0.5	0.6
611737	BLA2	3.40	1.21	0.86	0.45	2.5	3.1
611740	GK1	3.20	1.24	1.43	0.48	2.8	3.7
611742	YK3	2.07	1.20	0.90	0.50	4.5	5.8
611743	KN4	33.68	1.58	0.96	0.42	0.4	0.5
611747	YM1	3.97	1.49	1.08	0.48	8.7	11.5
611749	TC1	3.33	1.26	1.02	0.53	2.8	3.6
611752	KNA1	3.07	1.04	0.86	0.51	0.5	0.7
611753	CFB1	21.97	1.15	0.87	0.50	0.7	0.9
611754	TC7	2.66	1.13	0.96	0.51	2.7	3.5
611757	ST2	4.20	1.18	1.38	0.48	1.2	1.6
611758	KNA2	2.77	1.06	0.86	0.49	0.7	0.9
611759	MM1	6.84	1.11	0.89	0.48	2.1	2.6
611764	GN2	3.87	1.03	0.86	0.54	0.9	1.1
611767	NC2	3.08	0.97	1.00	0.47	0.9	1.2
611772	BLD1	2.60	1.45	6.74	0.46	0.9	2.2
611773	KN7	5.18	1.13	1.46	0.51	1.3	1.7
611776	KN2	4.94	1.22	1.01	0.52	1.9	2.4
611777	YK1	6.45	1.19	0.97	0.46	1.1	1.4
611780	BLC1	4.28	1.00	1.01	0.56	1.6	2.1
611782	N4	40.74	1.81	0.76	0.38	0.1	0.2
611784	MO5	2.94	1.31	0.85	0.48	6.0	7.6
611785	YM3	1.78	1.61	1.44	0.35	61.2	79.8
611790	A2	4.50	1.12	1.30	0.46	0.9	1.2
611791	NC1	2.89	0.98	1.47	0.32	1.0	1.3
611794	CL2A	3.86	1.24	1.02	0.50	7.2	10.0
611795	WC2	3.39	1.08	0.88	0.42	1.7	2.3
611796	KK1	3.74	1.20	1.02	0.54	10.9	14.4
611798	CL4	3.04	1.27	1.34	0.53	20.0	26.3
611801	KTB1	3.24	1.23	1.17	0.52	6.7	8.7
611805	AH3	4.29	1.24	0.97	0.49	3.1	4.1
611819	AH1	2.74	1.34	1.00	0.57	2.0	2.7
611822	LV4	15.30	0.72	0.41	0.28	0.1	0.2
611823	WC7	3.40	1.28	0.97	0.64	0.6	0.8
611827	MO2	4.17	1.35	0.97	0.43	3.2	4.2
611834	BK2	5.39	1.16	0.88	0.54	0.4	0.5
611838	WCC2	8.93	1.36	0.95	0.53	0.5	0.8
611876	WC10	3.92	1.12	1.00	0.56	1.2	1.6
611896	WCA1	3.94	1.20	0.90	0.51	3.0	4.1

5.6.4 Poly-Chlorinated Biphenyls (PCB)

The class of organic compounds known as Polychlorinated Biphenyls (PCB) are manufactured by the addition of elemental chlorine to biphenyl to yield a product with 20-70 % chlorination. PCB are persistent in the environment and accumulate in soils, freshwater and marine sediments, seawater, sewage sludge and vegetation as well as the fatty tissues of animals. The River Clyde has received polluted waste from shipbuilding, textile, paper and engineering industries (Edgar et al., 1999; Edgar et al., 2003). Additional sources of anthropogenic contaminants such as PCB include effluent and accidental discharges from military bases and from sewage sludge disposal site in the firth of Clyde (Kelly, 1995). However, single point source apportionment is not generally possible because of redistribution, remobilisation and biodegradation of the original PCB congener mixtures (Yanik et al., 2003; Harrad et al., 1994). Further it has been postulated that low concentrations of PCB enter marine and estuarine systems by atmospheric transport, thus, PCB have been detected in many parts of the world. The combination of high population density and heavy industry has consequently created the issue of PCB pollution in the Clyde.

After entering estuarine systems PCB accumulate in sediments and or biological tissues as compared to water because of physiochemical factors such as low vapour pressures and low solubility. Although laboratory studies have demonstrated that sorption of compounds such as PCB is correlated to the organic C content of the sediment matrix (sorbent) recent investigations in the Clyde estuary have not found a definitive link between PCB and total organic carbon (TOC) or sediment particle size (Edgar et al., 1999, Edgar et al., 2003). It has however been shown that a polychlorinated dibenzo-para-dioxins and dibenzofurans (PCDD/F) that chlorinated contaminants can be correlated to the type of organic matter namely, lipids (Tyler et al., 1994).

Each clearly defined chemical compound in the PCB family is named a congener. The 209 known PCB congeners maybe grouped into subclasses (homologs) on the basis of the number of chlorine atoms; thus tri, tetra, penta, hexa, hepta and octachlorophenyls have 3, 4, 5, 6, 7 and 8 chlorine substituents respectively. Further, the naming system introduced in 1980 by Ballschmitter and Zell and refined up until about 1993 has been widely adopted as an accurate method to identify individual PCB congeners in parallel with classical nomenclature.

An estimated 40,000 tonnes of total PCB were commercially manufactured in the UK from 1954 onwards, peak production was achieved in mid-1960s before declining throughout the 1970s due to restrictions and eventual UK sales ban in 1977. Interestingly, PCB have been detected in sediment cores and soils dated prior to UK production and these have been attributed to PCB imports and environmental transport of PCB from North America and Europe (Harrad et al., 1994). No precise sales records of mixtures of PCB manufactured in the UK are known although the most common contemporary formulations in the USA were aroclors 1242, 1254 and 1260 which contain 42, 54 and 60 % chlorine respectively and are comprised of congeners 28, 52, 101, 138, 153 and 180. The commercial manufacture of these toxic compounds was subject to eventual ban in 1985 under the OSPAR convention (OSPAR, 1997). PCB are known to cause cancer and effect immune, reproductive, nervous and as well as endocrine systems in animals. Studies on humans confirm their potential carcinogenic and non-carcinogenic effects. Mixtures of PCB tend to be chemically stable, non-flammable and insulating with high boiling points. These properties made PCB ideal for use in the electricity and mining industries as cooling, insulating and hydraulic fluids. With the exception of production and disposal sites the main sources of PCB emissions include power transformers, capacitors, hydraulic oils, thermal and lubricating oils. Alternative sources include release from paints, printing inks, sealants and adhesives as well as rubber plasticizers.

During the present study, PCB were detected in 19 of the 23 Clyde tributary sediment samples analysed, within the range of 2.2 to 809 ng g^{-1}, with a mean concentration of 137.2 ng g^{-1} for total PCB (Tables 5.1 and 5.7). Maps of the distributions of the total 7 most common PCB compounds and of total PCB are shown in Annex 6.

Comparison of the TOC content of sediments with total PCB showed no significant correlation (r^2=0.00006) (Figure 5.8). However, it was observed that some of the sediments contained substantial plant fragments and oily residue, which, could increase the % TOC values and thus mask any relationship with PCB concentration. In this current study the influence of local inputs is not unexpected given point sources of possible PCB contamination from for example shipyards, heavy engineering, steelworks and ironworks infill, coal mining, gasworks and mills as well as other mixed industries. A previous study by Lead et al., (1997) reported no significant correlation between PCB concentration and organic matter content, soil type or land use in peat, clay, loam, clayloam and sandy loam soils from UK. The statistical data was suggested to partly reflect thorough environmental mixing.

All sample sites showed some degree of PCB contamination, with the exception of sediments from NT1, YM1, CL4, YM3, where interferences from the other compounds in the sediment matrix inhibited clear confirmation (Table 5.7). However, this does not indicate that these samples do not contain PCB but that the compounds of interest could not be quantified using the experimental methods employed in this study. The range of total PCB concentrations (2.2–809 ng g^{-1}, Table 5.1) is consistent with findings of a recent study of the PCB where 95 sediments from the Clyde estuary area were reported to have values ranging from 0.5 to 1822 ng g^{-1} for the summed concentrations of 22 chlorobiphenyls (Edgar et al., 1999). To place the range of total PCB values in context, previous studies reported contemporary UK soil concentrations as being 20 to 30 ng g^{-1} and 4 ng g^{-1} for soils from grassland and pasture respectively (Alcock et al., 1993; Lead et al., 1997). Similarly, Creaser and Fernandes (1986) reported PCB concentrations within a range of 2.3 to 444 ng g^{-1} with a mean of 22.8 ng g^{-1} for 99 samples collected from rural and urban locations in the UK.

Comparison of the total concentrations of PCB in this study with UK background levels suggests that many of the samples contain high concentrations of PCB contamination. However, presently there is considerable international debate and even conflicting reports with respect to maximum permitted concentrations of specific toxins such as PCB. The concentrations of 7 individual PCB congeners are presented in Table 5.7 and are compared to the background values reported by OSPAR (Table 5.8). Under the OSPAR criteria for Norwegian Sea sediments, the Clyde sediments in this study would be classed as approximately 100-5000 times above that of background (Table 5.8). These conclusions are based on a very limited number of sample sites and do not preclude the possibility that even higher concentrations of PCB could exist in sediments which maybe readily remobilised/redistributed in the Clyde estuary. Although PCB contamination of 19 sites was demonstrable, the risk to human health is more difficult to evaluate since the most immediate concerns are raised when residue levels in the food chain increase above concentrations harmful to human health. Other routes of PCB entry other than from direct ingestion of sediment, water and food include skin contact with soils/sediments.

To examine the distribution patterns further, the samples average PCB homologue percentages were determined from the total sum of PCB congeners; these are presented in Table 5.9 and Figure 5.9. It will be observed that in the general, the relative proportions of PCB are broadly similar and independent of total concentration. The main components of the PCB mixtures were tetra, penta and hexa-chlorinated homologues with lower percentages of tri and hepta-chlorinated PCB moieties (Figure 5.9). Their distribution is partly indicative of the precursor industrial mixtures such as Arcolor 1254, which is comprised of tetra-, penta- and hexa-chlorinated biphenyls. In contrast, inspection of the PCB homologue percentages for sites KN5 and PM1 show that they are dominated by mainly tri-chlorinated biphenyls (Figure 5.9) one possible explanation is that these sites have a different point source of contaminants than the other sites. However this is difficult to ascertain without either greater sampling density and/or use of compound specific isotope analysis of individual PCB congeners (Yanik et al., 2003). In general PCB with lower chlorination (PCB 28, 52) exhibit enhanced volativity and aqueous solubility as compared to their higher chlorinated counterparts (eg. PCB 153, 138) (Harrad et al., 1994).

Table 5.7 PCB concentrations in Clyde tributaries sediment samples

		Concentration Individual Congeners ng g^{-1}							
BGS Code	**GCC Code**	**PCB 28**	**PCB 52**	**PCB 101**	**PCB 118**	**PCB 153**	**PCB 138**	**PCB 180**	**Total of 7 PCB**
611704	LH1	0.00	2.97	30.55	21.49	21.12	28.37	13.56	118.06
611707	NT1	int	int	int	int	int	int	int	int
611711	PM1	222.37	22.45	6.80	9.27	2.87	3.00	1.43	268.19
611714	N2	4.26	0.33	0.13	0.76	1.28	0.17	0.20	7.13
611725	EF1	5.13	2.89	1.94	2.74	5.52	0.49	0.00	18.71
611726	CL5	2.27	1.42	1.53	1.22	2.65	2.85	2.59	14.53
611729	KN5	0.91	0.00	0.31	0.00	0.00	0.00	0.00	1.23
611736	MO3	0.99	0.36	0.83	0.38	1.77	0.86	1.86	7.04
611740	GK1	2.48	0.38	2.00	3.06	0.86	2.99	2.69	14.46
611743	KN4	0.59	0.00	250.78	7.74	0.00	0.00	0.00	259.11
611747	YM1	int	int	int	int	int	int	int	int
611754	TC7	1.89	0.33	0.90	0.65	0.86	0.48	0.56	5.68
611777	YK1	2.35	1.76	8.66	7.58	158.85	18.13	18.22	215.55
611791	NC1	7.59	2.43	3.66	4.02	4.53	4.41	3.84	30.48
611794	CL2A	8.94	2.02	5.64	5.61	7.16	10.13	5.33	44.83
611798	CL4	int	int	int	int	int	int	int	int
611805	AH3	4.78	1.02	2.31	2.77	3.20	2.55	2.09	18.72
611819	AH1	2.64	0.98	0.19	1.05	2.51	3.12	3.65	14.15
611822	LV4	2.32	1.59	3.00	2.89	3.27	3.58	0.88	17.53
611823	WC7	25.05	3.04	2.39	2.46	1.52	4.01	1.54	40.02
611827	MO2	6.35	1.40	8.16	16.19	8.44	10.27	7.30	58.11
611876	WC10	26.34	9.86	16.06	12.09	5.59	8.20	2.73	80.87
611785	YM3	int	int	int	int	int	int	int	int

