

**CHEMICAL RELATIONSHIPS IN WATERS AND
SEDIMENTS OF SOME URBAN STREAMS,
WITH PARTICULAR REFERENCE TO
HEAVY METALS AND PHOSPHORUS**

by

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CERTIFICATE

I certify that this thesis has not already been submitted for any degree and is not being submitted as part of candidature for any other degree.

I also certify that the thesis has been written by me and that any help that I have received in preparing this thesis, and all sources used, have been acknowledged in this thesis.

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Part 1

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List of Abbreviations

AAS	=	atomic absorption spectrophotometry
ANOVA	=	analysis of variance
ANZECC	=	Australian and New Zealand Environment and Conservation Council
AT	=	Appendix Table
bdl	=	below detectable limit
BOD	=	biochemical oxygen demand
CEC	=	cation exchange capacity
Ck.	=	creek
diss.	=	dissolved
DO	=	dissolved oxygen
EDTA	=	ethylenediamine tetraacetic acid
F	=	flow group
Fig.	=	Figure
G	=	geology category
GC	=	Gwawley Creek
HMO	=	hydrous metal oxides *
IW	=	interstitial water
Kjeld-N	=	kjeldahl nitrogen
L	=	land use category
LC50	=	the lethal concentration for 50% of the test organisms
log	=	natural logarithmic transformed data
MDS	=	multidimensional scaling
mmolNa	=	millimoles of sodium
NSW	=	New South Wales
OMS	=	organic matter and sulfides *
o-	=	ortho-
ppm	=	parts per million
QC	=	quality control
R	=	residual *
RE	=	rapidly exchangeable *
redox	=	reduction / oxidation potential
SC	=	Savilles Creek
sedOP	=	sediment organic phosphorus
sedS2P	=	sediment sum secondary phase
sedTP	=	sediment total phosphorus
SFA	=	segmented flow analyser
SPCC	=	State Pollution Control Commission #
sq	=	square root transformed data
SRP	=	soluble reactive phosphorus
SS	=	sample station
SW	=	surface water
TC	=	Temptation Creek
TOC	=	total organic carbon
trib.	=	tributary
TWINSpan	=	two-way indicator species analysis
UDP	=	Urban Development Program
v/v	=	volume per volume
w/v	=	weight per volume

* categories of sediment heavy metal speciation analysis

now the NSW Environment Protection Authority (EPA)

Part 2

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Abstract

This thesis describes two studies of the chemistry of freshwater streams in the Sydney basin.

The first was a survey of 86 waterways, sampled under low flow conditions. Samples were generally low in salinity, soft, of poor buffering capacity and dominated by sodium and chloride. Co-dominance by calcium, magnesium and (bi-)carbonate occurred in a number of particular cases. Multivariate analyses indicated three groups, separated primarily by levels of dissolved nutrients, trace metals, turbidity and colour. Groupings were associated strongly with the type of catchment development. Streams in areas relatively unaffected by human influence had notable uniformity in chemistry, while those from developed catchments were varied. Heavy metal contamination was relatively low, although a few of the samples displayed inordinately large levels of one or more metals. In such cases the more extreme measurements of phosphorus and nitrogen were also seen. These findings were consistent with occasional or localised elevation of contaminant levels.

The second study involved monitoring of three Hawkesbury Sandstone streams. Sampling of surface waters, interstitial waters and sediments was performed at irregular intervals over a two year period at three stations within each site. The streams predominantly existed under low flow conditions and showed similar major ion chemistries to the majority of the survey samples. Levels of calcium and total carbonate, plus heavy metals and nutrients were generally higher in the urbanised creeks, compared to the reference stream. During a heavy storm, high levels of nutrients, suspended solids and colour were detected in all surface waters at peak-flow, as well as alkaline pH, oxidising redox, and reduced conductivity, alkalinity and hardness.

The sandy sediments were characterised by very low levels of organic matter and cation exchange capacity. Sequential extractions identified that the sums of secondary phase lead, zinc and copper were over nine, four and two times that of the corresponding residual, respectively. Greatest proportions of zinc and lead were associated with coatings of iron and manganese oxides, or coarse waste particles. Copper was preferentially associated with organic matter. Concentration gradients between interstitial and surface waters were rare and release of sedimentary constituents should occur rapidly from the upper-most particulates.

Poor water and sediment qualities were often observed in the urban sites. Poor water quality was also seen on occasion in the reference stream. However, since poor sediment quality was not detected at those times and interstitial waters for all sites displayed high within-site variability, surface waters were considered the most reliable short-term indicator of condition for Hawkesbury Sandstone streams. Multidimensional scaling showed that all streams had distinct water and sediment chemistries. High levels of temporal and spatial variability were apparent within the urbanised sites - particularly in interstitial waters - mostly due to concentrations of heavy metals, phosphorus and suspended solids. Seasonal differences were detected, but only in terms of the level of variability between summer and winter samples.

1 INTRODUCTION

Hart (1982) recommended that the chemistry of sediments and particulate matter of water bodies be studied because information was lacking on the mechanisms that result in enrichment of these media. This has been emphasised also by Hart and McKelvie (1986), who highlighted a need for detailed understanding of the cycling of trace constituents in Australian inland waters, and in particular the role of seston in the cycling process. Contaminants most likely to be affected by sediments are heavy metals, nutrients, pesticides, PCBs and polycyclic aromatic hydrocarbons (Hart and McKelvie, 1986; Beckett, 1986; Hart, 1982; Förstner, 1982; Harms *et al.*, 1978), in fact those substances on which water quality studies focus.

In addition, Hart *et al.* (1992) noted that there have been very few *in situ* field studies which have investigated 'the biogeochemistry of reactive heavy metals with the wide range of natural variations that are characteristic of stream ecosystems'. This can be extended to include the other constituents mentioned above. With respect to the freshwater streams of the Sydney Basin, no chemical data base exists in the published literature at all, whether it be for waters or sediments.

This thesis addresses these issues through two studies of freshwater streams in the Sydney basin. The first study involves a survey of the general current water chemistry. The second involves an examination of the relationships between waters and sediments in some streams of urban Sydney. Particular reference has been made to heavy metals and phosphorus.

1.1 The Chemical Composition of Lotic Waters

It is well established that three mechanisms heavily control the chemical composition of natural surface waters - atmospheric precipitation, geochemical processes and evapotranspiration (Gibbs, 1970). Water systems that are situated in coastal regions and/or tropical areas of low relief and high leaching rates are rainfall dominated and the sea-salt aerosols, high in sodium, chloride, magnesium and sulfate, make a direct contribution to the water chemistry (Gibbs, 1970). In urban and inland catchments, atmospherically transported dusts containing potassium, calcium, bicarbonate, nutrients and contaminants are a major source of constituents (Hart and McKelvie, 1986).

Rock-dominated systems consist of those in which the water is in at least partial equilibrium with the underlying basin constituents (Gibbs, 1970). Minerals are dissolved or precipitated, thus modifying the chemical properties of the water (Stumm and Morgan, 1970). A shift in equilibrium is mediated by the physico-chemical conditions, with temperature, pH and redox conditions being perhaps the most influential (Buckney, 1980; Stumm and Morgan, 1970). In general, dissolution is favoured by increased temperature and acidic pH, although importantly, a number of inorganic salts of interest (e.g. CaCO_3 , CaSO_4) decrease in solubility as temperature is raised (Stumm and Morgan, 1970). This is most relevant in warmer areas where evaporation is highest.

Waters that are principally controlled by the evaporation-fractional crystallisation process are usually located in arid regions (Buckney, 1980; Gibbs, 1970). These tend to be sodium-rich systems (particularly those which are closer to oceans) due to the marked insolubility of calcium and magnesium carbonates, although calcium-dominated (rock source) freshwaters are also observed (Gibbs, 1970).

Other factors that influence the composition of surface waters include the origin of inflowing water, flow rate, relief and vegetation. However, in comparison such factors are regarded as having second-order importance since they generally dictate only minor deviations in the basic chemistry defined by the three prime mechanisms (Buckney, 1980; Gibbs, 1970).

External inputs and flow rate can lead to both temporal and spatial variations. The inflowing water includes groundwater, water from the surface-soil layers and surface runoff, the quantities of the latter two depending on rainfall and other factors relating to the catchment. Hence, during low flow conditions, the water is predominantly groundwater, but with precipitation the other sources contribute to increase the flow (Hart and McKelvie, 1986).

Groundwater usually contains the highest levels of dissolved materials because of the long time for water-rock contact. Surface runoff, however, may be similar to the composition of initial rainwater, although it generally contains high levels of suspended particulate matter as well (Hart and McKelvie, 1986). The suspended solids also contribute those constituents which show marked association with particulate matter, such as phosphorus and heavy metals (Gabric and Bell, 1993; Ellis, 1976).

Since the relative contributions of groundwater, surface-soil and runoff waters can vary quite markedly, especially during high flows, rate of discharge significantly affects the

concentrations of dissolved compounds (King and Tyler, 1982; Norris *et al.*, 1980; Buckney, 1979; Buckney, 1977). For example, Buckney (1977), in his study on the nature of chemical changes in the Derwent River, Tasmania, reported that with increasing discharge (up to a certain point), the concentrations of sodium, potassium, chloride and silica rose, while pH and the concentrations of calcium, magnesium, bicarbonate and sulfate fell. In another study of loadings in the Onkaparinga River, South Australia, Buckney (1979) found that the high flow period was chemically distinctive due to mobilisation of nutrients and other substances.

1.2 Stream Water Quality and Urban Runoff

Streams situated in developed catchments commonly exhibit stresses arising from non-point source pollution, most of which is introduced following storm events. Campbell (1978a) stated that this problem had become quite serious in urban Australia.

Rather than addressing the issue of storm water runoff, past major expenditures in water pollution control have been directed toward point sources such as municipal and industrial waste discharges. The continual tightening of effluent standards and improved efficiency in the treatment of such wastes, although worthwhile, has meant that stormwater pollution is the major degrading factor for many urban streams.

Part of the concern about urban waters is that the status of water quality is difficult to assess, due to the complexity of pollution sources. A single precipitation event can directly transport a wide range of pollutants (e.g. sediment, oxygen-demanding wastes, coliform bacteria, nutrients, heavy metals, insecticides and herbicides) in large quantities to receiving surface waters (Marsh, 1993). Sources include sewer overflows, solid waste litter, vegetation, chemical spills, atmospheric deposits, roof and road surface materials and vehicle pollutants (Ellis, 1989; DeGuida and Clarkson, 1987; Duda *et al.*, 1982; Weeks, 1981; Wanielista *et al.*, 1977; Ellis, 1976). The runoff also leads to a variety of other problems including overloading of treatment plants, blocking and impairment of road drains, sewers, catchbasins and channels, as well as ecological damage to flora and fauna (Ellis, 1976). As urban sprawl proceeds, there is increased impermeable surface content, coupled with reduction in infiltrative capacity, hence a greater area for the water to wash and accumulate contaminants.

Gabric and Bell (1993) reported that nutrient levels in non-point source runoff from urban and rural areas can sometimes be greater than certain common point source loadings. Indeed, it has been shown that the quality of urban stormwater runoff can, for transient

periods, be worse than that of domestic sewage (Cordery, 1977; Ellis, 1976; Radziul *et al.*, 1975). This water usually enters a stream at a number of dispersed points (i.e. non-point source pollution), often due to the lack of drainage control measures, and the result is a general depression of water quality along a considerable length of the system (Arthington *et al.*, 1982). The extent of any effects is at least partly controlled by the nature and frequency of rainfall events. Hence the type of season becomes a critical factor.

With the onset of surface flow, a strong pulse of pollutant materials is usually discharged (Marsh, 1993; Weeks, 1981). In accordance with its highly sporadic and variable nature, however, multiple peak concentrations may occur, reflecting the variety of pollutant sources, size sorting, different mobilisation rates and chemical changes at the solid surface during transport. For instance, a recent study of pollutant levels in stormwater runoff in Louisville, Kentucky (Marsh, 1993), observed extreme variability in contaminant concentrations for both 'first flush' (first 20 minutes) and composite (first 3 hour) samples. Factors causing the variation included the size of the storm, weather patterns, season and time since previous rainfall events. High variability was also observed by Florence and Morrison (1992), who noted that maximum suspended solid and heavy metal concentrations are not necessarily observed in the initial pulse.

Despite the irregular composition of urban stormwater runoff, the discharge can exhibit toxicological effects (Marsh, 1993). This is partly because a considerable fraction of the pollutant loading may be in the dissolved phase and rapid changes in receiving water quality are possible (Florence and Morrison, 1992; Cordery, 1977; Ellis, 1976).

Table 1 lists urban stormwater quality data obtained in the literature. Values from three Australian studies by Weeks (1981), Gutteridge, Haskins and Davey Pty. Ltd. and the Environment Protection Authority of Victoria (GHD & EPA, 1981) and Cordery (1977), are presented and represent mean concentration ranges observed for Melbourne and Sydney, while those from Roesner (1982) are for Seattle, in the United States. Table 1 also includes toxicity information, obtained from Hart (1974), for some of these constituents in aquatic (fresh water) systems. Although the information is generalised and may vary depending on species, water temperature, dissolved oxygen, hardness, pH, alkalinity and time of exposure (etc.), it nevertheless puts into perspective how toxic urban runoff can be.

Both acute and chronic toxicological effects are likely following runoff release into urban reaches of a watercourse (Marsh, 1993; Harremoës, 1989; Ellis, 1989; Ellis, 1976). Acute effects are principally caused by depletion in dissolved oxygen (DO) and/or

Table 1. Reported data for urban stormwater runoff and toxicity of constituents to freshwater life.

Variable	Mean concentration range (mg/L)				Toxicity in freshwater systems
	Weeks (1981)	GHD & EPA (1981)	Cordery (1977)	Roesner (1982)	
Pb	0 - 0.69	0.16 - 0.53	0.5	0 - 0.51	<p>Hart (1974)</p> <p>96 hour LC50s vary from 1 - 7 mg/L for certain trout and minnows</p> <p>LCs for fish : 0.01 - 330 mg/L</p> <p>LCs for fish : 0.01 - 10 mg/L</p> <p>Toxicities vary from 0.015 - 3 mg/L for aquatic life</p> <p>Toxicities to zooplankton and phytoplankton vary from 0.016 - 0.7 mg/L</p> <p>96 hour LC50 to fathead minnows = 5 mg/L (limited data available)</p> <p>0.006 mg/L lethal to water fleas; 0.02 mg/L lethal to certain fish</p> <p>0.1 mg/L : limit for prevention of nuisance plant growth in streams</p> <p>96 hour LC50s for fish : 0.29 - 5.1 mg/L; 8 mg/L lethal to water fleas</p> <p>150 mg/L : no light transmitted beyond 8cm depth</p> <p>1000 - 2000 organisms/100mL : distinct pollution of the water</p> <p>200 organisms/100mL : level at which presence of pathogens likely</p>
Zn	0 - 5.8	0.21 - 1.23		0 - 0.25	
Cd	0 - 0.01	0.009 - 0.011		0 - 0.057	
Cu	0 - 0.48	0.026 - 0.48		0.001 - 0.21	
Cr	0 - 0.58	0.02 - 0.58		0.001 - 0.01	
Ni	0 - 0.07	0.02 - 0.026			
Hg	0 - 0.0002	0 - 0.0001		0 - 0.0002	
total P	0.21 - 1.7	0.31 - 1.2			
ortho-phosphate	0 - 0.33	0.15 - 0.33	1.6 - 2.95	0.03 - 0.22	
nitrate-N	0.47 - 12	0.87 - 5.9	0.61 - 0.96	0.49 - 1.38	
ammonia-N	0.1 - 0.68	0.104 - 0.67	1.92 - 2.75	0 - 0.75	
nitrite-N	0 - 1.2	0.055 - 1.2		0.05 - 0.22	
Kjeld-N	0 - 5.6	1.94 - 5.6			
suspended solids	22 - 597	146 - 597	236 - 275	36 - 390	
filterable residue	94 - 1321	144 - 1321	118 - 137	78 - 199	
BOD	0 - 38	0 - 23	18 - 30	5.8 - 100	
TOC	19 - 61	21-61			
coliforms					
(1000 organisms/100mL)					
total			2000 - 5600	6.8 - 620	
fecal			65 - 410	0.36 - 13	
E. coli	0 - 350	0 - 350			

increased turbidity. For example, in performing bioassay assessments of urban runoff on fathead minnows, Marsh (1993) observed mortality was most influenced by low dissolved oxygen levels, although turbidity was also an important factor.

Reduced DO concentration occurs as discharges loaded with organic materials stimulate microbial respiration, using up the available supply as oxidation of organic carbon, nitrogen, phosphorus and sulfur takes place, the latter three elements forming oxidised salts (Arthington *et al.*, 1982; Campbell, 1978a). The mechanism of toxicity from high turbidity is a more physical process, rather than chemical, involving abrasive action on the organism, as well as gill clogging and covering of the habitat or deposited eggs (Marsh, 1993).

The effects of runoff are also not necessarily confined to the periods immediately following heavy rains. A number of constituents show strong association with particulate matter (such as very fine silt, clay and hydrous aluminium, iron and manganese oxides) and can remain in the system, mainly localised in or near the stream bed (Marsh, 1993; Pratt *et al.*, 1981; Ellis, 1976; Sartor *et al.*, 1974). Those organisms which survive the short term impact may, therefore, perish later on exposure to contaminants resolubilised from the sediments and prolonged oxygen depletion in high organic matter environments (Ellis, 1989; Harremoës, 1989).

A number of studies have looked at the distinctive patterns of contaminant dispersal and aquatic biota that occur in urban catchments (Hogg and Norris, 1991; Arthington *et al.*, 1982; Pratt *et al.*, 1981; Campbell, 1978a). For instance, following a study of the Green River in Massachusetts, Pratt *et al.* (1981) reported that pollutants appeared to remain in the system and most seriously affected the benthic community during the normally stress-free season of low stream flow.

The individual discharge event, whether rare or frequent, may therefore have less significance compared to the accumulated discharge because the sediment acts as a reservoir for numerous contaminants (Oschwald, 1972). Two important pollutant types which behave in this manner are the heavy metals and phosphorus, due to their strong tendencies to form insoluble precipitates, adsorb to oxides and hydrous oxides of iron and aluminium, and associate with other organic and inorganic compounds, such as calcium carbonate (Pardo *et al.*, 1990; Löfgren and Boström, 1989; Istvánovics, 1988; Gupta and Chen, 1975; DeGroot and Allersma, 1975; Syers *et al.*, 1973).

Chronic stress, or prolonged detrimental effects, on stream biota thus becomes a problem through continuous remobilisation of toxicants from this sediment (Pratt *et al.*, 1981).

Substances accumulate on a time scale governed by the hydraulic residence time in the stream and the seasonal cycle of turnover in the water and sediments. In the case of nutrients, accumulation/turnover rates are of the order of a month to a year, while for heavy metals a year or decade is normally involved (Harremoës, 1989).

1.3 Suspended Solids and Stream Sediment

Surface runoff provides the necessary detachment and transport energy for displacement of particulates from land to water (Oschwald, 1972). In developed and cleared catchments, significantly higher rates of particle movement are observed in comparison to natural areas (Neller, 1985; Bliss *et al.*, 1983; Ellis, 1976). The difference is due to a number of factors including greater incidence and magnitude of runoff, changes in catchment hydrology and increased impervious surface content; it also reflects the larger area of exposed soil surface providing a more regular supply of solids (Neller, 1985).

The rapid and massive increase in stream flow due to storms is accompanied by very efficient flushing effects. Ellis (1976) reported the first flush of suspended solids can range in concentration between 350 and 3000 mg L⁻¹ and has an apparent linear relation to total discharge, with the peak of solids and discharge being almost coincident. The increased turbidity reduces light penetration, in turn restricting photosynthesis and food production (Oschwald, 1972).

Most of this solid material is dominated by fine inorganic fractions, which make up 45 to 70 per cent of the total weight and are derived primarily from soil, roof, pavement and street surfaces (Ellis, 1976). Considerable amounts of brick, glass, concrete and ash are also included, as well as small amounts of plastics, aggregate and metallic particles. The organic component is normally quite variable, but can contribute up to a third of the total sample weight. Typically, plant debris comprises 3%, humic fractions 2%, bitumen 4%, whilst the rubber fraction can vary from 1 to 20% (Ellis, 1976).

Surface soil is perhaps the greatest source of particulate matter. Soil constituents can be subdivided into the coarse fraction (>2µm diameter), colloid fraction (<2µm), and organic fraction (Huang *et al.*, 1977). The coarse fraction comprises 5 to 90% (dry weight) and may be separated into gravel, sand and the larger silts. The colloidal fraction (i.e. fine silt and clay) comprises 10 to 80% and heavily influences the colour, texture and ion-exchange properties of the solid material. The organic matter (1-40%) includes a large number of small, water soluble molecules (mainly acids), plus insoluble polymeric

humus particles which are also colloidal, binding strongly to clays and hydrous oxides, and having cation-exchange properties (White, 1979; Huang *et al.*, 1977).

Sediments of natural waters are thus heterogeneous mixtures of various solid phases, including clays, silica, organic matter, metal oxides (e.g. FeOOH, MnO₂, Al₂O₃), carbonates, sulfides, various minerals and a bacterial population (Hart, 1982). Particle size distribution resembles that for most surface soils with the colloidal fraction (or more simply, the 'fines') being especially important in acting as a mechanical substrate upon which organic matter and secondary minerals are coated (Förstner, 1985; Hart, 1982; Huang *et al.*, 1977). This fraction dominates sorption reactions involving heavy metals, nutrients (like ammonium nitrogen, phosphorus and potassium) and pesticides due to their large surface area per unit weight and high adsorptive capacity, generated by alternate positive and negative charges on the plate-like surfaces and edges (White, 1979; Oschwald, 1972).

Suspended material is released into stream channels and deposition takes place in the pool areas. This alone often has a serious impact on the aquatic system as such sediment changes the composition of the substratum, smothers organic food particles and interferes with feeding and respiration, especially in the Odonata, Trichoptera and Bivalvia (Hogg and Norris, 1991). For instance, Hogg and Norris (1991) concluded that inputs of fine inorganic particulate material from Tuggeranong Creek into the Murrumbidgee River were responsible for the low macroinvertebrate numbers in pools downstream of a cleared catchment.

From a chemical water quality point of view, sediment-water interactions can be considered both beneficial and detrimental. During low flow, deposited solids enter into sorption-desorption reactions with the surrounding water, basically functioning as an ion-exchange column in removing and releasing constituents from solution (Oschwald, 1972). Pollutants may, therefore, be removed from the water column initially, remaining undisturbed for relatively long periods of time and then be suddenly released due to a change in environmental conditions or as the particles are moved by a change in flow. Thus, sediment sorption can also remove a dissolved substance at one location, only to have it reappear elsewhere (Oschwald, 1972). Particulate-feeding aquatic organisms are at risk directly as they may extract the contaminants upon ingestion, depending on the binding strength on the solids.

1.4 Heavy Metals

1.4.1 General Chemistry, Sources and Ecology

Transition metals, more often known as the heavy metals, comprise those elements found in the middle section of the Periodic Table (Petrucci, 1972) : atomic numbers 21 to 30, 39 to 50 and 57 to 82. While the majority are non-essential for normal cellular processes of organisms, a few are required in trace amounts. These include iron, copper, zinc, manganese, cobalt and molybdenum, and owe their roles in biological systems mainly to an ability to form complexes with a variety of donor groups (Brown and LeMay, 1981; Cotton and Wilkinson, 1980; Petrucci, 1972).

All heavy metals possess a common feature in relation to biological life - in excessive quantities they become acutely toxic to most living organisms (Duffus, 1980), and environmental pollution has become a major global problem for this reason. Some of the sources from which heavy metal-containing products are released to the environment include mining, smelting, metal plating, pesticides, liquid waste discharges, water pipes, spills, acidic rainfall corrosion of metal roofs and gutters, and emissions from coal-fired power plants and automobile engines (Yaziz *et al.*, 1989; Ormrod, 1984; Kormondy, 1984; Mason, 1981; Brown and LeMay, 1981; Duffus, 1980). Natural release processes include volcanic activity and weathering of rocks (Kormondy, 1984; Duffus, 1980).

Most heavy metals are transported through the environment in particulate form, mainly as precipitates or associated with metal oxides and coated clay minerals (Förstner, 1982; Gibbs, 1973). A few metals can also be present in gaseous form, such as mercury vapour and the alkylleads (Chakraborti *et al.*, 1989; Ormrod, 1984). Gaseous organoleads occur in the environment mainly due to the use of tetraalkyllead compounds as anti-knock additives in gasoline. These compounds are believed to undergo natural biomethylation and degradation to inorganic lead via numerous highly toxic alkyllead molecules (Chakraborti *et al.*, 1989). Vaporised heavy metal is carried in the atmosphere until released to waterbodies by wet and dry deposition.

Like many pollutants, there is particular concern for impact on all types of natural waterways, since there is a distinct transfer from land to water (Nürnberg, 1984). In water systems they are carried by the flow of water before further sedimentation, impaction and/or the release of dissolved forms. Importantly, heavy metals are not biologically degradable and may be accumulated by plants and animals, entering a biogeochemical cycle in which they are transformed into various organometallic compounds (Nürnberg, 1984; Hart and Davies, 1978).

1.4.2 Aquatic Chemistry

Heavy metal input into inland waters (streams, rivers and lakes) occurs through wastewater discharge, runoff and wet and dry deposition of atmospheric aerosols (Hamilton-Taylor *et al.*, 1993; Nürnberg, 1984). Depending upon the form (particulate, complexed or free), metal may either be taken up by organisms directly or interact with the sediments (Hart, 1982).

For most water bodies, dissolved levels are normally found in the trace or ultra-trace range. This is typically several hundred micrograms per litre in highly polluted rivers, to 0.001 microgram per litre in unpolluted open ocean (Nürnberg, 1984). Studies on coastal waters have shown that, with only a small number of exceptions (such as lead), the actual concentration at any given site is usually inversely proportional to salinity (Balls, 1985; Huizenga and Kester, 1983), an observation consistent with the hypothesis that the nearby land is the main source of these metals via rivers.

The same relationship can be expected with the loading of suspended particulate matter which has been found to regulate metal fractionation between dissolved and particulate phases (Balls, 1988). This distribution will of course vary from element to element due to their different reactivities with surfaces. For example, in a study of metal levels in coastal waters of the western North Sea, Balls (1985) observed lead was most strongly associated with particulate material, cadmium existed almost entirely in the dissolved phase and copper was intermediate in behaviour. Ramamoorthy and Rust (1978) reported a cation-exchange order, including these three metals, after experiments on bed-sediments from the Ottawa River, Canada. The capacity to bind was found to decrease as follows : $\text{Hg} > \text{Pb} > \text{Cu} > \text{Cd}$.

For lotic fresh waters, salinity is unlikely to have a major influence. Instead, suspended particulates are expected to exert the primary control on fractionation and metal transport (Sabri *et al.*, 1993; Balls, 1989; Sinclair *et al.*, 1989). This will be particularly so for streams in urban catchments, due to high variability in flow, turbulence and resuspension of solids, as well as the incidence of turbid discharges generated by runoff.

The composition and size of suspended matter thus becomes important, material with the higher surface area to volume ratio showing the greatest capacity for adsorption (Balls, 1988). A range of particle types can exist in the water column, all having different surface chemistries, including those of biological and organic nature (plankton, bacteria) and their degradation products (detritus), fecal debris and humic materials, as well as

inorganic particles (clay, silica) from the sediment, often coated by a sorbed layer of hydrous metal oxide or organic matter which exhibit specific complexation properties (Pardo *et al.*, 1990; Förstner, 1985; Nürnberg, 1984; Shotyk, 1984; Hart and Davies, 1978; Schnitzer, 1971).

Obviously there are numerous physico-chemical forms in which trace metals may be present in the aqueous phase. These can be summarised into five major groups (Pardo *et al.*, 1990; Hart and Davies, 1978; Gibbs, 1973) :

- (1) free (hydrated) metal ions e.g. Cd^{2+} , Cu^{2+} , Zn^{2+}
- (2) inorganic complexes e.g. CdCl^+ , $\text{CuCO}_3(\text{aq})$, $\text{Pb}(\text{OH})_2(\text{aq})$
- (3) organic complexes e.g. Cu(II)-salicylic acid, Zn(II)-fulvic acid
- (4) bound to reducible phases e.g. Zn-silicate, Pb(II)-FeOOH
- (5) associated with colloidal and particulate material (e.g. clay, sulfide precipitates), or organic material (e.g. detritus).

Groups 1 to 3 represent the dissolved component. Of these, organic complexation is a significant mechanism in regulating dissolved metal speciation (Balls, 1988).

A master variable affecting the chemistry of heavy metals is pH. High pH (8-9) induces rapid precipitation of metal hydroxides, carbonates and phosphates, while also encouraging sorption of metal onto organic and inorganic particles. On the other hand, acidic pH (<6) stimulates metal dissolution and complex formation (Nicholas and Thomas, 1978; Helz *et al.*, 1975).

The wide range of ionic, colloidal and particulate species all have differing toxicities, although hydrated and lipid soluble forms are regarded as having the highest, due to their great speed in being able to diffuse through a biomembrane (Florence and Morrison, 1992). However, the dissolved phase is most relevant to the fate of heavy metals because it is the phase through which transfer predominantly occurs between components (e.g. suspended particles and organisms) of aquatic systems. In urban environments, soluble metal concentrations are often highest during summer low-flows when dilution is least and high evapotranspiration losses prevail, or during the initial stages of contaminated storm runoff (Grimshaw *et al.*, 1976).

Various organisms are able to concentrate heavy metals in their tissues, resulting in the entry into aquatic food chains. Dissolved metals are taken up by phytoplankton and macroalgae via adsorption and ion exchange processes (involving organic molecules such as proteins and polysaccharides), followed by diffusion through cell membranes (Nürnberg, 1984). In higher organisms, such as molluscs, polychaetes, crustaceans and fish, metal uptake occurs by both adsorption on body surfaces and ingestion of particles during feeding. Attachment to mucus promotes diffusion through the external body surface or digestive tract (Nürnberg, 1984; Miettinen, 1975; Hart, 1974).

1.4.3 Metal Accumulation in Sediments

Sediment accumulation of heavy metals takes place by way of five major processes, which have been summarised by Förstner (1982) and Gibbs (1973) :

- (1) precipitation of discrete compounds
- (2) binding to fine, surface-active solids (present in the discharge or suspended during turbulence)
- (3) co-precipitation by hydrous Fe and Mn oxides and by carbonates
- (4) association with organic molecules
- (5) incorporation in crystalline minerals.

Essentially these can be generalised as either precipitation (1 and 3) or adsorption (2, 4 and 5). The relative balance between these two mechanisms will depend on the metal concentration, available solid surface area and the concentrations of complexing agents present in the waters (Pagenkopf and Cameron, 1979).

Inorganic precipitates include oxides, hydroxides, carbonates, sulfates and sulfides (Cotton and Wilkinson, 1980; Huang *et al.*, 1977; Petrucci, 1972). Reaction with carbonates and hydroxides is most common in pH-buffered, hard water systems (Förstner 1982). As most heavy metals (Zn, Ag, Hg, Cu, Cd, Pb) show a particularly strong affinity for sulfide ions and subsequently very low solubility of the resulting precipitate (Jackson, 1978), such associations prevail under reducing conditions and when sulfide is released following decomposition of organic matter.

The sulfide content of sediment is in the form of solid iron and manganese sulfides, or associated with organic matter, all of which vary in their reactivity. The most reactive or labile fraction, defined as 'acid volatile sulfide' due to solubility in cold acid (HCl), includes the iron/manganese monosulfides and are common to both marine and freshwater sediments, although mainly under anaerobic conditions. Their production is via diagenesis of particulate organic carbon coupled to reduction of sulfate to form sulfide, the precipitation of iron and manganese monosulfides thus resulting (Di Toro *et al.*, 1990).

These acid volatile sulfides are a reactive pool of solid sulfide which can interact with free heavy metals. Any such metal added to the sediment causes dissolution of these monosulfides and the release of free sulfide which then forms more insoluble heavy metal-sulfide precipitate (Di Toro *et al.*, 1990). Such reactions can dramatically influence heavy metal bioavailability and thus have important toxicological implications which will be further discussed later.

In the presence of excess free sulfide, heavy metals will also not remain adsorbed to clay and hydrous metal oxide surfaces. The metals become immobilised in the mud as insoluble sulfides or as a network of interconnected sulfide gels and organic complexes (Jackson, 1978; Petrucci, 1972). Substantial accumulation thus occurs in sediments rich in organic matter and hydrogen sulfide. Organic chelators compete with sulfide and the metals are partitioned to varying degrees between the two forms. The partitioning is strongly dependent on the stability of the inorganic metal sulfide. Jackson (1978) for example, found that the proportion of sulfide-bound metal relative to organically-bound metal decreased in the order $\text{Hg} > \text{Cd} > \text{Cu} > \text{Fe} > \text{Zn}$.

Removal of dissolved heavy metals through surface adsorption phenomena include : surface coordination of metal ions on hydrous oxides and carbonates, ion exchange through electrostatic bonding with clay minerals, covalent binding by organically coated particulate matter or organic colloidal material, or particulate adsorption of a metal-ligand complex (Davis and Leckie, 1978). A general sequence for the capacity of common materials to sorb heavy metals is as follows (Förstner *et al.*, 1981) :

Mn oxides > humic acids > hydrous Fe oxides > clay minerals.

Since heavy metals exhibit different chemistries, there can be preferences for certain phases. Pardo *et al.* (1990), for example, identified speciation patterns for a number of

Organic matter consists of a diverse mixture of molecular species, arising from three main sources (Förstner, 1985; Hart, 1982) :

- (1) organisms, such as bacteria and algae which take up heavy metals directly, or adsorb them onto their cellular surfaces
- (2) breakdown of plant and animal material and condensation of lower molecular weight organics, generating a diverse mixture of compounds having large molecular weights and polyelectrolyte and colloidal properties
- (3) low molecular weight compounds adsorbed onto clay or metal oxide substrates.

The breakdown of large molecular weight organics can have other implications as well. Decomposition occurs primarily through biological activity, as microorganisms use organic and inorganic molecules for carbon and energy sources. The sequential oxidation may change the environment from aerobic to anaerobic, leading to reduction of certain inorganics and lowering of redox potential in the soil-water system (Huang *et al.*, 1977). Certain heavy metals may thus become more soluble and mix with dissolved organic ligands to form organo-metallic complexes.

Despite this diverse range of compounds, natural organic matter can be simply classified into two broad categories of insoluble and soluble material (Day *et al.*, 1991). Active sites for binding are basically the same and involve carboxylic acid and phenolic functional groups (from salicylic and fulvic acids), nitrogen atoms or peptides (Förstner, 1985; Hart, 1982).

The more water insoluble fraction is principally composed of humic substances, accounting for 20 to 80% of the total organic matter of natural waters, and result from the chemical and biological degradation of plant and animal remains, or from the synthesising ability of microbes (Shotyk, 1984; Schnitzer, 1971). The hydrophilic, nonhumic organics are less complex, having clearly recognisable chemical and physical properties; they include, amino acids, phenolic acids and sugars. These, too, result from breakdown of biological macromolecules but are usually in lower concentrations because of rapid turnover via transformations, being consumed almost as fast as they are produced. They are still important as complexing agents, however, because of the generally high stability of the metal complexes (Shotyk, 1984).

Humic compounds are acidic, dark coloured, chemically complex biopolymers of molecular weights ranging from 500 to 500 000. They exhibit an appreciable exchange capacity, due to a large content of carboxyl (-CHO and -COOH) and phenolic hydroxyl groups attached to a predominantly aromatic 'nucleus', enabling coordination of metal ions and reaction with clay minerals (Schnitzer, 1971).

Based on solubility, humic substances are grouped into three main fractions : fulvic acids, humic acids and humin. The fulvic acid fraction is the largest of the three, having lowest molecular weight and tends to be soluble in both alkali and acid. It generally accounts for 25 to 75% of the total organic matter content and affects practically all reactions that occur in sediment systems (Schnitzer, 1971). Day *et al.* (1991) observed that the humic component of natural organic matter from four Victorian freshwater systems was dominated (>80%) by fulvic acids and a constant fulvic acid to humic acid ratio occurred.

About 61% (by weight) of a fulvic acid molecule is in oxygen-containing functional groups, the ratio of COOH to total OH groups being approximately one (Schnitzer, 1971). Due to their high water solubility these acids are involved in metal mobilisation, as they can complex di- and tri-valent metal ions, releasing into solution metals from insoluble hydroxides and oxides. Fulvic acid can also interact with clay minerals and hydrous metal oxides by adsorbing onto external surfaces, regardless of pH, and in interlayer spaces under quite acidic conditions. Aluminium oxide shows particularly strong affinity for fulvic acid (DeGroot and Allersma, 1975; Schnitzer, 1971).

Humic acids are intermediate in molecular weight, compared with the fulvic acids and humin, and are soluble in alkali but insoluble in acid (Schnitzer, 1971). Representatives of this group are salicylic acid, protocatechuic acid, glutamic acid, picolinic acid and pyrazinedicarboxylic acid. These complexing ligands, like fulvic acid, have been shown to interact strongly with clay surfaces and hydrous oxides, as well as heavy metals - see Figure 1. It would appear they are at least partly responsible for the metal fraction transported by association with suspended particles (Davis and Leckie, 1978).

The third, or humin, group concerns the most insoluble organic matter. These constitute a relatively small number of large molecular weight compounds that tend to be insoluble in both alkali and acid (Schnitzer, 1971). Being a target for microbial degradation, it is an important group in metal deposition, as described above (Huang *et al.*, 1977).

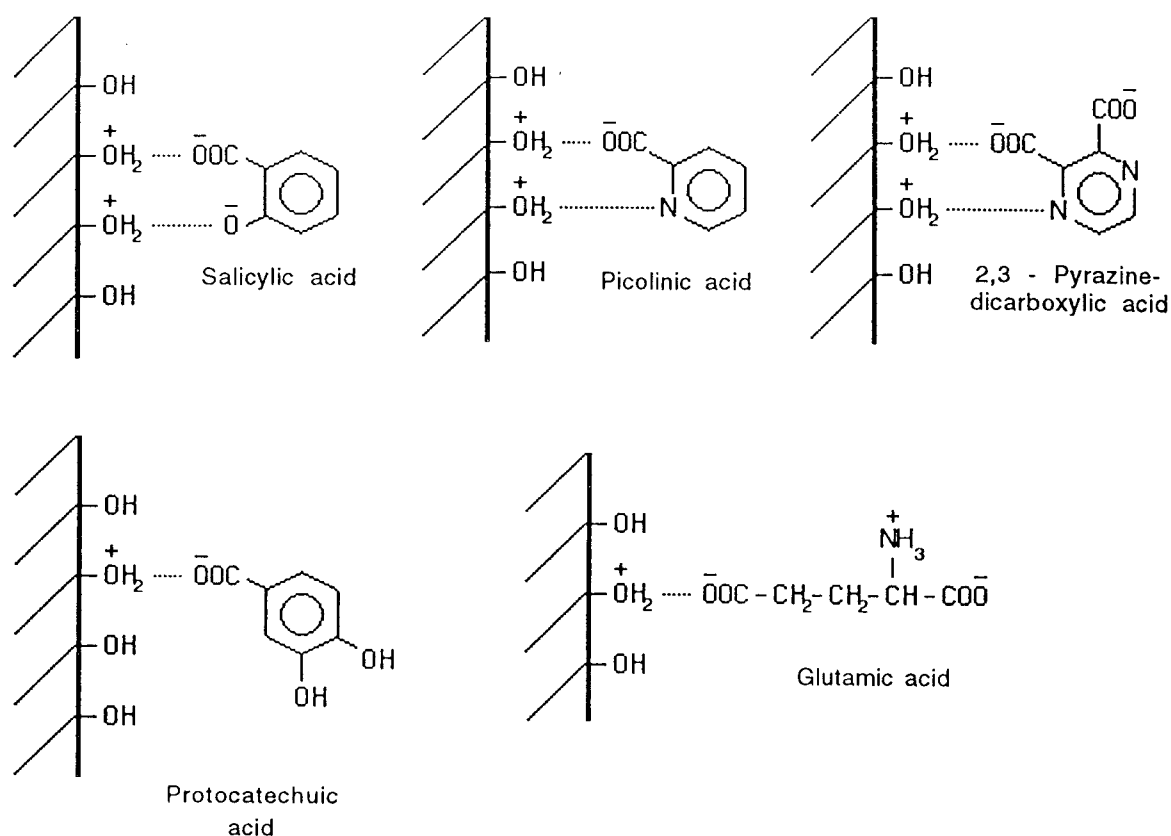


Figure 1. Adsorption of organic acids on hydrous metal oxide surfaces (Davis and Leckie, 1978).

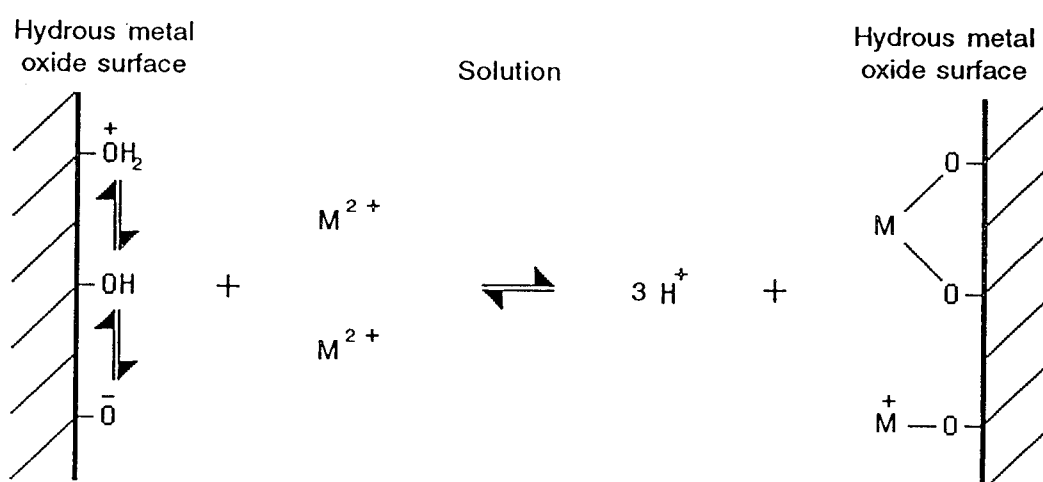
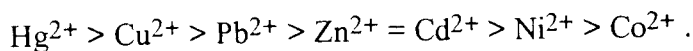


Figure 2. Reactions of divalent metal ions with surface bound hydroxyl groups at the water-oxide interface (Hart, 1982).

A general order of binding strength for a selection of heavy metal ions onto humic and fulvic acids is as follows (Förstner, 1985) :



Copper shows a marked association with all types of organic matter due to the strength of binding. Complexation thus plays an important role in regulating its environmental chemistry (Pardo *et al.*, 1990; Hart and Davies, 1978).

1.4.5 The Role of Hydrous Metal Oxides

Hydrous metal oxides of iron, manganese and also aluminium are extremely common in soils and sediments, existing as partial coatings on other mineral and detrital surfaces, or as discrete oxide particles (Lee, 1975; Gibbs, 1973). They are commonly regarded as accessory minerals and arise from a variety of sources such as weathering of resistant primary minerals and precipitation (Förstner, 1982; White, 1979; Lee, 1975).

Precipitation is perhaps the more usual source and is particularly important since co-precipitation with available heavy metals may occur. As reduced metal (i.e. Fe(II), Mn(II)) migrates in anoxic sediment or groundwater, oxidation occurs upon contact with dissolved oxygen, resulting in the precipitation of the hydrous oxide (Lee, 1975). The procedure is somewhat pH dependant - ferrous iron is readily oxidised to the ferric form in an alkaline-neutral to slightly acidic environment and manganese requires quite highly alkaline conditions for equivalent rates of transformation. Considerable manganese oxidation thus takes place on the surface of carbonate minerals (e.g. calcite) where a microzone of higher pH exists. It may also be mediated by microorganisms (Förstner, 1982; Lee, 1975).

Much experimentation, both as laboratory tests and in the field, has been conducted using hydrous metal oxides such as amorphous iron oxide (FeOOH), manganese dioxide (MnO₂) and alumina (Al₂O₃) (Johnson, 1986; Tessier *et al.*, 1985; Benjamin and Leckie, 1981a; Benjamin and Leckie, 1981b; Huang *et al.*, 1977; Gadde and Laitinen, 1974). This has led to improved understanding of the mechanisms of heavy metal uptake in sediments and the influences of other species, like competing cations and organics.

From such work it has become clear that heavy metal accumulation in sediments is dominated by associations with these metal oxides, especially under aerobic conditions. Despite the possible interactions with sulfides, mainly through acid volatile sulfides (Di

Toro *et al.*, 1990), certain studies (Förstner, 1982; Oakley *et al.*, 1980) dispute the effectiveness of coprecipitation of heavy metals with the iron sulfide phase in comparison with incorporation into hydrous iron oxides. Being the major accumulative phase, these oxides thus play dominant roles in determining reservoirs and modes of transport for metals, such as copper, cadmium, lead, zinc, nickel, mercury, iron and manganese, in natural waters (Hart and Davies, 1978; Lee, 1975; Gibbs, 1973).

In an aqueous environment, the metal oxide surface is covered with surface hydroxyl groups and a variety of binding site types occur, each having a different characteristic affinity for adsorbate (Hart, 1982, Benjamin and Leckie, 1981*b*). The variability in surface sites is caused by pits, edges and other surface defects, or the manner in which a particular oxygen atom is coordinated to an iron centre. Adsorption can be regarded as reactions with these surface-bound hydroxyl groups at the water-oxide interface (Benjamin and Leckie, 1981*b*; Stumm and Morgan, 1970).

Various mechanisms have been proposed to explain the sorption process and many characteristic features of each have been observed. Ion exchange with hydrogen ions or other cations (Ca^{2+} , Mg^{2+}) appears to be a principal mode of metal ion adsorption - see Figure 2. The exchange capacity arises from the existence of a pH-dependent surface charge that determines the mode in which the solids act (Lee, 1975). In acidic solutions, the surface charge is positive and the hydrous metal oxides act as anion exchangers. In basic solutions, the surface charge is negative and they are cation exchange particles. The adsorption processes are generally reversible, although not always, and an ion can be replaced by other competing ions (Gadde and Laitinen, 1974).

Surface complexation with organic coatings is another important mechanism, especially for iron oxides. As described above, adsorption of organic ligands, such as organic and amino acids or fulvic and humic materials, occurs readily. The process is also pH dependent, natural organic matter, for example, showing maximum adsorption in acid conditions, around pH 5 (Hart, 1982).

Uptake or release of heavy metals is a function of metal ion concentration in the water, the concentrations of other heavy metals, pH, and the amount and type of organic and inorganic ligands in solution (Lee, 1975). The age of an oxide precipitate also plays a significant role in the ability to interact with any constituents present (Lee, 1975). Freshly precipitated oxides have rapid and marked sorption capacities, the capacity becoming greater with increasing pH. Aging tends to reduce the ability to sorb ions through molecular rearrangements which affect crystallinity, and sorption of other materials leading to reduction in the number of available sites. Freshly precipitated

'coatings' (usually of ferric hydroxide) on clay minerals, carbonates, insoluble organics and other suspended materials are extremely reactive, exerting a chemical activity far in excess of their total concentrations (Förstner, 1982; Lee, 1975).

The degree of interaction between heavy metals and hydrous oxides therefore depends greatly on whether the metal was present at the time of oxide formation. In natural water systems, regions of maximum hydrous oxide formation (e.g. at the anoxic/oxic interface with alkaline pH) would therefore have greatest influence on heavy metal transport (Lee, 1975).

1.4.6 Sediment Heavy Metal Bioavailability

The heavy metal content of a sediment can be divided into two principal phases : a primary mineral phase, involving that which is fixed within the inert, coarse-grained crystalline lattice, and a secondary phase, which includes all the remaining fractions generated through various physical and chemical processes of weathering of primary minerals and anthropogenic inputs (Chen *et al.*, 1989). A comparison of the totals for these two phases provides an indication of the extent of pollution - the greater the percentage of primary phase metal, the lower the contamination of the site since such metal is essentially unavailable and cannot be mobilised under normal conditions (Pardo *et al.*, 1990; Chen *et al.*, 1989). The distribution of metals among the different geochemical phases is therefore controlled by the relative amounts of the geochemical phases (Chen *et al.*, 1989).

Particulate secondary phase metals are usually in relatively unstable forms and therefore still chemically and physically active, creating a dynamic relationship between the metal pools in the sediment phase (Förstner, 1985; Förstner, 1982). Considering that a diverse range of biota usually exists in the surficial sediments, this relationship must include biological activity as well, whereby aquatic organisms become exposed to metal contamination.

Basically there are two means by which metals become bioavailable - exposure to dissolved forms in solution and through ingestion of metal-enriched particulate material by filter and deposit feeders (Luoma, 1989; Salomons and Förstner, 1984). With respect to the release or mobility of sediment heavy metals, bioavailability depends on the properties which influence the distribution and rates of transfer between the solid and aqueous phases, in addition to sediment geochemistry. Important chemical factors include mass action, pH, redox potential and the aerobic or anaerobic nature of the water, the presence of organic chelators, concentrations of the major anions and cations, and the

type and amount of colloids and particles present (Hart *et al.*, 1992; Pardo *et al.*, 1990; Chen *et al.*, 1989; Batley, 1987; Förstner, 1985; Hart and Davies, 1978). Physical and biological factors which affect the distribution of metals in the sediment include the types of sediment components, particle size distribution and pore size, flow, turbulence at the sediment surface, water content, bioturbation and biological activity (Luoma, 1989).

While the ease of metal dissolution differs from metal to metal, generally the components from which metals are most readily remobilised are (in order) the clays, silicates, carbonates, metal oxides and some organics (Pardo *et al.*, 1990). These categories are regarded as the more mobile fractions since their metal loads can be released by simply a lowering of pH, a change in the redox potential or the ionic environment, and in the case of organic materials, degradation (e.g. oxidation). This makes them the most important in respect to possible environmental impacts (Pardo *et al.*, 1990). Jackson *et al.* (1993), for example, found that low sediment pH (e.g. $4.8 \leq \text{pH} \leq 7.1$), in the presence of mildly oxic conditions (e.g. $0 < E_h < 200 \text{ mV}$), increased the bioavailability of nonresidual aluminium, copper, iron, manganese and zinc to rooted aquatic macrophytes from freshwater lakes in southern Quebec.

The influence of pH is fairly straightforward and involves neutralisation reactions or an ion-exchange mechanism (Lee, 1975). As described previously, reduction in pH promotes alteration in the surface charge properties of particles (e.g. hydrous oxides), followed by replacement of metals with protons (Gadde and Laitinen, 1974).

Redox potential is more complicated because of competition. A switch from reducing to oxidising conditions can significantly increase the mobility of various metals such as Hg, Cu and Cd, and to a lesser extent Zn, Co, Ni and Pb (Förstner, 1985). However, this potential mobility could be restricted since iron and manganese readily form hydrous oxides in an oxic environment and coprecipitation or adsorption may take place (Lee, 1975).

Under reducing conditions iron and manganese oxides dissolve, releasing their heavy metal load. However, build-up of the dissolved forms does not necessarily occur due to concomitant production of sulfides that immobilise the metals through reprecipitation (Batley, 1987; Lee, 1975).

There is yet a further complication. In Section 1.4.3, it was described how heavy metals may react with the acid volatile sulfide content of anoxic sediment to form a highly insoluble (non-bioavailable) precipitate. The amphipod sediment toxicity experiments of Di Toro *et al.* (1990) involving cadmium, determined that if the quantity of added metal

was exceeded by the quantity of sediment acid volatile sulfides, metal was undetectable in the interstitial water and no mortality occurred. Once the added cadmium reached an excess with respect to the acid volatile sulfides, free cadmium was measured in the interstitial water and amphipod mortality resulted at $>1\mu\text{gCd}^{2+} \text{ L}^{-1}$. These findings for cadmium are qualitatively applicable to other heavy metals since they too can displace iron and manganese sulfides to form highly insoluble precipitates.

Obviously there are numerous chemical and physical phenomena that need to be considered when assessing this form of bioavailability. Of course, bioavailability does not just involve the release of dissolved forms into the interstitial and surface waters. Detritus- and filter-feeding animals may ingest contaminated sedimentary particles and in the highly acidic environment of the gut, they may become exposed directly (Guerrero and Kesten, 1994). Compared to uptake from solution, metal assimilation from ingested solids is inefficient but as the source is highly concentrated (i.e. orders of magnitude greater), effects might be more acute in certain organisms (Luoma, 1989; Salomons and Förstner, 1984). Again, the geochemical characteristics of the sediment will control the availability and, ultimately, the bioaccumulation.

1.5 Phosphorus

1.5.1 Sources, Ecology and Biological Importance

Phosphorus is the twelfth most abundant element in the earth's crust and essential for all life (Kormondy, 1984; Brown and LeMay, 1981). It occurs as phosphate minerals, the principal source being phosphate rock, which has high levels of $\text{Ca}_3(\text{PO}_4)_2$ and is mined and converted to fertilisers, or used in the production of detergents (Brown and LeMay, 1981). Many naturally occurring organophosphorus compounds have also been identified and their dissolved forms can represent up to 60% of the total phosphorus content of natural waters (Scharpf, 1973).

In living cells, the phosphorus content varies from 0.5 to 1.5% of dry weight (Gerritse, 1993). Its importance in the metabolism of biological systems stems from being a component of the prime energy carrier, adenosine triphosphate (ATP). It also has a central role in photosynthesis, and is a constituent of nucleic acids, phospholipids and numerous other compounds (Kormondy, 1984; Lehninger, 1982; Hodson, 1973). Plants require inorganic phosphate, made available by mineralising decomposition which is mediated by microorganisms (Kormondy, 1984; Scharpf, 1973). However, it is

transferred to consumers and decomposers in organic forms (Kormondy, 1984; Scharpf, 1973).

Like heavy metals, phosphorus has a strong association with particulate matter (Gerritse, 1993; Syers *et al.*, 1973). In water systems, both inorganic and organic forms commonly occur; however, both tend to be insoluble, while any component that exhibits greater solubility generally becomes adsorbed to the sediment matrix (Gabric and Bell, 1993). Sorption onto clays, for instance, occurs by two mechanisms - chemical bonding of the anions to positively charged edges and substitution for silica (Scharpf, 1973). Transportation is thus mediated mainly through the movement of suspended solids and plant material (Gabric and Bell, 1993).

Australian soils are characteristically limiting in phosphorus (Wild, 1957). With the rapid expansion of urban and rural development, increased sewage discharges and the extensive use of detergents and fertilisers have dramatically raised the levels of all forms of phosphorus in many soils, waters and sediments (Gabric and Bell, 1993; Bliss *et al.*, 1983). Sensitive ecosystems, such as bushland catchments and freshwater streams, have consequently been subject to heavier loads of phosphates, to their detriment (Bliss *et al.*, 1983; Clements, 1983).

A fundamental concept of ecology is that primary production increases until an essential factor becomes limiting (Syers *et al.*, 1973). It is common for phosphorus to be the limiting factor in waters as usually only a small fraction of the total concentration is available. Any increased input of reactive forms of phosphorus immediately raises primary productivity and hence the biomass of phytoplankton, algae and macrophytes (Kormondy, 1984; NAS, 1969).

Continuous inputs result in accelerated eutrophication. This process follows a sequence of steps approximated by general deterioration of water quality, dramatic oxygen depletion as organic matter is decomposed with subsequent mortality of benthic biota, reduced water clarity and aesthetic appeal, plus production of obnoxious odours and toxins. Proliferation of algae and cyanobacteria are often the final stages (Gabric and Bell, 1993; Cullen, 1986; Simmons and Cheng, 1985; Kormondy, 1984; NAS, 1969).

Flood flows of accumulated surface runoff carry large loads of soluble phosphate along with much larger loads of insoluble suspended forms, particularly in the first flush (Harms *et al.*, 1978). For example, in a 12-month study of Lake Ginninderra in the Australian Capital Territory, Cullen *et al.* (1978) determined that of the total phosphorus load entering the lake from the surrounding lands, 96% did so during storm events which

occupied only 12% of the time. Most of the phosphorus was particulate, the bulk (83%) being retained in the waterbody.

The phosphorus in waters originates from fertilisers, plant material, animal excreta and other substances (Cullen, 1986; Harms *et al.*, 1978; Cordery, 1977). Vegetation contributes in two ways. Firstly, the surface of tree leaves (including grasses) present a huge surface area for collection of aerosols that are deposited from the atmosphere. These surfaces are washed by rainwater, hence transporting and dissolving constituents in the process. Secondly, they are subject to leaching when soaked. Highest concentrations are derived from leaf-litter and grass clippings that have been dumped into gutters (Dorney, 1986).

Attempts to prevent, or reverse, eutrophication by limiting phosphorus inputs are complicated by the contribution of dissolved forms made by the sediment. Advanced eutrophication is associated with the deoxygenation of the bottom waters, yet such conditions enhance further release - particularly from sediments high in hydrous metal oxides - thus perpetuating a eutrophic condition, even after external sources are diverted (Syers *et al.*, 1973).

1.5.2 Aquatic Chemistry and Accumulation in Sediments

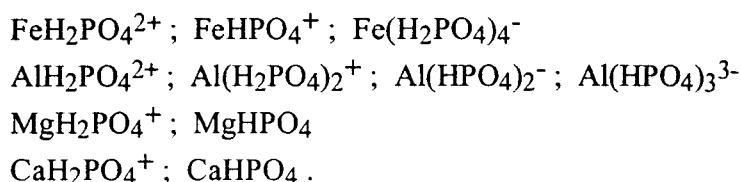
The aquatic chemistry of phosphorus has many similarities to that of the heavy metals, as highlighted by the following general points (Gabric and Bell, 1993; Cullen *et al.*, 1978; Syers *et al.*, 1973; Jitts, 1959) :

- agricultural and urban runoff are major mechanisms for the transport of phosphorus from land to water;
- the bulk of the elemental load is found in insoluble forms, whether it be in the sediment or as suspended particulate matter;
- sediments are a 'sink' for phosphorus;
- hydrous metal oxides and organic matter play important roles in partitioning and sediment adsorption;
- usually only a small fraction is in the dissolved state;
- the dissolved fraction is the most biologically significant;
- changes in certain environmental parameters affect uptake and release of ionic forms by solid material.

In water systems, phosphorus exists in four main fractions (Oliver *et al.*, 1993), as follows :

- (1) dissolved P (both inorganic and organic)
- (2) suspended particulate P (including P associated with solid matter and colloidal forms)
- (3) biological P
- (4) sediment P.

Of the dissolved fraction, orthophosphates in the forms H_2PO_4^- , HPO_4^{2-} or PO_4^{3-} , comprise the greatest portion, although over the 4 to 9 pH range, the first two predominate (Oliver *et al.*, 1993; White, 1980). As well as being in the free, or hydrated state, the phosphate can also form complexes with metal cations, such as ferric and aluminium ions in acid conditions and calcium and magnesium ions under neutral and alkaline conditions. Examples include (White, 1980) :



Obviously, the organic phosphorus component is important. Particulate organic forms tend to be insoluble, while dissolved organic forms are derived from the breakdown of particulate matter (Kormondy, 1984; Syers *et al.*, 1973). Thus, particulates become soluble after decomposition.

Transfers between the four compartments depend on the immediate physical, chemical and biological conditions (Oliver *et al.*, 1993). However, accumulation in the sediments is a particularly dominant force, the overall amounts of each of the mobile components (i.e. fractions 1 to 3) being controlled by two natural physical processes : sedimentation and adsorption (White, 1980; Syers *et al.*, 1973).

Sedimentation via precipitation involves the reaction of orthophosphate with cations like aluminium (forming AlPO_4), iron (forming FePO_4) and calcium (forming $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$). Mixed ferric hydroxy-phosphates and ferrous phosphates ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) can also precipitate (Syers *et al.*, 1973). Given that the required

cation and anion solubility products are satisfied, the precipitation of these insoluble compounds depends on pH and redox conditions. In general, pH of 5 to 6 is the lowest possible level before resolubility, while oxidising conditions promote ferric ion formation.

In calcareous systems, the deposition of phosphorus is strongly influenced by the biogenic precipitation of CaCO_3 minerals such as calcite, aragonite, Mg-calcite and dolomite (Boström *et al.*, 1988). Sedimentation via self-flocculation, which involves aggregation of algae, bacteria and CaCO_3 crystals, is also known to occur (Boström *et al.*, 1988).

Precipitation of calcium phosphates (such as hydroxyapatite) is generally slow but favoured by high temperature and photosynthetic activity, which in turn promotes increased pH (Boström *et al.*, 1988; Istvánovics, 1988). In the range 8 to 10, co-precipitation is significantly enhanced. For example, Gerritse (1993) reported that with increasing pH and levels of calcium and fluoride, theoretically greater than 95% of phosphate in wastewater could be removed as sparingly soluble salts (hydroxyapatite and fluoroapatite).

Of course, the sedimentation of other insoluble materials is continually taking place. Such materials include settling-out of detrital P minerals, organic P-containing or P-adsorbing matter and direct assimilation by sediment biota (Boström *et al.*, 1988).

Adsorption by sediment mineral particles, such as clays, hydrous metal oxides and calcite, occurs with dissolved phosphorus, both the inorganic and the organic forms (Syers *et al.*, 1973). For crystalline clay minerals (e.g. kaolinite), interaction is primarily through the cations in the electrical double layers at their planar surfaces. Hydrated oxides of iron, aluminium and manganese provide most effective surfaces for adsorbing phosphates and a form of ion exchange with hydroxyl ions is the likely mechanism (White, 1980). In both cases, the immediate pH and ionic strength greatly affect the adsorption capacity by changing the surface charge of the solids. Usually a negative correlation is found between pH and the binding of phosphorus (Enell and Löfgren, 1988). However, adsorption onto carbonates dominates at pH 7 to 9 (Boström *et al.*, 1988). Normally the surface potential-determining ions are Ca^{2+} and CO_3^{2-} , but if present, OH^- and metal cations can exert influence. Impure calcites and those of high specific surface area show extensive adsorption of phosphorus (Boström *et al.*, 1988; White, 1980).

Specific organic phosphorus compounds that have been identified in the sediments adhere to the mineral fraction through the phosphate group (Syers *et al.*, 1973). Examples include ATP, inositol hexa- and penta-phosphates, choline, nucleic acids and nucleotides.

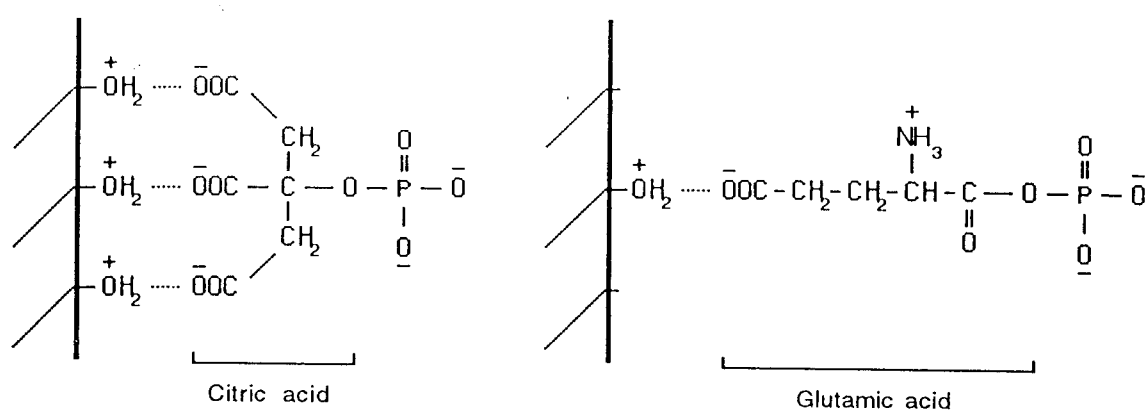
The organic matrix is generally regarded as less efficient in adsorbing phosphate, although the humic-iron complexes are an exception to this rule (Enell and Löfgren, 1988). From experiments with two different estuarine sediments, Jitts (1959) observed that high organic matter content depressed phosphate adsorption and proposed this was probably due to a masking of mineral particles from the phosphate ions in solution. However, Hart *et al.* (1976) found a strong correlation of total phosphorus with organic matter, while Istvánovics (1994) observed that sediments of the Kis-Balaton reservoir in Hungary with high humic contents were able to adsorb phosphate efficiently, releasing only small amounts regardless of environmental conditions.

Such adsorption should involve the formation of phosphate esters (Figure 3). White (1980) indicated that for this process H^+ and OH^- species determine the overall charge and potential, as with uncoated metal oxides, although it can often be the Al and Fe adsorbed by the organic colloids which are most active in the adsorption. Hence, the ability of organic matter to adsorb phosphorus seems to depend on the amount of humic-iron complexes present, as suggested by Enell and Löfgren (1988).

1.5.3 Role of Oxygen and (Hydrous) Metal Oxides in Sediments

Uptake or release of phosphorus is determined by sediment composition and the limnological conditions (Syers *et al.*, 1973), including pH, redox status (Löfgren and Boström, 1989), decomposition of organic matter (Istvánovics, 1988), and the levels of phosphorus-accumulating bacteria in the surface layers (Sinke *et al.*, 1993; Kern-Jespersen and Henze, 1993). One particularly important physico-chemical parameter is oxygen content and its influence on oxidation-reduction reactions involving hydrous metal oxides.

When deoxygenated (hypolimnetic) water containing ferrous ion is reoxygenated during overturn, Fe^{2+} is oxidised and in slightly acidic to alkaline solutions hydrous ferric oxide ($FeOOH$) is precipitated (Syers *et al.*, 1973). Under some conditions, $Fe(OH)_3$ may also form to settle on the oxidised microzone at the sediment-water interface, imparting a reddish colour (Williams *et al.*, 1971). Oxides of aluminium, such as Al_2O_3 and $Al(OH)_3$, are also able to form under these conditions, and at high pH manganese(II) is oxidised to form manganese dioxide (Lee, 1975; Syers *et al.*, 1973; Williams *et al.*, 1971).



Mechanism for esterification :

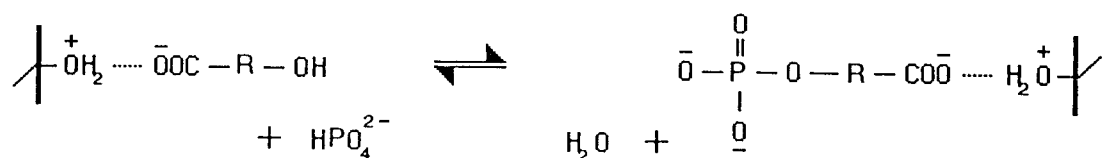


Figure 3. Esterification of phosphate to organic matter - iron oxide complexes (Shotyk, 1984; Brown, 1982; Davis and Leckie, 1978).

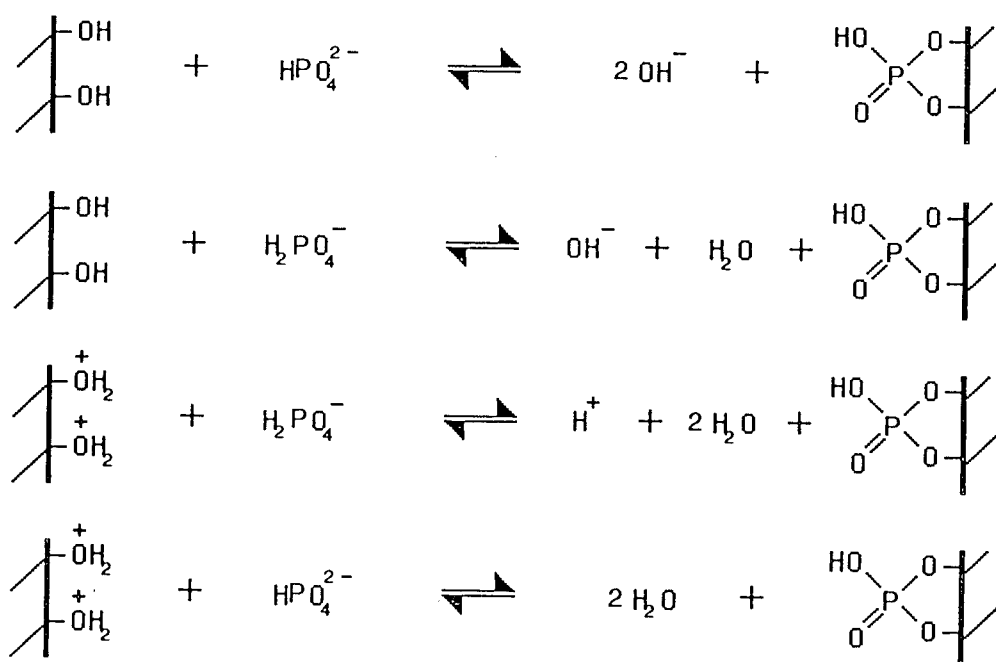


Figure 4. Examples of ortho-phosphate adsorption/desorption reactions with hydrous metal oxide surfaces (Salomons and Forstner, 1984; White, 1980).