Int = could not be calculated due to high matrix interference

Table 5.8. Ranges of background concentrations of PCB congeners in surface sediments for specific regions of the OSPAR Convention Area

Substances	**Norwegian Sea**	**Iceland Sea / Norwegian Sea**	**South Norway / Skagerak**
TOC (%)	0.5	0.5	0.6
PCB 28 ng g^{-1} dw	<0.01	<0.01	0.030
PCB 52 ng g^{-1} dw	<0.01	<0.01	0.035
PCB 101 ng g^{-1} dw	0.012	0.016	0.065
PCB 153 ng g^{-1} dw	0.025	0.020	0.090
PCB 138 ng g^{-1} dw	0.025	0.026	0.120
PCB 180 ng g^{-1} dw	0.015	<0.01	0.060

Source: OSPAR (1997)   dw = dry weight

Table 5.9 PCB homologue groups in Clyde tributaries sediment samples

		Chlorination ng g^{-1}					
BGS Code	**GCC code**	**Tri**	**Tetra**	**Penta**	**Hexa**	**Hepta**	**Total of all PCB ng g^{-1}**
611704	LH1	13.72	30.06	120.89	55.21	22.39	242.27
611707	NT1	int	int	Int	int	int	int
611711	PM1	538.75	213.19	45.45	9.67	1.93	808.99
611714	N2	4.26	0.88	2.51	1.54	0.20	9.39
611725	EF1	10.94	2.89	9.29	8.81	0.00	31.93
611726	CL5	5.82	1.42	11.07	5.48	2.59	26.38
611729	KN5	1.84	0.00	0.31	0.00	0.00	2.16
611736	MO3	2.11	1.57	2.71	4.99	4.36	15.75
611740	GK1	4.80	4.43	13.46	10.71	2.69	36.08
611743	KN4	1.52	0.01	292.65	0.00	0.00	294.19
611747	YM1	int	int	Int	int	int	int
611754	TC7	4.58	2.23	4.04	2.63	0.79	14.27
611777	YK1	5.06	8.25	31.44	219.90	46.73	311.38
611791	NC1	12.05	9.32	23.05	9.54	5.35	59.31
611794	CL2A	23.32	6.69	31.58	27.73	7.76	97.08
611798	CL4	int	int	Int	int	int	int
611805	AH3	9.04	3.80	14.52	16.53	2.09	45.98
611819	AH1	2.64	0.98	1.56	8.09	3.65	16.92
611822	LV4	2.32	5.87	23.00	8.31	0.88	40.37
611823	WC7	59.80	25.26	16.32	8.95	1.54	111.87
611827	MO2	14.47	10.36	93.25	33.98	22.91	174.97
611876	WC10	50.06	73.60	120.65	19.92	2.73	266.96
611785	YM3	int	int	Int	int	int	int

Int = could not be calculated due to high matrix interference

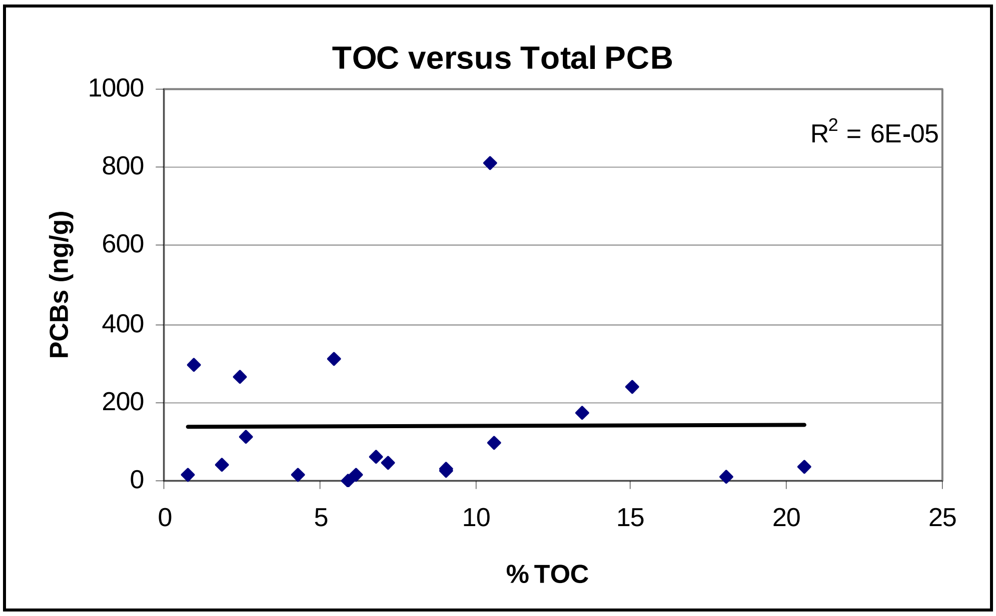
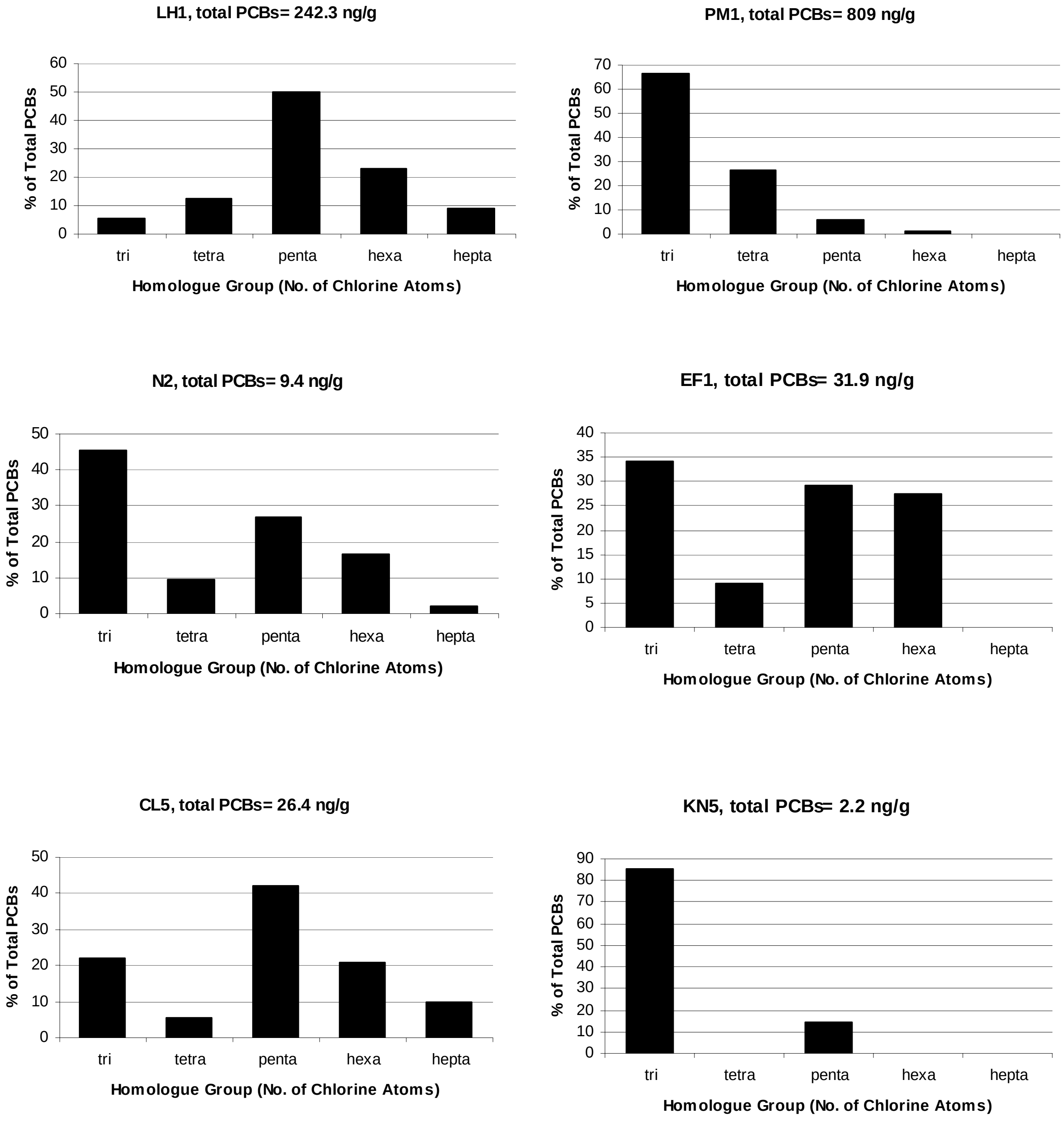


Figure 5.8. Scatter plot showing the relationship between %TOC and total PCB concentrations in Clyde tributaries sediments.



LH1, total PCBs= 242.3 ng/g

PM1, total PCBs= 809 ng/g

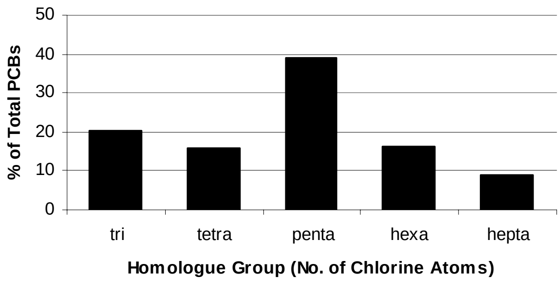
N2, total PCBs= 9.4 ng/g

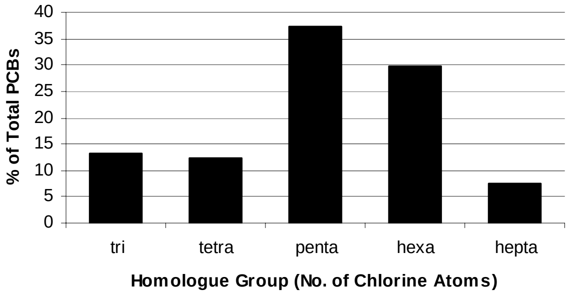
EF1, total PCBs= 31.9 ng/g

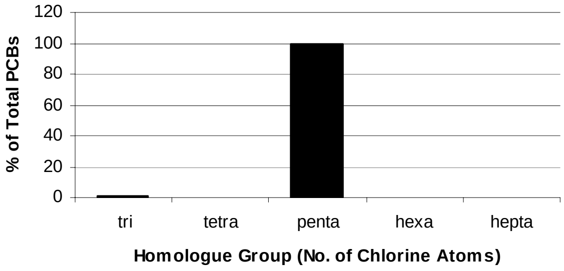
CL5, total PCBs= 26.4 ng/g

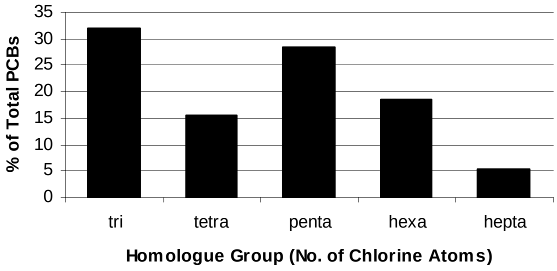
KN5, total PCBs= 2.2 ng/g

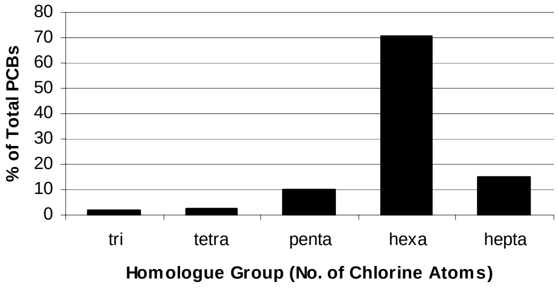
Figure 5.9 Bar charts showing homologue groups of PCB in Clyde tributary sediments

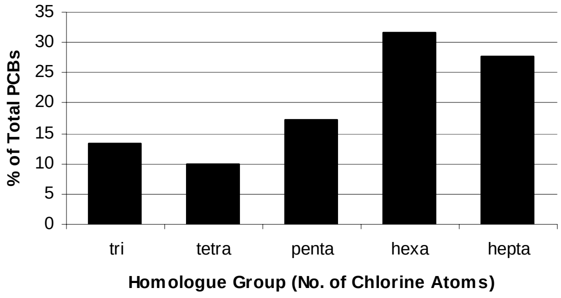

NC1, total PCBs= 59.3 ng/g

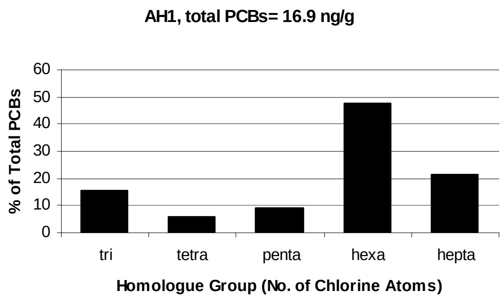

GK1, total PCBs= 36.1 ng/g

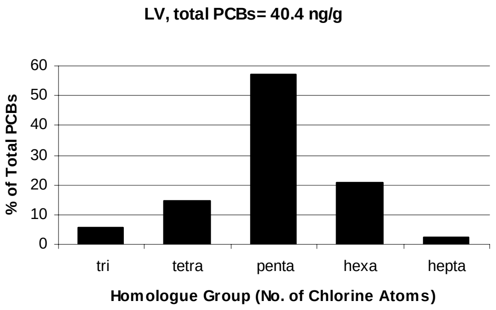

KN4, total PCBs= 294.2 ng/g

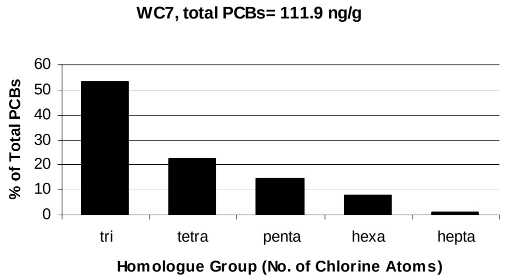

TC7, total PCBs= 14.3 ng/g

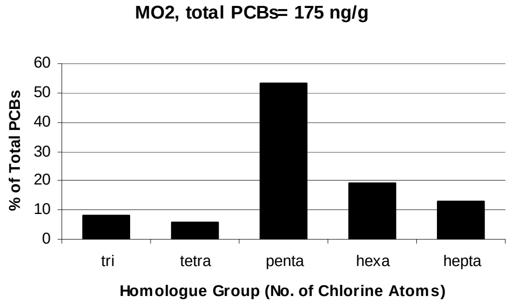

YK1, total PCBs= 311.4 ng/g

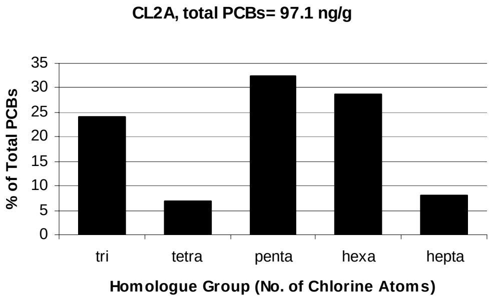

MO3, total PCBs= 15.7 ng/g

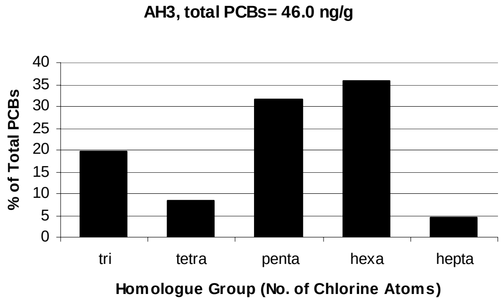

AH1, total PCBs= 16.9 ng/g

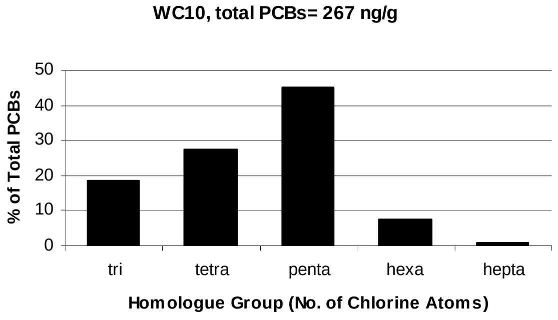

LV, total PCBs= 40.4 ng/g


WC7, total PCBs= 111.9 ng/g


MO2, total PCBs= 175 ng/g


CL2A, total PCBs= 97.1 ng/g


AH3, total PCBs= 46.0 ng/g


WC10, total PCBs= 267 ng/g

5.6.5 Organo-Tin

Tributyltin (TBT) is a widespread contaminant of coastal waters and sediments as a result of its use as an antifouling agent on marine structures, nets and vessel hulls. It can be very persistent in the environment and demonstrates high toxicity to marine organisms, notably endocrine disruption in gastropod molluscs which is responsible for the decline of dogwhelk populations whereby female dogwhelks develop male sex genitalia (called "imposex") which results in reproductive failure (Bryan, et al., 1986). This phenomenon has also been found the around the Clyde Sea, but since the introduction of regulations prohibiting TBT-based anti-fouling paint on vessels <25m in length, the dogwhelk populations have made a widespread recovery (Evans, et al., 1996; Nicholson and Evans, 1997). However TBT residues persist in many coastal locations. Recent surveys have shown that TBT is common in the vicinity of ports, shipping channels and smaller harbours and marinas where there are facilities for small boat maintenance.

Sediments are sinks for TBT. However, resuspension can sustain higher concentrations in overlying waters. TBT is highly persistent in anaerobic sediments. The concentrations in sediment vary over a wide range. The highest concentrations of organotins are observed in harbours, marinas and along major shipping routes (for example, as high as 10 mg kg^{-1}).

The status of sediment contamination in the Clyde estuary has been routinely studied to determine the distribution, transport and fate of various types of anthropogenic contaminants. Previous studies of the Clyde estuary have focused on PCB (Edgar et al., 1999; Edgar et al., 2003), but there are very few data relating to TBT concentrations in Clyde river or estuary sediments.

Presently there remains much international debate and conflicting reports with respect to maximum permitted concentrations of specified organic toxins in marine / estuarine sediments. OSPAR has given some advice about how background concentrations of organic toxins can be used as assessment tools (OSPAR, 1997) this includes:

- Values that can be applied throughout the maritime area, however some of these values can only be applied on a regional basis.
- Due to expected high natural variability within the different environments of the maritime area, assessments should be carried out by relevant experts in order to avoid misinterpretation and misevaluation of monitoring data.
- Background values do not represent target values and should not be used as such.

In some literature TBT concentration values do not specify if the units of are either: weight as Sn / weight of dry sediment or weight of tributyltin chloride / weight of dry sediment. Normally certified reference material literature (e.g. PACS-2) and analytical papers express concentrations as weight of Sn / weight of dry sediment (e.g. mg of Sn kg^{-1} dw). This was format used to present the data from the present study.

Although there are currently no guidelines relating to organo-tin in freshwater sediments in the UK, marine Ecotoxicological Assessment Criteria (EAC) values are defined as concentration levels of a substance above which concern is indicated. The EAC for TBT is 0.005 – 0.05 mg kg^{-1} dry weight (OSPAR, 2000).

OSPAR reported that typical concentrations of TBT in sediments of estuaries on the eastern Irish Sea are in the range < 0.0 to 1.0 mg kg^{-1} but higher concentrations were found in Swansea Bay (< 0.01 to 2.7 mg kg^{-1}) and the Mersey estuary (0.6 to 12.9 mg kg^{-1}) in 1995. Concentrations in offshore sediments are generally < 0.01 mg kg^{-1} (OSPAR, 2000). A recent study of the Mersey estuary (Kim and Spiro, 2003), where TBT was found in all sediments, showed ranges of 0.4 to 2.4 mg kg^{-1} (mean = 1.3 mg kg^{-1}).

The Ministry of Agriculture, Fisheries and Food, Directorate of Fisheries Research (MAFF 1994), use an 'Equilibrium Partitioning Approach' which involves the setting of a quality standard for a contaminant in a marine sediment at a concentration which, in equilibrium with the surrounding water, does not lead to a breach of the relevant water quality criterion for that contaminant and is normalised to 10 % TOC. The 'Sediment Safe Level' for TBT is 0.0014 mg kg –TOC^{-1}, however this document does not specify if this value is as 'Sn' or as 'TBT chloride'.

Of the 10 sediment samples examined during the present study, only three contained detectable concentrations of TBT or DBT. The locations of these samples are shown in the maps presented in Annex 6 and correspond to the following sites:

LH1	TBT = 0.35 mg Sn kg^{-1}
MO2	TBT = 0.18 mg Sn kg^{-1}
YM1	DBT = 0.15 mg Sn kg^{-1}

These concentrations are above the EAC limits for TBT (0.005 – 0.05 mg kg^{-1}) and are therefore a possible cause for concern, however, it should be noted that the samples are stream sediments not river or estuary sediments. Most of the sediments contained less than 0.07 mg Sn kg^{-1}, which is not too surprising because the majority of sites are not strongly associated with shipping.

In a recent study, TBT, DBT and MBT concentrations were determined in the Clyde estuary (Kim, 2003). Only a few samples were found to have detectable concentrations of organotin compounds, these were King George V Docks (0.49 mg Sn kg^{-1} TBT, 0.90 mg Sn kg^{-1} DBT), Duntocher Burn (0.61 mg Sn kg^{-1} TBT), Upper Harbour (0.41 mg Sn kg^{-1} TBT) and Lower Harbour (0.18 mg Sn kg^{-1} TBT). A detectable concentration of MBT was found at Erskine (0.28 mg Sn kg^{-1} MBT). Compared to the Mersey, the Clyde estuary has a relatively reduced concentration of TBT in the sediment, a possible indicator of this is the recovery of dogwhelk populations in the Clyde Sea area due to the reduction of TBT used as an anti-fouling paint ingredient (Evans, et al., 1996; Nicholson and Evans, 1997).

5.7 SURFACE WATER DETERMINANDS

Maps showing the distribution of determinands in surface waters are presented in Annex 7 of this report and summary statistics in Table 5.10. Water guideline values and mean concentrations of parameters in surface waters from rural areas are included on the maps for comparison. Comparisons with land use and potential contaminant sources are not examined as part of this report but it is recommended that these issues be investigated in more detail as part of the proposed follow-on Clyde estuary-Clyde basin study.

5.7.1 Inter-parameter Relationships

The TOC content and pH of waters can exert significant controls on the amount and mobility of elements present. The results of this study show that the metal elements Fe, Al, Cu, Zn, Sn and Pb are significantly correlated (95% confidence level) with TOC in surface waters (Table 5.11). The parameters TOC, Mn, Fe, Al, Ni, Zn, Cd and Pb show significant (95 % confidence level) negative relationships with pH as expected as peaty waters with high organic matter content generally have low pH and many metal elements are mobilised in acid conditions. Interestingly Cr shows significant positive correlations with pH, Ca, and sulphate (SO_4) this may reflect the alkaline nature of chromite processing waste distributed in the Glasgow environment. Several of the metal elements (Al, Ni, Zn Cd and Pb) and ammonium (NH_4) are significantly positively correlated (95 % confidence level) with Fe and Mn and are probably associated with iron and manganese oxides as well as gross contamination related to industrial sources (Table 5.11). Dissolved oxygen (DO) shows a positive relationship with pH but is inversely correlated with TOC, NH_4, P, Mn, Fe and many of the other metal elements as expected as low oxygen waters tend to have high organic matter, iron and manganese oxide and contaminant contents (Table 5.11).

5.7.2 Relationships With Artificial Ground

In general, there is little difference in concentration range between parameters collected on sites underlain by artificial ground as defined in Figure 2.5 and those that are not (Figure 5.10). Ni, Cu, Sb, Pb, Se, U and Cr all show marginal elevation over artificial ground and probably reflect the use of coal mining and other waste as fill materials.

5.7.3 Inorganic Parameters

At the present time, water quality assessments are generally based on drinking water standards, which in Scotland refers to the Water Supply Scotland Regulations (WSR, 2000). The CEC water quality standards for aquatic life in Class I river waters also provide a useful indication of harmful concentrations of substances (CEC, 1978). For several contaminants there are no current UK water guidelines therefore distributions are compared to guidelines or limits from other countries as follows. References to the guideline values used in this section and on the maps in Annex 7 are given in the key to the annexes of this report.

5.7.3.1 NON WSR SUBSTANCES

Total organic carbon (TOC) contents are highest in peaty marshy waters around Bishop Loch as expected (Annex 7).

Dissolved oxygen (DO) is a measure of the oxygen freely available in water. DO is vital to fish and other aquatic life and for the prevention of odours. Traditionally, the level of DO has been accepted as the single most important indicator of a water body's ability to support desirable aquatic life. Secondary and advanced waste treatments are generally designed to protect DO in waste-receiving waters. Values below the CEC drinking water guideline of 5 mg L^{-1} are associated with the peaty marsh environments around Bishop Loch, GK1 and TC8. Low values were also recorded in the Camlachie, Battle, Pow, Linthouse White Cart and Polmadie catchments reflecting the poor quality of water in these systems. Extremely low values (0.1 mg L^{-1}) were recorded in the contaminated Molendinar Burn (Annex 7).

Barium (Ba), exceeds the CEC drinking water guideline of 0.1 µg L^{-1} in the Yoker, Molendinar, Tollcross and North Calder catchments as well as in the peaty environments around Bishop Loch whereas concentrations of Be are all below the US-EPA drinking water guideline of 4 µg L^{-1} (Annex 7).