The secondary metal oxides and hydroxides, particularly those containing ferric iron, all have a capacity to attach inorganic phosphorus, much more so than primary crystalline minerals. Williams *et al.* (1971), for example, observed the Fe to P atomic ratio varied between 5 and 10 for readily extractable complexes in Wisconsin lake sediments.

Any available phosphorus is quickly adsorbed or co-precipitated, the reaction occurring readily due to accessible hydroxyl groups and interactions with the metal component, especially ferrous iron (Williams *et al.*, 1971). If these substrates become saturated with phosphorus, further sorption reactions with sedimentary clays, either by ionic bonding or surface exchange reactions with silicates, are possible (Löfgren and Boström, 1989).

In anoxic sediment layers, phosphorus has greater mobility and tends to diffuse upwards, only to be trapped in the oxidised surface layers; this results in marked phosphorus enrichment in this region (Istvánovics, 1988). Carignan and Flett (1981) suggested that the upward movement was controlled by a dissolution-migration-precipitation cycle of metal, with phosphorus co-precipitating or co-dissolving with iron and manganese. The process occurs best in undisturbed sediments, since turbulence diffuses the anoxic-oxic interface (Boström *et al.*, 1988).

1.5.4 Release from the Sediment

There are essentially two basic mechanisms by which phosphorus may be released from the sediment to surface water. These are resuspension of particulate forms and mobilisation into the interstitial pool with subsequent upward transport of the dissolved species (Boström *et al.*, 1988).

The suspension of particulates is generated by any scouring disturbance, the turbulent mixing and diffusion also diluting interstitial orthophosphate anions. Such a disturbance can be generated by wind-induced currents, burrowing macroinvertebrates and for streams and rivers by rapid flow, often produced during storm events (Boström *et al.*, 1988). For example, in a study of inputs and outputs of phosphorus from four Victorian catchments, Campbell (1978*b*) found markedly increased concentrations of surface water phosphorus during periods of high flow and suggested this was due to the larger levels of particulates present at such times.

Mobilisation of soluble phosphates is more complicated, involving interrelated chemical, biological and physical processes, such as dissolution of precipitates, desorption, ligand exchanges (i.e. ion exchange of orthophosphate with OH^- or other coordinating agents), microbial mineralisation of organic phosphorus compounds resulting in hydrolysis of

phosphate-ester bonds and production of refractory P compounds, cellular release and autolysis of cells (Gächter and Meyer, 1993; Boström *et al.*, 1988). Central to the effectiveness of such transfer from solid to water is the rate of molecular diffusion.

Dissolution of inorganic phosphorus into interstitial water will depend on solubility product relationships, which are themselves influenced by solution ionic concentrations and pH (Syers *et al.*, 1973). Desorption from metal oxide surfaces is a function of the nature of the sorbing surface (i.e. binding strength; degree of saturation) and environmental parameters, again including pH but also temperature and microbial activity (Syers *et al.*, 1973). These latter two are related to each other, since an increase in temperature raises biological activity which in turn stimulates mineralisation and fixation, while also modifying the chemical environment by increasing oxygen consumption and lowering redox potentials (Löfgren and Boström, 1989; Syers *et al.*, 1973). For carbonates, the additional factors of dissolved Ca^{2+} and Mg^{2+} activity and partial pressure of CO_2 are important (White, 1980).

Figure 4 helps to illustrate the effect of pH. Forward reactions (i.e. adsorption onto metal oxide surfaces) are favoured by acidic conditions, while high pH, produced during periods of intense primary production, encourages ligand (OH^-) exchange of the bound phosphates (Boström *et al.*, 1988). In calcareous systems the alkaline conditions will also induce precipitation of calcium carbonate and any free phosphorus could be co-precipitated or re-adsorbed (Boström *et al.*, 1988).

Sediment buffering capacity thus becomes important. For example, strong gradients of increasing acidity can often be detected on approach to the sediment surface, particularly in deeper waters. Normally these gradients significantly reduce the pH-mediated exchange of phosphorus, unless they are destroyed by bottom currents which at the same time suspend solids in water of higher pH (Drake and Heaney, 1987).

Given that iron, aluminium and manganese have major roles in retaining inorganic fractions, mobility also depends on redox potential. For instance, anoxic microzones - perhaps generated through sulfate reduction to sulfide, causing ferrous ion formation - at the sediment-water interface, reduce Fe(III) and hence retention capacity by returning Fe(II) and associated phosphorus to solution (Moriarty and Boon, 1990; Boström *et al.*, 1988).

The presence of nitrate has been found to have a dual effect on phosphorus transfer. In anaerobic conditions, high nitrate concentration helps generate a layer of oxidised sediment during the microbial fixation to N_2 , hence buffering the redox potential at a level

high enough to keep iron in the ferric form and prevent phosphorus release (Boström *et al.*, 1988). On the other hand, in shallow, aerobic systems, it is likely that nitrate stimulates microbial activity (e.g. iron-reducing bacteria) and thus mineralisation, leading to orthophosphate release and exchange (Jensen and Andersen, 1992; Boström *et al.*, 1988; Rosich and Cullen, 1981).

Given these various factors, some of which are in competition, mobilisation occurs from both anoxic and oxygenated sediment surfaces. In deep stratified lakes where a stagnant water body covers anaerobic sediment, release is brought about by low retention capacity and molecular diffusion, as high amounts of dissolved cations (e.g. Fe^{2+} and Mn^{2+}) occur in the interstitial water. The sediment surface of shallow lakes, billabongs and stream pools are exposed to a more heterogeneous environment since water circulation is greater. In such conditions, release depends on high levels of pH and temperature, physical suspension and rapidly formed microstratifications producing anaerobic microsites (Löfgren and Boström, 1989; Boström *et al.*, 1988).

Whether oxic or anoxic, if the upward diffusive flux of phosphorus is large, the concentration gradient between pore water and surface water induces continued upward movement and obviously a net phosphate release (Löfgren and Boström, 1989). In shallow waters this will be aided by suspension due to flow or wind-induced turbulence.

1.5.5 Biological Influences on Cycling and Chemistry

Many early studies underestimated the role of aquatic organisms, particularly microorganisms, in the exchange of phosphorus between sediment and water. Mobility around the sediment-water interface was regarded as being regulated by pH- and redox-dependent abiotic processes. Bacteria were not considered, or at most treated as catalysts which facilitated the oxidation of organic matter and reduction of various electron acceptors (Gächter and Meyer, 1993; Gächter *et al.*, 1988). More recently, however, it has been recognised that classical models of phosphorus sedimentology (e.g. the Einsele/Mortimer and Vollenweider models) are too simplistic and do not take into account the biological (microbial) activity in surface sediments (Gächter *et al.*, 1988; Boström *et al.*, 1988).

This activity affects phosphorus cycling both directly and indirectly (Boström *et al.*, 1988). Firstly, interchange between particulate and dissolved phosphorus can be mediated through biological uptake. Organisms such as periphyton, phosphorus-accumulating bacteria and rooted macrophytes incorporate dissolved inorganic forms, resulting in the formation of particulate organic forms, refractory organic P compounds

and polyphosphates (Kern-Jespersen and Henze, 1993; Sinke *et al.*, 1993; Gächter and Meyer, 1993; Boström *et al.*, 1988). Ultimately the organic sources are returned to the sediment along with the settling of particulate inorganic phosphorus.

In a study of sediments from Lake Sempach, in north-central Switzerland, Gächter *et al.* (1988) observed that a large fraction (up to 80%) of the total phosphorus which accumulated in the uppermost (≤ 1 cm) sediments was incorporated in the bacterial biomass as particulate phosphorus. Subsequent laboratory experiments demonstrated that unsterilised sediments sorbed up to 31% more soluble reactive phosphorus than sterilised samples, the uptake rate also being more rapid in the first case.

Such bacterial phosphorus represents only a transient sink (Gächter and Meyer, 1993). Decay and decomposition of the cellular materials result in phosphorus assimilation by the decomposers. Any microbial mineralisation transfers phosphorus from the biomass and detritus pools back to the mobile pool as P-containing organic matter is decomposed and simple (dissolved) phosphates are released (Boström *et al.*, 1988; Syers *et al.*, 1973). Rhizosphere bacteria, for instance, are exceptionally active and solubilise complex organic and inorganic forms of phosphorus (Moriarty and Boon, 1990).

This microbial decomposition also modifies the general chemical environment. For example, the consumption of available oxygen during oxidation of organic matter generates a reducing condition in the immediate area (Boström *et al.*, 1988). Such a change in redox potential will subsequently alter the adsorption-desorption characteristics of iron and manganese phosphate complexes, as described above.

Benthic macroinvertebrates enhance available phosphorus flux to the water mass by active transport of sediment particles and water across the sediment-water interface (Enell and Löfgren, 1988). They can also alter the chemical environment (for example, pH and redox properties) through bioturbation (Enell and Löfgren, 1988; Boström *et al.*, 1988).

Algae and macrophytes effectively compete to remove phosphorus from sediments in order to satisfy their growth requirements (Syers *et al.*, 1973). Roots of submerged vascular plants in vegetated sediments assimilate interstitial orthophosphate, depleting the available supply (Boon and Sorrell, 1991). In addition, the surrounding area is both aerobic (from oxygen release) and acidic, due to a flux of protons (also released from the roots). Hence, further loss of inorganic phosphorus results from precipitation and adsorption to the iron and manganese complexes co-produced under such favourable conditions (Jaynes and Carpenter, 1986).

1.6 Assessment of Sediment Bioavailability Using Sequential Extraction Techniques

As speciation controls the geochemical behaviour and biological activity of sediment-bound constituents (Luoma, 1989; Chen *et al.*, 1989), various sequential chemical extraction techniques have been developed to estimate the proportions in specific solid phases (i.e. clays, carbonates, hydrous metal oxides, organic matter and sulfides, residual), whereby their potential bioavailability (hence toxicity) may be assessed (Förstner *et al.*, 1981; Salomons and Förstner, 1980; Tessier *et al.*, 1979; Gupta and Chen, 1975). Most available procedures have concerned heavy metal studies - although procedures for other parameters do exist, those for phosphorus having been reviewed by Pettersson *et al.* (1988) - and involve relatively simple reactions such as ion-exchange, reduction of hydrous metal oxides, oxidation, chemical competition and dissolution (Salomons and Förstner, 1984).

Despite the numerous proposals for both single and sequential extraction schemes, none has been developed into a commonly accepted, or standard, technique (Fiedler *et al.*, 1994). One reason is that past work on aquatic sediments would indicate no single method alone can closely define the availability of all metals (Luoma, 1989). Another problem has been the lack of suitable reference materials, which limits the quality control. Fiedler *et al.* (1994) attempted to correct these deficiencies by preparing a homogeneous and stable standard reference river sediment, to be used in the certification of extractable trace metals upon application of their suggested procedure. This procedure involved dilute acetic acid (0.1 mol L^{-1}), hydroxylammonium chloride (0.1 mol L^{-1}) reducing agent and hydrogen peroxide (8.8 mol L^{-1}) oxidising agent.

It is also well documented that the accuracy of these procedures is confounded by non-selectivity of extractants, trace element redistribution and readsorption among phases and freshly exposed surfaces, and differences in chemistry of the elements concerned (Martin *et al.*, 1987; Kheboian and Bauer, 1987; Rendell *et al.*, 1980). Hence, the discrimination between forms of selected species may not be as selective as sometimes stated, often leading to misinterpretation of the relationship between speciation data and bioavailability (Martin *et al.*, 1987; Salomons and Förstner, 1984).

Nevertheless, while species extractions may have limitations they do provide a differentiated analysis, supplementing a comparison of total levels (Salomons and Förstner, 1984). They can also enable an insight into the chemical properties of the elements concerned, such as the relative bonding strength with the various solid fractions in natural systems (Martin *et al.*, 1987; Salomons and Förstner, 1984). Furthermore,

they are useful in predicting metal and nutrient chemistry and bioavailability among geochemically similar sediments (Luoma, 1989; Batley, 1987).

1.7 Sampling and Analysis of Interstitial Water

The sampling and analysis of interstitial waters is often performed in conjunction with sediment speciation studies. The most common collection methods include extraction from sediment cores (Howes *et al.*, 1985; Robbins and Gustinis, 1976; Sasseville *et al.*, 1974; Reeburgh, 1967; Shapiro, 1958) and the less destructive, or *in situ*, means involving dialysis bags or membranes (Morrison, 1989; Howes *et al.*, 1985; Carignan, 1984; Bottomley and Bayly, 1984; Mayer, 1976; Hesslein, 1976) and cylindrical water collector tubes (Whitman, 1989; Howes *et al.*, 1985; Hertkorn-Obst *et al.*, 1982; Makemson, 1972).

The interest in this sample type arises because surficial sediments release constituents to the overlying water column via the interstitial solution. Transport depends on particle composition, rates of diffusion, the extent of turbulent mixing and possibly on the upward movement of groundwater through the sediment layers (Enell and Löfgren, 1988; Hart and Davies, 1978). Environmental variables which influence pore water composition include pH, salinity, ionic composition of the water, redox potential and oxygen status (Enell and Löfgren, 1988; Hart and Davies, 1978; Huang *et al.*, 1977).

The solution can often contain substances in higher concentrations than the surface water, the levels being governed by sorption-desorption reactions (Enell and Löfgren, 1988; Hart and Davies, 1978). At least for heavy metals and phosphorus, much of this mobile material exists as free ions, complexes or associations with colloid and particulate phases (Hart and McKelvie, 1986; Hart and Davies, 1978; Davis and Leckie, 1978). Hence, the identification of pollutants and nutrients in stream sediment and interstitial water could be a better indicator of contamination than merely data on water column measurements, especially during dry weather low-flow conditions (Hart and McKelvie, 1986). Furthermore, by sampling these components the transfer of materials across the sediment-water interface can be investigated and so help to understand cycling in aquatic ecosystems (Enell and Löfgren, 1988; Hart and Davies, 1978).

1.8 Chemical Studies of Sydney Freshwater Streams

1.8.1 Australian Lotic Waters, with Reference to Sydney

Due to the vast range of geographic and climatic differences which are characteristic of the Australian continent, its aquatic environments are considered highly variable and unpredictable, the chemistry having the potential to change substantially in a short time (Hart and McKelvie, 1986; Buckney, 1980). Often these fluctuations are seasonal and coincide with major climatic changes; maximum and minimum concentrations occurring in the dry and wet seasons (Buckney, 1980; Williams, 1967). For instance, many areas in Australia experience long dry periods, resulting in considerable desiccation and increased dissolved salt concentration. With the onset of rain and catchment saturation, the first discharges may carry the dry season accumulation of chemical constituents. These turbid discharges typically have high colour, low pH and a predominance of sodium and chloride, along with high levels of bicarbonate and nutrients (Buckney, 1980).

Williams (1967) noted the importance of desiccation on water chemistry in the lakes of New South Wales. In fact, it was considered 'likely that seasonal fluctuations in chemical characteristics are governed principally by seasonal changes in the intensity of evaporation'.

In those situations where non-seasonal fluctuations occur, they are usually correlated to climatic irregularities and/or human developments (Buckney, 1980; Timms, 1970; Williams, 1967). For example, after a three year investigation into the variations in salinity of four small lentic freshwater bodies in the Hunter Valley of New South Wales, Timms (1970) observed no seasonal patterns, despite wide fluctuations in total dissolved solids during the period. Instead the variability was influenced by the rate of water renewal. In upland (i.e. eroding) and small urban streams a major source of variability stems from irregular flow patterns which are common in such systems (Lake, 1982).

Despite the high variability, certain chemical features of Australian streams and rivers are apparent and have been described in reviews by Hart and McKelvie (1986), Buckney (1980) and Williams and Wan (1972). A particularly distinguishing feature is the high content of total dissolved solids, regularly found to be greater than 200 mg L⁻¹ (Williams and Wan, 1972). The ionic content is usually dominated by sodium and chloride, even in fresh waters, although bicarbonate can often be the dominant, or co-dominant, anion (Buckney, 1980). Calcium, magnesium and bicarbonate become most significant in inland-flowing streams through prolonged interactions with the catchment lithology and

the regional groundwater. In arid areas, where annual evaporation exceeds precipitation, waters become more saline due to crystallisation of insoluble calcium and magnesium carbonates (Hart and McKelvie, 1986; Buckney, 1980).

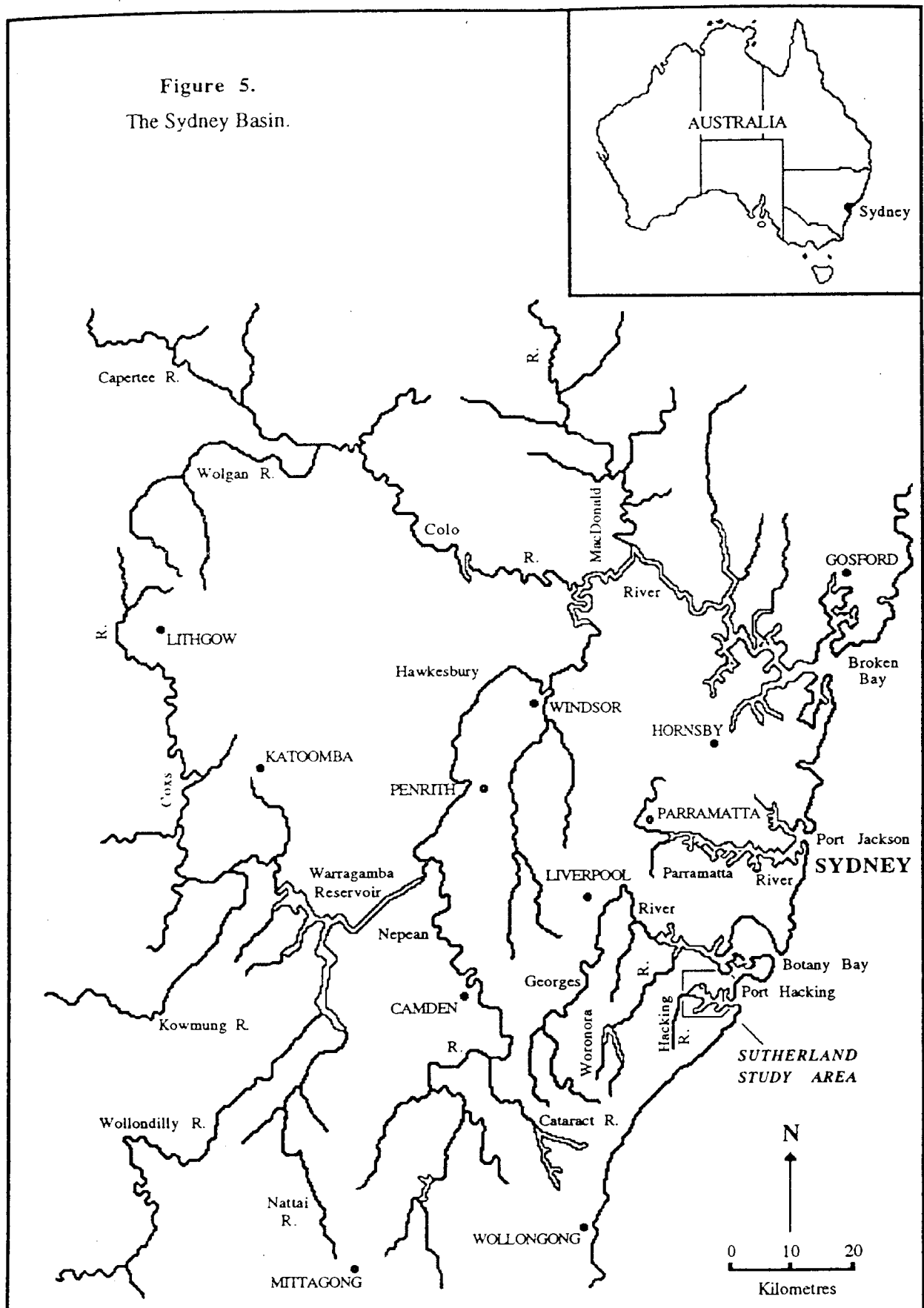
High turbidity is a feature of a large number of inland waters, particularly rivers, and a high proportion of nutrients are often in the particulate fraction (Buckney, 1980). Upon sedimentation and aggregation of particles, a major nutrient flux is generated. Later release of soluble and loosely bound ionic forms raises the amount of dissolved nutrients, such as ortho-phosphate, often found at high levels in many lakes and reservoirs (Williams and Wan, 1972).

Unfortunately, investigations into the chemistry (and for that matter, the ecology) of fresh waters in the Sydney basin are rare and so relatively little has been published about them. Being situated on the subtropical east coast of Australia (Figure 5), Sydney waters should be rainfall dominated and thus heavily influenced by aerosol salts originating from sea spray (Hart and McKelvie, 1986). Sodium, magnesium, chloride and sulfate are to be expected at the highest levels, with sodium and chloride dominating overall (Hart and McKelvie, 1986).

This is fairly consistent with the chemical data of Jolly (1966), obtained from a survey of six major reservoirs in the Sydney area. Five of these fresh waters were characterised by minimal annual temperature variation, low total dissolved solids, sodium chloride dominance and acidic pH. However, the sixth and largest reservoir, Warragamba Dam, demonstrated greater annual variation in temperature (except in the surface waters), greater proportion of mineral solutes with sodium/calcium and chloride/bicarbonate co-dominance, and alkaline pH.

Bowen and Smalls (1980) reported increased concentrations of nutrients (phosphorus in particular), colour and turbidity in a number of these reservoirs during the 1970s, leading to changes in their trophic status. For the Warragamba reservoir, the inputs were correlated with catchment events such as bushfires and stormwater flows. Given the higher level of urban and rural development since then (Urban Development Program, UDP, 1991), these increases should have continued and effects on smaller systems (e.g. streams) are likely to have been even more dramatic.

Figure 5.
The Sydney Basin.



1.8.2 Target Areas for Research

Lake (1982) reported that Australian lotic ecology had been sadly neglected, with studies of standing waters dominating the available literature. While there has since been a positive response to this deficiency, much more can still be done. For example, chemical cycling in lotic waters remains poorly understood and most studies to date have been concerned with monitoring various major and minor ions, rather than studying the mechanisms controlling distribution, circulation and effects of such chemical compounds (Hart and McKelvie, 1986). Without such knowledge, a complete picture of aquatic chemistry is not possible, hence limiting effective ecosystem management.

In their review 'Chemical Limnology in Australia', Hart and McKelvie (1986) highlighted this need for information concerning the distribution and biogeochemical cycling of chemical compounds between such compartments of inland waters as the dissolved fraction, organic matter, fine and coarse particulate matter, algae and macrophytes. The concept of spiralling, or the longitudinal displacement of heavy metals and nutrients due to flow, was discussed and they proposed the role of very fine particulate matter as being most crucial since it is carried the furthest and has the greatest capacity for surface adsorption.

Unfortunately, most of the current literature dealing with biogeochemical cycling has concerned studies from the Northern Hemisphere and it is uncertain whether the proposed mechanisms can be assumed to apply for Australian systems, given the various unique climatic and geographic traits. For instance, in surface waters of the Northern Hemisphere the chemistry of nutrients such as phosphorus often show distinct seasonal patterns. Highest interstitial concentrations of dissolved constituents are seen in summer (coinciding with the warmer temperatures) and early autumn, following the huge input of organic matter (primarily leaf litter) into the system. The higher levels reflect raised microbial activity, plus increased plant growth and benthic macroinvertebrate populations during these periods (Löfgren and Boström, 1989; Enell and Löfgren, 1988).

However, the paper by Lake (1982) would suggest that many Australian streams are likely to differ in nutrient chemistry, becoming aseasonal. This is because of greater variability in both water temperature and flow, while inputs of organic matter, the primary energy source, are more diverse (bark and branches being an important component) and determined by meteorological conditions.

For the fresh waters of the Sydney basin even fundamental studies describing the general chemical composition are scarce in the literature. Various reports, including New South

Wales State Pollution Control Commission (NSW SPCC, 1983), Bowen and Smalls (1980), Cordery (1977), New South Wales Department of Health (1971), Timms (1970), Williams (1967) and Jolly (1966), could be cited to establish a reference data bank of water quality for New South Wales, but the data are generally fragmentary and incoherent, being collected and analysed for specific purposes at particular times. Furthermore, major water courses, not necessarily lying in the Sydney basin, have usually been examined (Brymner, 1982; Muir and Johnson, 1978; Johnson and Muir, 1977; Williams *et al.*, 1970; Williams, 1967) and much smaller streams, of the sort predominating in an area the size of the Sydney basin, have tended not to be the subject of detailed study. In fact, of these listed papers only Cordery (1977) provides data for small watersheds in the Sydney region, comparing the surface water quality of three urban creeks during dry weather low flows and stormwater flood flows.

Chemical data for small watercourses, such as first order streams, have the advantage of reduced dilution effects, hence the greater likelihood of detecting changes compared with river and estuarine water monitoring (Balls, 1989). In many cases they are the initial and/or immediate sink for urban and rural discharges, thus representing the first contact of pollutants with the aquatic environment. This is most relevant to streams in intensely developed areas, such as the Sydney basin.

Geary (1981) noted that little research had been done on the temporal and spatial variation of sediments and solutes and their transport rates in Australian catchments. This variability would be most significant in streams (e.g. many small urban streams) that are heavily dependent on rainfall and subsequently experience irregular flow regimes and high rates of erosion.

1.8.3 Aims of this Research

This thesis attempts to address several research needs by way of two related studies. The first study aimed to provide a concise and coherent description of the general current water chemistry (inorganic) of Sydney basin freshwater streams in a regional perspective. To do this, a number of different stream samples were taken randomly and classified into groups based on their chemistries. These chemistries encompassed 18 standard water quality parameters, including heavy metal and nutrient (phosphorus and nitrogen) concentrations. An important objective of this survey was to assess the extent to which anthropogenic activities may have altered stream chemistry from the natural state, using heavy metal and nutrient levels as indicators of contamination. It was also a suitable reference point before attempting to evaluate some of the mechanisms of heavy metal and phosphorus distribution and cycling in certain streams.

The second study involved *in situ* monitoring of three representative freshwater streams from the basin - all lying on Hawkesbury Sandstone - sampling surface water, interstitial water and sediment over a two year period. Two of the streams were located in developed catchments, while the third was a suitable non-urbanised reference site. By monitoring these 'urbanised' streams a chemical comparison could be made between the stream types, while assessment of the effects of urban runoff was also possible.

The principal aim was to examine the possible influence of surficial sediments on the water chemistry of these Sydney streams, paying particular respect to heavy metals and phosphorus - these being principal contaminants found in urban runoff and strongly associated with the particulate fraction. At the same time, it was also concerned with a temporal survey of the three streams in order to describe any patterns of natural chemical variability.

In summary, the objectives of this second study were to :

- compare the chemistries of urbanised streams with a nearby undisturbed stream
- compare surface water composition during low and high flows
- assess the influence of surficial sediments on water chemistry
- assess the exchange mechanisms of heavy metals and phosphorus between sediments and water
- describe any patterns of natural chemical variability over time, in particular seasonal variability .

The research focuses heavily on heavy metals, phosphorus and suspended solids as specific water quality indicators of urbanisation. It should not be inferred, however, that these are always the most ideal parameters for such a purpose; indeed many others, including acidity, biochemical oxygen demand (BOD), pathogens, pesticides, polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs) and industrial wastes, also represent such indicators (Chapman, 1992). These three parameters were selected because they are :

- relatively easy to analyse
- common contaminants, particularly in urban runoff
- usually at readily detectable levels (\geq ppb)
- strongly associated with particulate matter
- of current interest, especially the role of nutrients in eutrophication and spread of blue-green algae (Fuller and Dunhill, 1994; Swan, 1994; Guillaud *et al.*, 1992) .

2 MATERIALS AND METHODS

2.1 Determination of Sampling Sites for Basin Survey

Sampling sites were selected by dividing the Sydney basin into squares, adopting the grid system of the NATMAP SI 56-5 Sydney Topographical Map (1 : 250 000 scale) series. At the intersection of a pair of grid lines, selected randomly, the nearest flowing watercourse was identified and sampled.

Ninety sites (covering 86 different waterways) were ultimately sampled between September and November 1990. The specific catchment geology for each site was determined using the Sydney Geological Sheet (1 : 250 000 scale). A brief description of the surrounding catchment (i.e. land use) was made at each site, with consultation of the relevant maps.

2.2 Pretreatment of Sampling and Laboratory Apparatus

Equipment used in the sampling and analysis of samples was soaked in a 2% nitric or hydrochloric acid bath for a minimum of two weeks to remove any surface contamination. When required, the item was carefully rinsed with reverse osmosis purified water (Batley and Gardner, 1977).

2.3 Collection of Stream Samples

2.3.1 Surface Water

Surface water samples were collected in high density polyethylene bottles (500mL and 120mL) and taken as close to the top of the sediment as possible, without disturbing it. This was done in order to obtain the interface, or 'microzone', component between the sediment and bulk surface water. The container was firstly immersed and then opened to prevent collection of the top surface film which can be enriched with various chemical species (Duce *et al.*, 1972).

2.3.2 Interstitial Water

Interstitial water was collected from a sediment depth of 5-10cm by drawing porewater slowly, but evenly, through a small, thin length of clear plastic tubing into a 50mL TERUMO® syringe. A section of fine nylon Nylal® ASTM 325 mesh (colourless, 44µm pore size) covered the end of the tube to prevent large particles being co-sampled and the original black rubber component of the syringe plunger was replaced with a seal of teflon wrapping. Sample was immediately released into a high density polyethylene bottle (500mL), or a suitable container to enable measurements. At all times care was taken to ensure that there was minimal disturbance and mixing of both sediment and water.

The suitability of this sampler was assessed and details of tests are presented in Appendix 1.

2.3.3 Sediment

The Hawkesbury Sandstone creeks had shallow depths (often <20cm) of loosely packed, sandy sediments. As the corer technique was found to be unsuitable for sampling such sediments, representative composite-grab samples were obtained by simply scooping sediment into a polyethylene bag.

2.3.4 Sampling Regime for Monitoring Study

Over a two year period (beginning on the 21st of March, 1991), three Sutherland Shire creeks were sampled twelve times. For each stream a short ($\leq 400\text{m}$) section represented the site and was divided into three sampling stations. The stations were selected at those points which were considered readily accessible on foot, while also being immediately down-stream of any distinctive urban features (e.g. stormwater drains and roadways).

Successive visits to a particular site were separated by at least two weeks, usually more than a month, to enable recovery from the previous disturbance. Given this limitation, a day selected for field work was chosen at random and at least one or two sites were sampled, depending on the requirement and time constraints, to enable sufficient time for immediate analyses and filtrations in the laboratory.

On every occasion, samples were taken from each of the three stations of that site, as close as possible to the mid-stream point. Surface waters were collected immediately on arrival, followed by measurement of quality parameters using the appropriate field meter. Sediment and interstitial water were then collected and further measurements taken. To

ensure independence the same spot, covering an area of approximately one metre in radius, was never sampled more than once.

On three of the twelve visits only surface water samples were collected. These samples allowed for the determination of the 'additional surface water chemistry' - see section 2.6.7. These data provided a more detailed description of the surface water composition.

2.4 Sample Storage and Water Filtration

Since there was a delay before returning to the laboratory, all samples were chilled to below 4°C (in ice) to inhibit bacterial growth and adsorptive losses (Clesceri *et al.*, 1989). For the Sydney basin survey, water samples were collected in batches and the time between sampling and filtration was 1-2 days.

On return, sufficient water sample was filtered under vacuum pump suction, using acid-washed Whatman GF/C 50 glass-fibre filters of nominally 0.45µm pore size. For surface waters the first 300mL of filtrate was used as a rinse and discarded. For interstitial waters, the initial rinse volume was 200mL. By filtering reverse osmosis water, blanks were prepared to allow background correction (Batley and Gardner, 1977).

Filtered water was divided into certain sub-samples, each for specific sets of analyses, in an attempt to minimise contamination. Those to be analysed for total dissolved heavy metals (i.e. free, complexed and colloidal metal ions) were acidified with BDH Aristar® high purity concentrated nitric acid to below pH 2, or 0.5-1% H⁺ (Noller, 1992; Clesceri *et al.*, 1989).

Alkalinity, acidity, hardness, suspended solids, turbidity and colour measurements were carried out before freezer storage. In the case of monitoring study samples this was on the day of sampling. All remaining samples were frozen until needed.

Sediments were placed in an oven (105°C) on return to the laboratory and remained there overnight until dry. Oven drying of sediment is not a recommended procedure when analyses such as heavy metal content, sequential extraction and cation exchange capacity are to be undertaken (Batley, 1989; Kersten and Förstner, 1989). However, for this study the relatively volatile elements (e.g. Hg) were not of interest, while changes to the CEC would have been negligible given the coarse (sandy) nature of the samples. Hydrous metal oxide and organic matter fractionation may have been altered (Kersten and Förstner, 1989), but since the sediments originated from environments that were relatively well aerated and

low in organic matter, further iron oxide crystallinity and losses due to organic matter solubility both should have been limited. Furthermore, as the study emphasised a comparison of sites and all sediments were treated the same, any effects would have been consistent for all samples.

2.5 Quality Assurance Protocols

For all chemical analyses the necessary reagents were analytical grade, or better. Suitable numbers of standards and blanks were analysed, following the recommendations of Clesceri *et al.* (1989).

Results from internal quality control analyses are presented in Appendix 2. For the Basin survey, purchased BDH analytical reagents (BDH-Merck Pty. Ltd., Kilsyth, Victoria, Australia) were co-analysed as internal standard reference waters and results are presented in Table A3. For the second study, BCSS-1 and PACS-1 Marine Sediment Reference Materials (produced by the National Research Council, Canada) were regularly analysed, in addition to the BDH analytical standards. Tables A4(i-iv), A5 and A6 list the results generated from these analyses.

2.6 Water Analysis

2.6.1 Chemical Analyses for Basin Survey

Measurements of pH, alkalinity, turbidity and colour were carried out immediately upon return to the laboratory, before dividing the samples into suitable aliquots for freezer storage.

The pH and alkalinity (in mg L^{-1} as CaCO_3 , to pH 4.5) were determined simultaneously using a Radiometer pH Meter 26 and automatic Titrator 11, coupled to an ABU 12 autoburette filled with 0.01M sulfuric acid (Clesceri *et al.*, 1989). The instrument detection limit for these alkalinity titrations was 0.2 mg L^{-1} as CaCO_3 and each value provided a measure of total (bi-)carbonate.

After initial persulfate digestion (Major *et al.*, 1972), total phosphorus was analysed colorimetrically as ortho-phosphate, following the ascorbic acid reduction method from Strickland and Parsons (1972). Dissolved ammonia was also determined from the colorimetric assay of Strickland and Parsons (1972). For these analyses unfiltered samples

were used and the detection limits at the 99% confidence level, as defined by the Analytical Methods Committee for the Royal Society of Chemistry (1987), were 0.03 mg L⁻¹ and 9 µg L⁻¹ respectively - refer to Appendix 3.

Dissolved heavy metals (Cu, Zn, Cd, Pb) were determined by graphite furnace atomic absorption spectrophotometry (AAS) using a Varian AA-1275 atomic absorption spectrophotometer with the Varian GTA-95 graphite tube atomiser (Rothery, 1982; 1980). Ammonium nitrate modifier (5%) was added where necessary. The 99% confidence level detection limits were 0.40, 0.25, 0.10 and 0.40 µg L⁻¹ for copper, zinc, cadmium and lead respectively (Analytical Methods Committee, 1987; refer to Appendix 3).

All remaining analyses (i.e. turbidity, colour, chloride, sulfate, sodium, potassium, calcium, magnesium and dissolved ortho-phosphate and nitrate) were as described in the corresponding sections below.

2.6.2 *In Situ* Physico-chemical Measurements

For the three Sutherland Shire sites, determinations of creek surface and interstitial water conductivity, dissolved oxygen, temperature, pH and redox potential were made at each sampling station using an appropriate field meter. Conductivity (mS m⁻¹) was determined with a YSI Model 33 S-C-T meter. Dissolved oxygen (DO, mg L⁻¹) was measured with a YEO-KAL Model 603 Dissolved Oxygen / Temperature meter, while temperature (°C), pH and redox (absolute millivolts) were all measured with an Orion Model 250A portable meter.

In both studies, stream water velocity was calculated from average pitometer height and the equation :

$$\text{Water velocity} = (2gh)^{1/2}$$

where, g is acceleration due to gravity (980 cm s⁻²) and h is the height (cm) of the water column in the pitot tube (Ward, 1967). Although the pitometer is not particularly suited for natural streams (Wisler and Brater, 1959), it is simple to use and reliable enough to distinguish between low and high water velocities. In view of its limitations, during the monitoring of the three Sutherland Shire streams values less than five millimetres water column height (corresponding to a velocity of 31.3 cm s⁻¹) were assumed to be below the detection limit of the method.

In taking the average of at least five stream width and depth measurements, an estimation of the discharge ($\text{m}^3 \text{s}^{-1}$) could be made.

2.6.3 Alkalinity, Acidity and Hardness

Surface (unfiltered) and interstitial (filtered) water alkalinity, acidity and hardness were all determined by the corresponding titration method of Clesceri *et al.* (1989). For each titration, results were expressed in milligrams per litre as calcium carbonate. Detection limits were 0.5 mg L^{-1} , 0.15 mg L^{-1} and 2.0 mg L^{-1} respectively.

In calculating anionic relative percentages, the alkalinity value was assumed to be equivalent to the total dissolved (bi-)carbonate content.

2.6.4 Suspended Solids

Suspended solids content of the surface water was determined gravimetrically following vacuum filtration of a measured volume of sample ($\geq 500 \text{ mL}$) through a pre-weighed Whatman GF/C 50 glass fibre filter (Clesceri *et al.*, 1989). Results were expressed in milligrams per litre. A 0.4 mg L^{-1} limit of detection applied.

2.6.5 Heavy Metals

2.6.5.1 Graphite Furnace AAS

Filtered surface and interstitial waters (acidified) of the three Sutherland Shire creeks were analysed by graphite furnace AAS for dissolved copper, cadmium and lead content. The instrument used was the Varian AA-1275 series spectrophotometer (Rothery, 1980) with a Varian GTA-95 atomiser (Rothery, 1982).

Two sets of furnace operating parameters were developed - one for copper and lead, the other for cadmium - following the work of Welz *et al.* (1988). These parameters are presented in Tables 2 and 3.

Sample plus palladium (0.15%) and magnesium (0.1%) nitrates modifier (Welz *et al.*, 1988) were pre-mixed 2:1 in small, acid-washed vials and injection volume onto a L'vov platform was $10 \mu\text{L}$ (L'vov, 1978). Results were expressed in micrograms metal per litre and detection limits at the 99% confidence level were $10.5 \mu\text{g L}^{-1}$ for copper, $4.75 \mu\text{g L}^{-1}$ for lead and $0.75 \mu\text{g L}^{-1}$ for cadmium (Analytical Methods Committee, 1987; refer to Appendix 3).

Table 2. Furnace operating parameters for copper/lead analysis.

Step	Temperature (°C)	Time (s)	Internal nitrogen flow (L min ⁻¹)	Read
1	90	60	3	
2	120	10	3	
3	120	20	3	
4	1000	10	3	
5	1000	20	3	
6	40	10	3	
7	40	1	0	
8	2200	1.1	0	*
9	2200	6	0	*
10	2700	1	3	
11	2700	2	3	

Cu : 327.4nm wavelength; 0.5nm slit; 6mA lamp current

Pb : 217nm wavelength; 1nm slit; 8mA lamp current

Table 3. Furnace operating parameters for cadmium analysis.

Step	Temperature (°C)	Time (s)	Internal nitrogen flow (L min ⁻¹)	Read
1	90	60	3	
2	120	10	3	
3	120	20	3	
4	800	10	3	
5	800	20	3	
6	40	10	3	
7	40	1	0	
8	1650	0.9	0	*
9	1650	6	0	*
10	2700	1	3	
11	2700	2	3	

Cd : 228.8nm wavelength; 0.5nm slit; 3mA lamp current

2.6.5.2 Flame AAS

Flame AAS was performed to determine dissolved zinc content in the filtered surface and interstitial waters (acidified) from the Sutherland Shire creeks. Again the Varian AA-1275 series spectrophotometer was used (Rothery, 1980; Varian Techtron, 1979). Concentrations were expressed in milligrams metal per litre. The detection limit at the 99% confidence level was 0.01 mg L^{-1} (Analytical Methods Committee, 1987; refer to Appendix 3).

2.6.6 Phosphorus

Dissolved ortho-phosphate was determined for surface and interstitial water samples using a Skalar SAN Plus segmented flow analyser (SKALAR, 1989). The phosphorus chemistry of this autoanalyser utilised an ascorbic acid reduction assay for ortho-phosphate ions, adapted from the method of Murphy and Riley (1962) for natural waters. Results were expressed in micrograms phosphate-P per litre and a detection limit of $1 \text{ } \mu\text{g L}^{-1}$, at the 99% confidence level, applied (Analytical Methods Committee, 1987; refer to Appendix 3).

Other components of the soluble reactive phosphorus (SRP), such as dissolved organic phosphorus and certain higher molecular weight polyphosphates, were not measured. However, as ortho-phosphate constitutes the major fraction of the SRP, this value was assumed to be a good estimation of the 'available' fraction (Hart and McKelvie, 1986; White *et al.*, 1981).

For surface waters, application of the assay to persulfate digested sample (Major *et al.*, 1972) provided an estimation of the total phosphorus concentration (Clesceri *et al.*, 1989). The detection limit at the 99% confidence level in this case was $1.3 \text{ } \mu\text{g PO}_4\text{-P L}^{-1}$ (refer to Appendix 3).

2.6.7 Additional Surface Water Chemical Analyses

2.6.7.1 Turbidity and Colour

Turbidity of unfiltered surface water was determined with a HACH 2100A turbidimeter. The readings were in nephelometric turbidity units (NTU) after calibration with Gelex® secondary turbidity standards (Clesceri *et al.*, 1989; Water Research Centre, 1979). Its detection limit was 0.5NTU.

Colour, or 'gilvin', was measured on filtered water as an absorbance at 440nm in an optical cell with a path length of 40mm (Water Research Centre, 1979; Kirk, 1976). A detection limit of 0.001 absorbance units was assumed.

Both turbidity and colour determinations were performed as soon as possible (<24 hours) after sampling. In the meantime, they were kept out of direct light (Water Research Centre, 1979).

2.6.7.2 Sodium, Potassium, Calcium and Magnesium

Unfiltered surface water was analysed for sodium, potassium, calcium and magnesium by flame AAS using the Varian AA-1275 series spectrophotometer (Rothery, 1980; Varian Techtron, 1979). Results were expressed in milligrams metal per litre. For each metal the instrument detection limit was 0.05 mg L⁻¹.

Prior to the analysis, strontium chloride was added to the samples and mixed standards to a final concentration of 5000 mg L⁻¹. The strontium acted as both a releasing agent for calcium and magnesium and as an ionization suppressant for sodium and potassium (Bennett and Rothery, 1983).

2.6.7.3 Chloride and Sulfate

Both chloride and sulfate concentrations were determined on unfiltered surface waters and expressed in milligrams chloride or sulfate per litre respectively. Chloride was measured using a Radiometer CMT10 chloride titrator (Radiometer Copenhagen, 1978). For a 20μL aliquot of sample, the instrument detection limit was 0.36μg chloride. For samples of very low concentrations, the pipetted volume was increased (up to 2mL) to ensure that the amount titrated was in excess of this limit. Hence, a final detection limit of 0.2 mg L⁻¹ applied.

Sulfate was measured by the turbidimetric technique of Clesceri *et al.* (1989). The detection limit at the 99% confidence level was estimated to be 2 mg L⁻¹ (Analytical Methods Committee, 1987; refer to Appendix 3). Samples with low levels of sulfate (<10 mg L⁻¹) were re-analysed using a buffer with sodium sulfate decahydrate added (252 mg L⁻¹), reducing the limit of detection to approximately 0.1 mg L⁻¹ (Clesceri *et al.*, 1989). Colour and turbidity corrections were performed for all samples by running blanks to which barium chloride was not added.

2.6.7.4 Ammonia and Nitrate

Both ammonia and nitrate were measured colorimetrically on filtered water using the appropriate chemistry of the Skalar SAN Plus segmented flow analyser (SKALAR, 1989). Levels were expressed in micrograms ammonia-N and nitrate-N per litre, respectively. Detection limits at the 99% confidence level were $4 \mu\text{g L}^{-1}$ and $5 \mu\text{g L}^{-1}$, respectively (Analytical Methods Committee, 1987; refer to Appendix 3).

Ammonia analysis was based on a modified Berthelot reaction, developed from the methods of Krom (1980), Verdouw *et al.* (1978) and Harwood and Kühn (1970). Nitrate determination involved a modified Griess-Ilosvay assay (Henriksen and Selmer-Olsen, 1970).

2.7 Sediment Analysis

2.7.1 Pre-treatment

Dry sediment was passed through an Endecotts BS410/1986 brass sieve, 2mm mesh, in order to remove any gravel and other large particles. All subsequent analyses were performed on the fractions being less than 2mm in diameter and recorded on a dry weight basis. For the chemical analyses, except cation exchange capacity, a suitable quantity was ground up to a fine powder.

2.7.2 Heavy Metals

Total heavy metal (Zn, Cu, Pb and Cd) content was determined on each sediment sample following the procedure of Section 2.7.2.4, which was derived from Tetra Tech (1986). If a detectable level was observed heavy metals were extracted in the four-step sequence, described below, to enable estimation of the basic forms.

This adopted sequential extraction technique was essentially a simplification of the methodology presented in Tessier *et al.* (1979). Although this is not regarded as the standard method for such work (there being, in fact, no standard method for this kind of analysis), it has been applied most widely and used as a benchmark for more recent procedures (Das *et al.*, 1995; Kheboian and Bauer, 1987).

Tessier *et al.* (1979) utilised both 1M sodium acetate (pH 8.2) and 1M magnesium chloride (pH 7.0) to estimate exchangeable trace metals (denoted as Fraction 1). The latter was

finally recommended as the initial reagent in the extraction procedure, mainly because the sodium acetate tended to also remove metals that were bound to carbonates (Fraction 2 in their paper). Since the Hawkesbury Sandstone sediments analysed here were low in readily exchangeable and carbonate fractions, it was considered not worthwhile to attempt both their estimation. Therefore, 1M sodium acetate was adopted as the same reagent was used for the determination of cation exchange capacity, allowing for a comparison of results if need be.

The first three speciation steps were performed using plastic tubes (polyethylene; 100mL) to enable separation of extract and solids via centrifugation, rather than filtration, since the latter is time-consuming, wastes sample and most importantly, a potential source of trace element contamination (Ahlers *et al.*, 1990). Heating stages were carried out in a laboratory oven.

Reagent blanks were prepared simultaneously and flame AAS with the Varian AA-1275 atomic absorption spectrophotometer was performed to determine the levels of the four metals (Rothery, 1980; Varian Techtron, 1979). A separate set of mixed standards, in the approximate sample matrix, was made for the metal analysis of each extraction type. All results were expressed in micrograms metal per gram and on analysis of individual extracts, the assumed detection limits were 0.01 mg L⁻¹ for zinc, 0.02 mg L⁻¹ for copper, 0.10 mg L⁻¹ for lead and 0.01 mg L⁻¹ for cadmium (Analytical Methods Committee, 1987; refer to Appendix 3).

2.7.2.1 Rapidly Exchangeable Metal

Sediment (1.5-2.5g) was shaken in 20mL of 1M sodium acetate, pH 8.2, for one hour. After centrifugation (2000rpm for five minutes), the supernatant was acidified to pH 2 with concentrated nitric acid and made up to a final volume of 25mL. The matrix was taken to be 80% v/v sodium acetate (1M), pH 2 (Tessier *et al.*, 1979; Gupta and Chen, 1975).

2.7.2.2 Metal Bound to Iron and Manganese Oxides

The residue from the previous step was extracted with 45mL of 0.04M hydroxylamine hydrochloride (NH₂OH.HCl) in 25%v/v acetic acid at 95°C for six hours with occasional agitation. The solution was centrifuged and made up to 50mL. The standard matrix was assumed to be 90%v/v hydroxylamine hydrochloride in 25% acetic acid (Tessier *et al.*, 1979).

2.7.2.3 Metal Bound to Organic Matter and Sulfides

To the residue from the previous step was added 7mL of 0.02M nitric acid, followed by 13mL of 30%w/v hydrogen peroxide (adjusted to pH 2 with 1:1 HNO₃). The mixture was heated at 85°C for two hours with occasional agitation. A second 7mL aliquot of 30% hydrogen peroxide (pH 2) was then added and the sample reheated as before for three hours.

After cooling, 13mL of 3.2M ammonium acetate in 20%v/v nitric acid were added, with mixing, to prevent adsorption of extracted metals onto the oxidised sediment (Gupta and Chen, 1975). The solution was centrifuged and the total volume made up to 50mL. The standard matrix was 7mL dilute nitric acid (0.02M) plus 13mL ammonium acetate (3.2M) in 20% nitric acid per 50mL (Tessier *et al.*, 1979).

2.7.2.4 Residual and Total Metal (excluding Lattice Metal)

The residue from the previous step, or 0.2-2g of original sediment, were transferred quantitatively to a suitable vessel with 10mL of 1:1 nitric acid. The mixture was heated at 95°C for ten minutes. After cooling, 5mL of concentrated nitric acid were added and the sample was refluxed (150°C) for at least two hours.

On completion of the second heating step, the mixture was again cooled and 2mL of water, followed by 3mL of 30%w/v hydrogen peroxide, were added. Gentle heating started the peroxide reaction but when effervescence subsided, heating was stopped. Further 1mL aliquots of the 30% peroxide were added, with warming, until any effervescence was minimal.

Upon cooling once more, another thirty minute refluxing step (110-120°C) was performed following the addition of 5mL of 1:1 hydrochloric acid and 10mL water. The final digestate was filtered and made up to 100mL. The residual matrix was taken as being 2.5% hydrochloric / 5% nitric acids (v/v) (Tetra Tech, 1986).

2.7.3 Phosphorus

2.7.3.1 Total Phosphorus

Sediment phosphorus was converted to ortho-phosphate by the sulfuric acid - hydrogen peroxide digestion of Allen (1989). The dissolved phosphate was then determined on the Skalar SAN Plus system, as per Section 2.6.6, assuming the same detection limit of 1 µg

$\text{PO}_4\text{-P L}^{-1}$. Amounts of sample used ranged from 0.25-0.4g and the total phosphorus concentration was given in micrograms phosphate-P per gram. Blank digests were prepared with each set of samples.

2.7.3.2 Organic Phosphorus

Determination of sediment organic phosphorus was performed by the multi-step acid and base extraction procedure of Allen (1989), which was based on the method of Anderson (1960). Extractions were carried out in polyethylene tubes (100mL) and amounts of sample used ranged from 1-2g. Blanks were prepared with each set of samples.

Both the inorganic (i.e. ortho-phosphate) and total phosphorus contents of the combined extracts were measured using the Skalar segmented flow analyser, as per the analysis of creek surface waters (Section 2.6.6), assuming the same detection limits of 1 and 1.3 $\mu\text{g PO}_4\text{-P L}^{-1}$, respectively.

2.7.4 Organic Carbon

Organic carbon was determined by the rapid titration procedure of Allen (1989), derived from the method of Kalembasa and Jenkinson (1973). For each sample, maximum refluxing temperature was 150°C (Charles and Simmons, 1986) and results were expressed as a percentage of dry weight (i.e. grams organic carbon per hundred grams dry sediment). A minimum of two blanks were prepared with each batch and sample titres were subtracted from the average value.

2.7.5 Particle Size Fractionation

A simplified mechanical analysis involving wet and dry sieving was devised from the methodologies of Tetra Tech (1986) and Day (1965) to determine the proportions of particles having defined diameter ranges of less than 2mm. ABICHEM ACA BS410 stainless steel laboratory sieves were used with a Fritsch® Analysette sieve shaker, Model 03502.

'Calgon' dispersant solution (5%w/v sodium hexametaphosphate; 300mL) was added to 100-150g of dry, 2mm sieved sediment. After ten minutes the solution was mixed and poured through a 106 μm mesh sieve. The residue on the sieve was washed under running water until the effluent was clear, then removed and dried at 105°C before weighing. The difference in weight between this and the initial gave the silt and clay content.

To partition the larger particles, the dry residue was shaken mechanically for five minutes through a stack of two sieves, having mesh sizes of 212 μ m and 106 μ m respectively. Each individual fraction retained was weighed and its percentage of the total dry weight calculated. Any material which passed through the 106 μ m sieve was measured and added to the weight of fines found previously. The appearance of such fines was a result of surface tension effects in wet sieving and differences in shaking technique in the wet and dry states (Kiff, 1973).

This scheme fractionated the particles into the following general classes :

Coarse sand	=	212 μ m - 2mm
Fine sand	=	106 - 212 μ m
Silt + clay	=	< 106 μ m.

These were as close as possible (given the sieves available) to the Atterberg scale, adopted by the International Society of Soil Science (Allen, 1989; White, 1979; McIntyre and Loveday, 1974; Kiff, 1973; Atterberg, 1905).

Removal of organic matter (by addition of peroxide) prior to analysis, as suggested by Kiff (1973), was not done to avoid decomposition of organic coatings found in agglomerated particles, which would otherwise lead to an increased number of smaller particles (Hart and McKelvie, 1986). In any case, sediment organic matter was expected to be low, making the step of limited use.

2.7.6 Cation Exchange Capacity

To complement each particle size analysis, the cation exchange capacity of the sediment was also estimated. The method was derived from that of Bower *et al.* (1952).

Un-ground sediment (4g) was shaken for five minutes in 1M sodium acetate (pH 8.2; 30mL) to replace exchangeable ions on the colloids with sodium ions. The mixture was centrifuged at 2500rpm for a few minutes (or until the supernatant liquid was clear) and the supernatant decanted. These steps were repeated three more times with further 30mL lots of the acetate solution. The sediment was then washed three times in 95% ethanol (v/v, 30mL), with shaking and centrifugation as above.

To replace the adsorbed sodium, the sediment was extracted three times with neutral 1M ammonium acetate (30mL), following the same shaking and centrifugation procedure. In this case, however, the supernatants were combined and made up to 100mL for flame AAS

using the Varian AA-1275 spectrophotometer (Rothery, 1980; Varian Techtron, 1979). Results were expressed in millimoles sodium per 100 grams of sediment. A minimum of two blanks were prepared with each batch of samples and the standard matrix included an appropriate amount of the ammonium acetate extractant.

2.8 Statistical Analyses and Data Manipulation

2.8.1 General Procedures

To simplify the data analysis, any constituent found to be at a level below the detectable limit was assumed to have a concentration of zero. Calculated anion relative percentages were based on molecular weights per charge of chloride (35.45), sulfate (48.0) and carbonate (50.0) only. Similarly, cation relative percentages were based on molecular weights per charge of sodium (23.0), potassium (39.1), calcium (20.0) and magnesium (12.1) only.

The statistical analyses of chi-square association measures, analysis of variance (ANOVA), correlation and regression were conducted using SYSTAT 5 (Wilkinson, 1989) at the 5% significance level, unless otherwise stated. Where necessary, reference was made to the texts Snedecor and Cochran (1980) and Sokal and Rohlf (1969). Where a statistical analysis may have been influenced by departures from normality and variance homogeneity, this has been highlighted.

Analysis of variance, by definition, is a parametric test. It is considered to be quite robust to many types and magnitudes of non-normality and departures from homogeneity of variances (Underwood, 1981). Nevertheless, to avoid possible Type I errors the data sets were consistently checked for non-normal distribution and variance heterogeneity.

SYSTAT 5 performs analysis of variance with a Bartlett test for homogeneity of group variances within treatments. Since this test is too conservative as a routine procedure (Underwood, 1981), the more lenient *F*-test or Cochran's test (Snedecor and Cochran, 1980) was applied in some cases before (and after) data transformation where both the ANOVA and Bartlett probabilities were significant (i.e. $p < 0.05$). Non-significant ANOVA results (i.e. $p > 0.05$) were assumed reliable regardless of homogeneity (Underwood, 1981; Bartlett 1947)

The monotonic techniques of square-root (i.e. $\sqrt{x+1/2}$) and/or natural logarithmic (i.e. $\log_e(x+1)$) transformation were used. Note that negative redox values became missing

data after performing either of these two transformations. Hence, before the calculation was applied a value of 1000 was added to the original data where necessary.

In general, only the observed significant differences from each ANOVA are listed. Where appropriate, the analysis included a Tukey pairwise matrix comparison to identify the source(s) of the difference(s). If the comparison was too conservative (i.e. matrix probabilities were greater than 0.05) for a particular analysis, such cases are noted.

Correlation analysis usually involved Spearman correlation coefficients, since the majority of variables tended not to represent samples taken from a normal distribution. Critical values were found in the corresponding appendix table of Zar (1984). However, since non-parametric tests are less powerful and imply a greater probability of a Type II error, Pearson correlation coefficients were obtained wherever possible.

For the Sutherland Shire creeks, grouping of individual sets of data involved certain fixed factors, such as water type, season and flow. Classification with respect to flow rate was based on two categories :

Low (F1)	=	< 31.3 cm s ⁻¹
High (F2)	=	≥ 31.3 cm s ⁻¹ .

In the analysis, flows which could not be detected (i.e. less than 5 mm pitometer height - refer to Section 2.6.2) were not taken as zero, but designated as 4.4 cm s⁻¹. This value was the average low-flow for these sites, after determination with surface floats following the techniques of Campbell (1978*b*) and Wisler and Brater (1959).

Individual replicates were also classified as either summer (including the spring months) or winter (including the autumn months) samples, according to the season when collected. Benson and Howell (1990) state that for the Sydney region the average frost period occurs mostly between May and September. For this study, September was therefore assumed to lie in the winter season, with March subsequently being regarded as a summer month.

2.8.2 Multivariate Statistical Methods

Considering the wide range of chemical parameters that were measured during these studies, multivariate data analysis was appropriate to complement the univariate statistical analyses. The neglect of multivariate techniques by chemists is quite apparent in the literature, despite them often being used by ecologists, geologists and agricultural, medicinal and social scientists (James and McCulloch, 1990). They are powerful tools for

describing and interpreting the relationships of variables from data sets that contain intercorrelations, for grouping samples and assessing their variability, while avoiding the possible insertion of mathematical artefacts (e.g. parabolic curves).

Given the design of the basin survey (i.e. large site numbers, each described by numerous parameters), the combination of two substantially different methods - a specific hierarchical classification (e.g. two-way indicator species analysis) and an ordination technique (e.g. nonmetric multidimensional scaling), as suggested by Gauch (1982) - was regarded as the most suitable approach to the data analysis in this case. The ease of use and success observed with the multidimensional scaling recommended it as a means of assessing stream chemical variability (spatial and temporal) in the monitoring study.

Two-way indicator species analysis (TWINSPAN; Hill, 1979) is a polythetic divisive classification technique which clusters a set of samples through reciprocal averaging and then successively divides the samples into a hierarchy of smaller and smaller clusters. The resultant hierarchy is displayed as a dendrogram, with the most similar samples being placed together in the sequence (Gauch, 1982).

Large data sets are easily analysed with lucid presentation of the results, the similarities and differences between samples being shown quite clearly compared to many other techniques (Wells *et al.*, 1995; Gauch, 1982). The analysis makes no formal assumptions about the nature of the data; the requirements of normality, linearity and homoscedasticity that are critical in other techniques have no importance here (Hair *et al.*, 1995; Hill, 1979). In addition, the analysis is relatively unaffected by noise (Gauch, 1982). Being both polythetic and divisive, it is effective and robust, making it far superior to related monothetic and agglomerative techniques (Gauch, 1982). Most importantly, it commences by examining overall, major gradients in the data, hence using all the available information to make the critical initial divisions (Gauch, 1982). This was especially relevant to the basin survey, where major groups were hoped to be expressed in the classification, rather than tiny, sample-to-sample differences. Such groupings may not have been as readily identified by utilising such techniques as principal components analysis or linear discriminant function analysis.

Multidimensional scaling (MDS) is an ordination technique which displays a set of samples, originally involving many dimensions, in a few dimensions (normally one to three), hence enabling some interpretation of the pattern in the data to be made. It uses sample proximities (e.g. Euclidean distances) as input, generating a spatial representation that consists of a geometric configuration of points, each point corresponding to one of the samples. Thus, the more dissimilar two samples are, the further apart they are in the

configuration (Gauch *et al.*, 1981; Kruskal and Wish, 1978). Its principal advantage lies in the fact that situations often occur where the relationship between objects is unknown, yet a distance matrix can still be estimated (Manly, 1994).

The technique requires no restraining assumptions on the methodology, the type of data, or form of the relationships among the variables (Hair *et al.*, 1995; Gauch *et al.*, 1981). Like various other ordination procedures it involves scaling, except that here only the rank order of inter-object distances is used and nonlinear monotonic relationships are estimated. Techniques such as principal components analysis, principal coordinates analysis, factor analysis and correspondence analysis are best suited for linear data and will not discover nonlinear relationships (James and McCulloch, 1990). While many of the parameters measured during these studies are well known as displaying certain relationships (usually linear), not all do so. Hence it was better to choose a technique that would not limit the analysis in this context. An additional point is that compared to certain interdependence techniques, such as factor and cluster analyses, MDS does not require the specification of the variables to be used in comparing objects (Hair *et al.*, 1995).

Nonmetric MDS was preferred over a metric method due to its greater power and flexibility, derived from there being no assumption of any specific type of relationship between the calculated distance and the similarity measure. This consequently enables better low-dimensional representations of the data (Hair *et al.*, 1995; Manly, 1994, Prentice, 1977). Furthermore, as quoted from James and McCulloch (1990), nonmetric MDS is 'potentially a robust ordination method for reducing the dimensions of data without a priori transformations'.

TWINSpan (Hill, 1979) and Kruskal nonmetric multidimensional scaling of Euclidean distance matrices (Wilkinson, 1989; Kruskal and Wish, 1978; Kruskal, 1964a; Kruskal, 1964b) were performed on range standardised data. For TWINSpan, the following cut levels were assumed :

Cut Level :	0	1	2	4	8	16	32	64	>64
Range Limit :	-	1	2	3	4	5	6	7	8

Following an MDS analysis, by using the most different values as extreme points, spread and group cluster plots were investigated. For each ordination, the final configuration stress, or 'goodness of fit' statistic, was noted. This value was qualified using the guidelines of Kruskal (1964a), given below :

<i>Stress</i>	<i>Goodness of fit</i>
>0.2	poor
0.15 - 0.2	be cautious
0.1 - 0.15	fair
0.05 - 0.1	good / satisfactory
<0.05	excellent
0	'perfect'

A 'perfect' fit indicates there is a perfect relationship between dissimilarities and the distances between points in the two-dimensional plot.

To aid in the presentation of results, final configuration diagrams involving large numbers of samples were simplified by plotting principal sample groups separately. Thus a set of scatter plots for the same analysis are sometimes presented, but these do not represent separate ordinations.

For data obtained from the Sutherland Shire creeks, scaling was performed on selected parameters from the surface and interstitial water chemistries, plus the sediment chemistries. The selection criterion was, in each case, that the sample attributes (i.e. analyses) were the same for each sample type. Mean values, single samples (i.e. sample collections) and groups of samples were analysed, while scalings involving combined surface and interstitial water data were also run. Replicates for ordinations using large groups of samples were chosen by excluding those with relevant data points missing. Stations, therefore, may not have been represented by equal numbers of replicates in some cases, but the data set was maximised by not excluding further.

3 THE INFLUENCE OF URBANISATION ON SYDNEY STREAMS

3.1 Summary

Streams near Sydney were sampled for 18 water quality parameters at 90 sites in 86 different waterways during low flow conditions. They were generally low in salinity, soft, of poor buffering capacity and dominated by sodium and chloride, consistent with their location in a coastal basin with a high sandstone content. Calcium, magnesium and (bi-)carbonate dominance, or at least co-dominance, occurred in a number of cases where other rocks, such as igneous and metamorphic formations, were present.

Multivariate analyses indicated three groups, separated primarily by levels of dissolved nutrients, trace metals, turbidity and colour. Chemical groupings were associated strongly with the type and level of catchment development. Streams in areas relatively unaffected by human influence had notable uniformity in chemistry; any observed variability was derived mostly from the major ions, reflecting geological influences. In comparison, streams in catchments affected by human development were highly varied.

Heavy metal contamination of these streams was relatively low, though a few of the samples displayed inordinately large levels of one or more metals. In such cases the more extreme measurements of phosphorus and nitrogen were also seen. Since very high concentrations of metals and nutrients were not frequent in samples, the findings were consistent with occasional or localised elevation of contaminant levels.

Climatic trends ensured the sampling period was dominated by low stream flow conditions, that is, conditions not favourable for an assessment of the influence that flow and discharge have on surface water chemistry.

3.2 Introduction

3.2.1 The Study Area

3.2.1.1 Location and Climate

The Sydney basin, situated on the subtropical east coast of Australia, is defined here as those catchments draining to the coast between Broken Bay and Botany Bay heads, also

including the Hacking River catchment which drains into Port Hacking (see Figure 5). The principal river systems are the large Hawkesbury River and the smaller Parramatta and Georges Rivers. The total area is approximately 20 000 square kilometres.

The climate is typically a warm, wet summer-autumn and cool, dry winter-spring. Rainfall is highest on the coast, where the annual average is over 1200mm and on the nearby elevated plateaus with an annual maximum of 1400mm. While rainfall is somewhat variable and unpredictable, near the coast the wettest period is during autumn; rainfall is low in winter and the spring months are the driest. Low intensity, prolonged rainfall is rare (Benson and Howell, 1990; Chapman and Murphy, 1989).

Mean maximum temperatures increase from less than 26°C along the coast to over 29°C on the Cumberland Plain (covering the region Windsor - Penrith - Camden - Liverpool on Figure 5), and mean minima drop from 7-8°C to 2-4°C respectively. January is normally the hottest month and July the coldest. Frosts are rare on the coast but common in the west of the area (Benson and Howell, 1990).

3.2.1.2 Geology

Figure 6 provides a simplified illustration of the basin geology, based on the New South Wales Department of Mines, Sydney Geological Sheet (1 : 250 000 scale) with accompanying booklet (Bryan *et al.*, 1966) and Benson and Howell (1990). Three fundamental rock types are depicted and represent the oldest formations, their development beginning in the late Permian period through to the early Tertiary period (300-50 million years ago). The first group, found mainly on the western reaches, includes a mixture of metamorphic and igneous formations with an occasional fine-grained sedimentary outcrop, often limestone. Beds of shale, including the Wianamatta Shales, mixed with small amounts of sandstone, comprise the flat Cumberland Plain and parts south to Mittagong.

Sandstone, the majority of which is Hawkesbury Sandstone, is the third fundamental rock type and comprises the largest proportion of the basin, particularly in the more mountainous northern and north-western regions. It produces shallow, sandy, infertile soils.

Although not able to be shown in Figure 6, the Wianamatta Group shales and occasional sandstones of the Cumberland Plain are also found on the inner western and southern areas. These may provide an important source of suspended materials to the creeks in this area.