Concentrations of Ca in water are below the CEC recommended value of 100 mg L^{-1} over much of western and southern Glasgow reflecting natural geological conditions namely the presence of Clyde Plateau Volcanic and sandstone rock types in this area. Similarly total alkalinity values below the WHO drinking water and CEC aquatic life recommended value of 200 mg L^{-1} are reported over much of southwest Glasgow and in the River Kelvin. Magnesium (Mg) and TDS concentrations are all below the CEC drinking water guidelines of 50 and 1500 mg L^{-1} respectively. However, high values of 178.8 Ca and 38.8 Mg mg L^{-1} at ST2 may reflect calcareous fill materials at this site. Potassium (K) concentrations in the Tollcross Burn and Malls Mire Burn are all above the CEC drinking water guideline of 12 mg L^{-1}. The relatively high alkalinities and concentrations of Ca, K, SO_4 and Mg in water in the Tollcross Burn and in the Battle, Kirk, Molendinar and Polmadie catchments may reflect the presence of calcareous coal mining and chromite processing wastes in these areas or low flow conditions in these streams. Sites ST1 and ST2 may also be affected by calcareous fill materials.

Chloride (Cl) and P are all below the CEC drinking water guidelines of 250 and 5 mg L^{-1} respectively, however, P concentrations are all in excess of the CEC aquatic life standard of 0.01 mg L^{-1} for Class I rivers (Annex 7). Cobalt (Co), V and Si concentrations are all below the respective Russian drinking water guidelines of 100 µg L^{-1}, 100 µg L^{-1} and 10 mg L^{-1}. Strontium and Th values are lower than the US-EPA drinking water guidelines of 4 mg L^{-1} and 50 µg L^{-1} (Annex 7). Uranium (U) concentrations are well below the WHO drinking water guideline of 9 µg L^{-1}, highest concentrations are associated with the Ca-rich waters of eastern Glasgow as the element is more mobile under alkaline conditions.

Lithium concentrations above the Russian drinking water guideline were recorded at ST1, ST2 and MM1. In the case of the Malls Mire Burn this probably reflects contamination whereas at ST1 and ST2, concentrations may be natural or related to fill materials in the area (Annex 7). Although only one site (CL3) exceeds the WHO drinking water guideline of 70 µg L^{-1} for Mo, the value (214 µg L^{-1}) indicates marked contamination of water in this catchment.

5.7.3.2 WSR SUBSTANCES

As outlined in Chapter 1 of this report, the WSR outline guidelines for substances in water. Maps of the distributions of these parameters in Glasgow stream waters are presented in Annex 7 of this report. Locations where these guideline values are exceeded in waters are presented in Annex 8.

Water pH values below the WSR drinking water and CEC aquatic life guidelines of 6.5 were recorded in the peaty marshy environments around Bishop Loch (Annexes 7 and 8) and these conditions are likely to affect the concentrations of many of the metal elements in water as follows.

Ammonium (NH_4) is environmentally hazardous both because of its toxicity to fish and because of its ease of oxidation, enabling it to deplete dissolved oxygen rapidly. The decay of nitrogenous organic wastes, breakdown of animal and vegetable wastes and effluent from sewage treatment works are the principal sources of ammonium in water. Ammonium concentrations in surface waters exceed the WSR guideline of 0.5 mg L^{-1} at a number of locations over the study area including the White Cart, Polmadie, Malls Mire, Yoker Mains, Kirk, Newton, Pow, Battle, Tollcross, Camlachie and Molendinar catchments as well as the peaty marshy areas such as ST1, ST2, KNA1 and Bishop Loch. These results are indicative of poor water quality in many of the urban streams in eastern Glasgow and probably reflect cross contamination of the streams by the sewer network (Annexes 7 and 8). Similarly the lower CEC aquatic life standard of 0.04 mg L^{-1} (Table 1.2) for Class I rivers is exceeded at all the sites.

Aluminium (Al) concentrations in excess of the WSR guideline value of 200 µg L^{-1} are reported in the Bishop Loch area associated with peaty marshy low pH waters where the element is likely to be mobilised into the water column. The element is toxic to aquatic life and affects salmanoid fish in particular, hence the low CEC guideline of 1.6 µg L^{-1} for Class I rivers (Table 1.2). This value is exceeded at approximately 95 % of the sites sampled, however, the guideline refers to pH conditions lower than 6.5 and the majority of the catchments in the Glasgow area have higher pH (Annex 7).

Chromium (Cr) concentrations exceed the 1 µg L CEC aquatic life guideline for Class I rivers at approximately 75 % of the sites indicating the widespread mineral extraction (coal) and industrial (metal processing) sources of the element in Glasgow. Concentrations above the 50 µg L^{-1} WSR guideline are reported in the Light, Molendinar, Polmadie, Hole and Merry catchments. These sites are all affected by chromite waste contamination and concentrations in water up to the excessively high 903 µg L^{-1} recorded at site LT1A indicate mobilisation of this contaminant into the aquatic system. Although below the WSR guideline, relatively high concentrations (18 µg L^{-1}) also occur in the Eastfield Burn. These results are of concern because of impacts on groundwater quality, the River Clyde and the likely form of Cr present in the waters. It is recommended that these issues be investigated further as part of the proposed follow-on Clyde estuary-Clyde basin study. Previous studies have indicated the impacts of Cr on water quality in the area. For example, very high concentrations of Cr (6700 µg L^{-1}) associated with chromite waste have been reported in stream waters in south-east Glasgow resulting in concentrations of 1100 µg L^{-1} in the River Clyde and 9100 µg L^{-1} in groundwater (Farmer et al., 2002). Similarly, Cr concentrations of 3100 – 6200 µg L^{-1} were reported in stream waters from the Polmadie Burn and 169000 µg L^{-1} in groundwater from a chromite waste site by Whalley et al. (1999). In contrast, Cr concentrations in samples of river water from 13 sites along the Clyde were below the limit of detection with the exception of waters immediately downstream of the Polmadie

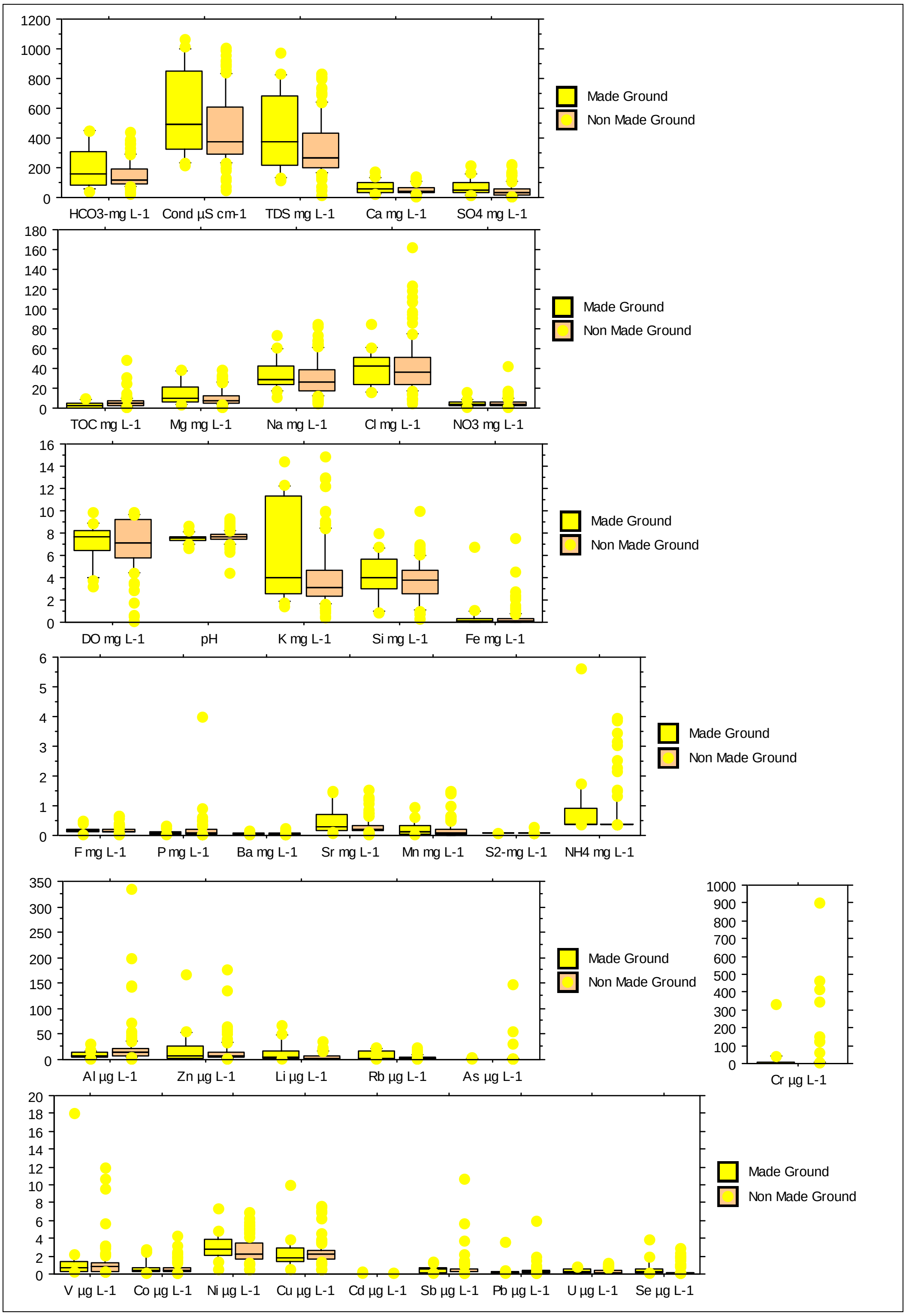
Burn inflow, which contained 1100 µg L^{-1}. However, at sampling points 1 and 4 km downstream of the inflow, values of 10 µg L^{-1} were recorded indicating rapid dilution of the stream water inputs in the river system. In terms of toxicity, the speciation of Cr is important. Under natural conditions Cr is normally present as the CrIII form and is an essential trace element for health. However, the CrVI hexavalent form is a known carcinogen to humans via inhalation. The studies by Farmer et al. (2002) demonstrated that > 90 % of the Cr present in south-east Glasgow was in the more toxic CrVI hexavalent form and was associated with humic substances in the waters. Similarly, Whalley et al. (1999) showed that the groundwaters from a chromite waste site in south-east Glasgow, stream waters from the Polmadie Burn and river waters from downstream the Polmadie Burn inflow to the Clyde contained Cr in the more toxic hexavalent form.

Iron (Fe) and Mn levels in almost all the catchments exceed the WSR guidelines of 0.2 mg L^{-1} and 0.05 mg L^{-1}respectively. In the case of peaty marsh areas to the north and north-east of Glasgow around Bishop Loch, ST1 and ST2 and the northern River Kelvin, this may reflect natural conditions and the mobilisation of Fe and Mn into the water column under acid conditions. In many of the other catchments Fe may indicate gross industrial contamination. The Fe and Mn water quality guidelines to a large degree relate to water colour rather than toxic effects and many natural waters in Scotland exceed the guidelines for these elements.

Cadmium (Cd), Cu, Pb, Hg, Ni, Se, Zn in addition to F and nitrate (NO_3) contents are all below the WSR guidelines of 5, 2000, 25, 1, 20, 10 and 5000 µg L^{-1} and 1.5 and 50 mg L^{-1} respectively (Annex 7). In contrast, Sb and As values greater than the WSR guidelines of 5 and 10 µg L^{-1} respectively in the Molendinar Burn are likely to reflect contamination (Annexes 7 and 8). The CEC aquatic life standard for Cd in Class I rivers (0.07 µg L^{-1}) is exceeded at sites on the Newton, Carntyne, Camlachie, Linthouse, Bishop Loch and North Glasgow catchments whereas approximately 75 % of the sites sampled are above the aquatic standard for Cu (2 µg L^{-1}); 90 % for nitrate (0.3 mg L^{-1}) and all the sites for Pb (0.1 µg L^{-1}). The latter standard is very low reflecting the high toxicity of Pb to aquatic life forms. In addition, the aquatic life guideline for Zn (45 µg L^{-1}) is exceeded in the Camlachie, Linthouse, North Glasgow, Bishop Loch and River Kelvin catchments (Annex 7).

Conductivities are below the WSR guideline of 1500 µS cm^{-1}, highest values are reported in the peaty marshy locations around north-east Glasgow and contaminated streams in the east of Glasgow (Annex 7).

Sodium (Na) and sulphate (SO_4) concentrations do not exceed the WSR guidelines of 200 and 250 mg L^{-1} respectively, highest concentrations are reported in the Tollcross, Battle and Camlachie catchments and concentrations of SO_4 are also high in the Malls Mire, Kirk, Newton and Pow Burns and may indicate the influence of coal mining or chromite processing waste in these locations. In contrast sulphide (S^-) concentrations are detectable only at site BK3 (Annex 7).



N Made Ground = 16 N Non-made Ground = 103 Made ground = artificial ground as defined in Figure 2.5

Figure 5.10 Box and whisker plots showing the 10th, 25th, 50th, 75th and 90th percentiles of element distributions in urban surface waters categorised according to location on artificial ground.

Table 5.10 Summary statistics for parameters in surface waters

Parameter	Units	Count	Minimum	Maximum	Mean	Median
DO	mg L^{-1}	122	0.1	9.9	7.1	7.3
pH		122	4.50	9.28	7.64	7.66
HCO_3^-	mg L^{-1}	122	0.012	451	164	124
Cond	µS cm^{-1}	122	50	1064	479	406
TDS	mg L^{-1}	122	13	975	359	283
TOC	mg L^{-1}	122	0.50	48.76	5.71	4.83
TIC	mg L^{-1}	122	2.50	98.64	34.24	26.32
Ca	mg L^{-1}	122	1.3	178.8	55.0	43.2
Mg	mg L^{-1}	122	0.6	39.3	11.2	7.4
Na	mg L^{-1}	122	4.4	84.7	31.1	26.1
K	mg L^{-1}	122	0.4	14.9	4.3	3.2
Cl	mg L^{-1}	122	0.0	162.7	42.7	36.0
SO_4	mg L^{-1}	122	0.37	222.00	49.43	30.80
NO_3	mg L^{-1}	122	0.01	41.97	4.93	4.10
F	mg L^{-1}	122	0.005	0.680	0.178	0.148
P	mg L^{-1}	122	0.035	4.019	0.169	0.087
S^{2-}	mg L^{-1}	122	0.100	0.280	0.101	0.100
NH_4	mg L^{-1}	122	0.385	5.630	0.706	0.385
Si	mg L^{-1}	122	0.35	10.05	3.73	3.76
Ba	mg L^{-1}	122	0.011	0.254	0.066	0.061
Sr	mg L^{-1}	122	0.009	1.551	0.349	0.220
Mn	mg L^{-1}	122	0.004	1.483	0.185	0.081
Fe	mg L^{-1}	122	0.01	7.58	0.44	0.13
Li	µg L^{-1}	122	0.3	67.8	6.9	2.7
Be	µg L^{-1}	122	0.025	0.287	0.036	0.025
Al	µg L^{-1}	122	1	335	21	12
V	µg L^{-1}	122	0.25	18.08	1.31	0.81
Cr	µg L^{-1}	122	0.25	903.00	25.23	0.56
Co	µg L^{-1}	122	0.06	4.26	0.62	0.36
Ni	µg L^{-1}	122	0.50	7.40	2.70	2.33
Cu	µg L^{-1}	122	0.50	9.99	2.39	2.15
Zn	µg L^{-1}	122	1	177	15	6
As	µg L^{-1}	122	0.5	148.7	2.6	0.5
Rb	µg L^{-1}	122	0.67	23.72	5.09	3.11
Y	µg L^{-1}	122	0.02	0.44	0.07	0.04
Zr	µg L^{-1}	122	0.01	0.76	0.08	0.05
Mo	µg L^{-1}	122	0.07	214.49	3.46	0.84
Cd	µg L^{-1}	122	0.01	0.30	0.02	0.01
Sn	µg L^{-1}	122	0.08	0.41	0.21	0.20
Sb	µg L^{-1}	122	0.05	10.68	0.60	0.35
Cs	µg L^{-1}	122	0.01	0.20	0.03	0.01
La	µg L^{-1}	122	0.005	0.385	0.039	0.019
Ce	µg L^{-1}	122	0.005	0.842	0.070	0.034
Ho	µg L^{-1}	122	0.005	0.015	0.005	0.005
Tl	µg L^{-1}	122	0.005	0.127	0.009	0.005
Pb	µg L^{-1}	122	0.1	6.0	0.3	0.2
Bi	µg L^{-1}	122	0.005	0.005	0.005	0.005
Th	µg L^{-1}	122	0.01	0.04	0.01	0.01
U	µg L^{-1}	122	0.01	1.24	0.28	0.17
Se	µg L^{-1}	122	0.125	3.883	0.360	0.125
Hg	µg L^{-1}	122	0.010	0.010	0.010	0.010

Table 5.11 Pearson correlation matrix of parameters in urban surface waters

	DO	pH	HCO3	Cond	TDS	TOC	Ca	Mg	Na	K	Cl	SO4	NO3	F	P	S2-	NH4	Si	Ba	Mn	Fe	Al	V	Cr	Ni	Cu	Zn	As	Cd	Sn	Sb	Pb	U
pH	**0.553**																																
HCO3	0.147	**0.175**																															
Cond	0.131	0.128	**0.860**																														
TDS	0.140	**0.142**	**0.911**	**0.985**																													
TOC	**-0.325**	**-0.494**	**-0.415**	**-0.459**	**-0.458**																												
Ca	0.067	0.094	**0.877**	**0.929**	**0.946**	**-0.429**																											
Mg	**0.218**	**0.191**	**0.891**	**0.870**	**0.918**	**-0.378**	**0.817**																										
Na	0.149	0.135	**0.527**	**0.737**	**0.692**	**-0.347**	**0.478**	**0.584**																									
K	**0.265**	**0.188**	**0.804**	**0.792**	**0.830**	**-0.375**	**0.722**	**0.852**	**0.587**																								
Cl	0.036	0.085	**0.314**	**0.630**	**0.557**	**-0.295**	**0.437**	**0.380**	**0.819**	**0.277**																							
SO4	**0.160**	0.106	**0.703**	**0.852**	**0.872**	**-0.370**	**0.870**	**0.819**	**0.514**	**0.736**	**0.431**																						
NO3	**0.238**	**0.182**	-0.006	0.089	0.071	-0.100	0.014	0.033	**0.160**	**0.250**	0.137	0.050																					
F	-0.109	**0.224**	**0.516**	**0.542**	**0.547**	**-0.177**	**0.575**	**0.456**	**0.293**	**0.304**	**0.329**	**0.452**	-0.126																				
P	**-0.227**	-0.138	-0.136	-0.104	-0.113	0.013	-0.136	-0.103	-0.031	-0.071	-0.086	-0.040	-0.003	-0.127																			
S2-	-0.030	0.034	-0.091	-0.092	-0.093	-0.013	-0.074	-0.068	-0.095	-0.066	-0.083	-0.058	-0.058	-0.062	-0.032																		
NH4	**-0.290**	-0.131	**0.156**	**0.176**	**0.192**	-0.059	**0.196**	**0.186**	0.055	**0.183**	-0.011	**0.278**	-0.001	0.075	**0.344**	-0.035																	
Si	**-0.210**	-0.127	**0.656**	**0.723**	**0.727**	**-0.335**	**0.796**	**0.534**	**0.384**	**0.451**	**0.408**	**0.609**	0.035	**0.566**	-0.108	-0.140	**0.185**																
Ba	-0.111	-0.086	**0.279**	**0.234**	**0.210**	0.032	**0.292**	0.113	0.045	0.002	0.130	0.025	-0.125	**0.306**	**-0.212**	-0.032	-0.048	**0.357**															
Mn	**-0.358**	**-0.389**	**0.256**	**0.210**	**0.219**	0.145	**0.263**	**0.171**	0.054	0.097	0.065	0.124	**-0.256**	**0.282**	-0.050	-0.050	**0.259**	**0.385**	**0.626**														
Fe	**-0.273**	**-0.381**	0.042	-0.029	-0.002	**0.488**	0.058	0.005	-0.142	-0.054	-0.122	0.003	**-0.163**	0.085	-0.056	-0.031	**0.284**	0.102	**0.276**	**0.645**													
Al	**-0.288**	**-0.416**	**-0.290**	**-0.311**	**-0.309**	**0.834**	**-0.299**	**-0.237**	**-0.235**	**-0.208**	**-0.208**	**-0.243**	-0.111	-0.118	0.072	-0.036	-0.031	**-0.271**	-0.042	0.094	**0.428**												
V	-0.146	-0.086	-0.044	0.069	0.061	-0.009	0.062	-0.004	0.101	0.039	**0.160**	0.153	0.011	0.025	**0.406**	-0.042	0.044	0.070	**-0.190**	-0.078	-0.043	0.115											
Cr	0.016	**0.169**	0.043	0.141	0.127	-0.061	**0.156**	0.021	0.103	0.089	0.127	**0.214**	-0.044	**0.452**	0.051	-0.021	-0.062	0.143	-0.044	0.009	-0.073	-0.050	0.071										
Ni	**-0.158**	**-0.250**	**0.631**	**0.631**	**0.661**	0.028	**0.684**	**0.622**	**0.303**	**0.528**	**0.278**	**0.596**	-0.044	**0.493**	**-0.165**	-0.105	**0.171**	**0.656**	**0.291**	**0.458**	**0.354**	0.060	0.001	0.144									
Cu	**-0.186**	-0.152	**-0.386**	**-0.312**	**-0.332**	**0.231**	**-0.355**	**-0.370**	-0.036	**-0.298**	-0.008	**-0.261**	-0.084	**-0.180**	0.079	-0.029	-0.114	**-0.163**	-0.136	-0.154	-0.146	0.121	0.039	0.078	-0.064								
Zn	**-0.331**	**-0.565**	-0.136	-0.062	-0.068	**0.461**	-0.031	-0.095	-0.086	-0.038	0.001	0.041	-0.042	-0.094	-0.013	-0.049	-0.016	-0.012	0.017	0.126	**0.200**	**0.465**	0.065	-0.055	**0.347**	**0.357**							
As	0.075	0.027	0.123	**0.250**	**0.255**	-0.091	**0.269**	**0.180**	**0.193**	**0.199**	**0.247**	**0.385**	-0.026	**0.194**	-0.020	-0.013	-0.048	**0.218**	-0.047	0.000	-0.043	-0.042	**0.486**	0.116	0.141	-0.069	-0.014						
Cd	**-0.158**	**-0.272**	-0.008	0.066	0.056	0.085	0.079	0.011	0.034	0.012	0.131	0.091	0.046	0.023	0.001	-0.025	-0.012	0.144	**0.156**	**0.228**	**0.160**	0.148	0.005	-0.022	**0.296**	**0.181**	**0.499**	-0.032					
Sn	**-0.173**	-0.129	-0.149	**-0.217**	**-0.203**	**0.327**	**-0.204**	-0.136	**-0.173**	-0.114	**-0.215**	-0.154	**0.178**	-0.003	**0.276**	-0.129	0.101	**-0.194**	-0.105	-0.037	0.090	**0.340**	**0.202**	0.043	-0.051	0.113	**0.215**	-0.050	0.009				
Sb	0.006	-0.006	0.099	**0.304**	**0.289**	-0.117	**0.293**	**0.159**	**0.306**	**0.194**	**0.400**	**0.428**	-0.021	**0.225**	0.042	-0.036	-0.040	**0.266**	-0.078	-0.016	-0.082	-0.048	**0.563**	**0.165**	**0.171**	0.054	0.087	**0.942**	0.067	-0.043			
Pb	**-0.424**	**-0.592**	**-0.317**	**-0.322**	**-0.315**	**0.701**	**-0.309**	**-0.269**	**-0.205**	**-0.232**	**-0.207**	**-0.209**	-0.122	**-0.199**	**0.205**	-0.033	0.060	**-0.279**	-0.122	0.027	**0.235**	**0.704**	0.137	-0.043	0.064	**0.326**	**0.722**	-0.037	**0.192**	**0.481**	0.001		
U	0.013	0.083	**0.708**	**0.854**	**0.858**	**-0.375**	**0.880**	**0.742**	**0.534**	**0.654**	**0.517**	**0.879**	0.029	**0.556**	-0.065	-0.077	0.149	**0.740**	0.098	0.118	-0.062	**-0.209**	**0.183**	0.125	**0.606**	**-0.266**	0.030	**0.331**	0.139	-0.161	**0.415**	-0.261	
Se	0.037	0.004	**0.292**	**0.521**	**0.492**	**-0.225**	**0.543**	**0.367**	**0.324**	**0.445**	**0.386**	**0.648**	0.140	**0.344**	-0.033	-0.036	0.004	**0.455**	-0.016	-0.035	-0.129	-0.113	**0.372**	**0.166**	**0.323**	-0.084	0.131	**0.463**	0.137	-0.110	**0.572**	-0.130	**0.715**

R95% = 0.156, n = 122 (Koch and Link, 1970)

5.8 GENERAL TRENDS AND POSSIBLE IMPACTS ON THE RIVER CLYDE

One of the aims of the survey was to establish broad trends in the sediment and water quality of tributaries draining into the River Clyde. Most regulatory water quality assessments are based on temporal monitoring of a few parameters at a limited number of sites. The temporal aspect of monitoring is important because water quality can change very markedly through time due to dilution effects from rainfall; wet and dry atmospheric chemical deposition; the amount of surface run-off and volume of flow. Indeed many chemical parameters show seasonal variation in concentration (Neal and Robson, 2000). In contrast, the GSUE survey examines a broad range of parameters over a spatially extensive area to provide an overview of stream water quality but it should be appreciated that the data generated are a temporal 'snap-shot'. None the less the effects of increased surface run-off are minimised by sampling during the summer months when baseflow conditions predominate in the catchments. Evidence from a stream hydrogeochemical survey of Wales carried out between 1988 and 1994 suggests that spatial differences in water chemistry related to underlying solid and drift deposits, land use and anthropogenic sources can be identified despite temporal variations in run-off (BGS, 1999).