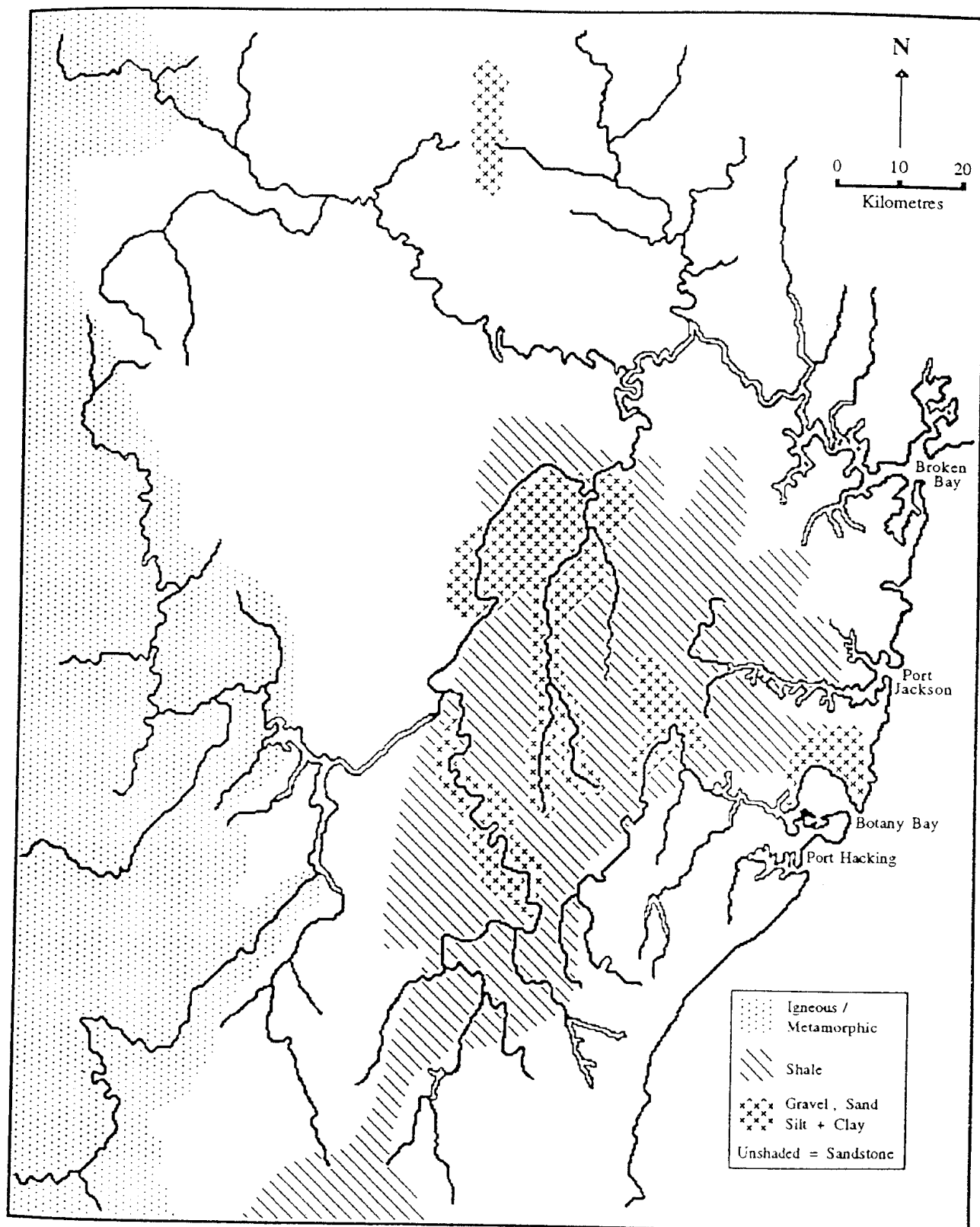


Figure 6. Geology of the Sydney Basin.

Between the Tertiary and Quaternary periods (50-1.8 million years ago), weathered alluvial sediments were laid down forming a series of gravel, sand, silt and clay terraces. These occur in the Windsor district, along the Georges River near Liverpool, on the flood plains of the Nepean-Hawkesbury River near Camden and along the major streams of the Cumberland Plain. Although having mixed composition, gravel and sand are usually the major components.

3.2.1.3 Land Use

A simplified map of the current state of basin land use, based on the NATMAP SI 56-5 Sydney Series, NSW Department of Main Roads Sydney and Surrounding Districts 1 : 100 000 Scale Map (1985) and Benson and Howell (1990), is provided in Figure 7. Over half of the Sydney basin has been developed, whether it be urban or rural, up to the present time. In the past, most cleared land was designated for farming purposes and both cultivation (concentrated in the region from Windsor to Liverpool and Camden) and grazing now occur. However, during the last few decades virtually no increase in such development has taken place because of greater demand to house the growing number of Sydney inhabitants. In fact, urban encroachment onto the rural areas, as well as previously undeveloped bush, has occurred (UDP, 1991; Benson and Howell, 1990).

Urban Sydney was originally concentrated around the two main harbours of Port Jackson and Botany Bay (Benson and Howell, 1990). The more recent expansion has been in all directions but particularly westwards beyond the Penrith district and south along the western bank of the Georges River. While specific data quantifying this rate of urbanisation are scarce, investigations by the Urban Development Program (UDP, 1991) of the New South Wales Department of Planning have tabulated the total number of dwelling commencements in the region between 1985 and 1990 :

85 / 86 :	26 000
86 / 87 :	25 500
87 / 88 :	30 000
88 / 89 :	33 500
89 / 90 :	25 000
TOTAL:	140 000

Approximately two-thirds of these are the construction of detached houses, while the remainder is comprised of multi-unit dwellings. Assuming an average of 500m² per

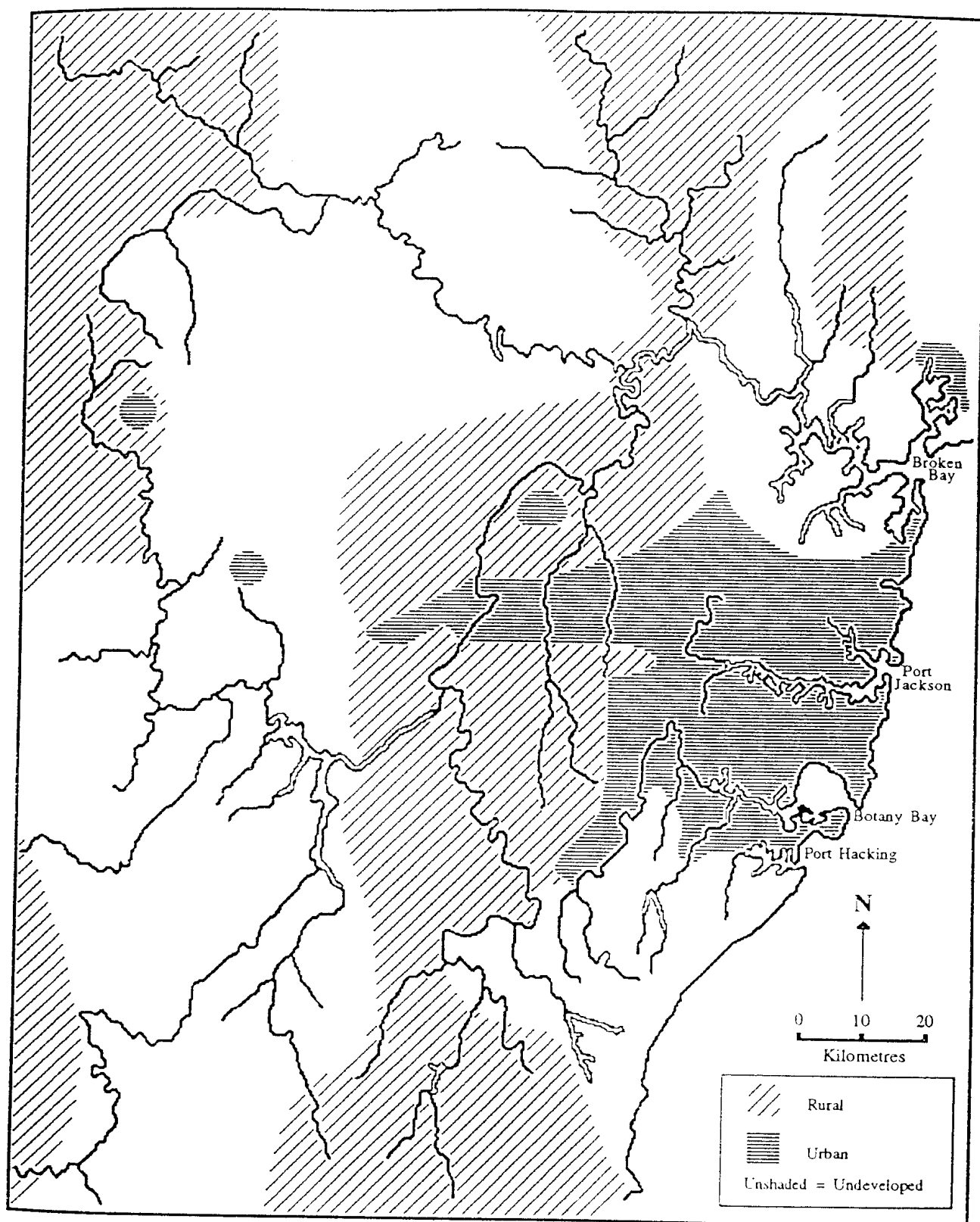


Figure 7. Land use of the Sydney Basin.

house and 2000m² per unit block, it is estimated that an area of 140km² (0.7% of the study area) have been recently modified for residential use alone.

As of June 1991, stocks of land under the control of the UDP could enable a further 133 000 potential dwellings, about half of which are expected to be completed, or at least started, by the end of 1995. Given that the UDP is responsible for about 39% of all new housing commencements in Sydney, a total of 341 000 future dwellings are thus possible (UDP, 1991). Following the same approach as above, this corresponds to an area of 341km² of land (1.7% of the study area) which would be developed. These calculated areas do not include the necessary amenities that accompany the building of houses, such as roads, parking facilities and shops, nor any industrial developments and consequently are expected to be underestimates, probably by about 5 to 10% overall.

The districts targeted for future developments are concentrated in the western and south-western areas, particularly around the Liverpool/Penrith/Camden subregions. However new releases in the northern districts of Sydney have also been included, mainly in the Windsor to upper Hornsby subregions (UDP, 1991). These are areas comprised primarily of natural vegetation.

3.2.2 Objectives and Experimental Design

The basic objective of this study was to answer the following questions :

- (1) What are the chemical characteristics of Sydney streams ?
- (2) What, in general terms, does urbanisation do to the chemical nature of streams in the Sydney basin ?

A secondary objective was to identify candidate streams for the intensive study described in Chapter 4.

The experimental design involved collection and analysis of surface water samples from a large number of randomly selected freshwater streams in the basin, as described in Chapter 2. In addition to analysis of the standard water parameters including pH, turbidity and colour, alkalinity (serving as a measure of (bi-)carbonate), the concentrations of major ions (sodium, potassium, calcium, magnesium, chloride and sulphate) and minor ions (lead, cadmium, zinc, copper, ammonium, nitrate and ortho-phosphate) were measured. Total phosphorus was also determined. Stream water velocity and discharge were estimated as described in section 2.6.2.

Assessment was directed to determining any correlations between the data and whether there was variation with flow, catchment type, geology and hence sediment type. The stream samples were classified into groups based on their chemistries using TWINSpan (Hill, 1979), as described in section 2.8. These groups were then compared to groupings based on catchment geology and land use. Since each site was sampled only once, the data for a particular sample were not expected to be an accurate picture of all the system's characteristics. Instead, the design hinged on sampling enough streams to ensure that each group would have sufficient numbers of samples (i.e. replicates) to allow statistical comparison between them and to assess spatial variability within them. The purpose, therefore, was to provide a general description and analysis of the pattern of chemical variability in the basin and to relate that to the geological and geographic influences.

3.3 Results

3.3.1 Initial Observations

A total of 90 sites in 86 different waterways were ultimately sampled. Figure 8 depicts the approximate location of each individual sampling site. Complete lists of the individual site descriptions and chemical data are provided in Appendix 4, tables A7 and A8. Table A9 lists the respective major cation and anion relative percentages.

The majority of samples (87%) had a salinity of less than 300 mg L⁻¹, approximately 30% being less than 50 mg L⁻¹. In order that only fresh waters be considered, fifteen sample sites (3, 18, 30, 31, 51, 56, 66, 72, 82, 83, 84, 87, 88, 89, 90) were omitted from the statistical analyses due to high (>200 mg L⁻¹) concentrations of one or more constituents, and were combined as a separate group. This cut-off level was much lower than a previously suggested value of 1000 mg L⁻¹ salinity (ANZECC, 1992; Buckney, 1980; or that of Williams (1967) (3000 mg L⁻¹)) to distinguish 'fresh' and 'saline' waters. However, it enabled confident elimination of samples affected by sea water. This separate group of samples is discussed later.

Although a number of samples contained high concentrations, trace metal levels on the whole were relatively low. Cadmium was not detected in any of the 90 samples and it would appear that this metal, plus others sharing similar chemistry, are unlikely to be

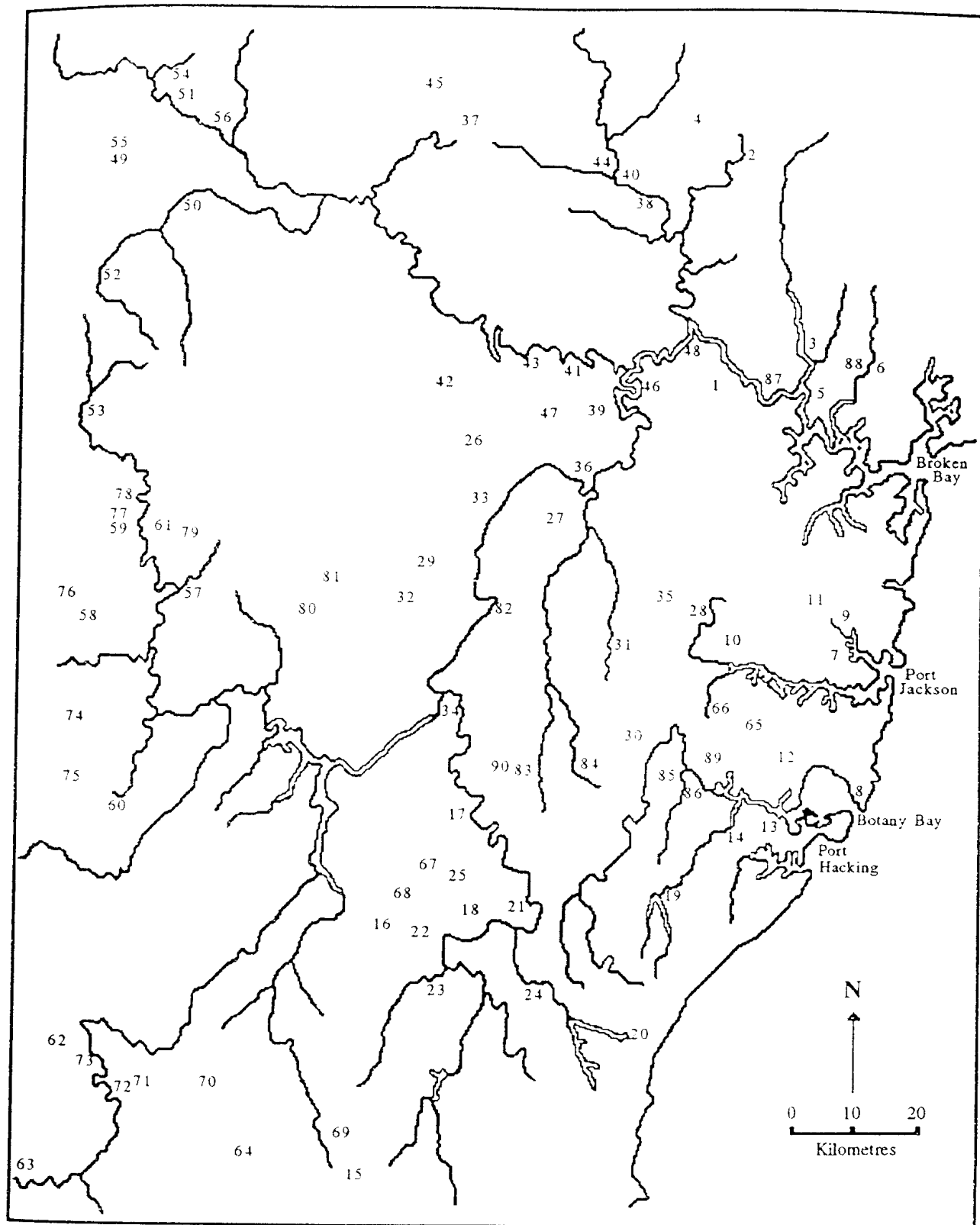


Figure 8. Locations of 90 sampling sites.

found at significant levels in the basin under normal conditions. Samples with high concentrations of one or more metals also had higher levels of phosphorus and nitrogen.

3.3.2 Two-way Indicator Species Analysis (TWINSpan)

The indicator species analysis classified the 75 sites into three main groups (Table 4), whose distribution in the sampling area are shown in Figures 8-10. The first group (23 samples; \triangle), represents those samples having very low or undetectable levels of the dissolved minor ions (i.e. nutrients and heavy metals). Group 2 (35 samples; \circ) was characterised by moderate nutrient enrichment and frequently detectable levels of heavy metals. Group 3 (\blacksquare), the most distinct group in the dendrogram, consisted of those samples (17) having substantial enrichment in both nutrients and heavy metals.

Table 4. Site order and groupings from the TWINSpan analysis (Groups 1 to 3).

Group 1	Group 2			Group 3	
	2 a	2 b	2 c	3 a	3 b
75	4	41	43	11	6
79	1	58	44	59	8
80	23	81	16	78	13
60	28	26	22	65	35
45	33	42	70	77	12
15	38	24	10	32	34
17	40	37	25	85	27
19	73	5	50	69	64
20	86	21	62	71	
29	2	36	67		
39	14	63	7		
47			53		
48			9		
52					
54					
55					
57					
68					
74					
76					
46					
61					
49					
n = 23	n = 35			n = 17	

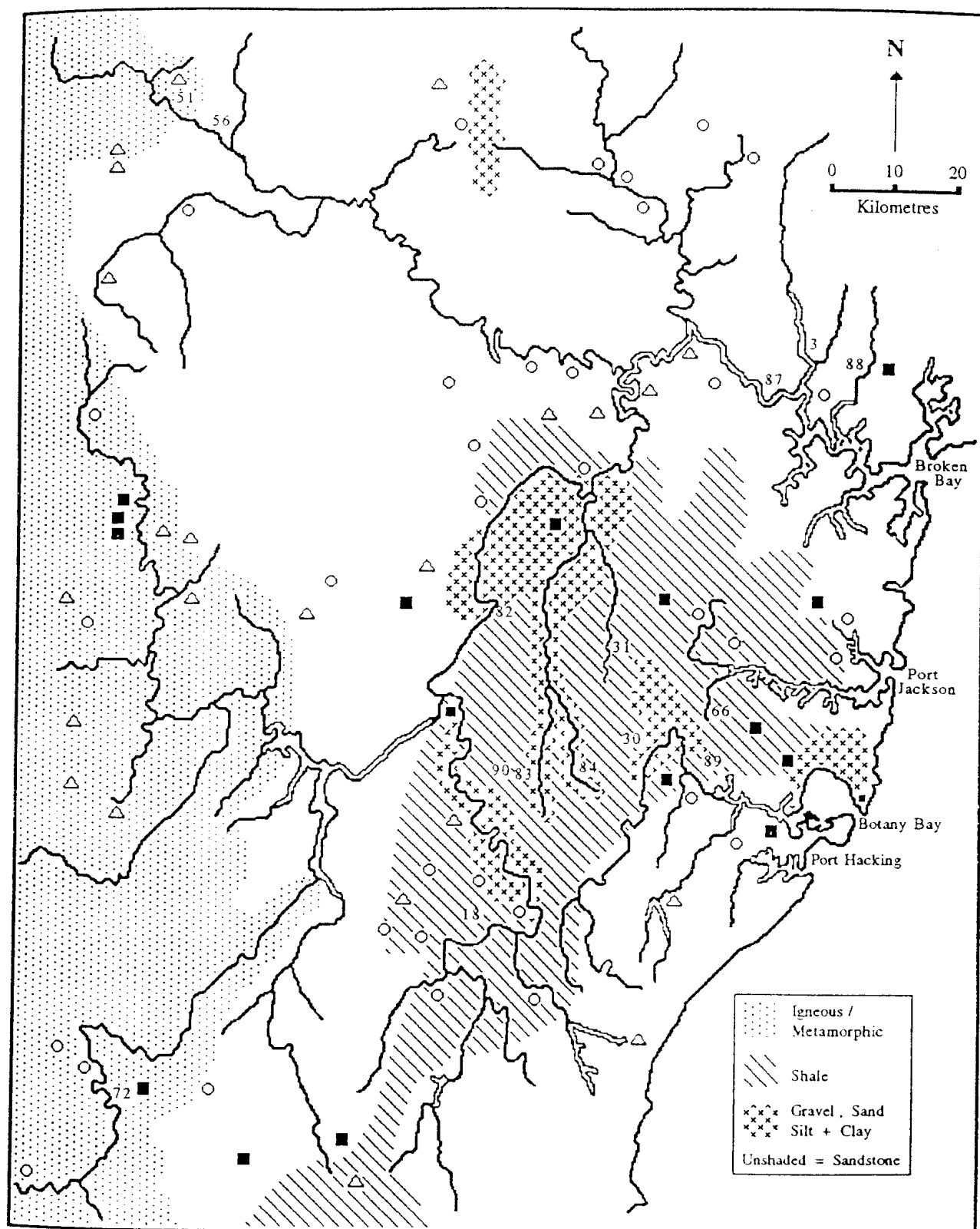


Figure 9. Basin geology with sampling sites.

△ = Group 1 sites; ○ = Group 2 sites; ■ = Group 3 sites

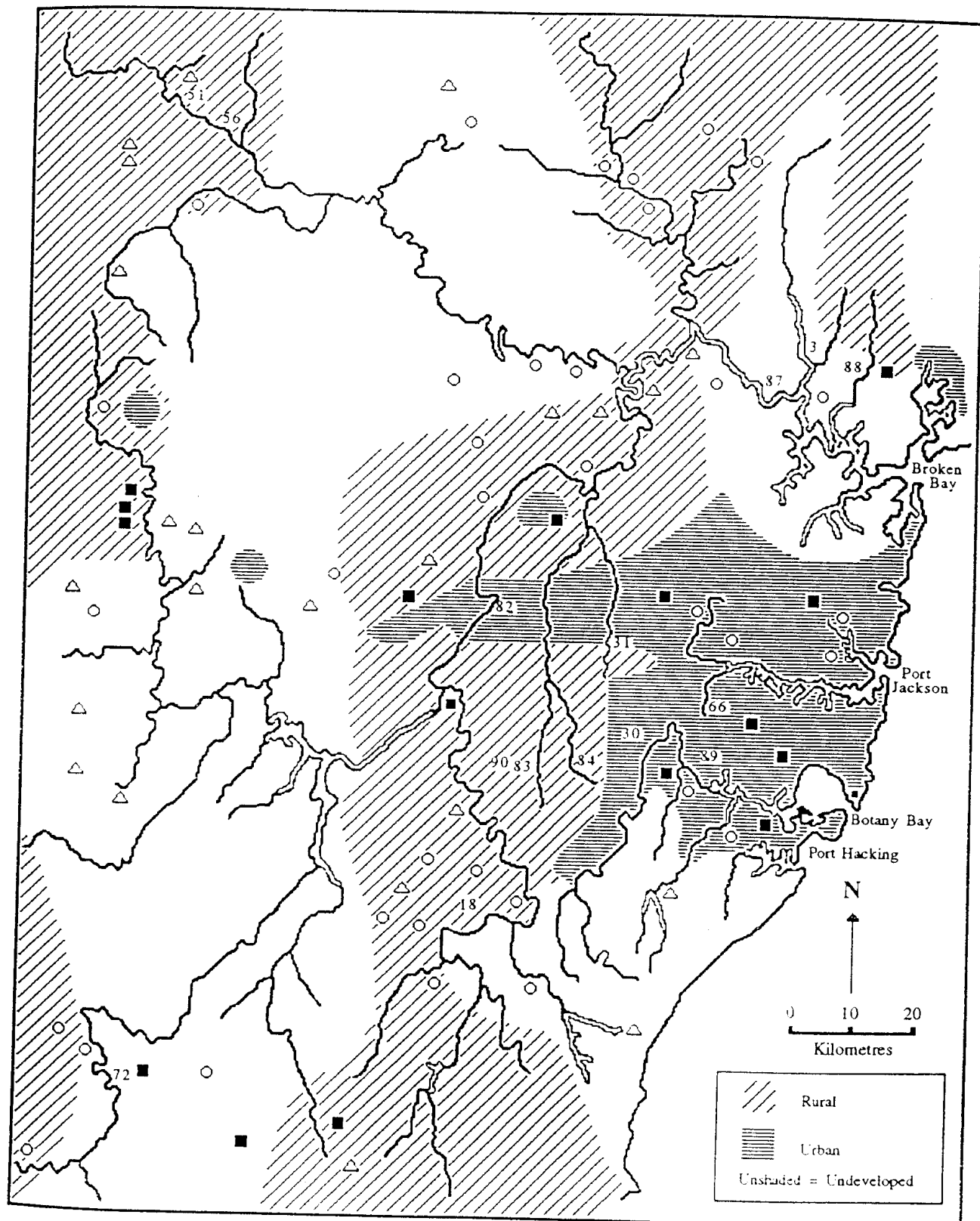


Figure 10. Basin land use with sampling sites.

△ = Group 1 sites; ○ = Group 2 sites; ■ = Group 3 sites

Further division of Groups 2 and 3 into three and two sub-groups respectively (see Table 4) was possible. Within Group 2, this was based on differences in the concentrations of potassium, nitrate, chloride, sulfate, ammonia, copper and zinc (in that order of importance). For Group 3, the sub-groups were due to differences in turbidity, orthophosphate, ammonia, copper, lead and zinc; that is, differences in minor ions and turbidity accounted for much of the variability between these sub-groups.

Correlation of TWINSPAN groupings with geology and land use was assessed by two-way chi-square association measures with significance evaluated at $p \leq 0.05$ - refer to appendix table A7 and Figures 9 and 10. Using the six groups displayed in Table 4, the Pearson chi-square probability was 0.039 for geology. Groups 1 and 2 showed significant association with igneous/metamorphic and sandstone dominated catchments, respectively.

A strong association with land use was also observed ($p=0.046$ for the six groups and 0.007 upon testing the original three TWINSPAN groups). Group 1 sites tended to be located in either purely undeveloped areas, or on the developed-bush interface. Only a small number of samples in this group were found in totally developed catchments. In contrast, Group 3 sites were principally obtained from urban and rural areas, highlighting how developments lead to detrimental changes to receiving water quality. The catchment descriptions of Group 2 were various, nearly half the samples being from some combination of land use, consistent with the intermediate chemistry of the group.

3.3.3 Analysis of Differences

Table 5 provides a list of the respective means, ranges and standard errors for the chemical parameters within each group (including the Group 4 samples; i.e. those excluded because of high levels of one or more constituents). Due to non-homogeneity of variances, even after transformation of the data, statistical comparisons between groups were not possible for most parameters.

Of the seventeen parameters, only pH and chloride showed homogeneous group variances and furthermore, only the pH data were normally distributed. Upon performing logarithmic transformations, homogeneity was obtained for sulfate, alkalinity, sodium and potassium, only. This indicated one group (at least) had substantial variability for the remaining parameters.

Table 5. Group means, ranges and standard errors for chemical parameters.

Parameter	Group 1 (n = 23)	Group 2 (n = 35)	Group 3 (n = 17)	Group 4 (n=15)
chloride (mg L ⁻¹)	25.2 ± 6.7 (<0.2 - 119)	39.4 ± 6.5 (<0.2 - 170)	46.5 ± 9.9 (<0.2 - 142)	1743 ± 599 (110 - 8091)
sulfate (mg L ⁻¹)	26.1 ± 12.3 (<0.1 - 194)	10.4 ± 5.0 (<0.1 - 174)	13.3 ± 3.1 (<0.1 - 38.8)	221 ± 70 (<0.1 - 890)
alkalinity (mgCaCO ₃ L ⁻¹)	4.3 ± 1.5 (0.2 - 26.2)	6.3 ± 1.8 (0.6 - 54.0)	6.8 ± 1.2 (0.6 - 19.2)	15.2 ± 3.0 (2.2 - 47.8)
sodium (mg L ⁻¹)	21.2 ± 6.2 (1.6 - 128)	25.1 ± 3.2 (3.5 - 70.1)	33.7 ± 6.6 (9.6 - 103)	1010 ± 341 (116 - 4576)
potassium (mg L ⁻¹)	1.3 ± 0.3 (0.1 - 6.0)	2.0 ± 0.2 (0.3 - 5.9)	3.9 ± 0.6 (0.7 - 9.0)	29.3 ± 12.8 (2.2 - 172)
calcium (mg L ⁻¹)	11.7 ± 5.0 (<0.05 - 94.0)	11.5 ± 2.5 (0.1 - 56.0)	17.0 ± 2.4 (1.0 - 33.6)	66.9 ± 12.7 (16.6 - 192)
magnesium (mg L ⁻¹)	11.3 ± 4.3 (0.3 - 86.0)	8.1 ± 1.3 (0.4 - 32.3)	9.3 ± 1.5 (1.4 - 22.8)	184 ± 54 (21.2 - 780)
pH	6.7 ± 0.2 (4.9 - 8.3)	6.9 ± 0.1 (5.3 - 8.5)	7.2 ± 0.2 (5.1 - 9.1)	7.7 ± 0.1 (6.7 - 8.4)
turbidity (FTU)	4.3 ± 1.1 (0.5 - 22.5)	11.2 ± 2.4 (0.5 - 65.0)	35.6 ± 15.3 (0.5 - 250)	28.8 ± 19.5 (1.0 - 300)
colour (A440)	0.012 ± 0.003 (<0.001 - 0.041)	0.015 ± 0.003 (<0.001 - 0.080)	0.075 ± 0.040 (<0.001 - 0.685)	0.028 ± 0.013 (<0.001 - 0.204)
total P (mgPO ₄ ³⁻ -P L ⁻¹)	0.38 ± 0.03 (<0.03 - 0.75)	0.52 ± 0.04 (0.22 - 1.2)	0.63 ± 0.14 (<0.03 - 2.48)	0.51 ± 0.08 (<0.03 - 1.16)
orth-PO ₄ ³⁻ (mgPO ₄ ³⁻ -P L ⁻¹)	<0.001	0.007 ± 0.004 (<0.001 - 0.15)	0.17 ± 0.13 (<0.001 - 2.21)	0.07 ± 0.04 (<0.001 - 0.49)
nitrate (mgNO ₃ ⁻ -N L ⁻¹)	0.08 ± 0.04 (<0.005 - 0.95)	0.16 ± 0.03 (<0.005 - 0.80)	0.87 ± 0.27 (<0.005 - 3.43)	0.35 ± 0.14 (<0.005 - 1.71)
ammonia (mgNH ₄ ⁺ -N L ⁻¹)	<0.009	0.05 ± 0.02 (<0.009 - 0.63)	0.91 ± 0.41 (<0.009 - 4.78)	0.20 ± 0.16 (<0.009 - 2.46)
lead (µg L ⁻¹)	<0.40	<0.40	10.6 ± 8.7 (<0.40 - 150)	0.69 ± 0.35 (<0.40 - 4.5)
zinc (µg L ⁻¹)	<0.25	0.11 ± 0.04 (<0.25 - 0.90)	10.5 ± 6.3 (<0.25 - 100)	10.1 ± 7.2 (<0.25 - 100)
copper (µg L ⁻¹)	<0.40	0.35 ± 0.11 (<0.40 - 2.9)	4.7 ± 1.5 (<0.40 - 25.0)	2.4 ± 0.9 (<0.40 - 13.8)

Note :

(1) Values in brackets are the observed minima and maxima

(2) Cd has been omitted as all values were below the detectable limit (i.e. <0.10 µg L⁻¹)

Group 1 was not expected to be a major source of this high variability since those parameters which showed the greatest variation were usually low in concentration in this group. For example, ortho-phosphate, ammonium, copper and lead levels were all below detectable limits.

A slight improvement occurred when the analysis was applied to the six TWINSpan groups. Still pH alone was normally distributed, while only pH, chloride, sodium and potassium had homogeneous group variances. Variability for turbidity, sulfate, alkalinity and calcium became homogeneous on logarithmic transformation.

It was concluded that a large number of groups would be necessary before satisfactory homogeneity could be obtained throughout the data. No group differences of statistical significance were subsequently observed for any of the variables. Nevertheless, consistent increases from Group 1 to Group 3 for pH, chloride, sodium, turbidity and the minor ions were apparent. In addition, sulfate means and maximum concentrations were lower for Groups 2 and 3 compared to the corresponding Group 1 values.

3.3.4 Multidimensional Scaling

Given the high level of heterogeneity in the data, it was appropriate to use an ordination method to help elucidate any patterns. Three separate analyses were performed using multidimensional scaling on Euclidean distance matrices. The first involved all the chemical parameters; the second and third were conducted after removing all parameters except the major ions (i.e. chloride, sulfate, (bi-)carbonate, sodium, potassium, calcium and magnesium) and turbidity, colour and minor ions (i.e. ortho-phosphate, nitrate, ammonia, lead, zinc, copper), respectively. The corresponding final configuration stresses were 0.117, 0.099 and 0.068, each indicating a satisfactory 'goodness of fit' (see section 2.8). Figures 11, 12 and 13 show the respective ordinations. In these diagrams, sample to sample dissimilarity is represented by the distance between the points. Hence, within-group variability can be assessed from the spread of points.

Figure 11 shows a gradation in the spread of points from Group 1 to Group 3 sites, with Group 3 being the most variable in the ordination (i.e. yielding the greatest spread). Note also the difference in direction (i.e. upwards and to the left) that the scatter takes for the Group 3 sites, indicating a further subtle difference compared with the other two groups. Group 2 sites are intermediate in spread.

A clear gradation is not apparent in Figure 12, indicating almost equal variability in major ion chemistry for the sample groups. If the three Group 1 outliers (Figure 12a) are

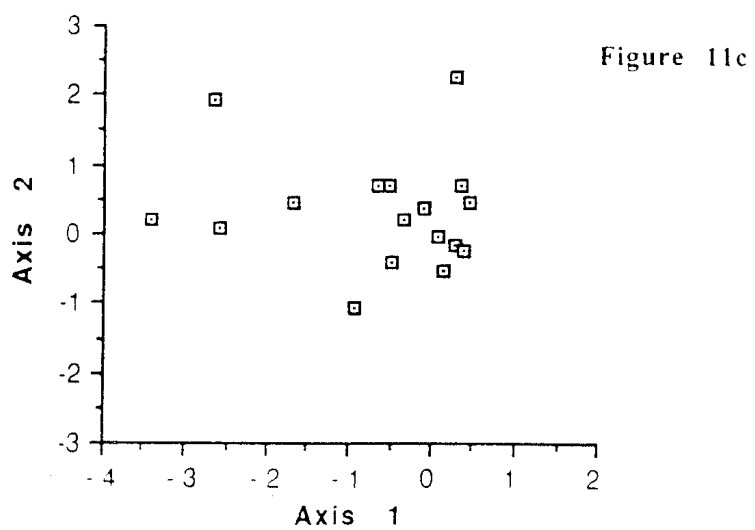
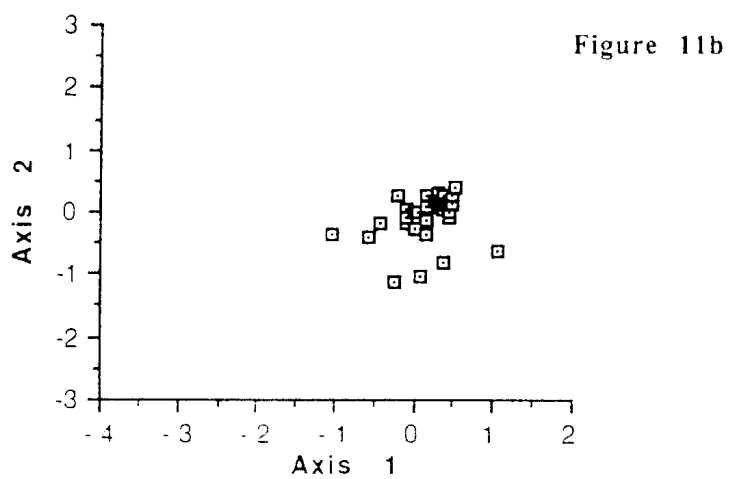
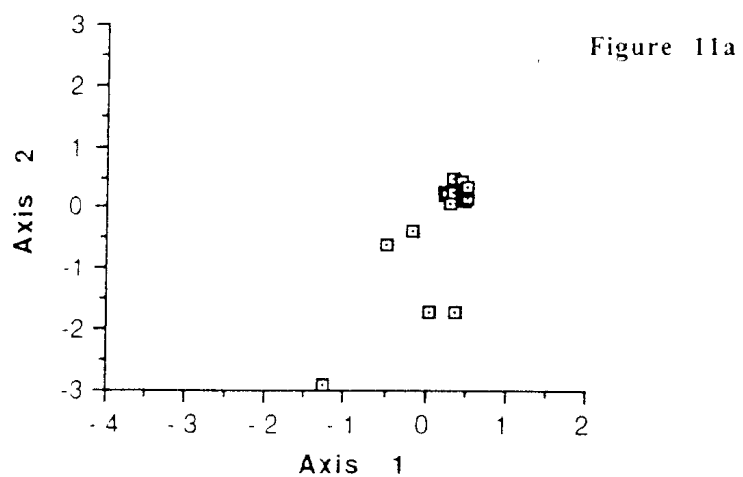


Figure 11. Multidimensional scaling ordination using all chemical parameters. a. Group 1 sites. b. Group 2 sites. c. Group 3 sites.

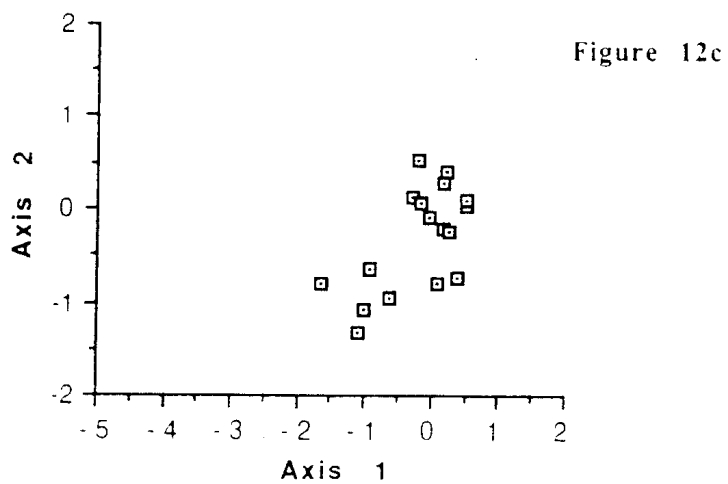
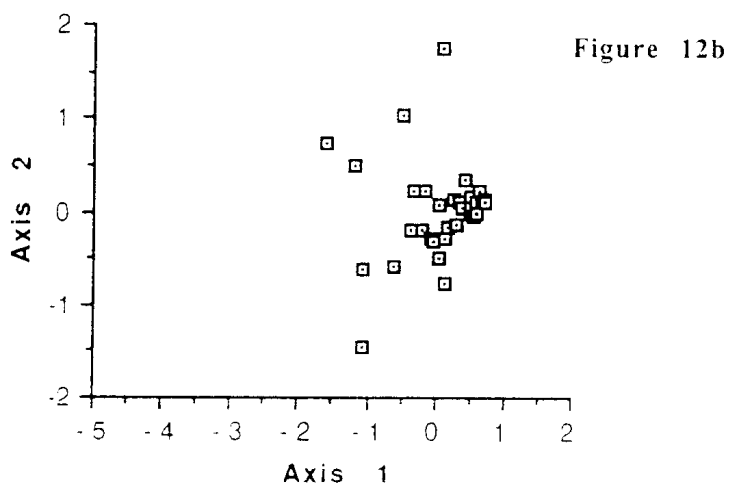
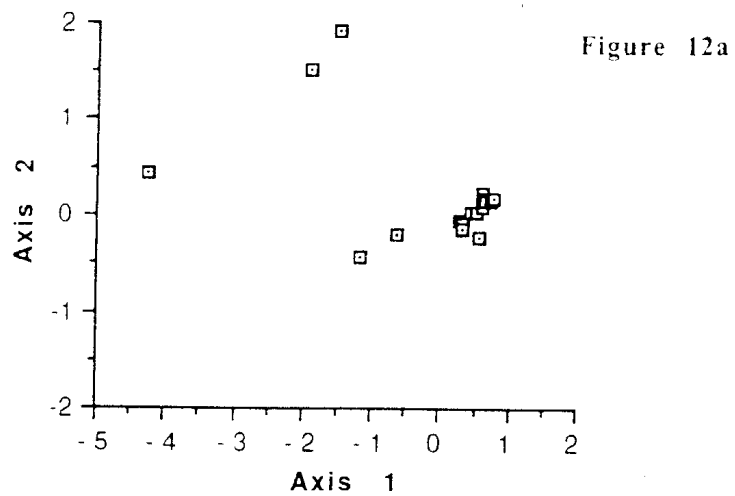


Figure 12. Multidimensional scaling ordination using the major ions. a. Group 1 sites. b. Group 2 sites. c. Group 3 sites.

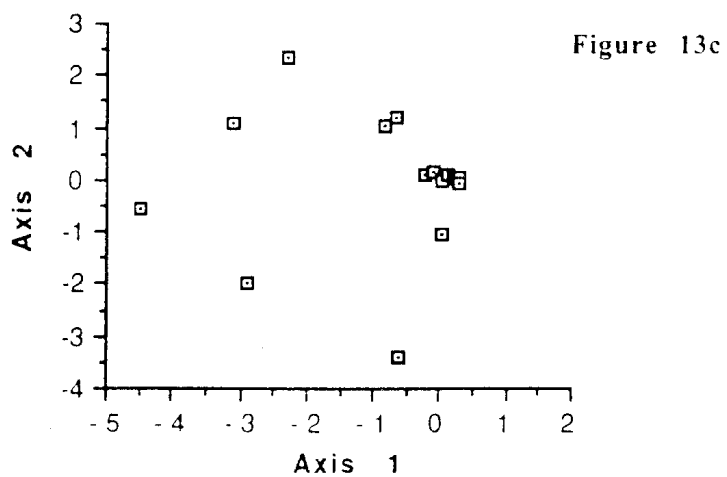
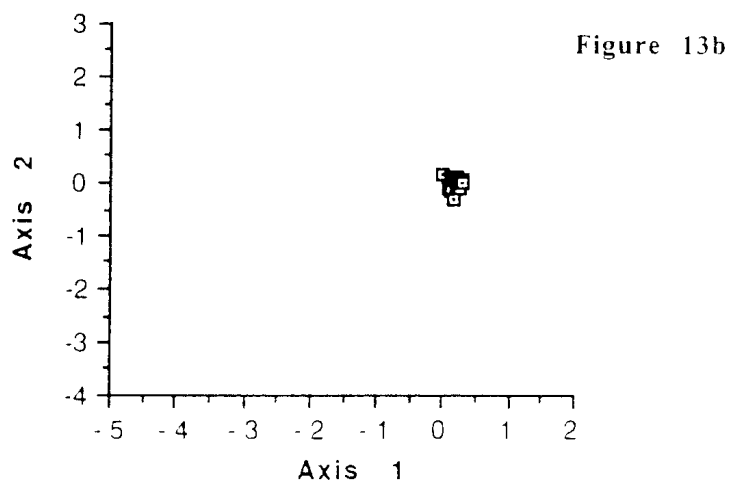
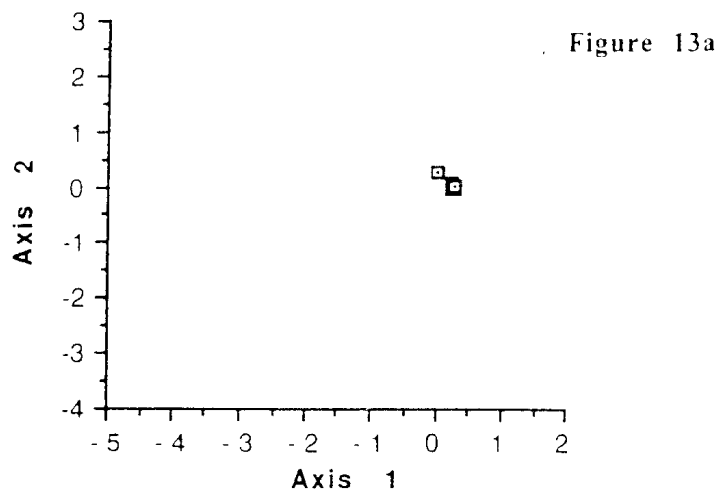


Figure 13. Multidimensional scaling ordination using the minor ions + turbidity and colour.
 a. Group 1 sites. b. Group 2 sites. c. Group 3 sites.

ignored, the sites of Group 2 generally show the most variability. This was consistent with the factors leading to the corresponding sub-groupings in the TWINSPAN dendrogram.

Figure 13 illustrates a difference in variability within the three groups. Groups 1 and 2 both show little separation. In comparison, Group 3 sites show relatively large variability in the minor ion concentrations.

3.3.5 Group 4 Samples

Group 4 included a number of samples (3, 30, 66, 87, 88, 89) which were clearly contaminated with marine water, being from or close to tidally-influenced reaches of the main rivers. Of the remaining samples, all but three were at very low altitude, within tidal zones of the Hawkesbury and/or Georges Rivers and potentially subject to tidal influence from time to time (i.e. 18, 31, 82, 83, 84, 90). These were excluded on the basis of high chloride or sodium levels; there is no firm evidence from this study on which to eliminate the possibility of marine contamination in these cases. Samples 51 (Capertee River), 56 (Capertee River) and 72 (Bullio Creek) were eliminated because of high sulfate, sulfate, and chloride, respectively. Samples 51 and 56 may have been contaminated by coal mine drainage. Sample 72 would otherwise have fallen into Group 1.

3.3.6 Effects of Stream Flow

Regression analysis (Table 6) on ungrouped data found that only turbidity and colour were significantly affected by water velocity. In both cases the coefficients were negative values.

Table 6. Parameters that showed significant regressions with water velocity.

Un-grouped Data (n=69)			Grouped Data			
Variable	Regression r ² value	Regression p value	Variable	TWINSPAN group	Regression r ² value	Regression p value
turbidity	0.055	0.029	pH	3	0.201	0.040
colour	0.049	0.038	colour	1	0.244	0.010
			sulfate	3	0.466	0.002
			alkalinity	3	0.257	0.022
			calcium	3	0.384	0.005

Note : r² is the adjusted squared multiple r value

When assessed group-wise, water velocity was seen to have an influence on pH, sulfate, alkalinity and calcium of Group 3 sites (positive coefficients) and colour of Group 1 sites (again a negative coefficient). Apart from these effects, discharge was found to have no significant influence on water chemistry.

3.4 Discussion

The low salinity of the majority of samples, coupled with equally low alkalinities (a maximum value of $54 \text{ mg CaCO}_3 \text{ L}^{-1}$), suggests Sydney Basin waters can be classified as not only very fresh, but also 'soft'. Taking into account the wide pH range observed, a generally low buffering capacity can be inferred.

A sodium and chloride dominance with a strong correlation between concentrations (Spearman correlation coefficient = 0.955; $p \leq 0.0005$) was observed for the fresh waters, highlighting the likely common origin of these ions (e.g. sea salt aerosols; Buckney, 1980) and high sandstone content of the basin, hence low weathering rate of underlying bedrock minerals (Reinson, 1976). This is best illustrated by Figure 14 which includes the omitted 15 'saline' samples for comparison. The sodium and chloride dominance was greatest in these Group 4 samples, as expected. The substantial contributions by sulfate in certain samples of this group (e.g. sites 51 and 56) are masked in this figure.

The high relative percentage for (bi-)carbonate in Group 1 was interesting, given that the alkalinity was lower than in the other two groups. Since this group also had the lowest sodium and chloride levels, these sites represented the freshest of the Sydney waters.

Figure 14 also indicated Sydney's fresh waters are relatively higher and much less variable in magnesium proportion compared to calcium. This was verified by analysis of variance of these relative percentages between the four groups ($p=0.475$ for Mg; $p=0.004$ for Ca).

By grouping the 75 sites on the basis of catchment geology, Figure 15 shows that a shift to calcium/magnesium and carbonate dominance, or at least co-dominance, occurred where no (or little) sandstone rock was present. This was most apparent in the areas where geology was principally composed of igneous/metamorphic formations.

The differences in chemistry for Group 1 can only be explained by differences in geological influences. These sites, most of which were located in undisturbed environments, showed a range of different substrate geologies and high variability in

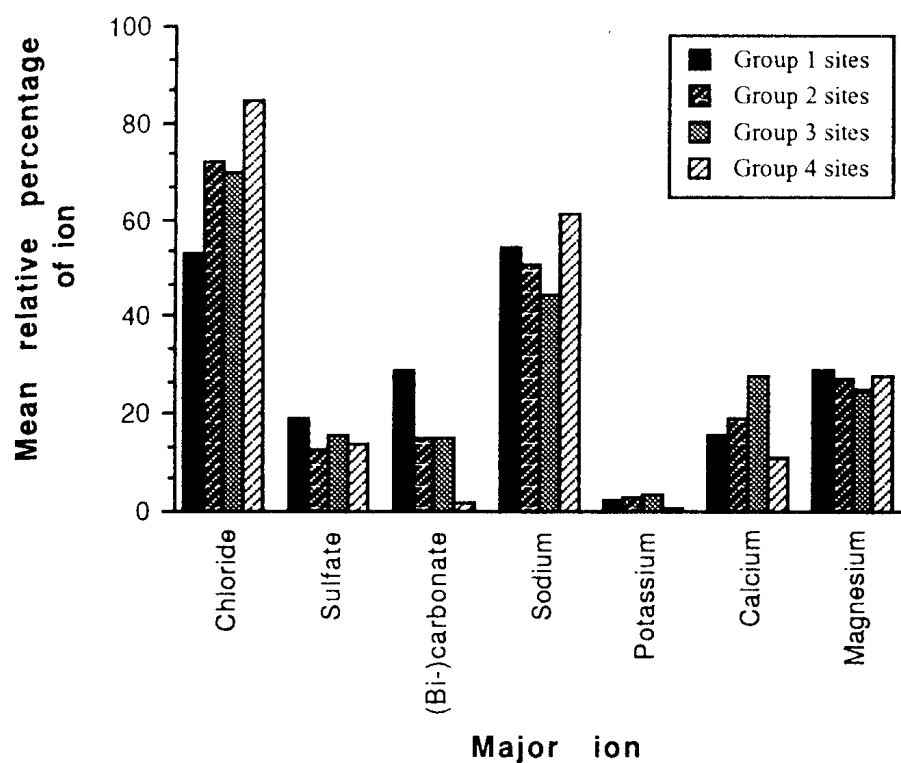


Figure 14. Major ion mean relative percentages for the four sample groups.

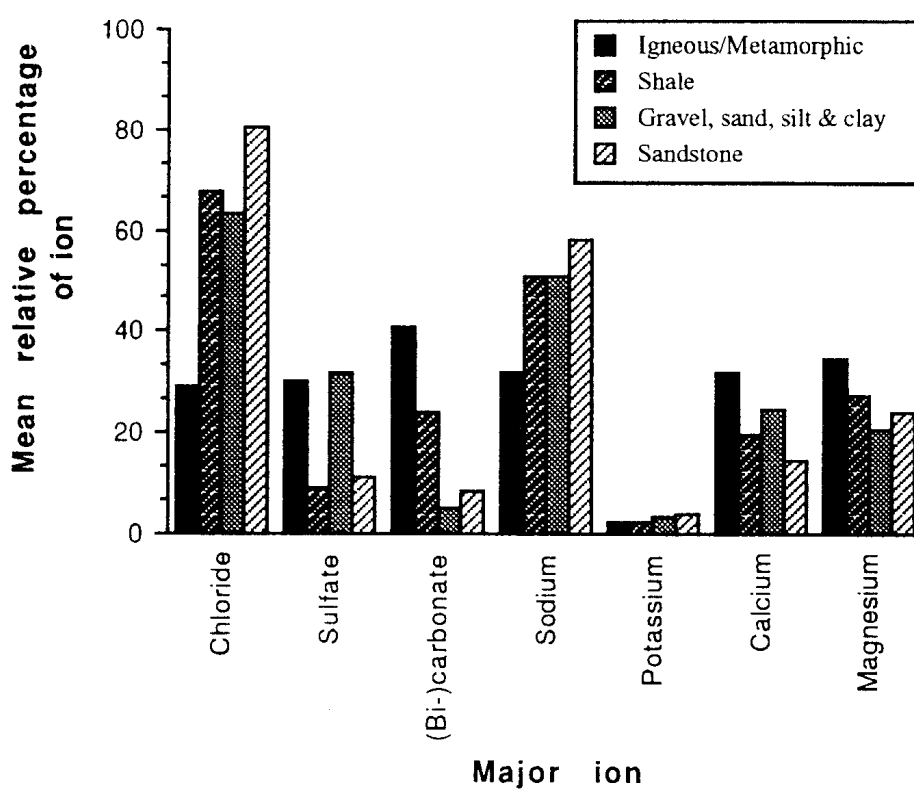


Figure 15. Major ion mean relative percentages for the 75 sites, as grouped by the principal basin geologies.

major ion chemistry, compared with the minor ion chemistry. Group 3 sites, on the other hand, showed greatest variability in minor ion chemistry.

As extreme values for metal and nutrient concentrations were not frequent in the data, severe contamination appears to be generated from occasional or localised pollution. Since the sites of Group 3 were mainly in developed catchments, it was concluded that modifications to freshwater chemistry arising from urban and rural influences have overridden other influences. Streams in such catchments have notable non-uniformity in their chemistries, particularly for the minor constituents.

Group 2 sites, found primarily on the interface dividing natural and developed catchments, represented those samples having less extreme modifications. In terms of the major ions, variability was still high, as should be expected. Enrichment in nutrients, metals, turbidity and colour, while not creating marked between-sample variability, was nevertheless noticeable. It was significant that this was the largest of the three groups and with increasing levels of urban/rural activity the water quality of such sites would be the first to deteriorate and reflect the characteristics of Group 3 samples.

Ayers and Gillett (1984) and Ayers *et al.* (1987) have reported on the composition of rainwater for Sydney. Despite considerable between-sample variability, samples were quite acidic, the typical annual average pH being about 4.6. Sulfuric acid (generated from SO₂ emissions) contributed about twice as much to the acidity as nitric acid (from NO_x emissions); hence relatively high levels of sulfate were seen as well. Some stationary source HCl emissions also contributed to the low pH, in addition to providing further chloride, the dominant anion. The acidity was partially balanced by certain neutralising agents, which were mainly gaseous ammonia and calcareous aerosols.

Despite the obvious influence on receiving water composition (and quality), rainwater is unlikely to be the main cause of major ion differences between streams, since gas and aerosol dispersion in the atmosphere would ensure that a wide range of streams are subjected to similar inputs. Hence, between-site variability in major ion chemistry should be more heavily influenced by catchment geology.

The relative influence of rain water composition and catchment lithology on surface waters of eastern Australia has been investigated previously (Reinson, 1976; Douglas, 1968). Douglas (1968) compared river water samples from tropical catchments in north-east Queensland with samples from catchments in the central and southern tablelands and highlands of New South Wales. It was concluded that atmospheric salts heavily influenced the composition of dilute waters, although catchment lithology was the more

dominant force of the two overall. Reinson (1976) found that precipitation was particularly important in the chemistry of stream waters of the Genoa River basin and expected this to hold for stream waters of eastern Australia in general. Furthermore, in areas of high chemical weathering, the chemistry of this basin would be controlled by a mixture of atmospheric and rock-weathered salts (i.e. a chloride - (bi-)carbonate mixture), while in cases of low weathering rate, the atmospheric inputs of sodium chloride would predominate.

The chemical characteristics of the Group 1 samples, and also the Group 2 samples, were consistent with these generalisations. Nevertheless, the chemistries of the majority of the Sydney basin streams would also appear to be subjected to an additional factor - namely catchment land use. The intensive human development which has taken place in this coastal zone has led to a significant increase in the loading of sediment, nutrients and contaminants from point and non-point sources. Being a region of higher population density, compared with rural activity, the local urban/industrial loadings have been especially important (Gabric and Bell, 1993). At the same time, given that nutrient loads in discharges from cropped lands are usually an order of magnitude greater than those from undeveloped forested areas (Gabric and Bell, 1993), the influence of rural activity cannot be underestimated in many cases.

Hence, a number of findings with respect to the general chemical composition of inland freshwater streams arise from this study. Streams situated in purely urban and rural catchments predominantly show poor water quality with higher levels of metals, nutrients, turbidity and colour compared to other waters. Increased salinity and pH could also be expected. In contrast, waterways surrounded by the original natural vegetation will predominantly show lower levels of all such constituents and good water quality. Those systems lying on the bush-developed interface should portray intermediate characteristics, reflecting their transitional status.

Chemical variability in streams from undeveloped catchments can be ascribed to catchment geology and concerns the major ions, especially (bi-)carbonate, sulfate and calcium. Variability in major ion composition can still be detected in streams from developed catchments, but it is less clear if this variability is due to geology alone. What more readily distinguishes these sites is extreme variation in the concentrations of trace constituents (i.e. those normally regarded as contaminants), along with increased pH and salinity.

Thus, in relative terms the influence of catchment land use is greater than that of geology for streams in the Sydney basin. This is no surprise considering the region is the most

intensely developed of any metropolitan area of Australia. To fully assess the influence of geology on stream chemistry, it is best to focus on sites that are unaffected by human developments.

While both phosphorus and nitrogen increased in concentration from bush to urban and rural sites, total phosphorus was high throughout, very often greater than the recommended guidelines of ANZECC (1992) and the New South Wales SPCC (1990), provided in Table 7. However, dissolved ortho-phosphate levels were invariably low, although these levels may have been influenced, at least partly, by algal uptake and metabolism, since the time lag between sampling and freezer storage was up to 2 days in length. Of the 75 samples, fourteen had some detectable phosphate and of these, nine and three were, respectively, in excess of the ANZECC (1992) lower ($10 \mu\text{g L}^{-1}$) and upper ($100 \mu\text{g L}^{-1}$) limits to control algal blooms.

Nitrogen levels were also elevated but generally less so than phosphorus. Again the total measurement is an underestimate since only dissolved nitrate plus ammonia are included. For the 75 samples, 36 were in excess of the ANZECC (1992) lower limit ($100 \mu\text{g L}^{-1}$) and of these, 12 samples were in excess of the corresponding upper limit ($750 \mu\text{g L}^{-1}$). The inference that Sydney fresh waters contain high concentrations of nutrients is also consistent with earlier work of Williams and Wan (1972) who found such conditions (e.g. phosphate phosphorus) to be a characteristic of many Australian inland waters.

It is known that any essential factor (e.g. P, N and other micronutrients) may become limiting for primary production in aquatic systems (Gabric and Bell, 1993), although phosphorus is the most common (Syers *et al.*, 1973). Since primary producers most readily assimilate dissolved inorganic forms of phosphorus and nitrogen (Gabric and Bell, 1993), and assuming that an N/P atomic ratio of <16 indicates nitrogen limitation (Triska *et al.*, 1993), the data suggested that nitrogen may be a limiting nutrient for primary production in some of these water systems from time to time (e.g. sites 7, 8, 22, 27, 58, 59, 84, 88 and 89).

Table 8 lists the proportion of each of the three principal TWINSpan groups which exceed, or fail to lie within the limits of, the ANZECC (1992) water quality criteria in Table 7. Although the group-sizes are unequal, general trends can be depicted.

Highest proportions were seen with Group 3 for all parameters other than pH, illustrating the generally poorer quality of these waters. Group 2 was intermediate, as expected. Group 1 samples satisfied each criterion except pH, a surprisingly high percentage falling outside the acceptable range, usually in the acidic region. This result, given the low

Table 7. Relevant water quality criteria for protection of freshwater ecosystems.

Indicator	ANZECC	NSW SPCC Level 1	NSW SPCC Level 2
pH	6.5 - 9.0	6.5 - 8.5 (should not fluctuate > 2.0 units)	6.0 - 9.0 (should not fluctuate > 2.0 units)
salinity	< 1000 mg L ⁻¹ (about 1500 μ S cm ⁻¹)	should not vary by > 2% from the background limits of variation	should not vary by > 10% from the background limits of variation
DO	> 6 mg L ⁻¹	> 6 mg L ⁻¹ (unless lower levels are natural)	> 4 mg L ⁻¹ (unless natural variations occur)
turbidity	< 10% change in seasonal mean concentration	combined effects of turbidity and colour should not reduce the depth of the compensation point for photosynthetic activity by > 10% from seasonal background value	combined effects of turbidity and colour should not reduce the depth of the compensation point for photosynthetic activity by > 50%
colour	< 10-20% change in euphotic depth		
alkalinity		should not be under 25% of background levels	should not decrease below 25% of background levels
total P	10-100 μ g L ⁻¹	0.02 mg L ⁻¹	0.05 mg L ⁻¹
total N	100-750 μ g L ⁻¹	0.2 mg L ⁻¹	0.5 mg L ⁻¹
	Suggested range dependent on water hardness	Heavy metal limits at 50, 100, 200 mg L ⁻¹ CaCO ₃ hardness	Heavy metal limits at 50, 100, 200 mg L ⁻¹ CaCO ₃ hardness
lead acute criterion chronic criterion	1.0-5.0 μ g L ⁻¹	34, 82, 200 μ g L ⁻¹ 1.3, 3.2, 7.7 μ g L ⁻¹	as per Level 1 "
zinc acute criterion chronic criterion	5.0-50.0 μ g L ⁻¹	65, 120, 210 μ g L ⁻¹ 50, 110, 190 μ g L ⁻¹	as per Level 1 "
copper acute criterion chronic criterion	2.0-5.0 μ g L ⁻¹	9.2, 18, 34 μ g L ⁻¹ 6.5, 12, 21 μ g L ⁻¹	as per Level 1 "
cadmium acute criterion chronic criterion	0.2-2.0 μ g L ⁻¹	1.8, 3.9, 8.6 μ g L ⁻¹ 0.66, 1.1, 2.0 μ g L ⁻¹	as per Level 1 "

Note :

- (1) Level 1 protection concerns maintenance of pristine aquatic ecosystems not subject to human interference
- (2) Level 2 protection concerns maintenance of modified aquatic ecosystems subject to human interference
- (3) NSW SPCC heavy metal limits represent the one-hour average which should not be exceeded more than once every three years on average

(ANZECC, 1992; NSW SPCC, 1990)

Table 8. Sample percentage for each primary TWINSpan group exceeding ANZECC (1992) quality criteria limits.

Indicator (Assumed range / limit for group comparison)	Group 1	Group 2	Group 3
pH (6.5 - 9.0)	39	29	18
Nutrients			
ortho-Phosphate (10 $\mu\text{gPO}_4^{3-}\text{-P L}^{-1}$)	0	9	35
(100 $\mu\text{gPO}_4^{3-}\text{-P L}^{-1}$)	0	3	12
Nitrogen as $(\text{NH}_3 + \text{NO}_3^-)\text{-N}$ (100 $\mu\text{gN L}^{-1}$)	13	54	82
(750 $\mu\text{gN L}^{-1}$)	4	6	53
Heavy Metals (hardness dependent)			
Lead (1.0 $\mu\text{g L}^{-1}$)	0	0	35
(5.0 $\mu\text{g L}^{-1}$)	0	0	18
Zinc (5.0 $\mu\text{g L}^{-1}$)	0	0	24
(50 $\mu\text{g L}^{-1}$)	0	0	6
Copper (2.0 $\mu\text{g L}^{-1}$)	0	6	59
(5.0 $\mu\text{g L}^{-1}$)	0	0	29

alkalinity values, provided further evidence that basin fresh waters have low buffering capacity.

Generally low stream flow conditions were observed throughout the sampling period, as a consequence of low rainfall - compare Figure 16, the average monthly totals for 1860 to 1990 inclusive, with Figure 17, the actual monthly totals for 1990. Data for 1990 indicated the sampling period was drier than normal, October and November having had less than half the average rainfall. This predominance of low water velocities probably accounts for the inconclusive results obtained from the statistical analyses (i.e. regression) described in Section 3.3.6.

Hence, such conditions were not favourable for assessment of the influence that water velocity and discharge may have on the surface water chemistry of Sydney streams. The samples therefore represented low-flow conditions, un- or minimally contaminated by surface runoff and experiencing high sedimentation rates.

Parts of the study area (approximately one-third) showed very high water quality, close to the expected pristine conditions prior to human settlement of the basin. Such samples were principally from non-developed catchments. However, the majority of samples (approximately two-thirds) indicated a number of modifications, including higher concentrations of heavy metals, nutrients, turbidity and colour, as well as increased salinity and pH. Catchment developments, whether they be urbanisation or ruralisation, correlated well with these modifications which override the mechanisms governing normal chemical variability.

Obviously the growth of the metropolitan area has had a significant influence on stream water chemistry - the basin geology and geography thus providing constraints for land development around Sydney, now recognisable in its stream water chemistry. If the rapid expansion continues, as has been the trend over the last few decades, then the number of clean, or higher quality, fresh waters must be expected to decline further.

Biological water quality may be expected to parallel physico-chemical quality, but a similar survey is needed for confirmation of this for the Sydney basin. True water quality can only be completely defined by a description which incorporates the chemical, physical and biological states of a system. Further monitoring work should also consider the value of including surficial sediments, since this medium should be both less temporally variable and active in regulating the chemistry of the water above.

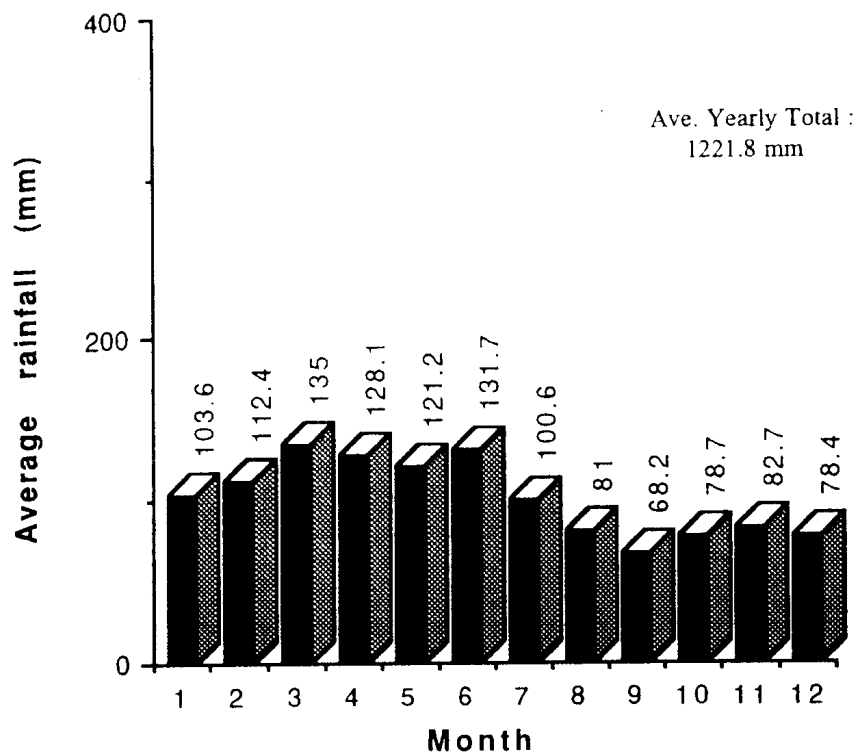


Figure 16. Average monthly rainfall for Sydney (1860-1990), as measured from Observatory Hill.

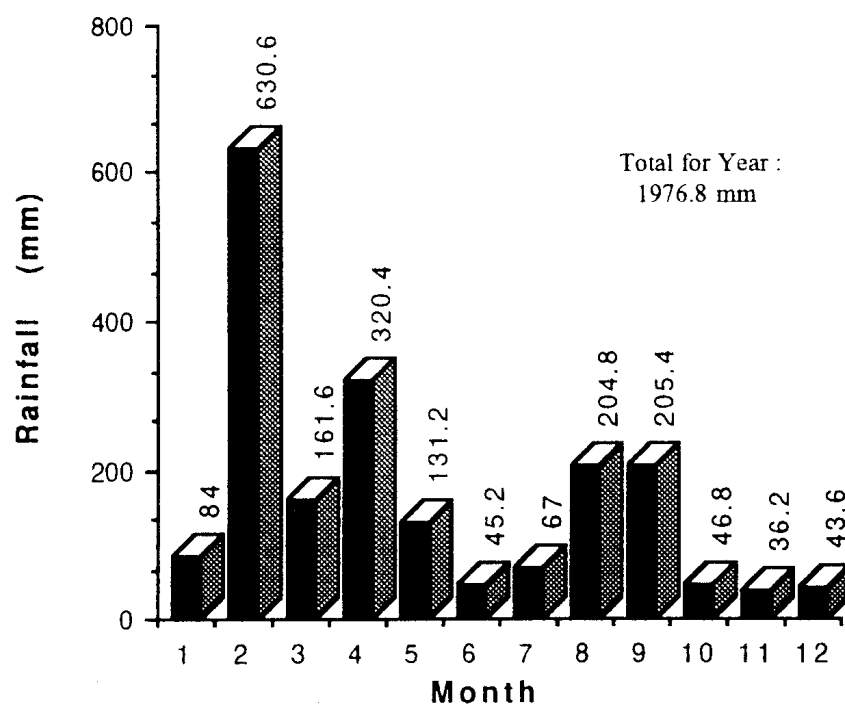


Figure 17. Monthly rainfall for Sydney during 1990, as measured from Observatory Hill.

(All data courtesy of The NSW Bureau of Meteorology, Sydney)

It is not possible, from this study, to determine how much of the between-sample variability can be attributed to temporal variation in water chemistry. Since flows remained low throughout the sampling period, temporal variation was probably very small. The following chapter examines temporal variability in three streams.

As many of the common pollutants (i.e. heavy metals, phosphorus, pesticides, organic matter) show strong associations with particulate matter, the surficial sediment of a water system becomes an important factor whereby the composition of the surface water is expected to be regulated or controlled by the sediment chemistry (Ellis, 1976; Oschwald, 1972). This issue is also addressed in the next chapter.

3.5 Conclusions

This survey developed a general chemical description for freshwater streams of the Sydney basin during low flows. The stream samples were characterised by :

- (1) low salinity, hardness and buffering capacity
- (2) sodium chloride dominance with a strong correlation between their concentrations
- (3) high total phosphorus and nitrogen concentrations
- (4) variability in major ion chemistry, due to catchment geology, in undeveloped areas.

In comparison with the Group 1 (undeveloped) samples, there were modifications in the chemical nature of samples from the urbanised streams, including :

- increased salinity, mostly from higher sodium and chloride levels
- lower sulfate
- higher pH
- higher concentrations of nutrients and heavy metals
- higher levels of turbidity and colour
- greater spatial variability in chemical composition, particularly with respect to the minor constituents.

These chemical modifications were associated with urban or rural development and have overridden other natural mechanisms.

Such features were also responsible for the increased incidence of poor water quality amongst those streams in developed areas. The greatest concerns about water quality arose with respect to nutrients and heavy metals, which are strongly associated with sediments (Hart and McKelvie, 1986; Hart, 1982). Since it has been claimed that the sediments are often the best medium for monitoring contaminants in aquatic systems (Chapman, 1992; Larsen and Jensen, 1989), it is thus important to assess the chemistry of this medium through a suitable study. In the next chapter this question is addressed.

4 THE ROLE OF SEDIMENTS IN SOME SMALL STREAMS

4.1 Summary

A short-term monitoring study of three Hawkesbury Sandstone freshwater streams is described. Two streams receive urban contaminants, one (the reference creek) has an undeveloped catchment. Sampling of surface waters, interstitial waters and sediments was performed at irregular intervals over a period of two years at three separate stations within each site. This regime sampled the major sources of chemical variability (monthly/seasonal). A total of 69 different physico-chemical parameters were measured.

The streams predominantly existed under low flow conditions ($<31.3 \text{ cm s}^{-1}$) during the study. Surface waters were low in salinity ($<200 \text{ mg L}^{-1}$), soft ($<100 \text{ mg L}^{-1}$ as CaCO_3) and of generally poor buffering capacity. Sodium and chloride dominance and correlation between these was observed, although high levels of calcium and total carbonate (up to co-dominant proportions) were apparent in the urbanised sites. Heavy metal and nutrient concentrations were also generally higher at these sites.

Runoff generated by a heavy storm created flood flows in all three streams. High levels of nutrients, suspended solids and colour were detected in surface waters during peak-flow, as well as alkaline pH, oxidising redox, and reduced conductivity, alkalinity and hardness. Changes in relative proportions of various constituents also occurred. Such distinctive chemistry was not observed in the remaining surface water samples, suggesting that extreme flows are needed to significantly change the composition.

Sediments were characterised by very low organic matter ($<2\%$) and poor cation exchange capacity ($<3 \text{ mmolNa/100g}$), due to high coarse + fine sand content ($>95\%$). Despite low accumulation of heavy metals and phosphorus in the long term, sediments were nevertheless a sink for these constituents.

Speciation studies identified that the sums of the secondary phase lead were over nine times that of the corresponding residual, while for zinc and copper the equivalent sums were four and two times larger, respectively. The lead contamination was probably derived from the emissions of automobiles. Greatest proportions of zinc and lead were associated with coatings of iron and manganese oxides, or coarse waste particles. This preference indicated that water quality would be particularly vulnerable to decreases in pH and oxidation-reduction potential. Apart from a substantial residual component, copper was preferentially associated with organic matter. Cadmium was rarely detected in any stream.

Poor water and sediment quality were often observed in samples from the two urban sites. Nevertheless, the streams were not grossly polluted as such conditions did not occur continuously. This natural resilience suggested that Hawkesbury Sandstone streams should be prioritised for management, being more likely to respond to remedial measures than streams in different geological environments.

Poor water quality was also seen on occasion in the reference creek. However, since poor sediment quality was not detected and interstitial waters for all sites displayed considerable within-site variability, surface waters were regarded as the most reliable indicator of stream condition for short stream lengths.

Concentration gradients between interstitial and surface waters were rare and surface water loads are believed to be more influenced by external inputs, rather than sediment fluxes, in these streams. Any release of heavy metals and phosphorus from sediments to the overlying water column should only occur rapidly from the upper-most particulates.

Multidimensional scaling identified that under low flow conditions the three sites had distinct water and sediment chemistries. However, high levels of temporal and spatial variability were apparent within the urbanised sites, particularly in interstitial waters, and were heavily influenced by concentrations of heavy metals, phosphorus and suspended solids. This was consistent with urban waterways regularly receiving discharges of diverse composition and supported a picture of non-seasonal fluctuation in chemistry. Seasonal differences were detected, but only in terms of the level of variability between summer and winter samples. During the winter seasons the chemistries of surface waters and sediments were more variable than in summer.

4.2 Introduction

4.2.1 Objectives

The need for information regarding the distribution and cycling of chemical compounds between the principal compartments of inland waters has already been highlighted. Most emphasis to date has been placed on the study of large systems (i.e. lakes and rivers) with little attention having been given to small streams. In terms of water quality management, there is great value in investigating and protecting such streams since most are tributaries to larger waterbodies.

This study attempted to address these deficiencies and had two principal aims. The first was to examine the influence of sediments on the water chemistry of certain Sydney streams lying on Hawkesbury Sandstone. The second was to characterise, or describe, any patterns of natural chemical variability occurring in the streams, paying particular

respect to heavy metals and phosphorus - these being principal contaminants found in urban runoff and strongly associated with the particulate fraction.

The objectives were encompassed by a series of specific questions, to be answered in relation to Hawkesbury Sandstone streams. These questions were as follows :

- (1) How do surface waters, interstitial waters and sediments differ between urbanised and undisturbed streams ?
- (2) How is surface water composition during low flow different to that at high flow in urban streams ?
- (3) What is the role of the sediment on stream chemistry ?
- (4) Do sediments and interstitial waters give a more reliable measure of stream quality than surface waters ?
- (5) What can be inferred about the exchange mechanisms whereby heavy metals and phosphorus are taken up or released by the sediment ?
- (6) What are the patterns of natural chemical variability for these Hawkesbury Sandstone-based streams, over time ?

Hawkesbury Sandstone streams were chosen for this study because of their frequency in the urbanised parts of Sydney, the close proximity on Hawkesbury Sandstone of both urbanised and undeveloped catchments and because their sediments are coarse and hence were expected to display different chemistry from that of the more-studied systems with high fines content.

4.2.2 Experimental Design

The experimental design involved *in situ* monitoring of three representative freshwater streams - all lying on Hawkesbury Sandstone - in the Sutherland shire of the Sydney basin (see Figure 5). Two of the streams were located in developed (urbanised) catchments, the third was situated in essentially undisturbed natural bushland. By monitoring these 'urbanised' streams, assessment of the effects of urban runoff was possible. One of the urbanised streams, Gwawley Creek, was sampled in the Sydney Basin survey (i.e. site 13) and was classed with the Group 3 replicates. The other two sites were expected to be examples of the remaining two groups defined in this survey.

Surface waters (12 samples), interstitial waters (9 samples) and surficial sediments (9 samples), from three stations at each of the three sites, were collected at random intervals over a two year period. These samples were analysed for a wide range of chemical and physical parameters. Various measurements (i.e. temperature, pH, conductivity, redox potential, dissolved oxygen, flow rate and discharge) were also made *in situ*, using appropriate field meters.

Sampling was somewhat stratified, since the selection of sampling days was not completely independent - each month of a year was to have some sort of sampling performed, in order to cover seasonal variability, while at least one storm event was to be captured. Furthermore, while there was replication of stations within each of the sites, there was limited replication on the basis of site-type (i.e. catchment geology). Hence, the conclusions from this study are relevant to Hawkesbury Sandstone-based freshwater streams, and by implication to similar streams elsewhere.

Field work was always carried out at the same time of day (mornings), hence, any diel patterns were ignored. However, hourly and daily fluctuations in water quality under low flow conditions were not expected to be as critical as seasonal and storm flow variabilities (Preston *et al.*, 1992; Mitchell and Furnas, 1992). The sampling therefore incorporated the major sources of chemical variability in these water systems, allowing for a more detailed chemical description than would be possible if diel variability was to be assessed.

According to the categories and principal characteristics of water quality assessment programs described by Chapman (1992), this field study would be classed as a combination of both impact and basic surveys. The duration of the investigation was relatively short (being approximately two years), while the number of sites (i.e. streams) and overall sampling frequency were not high. Instead the emphasis, or trade off, was based on analysing for a large but specific number of variables, to produce a comprehensive chemical description of the chosen freshwater streams.

Being descriptive, it attempted to identify different patterns of chemical variability between certain streams of the Sydney basin. The main advantage is that data were generated in the field under natural conditions. However, it was difficult to consider causality (e.g. stormwater runoff as the principal cause of poor water quality).

It is not possible to isolate causal factors in the field without replicated treatments - in this case, streams (Underwood, 1991). In the Sydney basin there are few non-urbanised

streams that are both sufficiently close to urbanised creeks and found on Hawkesbury Sandstone. In a macroinvertebrate survey of Sydney streams, R.P. Lim (unpublished data) identified only one such 'clean' stream, this being Bola Creek which is situated wholly within the southern reaches of the Royal National Park. However, this stream was considered not close enough to any urbanised catchment and is not convenient to sample.

This study proposes the chosen reference site to be a second non-disturbed stream, having the additional advantage of being in the vicinity of urbanisation. It was decided, therefore, to break down all sites into a triplicate of sub-sites, in order to satisfy experimental unit replication. By doing this the experiment then shared similarities with an asymmetrical design of replicated BACI (Before/After and Control/Impact) sampling (Underwood, 1992; Underwood, 1991).

4.2.3 The Study Sites

4.2.3.1 Characteristics of the Sutherland Shire

The Sutherland Shire of Sydney is predominantly a suburban region, extending along the southern parts of the Georges River from Cronulla to Como, down to the northern reaches of the Royal National Park and including Kirrawee to Port Hacking (see Figures 5, 18 and 19). Its geology is predominantly Hawkesbury Sandstone, capped in places with shale outcrops or pure sand (Benson and Howell, 1990). This has created a topography of steep hills and long narrow ridges with sandy soils tending to be shallow, acidic and infertile due to the high quartz sand content and very low levels of nutrients, particularly phosphorus (Benson and Howell, 1990).

Prior to european settlement this region was dominated by dry sclerophyllous vegetation, comprised of mostly Sandstone Heath/Woodland with smaller areas of Turpentine/Ironbark forests (Benson and Howell, 1990). Today only patches of the original vegetation remain and are concentrated along the more stable ridge-top sites. Subsequent invasion of weeds and exotic plants has been extensive, especially on the slopes and creek gullies, which although too steep to build on, have not necessarily been able to retain their indigenous species since they are more easily eroded and the most vulnerable to runoff and pollution (Benson and Howell, 1990).

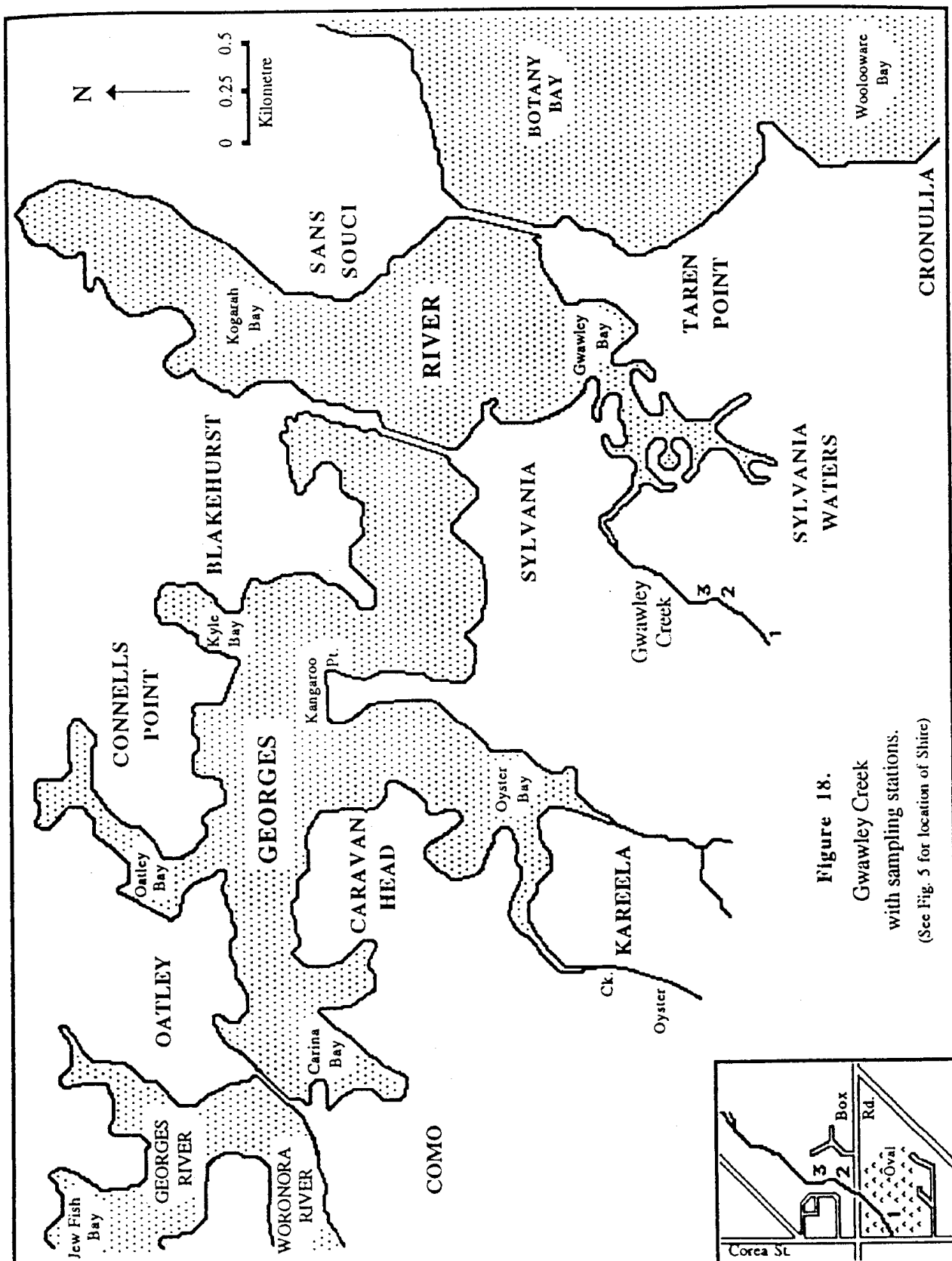
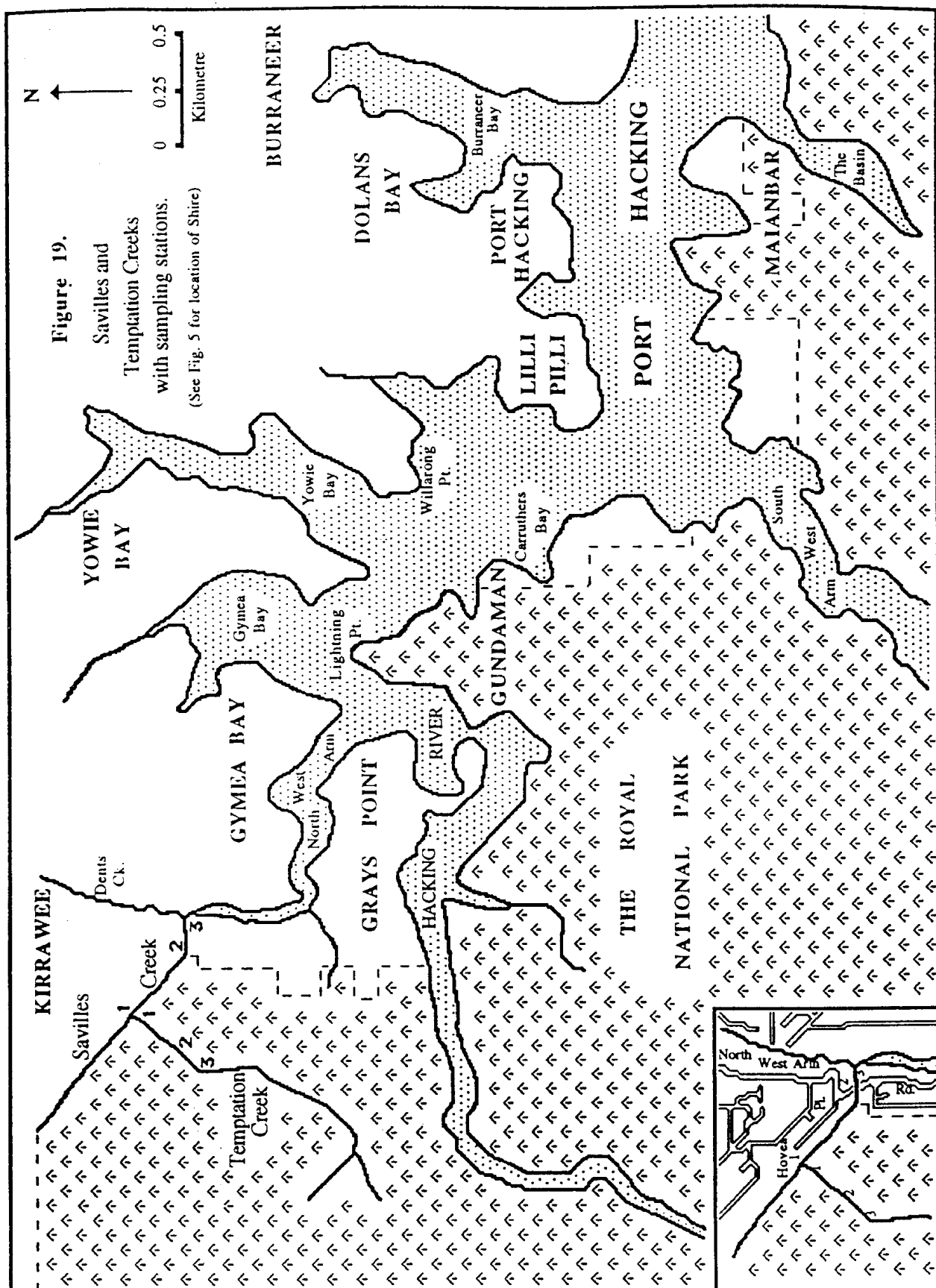


Figure 18.
Gwawley Creek
with sampling stations.
(See Fig. 5 for location of Shire)



4.2.3.2 Site Selection

The two urbanised sites were (Figures 18 and 19) :

- (1) Gwawley Creek, Sylvania Waters
- (2) Savilles Creek, Kirrawee/Gymea Bay

The third, non-urbanised, site was Temptation Creek in the upper north-western reaches of the Royal National Park, which, although joining Savilles Creek at the start of the second urban site, extends deep into the heart of the bush, rather than along the urban fringes (Figure 19).

All three sites were expected to have low levels of sediment organic matter, clays and other fine particles. Being flowing waters with coarse-grained beds of low absorptive capacity, it was therefore possible that sediment-water exchange processes may not necessarily be very important in these systems; but if they are, they would be controlled by the hydrous metal oxide fraction.

In addition, the creeks mainly receive anthropogenic constituents via non-point sources (particularly from the contributions in stormwater), rather than from any major point sources. As they are all first order streams, they were likely to show pollutant effects promptly and at the same time clear quickly. Furthermore, under most conditions there should be only minimal suspended particulate matter content. Hence, inputs can be more readily detectable since they should have higher concentrations in the dissolved fraction and be more sensitive to changes (Balls, 1989; Luoma, 1989). These properties could be exploited for water quality management.

4.2.3.3 Gwawley Creek

Gwawley Creek is a relatively short, first-order, freshwater stream situated in a residential catchment of Sylvania Waters (Figure 18). It begins as outlets of large stormwater pipes, running two to three kilometres before turning saline and draining into Gwawley Bay of the Georges River. For the first 200 metres the creek passes through sporting fields, but upon passing underneath a major road, it becomes lined with medium density housing for the remainder of its length.

The terrain of the district is classified as disturbed, landfill having been dumped prior to intensive human development (Chapman and Murphy, 1989). The creek gully slopes are

primarily sand and of high erosion hazard, while its sediments are usually of low depth (<50cm) and bare sandstone can be observed. The vegetation is mainly composed of weeds and non-native trees, becoming quite dense as the houses enclose around. Small drain pipes from individual houses empty at numerous points along the banks, while dumped rubbish and general litter are other characteristic features.

A section covering a few hundred metres of the creek was chosen for sampling. Three individual stations were selected as follows :

- (1) beginning of Gwawley Creek, close to large stormwater outlets
- (2) just below crossing of Box Road
- (3) end of chosen site, about 100m below station 2.

Refer to Plates 1-3 in Appendix 5 for station photographs. The catchment area of Gwawley Creek at the sample site is approximately 0.3km² and virtually 100% of this is urbanised.

4.2.3.4 Savilles and Temptation Creeks

Savilles and Temptation Creeks are located close to the upper boundary of the north-western reaches of the Royal National Park (Figure 19). Both originate as first-order streams until they meet.

Savilles Creek runs for a few kilometres along the residential-bushland interface at Kirrawee, in a short but steep gully. Upon approaching Gynea Bay, residential development lines both sides of the creek and it is then joined by Dents Creek, draining into the North West Arm bay of the Hacking River.

The creek thus lies primarily in a large urban bushland catchment. The bush is principally based on dry sclerophyll plant communities (of native xeromorphic species), although areas in closer proximity to the creek (e.g. the 'urban' slope) are dominated by invading weeds and other mesomorphic species, particularly downstream of the North West Arm Road.

The section selected as a sampling site involved approximately 300 metres of the creek length. The three sampling stations were as follows :

- (1) beginning of chosen site, below the end of Hovea Place
- (2) at North West Arm Road, below crossing
- (3) end of site, close to the meeting with Dents Creek.

Refer to Plates 4-6 in Appendix 5 for station photographs. The catchment area of Savilles Creek at the sample site is approximately 0.4km^2 and of this 50-60% is urbanised.

Temptation Creek arises in the same bushland catchment as Savilles Creek (Figure 19). The creek is basically protected from any urban influences since it cuts deep into the dry sclerophyll bush, rather than running along the urban-bushland fringe.

The substrate is again predominantly sandstone rock and sand. Being a relatively clean stream of similar substrate, it made for a suitable 'control' creek for reference purposes. Adjacent sampling stations were approximately 100 metres apart with sample station 1 being the furthest point downstream, located just above the junction with Savilles Creek.

Refer to Plates 7-9 in Appendix 5 for station photographs. The catchment area of Temptation Creek at the sample site is approximately 0.25km^2 and of this less than 5% is urbanised.

These sites have been selected in order to use a gradation of urbanisation, as measured by the percentage of development within each catchment. Gwawley Creek represents a highly developed area, Savilles Creek a moderately developed one and Temptation Creek is essentially undeveloped.

4.3 Results

Raw data for this field study are listed in Appendix 4, as tables A10 to A14.

Between the 21st of March, 1991 and the 17th of February, 1993, twelve surface water samples, nine interstitial waters and nine sediments were collected at each sampling station (see also Table 9). Missing data points are a consequence of contaminated or damaged samples and faulty meters. As the end points for both alkalinity and acidity titrations are not sharp, the values for samples with marked iron oxide (yellow-brown) colouration were also omitted.

'Sample collection 12' represented the chemistry of the three creeks at flood flow, or full bank load, caused by an intense thunderstorm during their sampling. Under such

Table 9. Sampling dates and rainfall data for the Sutherland Shire, as measured at Oatley.

Sample collection	Sampling dates	Season	Sites sampled	Time since previous rain (1)	Amount (mm) (1), (2)	Amount over week prior to sampling (mm) (1)	Average stream flow rate at time of sampling (cm/s) (3)
1	21/3/91	summer	GC	12 hours	0.2	0.2	4.4
1	4/5/91	winter	SC; TC	5 days	8.0	8.0	4.4 ; 4.4
2	6/5/91	winter	GC; SC; TC	0.5 hour	6.2	25.8	67.1 ; 24.3 ; 4.4
3	23/10/91	summer	GC; SC; TC	13 days	0.4	0	14.9 ; 4.4 ; 4.4
4	14/11/91	summer	GC; SC; TC	24 hours	0.2	0.2	23.9 ; 4.4 ; 4.4
5	16/12/91	summer	GC; SC; TC	24 hours	171.4	171.4	20.4 ; 44.0 ; 21.2
6	21/3/92	summer	SC; TC	14 days	5.6	0	4.4 ; 4.4
6	4/2/92	winter	GC	12 hours	1.0	51.6	4.4
7	5/2/92	winter	GC; TC	3 days	34.6	34.6	14.5 ; 14.0
7	5/7/92	winter	SC	0.5 hour	0.4	2.4	4.4
8	7/3/92	winter	GC; SC; TC	3 days	68.8	68.8	15.7 ; 4.4 ; 17.7
9	27/8/92	winter	GC	2 days	9.0	9.0	4.4
9	28/8/92	winter	SC; TC	0.5 hour	0.4	9.4	4.4 ; 4.4
10	9/10/92	winter	GC; SC; TC	24 hours	0.2	3.8	4.4 ; 4.4 ; 4.4
11	19/1/93	summer	GC; SC; TC	12 hours	5.8	5.8	4.4 ; 4.4 ; 4.4
12	17/2/93	summer	GC; SC; TC	0 hours	45.4	62.0	all flood flow

Note :

- (1) Rainfall data courtesy of the NSW Bureau of Meteorology
- (2) Column 6 indicates total precipitation for the previous rain event
- (3) Average stream flow rates are means of the three station estimates, assuming a value of 4.4 cm/s for a measurement that was below the detectable limit (see section 2.8)

conditions it was impossible to determine flow and discharge rates, or obtain interstitial water and sediment samples.

4.3.1 Stream Flow Rate

Data for water velocity and discharge can be found in the appendix table A10. Note that width and depth measurements were not taken if the water flow at that point was obviously nil, or rather, below the detectable limit - refer to Chapter 2.6.2.

On the basis of the twelve visits to each of the three sites, all creeks showed predominantly low surface flow conditions (i.e. $<31.3 \text{ cm s}^{-1}$ or Flow Group F1 - refer to section 2.8). For 108 individual estimations, 84 (approximately 78%) were low flow. Of the remaining high flow group (i.e. $>31.3 \text{ cm s}^{-1}$ or F2), on only fifteen occasions were flows greater than 50 cm s^{-1} , nine of these being the unmeasurable flood flow (full bank load) conditions of sample collection 12 during a thunder storm.

At Gwawley Creek 3 (GC3), six of the twelve measurements were Flow Group 2, the greatest incidence of higher flows for the nine stations. Nevertheless, water depth at this station was usually very low causing discharge not to be particularly substantial.

Climate information supplied by the NSW Bureau of Meteorology for the Oatley field station, approximately four kilometres from Sylvania (see Figure 18), provided a good indication of the rainfall prior to these samplings (Table 9). It appeared that to markedly raise the level of flow, a heavy storm ($>10 \text{ mm}$) was needed, although once rain (and hence runoff) ceased, flows rapidly returned to normal (i.e. low). For example, sample collection 2 (5/6/91) was begun some thirty minutes following showers which totalled 6.2 mm, yet Group 2 flows were only observed at Gwawley Creek, sample stations 2 and 3 (sampled first) and Savilles Creek (SC) 2. At Gwawley Creek 1, despite its location close to a stormwater drain, flow was not detectable, indicating the capacity of pools in urban creeks to absorb flow rate increases.

Up until 24 hours prior to the commencement of sample collection 5 (16/12/91), a total 171.4 mm of rain had fallen in the Sutherland area over a period of five days - 9.2 mm, 41.0 mm, 50.4 mm, 63.8 mm, 7.0 mm. Due to this large and continuous volume of water, Group 2 flow rates were observed at Gwawley Creek 2, Savilles Creek 1-3 and Temptation Creek (TC) 1. However, at the remaining stations, flows had already returned to normal.

4.3.2 Water Chemistry

The relevant raw data for the major water chemistry parameters (i.e. those monitored on each sampling) are displayed in the appendix tables A11(i)-(iii). Tables A12(i)-(iii) provide additional surface water chemistry (determined less frequently).

4.3.2.1 General Considerations : Surface Water Salinity

All three creeks showed salinity levels below the conservative criterion (200 mg L^{-1}) used in the Sydney streams survey. Low conductivity readings (i.e. $\leq 100 \text{ mS m}^{-1}$) were regularly observed, even in interstitial waters where constituents are usually more concentrated due to reduced dilution. Salinity for the surface waters of each site, determined by summing the average concentrations of the seven major ions, were approximately 97.4, 193 and 100 mg L^{-1} for Gwawley Creek, Savilles Creek and Temptation Creek respectively.

For surface water major ion chemistry of each site, matrices of Spearman correlation coefficients were determined and values significant at the 0.01 probability level can be identified in Table 10. The critical value of the Spearman rank correlation coefficient (r_s) was obtained from Zar (1984).

Strong sodium and chloride correlations were observed, as expected, while magnesium and chloride were also correlated with high significance. Subsequently so were magnesium and sodium. For the two urban creeks, calcium was correlated with all of the above three elements, but not at Temptation Creek. No significant correlation of a metal with total carbonate was seen, however, until the three data sets were pooled, upon which a significance for this anion with calcium was found ($r=0.583$; $n=36$), but not for magnesium.

Plots of the major ion mean relative percentages (i.e. site means), calculated both with and without the sample collection 12 (storm) values, are presented in Figure 20. The cationic and anionic orders of dominance were as follows :

Gwawley Ck.	$\text{Ca} > \text{Na} > \text{Mg} > \text{K} : \text{HCO}_3 + \text{CO}_3 > \text{Cl} > \text{SO}_4$
Savilles Ck.	$\text{Na} > \text{Ca} > \text{Mg} > \text{K} : \text{Cl} > \text{HCO}_3 + \text{CO}_3 = \text{SO}_4$
Temptation Ck.	$\text{Na} > \text{Mg} > \text{Ca} > \text{K} : \text{Cl} > \text{SO}_4 > \text{HCO}_3 + \text{CO}_3 .$

Table 10(i). Spearman correlation matrix for surface water major ion chemistry; pooled Gwawley Creek data.

	chloride	sulfate	carbonate	sodium	potassium	calcium	magnesium
chloride	1.000	0.933	0.310	0.886	0.713	0.881	0.855
sulfate		1.000	0.256	0.769	0.697	0.739	0.702
(bi-)carbonate			1.000	0.382	-0.263	0.351	0.369
sodium				1.000	0.708	0.967	0.945
potassium					1.000	0.698	0.650
calcium						1.000	0.919
magnesium							1.000

p<0.01; n=12 for all variables, hence rs=0.727; significant correlations in bold

Table 10(ii). Spearman correlation matrix for surface water major ion chemistry; pooled Savilles Creek data.

	chloride	sulfate	carbonate	sodium	potassium	calcium	magnesium
chloride	1.000	0.517	0.421	0.970	0.720	0.925	0.949
sulfate		1.000	0.814	0.494	0.524	0.511	0.571
(bi-)carbonate			1.000	0.392	0.168	0.508	0.548
sodium				1.000	0.718	0.939	0.968
potassium					1.000	0.694	0.662
calcium						1.000	0.958
magnesium							1.000

p<0.01; n=12 for all variables, hence rs=0.727; significant correlations in bold

Table 10(iii). Spearman correlation matrix for surface water major ion chemistry; pooled Temptation Creek data.

	chloride	sulfate	carbonate	sodium	potassium	calcium	magnesium
chloride	1.000	-0.581	-0.657	0.998	0.324	0.126	0.909
sulfate		1.000	0.545	-0.592	0.071	0.326	-0.357
(bi-)carbonate			1.000	-0.663	0.216	0.524	-0.553
sodium				1.000	0.318	0.123	0.902
potassium					1.000	0.804	0.285
calcium						1.000	0.209
magnesium							1.000

p<0.01; n=12 for all variables, hence rs=0.727; significant correlations in bold

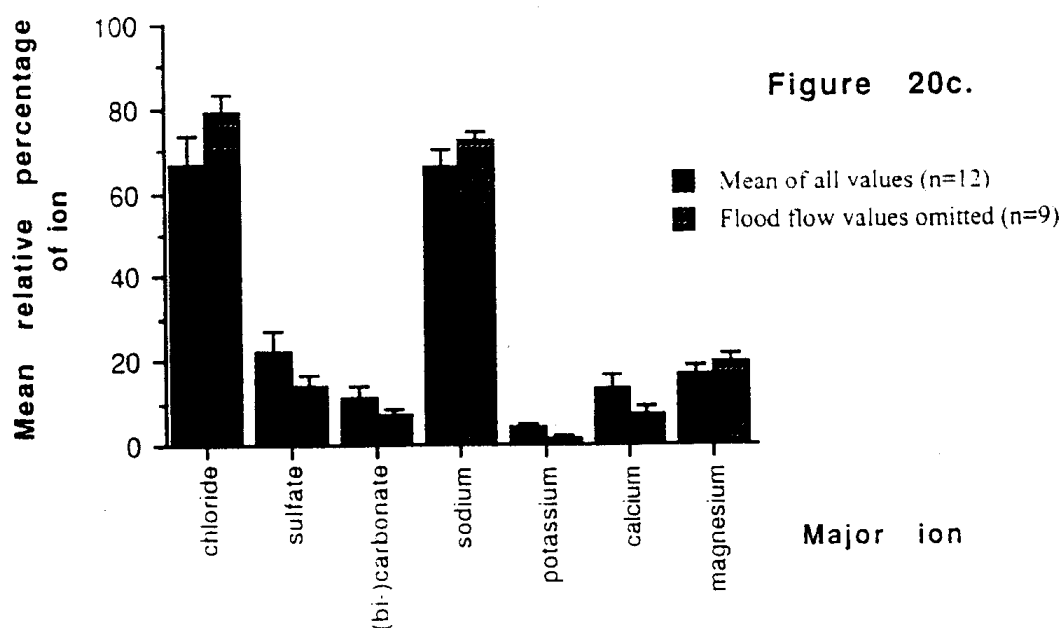
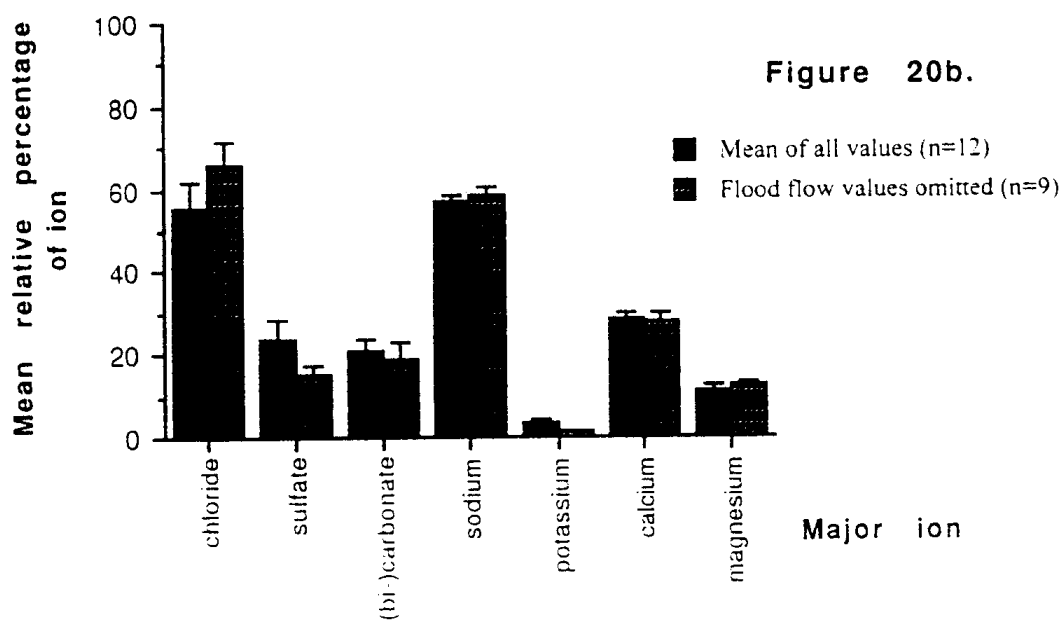
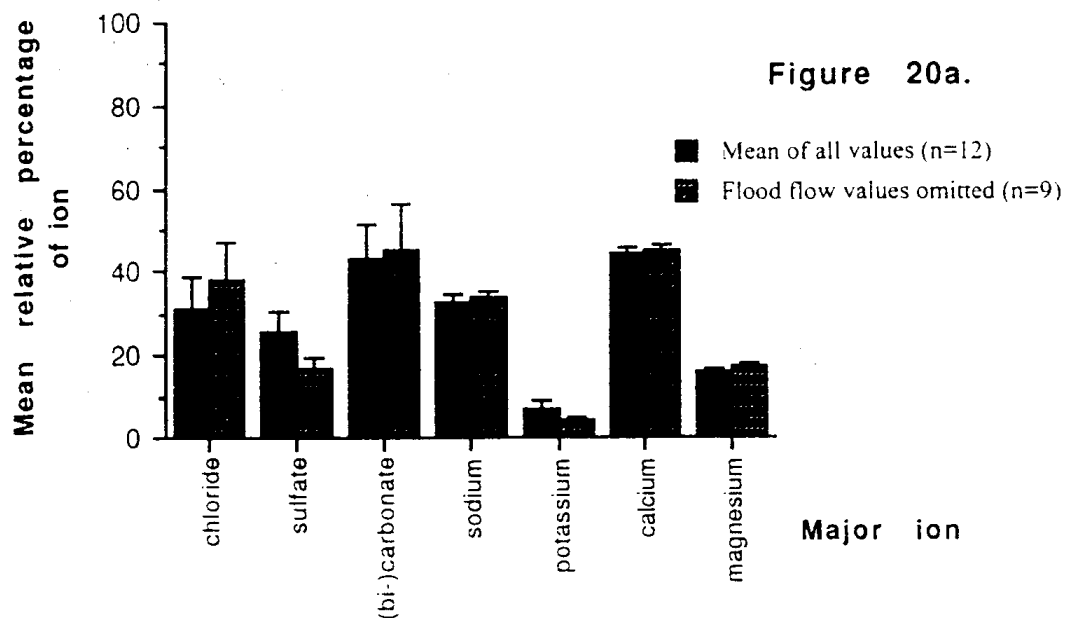


Figure 20. Major ion mean relative percentages (as equivalent weights) for the three sites. a. GC b. SC c. TC (Error bars are the standard errors)

According to Williams (1967), the orders of ionic dominance for Australian lentic freshwaters are usually either $\text{Na} > \text{Mg} > \text{Ca} > \text{K} : \text{Cl} > \text{HCO}_3 + \text{CO}_3 > \text{SO}_4$ or $\text{Na} > \text{Ca} > \text{Mg} > \text{K} : \text{Cl} > \text{HCO}_3 + \text{CO}_3 > \text{SO}_4$, although cationic proportions are known to show considerable variation. In comparison, these results illustrate variability for both ion types, the only consistency with this earlier work being that potassium was the least abundant of the cations.

A sodium and chloride dominance in Savilles and Temptation Creeks is demonstrated (Figure 20), the reference site showing the highest levels. For Gwawley Creek, however, a calcium, total carbonate, sodium and chloride co-dominance existed, with calcium and (bi-)carbonate each showing a slightly greater mean than the corresponding cation or anion.

Although this co-dominance did not occur in Savilles Creek, the mean relative percentage levels for calcium and (bi-)carbonate were obviously higher in the two urban sites than in the reference site. Magnesium differed, however, being about the same for Gwawley Creek and Temptation Creek, while the least in Savilles Creek. Despite characteristically low levels, least potassium was also observed at this site. Only sulfate levels did not appear to change amongst the three sites. Analysis of variance (using sample station means) verified these results (Table 11).

ANOVA (within-site) was also used to assess the effect of flood flow on the major ion composition of the surface waters. Results are presented in Table 12. The high flow samples caused increases in both sulfate and potassium mean relative proportions at all three sites, and although only significant at Savilles Creek, decreases in relative chloride percentage were apparent (Figure 20). Enhanced (bi-)carbonate was seen in Temptation Creek, but the analysis did not detect a significant difference for calcium or magnesium.

4.3.2.2 General Considerations : Surface and Interstitial Waters

Table 13 provides statistical evidence of the differences (between sites) observed for various parameters. The GC+SC abbreviation indicates pooled data from the two urbanised streams.

During the study, water temperatures were found to range from approximately 10°C to 25°C. On those occasions when all three sites were sampled, variability between sites was minimal and probably due to the individual readings being taken at different times of the day. More importantly, no significant difference between surface and interstitial waters was detectable - if anything, interstitial waters were slightly warmer.

Table 11. Results of between-site ANOVA using station mean major ion relative percentages for surface waters.

Major ion	Station means (all data)	p value	Flood flow values omitted	p value
chloride	GC < SC < TC	0.000	*	
(bi-)carbonate	TC < SC < GC	0.000	TC < SC < GC	0.000
sodium	GC < SC < TC	0.000	GC < SC < TC	0.000
potassium	SC < TC < GC	0.000	SC < GC; TC < GC	0.001
calcium	TC < SC < GC	0.000	TC < SC < GC	0.000
magnesium	SC < GC; SC < TC	0.012	SC < GC; SC < TC	0.006 (log)

* significant probability for chloride was observed (GC < SC < TC), however, variances were heterogeneous

(log) - indicates data were log transformed prior to ANOVA test

Table 12. Results of ANOVA using station mean major ion relative percentages, with and without sample collection 12 (storm) values.

	(i) Gwawley Ck.		(ii) Savilles Ck.		(iii) Temptation Ck.	
Major ion	Mean 1 v Mean 2	p value	Mean 1 v Mean 2	p value	Mean 1 v Mean 2	p value
chloride	M1 = M2	0.179	M1 < M2	0.002	*	
sulfate	M1 > M2	0.041	M1 > M2	0.002	M1 > M2	0.001
(bi-)carbonate	M1 = M2	0.613	M1 = M2	0.128	M1 > M2	0.013
sodium	M1 = M2	0.505	M1 = M2	0.273	M1 = M2	0.075
potassium	M1 > M2	0.001	M1 > M2	0.000	M1 > M2	0.000
calcium	M1 = M2	0.740	M1 = M2	0.542	M1 = M2	0.234
magnesium	M1 = M2	0.365	M1 < M2	0.009	M1 = M2	0.220

* significant probability for chloride was observed (M1 < M2), however, variances were heterogeneous

M1 = mean of all values

M2 = mean after sample collection 12 (i.e. flood flow) values omitted

Table 13. Significant probabilities resulting from ANOVA between site water chemistry data.

Surface water			Interstitial water	
Parameter	Difference	p value	Difference	p value
temperature conductivity	GC > SC	0.027		
	GC+SC > TC	0.000	GC+SC > TC	0.000
	GC > TC	0.022	GC > TC	0.000
pH	SC > TC	0.000 (log)	SC > TC	0.000
	GC+SC > TC	*	GC+SC > TC	0.008
	SC > TC	*	SC > TC	0.001
redox			GC < SC	0.003
	GC+SC < TC	0.013	GC > SC	0.001
alkalinity	SC < TC	0.006		
	GC+SC > TC	0.000 (log)	GC+SC > TC	0.000 (log)
	GC > TC	0.000 (log)	GC > TC	0.000 (log)
acidity	SC > TC	0.000 (log)	SC > TC	0.000 (log)
	GC+SC > TC	*	GC > SC	0.010 (log)
hardness	GC > TC	*	GC > TC	0.015 (log)
	GC+SC > TC	*	GC+SC > TC	*
	GC > TC	*	GC > TC	*
ortho-phosphate	SC > TC	*	SC > TC	0.000 (log)
	GC > TC	0.000 (log)	SC > TC	0.002 (log)
total phosphorus	GC > TC	0.033		
			GC+SC > TC	*
copper			GC > TC	*
			SC > TC	*
lead	GC > TC	*		
	GC > SC	*		
chloride	GC < SC	0.020 (log)		
sodium	GC < SC	0.027 (log)		
potassium	GC+SC > TC	0.036		
	GC > TC	0.031		
calcium	GC+SC > TC	0.000		
	GC > TC	0.018		
	SC > TC	0.001 (log)		
ammonia	GC > TC	0.018		
	GC > SC	*		
nitrate	GC+SC > TC	0.000 (log)		
	GC > TC	0.000 (log)		
	SC > TC	0.014 (log)		

* significant probability observed, however, variances were heterogeneous

GC+SC = pooled data from the urbanised streams

(log) = data were log transformed prior to ANOVA test

The non-saline character of all three creeks was complemented by low mean levels of acidity ($<10 \text{ mg L}^{-1}$ as CaCO_3) and hardness ($<100 \text{ mg L}^{-1}$ as CaCO_3 for surface water) - refer to appendix tables A11(i)-(iii). Constituents enabling buffering capacity against basic discharges must therefore be almost non-existent and the creek waters can be classified as 'soft', like the majority of Sydney basin waters.

For all alkalinity measurements performed, the value was almost entirely due to bicarbonate alkalinity, rather than some other component. Assuming a low-high cut level of 24 mg L^{-1} as CaCO_3 (Chapman, 1992), readings were high for the two urban creeks, especially in the interstitial water (note GC1; appendix table A11(i)), and values greater than 100 mg L^{-1} were common. For Temptation Creek, however, alkalinities were much lower and typical of the undeveloped streams sampled in the first study, although a small number of values were nevertheless greater than the maximum (54 mg L^{-1} as CaCO_3) observed during the earlier study.

The urban sites were generally neutral to slightly acidic in both surface and interstitial water pH. Temptation Creek water tended to be more acidic and values below 6 were not uncommon. The overall ranges were also larger at this site, even between the individual stations for a given sampling day, although note the values determined for Savilles Creek surface water on sample collection 1 : 6, 9 and 8.9 for stations 1 to 3 respectively (appendix table A11(ii)). Such a wide range at this site was not seen on any other samplings and was difficult to fathom, given that the increased pHs at sample stations 2 and 3 were accompanied by decreased levels of alkalinity, hardness, total carbonate, calcium and magnesium. Furthermore, the data from Temptation Creek (collected on the same day) suggested that an influence due to the discharge from this creek was unlikely to have affected the water quality at sample station 1. Nevertheless, these marked variations in pH along a stretch of creek suggested a reduced buffering capacity for both Savilles and Temptation Creeks.

Surface and interstitial water dissolved oxygen was not significantly different between the three creeks. However, interstitial water DO was usually lower than in the surface water, suggesting more reducing conditions. This was not unexpected of the sediment environment, which is often anaerobic, even in the surficial layers (Löfgren and Boström, 1989; Batley, 1987). A number of values similar to those of the surface water were observed, indicating oxidising conditions may occur in the sediments from time to time.

A high level of variability was observed with oxidation-reduction measurements, so comparisons need to be treated cautiously. Nevertheless, differences in surface water potentials between the sites were apparent. The two urban sites were more reducing overall (Table 13), with lower overall means and greater proportions (four to five of the eleven readings in each case) of negative values. In fact, for Temptation Creek surface waters, no negative values were observed.

Interstitial waters were considerably more reducing compared to the overlying water column, consistent with the reduced DO levels. This was especially the case for Savilles Creek, where nearly all readings were below zero. The pore waters of Gwawley Creek were perhaps the most oxidising and not greatly dissimilar to Temptation Creek.

Suspended solids content of the surface waters tended to be rather variable (note the large standard errors in appendix table A11), both within a site and between sites, making differences difficult to detect. Concentrations from zero up to almost one gram per litre were observed. Within-site variability was not as pronounced, however, for sample collection 12, which being the flood flow samples also contained some of the more extreme levels. The maximum at Savilles Creek station 3 was due to construction repairs on the North West Arm bridge at station 2, resulting in a particle laden discharge during the sampling. High solids concentrations were again seen here (349 and 268 mg L⁻¹ for sample collections 7 and 10, respectively) following turbid inputs that accumulated on the North West Arm Road and entered the stream just below station 2.

Surface water turbidity and colour were also quite variable (see appendix table A12), although within-site variability was considerably less compared with suspended solids concentration. The similarity of these results with those for suspended solids was not unexpected since both turbidity and colour can be categorised together, all being a measure of constituents generated by similar mechanisms (Water Research Centre, 1979).

Mean concentrations of surface water dissolved ammonia and nitrate were both highest in Gwawley Creek (appendix table A12; Table 13). Site differences in nitrate content were particularly noticeable (TC<SC<<GC) and a number of samples from Gwawley and Savilles Creeks contained excessive enrichment. Despite a nitrate enrichment, levels of ammonia in Savilles Creek waters were not different to those for Temptation Creek samples.

To substantiate the predicted differences between the surface and interstitial waters, analysis of variance utilising pooled data on the basis of site type (i.e. two groups :

combined urban sites and reference site) and site (i.e. three groups : GC, SC and TC) was performed. Such groupings with larger numbers of replicates were more powerful and complemented the analyses involving individual sampling stations (i.e. nine groups), each being a much smaller data set. Samples with missing measurements were selectively deleted to ensure an equal number and pairing of replicates.

On combining site data, the parameters which were significantly different in the two water types are listed in Table 14. Significant differences from analyses involving the separate sampling stations are listed in Table 15. Note that for Gwawley Creek 1, Temptation Creek 2 and 3, deletion of sample collection 12 meant no high flow (i.e. F2) data remained, hence the analysis with all data was equivalent to that with F2 removed. Furthermore, analysis after deletion of low flow (i.e. F1) samples was only possible on a very limited number of replicates (GC3 and TC1).

In general, the first impressions were reflected in the analysis, despite a high degree of non-homogeneity of variance. This lack of homogeneity possibly masked the detection of any differences for dissolved ortho-phosphate and the heavy metals; however dissimilarities between the surface and interstitial waters were not found.

4.3.2.3 Composition of Surface Waters at Flood Flow

The chemical characteristics of sample collection 12 surface waters made it necessary to treat these samples as a separate group in certain situations (e.g. assessment of major ion chemistry above). Being distinctly different to all other high and low flow samples, they were expected to be typical of the composition of the stream waters under high runoff discharge rate. These waters were not expected to include the first flush, however, since for each site flood flow had commenced at least 20 to 25 minutes prior to the collection of samples.

In all three sets of samples, the surface waters were neutral to basic in pH (i.e. slightly higher than the overall mean values) and had oxidising redox potentials, a consequence of mixing. The increased volume of water resulted in significant reduction in concentration of many major constituents, however - see appendix tables A11 and A12. Most obvious examples include the changes in conductivity, alkalinity, hardness, chloride, sodium and magnesium concentrations.

Compared to earlier samplings, marked increases in concentration occurred with phosphorus (both total and dissolved ortho-phosphate components), suspended solids, turbidity and colour. Apart from Temptation Creek nitrate levels, the other nutrients (i.e.

Table 14. Results of ANOVA between surface and interstitial waters for pooled data.

Parameter	Data pooled	All data SW v IW	p value	F2 removed SW v IW	p value	F1 removed SW v IW	p value
conductivity	GC+SC	SW < IW	0.011	SW < IW	0.032		
	GC	SW < IW	0.000 (log)	SW < IW	0.000		
DO	GC+SC	SW > IW	0.000 (sqr)	SW > IW	0.000 (sqr)	SW > IW	0.000
	GC	SW > IW	0.000	SW > IW	0.000	SW > IW	0.000
	SC	SW > IW	0.000	SW > IW	0.000	SW > IW	0.018
	TC	SW > IW	0.000	SW > IW	0.000		
pH	GC	SW > IW	0.011				
redox	GC+SC	SW > IW	0.021	SW > IW	0.001		
	SC	SW > IW	0.001	SW > IW	0.001		
	TC	SW > IW	*	SW > IW	*		
alkalinity	GC+SC	SW < IW	0.011 (log)	SW < IW	0.008 (log)		
	SC	SW < IW	0.003 (log)	SW < IW	0.020 (log)		
	TC	SW < IW	0.005	SW < IW	0.010		
acidity	GC+SC	SW < IW	*	SW < IW	*		
	GC	SW < IW	0.004 (log)	SW < IW	0.009 (log)		
	TC	SW < IW	*	SW < IW	*		
hardness	GC+SC	SW < IW	*	SW < IW	*		
	GC	SW < IW	*	SW < IW	*		
	SC	SW < IW	0.000 (log)	SW < IW	0.001 (log)		
	TC	SW < IW	0.034	SW < IW	0.040		
zinc	GC	SW < IW	*	SW < IW	*		
lead	GC+SC	SW < IW	*	SW < IW	*		

* significant probability observed, however, variances were heterogeneous

SW = surface water ; IW = interstitial water

F1 = low flow group ; F2 = high flow group

GC+SC = pooled data from the urbanised streams

(log) = data were log transformed prior to ANOVA test

(sqr) = data were square root transformed prior to ANOVA test

Table 15. Results of ANOVA between surface and interstitial waters of each sample station.

Parameter	Site/ Station	All data SW v IW	p value	F2 removed SW v IW	p value	F1 removed SW v IW	p value
conductivity	GC1	SW < IW	0.005				
	GC2	SW < IW	0.000	SW < IW	0.002		
	TC3	SW < IW	0.029	SW < IW	0.029		
DO	GC1	SW > IW	0.000				
	GC2	SW > IW	0.000	SW > IW	0.000		
	GC3	SW > IW	0.000	SW > IW	0.033	SW > IW	0.001
	SC1	SW > IW	0.004	SW > IW	0.014		
	SC2	SW > IW	0.002	SW > IW	0.004		
	SC3	SW > IW	0.001	SW > IW	0.003		
	TC1	SW > IW	0.001	SW > IW	0.005		
	TC3	SW > IW	0.001	SW > IW	0.001		
pH	GC2	SW > IW	0.014				
redox	SC1	SW > IW	0.042				
	SC2			SW > IW	0.039		
	SC3	SW > IW	0.027				
	TC3	SW > IW	0.002	SW > IW	0.002		
alkalinity	SC2	SW < IW	0.018	SW < IW	0.024		
	SC3	SW < IW	0.010	SW < IW	0.036		
	TC2	SW < IW	*	SW < IW	*		
	TC3	SW < IW	*	SW < IW	*		
acidity	GC2	SW < IW	0.014 (log)				
hardness	GC2	SW < IW	*	SW < IW	0.010 (log)		
	GC3	SW < IW	*				
	SC2	SW < IW	0.015	SW < IW	0.014		
	SC3	SW < IW	0.005	SW < IW	0.012		
	TC3	SW < IW	0.002	SW < IW	0.002		

* significant probability observed, however, variances were heterogeneous

SW = surface water; IW = interstitial water

F1 = low flow group; F2 = high flow group

(log) = data were log transformed prior to ANOVA test

dissolved ammonia and nitrate) were not necessarily increased, but they were still at high concentrations, nonetheless. Of the heavy metals, only zinc was detected, but the concentration was no greater than earlier measurements. These low levels were probably the effect of dilution of the stream surface water by the accumulated runoff.

4.3.2.4 Phosphorus Chemistry

Ortho-phosphate was readily detectable in both Gwawley Creek and Savilles Creek waters - see appendix table A11. Usually the level was less than $10 \mu\text{g PO}_4\text{-P L}^{-1}$; however, concentrations in excess of this lower limit for protection of freshwater ecosystems (ANZECC, 1992) were occasionally seen. Concentrations greater than the ANZECC (1992) upper limit ($100 \mu\text{g PO}_4\text{-P L}^{-1}$) were rare, although observed in samples from all three Gwawley Creek stations on sample collection 12. For Temptation Creek, samples with a concentration below the detection limit (i.e. $<1 \mu\text{g PO}_4\text{-P L}^{-1}$) were more frequent. Except for sample collection 12, surface and interstitial water levels were always below $10 \mu\text{g PO}_4\text{-P L}^{-1}$.

In relative terms, total phosphorus content of the surface waters was consistently high and comparable with the values seen for other Sydney streams. Mean values ranged from 0.05 to $0.1 \text{ mg PO}_4\text{-P L}^{-1}$ and higher levels ($>0.3 \text{ mg PO}_4\text{-P L}^{-1}$) were detected - see appendix table A11. Since interstitial waters required filtration prior to analysis, total phosphorus could not be determined; however, it is expected that a similar trend occurs.

Figure 21 shows the levels of total phosphorus and dissolved ortho-phosphate in the surface waters, as well as the relative proportions of these. For the Gwawley Creek stations, mean ratios of total to dissolved phosphorus were 4.7, 4.5 and 3.5, respectively. These ratios were larger, however, for Savilles and Temptation Creeks - 5.6, 7.7 and 6.8, respectively for Savilles Creek; 7.3, 7.0 and 5.7, respectively for Temptation Creek.

These results were compared to the corresponding data from sample collection 12. Apart from obviously higher amounts due to runoff, Figure 22 also illustrates a change in relative proportions with an increase of dissolved ortho-phosphate in these flood flow surface waters. Hence, the calculated ratios were generally lower in this case, particularly for Gwawley Creek (1.8, 2.3 and 2.3 for GC, respectively; 4.6, 5.2 and 6.4 for SC; 4.5, 4.7 and 4.7 for TC).

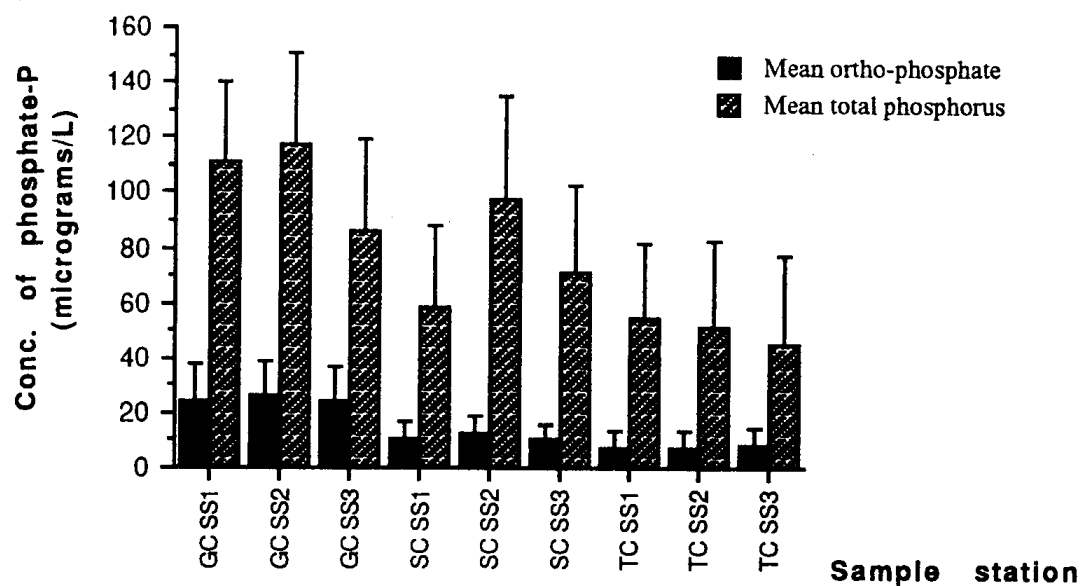


Figure 21. Mean surface water ortho-phosphate and total phosphorus levels (all data) for the nine sample stations. (Error bars are the standard errors)

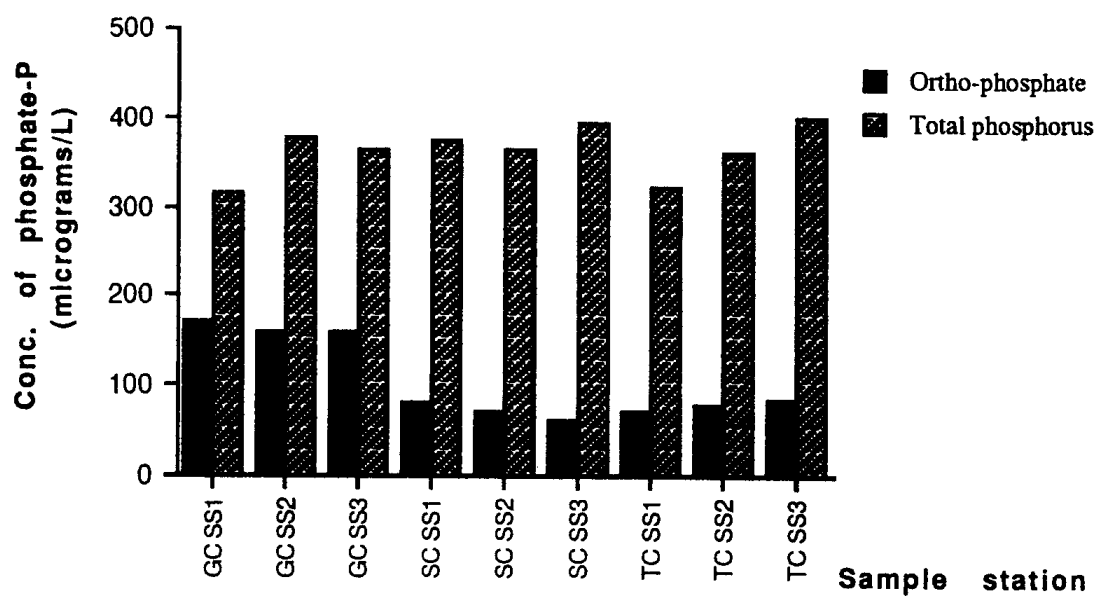


Figure 22. Flood flow surface water ortho-phosphate and total phosphorus levels for the nine sample stations.

Figure 23 shows the mean levels of surface and interstitial water dissolved ortho-phosphate. In this case the surface water means were determined on those samples when interstitial waters were also collected. Hence sample collection 12 values could not be included.

Only at Gwawley Creek sample stations 2 and 3 was there increased levels in the pore water compared to the surface water. For Gwawley Creek 1, ortho-phosphate levels were higher in surface water and for all other stations there appeared to be little difference. Analysis of variance failed to detect any significant differences in ortho-phosphate for the two water types, however. The large standard errors, indicating substantial variability, made differences difficult to detect. Nevertheless, it seemed that apart from two stations there could be only limited phosphate flux from pore waters to the surface water column.

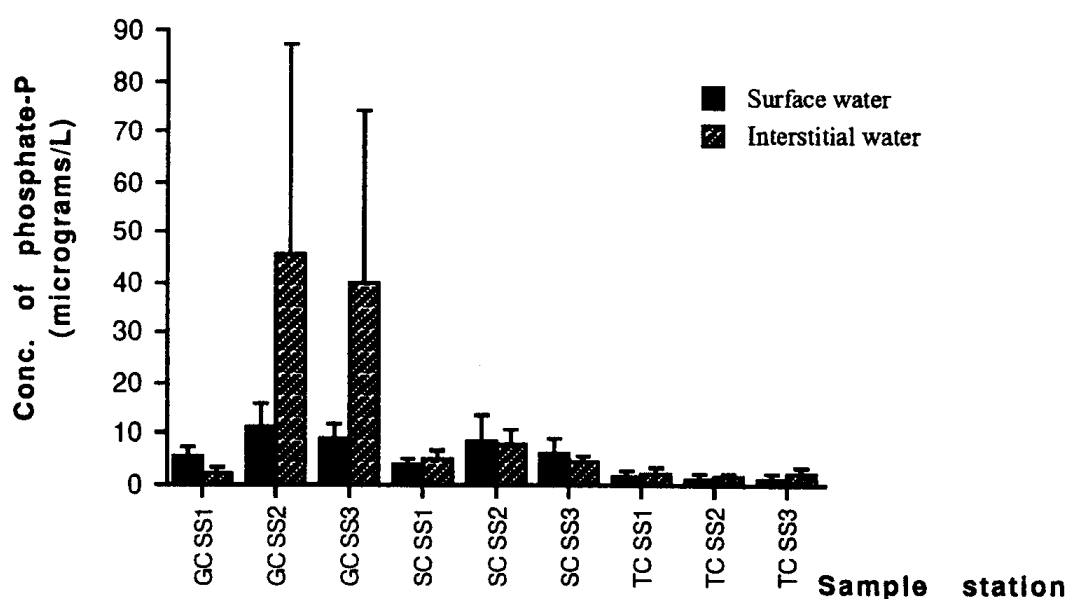


Figure 23. Mean surface and interstitial water ortho-phosphate levels, based on those samplings for which both water types were collected, for the nine sample stations. (Error bars are the standard errors)

4.3.2.5 Heavy Metal Chemistry

Dissolved heavy metals were detected sporadically, especially cadmium, although when present concentrations were usually high. This supported the findings of the Sydney streams survey, which also suggested cadmium (plus other metals sharing similar chemistry) would rarely be found at significant levels in surface waters under normal conditions.

Of the four metals studied, zinc was found at the highest concentrations. However, due to the high incidence of levels below the detectable limit and subsequent large standard errors, it was difficult to depict further trends or differences between the sites, as observed with the phosphate data. Figure 24, which presents the mean levels of surface and interstitial water dissolved heavy metals - again calculated for only those samples when both surface and interstitial waters were collected together - best illustrates the high variability seen. In general, though, it can be said that interstitial waters contained higher concentrations of metals than the respective surface waters, especially for zinc and lead, suggesting a sediment-to-water flux will occur on occasion.

4.3.2.6 Assessment of Water Quality

Table 16 lists the percentage of measurements for each site which failed to satisfy the relevant ANZECC (1992) water quality criteria, as provided in Table 7 (section 3.4). Results are based on pooled observations of all three stations, to generate a representative percentage. Interstitial waters are included; however, most relevance is with respect to the surface waters, especially in the case of dissolved oxygen. These results provide a general indication of how often unacceptable water quality can be expected, and a guide to the fluctuations possible.

Values outside the recommended pH range were seen at all three sites, but with greatest frequency at Temptation Creek. For each site the failures were all below the 6.5 lower limit and no value above 9 was observed. This was probably a reflection of very poor acid-buffering capacity. In the surface waters, dissolved oxygen levels were regularly above the ANZECC (1992) recommended limit of 6 mg L⁻¹, indicating well aerated streams. Some readings below 6 mg L⁻¹ were detected - more often at Temptation Creek compared to the two urbanised creeks - suggesting stresses on gill-breathing organisms may occur from time to time. This conclusion needs to be viewed with some caution, however, as the data have not included changes due to the diel cycle (ANZECC, 1992).

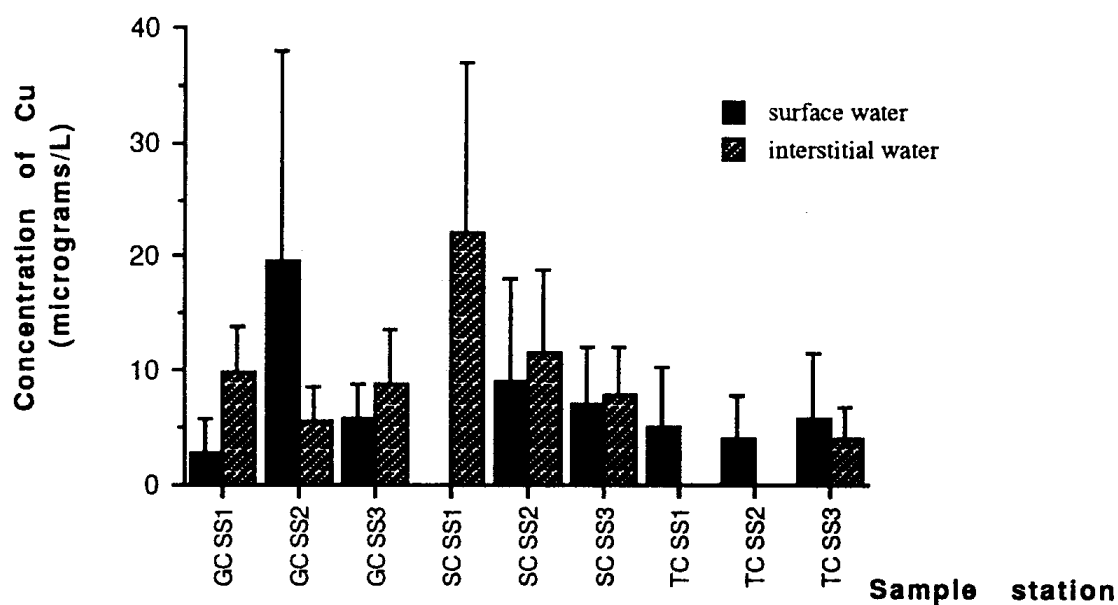


Figure 24a. Mean surface and interstitial water copper levels.