Hence the data generated by the present study are interesting because they provide evidence of catchments where contaminants have entered the water column, are mobile and have the potential to impact upon the River Clyde. On this basis ammonium dispersal is widespread in the upper reaches of the White Cart catchment but is diluted downstream over a 1 km distance between sites WC6 and WC 5 (Annex 7). Similarly, values exceeding the WSR guideline are reported in the upper reaches of the Tollcross and Camlachie catchments but appear to be diluted to low concentrations within short distances downstream (Annex 7). In contrast, high ammonium concentrations in the Malls Mire, Polmadie, Kirk, Newton, North Calder, Battle and Yoker Mains Burns are proximal to their inflows to the Clyde and probably affect river water quality (Annex 8). High As, Cr and Sb concentrations in the Molendinar waters and Cr in the Polmadie Burn also occur close to the Clyde inflows and have the potential to impact upon river water quality (Annex 8). Likewise, high Cr concentrations in the Light Burn appear to compromise water quality in the Camlachie and ultimately the Molendinar catchment draining into the Clyde and concentrations in the Hole-Merry catchment affect the quality of the White Cart water for several kilometres downstream (Annex 7).

However, it is emphasised again that these data provide a temporal snap-shot and because of the seasonal variability in water quality it is pertinent to consider trends in sediment quality as concentrations do not vary so markedly with time. Furthermore sediments act as source-sinks for contaminants, indeed many studies have demonstrated that the dominant control on contaminant migration in rural and urban drainage systems is the re-suspension of sediment particulates into the water column during storm events (for example Neal et al., 1999; Coyle et al., 2004).

Although element concentrations in the fine < 150 µm fraction of the sediments collected for the present study have not been considered in detail in relation to guideline values in the previous sections of this report, these data are important in terms of contaminant mobility as it is the fine sediment that is likely to be most readily mobilised and transported over greater distances during storm events.

In this context, based on the concentrations in < 2 mm AND < 150 µm sediment fractions outlined in Annexes 3 and 4, a range of contaminants in several of the catchments indicate either a degree of downstream dispersal (namely high values at adjacent sampling points) or proximity to the Clyde and are of potential concern with respect remobilisation of material into the river (Table 5.12). It is recommended that relationships between tributary inflows and sediment and water quality in the River Clyde be examined in more detail for these parameters once the Clyde estuary geochemical data are available (Jones et al., 2004).

Table 5.12 List of catchments draining into the River Clyde of potential concern in terms of sediment contaminant transport

Catchment	**Contaminants**
Camlachie	As, Cd, Cr, Pb, Ni, TPH
Polmadie	As, Cd, Cr, Ni, TPH, PCB
Molendinar	As, Cd, Cr, Ni, TBT
Linthouse	As, Cd, TPH, PCB, TBT
Yoker Mains	As, Cd, Cr, TPH, DBT
Eastfield	Cd, Cr, Ni, TPH
Malls Mire	Cr, Ni, TPH
White Cart	Cr, Pb, Ni
Auldhouse	Cr, Pb
Battle	Cr, Ni
Brock	As, Ni
Kelvin	As, Pb
Levern	As, Ni
Newton	Cd, Ni
North Calder	Cr, Ni
Yoker	Ni, PCB
Hole-Merry	Cr
Light	Cr
Tollcross	Ni

6 Conclusions and Recommendations

- The geochemical results for 118 stream sediment and 122 surface water samples collected from all tributaries draining into the River Clyde in the Glasgow City Council administrative area provide an overview of the drainage geochemistry in the urban environment and a bench mark against which future change can be measured particularly in light of the forthcoming CEC Water Framework legislation. The data also provide information on potential contamination problems that may require further investigation.

- Comparisons between the urban geochemical data with the surrounding rural G-BASE drainage survey data are useful to place the urban data in context and assess the levels of contamination in the urban environment against the rural background. The results of the present study indicate that many of the metal elements are enhanced 2-3 times in the urban environment regardless of solid geology and superficial deposit parent material type.

- No conclusive relationship between made ground and sediment or water geochemistry was evident in the present study. However, comparisons with land use and potential contaminant sources were not examined in detail as part of this report and it is recommended that these issues are investigated further as part of the proposed follow-on Clyde estuary-Clyde basin study (see below).

- Comparisons between the fine (< 150 μm) and coarse (< 2mm) fraction of stream sediments revealed that the majority of contaminants are concentrated in the fine fraction and are probably associated with clay minerals, heavy minerals and iron and manganese oxides. This has implications for the transport of contaminants into the Clyde estuary. Examining the dynamics of the Clyde tributary and estuary system were beyond the scope of the present study but it is recommended that further investigations be carried once the on-going Clyde estuary geochemical survey is completed.

- Parameter concentrations in sediments generally showed a poor correlation with levels in surface waters as the dissolution of minerals depends not only on the concentrations in the sediment but on factors such as the pH and redox conditions and presence of clay minerals, organic matter and iron and manganese oxides at the site. It was beyond the scope of this study to examine these issues in detail but it is recommended that the relationships between sediment and water and controls on contaminant mobility be examined in more detail as part of the proposed follow-on Clyde estuary-Clyde basin study.

- Although there are currently no UK guidelines on sediment quality, comparison with soil guideline values from this country and elsewhere reveal that many of the metal contaminants exceed the guideline values in streams in the north-west, east and south-east of Glasgow indicating contamination but also in peaty marshy streams to the north-east of the city where low pH and high organic and iron and manganese oxide contents in the sediments probably enhance the metal loading of the sediments. In contrast, cyanide and asbestos determinations in sediments were below guideline values. The organic contaminants TPH, PAH and PCB in sediments were evident at sites proximal to bus depots, gas works, heavy engineering and mixed industry. In contrast organo-tin compounds were identified at only 3 sites, 2 of which are proximal to the dockland areas of the city as expected.

- Comparisons between surface water parameters and guideline values from this country and elsewhere demonstrated that ammonium and dissolved oxygen levels are generally poor in streams in the east of Glasgow known to be contaminated and peaty marshy areas to the north-east of the city. Levels of Cr in stream water in the east and south-east of Glasgow are extremely high in a few localities (up to 903 $\mu g\ L^{-1}$) as a result of the widespread use of chromite processing waste as fill materials in the city. More detailed examinations of the distribution of Cr in the Clyde estuary in relation to inputs from the tributaries is recommended as part of the proposed follow-up Clyde estuary–Clyde basin study.

- The aim of the present study was to provide information on the geochemistry of Clyde tributaries to link to an on-going sister project investigating the geochemistry of the Clyde estuary. Once the Clyde estuary project is completed it is recommended that the data from the present survey be examined in the context of a wider geo-environmental characterisation of the Clyde basin to aid urban regeneration and mitigate environmental impacts. It is envisaged that a future project would consider, the hydro-dynamics and geochemistry of the Clyde estuary, the geochemistry of the Clyde tributaries and the BGS soils geochemical database for Glasgow, which will become available in 2004, to assess the implications of land use and contaminant mobility on environmental quality in the Clyde basin.

7 References

ALCOCK, RE, JOHNSTON, AE, MCGRATH, SP, BERROW, ML AND JONES, KC. 1993. Long-term changes in the polychlorinated biphenyl content of United Kingdom soils. *Environmental Science and Technology* 27, 1918-1923

API. 2001. *Risk-based Methodologies for Evaluating Petroleum Hydrocarbon Impacts at Oil and Natural Gas E&P Sites*, API Publication 4709. (Washington: American Petroleum Institute)

APPLETON, JD. 1995. *Potentially Harmful Elements from Natural Sources and Mining Areas: Characteristics, Extent and Relevance to Planning and Development in Great Britain.* Technical Report WP/95/3. (Keyworth, Nottingham: British Geological Survey)

ARNOLD C, BERG A, MULLER S, DOMMAN U, AND SCHWARZENBACH R. 1998. Dionex, Application Note 339. *Analytical Chemistry* 70, 3094-3101.

ASTM. 1995. *Standard E1739-95e1 Guide for Risk-based Corrective Action Applied at Petroleum Release Sites.* (Philadelphia: American Society for Testing Materials)

ASTM. 2000. *Standard E2081-00 Guide for Risk-based Corrective Action*. (Philadelphia: American Society for Testing Materials)

AYRIS, SA, CURRADO, GA, SMITH, D AND HARRAD, S. 1997. GC-MS procedures for the determination of PCBs in environmental matrices. *Chemosphere*, 35, 905-917.

BALBA, MT, YING, AC AND MCNEICE, TG. 1991. Bioremediation of contaminated land: bench scale to field applications. In: HINCHEE, RE. AND OLFENBUTTEL, RF. (Eds.) *On-site Bioreclamation: Processes for Xenobiotic and Hydrocarbon Treatment.* (Stoneham, MA: Butterworth and Heinemann)

BAUMARD, P, BUDZINSKI, H, MCHIN, Q, GARRIGUES, P, BURGEOT, T, AND BELLOCQ, J. 1998. Origin and bioavailability of PAHs in the Mediterranean Sea from mussel and sediment records. *Estuarine, Coastal and Shelf Science* 47, 77-90.

BOULOUBASSI, I AND SALIOT, A. 1993. Investigation of anthropogenic and natural organic inputs in estuarine sediments using hydrocarbon markers (NAH, LAB, PAH). *Oceanologica Acta* 16, 145-161.

BRIDGE, DM, BROWN, MJ AND HOOKER, PJ. 1997. *Wolverhampton Urban Environmental Survey: An Integrated Geoscientific Case Study.* Technical Report WE/95/49. (Keyworth, Nottingham: British Geological Survey)

BRITISH GEOLOGICAL SURVEY. 1993. *Regional Geochemistry of Southern Scotland and Part of Northern England.* (Keyworth, Nottingham: British Geological Survey)

BRITISH GEOLOGICAL SURVEY. 1999. *Regional Geochemistry of Wales and Part of West-central England: Stream Water.* (Keyworth, Nottingham: British Geological Survey)

BRITISH GEOLOGICAL SURVEY. 2000. *Regional Geochemistry of Wales and Part of West-central England: Stream Sediment and Soil.* (Keyworth, Nottingham: British Geological Survey)

BROWN, MJ AND MARCHANT, A. 2000. Providing GIS solutions for local authorities. *Earthwise* 16, 22-23.

BROWNE, MAE, FORSYTH, IH AND MCMILLAN AA. 1986. Glasgow, a case study in urban geology. *Journal of the Geological Society of London* 143, 509-520.

BRYAN, SK, GIBBS, PE, BURT, GR AND HAMMERSTONE, LG. 1986. The decline of the gastropod *Nucella lapillus* around south-west England: evidence for the effects of tributyltin from anti-fouling paints. *Journal of the Marine Biological Association UK* 66, 611-640.

BUDZINSKI, H, JONES, I, BELLOCQ, J, PIÉRARD, C, AND GARRIGUES, P. 1997. Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary. *Marine Chemistry* 58, 85-97.

CEC. 1978. *The Quality of Fresh Waters Needing Protection or Improvement in Order to Support Fish Life.* EU Directive 78/659/EEC (Brussels: Commission of the European Community)

CEC. 1998. *Water Quality Framework.* EU Directive 98/83/EC. (Brussels: Commission of the European Community)

CEC 2000. *Establishing a Framework for Community Action in the Field of Water Policy.* EU Directive 2000/60/EC. (Brussels: Commission of the European Community)

COYLE, J, TAYLOR, KG AND DOBSON M. 2004. Sediment and associated contaminant flux through an urban river system, Greater Manchester, UK. *Abstracts of the 22nd Society for Environmental Geochemistry and Health European Conference*. Brighton.

CREASER, CS AND FERNANDES, AR. 1986. Background levels of polychlorinated biphenyls in British soils. *Chemosphere* 15 (4), 499-508.

D'ARCY, BJ, ELLIS, JB, FERRIER, RC, JENKINS, A AND DILS, R. (eds). 2001. *Diffuse Pollution Impacts*. (Lavenahm, Surrey: CIWEM, Terence Dalton Publishers)

DAVIES, BE. 1995. Lead. In: *Heavy Metals in Soils*. ALLOWAY, BJ. (editor). (London: Blackie Academic & Professional.) 206-223.