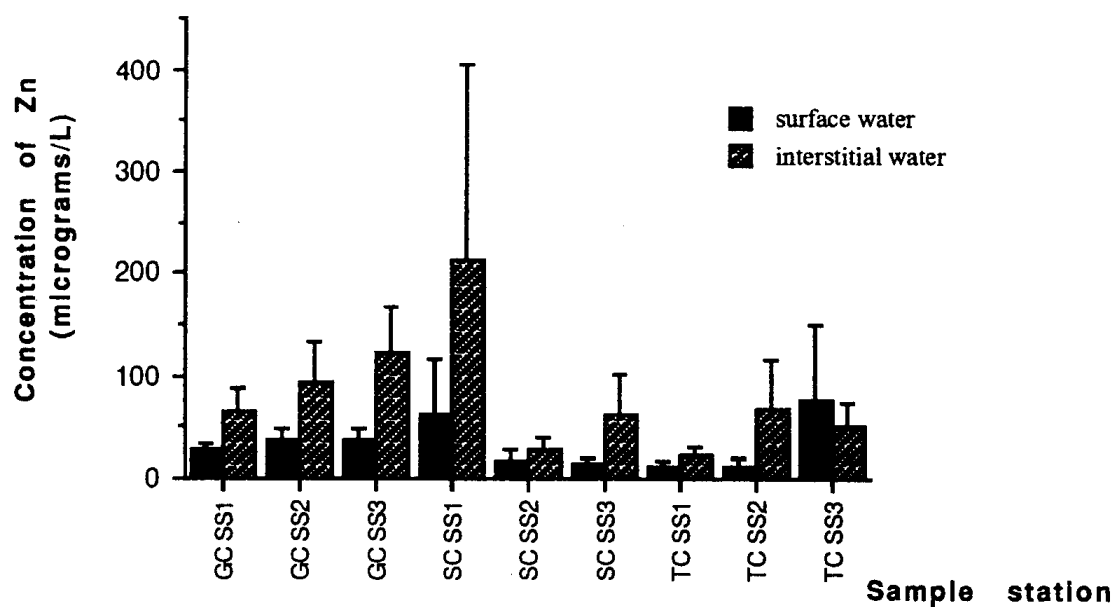


Figure 24b. Mean surface and interstitial water zinc levels.

(Means based on samplings when both water types collected. Error bars are the standard errors)

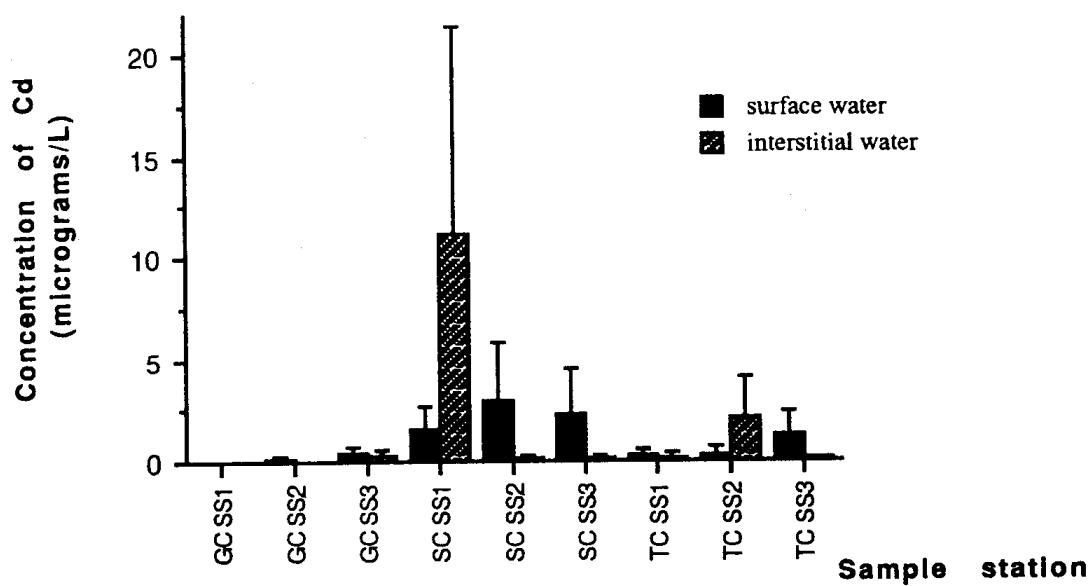


Figure 24c. Mean surface and interstitial water cadmium levels.

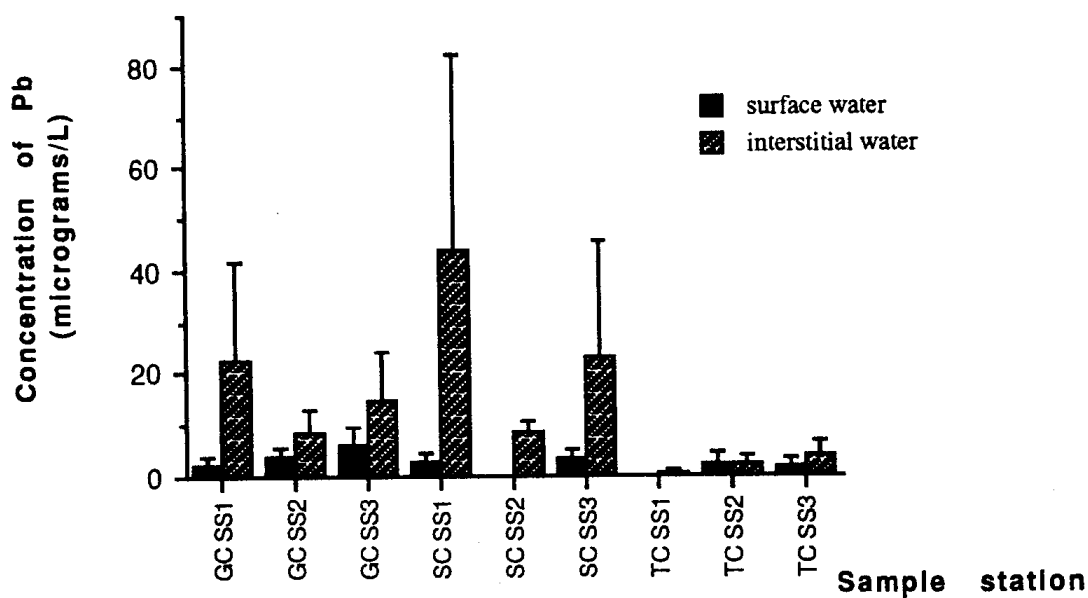


Figure 24d. Mean surface and interstitial water lead levels.

(Means based on samplings when both water types collected. Error bars are the standard errors)

Table 16. Percentage of measurements for each site which fail the ANZECC (1992) water quality criteria

Indicator (Assumed range / limit for group comparison)	GC SW	GC IW	SC SW	SC IW	TC SW	TC IW
pH (6.5 - 9.0)	8 (0)	26 (0)	11 (0)	4 (0)	44 (67)	44 (60)
DO (6.0 mg L ⁻¹)	12 (50)	92	13 (0)	87	23 (20)	83
Nutrients						
total phosphorus (10 µgPO ₄ ³⁻ -P L ⁻¹)	89 (75)		67 (70)		42 (67)	
(100 µgPO ₄ ³⁻ -P L ⁻¹)	36 (29)		22 (20)		14 (33)	
ortho-phosphate (10 µgPO ₄ ³⁻ -P L ⁻¹)	36	8	19	45	8	4
(100 µgPO ₄ ³⁻ -P L ⁻¹)	8	6	0	0	0	0
total nitrogen as (NH ₃ +NO ₃ ⁻)-N						
(100 µgN L ⁻¹)	100		75		33	
(750 µgN L ⁻¹)	58		17		0	
Heavy metals (hardness dependent)						
copper (2.0 µg L ⁻¹)	25 (20)	25 (20)	14	30	17	7
(5.0 µg L ⁻¹)	25 (20)	25 (20)	14	30	17	7
zinc (5.0 µg L ⁻¹)	81 (67)	85 (67)	44	59	39	78
(50 µg L ⁻¹)	22 (20)	56 (43)	8	26	8	11
cadmium (0.2 µg L ⁻¹)	11	4	17	15	11	11
(2.0 µg L ⁻¹)	3	4	11	7	11	4
lead (1.0 µg L ⁻¹)	39 (29)	44 (33)	14 (0)	44 (12)	14 (0)	18 (0)
(5.0 µg L ⁻¹)	36 (29)	41 (33)	14 (0)	44 (12)	14 (0)	15 (0)

Note :

GC = Gwawley Creek ; SC = Savilles Creek ; TC = Temptation Creek

SW = surface water ; IW = interstitial water

Values in brackets signify the level of poor quality compliance for the three stations of each site

High percentages occurred with the total nutrient levels, frequencies following the trend : GC>SC>TC. For nitrogen this is most significant since the total load was based on a sum of the two common dissolved forms only, unlike total phosphorus which included essentially bio-unavailable particulate (bound) forms as well. Frequencies for dissolved ortho-phosphate were much lower but still followed the same trend.

Each of the four heavy metals occurred at concentrations in excess of the respective quality criteria at some point, especially zinc. As with nitrogen, the actual concentrations included only the dissolved forms which represent a potentially toxic fraction (Florence and Morrison, 1992). On comparing percentages for the three sites, trends were less distinct than for nutrients, reflecting the highly variable nature (sporadic detection frequency) of dissolved heavy metals. Nevertheless, higher values were generally seen at the urbanised sites.

The levels of spatial and temporal compliance were also assessed for each stream. Spatial compliance was a percentage measure of the number of sample collections when all three sampling stations failed a certain quality criterion, per total number of sample collections when a corresponding failure was observed for the site. The larger the percentage, the greater the spatial compliance. For this data set, the statistic was mostly of relevance to pH, surface water dissolved oxygen, total phosphorus, lead, plus Gwawley Creek copper and zinc concentrations. Values are given as the bracketed numbers in Table 16.

Largest percentages were observed for total phosphorus ($10 \mu\text{g L}^{-1}$ limit) - reflecting the high levels regularly detected in these surface waters - Temptation Creek pH values and Gwawley Creek zinc concentrations ($5 \mu\text{g L}^{-1}$ limit). However, in no instance was there a 100% value. Furthermore, for each site no one sampling station consistently displayed poor quality for any given parameter. These results suggest a general pattern of spatial and temporal non-compliance, hence reflecting a high level of chemical variability.

4.3.2.7 Surface Water Loadings

A summary of the surface water loading statistics is presented in Table 17. Loading was calculated by multiplication of constituent concentration and discharge, then converting the value into Mg, kg, g, or mg per hour. The results were based on those sample collections for which reliable flow measurements were obtained; hence, sample collection 12 was not included. Where flow was below the detectable limit (i.e. <5mm pitot tube height), the 4.4 cm s^{-1} value was assumed.

Parameter	Gwawley Creek			Savilles Creek			Temptation Creek		
	SS1	SS2	SS3	SS1	SS2	SS3	SS1	SS2	SS3
suspended solids (kg/h)	4.53 (3.45) <i>0.11-32.0</i>	26.6 (13.5) <i>0.10-104</i>	2.57 (1.82) <i>0.03-20.0</i>	7.94 (3.20) <i>bdl-25.4</i>	3.50 (1.52) <i>bdl-12.6</i>	41.1 (21.9) <i>bdl-171</i>	1.40 (0.44) <i>bdl-3.60</i>	10.3 (8.73) <i>bdl-53.8</i>	7.06 (1.81) <i>0.61-10.9</i>
total P (g/h)	15.0 (8.5) <i>0.39-79.8</i>	141 (92) <i>1.27-756</i>	29.5 (26.3) <i>bdl-292</i>	7.58 (2.62) <i>bdl-20.9</i>	36.9 (27.3) <i>bdl-225</i>	8.43 (4.13) <i>bdl-33.4</i>	4.76 (2.55) <i>bdl-17.3</i>	1.63 (0.87) <i>bdl-5.40</i>	6.66 (3.43) <i>bdl-20.9</i>
ortho-phosphate (g/h)	1.36 (0.73) <i>0.06-6.85</i>	35.5 (30.5) <i>0.23-248</i>	5.49 (4.29) <i>0.06-48.0</i>	6.62 (5.64) <i>bdl-46.1</i>	8.82 (4.80) <i>0.34-34.2</i>	7.49 (5.63) <i>0.19-46.1</i>	2.14 (2.03) <i>bdl-16.4</i>	0.73 (0.73) <i>bdl-4.38</i>	1.52 (1.32) <i>bdl-8.09</i>
copper (g/h)	0.26 (0.18) <i>bdl-1.50</i>	0.84 (0.64) <i>bdl-5.13</i>	1.56 (0.83) <i>bdl-8.53</i>	0.22 (0.22) <i>bdl-1.75</i>	3.06 (3.06) <i>bdl-24.5</i>	2.14 (1.36) <i>bdl-10.7</i>	6.22 (4.26) <i>bdl-31.5</i>	bdl <i>bdl-6.85</i>	1.14 (1.14) <i>bdl-6.85</i>
zinc (g/h)	5.14 (2.31) <i>bdl-19.0</i>	80.0 (75.8) <i>bdl-610</i>	13.4 (9.8) <i>bdl-111</i>	32.6 (32.6) <i>bdl-261</i>	11.8 (5.8) <i>bdl-45.2</i>	4.31 (2.67) <i>bdl-22.2</i>	4.10 (1.86) <i>bdl-13.7</i>	1.46 (1.35) <i>bdl-8.21</i>	54.4 (46.7) <i>bdl-287</i>
cadmium (mg/h)	bdl <i>bdl-152</i>	21.6 (18.8) <i>bdl-172</i>	21.9 (18.2) <i>bdl-200</i>	746 (679) <i>bdl-5481</i>	1843 (1819) <i>bdl-14582</i>	948 (924) <i>bdl-7416</i>	48.4 (48.4) <i>bdl-387</i>	5.18 (5.18) <i>bdl-31.1</i>	942 (756) <i>bdl-4627</i>
lead (g/h)	0.48 (0.33) <i>bdl-2.99</i>	22.6 (21.3) <i>bdl-172</i>	3.61 (2.84) <i>bdl-31.7</i>	0.89 (0.89) <i>bdl-7.10</i>	bdl <i>bdl-2.99</i>	0.64 (0.43) <i>bdl-3.15</i>	1.10 (0.76) <i>bdl-5.76</i>	bdl <i>bdl-1.74</i>	0.29 (0.29) <i>bdl-1.74</i>
Sample collections	1 to 3, 5 to 8, 10 & 11	1 to 5, 8, 10 & 11	1 to 11	1 & 2, 4 to 6, 8, 10 & 11	1 & 2, 5 to 8, 10 & 11	1 & 2, 5 to 8, 10 & 11	1 & 2, 5 to 8, 10 & 11	1 & 2, 5, 8, 10 & 11	1 & 2, 5 & 6, 10 & 11
chloride (Mg/h)	1.10 (0.76) <i>0.00-2.56</i>	2.74 (2.27) <i>bdl-7.24</i>	8.81 (7.23) <i>bdl-23.1</i>	56.0 (35.8) <i>6.88-126</i>	63.2 (43.3) <i>8.88-149</i>	15.3 (4.58) <i>6.25-21.1</i>	16.8 (4.97) <i>7.09-23.5</i>	6.40 (3.69) <i>0.86-13.4</i>	22.5 (4.79) <i>17.7-27.3</i>
sulfate (kg/h)	0.89 (0.42) <i>0.37-1.73</i>	6.46 (3.33) <i>0.39-11.9</i>	3.79 (2.89) <i>bdl-9.46</i>	10.7 (3.69) <i>3.45-15.4</i>	25.7 (23.4) <i>bdl-72.4</i>	5.54 (1.72) <i>3.03-8.83</i>	3.35 (2.14) <i>bdl-7.34</i>	2.31 (1.51) <i>0.06-5.18</i>	4.59 (1.84) <i>2.74-6.43</i>
(bi-)carbonate (kg/h)	1.60 (0.93) <i>0.15-3.33</i>	14.7 (10.3) <i>0.11-34.6</i>	7.75 (4.53) <i>0.38-16.0</i>	5.58 (1.67) <i>3.65-8.91</i>	17.6 (14.0) <i>2.60-45.6</i>	3.48 (1.44) <i>1.11-6.08</i>	1.60 (0.82) <i>0.74-3.24</i>	0.40 (0.19) <i>0.15-0.65</i>	0.74 (0.27) <i>0.47-1.00</i>
sodium (kg/h)	1.06 (0.20) <i>0.77-1.45</i>	6.16 (4.04) <i>0.65-14.0</i>	4.77 (2.64) <i>2.07-10.1</i>	37.2 (25.1) <i>3.20-86.1</i>	43.8 (30.2) <i>4.90-103</i>	9.86 (3.31) <i>3.30-13.9</i>	10.5 (3.0) <i>4.83-14.9</i>	3.53 (2.09) <i>0.53-7.56</i>	14.0 (3.9) <i>10.1-17.9</i>
potassium (kg/h)	0.14 (0.02) <i>0.11-0.18</i>	2.49 (2.26) <i>0.10-7.02</i>	0.76 (0.31) <i>0.29-1.36</i>	1.01 (0.55) <i>0.16-2.03</i>	1.93 (1.37) <i>0.22-4.63</i>	0.42 (0.13) <i>0.16-0.56</i>	0.39 (0.09) <i>0.21-0.51</i>	0.15 (0.10) <i>0.01-0.35</i>	0.76 (0.22) <i>0.54-0.98</i>
calcium (kg/h)	1.03 (0.17) <i>0.84-1.38</i>	9.55 (7.17) <i>0.72-23.8</i>	5.75 (2.62) <i>1.91-10.8</i>	12.3 (6.1) <i>1.12-22.1</i>	25.1 (19.8) <i>1.53-64.6</i>	4.84 (2.06) <i>1.11-8.22</i>	2.03 (1.37) <i>0.36-4.75</i>	0.20 (0.17) <i>0.02-0.54</i>	0.59 (0.01) <i>0.58-0.60</i>
magnesium (kg/h)	0.29 (0.06) <i>0.20-0.39</i>	2.02 (1.44) <i>0.17-4.86</i>	1.04 (0.41) <i>0.54-1.87</i>	2.90 (1.46) <i>0.49-5.53</i>	5.77 (4.44) <i>0.56-14.6</i>	1.17 (0.46) <i>0.40-2.00</i>	1.17 (0.14) <i>0.89-1.32</i>	0.73 (0.57) <i>0.07-1.86</i>	2.50 (0.20) <i>2.30-2.70</i>
ammonia (g/h)	9.69 (6.14) <i>1.00-21.5</i>	250 (242) <i>0.20-734</i>	50.5 (39.9) <i>0.75-129</i>	7.53 (4.11) <i>1.94-15.6</i>	14.3 (6.87) <i>2.59-26.4</i>	3.81 (0.90) <i>2.01-4.82</i>	4.66 (0.63) <i>3.86-5.90</i>	1.77 (0.33) <i>1.11-2.11</i>	5.61 (0.90) <i>4.71-6.51</i>
nitrate (g/h)	93.8 (29.5) <i>43.6-146</i>	10521 (10400) <i>11.3-31320</i>	452 (248) <i>40.6-898</i>	127 (86) <i>4.91-292</i>	340 (294) <i>7.35-927</i>	86.1 (68.7) <i>6.34-223</i>	8.29 (6.48) <i>1.36-21.2</i>	3.25 (1.59) <i>0.11-5.29</i>	6.93 (3.76) <i>3.17-10.7</i>
Sample collections	1, 2 & 8	1, 2 & 8	1, 2 & 8	1, 2 & 8	1, 2 & 8	1, 2 & 8	1, 2 & 8	1, 2 & 8	1 & 2

Values in brackets are the standard errors; values in italics are the observed minima and maxima.

The data displayed extreme variability, as seen in the large standard errors and ranges, while variances were regularly heterogeneous. Highest loadings were observed for suspended solids, chloride and nutrients (nitrate in particular).

Analysis of variance detected only a few significant differences. On the basis of site type and sampling station no differences were observed. At the site level two differences were identified, wherein Savilles Creek was found to be more saline compared with the other sites, with high chloride ($p=0.037$, although variances remained heterogeneous, even after transformations) and sodium ($p=0.009$, logged data). The discharges themselves were no different at these levels (site type : $p=0.490$; site : 0.571 ; sampling station : $p=0.326$).

A number of significant differences were detected when the data were assessed by flow grouping. For the loadings of dissolved ortho-phosphate ($p=0.000$, logged data), (bi-) carbonate ($p=0.003$, logged data), potassium ($p=0.003$, logged data), magnesium ($p=0.038$, logged data), ammonia ($p=0.000$, logged data) and nitrate ($p=0.003$, logged data), high flow means were greater than the corresponding means for the low flow samples.

4.3.3 Sediment Chemistry

4.3.3.1 General Considerations

Appendix tables A13(i)-(iii) and A14(i)-(iii) list the sediment chemistry and particle size/cation exchange capacity data, respectively.

Comparing the raw data of the three sites (see appendix table A14), particle size measurements indicated the substrates were similar in terms of physical characteristics, although differences in coarse and fine particle contents were found from the ANOVA performed on this data set (Table 18). The urbanised creeks had greater cation exchange capacity (CEC); however, in all instances the values were quite low. As a consequence of the low level of silt and clay, fractionation was not performed on each sediment collected.

Sediments from the two urban creeks were clearly higher in organic carbon, total and organic phosphorus, copper, zinc and lead concentrations than Temptation Creek (appendix table A13; Table 18). In fact, apart from organic carbon and total phosphorus, the remaining parameters (especially lead) were regularly non-detectable at each of the three reference creek sampling stations.

Table 18. Significant probabilities resulting from ANOVA between site sediment chemistry data.

Parameter	Difference	p value
organic carbon	GC+SC > TC	0.004
	GC > TC	0.004
	SC > TC	0.031
total phosphorus	GC+SC > TC	*
	GC > TC	0.000 (log)
	SC > TC	0.000 (log)
	GC > SC	*
organic phosphorus	GC+SC > TC	*
	GC > TC	*
	SC > TC	*
total copper	GC+SC > TC	*
	GC > TC	0.000 (log)
	SC > TC	*
	GC > SC	0.000 (log)
total zinc	GC+SC > TC	0.000 (log)
	GC > TC	0.000 (log)
	SC > TC	*
total lead	GC > SC	0.000 (log)
	GC+SC > TC	*
	GC > TC	0.000 (log)
	SC > TC	*
coarse sand	GC > SC	0.000 (sqr)
	GC+SC > TC	*
	SC < TC	0.001
fine sand	GC > SC	0.030
	GC+SC > TC	0.011 (log)
	SC > TC	0.000
silt + clay	GC < SC	0.016
	GC+SC > TC	*
	GC > TC	*
CEC	SC > TC	*
	GC+SC > TC	0.001
	GC > TC	0.002
	SC > TC	0.008

* significant probability observed, however, variances were heterogeneous

(log) = data were log transformed prior to ANOVA test

(sqr) = data were square root transformed prior to ANOVA test

Of the 'impacted' sites, total heavy metal, phosphorus and organic carbon levels in Gwawley Creek sediments were greater than in Savilles Creek, although only valid significant differences were detected for copper, zinc and lead (Table 18). The stormwater drain outlet, situated just above Gwawley Creek 1, was expected to be a major source of these materials since particularly high levels were consistently observed at this station (appendix table A13). The latter sample collections (9, 10 and 11) from this site had substantial increases in organic carbon, total phosphorus, copper, zinc and lead, compared to earlier samples, suggesting large pulses of additional load occurred at some stage. Despite this, the data for all three sites did not provide evidence of any accumulative ability since considerable variability was present.

Although often high levels of sediment total phosphorus were seen, organic fractions were relatively insignificant (Figure 25), especially at Temptation Creek. This matched the generally low organic carbon results. The majority of the total phosphorus load in streams such as these must, therefore, be in inorganic forms (i.e. as ortho-phosphates).

Consistent with the water chemistry results, sediment cadmium was detected very rarely at all three sites. As a consequence of the low occurrence of this heavy metal in both waters and sediments, cadmium was subsequently excluded from further analysis.

Figure 26, representing the mean total copper, zinc and lead contents, illustrates the differences in sediment heavy metal content between the sites and also stations. Comparing concentration values, zinc and lead were present in relatively greater amounts, possibly reflecting the dominant role that organic matter plays in accumulating copper (Pardo *et al.*, 1990; Chen *et al.*, 1989; Hart and Davies, 1978) - in view of the low organic matter content in these sediments.

4.3.3.2 Assessment of Sediment Quality

Table 19 provides relevant sediment quality criteria, as obtained from Baudo *et al.* (1990). Table 20 lists the percentage of individual measurements for each site which failed to satisfy the 'lowest effect level' criteria recommended by the Ontario Ministry of Environment - the percentage taken to indicate the proportion of samples which could lead to some detrimental effect on the "most sensitive" organisms. As in the case for waters, the results are based on pooled observations from all three stations, to generate a more representative number. Despite the questionable validity in assuming these values as a standard reference - based on sediments of probably different physical characteristics

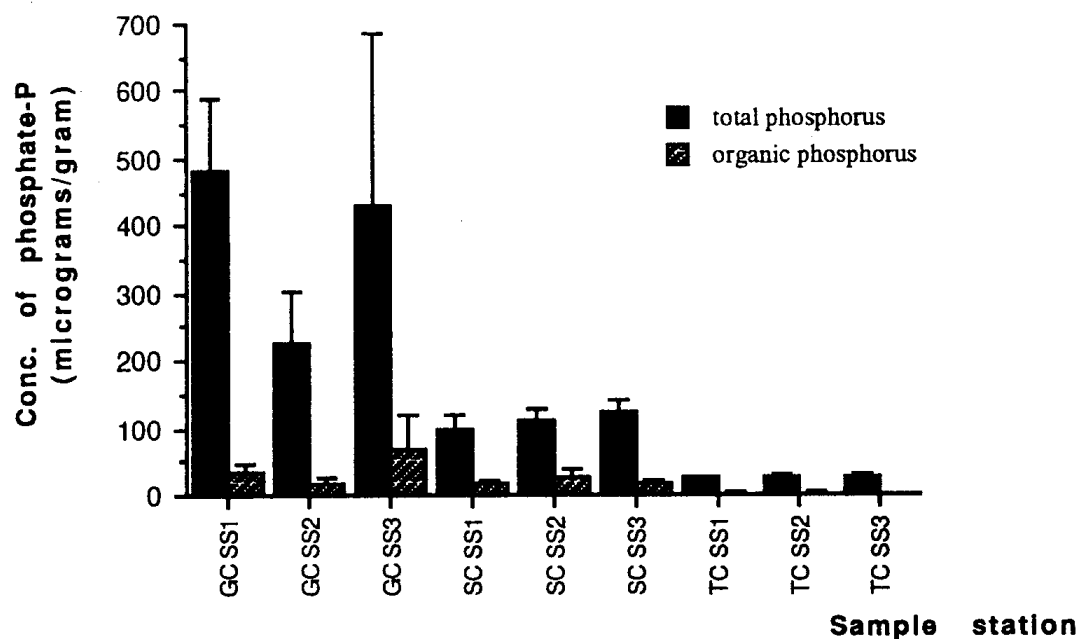


Figure 25. Sediment mean total and organic phosphorus concentrations for the nine sampling stations. (Error bars are the standard errors)

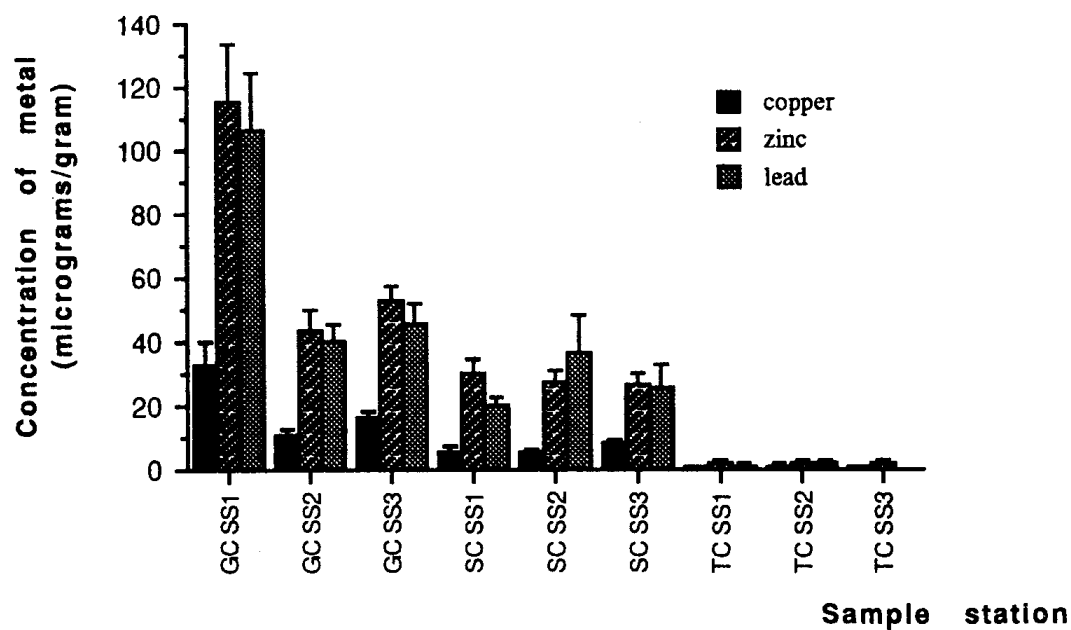


Figure 26. Sediment mean total heavy metal concentrations for the nine sampling stations. (Error bars are the standard errors)

Table 19. Sediment quality criteria from Baudo *et al.* (1990).

Indicator	US EPA (1977) Nonpolluted (ppm)	Ontario MOE Lowest effect level (ppm)	Ontario MOE Limit of tolerance level (ppm)
total P	< 420	600.0	2050.0
total N	< 1000	545.0	4800.0
lead	< 40	31.0	250.0
zinc	< 90	110.0	800.0
copper	< 25	25.0	114.0
cadmium	0	1.0	10.0

Note :

(1) US EPA (1977) = US Environment Protection Authority, Region V

Guidelines for classifying sediments of Great Lakes Harbors

(2) Ontario MOE = Ontario Ministry of Environment

Quality criteria are based on overt toxicity to benthic invertebrates .

Table 20. Proportion of measurements for each site which fail the Ontario MOE 'lowest effect level' sediment quality criteria.

Indicator (Assumed limit)	Gwawley Creek	Savilles Creek	Temptation Creek
total phosphorus (600 ppm)	15	0	0
<i>(134 ppm)</i>	<i>81</i>	<i>33</i>	<i>0</i>
copper (25 ppm)	23	0	0
zinc (110 ppm)	19	0	0
cadmium (1 ppm)	8	11	4
lead (31 ppm)	81	22	0

Values in italics represent the proportion which exceeded the Clements (1983) upper TP value (134ppm) for Hawkesbury Sandstone soils of the Sydney Basin.

- the results nevertheless provide an indication of the frequency of unacceptable sediment quality in these streams.

Gwawley Creek sediments were found to be of the poorest quality with significant percentages in excess of the specified limits being observed for all metals (including cadmium) and phosphorus. For one sample (SS3, sample collection 11) the total phosphorus concentration ($2212 \mu\text{g g}^{-1}$) was also in excess of the 'limit of tolerance level' (Baudo *et al.*, 1990). With the exception of lead, however, these percentages were heavily influenced by consistently excessive levels in samples from sample station 1.

Results for Savilles Creek sediments indicated lead and cadmium levels may cause problems from time to time, while from Temptation Creek one sample had a concentration of cadmium greater than the recommended limit. For the two urban sites (Gwawley Creek in particular), the proportion of samples with high levels of lead was a point of concern, indicating the ubiquity of this contaminant.

It was only relevant to make an assessment of the compliance of sediment quality (spatial and temporal) for Gwawley Creek (Cu, Zn and Pb) and Savilles Creek (Pb only). For Gwawley Creek copper and zinc, the samples were spatially non-compliant (i.e. 0% compliance observed for each - see section 4.3.2.6), a reflection of the low incidence of poor quality for sediments of Gwawley Creek sample stations 2 and 3. For lead, values of 50% (GC) and 33% (SC) were observed.

Because of the regularly high concentrations of heavy metals at sample station 1 of Gwawley Creek, temporal compliance was apparent. For instance, every sample from this station contained a concentration of lead which exceeded the assumed quality criterion of 31ppm.

In order to relate the phosphorus levels to values for Sydney Hawkesbury Sandstone soils (and sediments), 'normal' concentrations have been obtained from Clements (1983). The author is unaware of any similar data for heavy metals. Williams and Raupach (1983) stated that nitrogen content ranges from 100 to 8000ppm in the surface horizon of normal Australian mineral soils, the majority having less than 2000ppm. The values in Table 19 thus remain comparable for this parameter.

Clements (1983) provided a list of soil characteristics for an extensive range of samples collected throughout the Sydney Basin. Total phosphorus concentrations in soils based on the parental rock type of Hawkesbury Sandstone ranged from 19 to 134ppm. Assuming this upper value of 134ppm as the sediment quality criterion, the percentage of

measurements which exceeded such a level were markedly increased for both Gwawley and Savilles Creeks. All samples from GC1 were in excess of 134ppm, showing maximum temporal compliance, while the other two stations did so for 78 and 62% of samples, respectively. For Savilles Creek, the three stations exceeded the 134ppm criterion in 22, 33 and 44% of samples, respectively. Spatial compliance was now greater at 56% for Gwawley Creek and 11% for Savilles Creek.

The results (as per Table 20) for Temptation Creek remain unchanged, reflecting the low phosphorus concentrations in the sediments of this system. In fact certain samples (i.e. sample collections 6, 7, 9 and 10) displayed values below the minimum level (19ppm) reported by Clements (1983) - see appendix table A13.

4.3.3.3 Heavy Metal Speciation

On only one occasion was cadmium detected, that being for a hydrous metal oxide fraction from Temptation Creek SS2 - see appendix table A13. For copper, zinc and lead, the sums of the four speciated fractions were compared with the corresponding total determination. The entire data sets were pooled (i.e. all three sites, making 80 replicates) for correlation and ANOVA. Results are presented in Table 21 and indicate recovery by the speciation technique was more than satisfactory - the observed correlation coefficients being highly significant at the 0.01 probability level and no significant differences between each of the two respective groups were observed. The mean sum of speciated metal was slightly lower than the mean direct total for all three metals, but less than 100% recovery was to be expected considering a four step extraction was involved.

Table 21. Results of correlation and ANOVA between sediment total and sum of speciated heavy metal concentrations ($\mu\text{g g}^{-1}$).

Metal	Mean sediment total	Mean sum speciated	Pearson correlation coefficient	ANOVA p value
copper	8.96 (12.6)	8.10 (13.1)	0.975	0.675
zinc	33.3 (39.5)	32.7 (39.5)	0.962	0.925
lead	30.5 (39.4)	28.8 (41.6)	0.968	0.792

$p < 0.01$; number of replicates, $n = 80$; the value in brackets is the corresponding standard deviation

Figure 27 plots the mean fraction concentrations for the three urban creeks. Despite the low levels for Temptation Creek samples (often below detectable limits), similar trends in metal speciation were depicted, especially for zinc, making the reference site useful in illustrating the phase-preference that the metals exhibit.

For copper, the major component (>50% of the total sum) was in the organic matter and sulfide phase. As pointed out by Martin *et al.* (1987), normally such sequential extractions do not allow the separation of organic fractions from sulfidic ones. However, the sediments here are surficial, usually well aerated and low in sulfur-containing minerals, so it is unlikely that sulfides are present to any great extent, thus suggesting that organic matter is the copper source. Residual metal was also a substantial phase (approximately 30% of the total), but only a small amount of metal was associated with hydrous metal oxides (approximately 15%).

Partitioning of zinc and lead were generally similar. This has also been reported by Sinclair *et al.* (1989), Batley (1987) and Hart and Davies (1978). Both these metals were concentrated in the hydrous metal oxide fraction, lead particularly so (60% for Zn; 70% for Pb), highlighting the importance of this phase for these metals. In the case of zinc, the next most important phase was the residual component (22%), followed by that which was associated with organic matter (12-15%). For lead, there appeared to be an almost equal partitioning between these two phases (approximately 10% each).

For all metals, the rapidly exchangeable component was virtually negligible (<10%), consistent with the low fines content and CEC of these sediments. Nevertheless, concentrations of heavy metal in this fraction were higher in the urban creeks (e.g. $p=0.040$ from ANOVA between pooled zinc data from the urbanised creeks and TC zinc data, although variances were heterogeneous; both rapidly exchangeable copper and lead were constantly below detectable limits in Temptation Creek). In addition, analysis of variance detected no significant differences between Gwawley and Savilles Creeks for each metal ($p=0.639$ for Cu; $p=0.284$ for Zn; $p=0.092$ for lead).

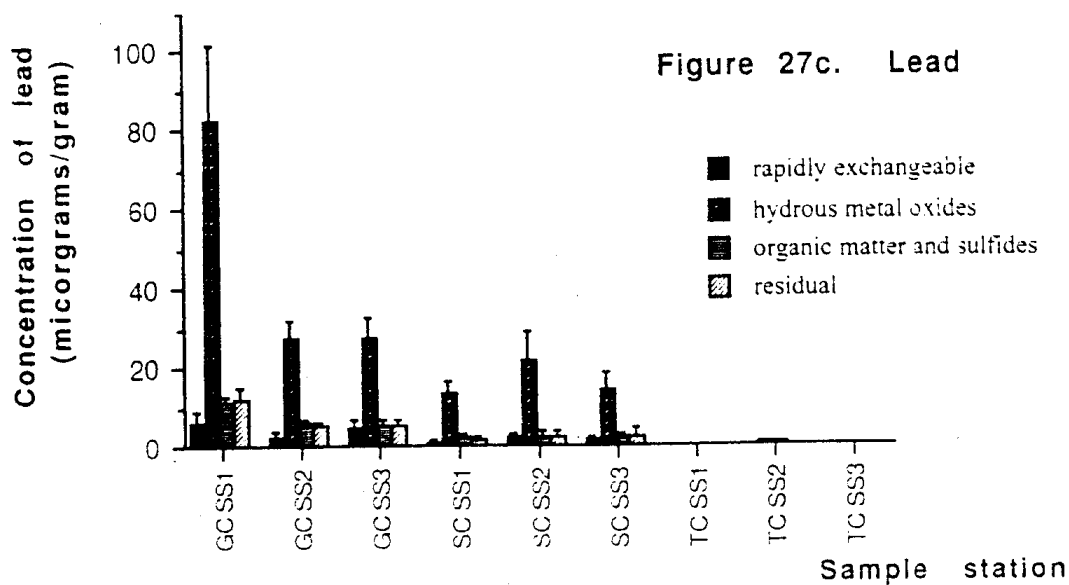
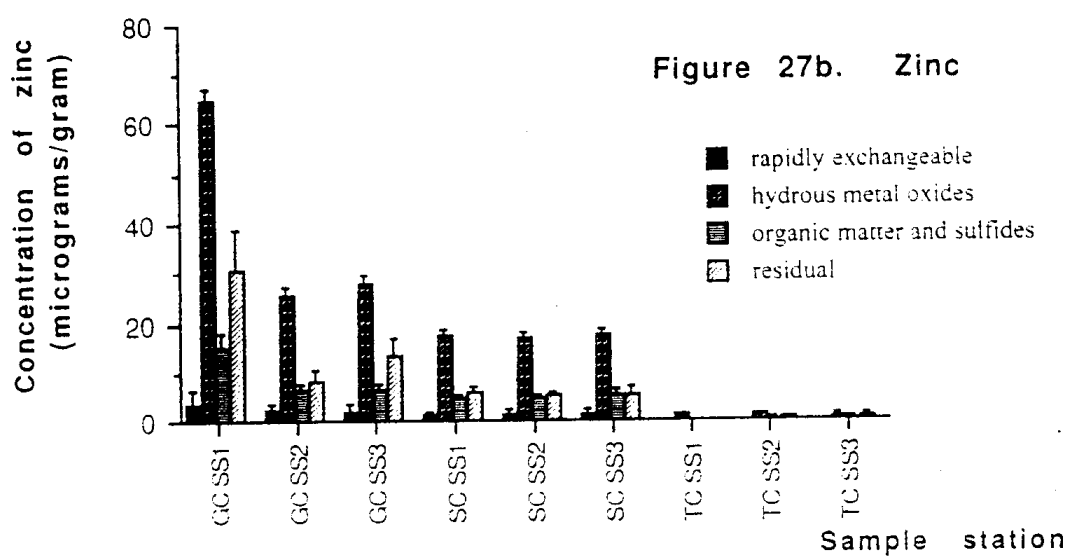
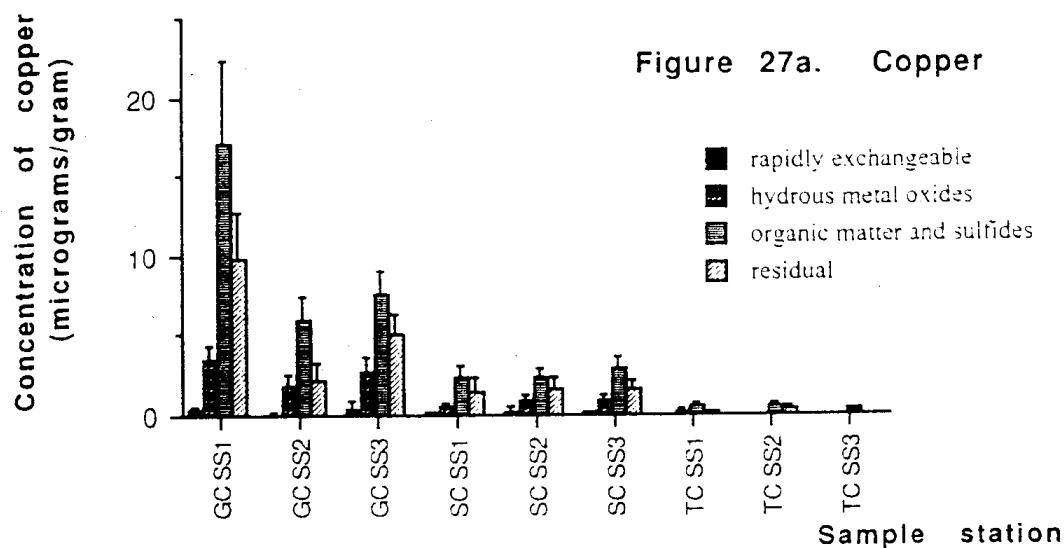


Figure 27. Mean concentrations from heavy metal speciation studies of urban creek sediments. (Error bars are the standard errors)

4.3.4 Associations Between Chemical Variables

Correlation analysis enabled identification of the associations (linear) between chemical variables in the three creeks. Pooled data were analysed and matrices of Spearman coefficients were generated from three sequential analyses (utilising the 'pairwise deletion' option) as follows :

- all available data
- combined Gwawley Ck. and Savilles Ck. data (i.e. TC data removed)
- Temptation Ck. data (i.e. GC and SC data removed).

GC+SC is used to indicate the results for pooled data from the urbanised sites. Significance was assessed at the 5% level, unless otherwise stated. Critical values of the Spearman rank correlation coefficient (r_s) were obtained from Zar (1984).

4.3.4.1 Surface Water Chemistry

Significant correlations (all data : 0.485 (n=108); GC+SC data : 0.430 (n=72)) of dissolved ortho-phosphate and total phosphorus were observed, except for the Temptation Creek data. Total phosphorus and zinc were significantly correlated (all data : 0.387 (n=108); GC+SC data : 0.241 (n=72); TC data : 0.451 (n=36)), although zinc and ortho-phosphate were not. Between the heavy metals, only copper and lead were significantly correlated (all data : 0.303 (n=108); GC+SC data : 0.328 (n=72)), but again not for the Temptation Creek data. However, both these metals were usually not detected at Temptation Creek.

Discharge, temperature and dissolved oxygen were all poorly correlated with heavy metal and total phosphorus levels, negative coefficients often occurring. For dissolved ortho-phosphate, no correlation with discharge or DO was observed. However, significant positive coefficients were seen with temperature (all data : 0.360 (n=99); GC+SC data : 0.477 (n=66); TC data : 0.367 (n=33)), suggesting that as water temperature was raised, so were rates of decomposition, leading to increased phosphorus concentrations in the water.

Suspended solids was significantly correlated with total phosphorus (all data : 0.474 (n=105), GC+SC data : 0.495 (n=69), TC data : 0.406 (n=36)), as expected. No significant correlation with any of the dissolved metals or ortho-phosphate was obtained, however.

Significant coefficients involving conductivity and hardness, were only observed on analysing the combined Gwawley Creek and Savilles Creek data. For conductivity (n=72), significant negative coefficients with ortho-phosphate (-0.476), total phosphorus (-0.260) and zinc (-0.302) were seen. For hardness, a significant negative correlation with ortho-phosphate was obtained (-0.467, n=72). For alkalinity, acidity, pH and reduction/oxidation potential, a number of significant coefficients were observed. These are presented in Table 22(i-iii).

4.3.4.2 Interstitial Water Chemistry

For the interstitial water chemistry, the only correlations of significance amongst ortho-phosphate and the heavy metals were between copper and lead (all data : 0.453 (n=81), GC+SC data : 0.465 (n=54)). This reflected those obtained for the surface water data. Results for correlation of interstitial water temperature, conductivity and hardness with the corresponding dissolved ortho-phosphate and heavy metal concentrations reflected those previously described for the surface water chemistry. Coefficients for the remaining variables, including dissolved oxygen, are presented in Table 23(i-iii).

Dissolved oxygen was positively correlated with dissolved zinc concentration, while DO and copper were correlated in combined Gwawley and Savilles Creek data. This result for zinc was consistent with the significant correlations from the first two analyses involving redox potential. Apart from the DO-Cu relationship in the urban creek data, copper and lead appeared to differ from zinc - compare the correlations involving acidity and pH. Only with alkalinity were all three metals associated in the same manner (i.e. negative correlations). It was also interesting that significant correlations involving metals with alkalinity and acidity occurred for the urban creek data, but not for the corresponding Temptation Creek data.

Interstitial ortho-phosphate was poorly associated with most variables. A significant correlation with acidity was observed, however - the negative coefficients being consistent with results involving the combined urban creek surface water data.

Table 22(i). Spearman correlation coefficients for surface water alkalinity, acidity, pH and redox with heavy metals and phosphorus; total data set.

SW variable	Alkalinity	Acidity	pH	Redox
dissolved o-phosphate	0.285	-0.002	0.284	0.251
total P	0.238	0.238	0.394	0.313
dissolved Cu	0.045	-0.003	-0.123	-0.275
dissolved Zn	0.018	0.269	0.073	0.024
dissolved Pb	0.068	-0.126	0.052	0.008
	n=108	n=99	n=108	n=99

p<0.05; significant correlations in bold

Table 22(ii). Spearman correlation coefficients for surface water alkalinity, acidity, pH and redox with heavy metals and phosphorus; GC and SC data.

SW variable	Alkalinity	Acidity	pH	Redox
dissolved o-phosphate	-0.448	-0.336	0.191	0.502
total P	-0.270	0.008	0.105	0.466
dissolved Cu	0.130	0.130	-0.084	-0.266
dissolved Zn	-0.235	0.304	-0.136	0.067
dissolved Pb	-0.094	-0.097	0.152	0.140
	n=72	n=66	n=72	n=66

p<0.05; significant correlations in bold

Table 22(iii). Spearman correlation coefficients for surface water alkalinity, acidity, pH and redox with heavy metals and phosphorus; TC data.

SW variable	Alkalinity	Acidity	pH	Redox
dissolved o-phosphate	0.505	-0.131	0.261	0.389
total P	0.337	0.254	0.622	0.562
dissolved Cu	-0.183	-0.146	-0.136	-0.393
dissolved Zn	-0.168	0.104	0.161	0.288
dissolved Pb	0.128	-0.218	-0.112	-0.432
	n=36	n=33	n=36	n=33

p<0.05; significant correlations in bold

Table 23(i). Spearman correlation coefficients for interstitial water dissolved oxygen, alkalinity, acidity, pH and redox with heavy metals and phosphorus; total data set.

IW variable	DO	Alkalinity	Acidity	pH	Redox
dissolved o-phosphate	-0.116	0.152	-0.409	0.054	-0.110
dissolved Cu	0.220	-0.137	-0.259	0.164	-0.048
dissolved Zn	0.419	-0.290	0.333	0.177	0.248
dissolved Pb	0.122	-0.160	-0.211	0.358	-0.118
	n=74	n=76	n=68	n=80	n=72

p<0.05; significant correlations in bold

Table 23(ii). Spearman correlation coefficients for interstitial water dissolved oxygen, alkalinity, acidity, pH and redox with heavy metals and phosphorus; GC and SC data.

IW variable	DO	Alkalinity	Acidity	pH	Redox
dissolved o-phosphate	-0.096	-0.182	-0.539	-0.086	-0.180
dissolved Cu	0.315	-0.444	-0.386	0.119	-0.006
dissolved Zn	0.368	-0.438	0.301	-0.308	0.386
dissolved Pb	0.156	-0.412	-0.198	0.278	-0.192
	n=50	n=53	n=48	n=53	n=48

p<0.05; significant correlations in bold

Table 23(iii). Spearman correlation coefficients for interstitial water dissolved oxygen, alkalinity, acidity, pH and redox with heavy metals and phosphorus; TC data.

IW variable	DO	Alkalinity	Acidity	pH	Redox
dissolved o-phosphate	-0.185	0.350	-0.407	0.031	-0.013
dissolved Cu	-0.084	-0.097	-0.080	0.079	-0.269
dissolved Zn	0.565	-0.133	0.430	-0.213	0.123
dissolved Pb	0.027	-0.166	-0.399	0.393	-0.067
	n=24	n=23	n=20	n=27	n=24

p<0.05; significant correlations in bold

4.3.4.3 Sediment and Interstitial Water Chemistry

Including all the available data, significant positive correlations were observed between the sediment heavy metal and phosphorus totals and interstitial water conductivity, alkalinity, acidity and hardness - the largest values being with hardness (Table 24(i)). In contrast, pH and redox potential were poorly correlated with sediment totals, apart from a weak correlation of pH and total phosphorus.

Excluding acidity, this pattern was virtually reversed on performing the analysis without Temptation Creek data (Table 24(ii)), pH and redox becoming significantly correlated (with the exception of pH and total P). Largest values were seen for redox potential, while the coefficients were negative for pH and total content of metal.

Analysis of Temptation Creek data remained generally similar for conductivity, alkalinity and hardness, but differences occurred once more for pH and redox (Table 24(iii)). It was concluded that overall, these latter two variables appeared to have greater influence on copper and phosphorus, compared with zinc and lead. The correlation of pH and sediment total phosphorus was highly significant at this site ($p < 0.005$) and probably accounted for the similar result when all data were pooled.

Only acidity was consistent throughout all three creeks. All pairs of variables were positively correlated and the only two coefficients which were not significant were with phosphorus and zinc for the TC data.

Acidity in these three creeks is likely to be controlled by the content of various organic acids (e.g. fulvic and humic acids), which are of course derived from the available organic matter (Schnitzer, 1971). To verify this, correlation between water acidity (surface and interstitial) and organic carbon identified positive coefficients, significant at the 0.005 level at least (Table 25). Furthermore, given the extremely low amounts of sediment organic carbon that were detected, it is consistent that acidity values were correspondingly low for the water samples.

Table 24(i). Spearman correlation coefficients for interstitial water parameters and sediment heavy metals and phosphorus; total data set.

Sediment	total	Conductivity	Alkalinity	Acidity	Hardness	pH	Redox
P		0.560	0.525	0.432	0.716	0.305	-0.048
Cu		0.307	0.485	0.507	0.594	-0.003	0.214
Zn		0.451	0.528	0.387	0.662	0.130	0.100
Pb		0.442	0.560	0.447	0.690	0.056	0.137
		n=79	n=75	n=67	n=80	n=79	n=71

p<0.05; significant correlations in bold

Table 24(ii). Spearman correlation coefficients for interstitial water parameters and sediment heavy metals and phosphorus; GC and SC data.

Sediment	total	Conductivity	Alkalinity	Acidity	Hardness	pH	Redox
P		0.120	0.212	0.555	0.276	-0.025	0.310
Cu		-0.177	0.191	0.548	0.174	-0.306	0.495
Zn		-0.156	0.183	0.502	0.134	-0.352	0.533
Pb		-0.082	0.234	0.545	0.235	-0.413	0.535
		n=52	n=52	n=47	n=53	n=52	n=47

p<0.05; significant correlations in bold

Table 24(iii). Spearman correlation coefficients for interstitial water parameters and sediment heavy metals and phosphorus; TC data.

Sediment	total	Conductivity	Alkalinity	Acidity	Hardness	pH	Redox
P		0.472	-0.040	0.191	0.274	0.562	-0.461
Cu		-0.130	0.519	0.837	-0.051	-0.530	0.417
Zn		0.095	-0.130	0.178	-0.044	0.116	-0.012
Pb		-0.056	0.385	0.489	0.068	-0.353	0.243
		n=27	n=23	n=20	n=27	n=27	n=24

p<0.05; significant correlations in bold

Table 25. Spearman correlation coefficients for water acidity and sediment organic carbon.

Data pooled	surface water	interstitial water
all data	0.681 $p < 0.001$; $n = 71$	0.611 $p < 0.001$; $n = 67$
GC + SC	0.665 $p < 0.001$; $n = 47$	0.582 $p < 0.001$; $n = 47$
TC	0.632 $p < 0.002$; $n = 24$	0.652 $p < 0.005$; $n = 20$

Correlation of sediment metal and phosphorus totals with the corresponding dissolved levels in interstitial water samples, identified significant coefficients for only zinc and phosphorus (Table 26(i-iii)). Although for both constituents the values were low (< 0.500), indicating at best only weak correlations, the results still suggest that only zinc was equilibrating between the sediment and interstitial water phases, while phosphorus was either in the sediment or in the interstitial water, hence exhibiting near-complete transfer.

4.3.4.4 Sediment Chemistry

For the total data set, parameters providing a total measure in the sediment (i.e. organic carbon, total phosphorus, copper, zinc and lead), as well as the silt + clay fraction, were all positively and significantly correlated, although very high values were observed only for the associations amongst the metals and phosphorus (Table 27(i)). Only total zinc and lead were significantly correlated with the sediment cation exchange capacity, while only lead showed significant correlations with the two sand fractions. In both cases, however, the values were not large (< 0.500).

Differences in the overall result (i.e. fewer significant correlations) occurred when the analysis was performed without the Temptation Creek data (Table 27(ii)). Sediment heavy metals, phosphorus and organic matter still had significant and positive correlations, although total phosphorus was no longer correlated with the organic carbon content. Correlation of organic phosphorus with both these parameters also yielded non-significant coefficients (0.041 with organic C; 0.016 with total P). These results are

Table 26(i). Spearman correlation coefficients for interstitial water and sediment heavy metals and phosphorus; total data set.

Interstitial water variable	Sediment variable	Coefficient
diss. ortho-phosphate	total P	0.051
dissolved Cu	total Cu	0.193
dissolved Zn	total Zn	0.317
dissolved Pb	total Pb	0.084

p<0.05; n=80; significant correlations in bold

Table 26(ii). Spearman correlation coefficients for interstitial water and sediment heavy metals and phosphorus; GC and SC data.

Interstitial water variable	Sediment variable	Coefficient
diss. ortho-phosphate	total P	-0.414
dissolved Cu	total Cu	-0.102
dissolved Zn	total Zn	0.317
dissolved Pb	total Pb	-0.268

p<0.05; n=53; significant correlations in bold

Table 26(iii). Spearman correlation coefficients for interstitial water and sediment heavy metals and phosphorus; TC data.

Interstitial water variable	Sediment variable	Coefficient
diss. ortho-phosphate	total P	-0.462
dissolved Cu	total Cu	-0.195
dissolved Zn	total Zn	0.338
dissolved Pb	total Pb	-0.167

p<0.05; n=27; significant correlations in bold

Table 27(i). Spearman correlation matrix for selected sediment parameters;
total data set.

	organic carbon	P	Cu	Zn	Pb	CEC	coarse sand	fine sand	silt + clay
organic carbon	1.000	0.485	0.626	0.589	0.649	0.186	-0.137	0.123	0.482
phosphorus		1.000	0.810	0.847	0.787	0.254	-0.146	0.151	0.379
copper			1.000	0.886	0.846	0.251	-0.112	0.132	0.381
zinc				1.000	0.901	0.443	-0.218	0.209	0.460
lead					1.000	0.441	-0.342	0.347	0.614
CEC						1.000	-0.584	0.505	0.584
coarse sand							1.000	-0.974	-0.764
fine sand								1.000	0.726
silt + clay									1.000

p<0.05; n=80 for all chemical variables, n=36 for the four physical characteristics; significant correlations in bold

Table 27(ii). Spearman correlation matrix for selected sediment parameters;
GC and SC data.

	organic carbon	P	Cu	Zn	Pb	CEC	coarse sand	fine sand	silt + clay
organic carbon	1.000	0.266	0.457	0.405	0.502	0.006	-0.003	-0.035	0.436
phosphorus		1.000	0.675	0.564	0.449	-0.255	0.259	0.241	0.157
copper			1.000	0.817	0.700	-0.178	0.257	-0.235	0.127
zinc				1.000	0.778	0.079	0.212	-0.234	0.188
lead					1.000	0.108	-0.096	0.113	0.415
CEC						1.000	-0.247	0.064	0.347
coarse sand							1.000	-0.956	-0.716
fine sand								1.000	0.625
silt + clay									1.000

p<0.05; n=80 for all chemical variables, n=36 for the four physical characteristics; significant correlations in bold

Table 27(iii). Spearman correlation matrix for selected sediment parameters; TC data.

	organic carbon	P	Cu	Zn	Pb	CEC	coarse sand	fine sand	silt + clay
organic carbon	1.000	-0.066	0.746	0.318	0.546	-0.643	0.629	-0.545	-0.259
phosphorus		1.000	0.042	0.584	0.201	-0.550	0.518	-0.585	-0.609
copper			1.000	0.155	0.651	-0.862	0.850	-0.696	-0.448
zinc				1.000	0.299	-0.414	0.381	-0.444	-0.414
lead					1.000	-0.218	0.218	-0.044	-0.044
CEC						1.000	-0.951	0.902	0.601
coarse sand							1.000	-0.951	-0.755
fine sand								1.000	0.699
silt + clay									1.000

p<0.05; n=80 for all chemical variables, n=36 for the four physical characteristics; significant correlations in bold

consistent with the hypothesis that most of the sediment phosphorus is in inorganic forms and shows minimal association with organic matter.

The sediment physical characteristics of CEC and silt + clay both showed much less association with the chemical parameters in this case. In fact, only organic carbon and lead concentration remained significantly correlated with the silt + clay content. There was also no association between these two variables which are normally strongly related.

A different pattern emerged again with the analysis of Temptation Creek data (Table 27(iii)). Fewer significant correlations were observed amongst the metals, phosphorus and organic carbon, indicating that different association mechanisms occur in the urbanised and non-urbanised creeks, although zinc and phosphorus seem to follow similar mechanisms in all three cases. However, a larger number of significant correlations involving the sediment physical characteristics were apparent.

For the three data sets used, the concentrations of heavy metals in the hydrous metal oxide, organic matter plus sulfide and residual fractions were usually significantly correlated (positive values) with the corresponding metal totals. The rapidly exchangeable zinc and lead fractions were significantly correlated with the respective totals for the complete pooled data set, but not for either combined Gwawley Ck. and Savilles Ck. data, or Temptation Creek data. Rapidly exchangeable copper showed no significant association with sediment totals at all.

4.3.5 Chemical Variability

In order to assess and compare natural chemical variability (both spatial and temporal) within and between the three sites, nonmetric multidimensional scaling (MDS) to two dimensions was performed using various combinations of selected parameters. The multivariate technique also enabled assessment of whether the factor of season affected this variability.

The chosen surface water parameters included conductivity, DO, pH, redox, alkalinity, acidity, dissolved ortho-phosphate, dissolved copper, zinc and lead, and suspended solids. MDS involving mean values included average dissolved nitrate as well.

The same set of variables was used from the interstitial water chemistry, excepting of course suspended solids and nitrate. Likewise on combining surface and interstitial waters, these two parameters were omitted.

Sediment variables included organic carbon and the total measures for phosphorus, copper, zinc and lead. MDS using mean values incorporated the average fine sand and silt + clay data.

4.3.5.1 Variability in Surface Water Chemistry

The ordination involving sample station means is presented in Figure 28. The iteration stress of the final configuration was 0.051, indicating the configuration of points represents a good fit (Kruskal, 1964a).

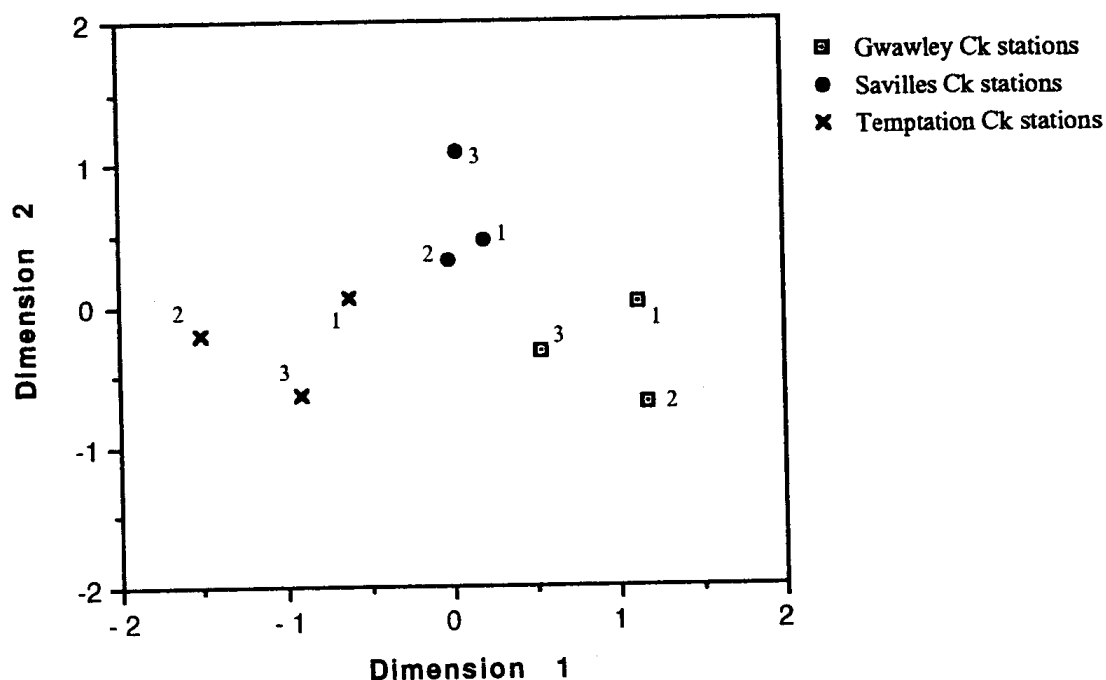


Figure 28. MDS ordination using sample station mean values of surface water chemical parameters.

The nine stations were distinctly grouped in threes by their respective sites and a gradation from reference (TC) to urban-bush (SC) to urban (GC) creek was apparent, consistent with the overall relative amounts of dissolved constituents - low (TC) to high (GC). This gradation was almost perfectly in sequence from station 1 (GC1, nominally the most polluted) to station 9 (TC3, furthest site from urban influences). Hence, in terms of overall means, the three sites had distinct chemical composition.

Compared to the other two creeks, the spatial distribution between the Temptation Creek stations was greatest, indicating highest within-site variability. This was probably a consequence of using means - for Temptation Creek, where levels are normally low, the incidence of one or two high values can greatly influence the overall average. The separation between the Savilles Creek stations was lowest, stations 1 and 2 being very similar.

An ordination using individual samples was based on the following replicates (74), after exclusion of those with missing data :

Sample collections 1, 2, 4, 5, 6, 7, 8, 9, 10 for GC1-3

Sample collections 1, 2, 4, 7, 8, 9, 10 for SC1

Sample collections 1, 2, 4, 5, 7, 8, 9, 10 for SC2-3; TC1-3.

The configuration had an iteration stress of 0.154. On grouping the 74 points into their corresponding site and station, Figure 29 illustrates that, unlike the earlier ordination involving mean values, within-site variability was greatest for Gwawley Creek, intermediate for Savilles Creek and lowest for Temptation Creek (especially if the two outliers in Figure 29c are ignored). This is consistent with urban waterways being subjected to discharges (runoff) of highly diverse composition. At each site, no one station displayed markedly different scatter compared to the other two.

Using the data set involved, analysis of variance did not identify any significant differences between Gwawley and Savilles Creeks. Lead concentration was greater at Gwawley Creek, but the variances were not homogeneous. Temptation Creek was high in surface water oxidation-reduction potential ($p=0.029$), but low in alkalinity ($p=0.000$; logged data), dissolved ortho-phosphate ($p=0.000$; logged data) and possibly conductivity and acidity as well, however, variances were heterogeneous for the latter two.

Gwawley Creek replicates (Figure 29a) were markedly spread across Dimension 1. The triplicate of samples on the far left corresponded to sample collection 2 in each case. Apart from low alkalinities (17.8, 10.7, 11.0 mg L⁻¹ as CaCO₃, respectively), these surface waters were noted for extremely high dissolved zinc (0.13, 0.11, 0.11 mg L⁻¹), lead (24.4, 31.8, 30.4 µg L⁻¹) and ortho-phosphate (56, 46, 46 µg L⁻¹) concentrations (see appendix table A11). In contrast, the samples placed on the far right (e.g. sample collection 8; GC2, sample collection 7) all displayed high levels of alkalinity (103, 108, 103; 104 mg L⁻¹ as CaCO₃) and dissolved copper (15.7, 35.6, 32.9; 166 µg L⁻¹).

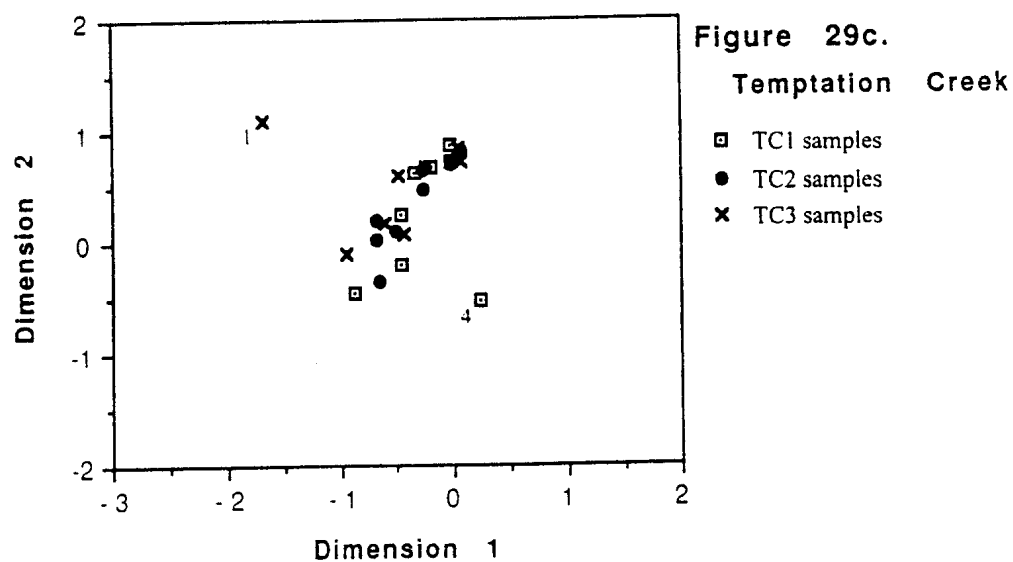
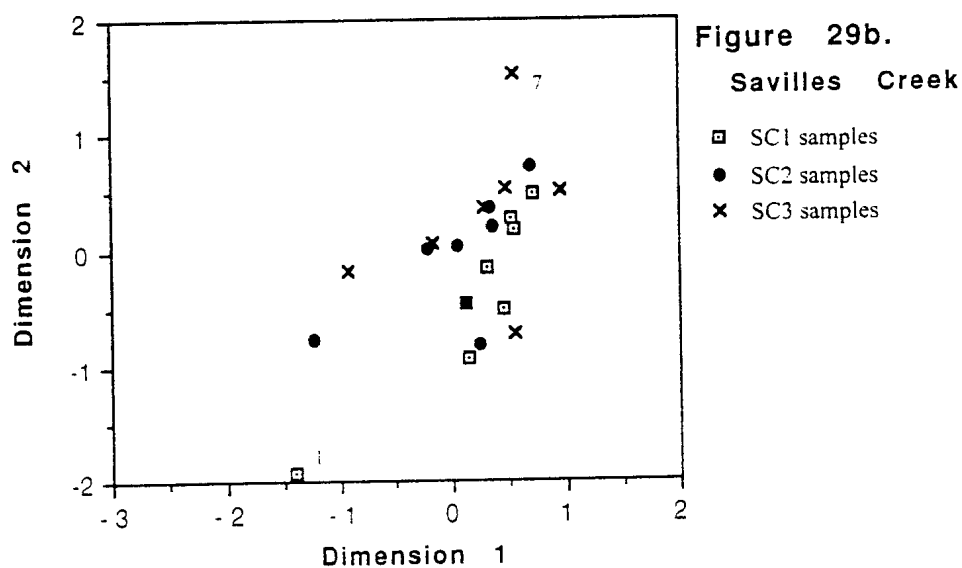
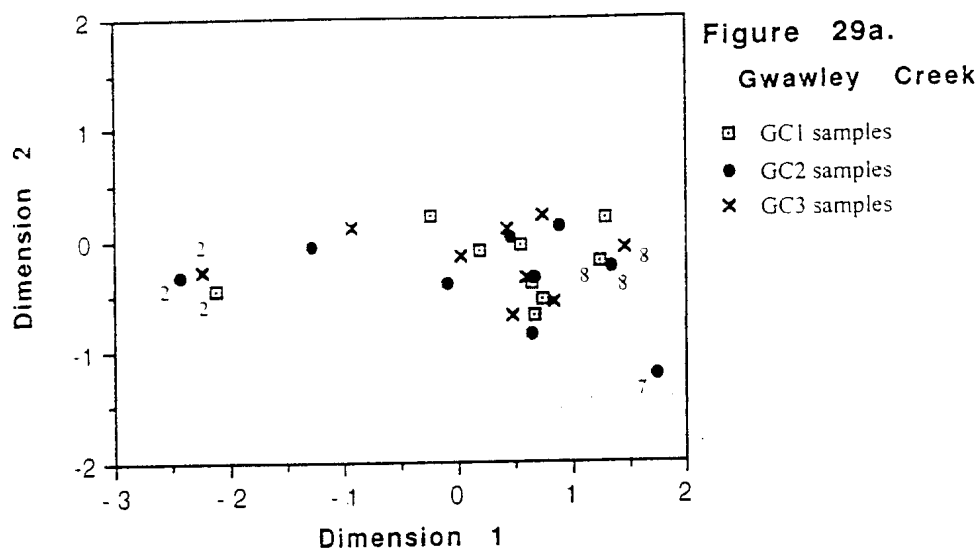


Figure 29. MDS ordination using chemical parameters from the surface waters, grouped by station. (Numbers denote particular sample collections)

The scatter of Savilles Creek samples tended to be vertical, rather than horizontal (Figure 29b). The position of the uppermost outlier (SC2, sample collection 7) was strongly influenced by high suspended solids (349 mg L^{-1}). The low outlier (SC1, sample collection 1) was characterised by very high oxidation-reduction potential (275mV) and zinc (0.50 mg L^{-1}). High zinc (0.67 mg L^{-1}) also influenced the positioning of a Temptation Creek outlier (TC3, sample collection 1; Figure 29c), along with high pH (8.8) and low alkalinity (1.8 mg L^{-1} as CaCO_3). High alkalinity (73 mg L^{-1} as CaCO_3) was a feature of the other outlier (TC1, sample collection 4). These results demonstrate that the common contaminants (i.e. heavy metals, phosphorus, suspended solids) were heavily responsible for surface water variability.

Figure 30 shows the ordination on classifying each point on the basis of season when collected (see also Table 9). Substantial spread is apparent for the winter, or wet season, samples. In comparison, the summer samples are confined to a distinct grouping.

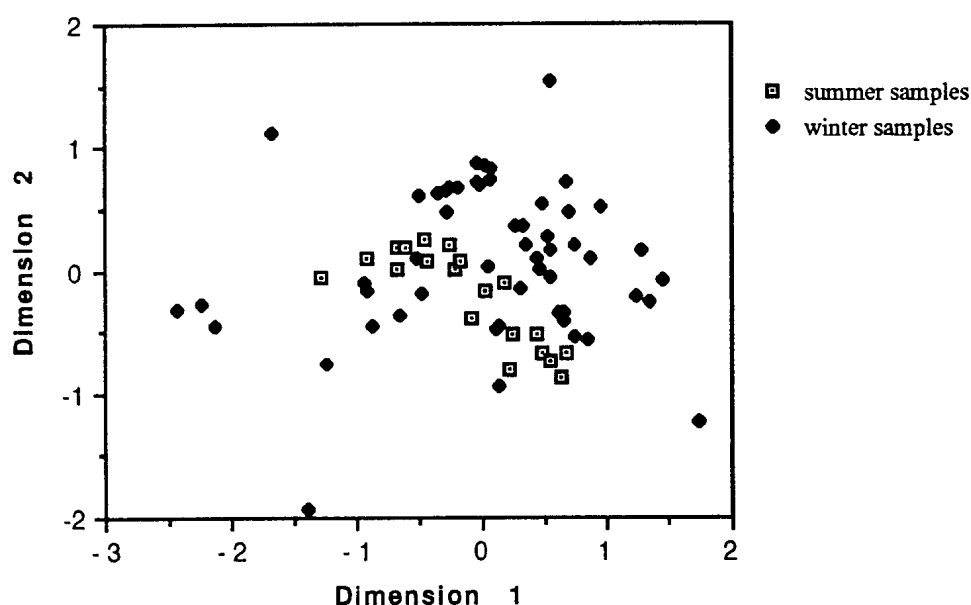


Figure 30. MDS ordination using chemical parameters from surface water samples, classified by season when collected.

ANOVA identified significant differences in oxidation-reduction potential ($p=0.020$) and dissolved oxygen ($p=0.000$; logged data) between these two groups. Winter samples were more reducing, despite a wider range of values. Dissolved oxygen, however, was

higher for the winter samples. The analysis showed a difference in acidity - winter samples showing greater levels than summer ones - but variances were not homogeneous.

4.3.5.2 Variability in Interstitial Water Chemistry

MDS of the mean interstitial water chemistry (Figure 31) produced a final iteration stress of 0.056, representing a good fit. Each triplet of stations could be grouped by the corresponding site, although the groupings were less distinct here, in contrast with the surface water ordination, since overlaps could be visualised (e.g. GC3 could be grouped with TC sites) due to wider separation of the stations. Consequently, a gradation effect was less pronounced.

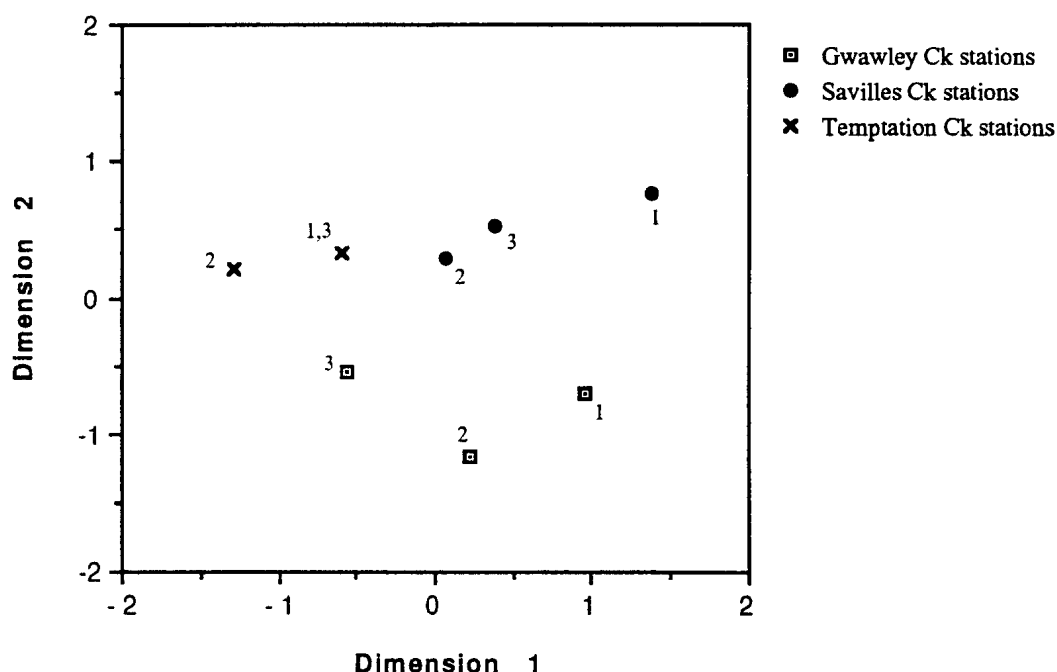


Figure 31. MDS ordination using sample station mean values of interstitial water chemical parameters.

Greatest variability in station interstitial water composition occurred within Gwawley Creek, the least within Temptation Creek - stations 1 and 3 being seen as identical. Compared to the corresponding surface water ordination (see Figure 28), Savilles Creek stations had a lower degree of proximity in this ordination, while stations 2 and 3 were

closer, rather than 1 and 2, reflecting a greater similarity in the interstitial water (and perhaps the sediment environment).

The ordination using individual samples was based on the following replicates (55) :

Sample collections 4, 5, 6, 7, 9, 10 for GC1

Sample collections 1, 4, 5, 6, 7, 9, 10 for GC2-3

Sample collections 1, 4, 5, 7, 9, 10 for SC1-3; TC1-2

Sample collections 1, 5, 7, 9, 10 for TC3.

Iteration stress of the final configuration was 0.118, providing an acceptable fit. However, an outlier, corresponding to sample collection 1 from Savilles Creek 1 (marked by very high concentrations of dissolved zinc and lead, as well as elevated copper, acidity and conductivity), resulted in aggregation of the vast majority of points. After elimination of this sample, the subsequent configuration had an increased iteration stress of 0.160, but at least an improved illustration of the spread of these samples was obtained.

On grouping these points by sampling station (Figure 32), the Gwawley Creek and Savilles Creek samples showed spatial distributions of generally similar magnitude. However, two principal clusters could be depicted - the Gwawley Creek samples being positioned towards the top left-hand corner; the Savilles Creek samples being positioned in the lower half of the plot.

Variability amongst Temptation Creek samples was again lower in comparison to the other two sites. Apart from a few points, including the low outlier, all samples were clustered in a relatively tight group, separated mostly across the horizontal axis. If superimposed onto the plots for the two other streams, the Temptation Creek samples lie almost removed from the two principal clusters mentioned above, with minimal overlapping (mostly with the Savilles Creek samples). The bottom outlier (TC1, sample collection 4) was the result of a combination of high conductivity, pH, alkalinity and lead, accompanied by very low (highly reducing) redox - the reading being -265mV, the lowest observed during the study.

Such separate clustering was not present in the equivalent surface water chemistry ordination and suggested different chemical effects between the groups. Using the data set involved, analysis of variance identified significant differences in conductivity ($p=0.000$; logged data; GC>SC>TC) and alkalinity ($p=0.000$; logged data; GC>SC>>TC) between the three sites. Redox ($p=0.022$; GC>SC), acidity ($p=0.001$;

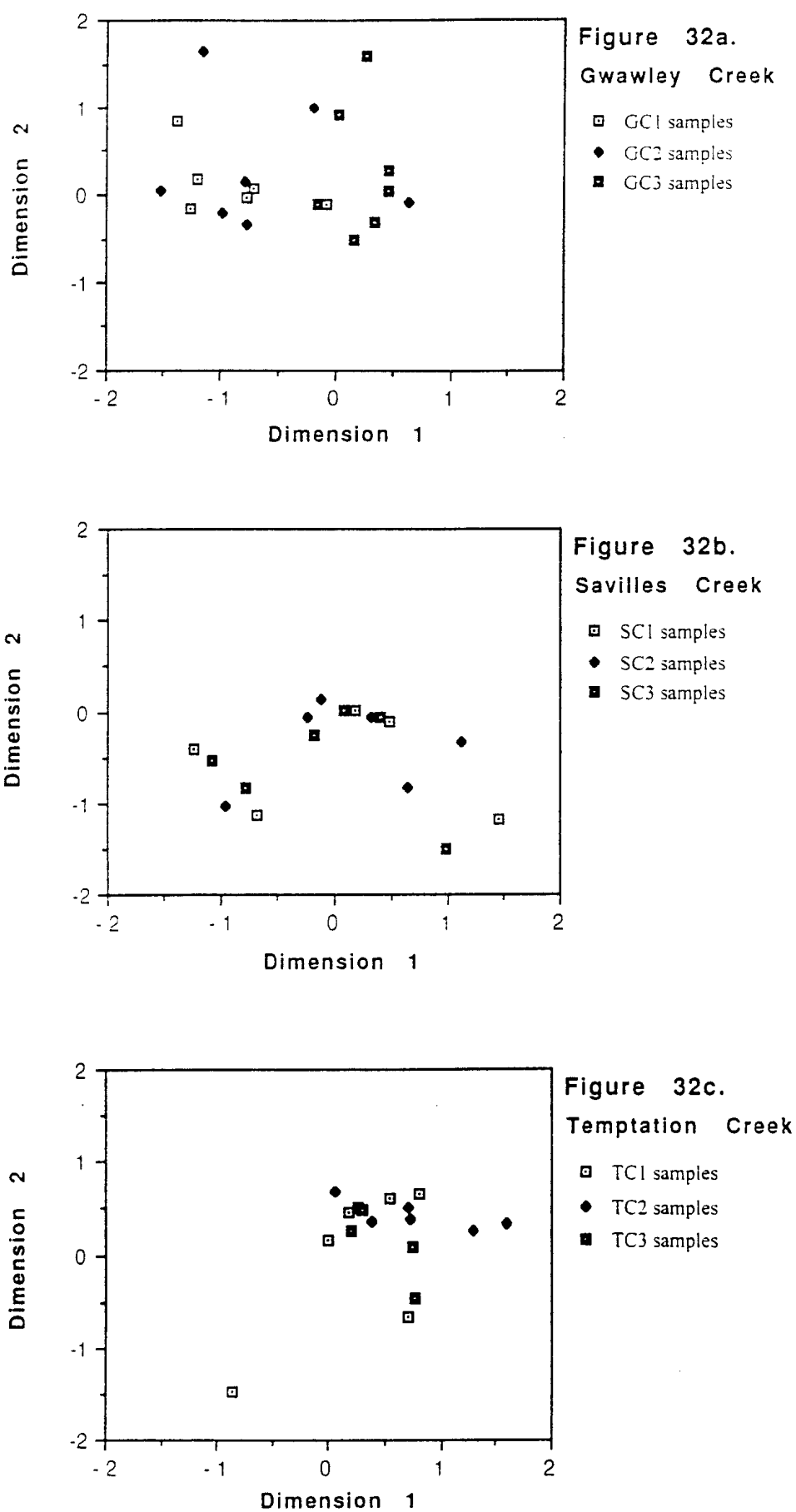


Figure 32. MDS ordination using chemical parameters from the interstitial waters, grouped by station.

logged data; $GC > SC = TC$) and pH ($SC > TC$) were also found to differ amongst certain pairs, although variances were heterogeneous for the latter. Assessment of the complete raw data (see appendix table A11) indicated dissolved ortho-phosphate and heavy metals could have lead to some displacement, since levels were usually higher in the urban sites.

Figure 33 illustrates the distribution of these samples, classified by the season they were collected. Unlike the surface waters, the scatters of summer and winter samples would appear to be equal, meaning the relative scatter of summer samples is greatly increased compared to that of the surface water.

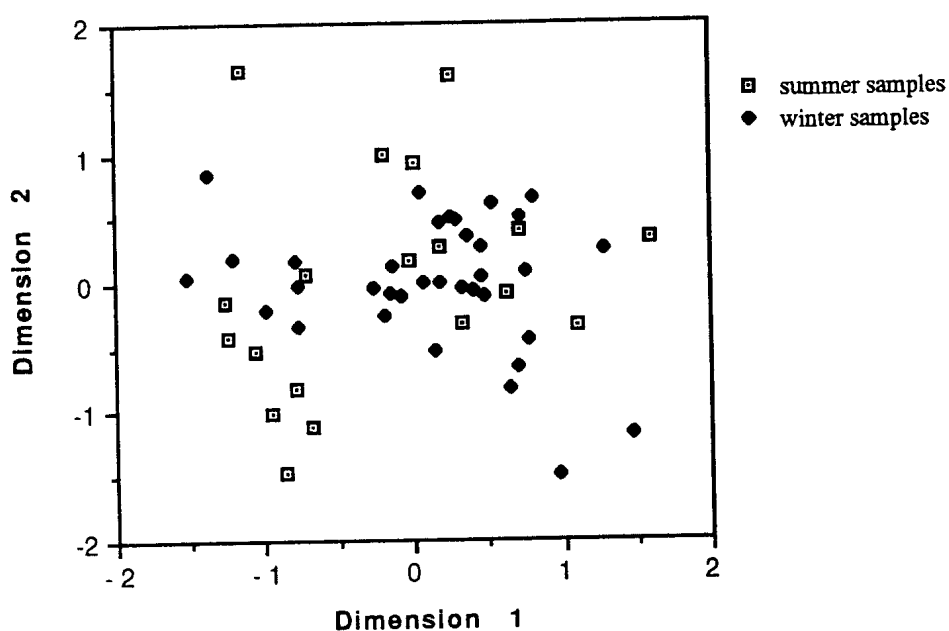


Figure 33. MDS ordination using chemical parameters from interstitial water samples, classified by season when collected.

Analysis of variance between the two groups identified that winter samples were significantly higher in DO ($p=0.000$) and also acidity ($p=0.012$; logged data). A further significant difference was observed for conductivity ($p=0.007$; logged data), whereby the summer mean was greater. A difference in dissolved ortho-phosphate was also possible - the levels in summer samples being much greater - however, variances were not homogeneous.

4.3.5.3 Comparison of the Variabilities in Surface and Interstitial Water Chemistry

The ordination involving mean values for combined surface and interstitial parameters (omitting suspended solids and nitrate) is illustrated by Figure 34. The iteration stress was 0.143.

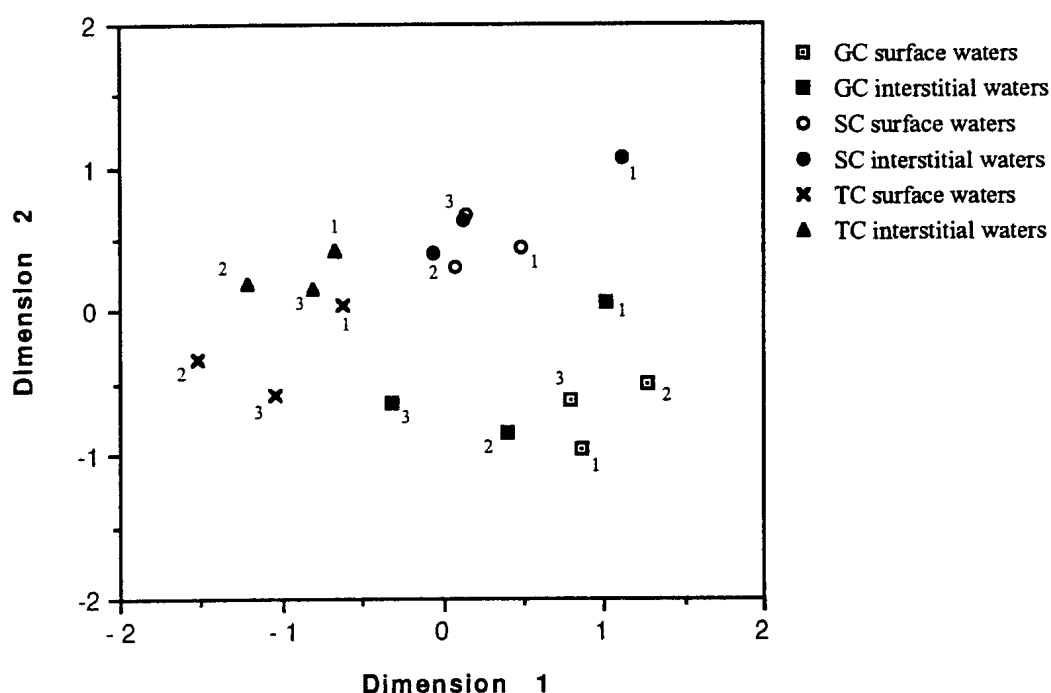


Figure 34. MDS ordination using sample station mean values of combined surface and interstitial water chemical parameters.

The plot indicated three principal groups of six points, each representing one of the creeks since all sextets were comprised of the respective surface and interstitial waters. A gradation (TC to GC) linking the groups was apparent, although best seen with the surface waters, as in the equivalent surface water ordination above (Figure 28).

For Gwawley Creek the interstitial samples were more scattered than their accompanying surface samples. Indeed, the two most separated Gwawley Creek interstitial waters (GC1 and GC3) could be re-grouped with the Savilles Creek and Temptation Creek points, respectively. In contrast, Temptation Creek surface waters showed wider

separation than the corresponding interstitial waters. For Savilles Creek, interstitial waters were also more varied than the surface waters overall, but this was mainly due to Station 1 interstitial waters. Chemistries of both water types from stations 2 and 3 were virtually identical.

In order to further compare the variabilities of these two water types, the relevant surface and interstitial water data from sample collections 5, 7, 9 and 10 were scaled individually. The ordinations are presented as Figure 35(a-d) and final iteration stresses were 0.084, 0.123, 0.050 and 0.069, respectively.

Markedly different configurations were seen, suggesting significant changes over time. Groups of stations were hard to isolate (except perhaps in the scaling of sample collection 10), but in general the surface waters were much easier to group by the corresponding creek than interstitial waters, due to considerable overlapping of the latter samples. This is best shown in Figures 35a,c and d. In these three ordinations the groups of surface waters lined up remarkably well horizontally and were ordered Gwawley Ck. to Savilles Ck. to Temptation Ck. on going from left to right. Notice too, that for Figures 35c and 35d there is almost perfect separation (vertical) of the two water types. Of the significant differences between surface and interstitial waters already listed in Tables 14 and 15, dissolved oxygen, alkalinity, redox potential and conductivity were the most likely sources of the separation. This was supported by assessment of the raw data for the sample collections concerned (appendix table A11) with widespread differences being noted for DO and alkalinity.

Except for the ordination of sample collection 7 data, interstitial waters were much more widely spread than the respective surface waters, consistent with earlier observations. This also included Temptation Creek samples here; however, on comparison with the other two sites, dissimilarities amongst both surface and interstitial waters were less each time.

Differences between the sites and stations were unlikely to be due to varying flow regimes. Conditions for these four collections would be regarded as essentially low flow, since only sample collection 5 saw a number of high flow ($\geq 31.3 \text{ cm s}^{-1}$) conditions.

The composite sample ordination, with replicates grouped by site, is illustrated by Figure 36. Due to a large data set, MDS on the Euclidean distance matrix obtained from 110 samples (i.e. 2 x 55 sample collections; see section 4.3.5.2) generated an unacceptable (>0.2) iteration stress (Kruskal, 1964a). The matrix was subsequently reduced to 72

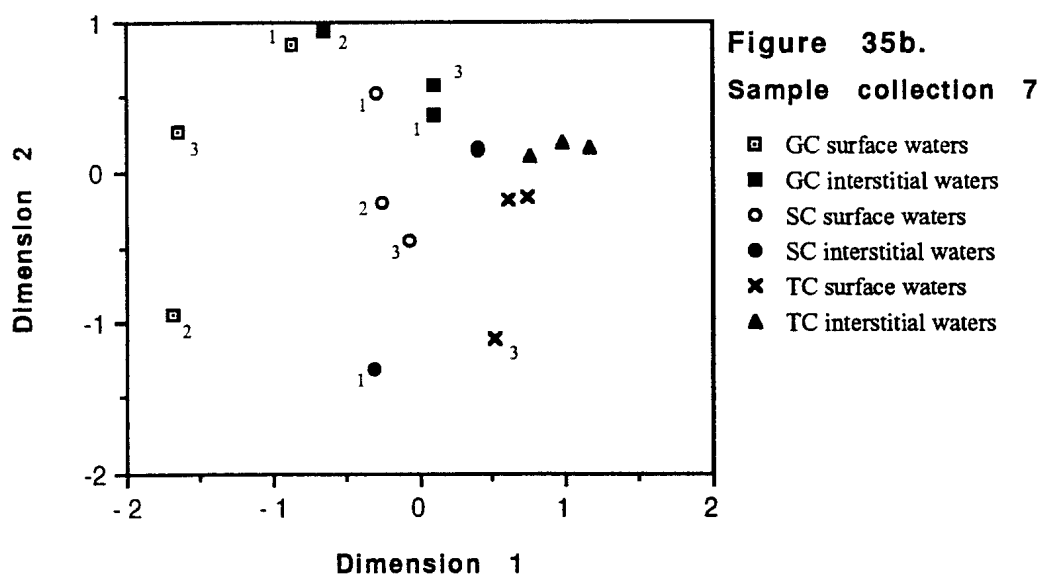
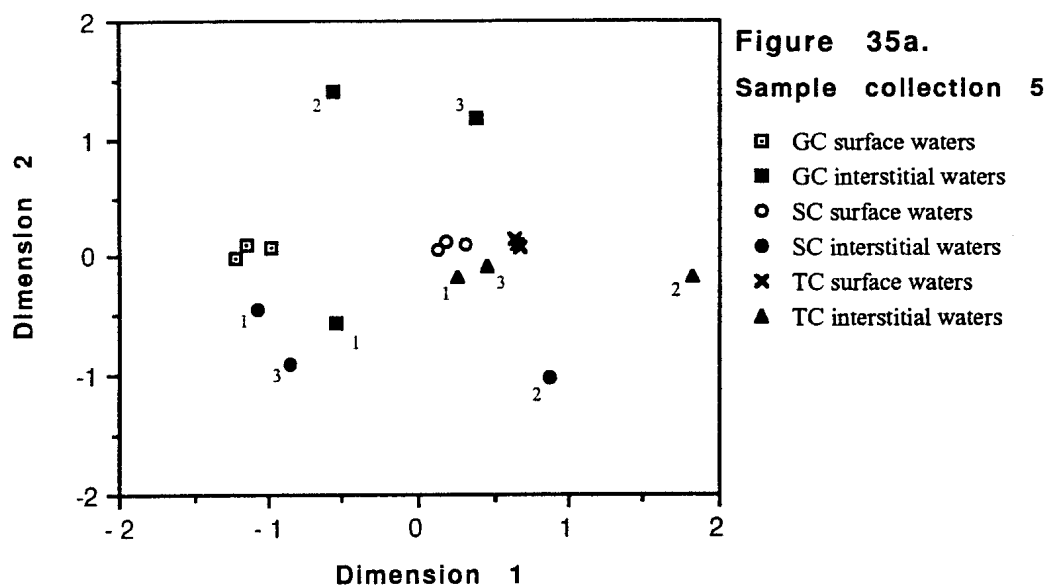


Figure 35. MDS ordinations using chemical parameters from station surface and interstitial waters of single sample collections.

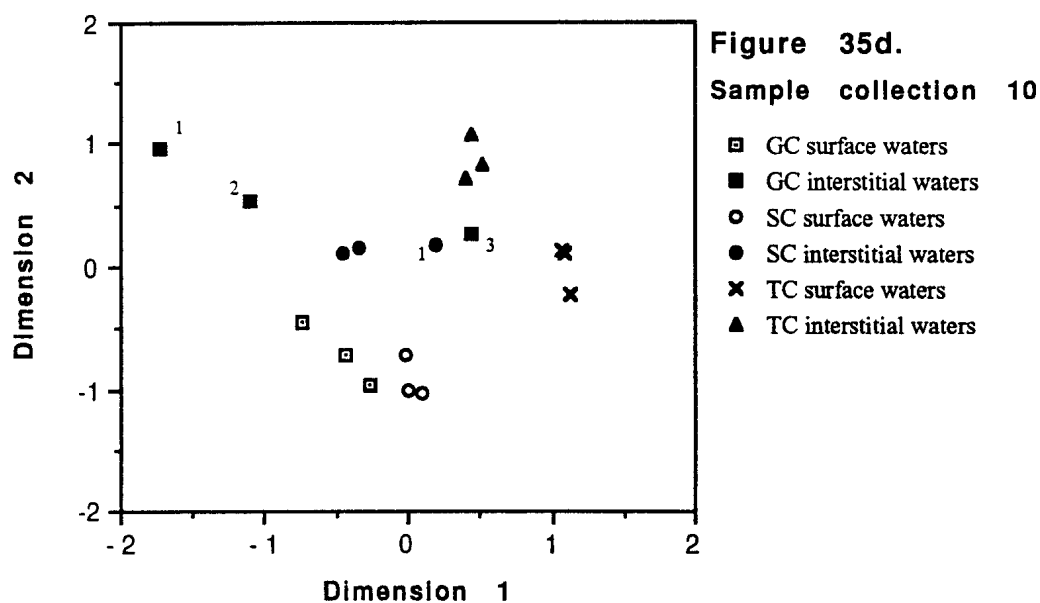
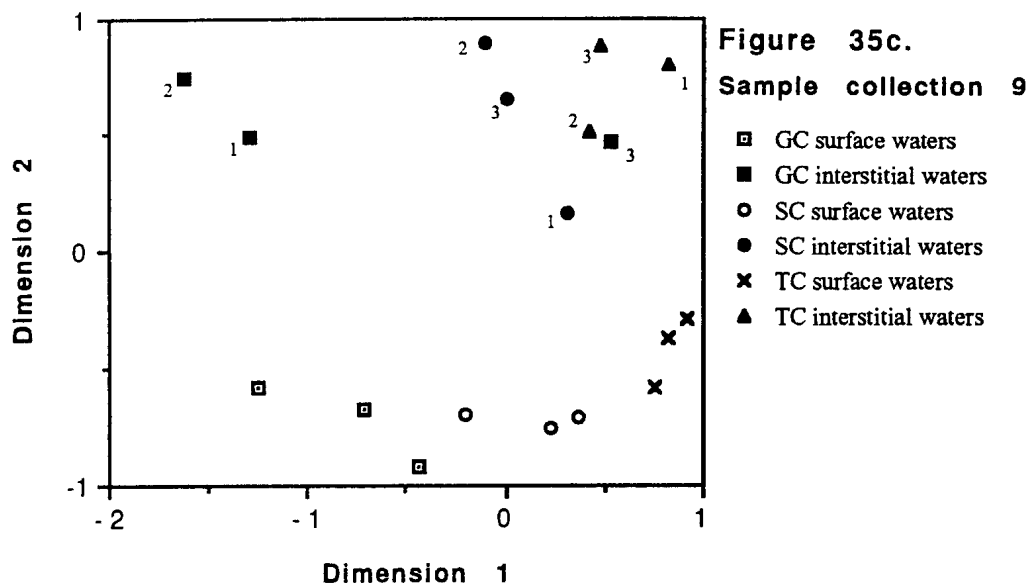


Figure 35 (continued). MDS ordinations using chemical parameters from station surface and interstitial waters of single sample collections.

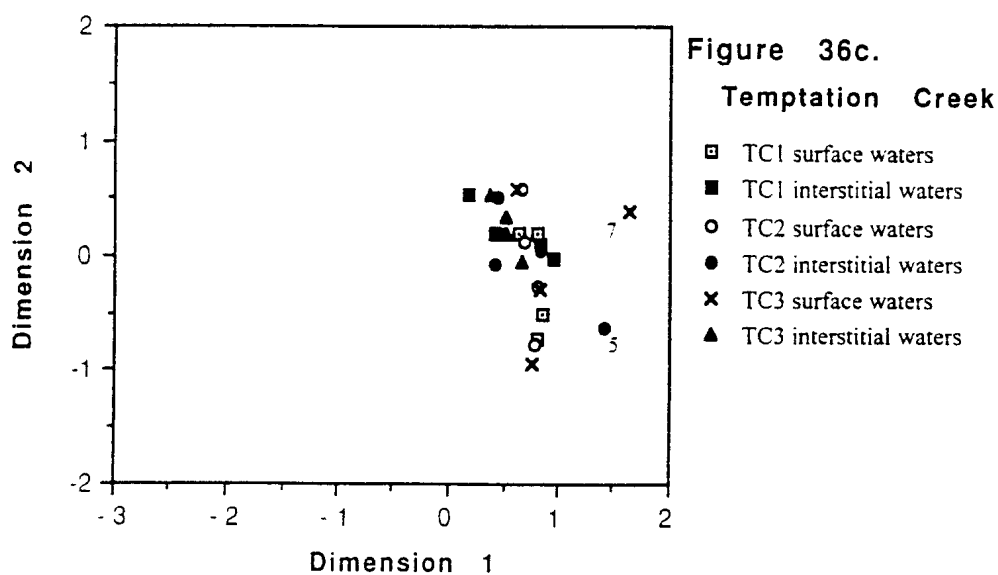
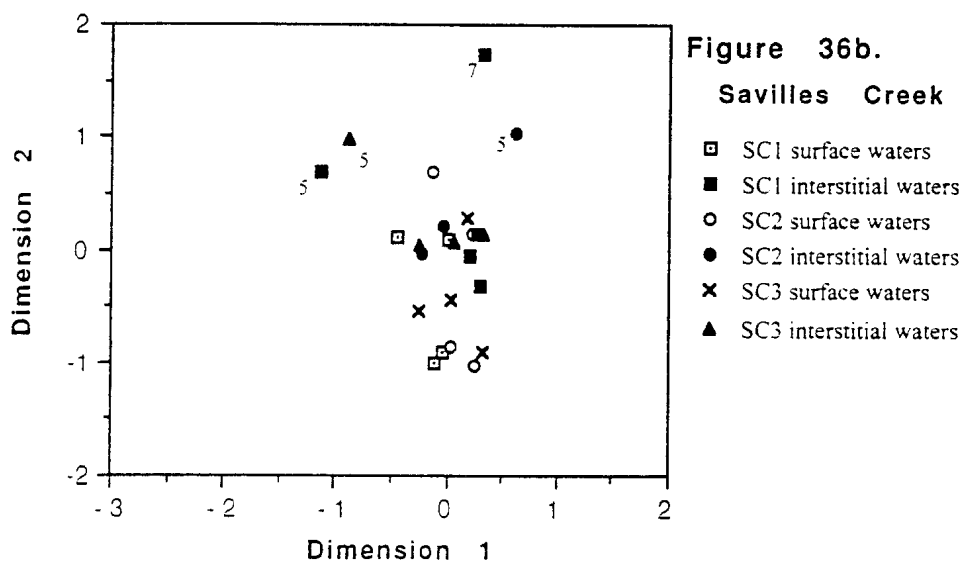
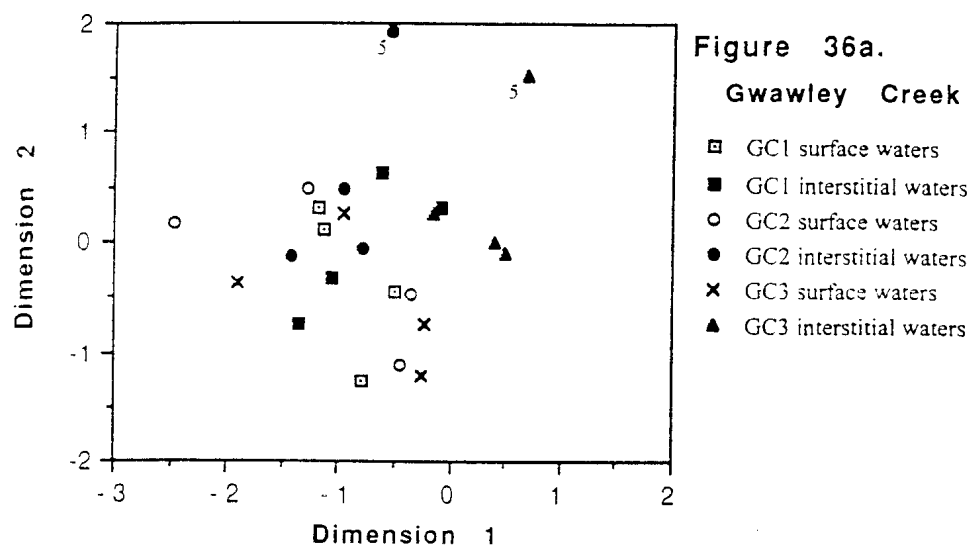


Figure 36. MDS ordination using chemical parameters from combined surface and interstitial waters, grouped by station. (Numbers denote particular sample collections)

samples (2 x 36) by further omitting sample collections 1, 4 and 6 - leaving each station to be represented by collections 5, 7, 9 and 10. Final configuration iteration stress was still high, but now more acceptable at 0.159.

Clearly, Figure 36 illustrates that the dissimilarity of samples was greatest for Gwawley Creek, intermediate for Savilles Creek and least for Temptation Creek, giving an impression that the points were converging into a tight cluster on moving from the urban to urban bush to reference site. This reflected the findings of earlier ordinations that urban waterways were more variable in chemistry. On comparing the two waters types from individual stations, the spread of interstitial waters appeared approximately equal to that of the corresponding surface waters in each plot. However, in Figures 36a and b most station outliers were interstitial samples.

As with the ordination of surface waters (Figure 29), much of the variability could be explained by different concentrations of dissolved heavy metals and phosphate. For example, in Figure 36a the two most removed samples (GC2 and GC3, sample collection 5) displayed very high dissolved ortho-phosphate concentrations (380 and $315 \mu\text{g L}^{-1}$, respectively; see appendix table A11), in addition to below mean dissolved oxygen levels (1.7 , 2.7 mg L^{-1}). Of the four Savilles Creek outliers (Figure 36b), two of these (SC1 and SC3, sample collection 5) displayed low dissolved oxygen (1.4 and 2.0 mg L^{-1} , respectively) and pH (6.71 , 6.07), along with high alkalinity (214 , 137 mg L^{-1} as CaCO_3) and dissolved ortho-phosphate (14.4 , $8.3 \mu\text{g L}^{-1}$). The other two were noted for high levels of copper (SC1, sample collection 7 : $101 \mu\text{g L}^{-1}$; SC2, sample collection 5 : $66 \mu\text{g L}^{-1}$), ortho-phosphate (SC2, sample collection 5 : $27.3 \mu\text{g L}^{-1}$) and oxidation-reduction potential (SC2, sample collection 5 : 120mV).

Two outliers in the Temptation Creek sub-plot were observed (Figure 36c). The surface water sample (TC3, sample collection 7) displayed low oxidation-reduction potential (19mV) and high concentrations of copper ($52.0 \mu\text{g L}^{-1}$) and lead ($11.1 \mu\text{g L}^{-1}$). The interstitial water (TC2, sample collection 5) was characterised by high levels of dissolved oxygen (9.5 mg L^{-1}), oxidation-reduction potential (160mV) and dissolved ortho-phosphate ($6.4 \mu\text{g L}^{-1}$).

Upon reclassifying these replicates by season when collected and separating the two water types (Figures 37a and b), distinct clustering is observed. For both surface and interstitial waters, summer samples are concentrated above the winter samples (apart from one summer interstitial water outlier in Figure 37b). Summer surface waters were generally less varied than the equivalent winter samples - consistent with earlier results

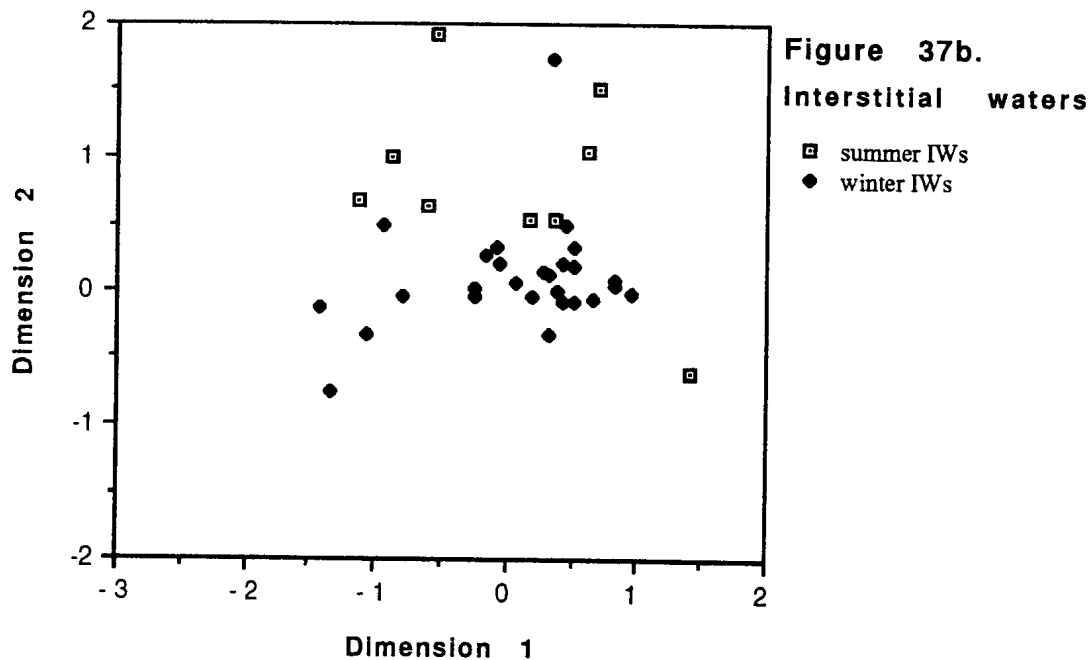
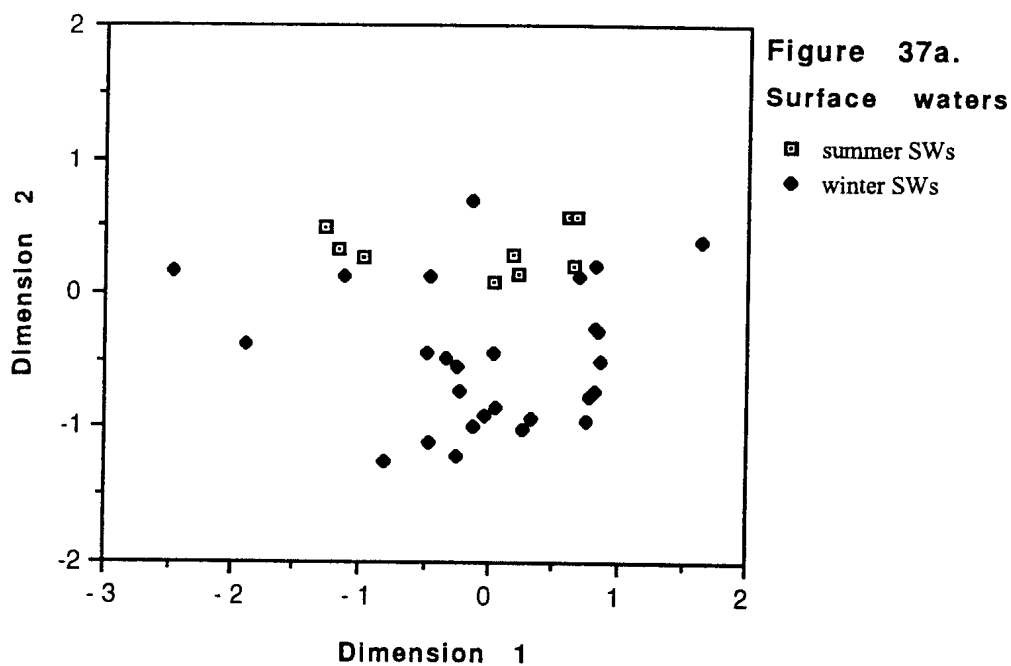


Figure 37. MDS ordination using chemical parameters from combined surface and interstitial water samples, classified by season when collected.

(see Figure 30) - however, summer and winter interstitial waters showed generally equal spread.

These clustering features are at least partly due to higher levels of dissolved orthophosphate, coupled with lower levels of dissolved oxygen, acidity and zinc, in the summer samples, although there was marked lack of variance homogeneity on performing ANOVA. For the comparison involving summer surface waters (i.e. Figure 34a), the levels of dissolved copper and lead should also have been important since neither metal was at a detectable concentration in this group.

4.3.5.4 Variability in Sediment Chemistry

The ordination involving the chosen sediment variable means is presented as Figure 38. A final iteration stress of 0.010 was observed, suggesting an almost perfect fit for this particular configuration.

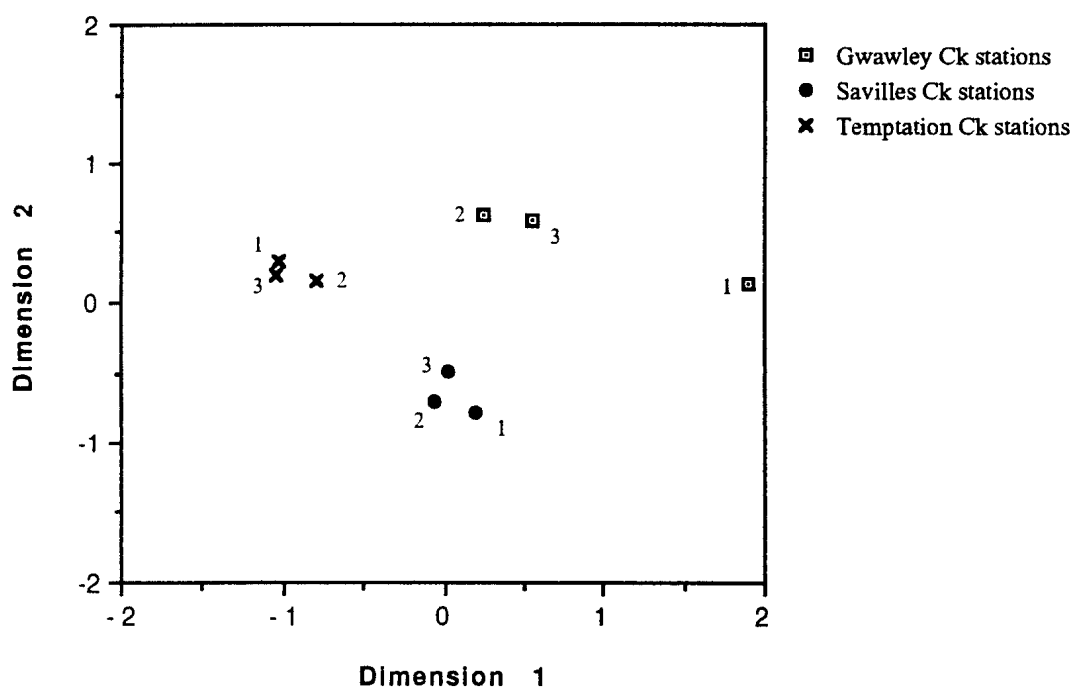


Figure 38. MDS ordination using sample station mean values of sediment variables.

Three groups, comprised of the three stations from each of the sites, were again present and indeed most distinct. The position of Gwawley Creek 1, however, could be regarded as a separate 'group', being quite remote in its location with respect to both the remaining pair of Gwawley Creek points and the Savilles Creek and Temptation Creek stations. This feature provided evidence that the stormwater outlet, in the immediate vicinity of the sampling station, has a major effect on the sediments. Moreover, this effect is shown to be localised.

A Temptation Creek to Gwawley Creek gradation was also apparent. This was consistent with Gwawley Creek sediments being high in contaminants, while Savilles Creek sediments were intermediate and Temptation Creek sediments were low. The compact station groupings suggested less within-site variability - except of course for Gwawley Creek with respect to station 1 - compared to the overall creek differences.

Relevant sediment data from sample collections 5, 7, 9 and 10 were analysed singularly to complement the above ordination. The results are illustrated by Figure 39(a-d) and final iteration stresses were negligible (≤ 0.014) in all cases.

Station groupings could be depicted, although they were less distinct for 39c and d as considerable overlapping was possible due to wider separations of points (particularly GC stations 2 and 3), signifying higher levels of within-site variability. The dissimilarity (i.e. separation) of individual stations was always greatest for Gwawley Creek and intermediate for Savilles Creek, as expected. Apart from the ordination of sample collection 10 data, variability between Temptation Creek stations was consistently minimal. The outlier in Figure 39d (i.e. TC2) was principally due to substantially high organic carbon content (1.79%, compared with the overall mean value of 0.336%), although elevated levels of copper, zinc and lead were also detected.

Overall differences between the separate analyses were not as marked as those involving water chemistry (see Figure 35). Points were shifted towards the right hand side of the plot, except those representing Gwawley Creek 1, which were always removed to the far left, highlighting a 'unique' composition at this station. The right-side points in Figures 39a,b and c, indicated a general linear (diagonal) gradation, from lower left (GC2 and 3) to upper right (TC stations) in the graph. Note also the relative positions of the three Gwawley Creek stations were very similar in the four ordinations, suggesting that the station sediment compositions, while all different, did not necessarily change much - or that all three changed similarly - over time. The same can also be said for the other two sites, if only Figures a,b and c are considered.

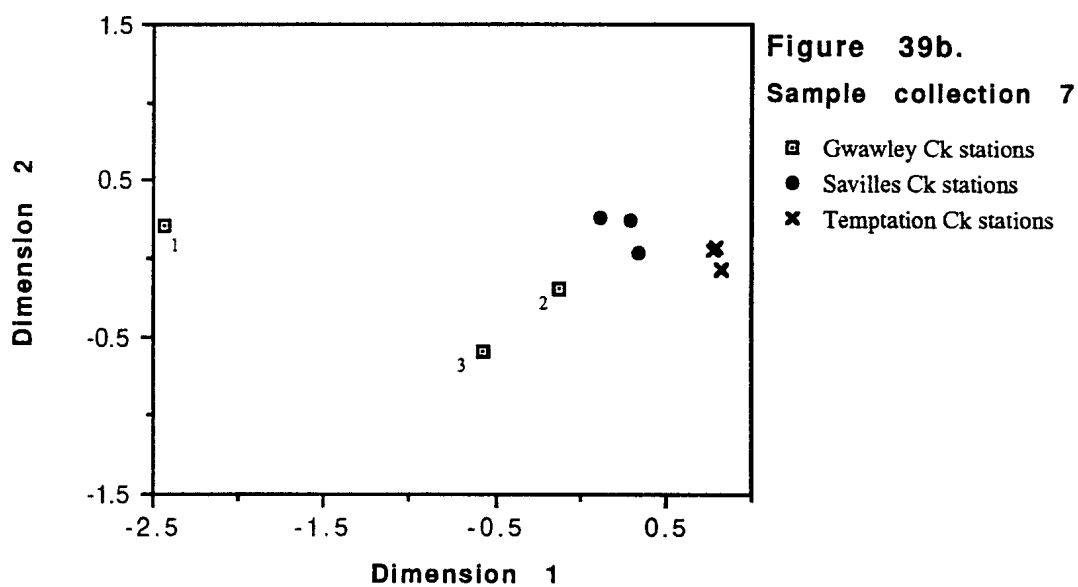
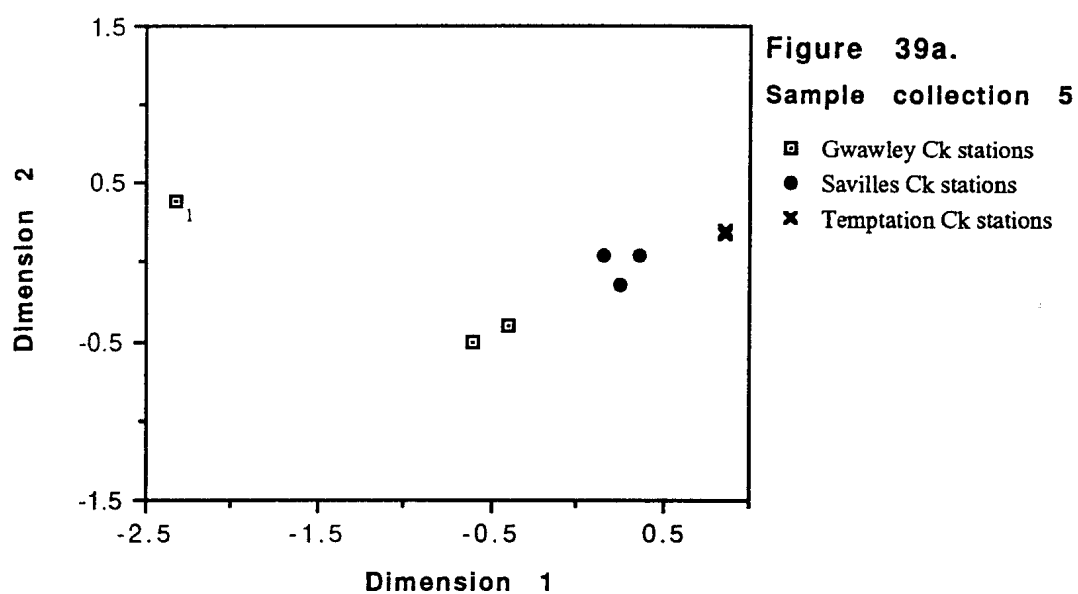


Figure 39. MDS ordinations using chemical parameters from station sediments of single sample collections.

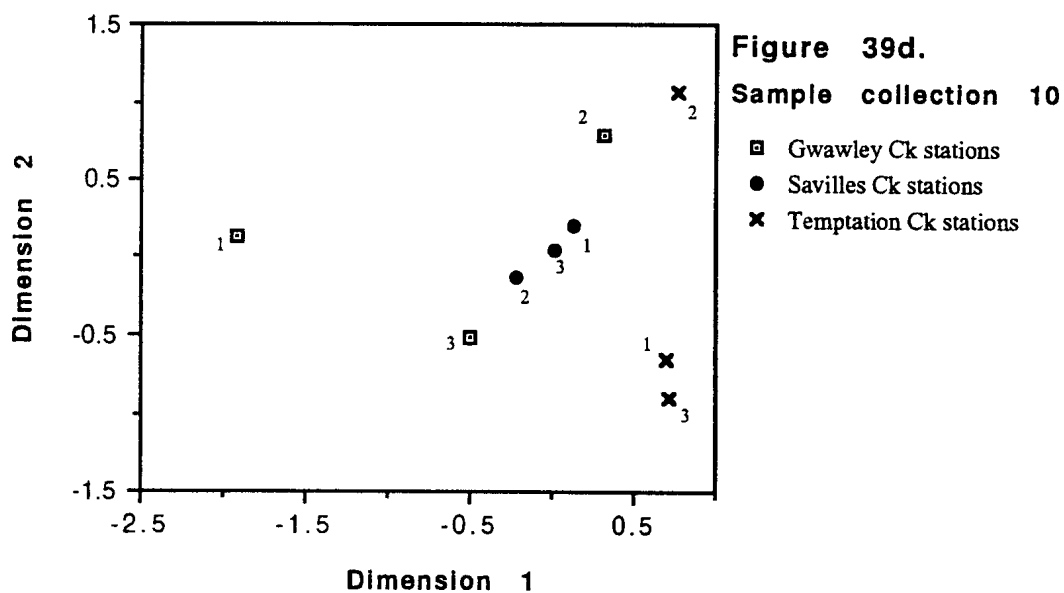
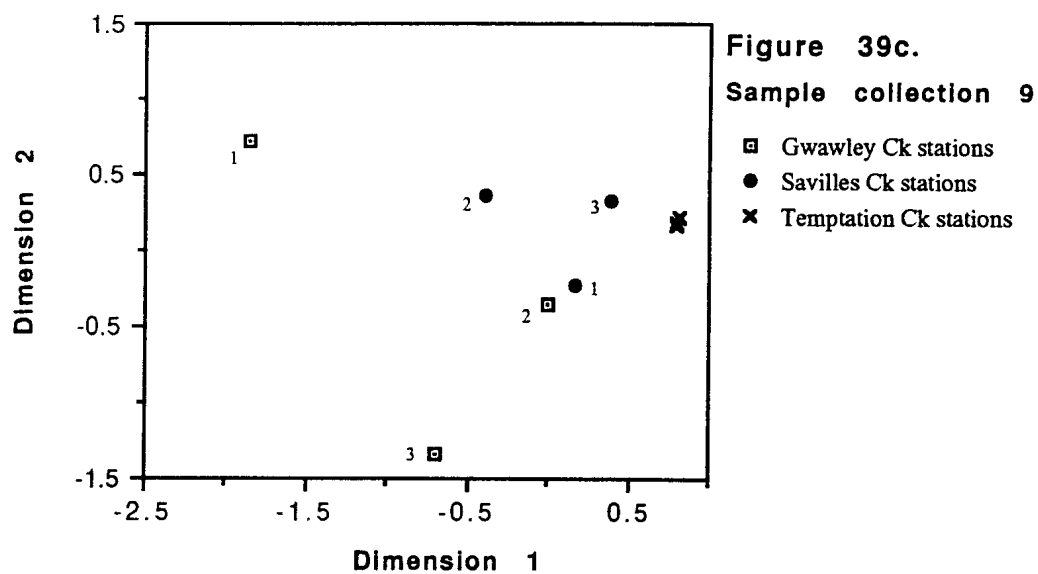


Figure 39 (continued). MDS ordinations using chemical parameters from station sediments of single sample collections.

While the ordinations for sample collections 5 and 7 were almost identical, comparisons with the remaining examples indicated sufficient differences to confirm there was still considerable temporal variability in the sediment chemistry of these streams. However, it is likely this temporal variability in composition is less than that shown by interstitial waters, or the surface waters.

The spatial distribution generated from multidimensional scaling of a large group of individual sediment samples reflected the previous results. This ordination was based on sample collections 1, 3, 5, 6, 7, 9, 10 and 11 from each station, hence comprising a data set involving some 72 replicates. The iteration stress for the final configuration was 0.058, indicating a good fit.

On organising the points into their corresponding site and station (Figure 40), Gwawley Creek samples were particularly scattered. Of the five parameters selected to make the data set, ANOVA identified significant differences for organic carbon ($p=0.003$; logged data; GC>TC), total phosphorus ($p=0.000$; logged data; GC>SC>TC) and total copper ($p=0.000$; logged data; GC>SC>TC). Total zinc and lead were expected to follow the same trend as copper, however, variances were not homogeneous - refer also to Table 18.

For Gwawley Creek (Figure 40a), sample station 1 replicates tended to show variability across the horizontal axis. Sample collection 3, located amongst a dense group of samples on the right-hand side, was characterised by low to average levels of all the constituents involved (see appendix table A13). The far left point (sample collection 11) was noted for very high organic carbon (1.57%), total phosphorus ($1195 \mu\text{g g}^{-1}$) and copper ($85.5 \mu\text{g g}^{-1}$). High lead concentration ($209 \mu\text{g g}^{-1}$) was observed for the uppermost point, corresponding to sample collection 9.

The other two stations were more varied across the vertical axis. Three low outliers (GC2, sample collection 10; GC3, sample collections 9 and 11) all shared high organic carbon levels (1.56%, 1.83% and 0.931%, respectively). High total copper (GC3, sample collection 9 : $25.2 \mu\text{g g}^{-1}$) and total phosphorus (GC3, sample collection 11 : $2212 \mu\text{g g}^{-1}$) were also apparent.

The scattering of Savilles Creek samples (Figure 40b) was again intermediate, consistent with its catchment type. The reference site showed only a minor spread (Figure 40c), except for one outlier (TC2, sample collection 10) which displayed extreme levels for all the relevant constituents. In this case, slightly greater spread of the replicates was distributed vertically, rather than horizontally. Since metal levels were usually non-

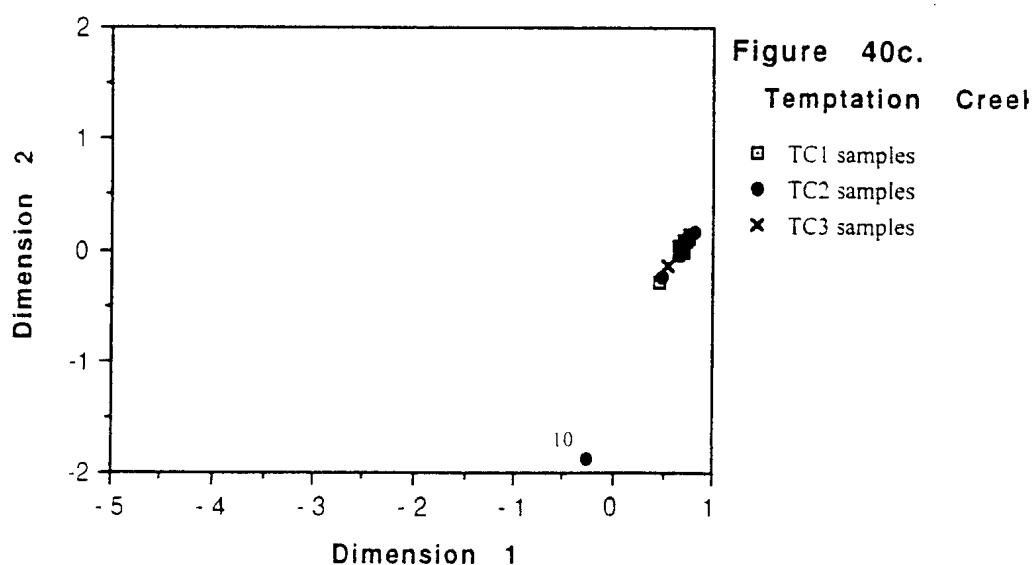
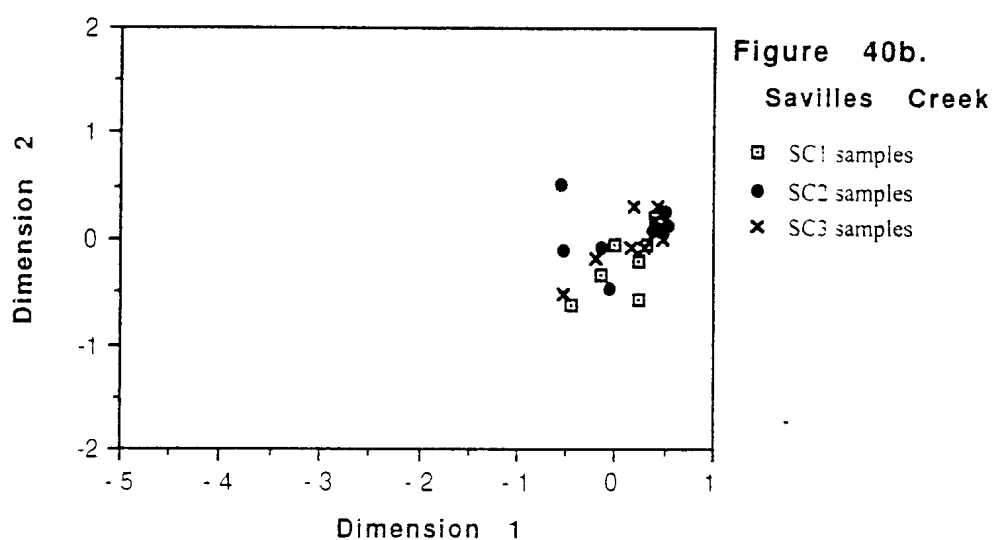
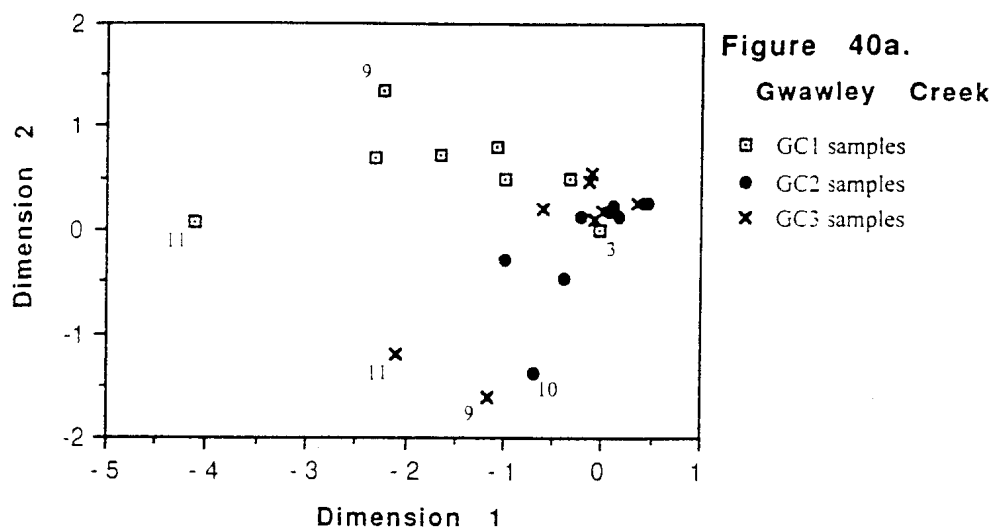


Figure 40. MDS ordination using chemical parameters from the sediments, grouped by station. (Numbers denote particular sample collections)

detectable, this suggested differences in organic carbon and phosphorus (see appendix table A13).

By identifying the summer and winter samples in this ordination, Figure 41 does not depict any distinct seasonal groupings and most replicates are clustered together on the middle right-hand side of the plot. However, if the two most extreme left summer samples (marked x) are ignored, then it is clear the winter samples show greater variability. Analysis of variance between the summer and winter sample groups identified only one significant difference, that being for organic carbon ($p=0.018$; logged data). For this variable, the mean for the winter samples was greater than that for the summer samples.

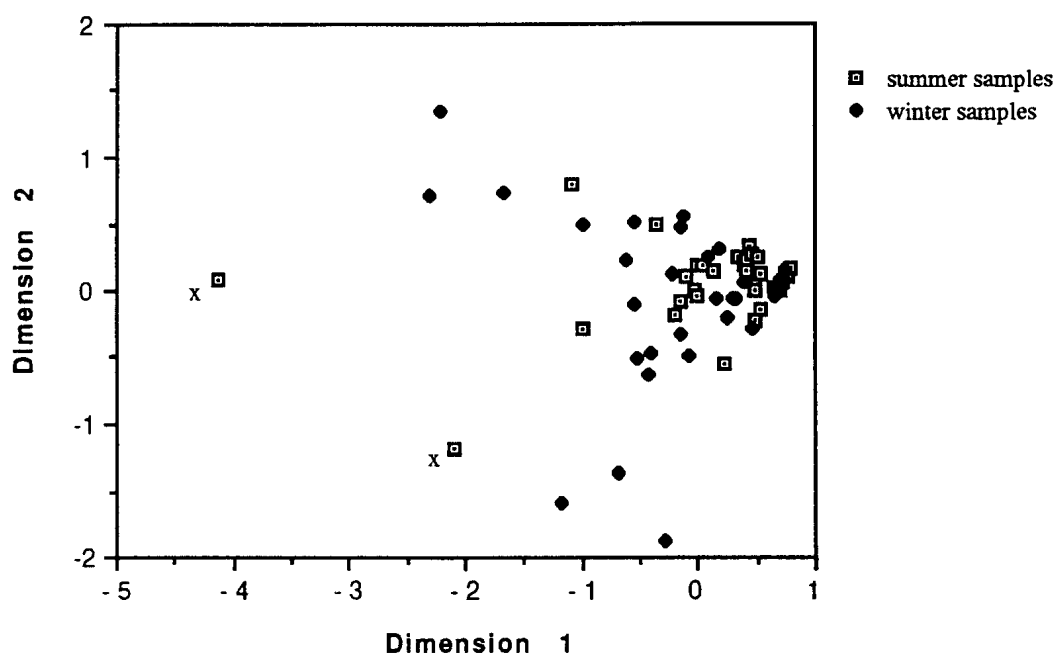


Figure 41. MDS ordination using chemical parameters from sediment samples, classified by season when collected.

It should be remembered that given the high incidence of collinearity between the chosen sediment parameters - see section 4.3.4.4 - the effects of these variables were to a degree confounding in these ordinations. However, the data set was not pruned further to generate suitable representatives (i.e. each to stand as a proxy for the corresponding variables), as suggested by Clarke and Ainsworth (1993), since the mutual correlation

coefficients did not average more than 0.95. Thus any confusion due to confounding should be extremely minimal. This feature would be even less critical for all previous ordinations due to the high level of inconsistency in correlations between pairs of water chemistry variables.

4.4 Discussion

4.4.1 Comparison of Urbanised and Undisturbed Streams

4.4.1.1 Stream Flow Rates and Discharges

All three streams predominantly showed low flow conditions. After consideration of the flow measurements and supplied rainfall data, it appeared discharges were quickly reduced (within approximately 12 hours) once precipitation ceased. As most of Sydney's rain falls during major storms and low intensity prolonged rainfall is rare (Chapman and Murphy, 1989), these systems will mainly experience such conditions, except during and within the short spaces of time following heavy storms or significant dry weather runoff events. Thus, for most of the time they can be described simply as a series of pools, connected by short, shallow stretches having low to moderate flows.

Besides a dependence on runoff quantity, this predominance of low flows could also be explained in terms of the Manning's roughness coefficient and the factors which affect it, as described by Chow (1959). In comparison with more even, artificial channels, most natural creeks have a high Manning's roughness coefficient for one or more of the following reasons (Chow, 1959) :

- higher surface roughness of the wetted perimeter due to exposed rock, coarse gravel and boulders
- dense vegetation on the side slopes, as well as marked macrophyte growth close to the banks and within the water channel
- a high degree of channel irregularity and frequently alternating cross section due to presence of sand bars, ridges, holes and humps in/on the wetted perimeter
- regular occurrence of obstructions such as fallen logs and bridge piers .

These characteristics were certainly common features of the three creeks studied here and indeed of the majority of the Sydney Basin streams surveyed. The result is that such

streams can maintain low flow rates when receiving small discharges (e.g. light rains) and quickly return to these baseline conditions after heavy storms.

It appeared that to magnify the flow of water, rapid downpours (e.g. 10mm in 15 minutes) or prolonged moderate storms (e.g. 10mm in 2 hours) were needed. Of these sorts of rain events, the former are known to pose the most significant chronic impact on stream water quality, especially if frequent (Marsh, 1993).