DEFRA. 2004. *Contaminated Land Exposure Assessment Guidelines (CLEA)*, Department of the Environment and Rural Affairs, http://www.defra.gov.uk/environment/landliability/pubs.htm

DETR. 2000. *Environment Agency and Institute for Environment and Health Guidelines for Environmental Risk Assessment and Management* (London: HMSO).

DODD, J, LARGE, DJ, FORTEY, NJ, KEMP, S, STYLES, M, WETTON, P AND MILODOWSKI, A. 2003. Geochemistry and petrography of phosphorus in urban canal bed sediment. *Applied Geochemistry* 18(2), 259-268.

EA. 2002. *Contaminants in Soil: Collation of toxicological data and intake values for humans. Benzo(a)pyrene*. Environment Agency R&D Publication Tox 2. (Bristol: Environment Agency)

EA. 2003. *Principles for Evaluating the Human Health Risks from Petroleum Hydrocarbons in Soils: A Consultation Paper*. R&D Technical Report P5-080/TR1 (Bristol: Environment Agency)

EDGAR, PJ, DAVIES, IM AND HURSTHOUSE, AS 1999. The biogeochemistry of polychlorinated biphenyls (PCBs) in the Clyde: Distribution and source evaluation, *Marine Pollution Bulletin*, Vol. 38 (6), 486-496.

EDGAR, PJ, HURSTHOUSE, AS, MATTHEWS, JE AND DAVIES, IM. 2003. An investigation of geochemical factors controlling the distribution of PCBs in intertidal sediments at a contamination hot spot, the Clyde Estuary, UK, *Applied Geochemistry* 18 (2), 327-338.

ELLISON, RA, ARRICK, A, STRANGE, PJ AND HENNESSEY, C. 1998. *Earth Science Information in Support of Major Development Initiatives*. Technical Report WA/97/84. (Keyworth, Nottingham: British Geological Survey)

ENVIRONMENTAL PROTECTION ACT PART IIA. 1990. *Contaminated Land* (London: HSMO)

EVANS, SM, EVANS, PM AND LEKSONO, T. 1996, Widespread recovery of dogwhelks, Nucella lapillus (L), from tributyltin contamination in the North Sea and Clyde Sea. *Marine Pollution Bulletin* 32 (3), 263-269.

FARAGO, ME, KAVANAGH, P, BLANKS, R, KELLY, J, KAZANTIS, G, THORNTON, I, SIMPSON, PR, COOK, JM, PARRY, S AND HALL, GEM. 1996. Platinum metal concentrations in urban road dust and soil in the United Kingdom. Fresenius *Journal of Analytical Chemistry* 354(5-6), 660-663.

FARMER, JG, THOMAS, RP, GRAHAM, MC, GEELHOED, JS, LUMSDON, DG AND PATERSON, E. 2002. Chromium speciation and fractionation in ground and surface waters in the vicinity of chromite ore processing residue disposal sites. *Journal of Environmental Monitoring* 4(2), 235-243.

FERGUSSON, JE. 1990. *The Heavy Metals: Chemistry, Environmental Impacts and Health Effects*. (Oxford: Pergamon Press)

FORSYTH, IH, MCMILLAN, AA, BROWNE, MAE AND BALL, DF. 1984a. *Account Accompanying Environmental Geology Maps of Glasgow (National Grid Sheet NS66).* Central Scotland Research Programme Technical Report WA/LS/84/2 (Edinburgh: British Geological Survey)

FORSYTH, IH, MCMILLAN, AA, BROWNE, MAE AND BALL, DF. 1984b. *Account Accompanying Environmental Geology Maps of Glasgow (National Grid Sheet NS56).* Central Scotland Research Programme Technical Report WA/LS/84/3 (Edinburgh: British Geological Survey)

FORSYTH, IH, PATERSON, IB, AND HALL, IHS. 1984c. *Account Accompanying Environmental Geology Maps of Glasgow Phase 2 Parts of National Grid Sheets NS 55, 57 and 65.* Central Scotland Research Programme Technical Report WA/LS/84/2 (Edinburgh: British Geological Survey)

FORSYTH, IH, PATERSON, IB, AND HALL, IHS. 1985. *Account Accompanying Environmental Geology Maps of Glasgow Phase 3 Parts of National Grid Sheets NS 55, 57 and 65.* Central Scotland Research Programme Technical Report WA/LS/85/2 (Edinburgh: British Geological Survey)

GSCHWEND, PM AND HITES, RA. 1981. Fluxes of polycyclic aromatic hydrocarbons to marine and lacustrine sediments in the northeastern United States. *Geochimica et Cosmochimica Acta* 45, 2359-2367.

GUSTAFSON, JB. 2002. Using TPH in Risk-Based Corrective Action. http://www.epa.gov/swerustl/rbdm/tphrbca.htm.

HALL, IHS, BROWNE, MAE AND FORSYTH, IH. 1998. *Geology of Glasgow District.* British Geological Survey Memoir for 1:50 000 Geological Sheet 30E (Scotland). (London: HMSO)

HARRAD, S, STUART, AP, ALCOCK, R, BOUMPHREY, R, BURNETT, V, DUARTE-DAVIDSON, R, HALSAL, C, SANDERS, G, WATERHOUSE, K, WILD, SR AND JONES, KC. 1994. Polychlorinated biphenyls (PCBs) in the British environment: sinks, sources and temporal trends. *Environmental Pollution* 85, 131-146.

HARRIS, JR, AND COATS, JS. 1992. *Geochemistry Database: Data Analysis and Proposed Design.* Technical Report, WF/92/5. (Keyworth: British Geological Survey)

HARRISON, I. 2002. *Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Sediments from the Irish Sea*. Internal Report IR/02/029. (Keyworth: British Geological Survey)

HEM, J. 1992. *Study and Interpretation of the Chemical Characteristics of Natural Water*. (Reston: US Geological Survey).

HOOKER, PJ, ELLISON, RA, MARCHANT, AP, SHAW, RP, LEADER, RU, NEWSHAM, R, BROWN, MJ, WARD, RS, VEITCH, N, HART, AJ AND MORRIS JL. 2000. *Some Guidance on the Use of Digital Environmental Data.* Technical Report WE/99/14. (Keyworth, Nottingham: British Geological Survey)

HUDSON-EDWARDS, KA. 2003. The geochemistry of sediment-borne contaminants in fluvial, urban and estuarine environments. *Applied Geochemistry* 18(2), 155-158.

HURSTHOUSE, AS, MATTHEWS, JE, FIGURES, P, IQBAL-ZAHID, P, DAVIES, IM, AND VAUGHAN DH. 2003. Chromium in intertidal sediments of the Clyde, UK: potential for remobilisation and bioaccumulation. *Environmental Geochemistry and Health* 25(2), 171-203.

ICRCL. 1987. *Guidance on the Assessment and Redevelopment of Contaminated Land.* Interdepartmental Committee on the Redevelopment of Contaminated Land Guidance Note No. 59/83 (2nd Edition). (London: Department of the Environment)

INGHAM, MN AND VREBOS, BAR. 1994. High Productivity Geochemical XRF Analysis. *Advances in X-ray Analysis*, Vol.37, 717-724.

JOHNSON, CC, BROWN, SE AND LISTER, TR. 2003. *G-BASE Field Procedures Manual.* Internal Report IR/03/096N. (Keyworth: British Geological Survey)

JONES, DG, LISTER, TR, STRUTT, MH, ENTWISTLE, DC, HARRISON, I, KIM, AW, RIDGWAY, J AND VANE CH. 2004. *Estuarine Geochemistry: Report for Glasgow City Council.* Commissioned Report CR/04/057 (Keyworth: British Geological Survey).

KELLY, AG. 1995. Accumulation and persistence of chlorobiphenyls, oprganochlorine pesticides and faecal sterols at the Garroch Head sewage sludge disposal site, Firth of Clyde. *Environmental Pollution*, 88, 207-217.

KELLY, JJP. 1997. *Influence of Geology and Anthropogenic Activity on the Geochemistry of Urban Soils.* Unpublished Thesis, Imperial College Centre for Environmental Technology, London.

KELLY, JJP, THORNTON, I AND SIMPSON PR. 1996. Urban geochemistry: a study of the influence of anthropogenic activity on the heavy metal content of soils in traditionally industrial and non-industrial areas of Britain. *Applied Geochemistry*, Vol. 11, 363-370.

KIM A. 2003. Estuarine Contamination (Clyde, UK): *Determination of Tributyltin (TBT) and Other Organotin Compounds in Sediment*. Clyde Estuarine Contamination Study. (Keyworth: British Geological Survey)

KIM, A AND SPIRO, B. 2003. *Estuarine Contamination (Mersey, UK): Determination of PCBs, Organotin and Organolead Compounds in Sediments as a Tool for Fingerprinting Contaminant Sources*. NIGL-BGS Programme No. 40149. (Keyworth: British Geological Survey)

KOCH, G AND LINK, R. 1970. *Statistical Analysis of Geological Data*. (New York: John Wiley and Sons)

LEAD, WA, STEINNES, E, BACON, JR AND JONES, KC. 1997. Polychlorinated biphenyls in UK and Norwegian soils: spatial and temporal trends. *The Science of the Total Environment*, 193, 229-236.

LEHR, RE AND JERINA, DM. 1977. Metabolic activations of polycyclic hydrocarbons: Structure-activity relationships. *Archives of Toxicology*, Vol. 39, 1-6.

ŁOBIŃSKI, D, DIRKX, WMR AND CEULEMANS, M. 1992. Optimisation of comprehensive speciation of organotin compounds in environmental samples by capillary gas chromatography/helium microwave-induced plasma emission spectrometry. *Analytical Chemistry* 64 (2), 159.

MAFF. 1994. *Aquatic Environment Monitoring*. Marine Pollution Monitoring Group, Sixth Report of the Group Co-ordinating Sea Disposal Monitoring. Report No. 43. (London: Ministry of Agriculture, Fisheries and Food)

MASTRAL, AM, LÓPEZ JM, CALLÉN, MS, GARCIA, T, MURILLO, R AND NAVARRO, MV. 2003. Spatial and temporal PAH concentrations in Zaragoza, Spain. *The Science of the Total Environment* 3078, 111-124.

MCCREADY, S, SLEE, DJ, BIRCH, GF AND TAYLOR, SE. 2000. The distribution of polycyclic aromatic hydrocarbons in surficial sediments of Sydney Harbour, Australia. *Marine Pollution Bulletin* 40 (11), 999-1006.

MCMILLAN, AA, ELLISON, RA, FORDYCE, FM, Golledge, NR. and 7 others. 2001. *Superficial Deposits Characterisation in the Urban Environment; A Best Practice Guide to Mapping and Research*. Internal Report IR/01/68. (Keyworth: British Geological Survey)

MORGAN, P AND WATKINSON, RI. 1989. Hydrocarbon degradation in soils and methods for biotreatment, *Critical Reviews in Biotechnology* 8, 305-333.

NEAL, C, JARVIE, HP AND OGUCHI, T. 1999. Acid-available particulate trace metals associated with suspended sediment in the Humber rivers: a regional assessment. *Hydrological Processes,* Vol. 13 (7), 1117-1136.

NEAL, C AND ROBSON, AJ. 2000. A summary of river water quality data collected within the Land-Ocean Interaction Study: core data for eastern UK rivers draining to the North Sea. *Science of the Total Environment,* Vol. 251, 585-665.

NICHOLSON, G.J AND EVANS, S.M. 1997. Anthropogenic impacts on the stocks of the common whelk Buccinum undatum (L). *Marine Environmental Research* 44 (3), 305-314.

NOAA. 1999. *Sediment Quality Guidelines Developed for the National Status and Trends Program*. HAZMET Report 99-1. (Washington: National Oceanographic and Atmospheric Administration)

O'DONNELL, KE. 2004. *Geochemical Baseline Data for the Urban Area of York*. Internal Report IR/02/085. (Keyworth: British Geological Survey)

OSPAR. 1997. *Oslo And Paris Conventions For The Prevention Of Marine Pollution Joint Meeting Of The Oslo And Paris Commissions, Brussels: 2-5 September 1997.* Agreed Background / Reference Concentrations for Contaminants in Sea Water, Biota and Sediment. (London: OSPAR Commission)

OSPAR. 2000. *Commission for the Protection of the Marine Environment of the North-East Atlantic, Quality Status Report 2000.* (London: OPSAR Commission)

PLANT, JA. 1973. A random numbering system for geochemical samples. *Transactions of the Institute of Mining and Metallurgy* B82, 63-66.

POLLARD, SJT, WHITTAKER, M AND RISDEN, GC. 1999. The fate of heavy oil wastes in soil microcosms I: A performance assessment of biotransformation indices, *Science of the Total Environment* 226, 1-22.