Intense storms quickly saturate the catchment, resulting in large, fast-moving volumes of water being generated and causing high levels of contaminants, including suspended solids, to be released into the system (Marsh, 1993). Once precipitation ceases, the remaining quantity of suspended solids, with its load of contaminants, settles out as flows return to normal. The more violent the flow regime, the greater the bank and wetted perimeter erosion, leading to sediment displacement as well as replacement. This would be especially critical for streams having only shallow sediment depths and little bank vegetation, which is often the case with Hawkesbury Sandstone-based streams. Gwawley Creek, for example, is located on a terrain described as 'disturbed' and is easily eroded (Chapman and Murphy, 1989).

If precipitation is of low intensity but over a lengthy period, then the catchment can still become saturated. However, even though an equivalent amount of rain may be deposited, the longer time length enables greater infiltration, storage and evaporation. The ensuing discharges into a receiving stream are unlikely, therefore, to contain the same immediate load of contaminants (Marsh, 1993). On the other hand, flushing effects would be reduced, encouraging an addition to the surficial sediment layers, rather than removal.

The storm sampled during collection 12 involved approximately 45mm of precipitation over a period of approximately one hour, hence categorising it as a 'rapid downpour', following the description above. Surface water sampling commenced at Gwawley Creek, about 20 minutes after the storm's commencement and all three sites were completed as the rain was easing to a light shower.

In terms of flow and water appearance the three sites were essentially the same. At each of the nine stations, flows were extremely rapid, turbulent and turbid - the water having a milky-brown appearance. Water depths were markedly increased ($>>1\text{m}$) compared to the previous low flow levels measured (i.e. $<1\text{m}$); in fact at Savilles Creek 1 and Temptation Creek 1 and 2, the water levels had risen to above full-bank height in each case. At other stations, bank erosion was observed.

Multidimensional scaling illustrated there was considerable temporal variability in the sediment chemistry of these three streams (see section 4.3.5.4). It is logical to assume the displacement and subsequent replacement of sediment that results from storm events, such as the one just described, can at least partly explain this variability.

Surface water loadings at all three sites were also highly variable and few results of interest were detected by analysis of variance (see Section 4.3.2.7), suggesting that concentrations should be used when comparing site types, sites and sampling stations. Nevertheless, the significant differences based on flow grouping for dissolved orthophosphate, (bi-)carbonate, potassium, magnesium, ammonia and nitrate were important given that sample collection 12 samples were not included in this data set. Considering the high concentrations of various constituents in these flood flow surface waters, this provided evidence that flood flows represent a major mechanism for transport of constituents into and out of stream catchments, urban or otherwise.

4.4.1.2 Major Ion Composition of Surface Waters

The low salinities or total dissolved solids contents ($<200 \text{ mg L}^{-1}$) observed for the three creeks meant they easily classified as fresh waters. This feature would seem to be typical of the basin's freshwater systems, given the findings of the survey and also the study of six Sydney reservoirs by Jolly (1966). This is in contrast to Williams and Wan (1972), however, who remarked high total dissolved solids ($>200 \text{ mg L}^{-1}$) was a characteristic of many Australian inland waters, but can be accounted for by the fact that Sydney is coastal and receives greater rainfall compared to regions further inland.

Strong sodium and chloride dominance and correlation was observed (Table 10; Figure 20) and in accord with the basin survey. Most of this sodium chloride should originate from sea spray, which is a major contributor of magnesium and sulfate as well (Hart and McKelvie, 1986). However, significantly higher levels of calcium and (bi-)carbonate were also observed in samples from the urbanised sites (Table 11), such levels approaching co-dominant proportions in many of those from Gwawley Creek. As soil and dust are believed to be an important source for calcium, (bi-)carbonate and potassium (Hart and McKelvie, 1986), this illustrates the relative importance and variability of sea salt aerosols and soil material as sources of the major ions in these areas. These results also imply that catchment influences on urbanised streams are varied.

Given that hardness ($<100 \text{ mg L}^{-1}$) and acidity ($<10 \text{ mg L}^{-1}$) were both low (Clesceri *et al.*, 1989), the surface waters of these creeks can be regarded as soft and of poor base-

buffering capacity. Alkalinity levels in Temptation Creek were representative of the poor acid-buffering capabilities typically observed in the Sydney streams survey. In contrast, alkalinities of the two urbanised creeks were higher and should ensure greater buffering capacity towards inputs of acid. Gwawley Creek was particularly exceptional with its increased levels of calcium, alkalinity and hence (bi-)carbonate, considering the creek lies on Hawkesbury Sandstone and the supply of calcium bicarbonate from catchment lithology would be minimal. This reiterates how atmospherically transported dusts and building materials (e.g. concrete and plastering materials; Kirk-Othmer, 1978) must be an important source of these major ions, especially for Gwawley and Savilles Creeks. It is also possible, however, that additional carbonate could be generated by more intensive respiration in the system. Indeed the two creeks each have dense macrophyte and algal growth over much of their length, especially in the vicinity of sample station 1 at Savilles Creek.

4.4.1.3 Minor Ion Composition of Waters

At all three sites substantial variabilities (i.e. large standard errors) were observed for the minor ions, including phosphorus, copper, zinc, lead, nitrate, turbidity and colour (see appendix tables A11 and A12). For heavy metals the variation was derived from a low detection frequency, coupled with the fact that when measurable the level was often extreme. This was partly due to high furnace AAS detection limits.

The Basin survey indicated that total phosphorus concentrations can be high ($>0.1 \text{ mgPO}_4^{3-}\text{-P L}^{-1}$) in Sydney streams. During this study, elevated levels were regularly observed in surface waters taken from the urbanised creeks and occasionally in Temptation Creek samples (see appendix table A11). Dissolved ortho-phosphate concentrations in excess of the quoted quality criteria (Table 7) were also detected in both the surface and interstitial waters - the flood flow samples of collection 12 being particularly obvious (≥ 0.16 , 0.060 and $0.070 \text{ mgPO}_4^{3-}\text{-P L}^{-1}$ for GC, SC and TC respectively). This was consistent with the findings of Williams and Wan (1972), who reported that high ($>0.020 \text{ mg L}^{-1}$) phosphate phosphorus concentrations were a distinctive feature of many mainland lakes and reservoirs in south-eastern Australia.

Excessive levels of nutrients in stream waters from undeveloped catchments are possible as the surrounding vegetation and soil can easily be leached of soluble phosphorus and nitrogen during rain events (Dorney, 1986), while the precipitation itself may deposit substantial loads (Betson, 1978; Campbell, 1978*b*). The high levels in sample collection 12 waters from Temptation Creek provide a good example of this. Heavy metal enrichment can also be derived from atmospheric deposits (Hamilton-Taylor *et al.*, 1993;

Florence and Morrison, 1992). In a coastal zone of high population density, such as the Sydney Basin, all surface waters will be subjected to heavy aerosol deposition.

The data also indicated high variability with regards to the concentrations of suspended particulate matter in surface waters. Values for Temptation Creek were just as substantial as those for the streams in developed catchments, during high or low flow (see appendix table A11).

Under low flow conditions, a large proportion of the particulate matter was fine detrital material (decomposing organic matter), apparent as a thin layer on the surface of the sediment. Being of minimal density, this material would be readily resuspended, even by the slightest disturbance. The primary source appeared to be the surrounding vegetation, since a common feature of the sites was the often intense vegetation cover. In the cases of Gwawley and Savilles Creeks, the cover was principally composed of an entangled mass of weeds and other plants. The high rates of foliage deposition that subsequently occur provide the surface water with a continuous and rapidly degradable supply of natural organic matter and intact (but decaying) leaves and other plant parts were usually found lying on the sediment surface.

Such matter is believed to play a key role in the biogeochemical cycling and spiralling of nutrients and heavy metals (Hart and McKelvie, 1986), due to its absorptive properties and the ease with which it can be carried by water currents. Thus, in these systems, despite occasional extreme concentrations and rapid break-down, this organic matter did not accumulate in the sediments due to sediment flushing by surface water flow rates.

4.4.1.4 Differences Between Surface and Interstitial Waters

On comparing surface and interstitial waters under low flow conditions, certain significant differences in chemical composition were identified, mainly with respect to conductivity, alkalinity, acidity, hardness, DO and redox (Tables 14 and 15). These differences were consistent across each of the three sites.

For the first four of these parameters, higher levels were regularly seen in the interstitial waters due to restricted dilution. Dissolved oxygen and oxidation-reduction potentials were lower in the pore waters - consistent with the anoxic nature of the sediment environment - although conditions would not necessarily have been classed as highly anaerobic since aerobic conditions were observed from time to time, especially in Gwawley and Temptation Creeks. High interstitial oxygen levels were not unusual

considering the often shallow surface water and sediment depths, large pore size and regularly high dissolved oxygen levels in the water column.

Concentrations of phosphorus and heavy metals were greater in interstitial waters than in surface waters (Figures 23 and 24), if only slightly. However, the high variability indicated distinct concentration gradients between the two water types were rare. This was not surprising given the very sandy (and hence porous) nature of the sediments.

4.4.1.5 Sediment Composition

Certain general compositional features were apparent for the surficial sediments of the three Sutherland Shire creeks :

- (1) very low organic matter (<2%)
- (2) very low fines (i.e. silt + clay) content (<3%)
- (3) particle size dominated by coarse and fine sands (>95%)
- (4) low cation exchange capacity (<3 mmolNa/100g) .

These four characteristics are expected to be typical of most Hawkesbury Sandstone sediments, although there are no data in the literature to verify this.

On comparing the sites, the urbanised creeks displayed higher levels of heavy metals, phosphorus, organic carbon, cation exchange capacity and fines compared to Temptation Creek. Particularly high levels of these constituents were regularly observed at sample station 1 of Gwawley Creek, located at the outlet of a large stormwater drain. This result provided an indication of how localised urban discharges affect a receiving lotic system.

Having particle size fractionation being dominated by sand (derived from the underlying sandstone), plus only minimal percentages of fines and organic matter, these sediments were expected to exhibit low adsorption capacity compared to most other examples (Förstner, 1982). This property, accompanied by the effects of high flushing rates, can explain the poor accumulation of heavy metals and phosphorus observed in the raw data (appendix table A13).

While perhaps not exemplifying the heavy metal and phosphorus reservoirs that sediments are capable of being (Larsen and Jensen, 1989; Davis and Leckie, 1978; Hart *et al.*, 1976; Syers *et al.*, 1973), they still represented a substantial sink, since totals in excess of the presented quality criteria were observed in the urbanised streams (particularly at the Gwawley Creek stations), and hardly at all in Temptation Creek. This

illustrates the significance of the external inputs involved. After a study of the Ottawa River in Canada, Ramamoorthy and Rust (1978) also reported that substrates dominated by well-sorted sand were efficient sinks of heavy metals, although the accumulation in that case was partly due to increased loading of organic material generated from commercial logging activities. As indicated, organic matter levels for this study were low.

4.4.2 Surface Water Chemistry Under Flood Flow Conditions

Quite distinct chemistry was observed for the flood flow (i.e. sample collection 12) surface water samples, consistent with the data from other papers that assessed the composition of urban stormwater runoff (Roesner 1982; Weeks 1981; Betson, 1978). The most significant features of these samples included higher pH, oxidising redox, nutrient enrichment and increased suspended solids, turbidity and colour, along with reduced conductivity, alkalinity and hardness (appendix tables A11 and A12). Despite reduction in conductivity (with accompanying reduced relative proportions of chloride), expected to have been a consequence of heavy dilution, increased relative proportions of sulfate and potassium were nevertheless apparent (see Figure 20 and Table 12). In general, such chemistry was not apparent for the other high flow rate (F2) samples, indicating extreme flow regimes are required to significantly alter the overall chemical composition of waters in these streams.

Flood flow runoff was found to be a major contributor to the total nutrient and suspended solids load in all three streams (see Figures 21 and 22, plus appendix tables A11 and A12). This has also been reported in previous studies of waterways receiving stormwater runoff (Hogg and Norris, 1991; Neller, 1985; Cordery, 1977; Ellis, 1976). For Temptation Creek, the increased nutrient levels (except for dissolved ammonia) were the highest observed throughout the study and were indistinguishable from those for the urban sites, especially Savilles Creek. Thus, enrichment of such constituents can at times be just as substantial in runoff waters of undeveloped catchments as they are in many developed catchments.

Such a result has been observed by Meister and Kefer (1981) in a chemical comparison of the urban and non-urban stormwater runoff received by an artificial lake in Southern Illinois University. For suspended solids, while values for both sources were of such magnitude to contribute a significant pollutional load, for the initial stages (≤ 30 minutes) of runoff non-urban waters had the highest concentrations, but thereafter the urban concentrations became higher. Excessive levels of both dissolved phosphate and nitrate in non-urban waters were also seen, although only during the latter periods of sampling.

At all three study sites high concentrations of nutrients and suspended solids were measured on other occasions, even under normal (i.e. low) flow conditions. However, the detection frequency was low and not usually consistent across all sample stations (i.e. poor compliance was observed). For the flood flow samples, similarity in values across each stretch of creek (i.e. minimal variability between the three stations within each site) was particularly noticeable for total phosphorus, suspended solids and ammonia, which otherwise were rarely uniform on a sampling occasion. This is not meant to imply that under intense flow rates water composition is continuously uniform - although Cordery (1977) found phosphate concentrations in stormwater runoff collected from three urban watersheds in Sydney remained approximately constant during each flood sampled. Instead, it is understood that considerable variability in the data is usually seen (Gutteridge, Haskins and Davey Pty. Ltd. and the Environment Protection Authority of Victoria, 1981; Cordery, 1977). However, for any given system this variability is more prevalent on a temporal scale, rather than a spatial one (especially along short lengths of stream).

The observed shift in proportions of total and dissolved phosphorus to increased dissolved ortho-phosphate concentrations at flood flow - see section 4.3.2.4, plus Figures 21 and 22 - was most likely a result of the turbulent conditions and the fact that a substantial proportion of the phosphorus having anthropogenic origin is only weakly associated with particulate matter (Cullen, 1986). Being principally composed of sands, Hawkesbury Sandstone sediments normally should exhibit relatively weak adsorptive capacity in any case. The sediment resuspension and greater mixing during flood flow hence increased dissolution of the more bioavailable, or soluble, forms.

Urban runoff is also known to be a source of heavy metal enrichment for receiving waters (Florence and Morrison, 1992; Roesner 1982; Weeks 1981; Gutteridge, Haskins and Davey Pty. Ltd. and the Environment Protection Authority of Victoria, 1981; Cordery, 1977), but from sample collection 12 this was not observed, with only traces of dissolved zinc being detected (appendix table A11). The samples, however, represented the peak flow period, rather than the first flush which is often the contaminant-laden portion for metals (Marsh, 1993; Cordery, 1977; Ellis, 1976). In addition, only the dissolved component and not a total concentration was determined. The total metal level may well have been quite high in these samples, given the substantial suspended solids contamination and the strong affinity of metals for particulate matter. Hence, any dissolved metal present may have been heavily diluted to below detectable limits, just as the levels of most major ions were drastically reduced compared to all previous readings. It was expected that had first flush waters been taken, their composition would also have

been significantly different to the earlier sample collections, as well as the latter flood flow waters themselves.

An important consideration was that the samples from all three sites were almost indistinguishable in composition, a result which was not apparent for all other sampling occasions. Thus, under heavy storm flooding conditions, urbanised and undeveloped streams may become very similar chemically. Again, this may not necessarily be true for the period of first flush, since it is unlikely that high levels of heavy metals would be detected in undisturbed stream waters at such times.

4.4.3 Surficial Sediment Chemistry

Considering the sediments analysed in this study were geochemically very similar, then in accordance with Luoma (1989), the observed fractionation results were a valid reference for the investigation of heavy metal (and to a certain extent phosphorus) chemistry in these sediments. This also made it possible to consider prediction of metal availability.

For the Hawkesbury Sandstone sediments studied, most of the metal (Cu, Zn and Pb) and phosphorus content was assumed to be associated with inert quartz grains via coatings of iron/manganese oxides and organic matter acting as substrates, or as coarse waste particles (Förstner, 1982). Supporting this, the heavy metal speciation studies identified the hydrous metal oxides and residual fractions to be major phases, particularly for zinc and lead (Figure 27). Considering that copper demonstrates strong association with organic materials (Pardo *et al.*, 1990; Chen *et al.*, 1989; Hart and Davies, 1978), it seemed reasonable that on comparing amounts of the three metals (Figure 26), total copper was considerably lower relative to the other two. This indicates the over-riding importance of the organic matter phase in accumulating copper (see also Figure 27a).

Earlier speciation work has shown that an appreciable proportion of cadmium can be found in the rapidly exchangeable fraction (Harrison *et al.*, 1981; Salomons and Förstner, 1980). Given the low cation exchange capacities of these sediments, coupled with extremely low dissolved cadmium concentrations in the surface and interstitial waters, the virtual non-detection of this heavy metal during the sediment speciation analyses was therefore not unexpected.

The negligible rapidly exchangeable component of each sample for all four heavy metals, although not surprising, was not necessarily the restrictive factor for potential adsorption. While certain previous studies have observed substantial association of heavy metals with

this rapidly exchangeable (i.e. clay mineral) fraction (e.g. Pardo *et al.*, 1990; Harrison *et al.*, 1981; Salomons and Förstner, 1980), others have found only minimal amounts (Tessier *et al.*, 1979; Gupta and Chen, 1975). In all cases, the remaining phases are regarded as having greater importance. Subsequently, the clay minerals themselves are not seen as a significant sink and instead have relevance in metal transport, acting as a substrate for the sediment components of higher metal affinity (Davies-Colley *et al.*, 1984; Förstner, 1982).

According to Martin *et al.* (1987) and Gupta and Chen (1975), the first extraction step should have included any heavy metal associated with carbonate fractions - at least present to some extent in Gwawley and Savilles Creeks, given the findings of significantly increased calcium and (bi-)carbonate in the waters, as discussed in section 4.3.2.1. The absence of metals in this 'rapidly-exchangeable' fraction indicates it is unlikely that heavy metal is associated with carbonates to any great degree in the sediments of these streams.

The speciation results were generally consistent with previous sediment heavy metal distribution studies (Pardo *et al.*, 1990; Batley, 1987; Davies-Colley *et al.*, 1984; Harrison *et al.*, 1981; Salomons and Förstner, 1980). However, both Pardo *et al.* (1990) and Davies-Colley *et al.* (1984) identified iron oxides (i.e. of the hydrous metal oxide, or reducible, fraction) as being significant contributors to copper binding, yet this was not apparent here.

The relatively low partitioning of lead in the residual fraction was also unusual considering the high levels present and that it has been found to show significant concentration in this phase (Pardo *et al.*, 1990). It is well known that one of the principal sources of this metal in surface waters is from the combustion of leaded fuel in motor vehicles (Hamilton-Taylor *et al.*, 1993; Chakraborti *et al.*, 1989). Betson (1978), for example, concluded that automotive emissions probably accounted for the high lead concentrations in one of the watersheds investigated, which was traversed by two major highways and had many commercial businesses and parking lots close by. Importantly, atmospheric aerosols release high proportions of the more labile (i.e. dissolved and readily soluble) forms (Hamilton-Taylor *et al.*, 1993). These forms should favour secondary phase accumulation, such as adsorption onto hydrous metal oxides.

This would seem the case on comparing the sum of the sediment secondary phase heavy metals (i.e. RE + HMO + OMS fractions) against the residual fraction, assumed here to represent the primary mineral phase (Figure 42). Considering the definition of residual metal given earlier (Chen *et al.*, 1989; see chapter 1.4.6), the determined values did not

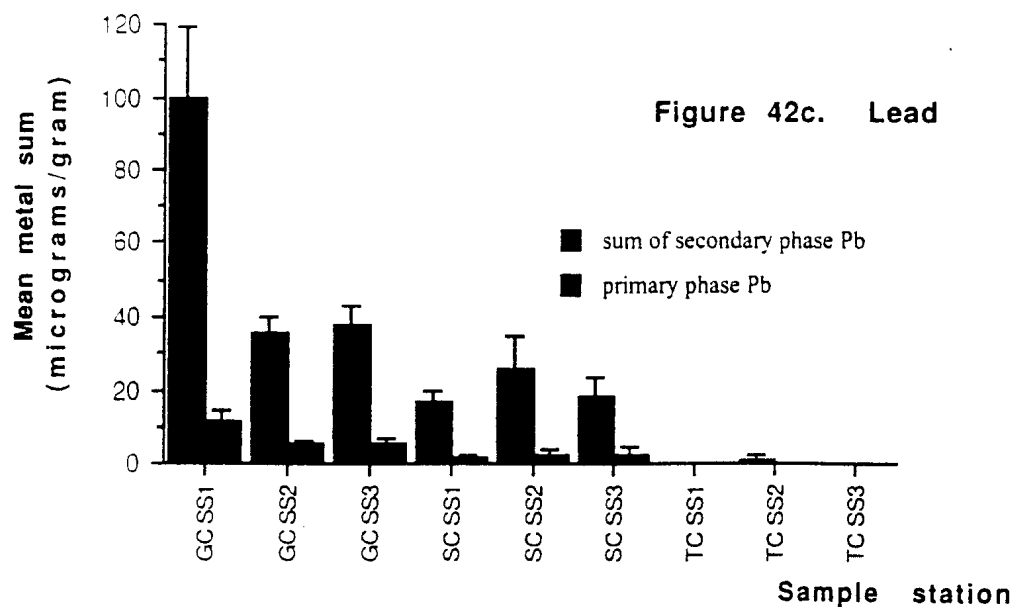
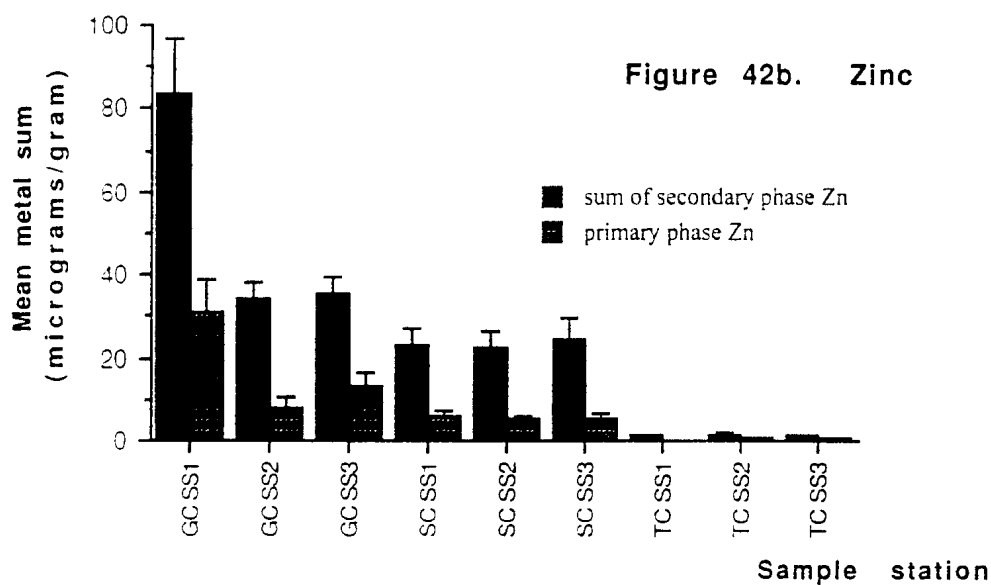
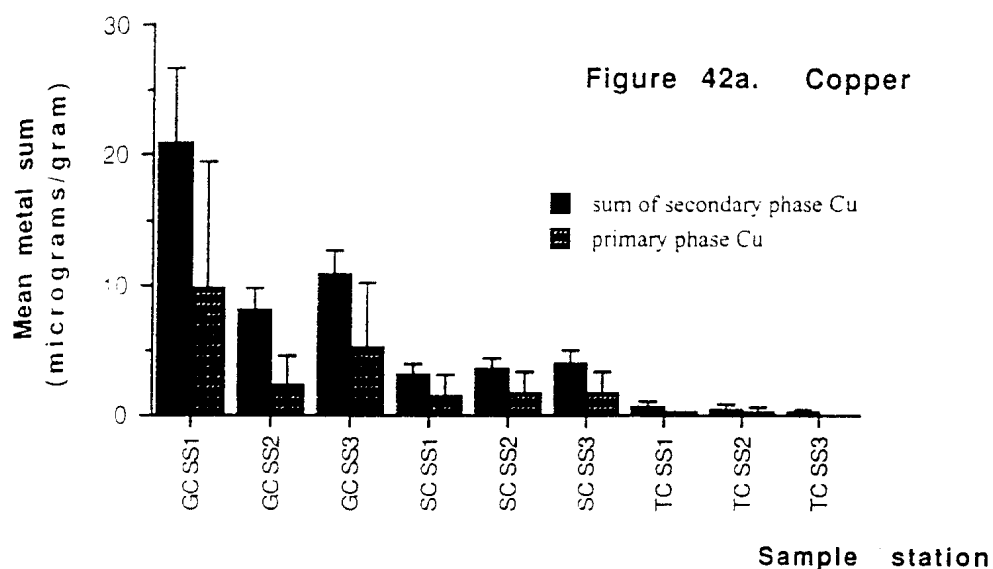


Figure 42. Sum of secondary phase metal versus primary (residual) phase metal. (Based on mean speciation values; error bars are the standard errors)

include any inert lattice-bound metal as the combination of nitric and hydrochloric acids used in this digestion, while providing a high degree of heavy metal extraction, did not dissolve silicates completely (Agemian and Chau, 1976). Since only a fraction of the lattice-bound metal was leached out, the method therefore does not enable true residual and total contents to be determined. Despite this, the designated residual fraction represented the least bioavailable fraction of the sediment, while the other three (pollution indicator) fractions contained the most bioavailable.

Results identified the sum of the secondary phase lead was over nine times larger than the corresponding residual, while for copper and zinc the secondary phase metals comprised totals which were approximately two and four times greater, respectively (Figure 42). These ratios exclude all Temptation Creek values, but even for this site the secondary phase metal was greater than the residual content. Figure 42 also illustrates that the sediments of Gwawley Creek sample station 1 are quite distinctive compared to the remaining eight stations, consistent with the multidimensional scaling of the sediment variable means (see Figure 38, section 4.3.5.4). These results are evidence that urban sediments are highly heterogeneous.

Given that all the sites have surface sediments which are low in fines and organic matter, and high sediment removal rates probably occur, the large secondary to primary phase heavy metal ratios emphasise significant pollutional loads in the urban streams, particularly in respect to lead. Furthermore, as the total levels occasionally surpassed sediment quality criteria and that metals are believed at least partly bioavailable in all phases except the residual (Batley, 1987), these loads could have deleterious consequences. For lead and zinc, considering the major proportions are associated with the hydrous metal oxide fractions - which are known to be reasonably mobile (Pardo *et al.*, 1990; Förstner, 1985) - water quality (and hence bioavailability) will be most susceptible to reductions in pH and oxidation-reduction potential.

Although not verified by analysis, phosphorus fractionation should also be concentrated towards the metal oxide and residual fractions. The organic component was usually negligible (see Figure 25) and phosphates readily adsorb to these oxides and form many insoluble compounds (Syers *et al.*, 1973).

4.4.4 Measurement of Stream Quality

The incidence of high levels of one or more of the minor ions made it necessary to estimate the number of samples that breached recommended guideline values. On comparison of the collected monitoring study data (including those for interstitial waters)

and the relevant water quality criteria, heavy metal and nutrient enrichment in the two urban creeks were obviously points of concern for aquatic ecosystem quality - see Table 16, section 4.3.2.6. This was most true of Gwawley Creek for which the highest numbers of samples were seen to fail the ANZECC (1992) standards. Considering where these waterways are located, the enrichment should principally be generated by non-point source discharges.

Of the dissolved heavy metals, the regular occurrence of undesirable concentrations of zinc highlighted these concerns for maintenance of biodiversity in these ecosystems. The occasional excessive levels of both copper and lead could also pose problems, prompting the suggestion that the phenomenon of synergism - i.e. enhancement of the toxicity of a substance by exposure to another substance, whether the exposure be simultaneous or with a time differential (Duffus, 1980) - could take place from time to time.

Excessive levels of heavy metals (as well as other constituents, such as suspended solids and ammonia) are known to promote both direct and synergistic effects. For instance, following a year-long intensive study of the benthic macroinvertebrates inhabiting the Green River, Massachusetts, Pratt *et al.* (1981) concluded that it was the synergistic and cumulative action of the components in urban runoff that caused the observed upstream-downstream differences in collection diversity and composition.

Table 16, and the lack of spatial and temporal compliance in water quality for the three sites, could also be interpreted such that both Gwawley and Savilles Creeks are not polluted systems, assuming Temptation Creek is not polluted. In other words, water quality of streams situated in developed catchments is quite localised and does not necessarily remain poor all the time, but fluctuates as external inputs, flow regimes and/or physico-chemical parameters are altered. Furthermore, water quality in theoretically unpolluted streams may also deteriorate from time to time, under high or low flow conditions. For example, certain pH, dissolved oxygen and heavy metal conditions that would be regarded as unacceptable were observed in Temptation Creek. Similar results for pH and nutrients were apparent in the Group 1 samples of the Basin survey - see Table 8, section 3.3. This suggests that contamination from the atmosphere may be a major source of nutrients and metals for surface waters - as suggested by Hamilton-Taylor *et al.* (1993), Florence and Morrison (1992) and Betson (1978).

On comparing the sediment data against the corresponding quality criteria - see Tables 19 and 20, section 4.3.3.2 - Gwawley Creek was quite obviously the most regularly contaminated site and Savilles Creek occasionally so. Unlike the water samples, however, lead alone stood out as a major metal contaminant of the sediments, rather than

zinc. In addition, apart from a low incidence of cadmium enrichment, Temptation Creek was regarded as an unpolluted site. Hence, while the water quality of streams located in undeveloped catchments may sometimes deteriorate, the sediments in this case did not.

Assessment of the incidence that poor sediment quality occurred simultaneously at each station of the two urban creeks suggested a pattern of spatial non-compliance, similar to that observed for the water samples. However, unlike the waters, the sediments of Gwawley Creek 1 demonstrated considerable temporal compliance; high levels of copper, zinc and lead (especially) being detected regularly at this station over the sampling period. For total phosphorus, temporal compliance was high at all three Gwawley Creek stations if the Clements (1983) upper limit for Hawkesbury Sandstone soils was considered. This emphasises the heterogeneity of sediment chemistry. It may also point to a very rapid assimilation of contaminants, since Gwawley Creek 1 (immediately downstream of a stormwater drain) is distinctive, even compared to those further downstream.

These results suggest that surface water monitoring, rather than sediment and interstitial water sampling, will provide the most reliable measure of stream condition in Hawkesbury Sandstone streams. Under low flows, subtle changes in quality (e.g. due to atmospheric inputs) are more likely to be detected in the surface water, particularly for systems in undeveloped catchments.

The sediment chemistry proved capable of distinguishing between urbanised and non-urbanised catchments, at least with respect to heavy metals, phosphorus, organic carbon, fine sand and silt + clay (see Figures 38 to 40). However, the chemical variability displayed did not support the sampling of this medium unless longer term ($>>2$ years) monitoring studies are to be performed. The low probability of any concentration gradient existing between the pore water and the water column above, coupled with the high variability of interstitial water composition, limits the value of sampling interstitial waters in these streams as well. Furthermore, under a high flow state, sediments and pore waters become difficult to sample and in any case are unlikely to be present, due to the turbulence and sediment suspension.

The streams were not grossly polluted and poor water and poor sediment quality did not occur all the time. They thus display an ability to recover from non-point source discharges. The nature of the bottom sediment must be a key factor in this mechanism as the coarse fractionation limits the amounts and types of constituents that can remain in the immediate system to cause prolonged exposures of contaminants to stream biota.

This restricted accumulation, or low storage capacity, thus becomes a natural 'self-protecting' mechanism which may have useful management implications. By reducing the input of non-point source discharges and/or the levels of contaminants, catchment management programs could see fast and effective results, as the streams probably have the capacity to regenerate following the cessation of a discharge. Hawkesbury Sandstone streams located in developed catchments could well be prioritised for management, being more likely to respond to remedial measures than some other streams in geologically different environments.

4.4.5 Sediment - Water Interactions

4.4.5.1 Sediment Release of Heavy Metals and Phosphorus

Analyses indicated total metal and phosphorus contents in the surficial sediments were orders of magnitude higher than in water (compare relevant data in appendix tables A11 and A13). Yet upon comparing dissolved levels for surface and corresponding interstitial waters, differences were inconsistent and/or undetectable (see also Figures 23 and 24) - even under nil flow conditions when mixing would be at a minimum. There was also poor correlation between sediment heavy metal and phosphorus totals with dissolved interstitial water levels (Table 26).

These results imply that heavy metals and phosphorus are quick to establish equilibrium conditions between the water and sediment phases in the streams studied. Assuming the presence of dissolved heavy metals and phosphorus in pore water (of the top 5-10 cm of sediment) indicates release to the overlying water (Batley, 1987), then transfer from the sediment environment through mass action and diffusion must be rapid and difficult to detect under low flow conditions. This release should occur directly from particulates located closest to the sediment-water interface.

The apparent lack of regular concentration gradients between the interstitial waters and the immediate surface waters was probably a consequence of the Hawkesbury Sandstone sediment type. Being of high coarse sand content, hence large pore size but low overall water volume (Townsend, 1973), upward release to the overlying water column by diffusion would occur quickly when surrounding physico-chemical conditions change.

For high flow rates (especially flood flows), the turbulence should suspend much, if not all, of the surficial sediment material. Hence during an intense storm, the interstitial waters may no longer exist due to complete resuspension of solids. In this instance, the vigorous mixing of resuspended and incoming solids with water of different chemical

composition would cause the immediate release of particulate-bound metals and phosphorus in the surrounding surface water. On subsequent return to normal conditions, sedimentation and aggregation of particles (promoted by favourable major ion chemistry in the water) generates a flux towards the sediment (Buckney, 1980), hence continuing the cycle.

4.4.5.2 Comparison of Surface Water Loads and Interstitial Water Diffusional Fluxes

In order to assess whether the sediments could have an effect on the water content of dissolved heavy metals and phosphate, calculations were performed. For selected sample collections (i.e. 1, 3, 4, 5, 10, 11), differences in surface water load (in milligrams per hour) between two adjacent stations were compared to the respective calculated amounts that could diffuse to/from the interstitial water.

The pore water diffusional flux (also in mg h^{-1}) was determined using the equation derived from Fick's first law (Williams and Williams, 1973) :

$$\text{Flux} = -D A (dC/dx) .$$

Where necessary, assumptions were made in order to generate a maximum final value.

Values for the diffusion coefficient (D) of each solute were calculated using the data supplied in the CRC Handbook of Chemistry and Physics (73rd ed.; Lide, 1992). Given that the particles of sandy sediments are mainly in contact, creating large pore size but low overall pore space, the cross-sectional area (A; with units of m^2) across which solute could diffuse was assumed to be 25% of the total sediment area between two stations (Townsend, 1973). For the three creeks, the total sediment areas (m^2) between each pair of stations were 600 (GC1-2), 300 (GC2-3), 1250 (SC1-2), 250 (SC2-3), 500 (TC1-2) and 500 (TC2-3). The change in concentration (dC) was approximated by the difference between the average interstitial water concentration and the average surface concentration for the two sampling stations. On dividing by 0.075m - the estimated distance between which the surface and interstitial water samples were collected - a value for dC/dx was obtained.

Poor agreement was observed between the two calculated values (refer to Appendix 6, Tables A15(i)-(iii)), indicating that no relationship existed between the difference in surface water loads and potential sediment-water fluxes. For ortho-phosphate, large differences in surface water loads were observed with the corresponding sediment fluxes

being extremely small - many orders of magnitude smaller in fact - while the positive and negative signs did not always match. The same trends were seen with the heavy metals, although the situation was confused due to a high incidence of samples with below detectable limit levels. Nevertheless, where pairs of numbers were present, the changes in surface water loads were usually large and calculated fluxes were small, with poor matching of signs. In addition, correlation analysis on the two load types (excluding those samples having undetectable values in both cases), found no significant correlation trends for any of the five parameters.

In a similar assessment of the fluxes of phosphate in the sediment column and across the sediment-water interface, Enell and Löfgren (1988) determined a sediment diffusion coefficient which took into account that the sediment hinders free diffusion through tortuosity and adsorption. These factors were not included here. However, any potential error should be minimal as the sediments were generally shallow, while being primarily of sand they were both porous and weak in adsorptive capacity.

Although the data used were obtained from studies of limnic ecosystems, Enell and Löfgren (1988) observed large discrepancies between calculated and measured phosphorus diffusive flux values, often up to more than one order of magnitude. As important mixing processes of bioturbation, gas ebullition and currents were considered negligible, it was suggested the release of phosphorus to the water mass must occur directly from particulates comprising the sediment surface, as a result of high pH and/or reducing conditions. For the compared low flow data of the present study, these mixing processes were also expected to be minimal and given the nature of the systems involved it was plausible to assume such a mechanism occurs for phosphorus and heavy metals.

In order to test this, the calculations were repeated using a much smaller value (0.5mm) for the estimated distance between which surface and interstitial water samples were collected (Appendix 7, Tables A16(i)-(iii)). However, weak agreement between the two sets of results was again observed, the diffusive fluxes still remaining significantly lower (in general) than the differences in surface water loads.

These results therefore implied that the flux of dissolved constituents from the sediment could not account for the differences in dissolved surface water content. Since the magnitude of downstream increase in surface water loads were consistently in large excess of the magnitude of flux loads, other sources or factors must have been responsible for the differences. This suggests that the surface water loadings are more influenced by external inputs, rather than the sediments.

4.4.5.3 Sediment Adsorption Isotherms

Solute adsorption onto a solid surface is known to continue until an equilibrium is established. This equilibrium reflects the capacity (or affinity) of the adsorbent for the given solute and may be expressed mathematically by way of an adsorption isotherm (Al Duri, 1996).

Hawkesbury Sandstone sediments are expected to exhibit low adsorption capacity, given their high sand content. A theoretical attempt to characterise the heavy metal and phosphorus adsorption behaviour is presented here, after reference to Al Duri (1996), Jenne (1995a), Jenne (1995b), McKinley and Jenne (1991), Duff *et al.* (1988) and Atkins (1982). Only low flow samples (which included the collection of sediments) were considered, so that conditions were as close to equilibrium as possible. Cadmium was not investigated since only a small data set was available.

The low flow samples that were combined to make up the data set were as follows :

Sample collections 1, 3, 4, 5, 6, 7, 9, 10, 11 for GC1; TC2-3

Sample collections 1, 3, 5, 6, 7, 9, 10, 11 for GC2

Sample collections 1, 6, 9, 10, 11 for GC3

Sample collections 1, 3, 4, 6, 7, 9, 10, 11 for SC1-3

Sample collections 1, 3, 4, 6, 9, 10, 11 for TC1.

For each plot, further samples were omitted where missing data points occurred, or where heavy metal or phosphorus concentrations were below the corresponding detection limit.

The Langmuir adsorption isotherm is commonly used to describe the relationship between amount of solute adsorbed (A , in moles or grams per unit mass of adsorbent) and the concentration of solute in solution at equilibrium (C , in moles or grams per litre). It may be written :

$$A = \frac{A_m KC}{(1 + KC)} ,$$

where A_m is the limiting (i.e. maximum) amount of solute that can be taken up by unit mass of adsorbent and, along with K , is a constant for a given system at a particular temperature (Al Duri, 1996; Duff *et al.*, 1988; Atkins, 1982). A plot of A against C

illustrates that as C increases there is an initial (sharp) increase in A , which then tends to a limit (the A_m value) for large C (Duff *et al.*, 1988).

This relationship can be rearranged into the linearised Langmuir adsorption isotherm as follows :

$$1/A = (1/A_m K) 1/C + 1/A_m .$$

A plot of $1/A$ against $1/C$ should be linear (with a slope of $1/A_m K$ and intercept on the $1/A$ axis of $1/A_m$), depending upon the applicability of the isotherm to a particular system.

From the monitoring study data set, interstitial water concentrations of dissolved metals (Cu, Zn and Pb) and ortho-phosphate were used as the solute equilibrium concentrations (i.e. C). Surface waters were not included since they were too influenced by external inputs, as discussed in the previous section. For metals, the corresponding amount of adsorbed solute (i.e. A) was approximated to the sum of secondary phase metal (i.e. RE + HMO + OMS fractions; see section 4.4.3). For phosphorus, the corresponding A was approximated as the sediment total P value. This may have been an overestimation in certain cases, as phosphorus was expected to be present to some extent in residual, or discrete precipitate, forms (see section 4.4.3). However, most was likely to be co-precipitated with and/or directly adsorbed onto metal oxide and organically coated surfaces (see section 4.4.5.4).

Subsequent plots did not display any relationship between the chosen pairs of variables (Figures 43 and 44). Nevertheless, there are explanations why the data did not fit the Langmuir model. Firstly, each sample (providing a pair of co-ordinates) was assumed to have been collected when the system was at equilibrium. Given that sample collections were performed at random and the Hawkesbury Sandstone streams were highly variable, especially the interstitial waters (see section 4.3.5), this assumption could not have been valid for all cases. Furthermore, there is no way of telling which samples did in fact represent such a condition.

Secondly, the isotherm applies for homogeneous adsorption and assumes a uniform adsorbent surface with energetically identical sorption sites (Al Duri, 1996). These sediments, despite being principally composed of sand, were heterogeneous in composition (see sections 4.3.3 and 4.3.5) and would not be restricted to only one (single layer) adsorption mechanism. Indeed the chosen 'A' data involved values that

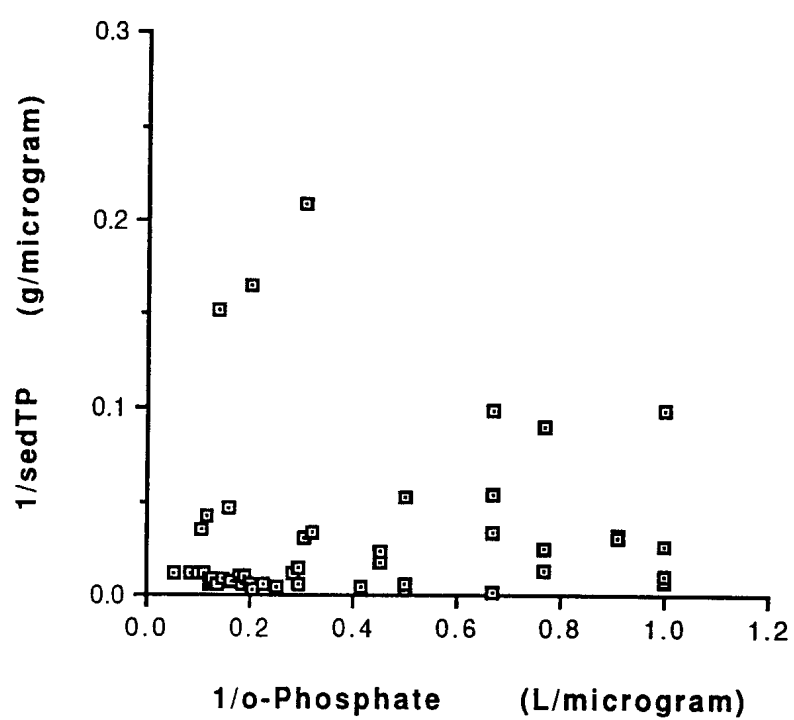


Figure 43. Langmuir adsorption isotherm plot for phosphorus and Hawkesbury Sandstone sediment. Sediment total P against IW dissolved ortho-phosphate.

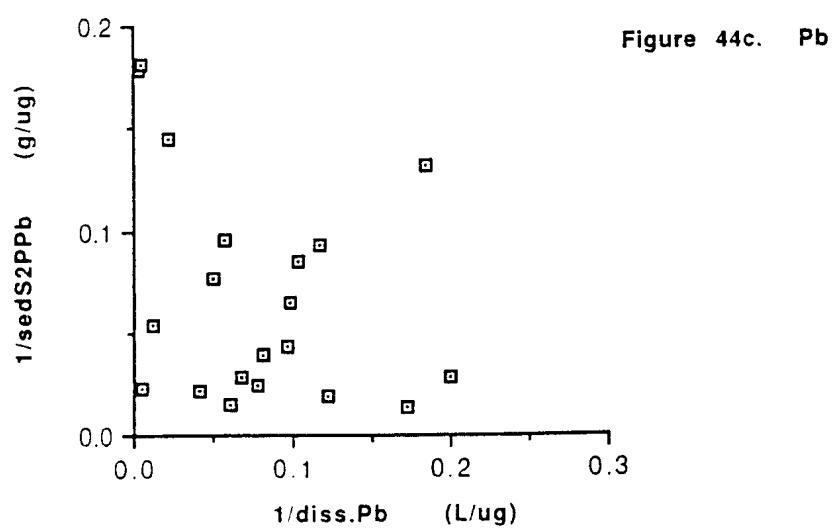
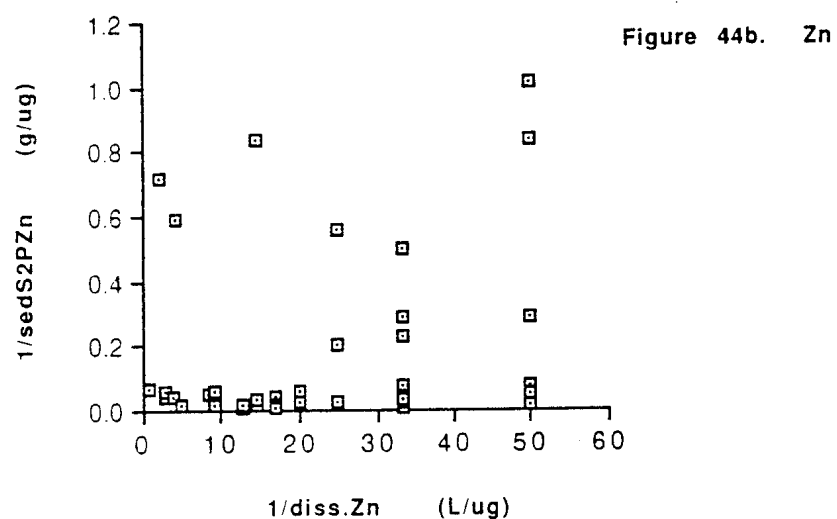
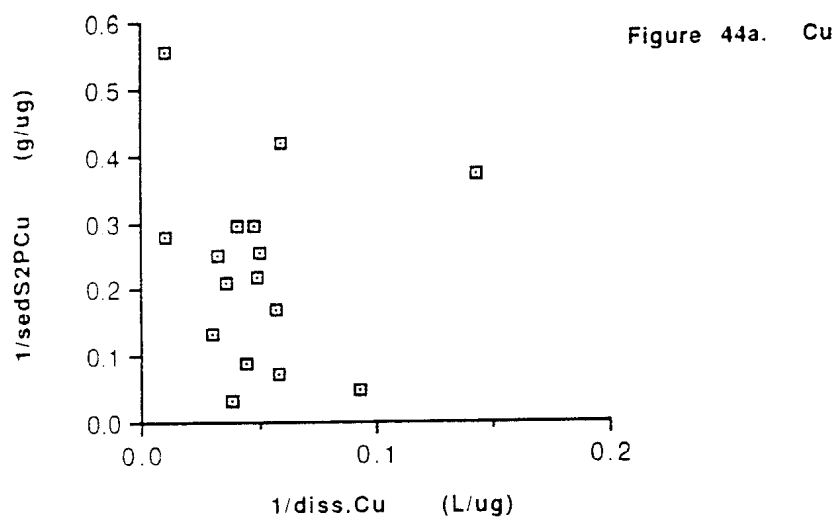


Figure 44. Langmuir adsorption isotherm plots for heavy metals and Hawkesbury Sandstone sediment. Sediment sum of secondary phase metal against IW dissolved heavy metal.

were a sum of numerous binding mechanisms (i.e. total; bound to clays + bound to hydrous metal oxides + bound to organic matter).

This second problem was addressed for phosphorus by replacing sediment total P (sedTP) with sediment organic P (sedOP), while for metals by separating the RE, HMO and OMS metal fractions and plotting each against the corresponding dissolved interstitial concentration. Again, however, the plots did not display any significant relationship between the chosen pairs of variables (Figures 45 and 46(i)-(iii)), except for weak linear correlation for rapidly exchangeable zinc and lead (Figures 46(i)b and 46(i)c; neither correlation coefficient was significant at the 5% level). It was concluded that the Langmuir model did not help describe heavy metal and phosphorus adsorption behaviour of the surficial Hawkesbury Sandstone sediments.

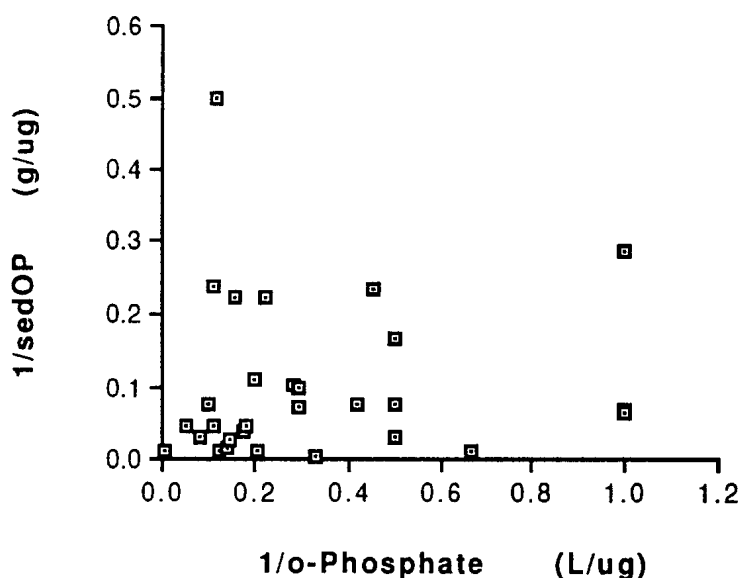


Figure 45. Langmuir adsorption isotherm plot for phosphorus and Hawkesbury Sandstone sediment. Sediment organic P against IW dissolved ortho-phosphate.

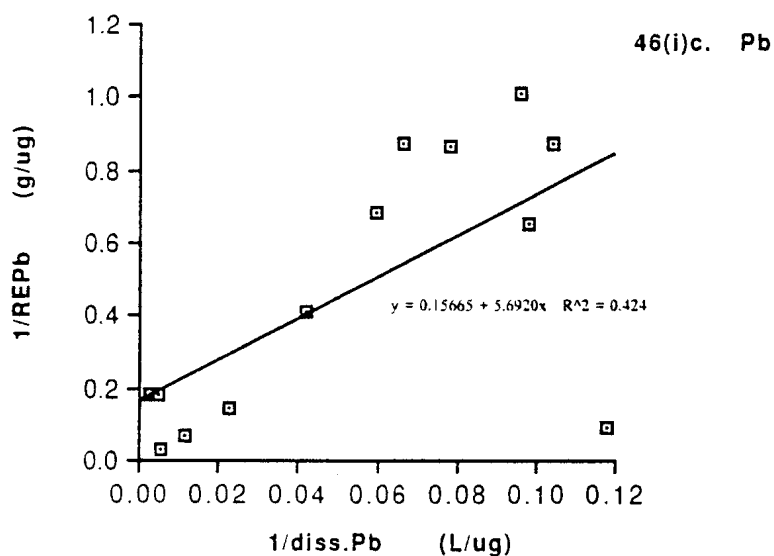
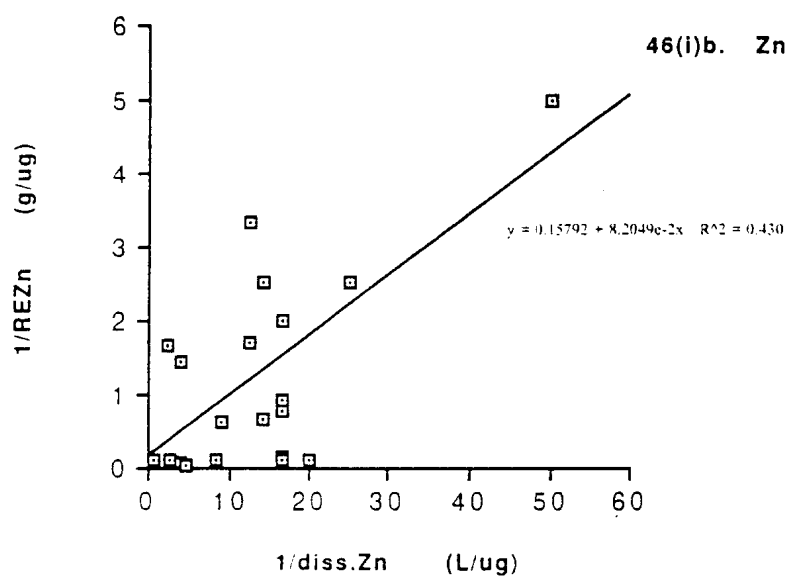
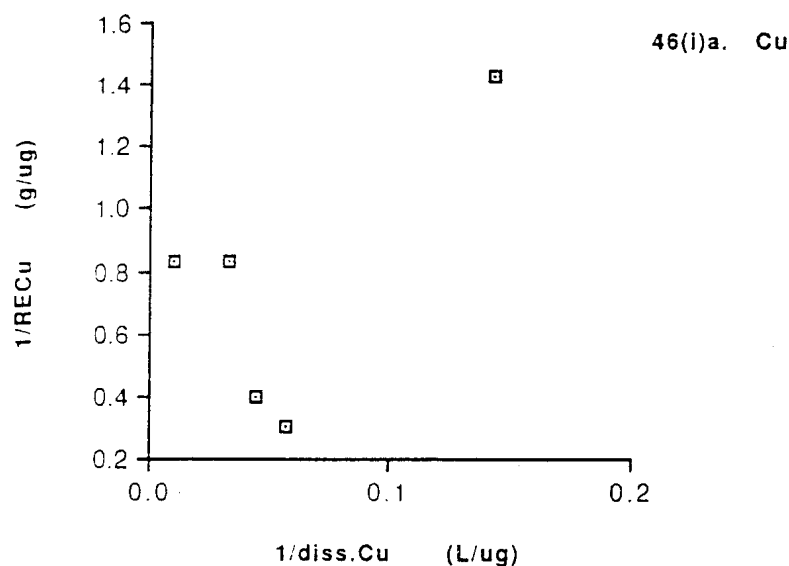


Figure 46(i). Langmuir adsorption isotherm plots for heavy metals and Hawkesbury Sandstone sediment. Sediment RE heavy metal against IW dissolved heavy metal.

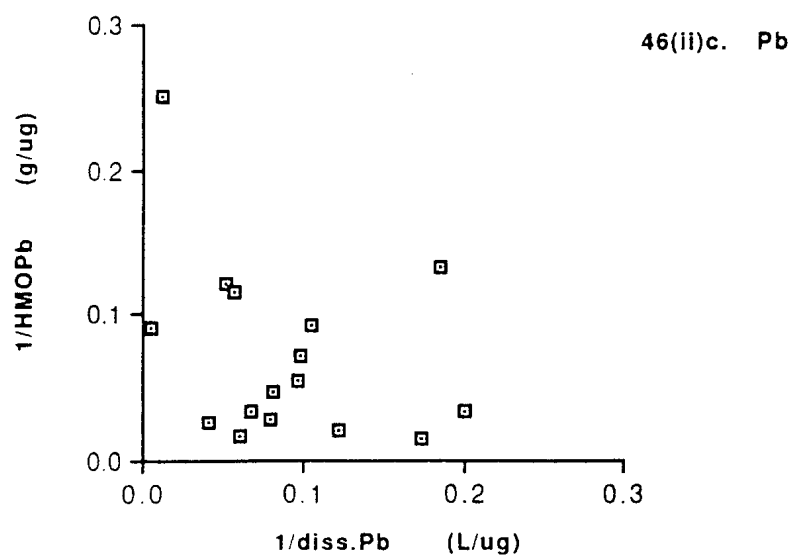
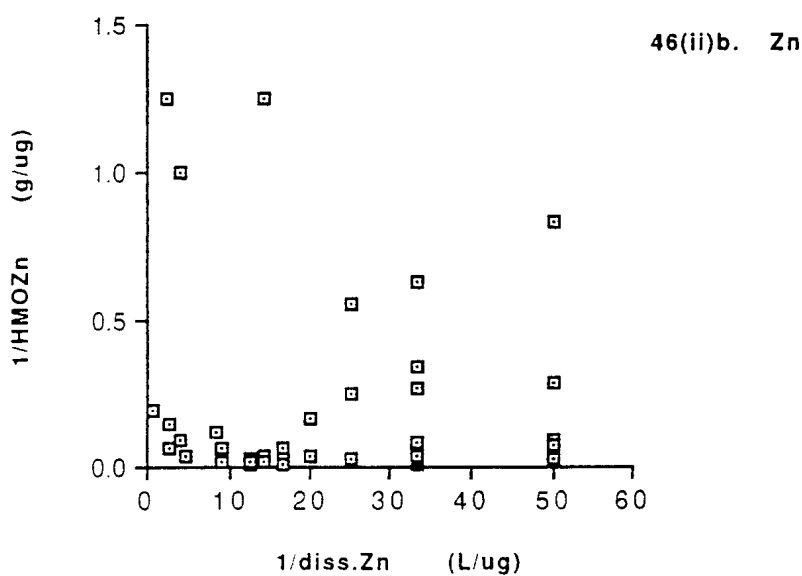
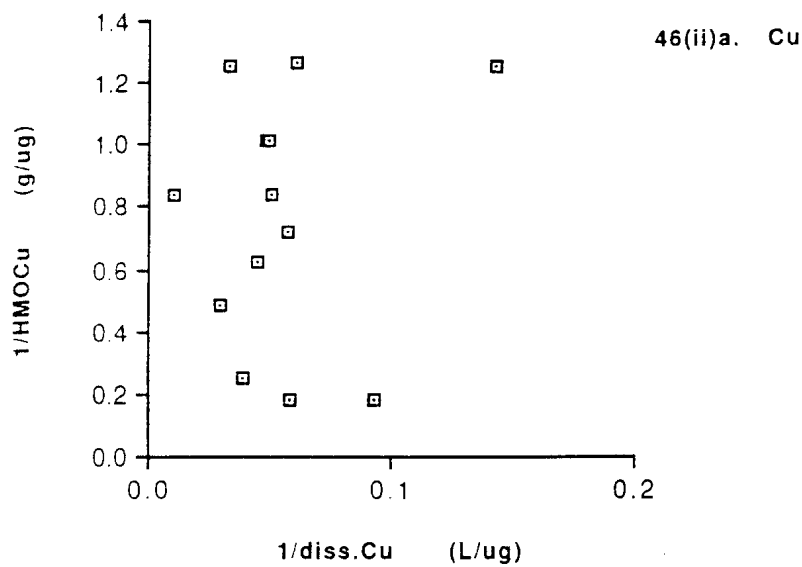


Figure 46(ii). Langmuir adsorption isotherm plots for heavy metals and Hawkesbury Sandstone sediment. Sediment HMO heavy metal against IW dissolved heavy metal.

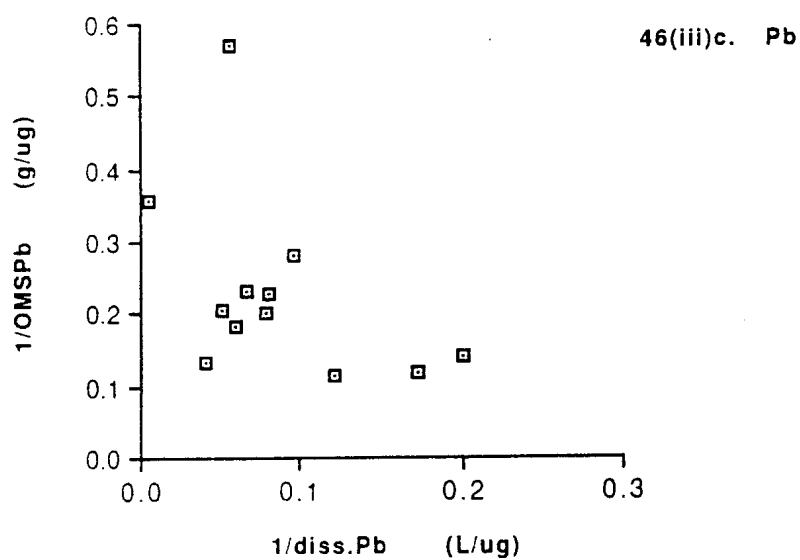
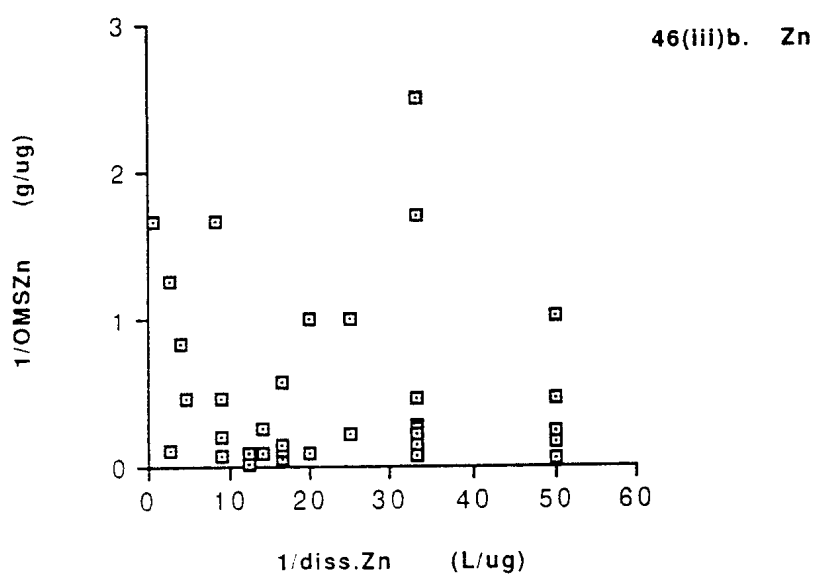
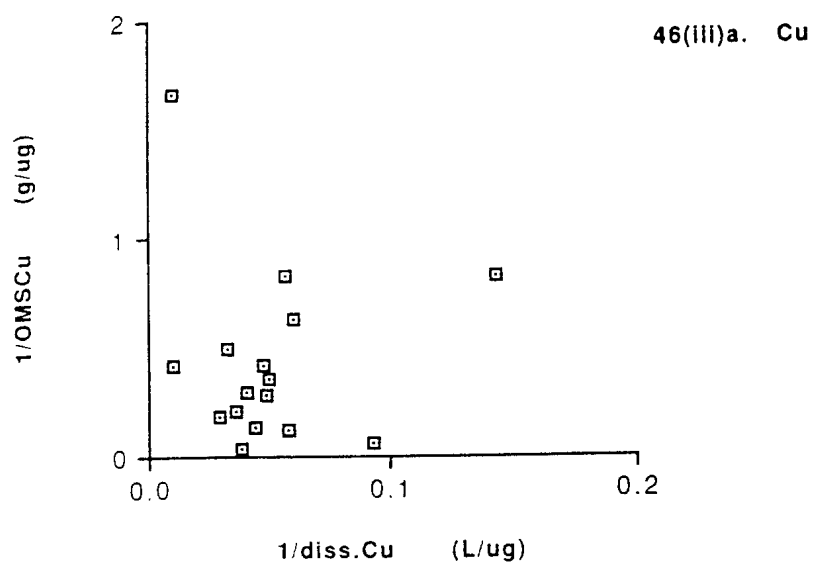


Figure 46(iii). Langmuir adsorption isotherm plots for heavy metals and Hawkesbury Sandstone sediment. Sediment OMS heavy metal against IW dissolved heavy metal.

McKinley and Jenne (1991) noted that experimental data often do not behave as predicted by the Langmuir model, but fit the empirical Freundlich isotherm. This isotherm differs from the Langmuir model in that it describes equilibrium on heterogeneous surfaces, hence it does not assume monolayer adsorption (Al Duri, 1996). It also does not have a limiting adsorbed concentration (McKinley and Jenne, 1991). The calculations remain mathematically convenient, however, and results have been accurate for a wide range of adsorption systems (Al Duri, 1996).

The Freundlich isotherm is expressed as :

$$A = a_F C^{b_F} ,$$

where a_F and b_F are the Freundlich constants, expressing the adsorbent capacity and heterogeneity factor, respectively. The value of the heterogeneity factor (b_F) ranges between 0 and 1; the more heterogeneous the surface, the closer the value is to 0 (Al Duri, 1996; McKinley and Jenne, 1991). A plot illustrates that as C increases, so does A , in a curved fashion (unless b_F is 1). Unfortunately, the isotherm fails to describe equilibria as C approaches 0 and is thermodynamically inconsistent (Al Duri, 1996). To overcome this, the relationship can be converted into a linearised form as follows :

$$\log A = \log a_F + b_F \log C .$$

A plot of $\log A$ against $\log C$ should be linear (with a slope of b_F and intercept on the $\log A$ axis of $\log a_F$), depending upon the applicability of the isotherm to a particular system.

Separate plots (of $\log A$ against $\log C$) involving sediment organic phosphorus, RE, HMO and OMS metal fractions were generated (Figures 47 and 48(i)-(iii)). Once again, no plot displayed any significant relationship between the chosen pairs of variables, apart from weak linear correlation for REPb (Figure 48(i)c; the correlation coefficient was not significant at the 5% level).

No improvement was observed if log-log scales were used for the x- and y- axes, as suggested by Al Duri (1996). It was concluded that the Freundlich model also did not help describe heavy metal and phosphorus adsorption behaviour of the surficial Hawkesbury Sandstone sediments.

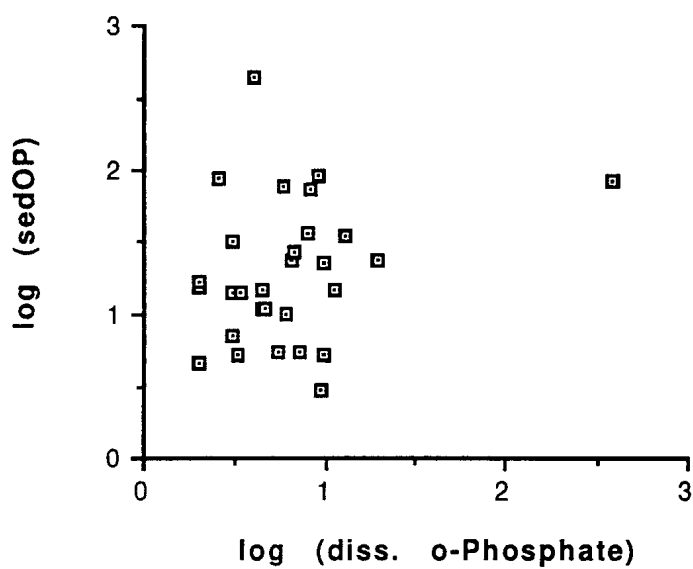


Figure 47. Freundlich adsorption isotherm plot for phosphorus and Hawkesbury Sandstone sediment. Sediment organic P against IW dissolved ortho-phosphate.