READMAN, JW, FILLMANN, G, TOLOSA, I, BARTOCCI, J, VILLENEUVE, J-P, CATINNI, C AND MEE, L D. 2002. Petroleum and PAH contamination of the Black Sea. *Marine Pollution Bulletin* 44 (1), 48-62.

REIMANN, C AND CARITAT, P. 1998. *Chemical Elements in the Environment.* (Berlin: Springer)

REMADE. 2004. *Bioremediation at Contaminated Gasworks Site: A Case Study*, http://www.remadeessex.org.uk/bioremediation.htm.

RIDGWAY, JM, BREWARD, N, CHENERY, SRN, REES, JG, LISTER, TR, GOWING, CJB AND INGHAM, MN. 2001. *Distinguishing between natural and anthropogenic sources of metals* *entering the Irish Sea*. Commissioned Report. CR/01/015 (Keyworth: British Geological Survey).

RIDGWAY, JM, BREWARD, N, LANGSTON, WJ, LISTER, TR, REES, JG AND ROWLATT, SM. 2003. Distinguishing between natural and anthropogenic sources of metals entering the Irish Sea. *Applied Geochemistry* 18(2), 283-310.

ROBERTSON, DJ, TAYLOR, KG AND HOON, SR. 2003. Geochemical and mineral magnetic characterization of urban sediment particles, Manchester, UK. *Applied Geochemistry* 18(2), 269-282.

ROGERS, HR. 2002. Assessment of PAH contamination in estuarine sediments using the equilibrium partitioning-toxic unit approach. *Science of the Total Environment*, Vol. 290 (1-3), 139-155.

ROWELL, DL. 1994. *Soil Science: Methods and Applications*. (UK: Longman Scientific and Technical)

SHIARIS, MP AND JAMBARD-SWEET, D. 1986. Polycyclic aromatic hydrocarbons in surficial sediments of Boston Harbour, Massachusetts, USA. *Marine Pollution Bulletin* 17 (10), 469-472.

SNIFFER. 2003. *Method for Deriving Site-Specific Human Health Assessment Criteria for Contaminants in Soil*. SNIFFER Report LQ1. (Stirling: Scottish Environmental Protection Agency)

TYLER, AO, MILLWARD, GE, JONES, PH AND TURNER, A. 1994. Dibenzo-para-dioxins and dibenzofurans in sediments from U.K. estuaries. *Estuarine and Coastal Shelf Science*, 39, 1-13.

US-EPA. 2004. *Water Quality Standards*. http://www.epa.gov/waterscience/standards/

US-EPA. 2004a. *Clean-Up*. http://www.epa.gov/ebtpages/cleanup.html

VAN ZYL, C. 1982. Rapid preparation of robust pressed powder briquettes containing a styrene and wax mixture as a binder. *X-ray Spectrometry* 11, 29-31.

WANG, X-C, ZHANG, Y-X AND CHEN, RF. 2001. Distribution and partitioning of polycyclic aromatic hydrocarbons (PAHs) in the different size fractions in sediments from Boston Harbor, United States. *Marine Pollution Bulletin* 42 (11), 1139-1149.

WARD, NI. 1990. Multielement contamination of British motorway environments. *Science of the Total Environment* 93, 393-441.

WESTLAKE, DWS, JOBSON, A, PHILLIPPE, R AND COOK, FD. 1974. Biodegradability and crude oil composition. *Canadian Journal of Microbiology* 20, 915-928.

WHALLEY, C, HURSTHOUSE, A, ROWLATT, S, IQBAL-ZAHID, P, VAUGHAN, H AND DURANT, R. 1999. Chromium speciation in natural waters draining contaminated land, Glasgow UK. *Water, Air and Soil Pollution* 112, 389-405

WOODHEAD, RJ, LAW, RJ AND MATTHISSEN P. 1999. Polycyclic aromatic hydrocarbons in surface sediments around England and Wales, and their possible biological significance. *Marine Pollution Bulletin*, Vol. 39 (9), 773-790.

WORLD HEALTH ORGANISATION. 1996 Guidelines *for Drinking Water Quality*. (Geneva: World Health Organisation)

WSR. 2000. *The Water Supply (Water Quality) (Scotland) Regulations* (HMSO: Edinburgh), http://www.scotland-legislation.hmso.gov.uk/

YANIK, PJ, O'DONNELL, TH, MAKO, SA, QIAN, Y AND KENNICUTT, MC. 2003. Source apportionment of polychlorinated biphenyls using compound specific isotope analysis. *Organic Geochemistry*, 34(2), 239-251.

YUNKER, MB, SNOWDON , LR, MACDONALD , RW, SMITH, JN, FOWLER, MG, SKIBO, DN, MCLAUGHLIN, FA, DANYUSHEVSKAYA, AI, PETROVA, VI AND IVANOV, GI. 1996. Polycyclic aromatic hydrocarbon composition and potential sources for sediment samples from the Beaufort and Barents Seas. *Environmental Science and Technology* 30(4), 1310-1320.

YUNKER, MB, MACDONALD , RW, VINGARZAN, R, MITCHELL, RH, GOYETTE, D AND SYLVESTRE, S. 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic Geochemistry* 33(4), 489-515.

ZEMANEK, MG, POLLARD, SJT, KENEFICK, SL AND HRUDEY, SE. 1997. Multiphase partitioning and co-solvent effects for Polynuclear Aromatic Hydrocarbons (PAH) in authentic petroleum- and creosote-contaminated soils, *Environmental Pollution* 98(2), 239-252

KEY TO THE ANNEXES – ANNEX REFERENCES

Soil (used as a proxy for sediments) Guideline Values

US-EPA Cleanup Standard = US-EPA. 2004a. *Clean-Up*, http://www.epa.gov/ebtpages/cleanup.html

CLEA Guideline = DEFRA 2004. *Contaminated Land Exposure Assessment Guidelines*, Department of the Environment and Rural Affairs, http://www.defra.gov.uk/environment/landliability/pubs.htm

Netherlands Remediation Guideline = Reimann C and Caritat P. 1998. *Chemical Elements in the Environment.* (Berlin: Springer)

German Guideline = Reimann C and Caritat P. 1998. *Chemical Elements in the Environment.* (Berlin: Springer)

ICRCL Guideline = ICRCL. 1987. *Guidance on the Assessment and Redevelopment of Contaminated Land.* Interdepartmental Committee on the Redevelopment of Contaminated Land Guidance Note No. 59/83 (2nd Edition). (London: Department of the Environment)

Water Quality Guideline Values

WSR Scotland = WSR. 2000. *The Water Supply (Water Quality) (Scotland) Regulations* (HMSO: Edinburgh), http://www.scotland-legislation.hmso.gov.uk/

CEC Drinking Water = CEC. 1998. *Water Quality Framework Directive* 98/83/EC. (Brussels: Commission of the European Community)

US-EPA = US-EPA 2004. *Water Quality Standards.* http://www.epa.gov/waterscience/standards/

Russian Guideline = Reimann C and Caritat P. 1998. *Chemical Elements in the Environment.* (Berlin: Springer)

WHO Guideline = World Health Organisation. 1996. *Guidelines for Drinking Water Quality.* (Geneva: World Health Organisation)

Environmental Values

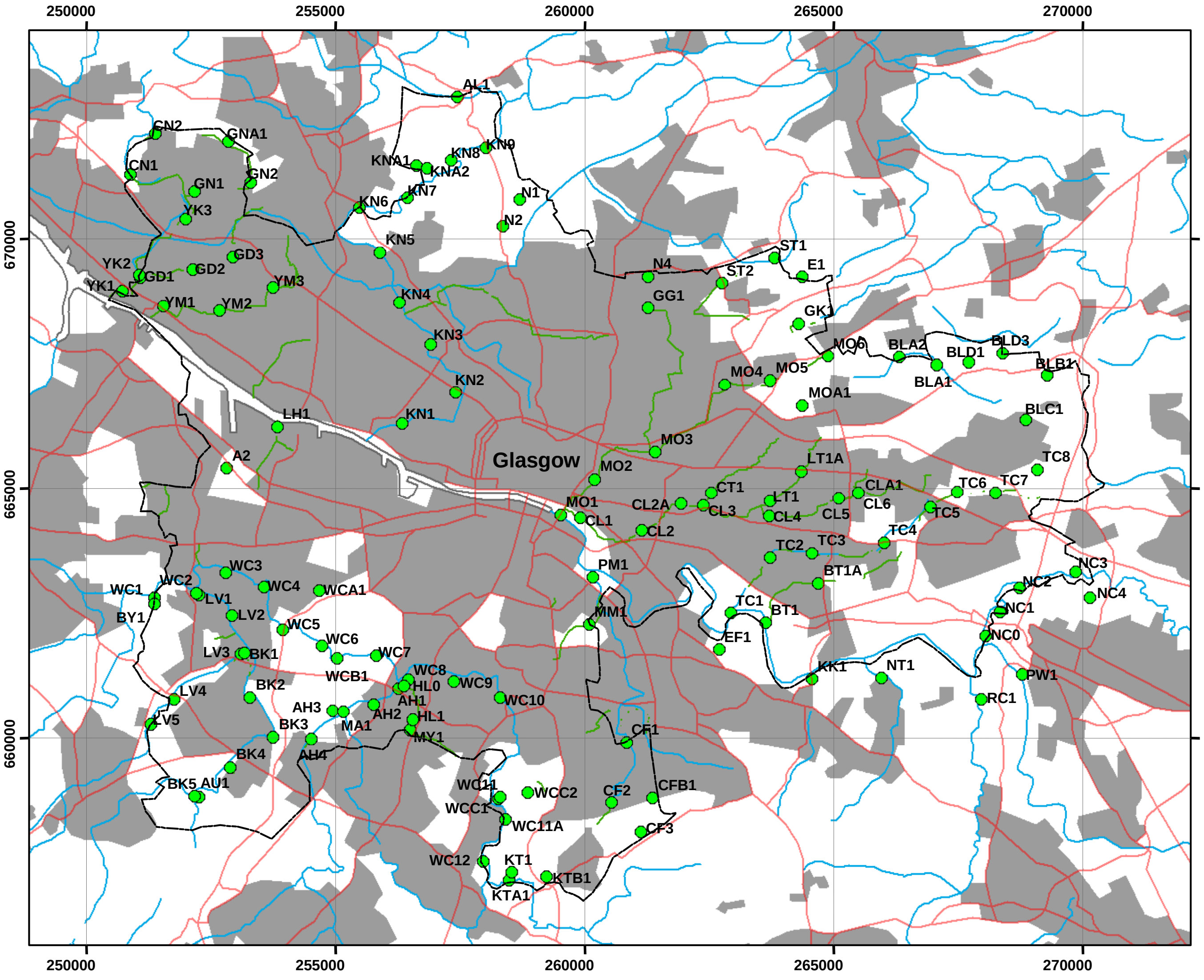
G-BASE Southern Scotland = British Geological Survey 1993. *Regional geochemistry of Southern Scotland and part of Northern England.* (Keyworth: British Geological Survey). Average = Median value

G-BASE Welsh = British Geological Survey. 2000. *Regional Geochemistry of Wales and Part of West-central England: Stream Sediment and Soil.* (Keyworth: British Geological Survey). Average = Median value

Seawater Average = British Geological Survey. 1999. *Regional Geochemistry of Wales and Part of West-central England: Stream Water.* (Keyworth: British Geological Survey).

Rainwater Average = British Geological Survey. 1999. *Regional Geochemistry of Wales and Part of West-central England: Stream Water.* (Keyworth: British Geological Survey)

KEY TO THE ANNEXES – SAMPLE LOCATION CODES



GCC Sample Code Catchment
A = Hillington
AH = Auldhouse Burn
AL = Allander Water
AU= Aurs Burn
BK = Brock Burn
BL = Bishop Loch
BT = Battle Burn
BY = Blacksey Burn
CF = Cityford Burn
CL = Camlachie Burn
CN = Cleddans Burn
CT = Carntyne Burn
E = Auchengree
EF = Eastfield Burn
GD = Garscadden Burn
GG = Garngad Burn
GK = Garnkirk Burn
GN = Garscadden Burn North
HL= Hole Burn
KK = Kirk Burn
KN = River Kelvin
KT = Kittoch Water
LH = Linthouse Burn
LT = Light Burn
LV = Levern Water
MA = Manse Burn
MM = Malls Mire Burn
MO = Molendinar Burn
MY = Merry Burn
N = North Glasgow
NC = North Calder
NT = Newton Burn
PM = Polmadie Burn
PW = Pow Burn
RC = Rotten Calder
ST = Stand Burn
TC = Tollcross Burn
WC = White Cart
YK = Yoker Burn
YM = Yoker Mains Burn

● Sample site locations
— Major roads
— Glagow City boundary
— Culverts
— Rivers
▨ Urban areas