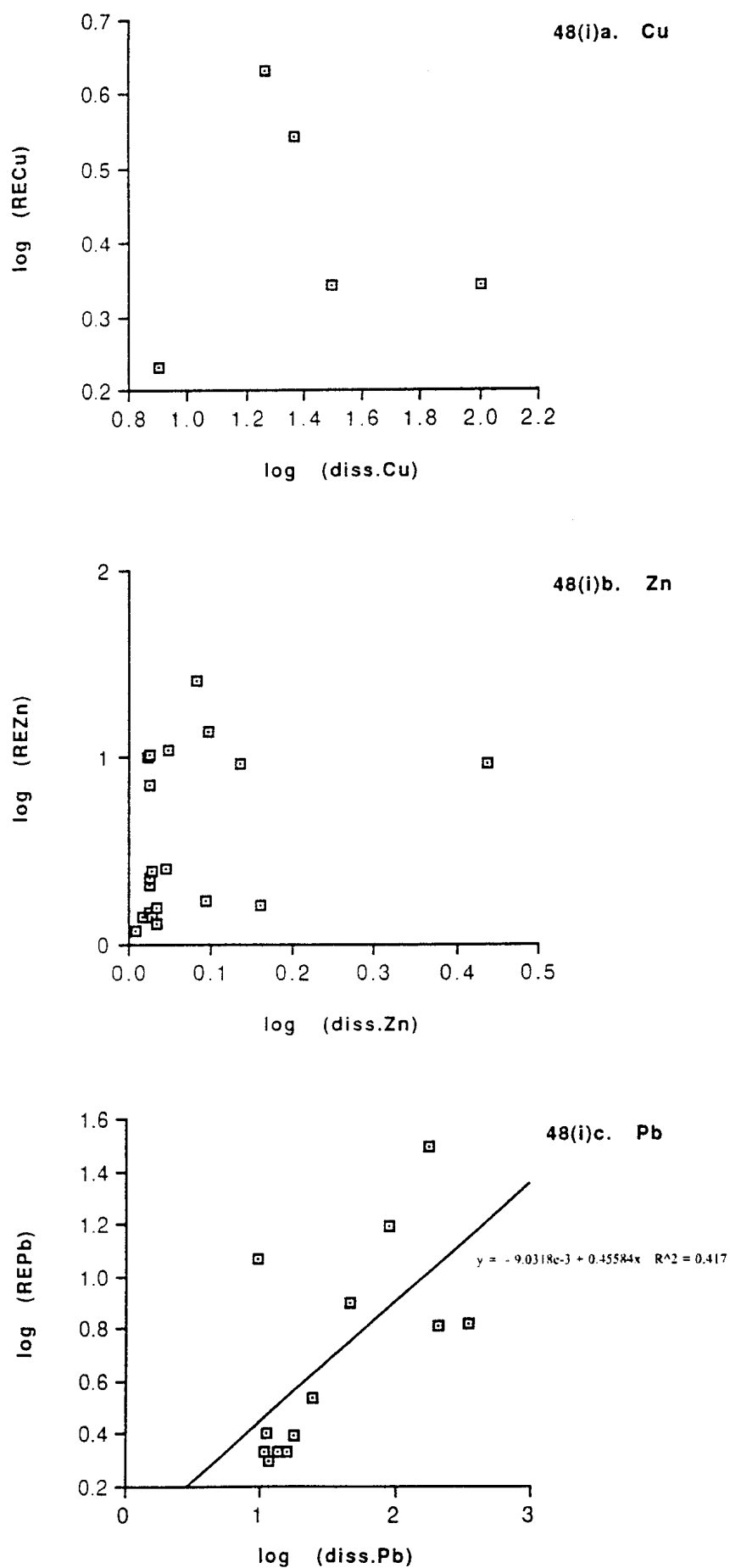


Figure 48(i). Freundlich adsorption isotherm plots for heavy metals and Hawkesbury Sandstone sediment. Sediment RE heavy metal against IW dissolved heavy metal.

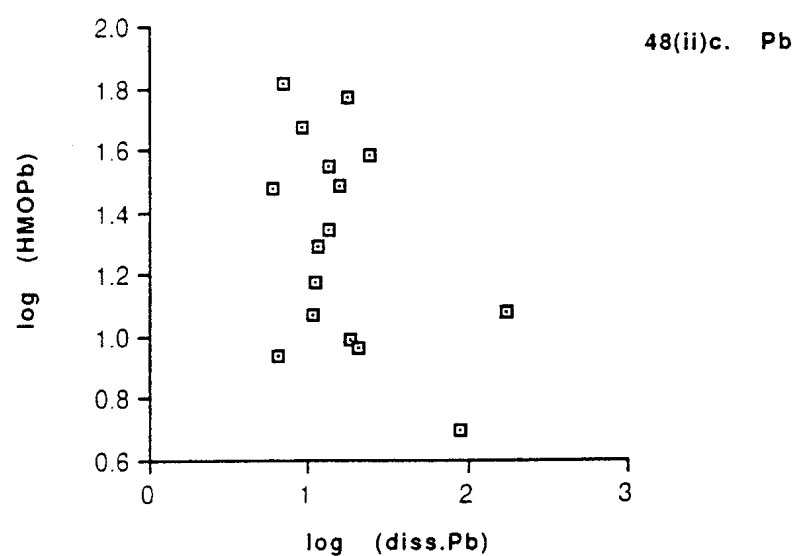
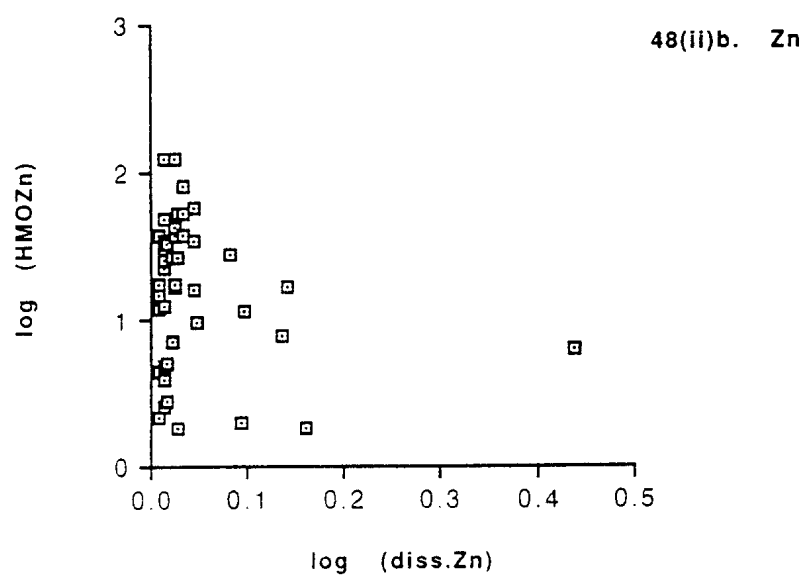
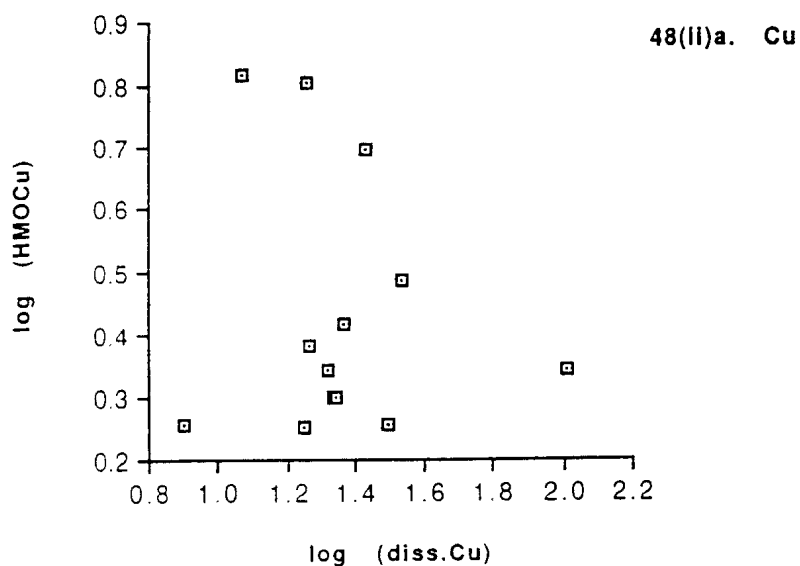


Figure 48(ii). Freundlich adsorption isotherm plots for heavy metals and Hawkesbury Sandstone sediment. Sediment HMO heavy metal against IW dissolved heavy metal.

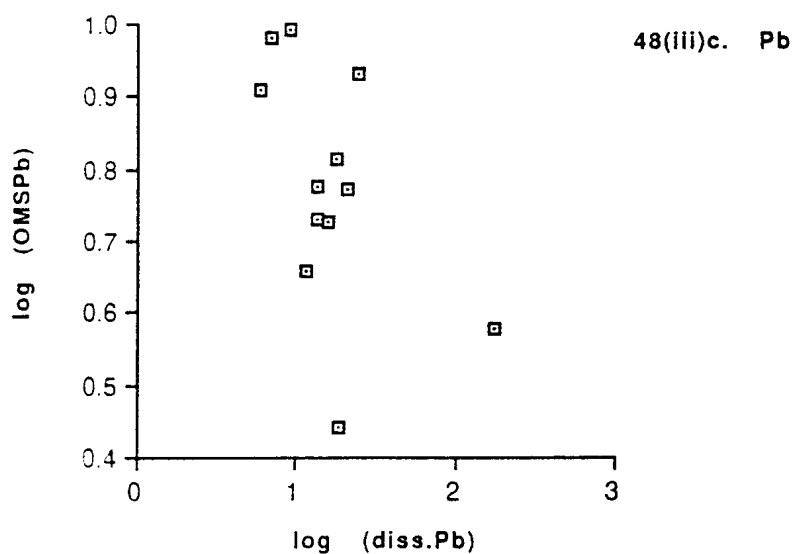
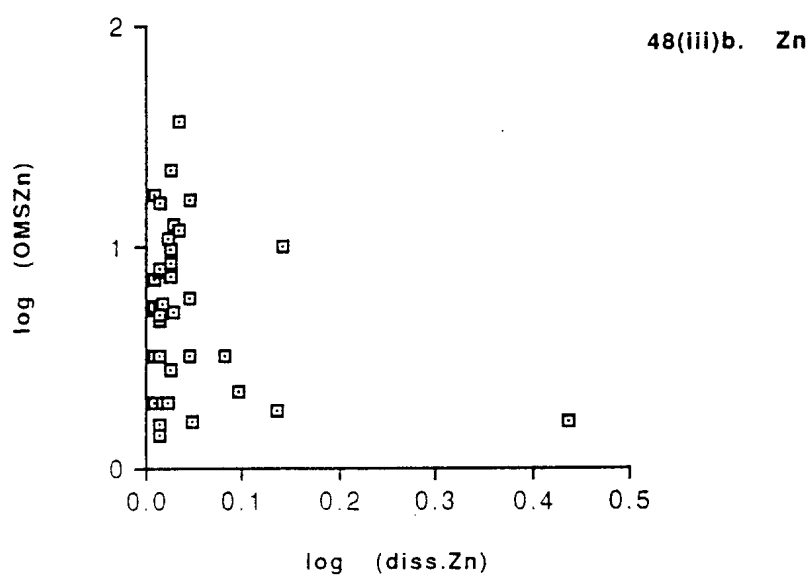
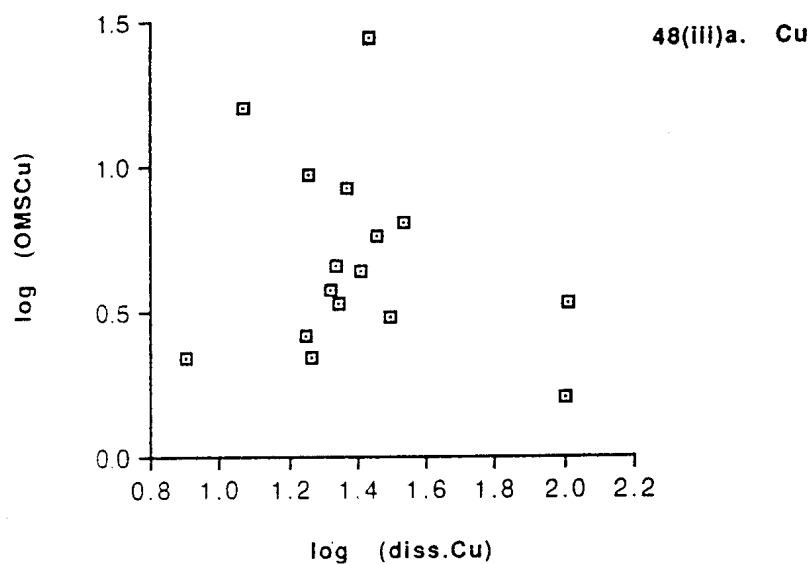


Figure 48(iii). Freundlich adsorption isotherm plots for heavy metals and Hawkesbury Sandstone sediment. Sediment OMS heavy metal against IW dissolved heavy metal.

This section demonstrates the difficulty in drawing conclusions concerning adsorption isotherms using field data. Without controlled experimental conditions and being uncertain when an equilibrium situation was present (i.e. being sampled), isotherm calculations are riddled with complications. After all, both isotherm models assume, or describe, an equilibrium process.

The empirical modelling does indicate, however, that the Hawkesbury Sandstone stream waters are rarely at equilibrium with their sediments, even at low flows. So while such a condition may be quickly established (see section 4.4.5.1), it is generally short-lived and easily shifted to a different status. This reflects the findings that these streams are highly variable in chemical composition.

4.4.5.4 Sediment Uptake of Heavy Metals and Phosphorus

Despite the significance at the 0.05 level, many of the determined correlation coefficients in Tables 22, 23, 24 and 26 were of small magnitude (<0.500) and thus the correlations were weak, accounting for only a low percentage of the linear variability. More importantly, on assessing each analysis the results were inconsistent and certain correlations implied improbable processes (e.g. oxidising conditions favouring release of both dissolved and total phosphorus forms, but reduction in dissolved heavy metal concentrations). Improbable processes suggested that more complex mechanisms, not as yet recognised, were taking place.

Nevertheless, numerous results were worth close consideration and helped the interpretation of other findings. For example, significant negative correlations were observed between specific water quality parameters (i.e. conductivity, alkalinity and hardness) and dissolved heavy metal and ortho-phosphate concentrations in both surface and interstitial waters (see sections 4.3.4.1 and 4.3.4.2, plus Tables 22(ii) and 23(i-ii)), accompanied by the positive correlations of these same quality parameters with sediment metal and phosphorus totals (Table 24). Hence, as the salinity of the water increased, so did the metal and phosphate precipitation rates, suggesting that precipitation is important for deposition of heavy metals and phosphorus to the sediments of these streams, especially in the urbanised sites. Since interstitial pH and redox potential also showed correlation with sediment totals at the urban sites (Table 24(ii)), the extent of precipitation should be at least partly influenced by these variables as well.

Given that alkalinity and hardness were involved, co-precipitation and association with calcium carbonate is possible, through the common ion effect (Petrucci, 1972). From the data in appendix table A12, comparison of calcium and total carbonate ionic products with

the theoretical solubility product ($5 \times 10^{-9} \text{ mol}^2 \text{ L}^{-2}$ or $50.1 \text{ mg}^2 \text{ L}^{-2}$ for CaCO_3 , as from Aylward and Findlay (1974)) indicated conditions which promote such precipitation do occur in the waters of these sites - even though of the total carbonate content most would favour the bicarbonate form. Such reactions would be expected to occur in the surface and interstitial waters with equal likelihood, given the poor correlation of sediment heavy metal and phosphorus totals with dissolved interstitial water levels (Table 26).

Some of this precipitation may result in a direct increase of the residual fraction, after all this fraction contributed a significant proportion of the heavy metal content in these sediments, especially for lead (see Figure 27 and section 4.4.3). However, upon considering the low partitioning of sediment heavy metal in the rapidly exchangeable fraction, from which most carbonate-bound metal is believed to be extracted (Martin *et al.*, 1987; Gupta and Chen, 1975), associations with carbonates must be relatively insignificant (again, see section 4.4.3).

In oxidised sediments, heavy metals and phosphorus are predominantly distributed among sites on hydrous metal oxides and various types of organic matter (Luoma, 1989; Syers *et al.*, 1973), due to the strong affinity of these substrates for such constituents (Salomons and Förstner, 1984; Förstner, 1982; Syers *et al.*, 1973; Williams *et al.*, 1971). As the Hawkesbury Sandstone sediments of these streams were relatively well aerated, high in iron oxide content - fine, orange-coloured precipitates being a common feature on the surface - and contained some organic matter, conditions are favourable for available heavy metals and phosphates to be co-precipitated with and/or directly adsorbed onto metal oxide and organically-coated surfaces. The sediment speciation results support this (Figure 27). These phenomena therefore remain the principal mechanisms for uptake of heavy metals and phosphorus in these sediments.

4.4.6 Patterns of Natural Chemical Variability for Hawkesbury Sandstone Streams

For both studies the data sets illustrated substantial chemical variability, particularly with respect to the minor ion chemistry in stream waters from developed catchments. This is consistent with the view that most Australian aquatic environments are highly variable and unpredictable (Norris and Georges, 1986). Multi-dimensional scaling was a suitable method to specifically identify, assess and compare the principal sources of this variability.

4.4.6.1 Site Variability

Ordinations using means identified that all three creeks had their own distinct chemistries, especially Gwawley and Temptation Creeks (Figures 28, 31, 34 and 38), highlighting that runoff is extremely varied. Between-site differences were most noticeable for surface waters and sediments. Greater separation of individual sampling stations was apparent for the urban interstitial waters, however, making site groupings less obvious.

Despite the sites having distinct water type and sediment compositions, the separate ordinations involving single and large groups of sample collections demonstrated that considerable variability, on both spatial and temporal scales, occurred in these chemistries under low flow conditions (Figures 29, 32, 35, 36, 39 and 40). For surface waters and sediments (Figures 29, 39 and 40), the variability was greatest for Gwawley Creek, intermediate for Savilles Creek and lowest for Temptation Creek.

Variability in interstitial water composition was virtually equal for the two urban sites, but still greater than for Temptation Creek (Figure 32). More importantly, there was also separate clustering of site replicates which indicated major chemical effects and analysis of variance identified significant differences in conductivity, alkalinity, acidity and oxidation-reduction potential for the groups. As acidity was extremely low for all three sites ($<10 \text{ mg L}^{-1}$ as CaCO_3 , see section 4.3.2.2), the other three water quality parameters were targeted as the main source of such effects.

Considering that heavy metal, phosphorus and suspended solids concentrations were highly variable, they were principal factors affecting the spatial distribution of the replicates. This was reflected in the outliers regularly displaying high levels of one or more of these constituents. Such results were consistent with the findings that urban waterways regularly receive discharges of diverse chemical composition (Ellis, 1976), and human developments create increased non-point discharges.

Single sample ordinations that included both water types found interstitial water to be generally more variable than surface water in composition (e.g. Figures 35a, 35c, 35d), especially in the two urban sites (refer also to Figures 31 and 34). In two analyses (Figures 35c and 35d) marked separation of the water types was observed, a result that was also seen in Figure 34, but for sites only in this latter case. Notable differences in dissolved oxygen and alkalinity levels were apparent, consistent with the sediment environment having a more anaerobic nature and less water.

Greater variability of interstitial waters was a reflection of the combined influences of the surrounding sediment and surface water compositions, which are both more variable in systems receiving inputs from urban catchments. For instance, from numerous ordinations the separation of stations 2 and 3 of Savilles Creek was often much less compared with station 1 (Figures 31, 34, 35b, 35c and 35d). At the site, the distance between these two stations was quite short - approximately 50m - reducing the opportunities for sediments and waters to alter in composition and hence so too the interstitial waters.

While surface waters affect pore water composition by dilution and/or providing constituent inputs (Enell and Löfgren, 1988; Boström *et al.*, 1988), the nature of the particulate material becomes very important. Sediment is normally of heterogeneous composition (Beckett, 1986; Hart, 1982), and influences the make-up of the water with which it is in direct contact (Enell and Löfgren, 1988; Oschwald, 1972). This becomes especially significant in urban sites, since the sediment changes regularly through high flushing rates and wide sources of replacing particulates (Neller, 1985; Ellis, 1976). Undeveloped sites are limited in the number and type of input sources, so sediment composition is more uniform over the sorts of distances (<1km) used here. Thus, the interstitial water chemistry of Temptation Creek was the least varied for the three systems studied, even showing less variability than the corresponding surface waters.

Changes in surface-sediment interstitial water chemistry are also derived from other factors including microbial activity, the hydrodynamics of the water column and seasonal variations in benthic populations (Enell and Löfgren, 1988). The combined influence of all these factors creates an extremely dynamic environment. For example, Enell and Löfgren (1988) reported that high levels of both temporal and spatial variability in interstitial phosphorus concentrations are known to occur within lakes, especially in shallow and eutrophic systems.

Between-site differences in surface water composition were quite obvious for the short stream reaches studied, the less pronounced within-site variability being attributed to dilution effects. Materials released from the sediments to the overlying water are quickly diluted and eventually spiralled (as described by Hart and McKelvie (1986)), so that localised pore water concentrations do not necessarily create zones of concentrated surface waters. Exceptions to this rule might include the headwater areas and isolated pools - generated after extended dry periods when connecting shallower reaches dry up - that lie over contaminated sediments. For both these environment types, flushes of upstream waters are not always possible, preventing the dilution of contaminants as they are released.

This natural 'buffering' capacity of the surface water creates greater compositional similarity over the creek length. On comparing the surface water loadings and potential diffusional fluxes for metals and phosphorus (section 4.4.5.2), it was concluded that for the stream reaches investigated, sediment diffusion/deposition in no way accounted for the difference in surface water load between two adjacent sampling stations (unless the concentration gradient is much steeper than reasonably assumed). Therefore the concentrations of these constituents are principally affected by external discharges into the system. Sites differ because of the relative amounts of external inputs - in urban areas there are more non-point (or point) sources compared to undeveloped sites.

For surface water it may, therefore, be possible to talk in terms of an overall stream quality (certainly for short distances of stream), and have relevance to surface water organisms. The quality of interstitial waters (and therefore sediments as well), however, may need to be characterised for local conditions as the organisms living in closer contact with the sediments, such as burrowers and other benthic macroinvertebrates, would be more directly influenced by this more variable water type.

Normally, surface sediments are a useful medium for the monitoring of numerous contaminants in aquatic systems, due to an ability to accumulate constituents while maintaining reasonably uniform composition (i.e. steady state grain size distribution, organic matter content etc.) over time (Chapman, 1992; Larsen and Jensen, 1989). However, the shallow, loosely packed sediments in these streams did not indicate heavy metal and phosphorus accumulation during the short-term monitoring study (appendix table A13). Instead they showed a reasonable amount of temporal variability, especially those from the urban sites (Figures 39 and 40). This is to be expected for water systems that have a high incidence of flood flow (and subsequent erosion in the immediate vicinity of the wetted perimeter), while incoming suspended solids from the surrounding catchment are varied in their contents. Nevertheless, the results diminish the value of sediments being used as an environmental monitor for Hawkesbury Sandstone streams located in developed catchments, unless long-term collections are used.

4.4.6.2 Differences in Seasonal Variability

Groups of distinct high and low values, coinciding with the main climatic changes of the year, were not apparent for any of the three monitored streams. However, from the composite sample collection ordinations, certain differences in chemical variability were observed between summer (including the spring months) and winter (including the autumn months) groups.

For both surface waters and sediments (Figures 30 and 41) greater variability occurred amongst the winter samples. However, from the ordination using only interstitial waters (Figure 33) there was little difference in the spatial distribution of summer and winter groups. This was a reflection of the highly variable nature of pore water in these streams, overriding any possible seasonal effects.

On combining the surface and interstitial water data sets, similar results were repeated (Figure 37). More importantly, however, distinct groups were generated in this case - summer samples being separated (vertically) from winter ones, whether the samples were of surface or interstitial origin. Despite consistent heterogeneity of variances, parameters that were responsible for these groupings included dissolved oxygen, acidity, zinc, copper and lead, with higher levels occurring in the winter samples; dissolved orthophosphate was lower in the winter samples.

Hence, seasonal fluctuations were detected in these Hawkesbury Sandstone streams, but in terms of changes in the level of chemical variability in surficial waters and sediments. Higher levels of variability were observed for the surface waters and sediments collected during the winter season (i.e. winter plus autumn months), compared to the summer season. In these streams, non-point discharges represent the major source of contaminants. Considering that autumn is normally the wettest season for the Sydney basin, while spring is the driest (Benson and Howell, 1990; Chapman and Murphy, 1989), these results support an hypothesis of runoff being a principal source of such chemical variability.

Riso *et al.* (1993) have reported seasonal influences in the water chemistry of heavy metals. Significant differences were seen in the concentration and distribution of copper, nickel and lead for Western Brittany coastal waters, sampled at monthly intervals for over a period of a year. These differences, while not the same for each metal, were attributed to seasonal changes; two of the main factors affecting the cycle of metal being the mixing of fresh and saline waters, and the phytoplankton development. Although not specifically runoff nor dealing with lotic fresh waters, this nevertheless helps to illustrate that environmental heterogeneity can be detected on a such a scale.

Marsh (1993) observed that for five of the six monitored sites in the metropolitan area of Louisville, Kentucky, the quality of runoff samples (including pH, DO, conductivity, turbidity, alkalinity, hardness and nutrients) was found to be much poorer for those taken during the winter season compared to summer. It was also noted that temporal variability in stormwater runoff was considerable, compositional differences occurring between the

first flush and latter end flows, from storm to storm, season to season and even year to year. The sources of this variability lay in the different weather patterns and the fact that land uses were able to contribute to a water system in a wide variety of ways. Importantly, the time of year rain occurred was regarded as much more important than the frequency and/or intensity of events.

4.5 Conclusions

This short-term monitoring study identified certain chemical characteristics and differences in the three small Hawkesbury Sandstone-based streams of the Sydney basin.

The streams predominantly existed under low flow conditions (i.e. $<31.3 \text{ cm s}^{-1}$) during this study, their physical nature being such as to hinder the passage of water. Flow rate was strongly influenced by runoff frequency and quantity. Rates of particle displacement/replacement were high and have influenced the observed variability in sediment composition.

Surface waters from all three sites were low in salinity ($<200 \text{ mg L}^{-1}$ total dissolved solids), soft ($<100 \text{ mg L}^{-1}$ as CaCO_3 for hardness) and of generally poor acid/base buffering capacity. Sodium and chloride dominance and correlation between these was observed, although high levels of calcium and total carbonate (up to co-dominant proportions) were apparent in the urban sites, especially Gwawley Creek. The increased concentrations of total carbonate at these sites caused a rise in the acid-buffering capacity ($>100 \text{ mg L}^{-1}$ as CaCO_3 alkalinity). Despite substantial variability, heavy metal and nutrient concentrations were generally higher in samples (waters and sediments) from the urbanised sites, compared to those from the reference site.

Runoff generated by a heavy storm created flood flows in all three streams. In this instance, the three streams were essentially indistinguishable and characterised by high levels of nutrients, suspended solids, turbidity and colour. These features were complemented by alkaline pH and oxidising redox, plus reduced conductivity, alkalinity and hardness through heavy dilution. Changes in the relative proportions of various constituents were also observed. Examples included decreased chloride with corresponding increased sulfate and potassium, as well as increased dissolved orthophosphate relative to the total phosphorus content.

Sediments were characterised by very low organic matter ($<2\%$), while particle size fractionation was dominated by coarse and fine sands ($>95\%$), leading to poor adsorptive

capacity (e.g. low cation exchange capacity; $<3 \text{ mmolNa/100g}$). Despite reduced accumulation of heavy metals and phosphorus in the long term, the sediments were nevertheless a sink for these constituents with observed concentrations being orders of magnitude higher than in the corresponding water samples.

Speciation studies on urban creek samples identified that the sums of the secondary phase lead were over nine times that of the corresponding residual, while for zinc and copper the equivalent sums were four and two times larger, respectively. The lead contamination was probably derived from the emissions of automobiles.

Greatest proportions of sediment zinc and lead were associated with coatings of iron and manganese oxides, or coarse residual particles. This preference indicated that stream water quality (or bioavailability) would be particularly vulnerable to decreases in pH and oxidation-reduction potential. Apart from a substantial residual component, copper was preferentially associated with organic matter and subsequently occurred at relatively lower levels compared to zinc and lead. Cadmium was rarely detected in any stream.

Heavy metal and nutrient levels in samples from the two urban sites (particularly Gwawley Creek) were often in excess of recommended quality criteria. However, the streams were not grossly polluted since poor water and sediment quality did not occur continuously. This suggested a natural tendency to regenerate following urban discharges. It is proposed that Hawkesbury Sandstone streams should be prioritised for management, being more likely to respond to remedial measures compared with many other streams.

Poor water quality - in the form of low dissolved oxygen and/or high concentrations of heavy metals and nutrients - was also seen on occasion in Temptation Creek, indicating that atmospheric aerosols may be a principal source of contamination (e.g. lead-containing aerosols). Given that interstitial waters displayed considerable within-site variability, surface waters were regarded as the most reliable measure of stream condition for short stream lengths.

Sediment quality was also varied, although it was possible to distinguish between the urban and reference streams. On this basis, prolonged sampling would be necessary if sediments were to be used as an environmental monitor for Hawkesbury Sandstone streams.

Concentration gradients between the interstitial and surface waters were rare. Release of heavy metals and phosphorus to the overlying water column was expected to occur

rapidly from the upper-most particulates at the sediment-water interface. Despite this, calculations indicated that sediment fluxes could not account for the changes in surface water loads between any two given sampling stations. Instead, these loads were believed to be influenced by external inputs (e.g. runoff, dissolved aerosols etc.).

Multi-dimensional scaling identified that under low flow conditions the three sites had distinct water and sediment chemistries. Substantial temporal and spatial variability was observed, however, particularly in the interstitial waters. This variability increased as follows : $TC < SC \leq GC$, and was heavily influenced by the concentrations of heavy metals, phosphorus and suspended solids. This was consistent with urban waterways regularly receiving discharges of more diverse composition than the stream in the undeveloped catchment.

High variability in the urban streams supported an overall picture of non-seasonal fluctuation in chemistry. Seasonal differences were detected, but in terms of the level of variability between summer (including spring) and winter (including autumn) samples. Hence, during the winter seasons the chemistries of surface waters and sediments were more variable than in summer. As winter represents the wet season for the Sydney basin, these differences support an hypothesis of runoff being a principal source of the variability.

4.6 Future Directions

This thesis has attempted to be as comprehensive as possible regarding the patterns in chemistry of freshwater streams in the Sydney basin. However, there were experimental limitations leading to some recommendations which future investigations on stream ecosystems could address.

For instance, these studies commenced from a limited data base. As mentioned previously, published data concerning the chemistry of small streams in the Sydney region is not readily available. More information is still required since most of the work presented here has centred on Hawkesbury Sandstone-based streams. Systems that lie over other geological formations also need to be investigated as sediments with higher concentrations of fines are expected to have different chemistries.

It was unfortunate that further storms failed to arise during the study. Different sampling strategies of flow-related events need to be performed, especially around the first flush and flooding periods, to help describe the immediate changes that take place in surface

water chemistry. Monitoring should also include assessment of the constituent deposition from rainwater (see Ayers and Gillett (1984) and Ayers *et al.* (1987)) and the time required for streams to return to low flow. Chemical data could be stratified on the basis of such characteristics as :

- flow rate
- time since rain
- amount of rain.

Organic matter plays an important role in the chemistry of aquatic ecosystems. Day *et al.* (1991) indicated that studies dealing with the isolation, quantification and identification of natural organic fractions are necessary.

A specialised procedure to determine the fractionation of sediment phosphorus should be developed. Since most of the phosphorus load in these sediments was in inorganic forms, it would have been interesting to identify and compare the levels of readily extractable forms with the non-occluded hydrous metal oxide forms.

Since the levels of dissolved heavy metals were often very low and variable, analyses should also include the measurement of the total concentration. Furthermore, characterisation of the size ranges of suspended particulate matter may provide an idea of changes in heavy metal and phosphorus partitioning.

Biological variables need to be described in order to effectively establish the complete status of a system and detect subtle changes in water quality (Norris and Georges, 1986). A biological survey of Sydney streams, for example, has never been reported in the literature and would provide relevant information on the limnology of the region. The monitoring of biomass for selected species in parallel with the measurement of heavy metal and phosphorus levels could provide assessment of bioavailability.

Laboratory based manipulative experiments have previously been performed in order to investigate sediment-water interactions. Such a controlled experiment needs to be undertaken for Hawkesbury Sandstone sediments, focusing on their sorption capacity and the role of iron oxides. Another experiment relevant to this work has been inspired by the studies of Hoff *et al.* (1982) and Lu and Chen (1977). Road-side particulates (<250µm) are added to polyethylene containers filled with creek water, simulating the release of first-flush solids following a runoff discharge. Changes in standard water quality parameters and the concentrations of heavy metal and/or phosphorus levels are monitored at set times. Triplicate tests (with suitable controls) are conducted for various

combinations of fixed, or random, factors including temperature, conductivity, alkalinity, pH and redox conditions. At the end of each experiment, bottom sediment is retained to check metal/phosphorus balance and speciation.

The use of a controlled environment could identify which parameters, or combination of parameters, are the most influential in sediment-water partitioning. Monitoring concentration levels would help establish when and how changes in chemical equilibria are brought about.

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APPENDICES

Appendix 1. The Interstitial Water Sampler

Appendix 1.1 The Sampler

A non-dialysis type of *in situ* sampler was thought to be suited for this project, since the selected urban creeks had sediments principally composed of sand. A technique adapted from Whitman (1989) and Makemson (1972) was devised, employing a modified TERUMO® plastic syringe (50mL volume).

The mesh-covered tube was inserted into the surficial sediment and the plunger drawn up, 50mL being obtained in under a minute. Further sample was taken after release of the porewater into a container. To prevent oxidation and loss of reduced compounds, the procedure was carried-out slowly and carefully to ensure no vigorous mixing and minimal disturbance of the sediment. Deep samples (i.e. >15cm) were not necessary and in some cases not possible, since the creeks often had only shallow layers of sediment. However, a depth of at least 5cm was required to avoid the oxygen contaminated layer near the surface (Makemson, 1972).

Most of the urban sediments were virtually silt-free, so clogging of the mesh was not usually a problem and sample could be released through the mesh without undue aeration of the sample. The sampler would not be recommended for sites of high fines content ($\geq 10\%$), however.

Appendix 1.2 Assessment of Suitability

Two tests were performed to establish the suitability of this sampler. The first involved determining whether the device did in fact sample interstitial water and not a mixture, including the water immediately above the sediment surface.

Sand, to a height of 5cm, was placed in a large beaker, followed by water to approximately 0.5cm above the sediment. When the water was no longer turbid, a solution of dark blue dye (100mL) was carefully added. The sampler was then inserted halfway into the sediment and the plunger slowly withdrawn. No dye was subsequently observed in the sample indicating only interstitial water was taken.

The second test concerned a statistical comparison of data for samples of surface water and syringe-sampled surface water to help decide whether any significant changes in composition of the interstitial water arise from the use of the syringe technique. This test included data for two additional creeks (Daylight Creek and Turpins Creek) at Sunny Corner, located in the central-west district of New South Wales, approximately 200km west of Sydney. Daylight Creek, whose headwaters arise just above abandoned mine workings, is heavily contaminated by acid mine drainage. Turpins Creek runs adjacent to the mine site but otherwise is relatively unaffected by it, until draining into Daylight Creek.

The test was done in two parts, the first involving simple t-test comparisons of individual temperature, conductivity, DO, pH and redox *in situ* measurements. The results are given in Table A1 and no significant difference between the two data sets was observed. In the second part, triplicate *in situ* measurements were compared, along with the results for dissolved ortho-phosphate, copper, zinc, cadmium and lead concentrations. The results are provided in Table A2.

No significant differences were seen for conductivity or any of the four heavy metals. On one occasion only, a difference in ortho-phosphate concentration was observed. It was concluded that the syringe should have no effect on the concentrations of most dissolved major and minor ions. Some differences were seen for the remaining parameters, however, in these cases the statistical significance could at least be partly explained, as described below. Another factor includes random fluctuations in readings, considering that field instruments were used.

Temperatures of syringe samples were found to be 0.1 to 1.0°C higher than normal surface water readings. Such an increase was due to warming of the sample on removal and in any case was relatively minor. Nevertheless, this stressed a need to perform temperature readings immediately on obtaining the sample.

Syringe DO values were generally 0.3 to 1.5 mg L⁻¹ lower, although a few increases were observed. The reduction in DO was probably the result of oxygen removal during the withdrawal of the plunger, which creates a substantial pressure. Redox and pH values varied up to ±15 and ±0.25 units respectively, but reflected the usual random fluctuations seen with the Orion Model 250A portable meter on measuring these two parameters. Furthermore, redox values were generally lower for the syringe samples which was consistent with reduction in DO.

Table A1. Paired t-test comparisons of single field measurements for surface water.

Date	Site Station	Temperature (oC)		Conductivity (mS/m)		Dissolved oxygen (mg/L)		pH		Redox (mV)	
		Direct	Syringe	Direct	Syringe	Direct	Syringe	Direct	Syringe	Direct	Syringe
14/11/91	GC 2	18.1	18.3	29.0	41.0	9.7	7.9	7.70	7.50	157	135
	SC 1	17.7	17.7	46.5	48.5	6.4	5.1	7.70	7.70	-30	20
	TC 3	20.1	21.1	23.0	24.0	7.3	6.6	8.00	8.00	74	128
16/12/91	GC 2	24.6	23.5	50.0	50.0	6.0	6.0	7.20	7.20	7	9
	SC 1	20.8	20.8	28.0	28.0	8.2	6.8	6.90	7.00	92	86
	TC 3	20.3	21.8	14.0	18.0	5.8	6.8	7.20	7.10	119	94
13/1/92	DC 3	18.7	18.9	24.0	23.5	7.3	6.3	6.00	5.90	260	247
	Turp.C 3	17.1	17.7	9.5	10.0	5.2	5.7	7.10	7.00	134	135
21/3/92	SC 1	19.6	21.6	48.5	44.0			7.51	7.31	-42	-35
	TC 3	22.1	23.0	16.0	17.0			6.20	6.30	29	24
2/4/92	GC 2	20.4	20.5	38.5	37.5	8.4	8.2	7.14	7.26	-27	-33
		t-test probability	0.082	t-test probability	0.312	t-test probability	0.119	t-test probability	0.341	t-test probability	0.676

Note : GC = Gwawley Creek ; SC = Savilles Creek ; TC = Temptation Creek ; DC = Daylight Creek ; Turp.C = Turpins Creek

Table A2. Paired t-test comparisons of triplicate field and laboratory measurements for surface water.

Date	Site station	Temperature (oC)			Conductivity (mS/m)			Dissolved oxygen (mg/L)			pH			Redox (mV)		
		Direct	Syringe	T-test	Direct	Syringe	T-test	Direct	Syringe	T-test	Direct	Syringe	T-test	Direct	Syringe	T-test
2/5/92	GC2	16.7	16.9		31.0	36.0		6.7	5.6		7.33	7.31		-37	-38	
		16.8	16.9	0.038	31.0	36.0	0.272	6.7	5.7	0.016	7.31	7.33	0.667	-39	-39	0.423
		16.7	16.9		37.0	36.0		6.7	5.2		7.33	7.35		-41	-41	
7/5/92	TC3	15.6	16.0		13.5	13.0		7.2	6.1		6.31	6.28		19	20	
		15.7	16.0	0.010	13.5	13.0	0.184	7.2	6.2	0.001	6.22	6.40	0.254	23	14	0.248
		15.6	15.9		13.0	13.0		7.2	6.1		6.00	6.25		36	21	
14/6/92	SC1	16.1	16.1		26.5	27.5		6.2	6.2		7.04	7.25		-22	-37	
		16.2	16.2	0.423	28.0	27.0	0.465	6.1	6.3	0.840	7.06	7.25	0.128	-26	-35	0.176
		16.0	16.4		29.5	26.0		6.2	5.9		7.24	7.27		-35	-36	
14/6/92	DC3	7.4	8.4		17.0	18.0		14.5	14.8		4.91	5.03		91	88	
		7.7	8.3	0.044	16.5	18.0	0.199	14.7	15.9	0.726	4.99	5.05	0.039	91	88	0.008
		7.8	8.3		18.0	18.0		15.9	15.1		4.99	5.07		91	87	
14/6/92	Turp.C3	7.4	8.0		7.5	7.5		15.3	14.6		7.60	7.48		-45	-40	
		7.4	8.0	0.003	7.0	7.5	0.423	15.1	14.8	0.070	7.60	7.52	0.015	-43	-42	0.106
		7.7	8.2		7.0	7.0		15.4	14.5		7.61	7.49		-44	-41	

Note : GC = Gwawley Creek ; SC = Savilles Creek ; TC = Temptation Creek ; DC = Daylight Creek ; Turp.C = Turpins Creek

Table A2 (continued). Paired t-test comparisons of triplicate field and laboratory measurements for surface water.

Date	Site station	o-Phosphate (ug/L)			Zinc (mg/L)			Copper (ug/L)			Cadmium (ug/L)			Lead (ug/L)		
		Direct	Syringe	T-test	Direct	Syringe	T-test	Direct	Syringe	T-test	Direct	Syringe	T-test	Direct	Syringe	T-test
2/5/92	GC 2	3.6	3.6		0.02	0.02		<10.5	<10.5		<0.75	<0.75		<4.75	<4.75	
		3.1	3.1	0.423	0.02	0.02	0.423	<10.5	<10.5		<0.75	<0.75		<4.75	<4.75	
		3.1	4.0		0.02	0.01		<10.5	<10.5		<0.75	<0.75		<4.75	<4.75	
7/5/92	TC 3	<1.0	<1.0		<0.01	<0.01		<10.5	<10.5		<0.75	<0.75		<4.75	<4.75	
		<1.0	<1.0		<0.01	<0.01	0.423	16.2	17.6	0.423	<0.75	<0.75		<4.75	<4.75	
		<1.0	<1.0		<0.01	<0.01		<10.5	<10.5		<0.75	<0.75		<4.75	<4.75	
14/6/92	SC 1	4.0	5.4		<0.01	<0.01		<10.5	<10.5		<0.75	<0.75		<4.75	<4.75	
		3.6	4.5	0.024	<0.01	<0.01		<10.5	<10.5		<0.75	<0.75		<4.75	<4.75	
		3.6	4.5		<0.01	<0.01		<10.5	<10.5		<0.75	<0.75		<4.75	<4.75	
14/6/92	DC 3	1.0	1.0		17.7	17.5		850	840		<10	10.0		200	240	
		1.0	1.0	0.423	17.3	17.2	0.118	840	840	0.423	<10	<10	0.423	240	200	0.618
		<1.0	1.0		17.7	17.3		850	850		10.0	10.0		250	200	
14/6/92	Turp.C 3	1.4	1.4		0.01	0.02		<20	<20		<10	<10		<100	<100	
		1.0	<1.0	0.423	<0.01	0.01	0.667	<20	<20		<10	<10	0.423	<100	<100	
		1.4	1.4		0.02	0.01		<20	<20		10.0	<10		<100	<100	

Note : GC = Gwawley Creek ; SC = Savilles Creek ; TC = Temptation Creek ; DC = Daylight Creek ; Turp.C = Turpins Creek

Appendix 2. Internal Quality Control

Appendix 2.1 QC Measures for the Sydney Streams Survey (Study 1)

Purchased BDH analytical reagents (BDH-Merck Pty Ltd., Kilsyth, Victoria, Australia) were co-analysed as internal standard reference waters and results are presented in Table A3. Analytes in sample blanks were consistently below detection limits.

Table A3. QC mean percentage recoveries from analysis of internal reference standards during Basin survey.

Parameter	Concentration of reference standard	Number of replicates	Mean percent recovery (standard deviation)
Cl ⁻	100 mmol L ⁻¹	18	98.9 (4.7)
SO ₄ ²⁻	15 mg L ⁻¹	18	102 (6)
total P	0.05 mgPO ₄ ³⁻ -P L ⁻¹	7	105 (10)
ortho-PO ₄ ³⁻	50 µgPO ₄ ³⁻ -P L ⁻¹	13	100 (3)
NO ₃ ⁻	50 µgNO ₃ ⁻ -N L ⁻¹	12	100 (6)
NH ₃	60 µgNH ₄ ⁺ -N L ⁻¹	4	100 (1)
Pb	10 µg L ⁻¹	12	98.1 (4.9)
Zn	1 µg L ⁻¹	11	100 (2)
Cu	10 µg L ⁻¹	9	99.6 (2.7)
Cd	1 µg L ⁻¹	13	99.8 (6.4)

Appendix 2.2 QC Measures for the Monitoring Study (Study 2)

Internal-laboratory standardisation was performed for certain analytes (heavy metals, phosphorus and organic carbon), to check harmonisation of methods and instrument optimisation. Tables A4(i-iv), A5 and A6 list the results generated from regular analysis of reference standards (described at the end of this section), including each

Table A4(i). QC recovery data for copper analysis.

Date	Method / Sample	Theoretical recovery (micrograms Cu)	Actual recovery (micrograms Cu)	% Recovery
17/10/91	sediment total copper / PACS-1 sediment (g)	45.2	44.0	97.3
9/6/92	0.100	21.4	20.0	93.5
29/10/92	0.047	53.3	49.0	91.9
	0.118	45.2	45.0	99.6
9/12/92	0.100	17.6	22.0	125
	0.039	92.2	108	117
12/2/93	0.204	31.2	26.5	84.9
	0.069	44.3	40.5	91.4
	0.098	51.5	47.5	92.2
	0.114	71.0	66.5	93.7
	0.157	82.3	74.0	89.9
6/4/93	0.182	47.9	42.0	87.7
	0.106	95.0	85.0	89.5
	0.210	67.8	62.0	91.4
	0.150	slope / intercept of regression line	0.989 -1.82	
9/6/92	BCSS-1 sediment (g)	18.6	18.0	96.8
	1.007	22.9	24.0	105
12/6/92	1.238	18.4	16.0	87.0
	0.994	18.5	16.0	86.5
	1.000	25.2	21.0	83.3
31/7/92	1.362	15.3	14.0	91.5
9/12/92	0.826	12.4	11.0	88.7
	0.668	3.53	3.75	106
12/2/93	0.191	slope / intercept of regression line	0.898 0.329	
9/11/92	sediment speciation / PACS-1 sediment (g)	90.8	86.5	95.3
	0.201	89.9	83.0	92.3
	0.199	91.7	83.5	91.1
8/2/93	0.203	112	103	92.0
	0.249	71.0	63.3	89.1
	0.157	183	173	94.5
	0.405	slope / intercept of regression line	0.969 -4.41	

Table A4(ii). QC recovery data for zinc analysis.

Date	Method / Sample	Theoretical recovery (micrograms Zn)	Actual recovery (micrograms Zn)	% Recovery
17/10/91	sediment total zinc / PACS-1 sediment (g) 0.100	82.4	81.0	98.3
9/6/92	0.047	39.0	40.0	103
29/10/92	0.118	97.2	87.0	89.5
	0.100	82.4	73.0	88.6
9/12/92	0.039	32.1	33.0	103
	0.204	168	171	102
12/2/93	0.069	56.8	47.5	83.6
	0.098	80.7	72.0	89.2
	0.114	93.9	88.5	94.2
	0.157	129	132	102
	0.182	150	152	101
6/4/93	0.106	87.3	80.0	91.6
	0.210	173	162	93.6
	0.150	124	113	91.1
		slope / intercept of regression line	1.00 -4.94	
9/6/92	BCSS-1 sediment (g) 1.007	120	106	88.3
	1.238	147	132	89.8
12/6/92	0.994	118	109	92.4
	1.000	119	109	91.6
31/7/92	1.362	162	130	80.2
9/12/92	0.826	98.3	78.0	79.3
	0.668	79.5	57.0	71.7
12/2/93	0.191	22.7	18.5	81.5
		slope / intercept of regression line	0.889 -3.82	
9/11/92	sediment speciation / PACS-1 sediment (g) 0.201	166	162	97.6
	0.199	164	170	104
	0.203	167	156	93.4
8/2/93	0.249	205	197	96.1
	0.157	129	120	93.0
	0.405	334	337	101
		slope / intercept of regression line	1.04 -12.3	

Table A4(iii). QC recovery data for lead analysis.

Date	Method / Sample	Theoretical recovery (micrograms Pb)	Actual recovery (micrograms Pb)	% Recovery
17/10/91	sediment total lead / PACS-1 sediment (g) 0.100	40.4	42.0	104
9/6/92	0.047	19.1	20.0	105
29/10/92	0.118	47.7	47.0	98.5
	0.100	40.4	39.0	96.5
9/12/92	0.039	15.7	16.0	102
	0.204	82.4	95.0	115
12/2/93	0.069	27.9	23.0	82.4
	0.098	39.6	36.0	90.9
	0.114	46.1	47.0	102
	0.157	63.4	56.5	89.1
	0.182	73.5	65.0	88.4
6/4/93	0.106	42.8	43.0	100
	0.210	84.9	90.0	106
	0.150	60.6	66.0	109
		slope / intercept of regression line	1.07 -3.59	
9/6/92	BCSS-1 sediment (g) 1.007	22.9	28.0	122
	1.238	28.1	26.0	92.5
31/7/92	1.362	30.9	21.9	70.9
9/12/92	0.826	18.7	12.0	64.2
	0.668	15.2	10.0	65.8
12/2/93	0.191	4.34	6.00	138
		slope / intercept of regression line	0.801 1.28	
25/6/92	sediment total lead (furnace AAS) / BCSS-1 sediment (g) 0.994	22.6	16.8	74.3
	1.000	22.7	25.2	111
9/11/92	sediment speciation / PACS-1 sediment (g) 0.201	81.2	57.5	70.8
	0.199	80.4	54.0	67.2
	0.203	82.0	58.5	71.3
8/2/93	0.249	101	96.0	95.0
	0.157	63.4	65.0	102
	0.405	164	153	93.3
		slope / intercept of regression line	1.03 -17.8	

Table A4(iv). QC recovery data for cadmium analysis.

Date	Method / Sample	Theoretical recovery (micrograms Cd)	Actual recovery (micrograms Cd)	% Recovery
27/11/91	sediment total cadmium (furnace AAS) / PACS-1 sediment (g) 0.100	0.238	0.236	99.2

Table A5. QC recovery data for organic carbon analysis.

Date	Sample (g)	Theoretical recovery (mg OC)	Actual recovery (mg OC)	% Recovery
9/12/91	BCSS-1 sediment 0.229	5.01	5.76	115
	0.229	5.02	5.30	105
	0.230	5.03	5.92	118
	0.229	5.00	5.69	114
23/12/91	0.303	6.64	6.67	100
	0.306	6.69	7.21	108
26/3/92	0.487	10.7	10.4	97.2
	0.500	10.9	10.7	98.2
3/4/92	0.470	10.3	11.4	111
	0.512	11.2	12.4	111
25/5/92	0.447	9.79	10.8	110
	0.398	8.72	9.55	109
26/6/92	0.327	7.16	7.65	107
19/10/92	0.338	7.40	9.06	122
		slope / intercept of regression line	0.987 0.741	
19/10/92	PACS-1 sediment 0.198	7.31	10.6	145
29/1/93	0.165	6.09	6.01	98.7
	0.204	7.53	7.87	104
	0.250	9.22	10.6	115
	0.185	6.83	7.34	107
5/4/93	0.147	5.42	6.14	113
	0.231	8.52	9.45	111
		slope / intercept of regression line	1.25 -0.785	
19/10/92	glucose + sand 0.298	11.9	11.5	96.6
	0.299	12.0	12.2	102
29/1/93	0.217	8.68	8.25	95.0
	0.392	15.7	15.1	96.2
	0.331	13.2	12.3	93.2
	0.397	15.9	14.7	92.4
5/4/93	0.248	9.92	9.37	94.5
	0.342	13.7	13.4	97.8
		slope / intercept of regression line	0.928 0.384	

Table A6. QC recovery data for phosphorus analysis.

Date	Method / Sample	Theoretical recovery (micrograms P)	Actual recovery (micrograms P)	% Recovery
	sediment total P / BCSS-1 sediment (g)			
5/12/91	0.030	20.3	19.2	94.6
	0.030	20.2	20.3	100
26/3/92	0.057	38.3	27.9	72.8
	0.052	34.9	20.0	57.3
10/4/92	0.062	41.9	41.9	100
	0.061	40.9	42.6	104
29/5/92	0.062	41.7	41.9	100
	0.065	43.7	45.3	104
23/6/92	0.063	42.3	48.3	114
	0.064	43.0	44.0	102
29/10/92	0.064	43.0	39.8	92.6
	0.060	40.3	35.7	88.6
4/2/93	0.023	15.5	17.4	112
	0.014	9.41	10.2	108
		slope / intercept of regression line	0.963 -0.226	
	PACS-1 sediment (g)			
5/12/91	0.022	22.4	19.6	87.5
	0.023	23.2	21.5	92.7
26/3/92	0.033	33.7	17.2	51.0
	0.033	33.7	14.0	41.5
4/2/93	0.037	37.6	38.8	103
	0.013	13.2	15.6	118
	0.021	21.3	17.6	82.6
	0.025	25.4	25.2	99.2
8/3/93	0.032	32.5	31.0	95.4
	0.027	27.4	25.0	91.2
3/4/93	0.021	21.4	19.8	92.2
	0.038	38.4	38.3	99.7
7/4/93	0.017	16.9	16.1	95.3
		slope / intercept of regression line	0.696 4.46	

Table A6 (continued). QC recovery data for phosphorus analysis.

Date	Method / Sample	Theoretical recovery (micrograms P)	Actual recovery (micrograms P)	% Recovery
1/10/91 7/1/92	sediment total P / phosphate std. (100 mgP/L)	100	97.7	97.7
		100	106	106
		200	193	96.8
		500	525	105
		1000	1000	100
		10.0	11.3	113
		20.0	20.7	103
		30.0	32.1	107
		40.0	41.2	103
		50.0	49.9	99.8
		slope / intercept of regression line	1.01 1.30	
1/10/91	pyrophosphate std. (100 mgP/L)	100	109	109
		100	100	100
		200	179	89.5
		200	179	89.5
		500	461	92.3
		500	502	100
		1000	1014	101
		1000	1004	100
		slope / intercept of regression line	1.02 -13.6	

Table A6 (continued). QC recovery data for phosphorus analysis.

Date	Method / Sample	Theoretical recovery (micrograms P)	Actual recovery (micrograms P)	% Recovery
	water total P / phosphate std. (100 mgP/L)			
24/3/92		1.00	0.72	72.0
		2.00	1.82	91.0
10/4/92		2.00	1.88	94.0
		3.00	2.95	98.3
14/5/92		2.00	1.86	93.0
		2.00	1.87	93.5
29/7/92		2.00	2.26	113
		2.00	1.92	96.0
10/8/92		2.00	1.91	95.5
14/10/92		2.00	2.52	126
		2.00	2.30	115
25/2/93		1.00	0.96	96.0
		4.00	4.20	105
		5.00	5.08	102
3/4/93		1.00	1.02	102
		4.00	4.24	106
		5.00	5.27	105
		slope / intercept of regression line	1.07 -0.125	
	pyrophosphate std. (100 mgP/L)			
24/3/92		1.00	0.88	88.0
		1.50	1.09	72.7
10/4/92		3.00	3.09	103
		3.00	3.02	101
14/5/92		3.00	2.30	76.7
		3.00	2.41	80.3
29/7/92		3.00	2.33	77.7
		3.00	2.27	75.7
10/8/92		3.00	3.40	113
14/10/92		3.00	1.44	48.0
		3.00	2.39	79.7
25/2/93		2.00	2.00	100
		4.00	4.18	104
		5.00	5.20	104
3/4/93		2.00	2.30	115
		4.00	4.24	106
		5.00	5.05	101
		slope / intercept of regression line	1.09 -0.495	

respective regression line slope and y-intercept (with standard deviation) from correlation of the actual versus theoretical recovery values. Ideally, a slope of 1 (± 0.1) and an intercept of 0 (± 10) was desired, with values for individual percentage recoveries ranging between 90 to 110%. Failure to meet these criteria was most likely due to experimental limitations of the method (e.g. reduced sensitivity of lead detection with flame AAS). Nevertheless, since a comparison between sites was the prime interest, inaccuracy was not of the same concern as maintaining consistent or reproducible results (i.e. minimal variability).

Except for total organic carbon determinations, methods generally indicated underestimation of the analyte. Hence, levels of heavy metals and phosphorus in the creek samples could well have been higher. For the two marine sediments, recoveries of sediment organic carbon were regularly over 105%, suggesting the acid dichromate oxidises further carbon sources, or some other reductant.

Of the heavy metals, greatest variability was seen with lead, particularly for total content determination on BCSS-1 sediment. Usually recoveries were below 90%, however, lead was a difficult analyte for the flame AAS technique due to low sensitivity. Cadmium was not analysed regularly since at an early stage in the project it became apparent this metal was of very low concentration (i.e. below detectable limits).

A poor slope coefficient ($r=0.696$) was generated for total phosphorus recovery from PACS-1 sediment. However, this was heavily influenced by two low values, from analysis on 26/3/92. All samples in that batch were subsequently reanalysed.

Despite good correlation for persulfate digestion of the aqueous pyrophosphate standard, recoveries were often low, sometimes below 80%. This was not necessarily unusual as the digestion is considered a convenient and rapid method, but not as efficient in converting phosphorus compounds to ortho-phosphate in comparison with other techniques described by Clesceri *et al.* (1989).

The BCSS-1 and PACS-1 standards were 'Marine Sediment Reference Materials for Trace Elements and Other Constituents', available from the Marine Analytical Chemistry Standards Program of the National Research Council, Canada. The certified values (with 95% tolerance limits) for the constituents of interest were as below.

Trace Elements ($\mu\text{g g}^{-1}$)

	BCSS-1	PACS-1
Copper	18.5 ± 2.7	452 ± 16
Zinc	119 ± 12	824 ± 22
Cadmium	0.25 ± 0.04	2.38 ± 0.20
Lead	22.7 ± 3.4	404 ± 20

Other Constituents (g/100g)

	BCSS-1	PACS-1
Carbon	2.19 ± 0.09	3.69 ± 0.11
P-pentoxide	0.154 ± 0.016	0.233 ± 0.018

The remaining standards were prepared in the laboratory, using purchased BDH analytical reagents (BDH-Merck Pty Ltd., Kilsyth, Victoria, Australia).

Phosphate std. (100 mgP L^{-1}) :

0.2195g potassium dihydrogen ortho-phosphate (anhydrous) dissolved in
500mL water

Pyrophosphate std. (100 mgP L^{-1}) :

0.3600g tetra-sodium pyrophosphate decahydrate dissolved in 500mL water

Glucose + Sand ($4\text{g}/100\text{g OC}$) :

10% w/w D-glucose (anhydrous) in acid-purified sand, ground-up
to homogenise

Appendix 3. Determination of Detection Limits

For water samples, the detection limits for a number of methods were determined following the guidelines proposed by the Analytical Methods Committee for the Royal Society of Chemistry (1987). According to this Committee, the detection limit is defined as "the lowest concentration of the analyte that can be distinguished with reasonable confidence from a *field blank*, here defined as a hypothetical sample containing zero concentration of analyte". The formula for the detection limit concentration (C_L) was :

$$C_L = k s_B / S .$$

The term k is a numerical constant and a value of 3 was "strongly recommended" to ensure the equivalent of a 99% confidence level. s_B is the standard deviation of responses of the field blanks, while S is the sensitivity of the method and equals the slope of the linear calibration curve close to the origin.

It was stressed that the detection limit be determined for an analytical system - rather than for an analytical method. Therefore, not only is the analysis method *per se* taken into consideration, but also other factors such as the analyst, the instrument used, reagent quality, the nature of the samples, the laboratory and field environments, protocols used for calibration and reagent blank correction etc.

Those applied for the analysis of Sydney Basin streams (Study 1) were determined on laboratory reagent grade water blanks (10), collected in high density polyethylene bottles (prepared as normal) and filtered where appropriate. The following values were subsequently estimated.

(i) Heavy Metals (Varian AA-1275 + GTA-95 furnace AAS)

Cu	=	0.40 $\mu\text{g L}^{-1}$
Zn	=	0.25 $\mu\text{g L}^{-1}$
Cd	=	0.10 $\mu\text{g L}^{-1}$
Pb	=	0.40 $\mu\text{g L}^{-1}$

(ii) Dissolved ortho-Phosphate (SKALAR SAN Plus SFA)

$\text{PO}_4^{3-}\text{-P}$	=	1.0 $\mu\text{g L}^{-1}$
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(iii) Total P (Strickland and Parsons, 1972; after persulfate digestion)

$$\text{PO}_4^{3-}\text{-P} = 0.03 \text{ mg L}^{-1}$$

(iv) Sulfate (Turbidimetric method)

$$\begin{aligned}\text{SO}_4^{2-} &= 2.0 \text{ mg L}^{-1} \\ &= 0.1 \text{ mg L}^{-1} \text{ (Na}_2\text{SO}_4 \text{ buffer added)}\end{aligned}$$

(v) Nitrate (SKALAR SAN Plus SFA)

$$\text{NO}_3^-\text{-N} = 5 \text{ } \mu\text{g L}^{-1}$$

(vi) Ammonia (Strickland and Parsons, 1972)

$$\text{NH}_3\text{-N} = 9.0 \text{ } \mu\text{g L}^{-1}$$

The use of reagent grade water samples meant very low limits were established, especially for the heavy metals. However, such blanks were not strictly in accordance with the Analytical Methods Committee guidelines, which stipulate the need for true field blanks.

For the three-stream monitoring study, refinements were subsequently made for the methods of heavy metal, total phosphorus and ammonia analysis. The detection limits were therefore re-assessed by analysing ten 500mL surface waters collected from Temptation Creek Sample Station 3 (for graphite furnace AAS, flame AAS, and SKALAR SAN Plus SFA assays).

These limits were as follows.

(i) Heavy Metals (Varian AA-1275 + GTA-95)

Graphite Furnace AAS :

$$\begin{aligned}\text{Cu} &= 10.5 \text{ } \mu\text{g L}^{-1} \\ \text{Cd} &= 0.75 \text{ } \mu\text{g L}^{-1} \\ \text{Pb} &= 4.75 \text{ } \mu\text{g L}^{-1}\end{aligned}$$

Flame AAS :

$$\text{Cu} = 0.02 \text{ mg L}^{-1}$$

Cd	=	0.01 mg L ⁻¹
Pb	=	0.10 mg L ⁻¹
Zn	=	0.01 mg L ⁻¹

(ii) Total P (SKALAR SAN Plus SFA; after persulfate digestion)

PO ₄ -P	=	1.3 µg L ⁻¹
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(iii) Ammonia (SKALAR SAN Plus SFA)

NH ₃ -N	=	4.0 µg L ⁻¹
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For copper, cadmium and lead, the limits for furnace AAS were significantly increased - greater in fact than some respective values reported in the basin survey (see appendix table A8). The palladium/magnesium nitrate modifier is expected to have been at least partly responsible for these higher limits. In addition, the copper limit was high because of the operating parameters that were necessary. The 327.4nm resonance line is less sensitive than the usual 324.75nm primary resonance line, however the analysis is interference free, since a spectral interference due to the palladium modifier is observed at 324.75nm (Welz *et al.*, 1988). In hindsight, furnace AAS may have been unnecessary for copper determinations as the slight improvement in sensitivity could justifiably have been sacrificed for saved analysis time. Nevertheless, on checking the raw data (appendix table A11) a significant proportion of values (10.5 to 20 µg L⁻¹) would not have been recorded.

The limit for total phosphorus in the monitoring study (1.3 µg L⁻¹) was significantly lower than the corresponding limit in Study 1 (30 µg L⁻¹). This was due to different sensitivities of the spectrophotometers involved. For Study 1, absorbance measurements were made with a standard bench ultra-violet / visible spectrophotometer, calibrated by a working standard curve of 0 to 0.4 mg L⁻¹ phosphate-phosphorus. Consequently, a low (i.e. <20 µg L⁻¹) limit of detection was not viable. For the monitoring study, the phosphorus chemistry of the SKALAR SAN Plus autoanalyser was configured for true trace (<10 µg L⁻¹) analyses, at least partly due to the high sensitivity of the flow-through cell photometer (SKALAR, 1989).

All other detection limits quoted in this thesis were instrument detection limits, established after consultation with the accompanying instrument notes. Although expected to be satisfactorily accurate, they were not determined following the above guidelines and hence are not necessarily applicable at the 99% confidence level.

Appendix 4. Raw Data

Raw data from the Sydney streams survey and monitoring studies of the Sutherland Shire sites are displayed in the following sets of tables.

Table A7. Survey study sites and individual descriptions.

Table A8. Survey study analytical chemistry data.

Table A9. Survey study calculated relative percentages.

Table A10. Monitoring study sampling dates and flow data.

Table A10(i). Gwawley Creek.

Table A10(ii). Savilles Creek.

Table A10(iii). Temptation Creek.

Table A11. Monitoring study surface and interstitial water chemistry.

Table A11(i). Gwawley Creek.

Table A11(ii). Savilles Creek.

Table A11(iii). Temptation Creek.

Table A12. Monitoring study additional surface water chemistry.

Table A12(i). Gwawley Creek.

Table A12(ii). Savilles Creek.

Table A12(iii). Temptation Creek.

Table A13. Monitoring study sediment chemistry.

Table A13(i). Gwawley Creek.

Table A13(ii). Savilles Creek.

Table A13(iii). Temptation Creek.

Table A14. Monitoring study sediment particle size and cation exchange capacity.

Table A14(i). Gwawley Creek.

Table A14(ii). Savilles Creek.

Table A14(iii). Temptation Creek.

Table A7. Survey study sites and individual descriptions.

Site number	Site name	Catchment landuse	Landuse category	Catchment geology	Geology category	Water velocity (cm/s)	Discharge (L/s)
1	Ashdale Creek	bush	L1	Hawkesbury sandstone	G4	40	13
2	Mogo Creek	bush	L1	sandstone + some shale	G4	0	0
3	Mangrove Creek	bush/rural	L2	sandstone + some shale	G4	upm	upm
4	Big Boree Creek	rural/bush	L2	Hawkesbury sandstone	G4	50	60
5	Mooney Mooney Creek tributary	rural/bush	L2	Hawkesbury sandstone	G4	71	260
6	Piles Creek	rural/bush	L2	Hawkesbury sandstone	G4	54	20
7	Warners Park Creek	urban	L3	Hawkesbury sandstone	G4	44	165
8	Bunnerong Creek	urban	L3	gravel, sand, silt + clay	G3	83	180
9	Bates Creek	urban bush	L2	Hawkesbury sandstone	G4	71	14
10	Subiaco Creek	urban	L3	Hawkesbury sandstone	G4	31	640
11	Lovers Jump Creek	urban bush	L2	sandstone + shale	G4	38	620
12	Bardwell Creek	urban	L3	shale + some sandstone	G2	95	560
13	Gwawley Creek	urban	L3	Hawkesbury sandstone	G4	31	200
14	Forbes Creek	urban	L3	Hawkesbury sandstone	G4	61	80
15	Mittagong River	bush/rural	L2	shale + sandstone	G2	135	1720
16	Sandy Flat Creek tributary	rural/bush	L2	Hawkesbury sandstone	G4	77	160
17	Big Gully Creek	bush/rural/residential	L2	shale + some sandstone	G2	93	90
18	Crawford Creek	rural	L3	shale + some sandstone	G2	2	20
19	Woronora River tributary	bush	L1	Hawkesbury sandstone	G4	92	620
20	Loddon River	bush	L1	Hawkesbury sandstone	G4	94	1350
21	Nepean River	rural	L3	gravel, sand, silt + clay	G3	upm	upm
22	Matthews Creek	bush/residential/rural	L2	shale + sandstone	G2	52	360
23	Dogtrap Creek	bush	L1	Hawkesbury sandstone	G4	56	170
24	Catact River	bush	L1	shale + sandstone	G2	upm	upm
25	Monkey Creek	rural/residential	L3	shale + some sandstone	G2	upm	upm
26	Burrallow Creek tributary	bush	L1	sandstone + shale	G4	0	0
27	Rickabys Creek	rural	L3	gravel, sand, silt + clay	G3	83	320
28	Mill Creek	urban bush	L2	Hawkesbury sandstone	G4	106	550

Table A7. Survey study sites and individual descriptions.

Site number	Site name	Catchment landuse	Landuse category	Catchment geology	Geology category	Water velocity (cm/s)	Discharge (L/s)
29	Fraser's Creek	urban bush	L2	Hawkesbury sandstone	G4	28	20
30	Cabramatta Creek	urban/rural	L3	shale + some sandstone	G2	52	30
31	Eastern Creek	urban/rural	L3	shale + some sandstone	G2	70	460
32	Glenbrook Creek	bush	L1	Hawkesbury sandstone	G4	0	0
33	Grose River	rural/urban	L3	shale + sandstone	G2	upm	upm
34	Baines Creek	rural/bush	L2	shale + sandstone	G2	0	0
35	Cattai Creek	rural/bush	L2	Hawkesbury sandstone	G4	96	420
36	Buttsworth Creek	rural	L3	shale + sandstone	G2	31	70
37	Howes Waterhole Creek	bush	L1	Hawkesbury sandstone	G4	44	320
38	Macdonald River	rural	L3	sandstone + some shale	G4	upm	upm
39	Roberts Creek	rural	L3	Hawkesbury sandstone	G4	93	600
40	Macdonald River	rural	L3	sandstone + some shale	G4	44	2600
41	Wheeny Creek	rural/bush	L2	Hawkesbury sandstone	G4	87	2250
42	Mountain Lagoon	rural	L3	sandstone + some shale	G4	0	0
43	Colo River tributary	rural/bush	L2	sandstone + some shale	G4	52	50
44	Melon Creek	rural	L3	sandstone + some shale	G4	31	7
45	Long Weeney Creek	bush	L1	Hawkesbury sandstone	G4	31	10
46	Doyle's Creek	rural	L3	Hawkesbury sandstone	G4	56	240
47	Roberts Creek	bush/rural	L2	Hawkesbury sandstone	G4	78	740
48	Mill Creek	bush	L1	Hawkesbury sandstone	G4	36	10
49	Crown Creek tributary	rural	L3	igneous + sedimentary	G1	37	20
50	Wolgan River	rural/bush	L2	sedimentary + coal	G2	97	2620
51	Capertee River	rural	L3	siltstone, shale + sandstone	G2	85	2060
52	Wolgan River	bush/rural	L2	igneous + sedimentary	G1	141	750
53	Coxs River	rural/power station	L3	granitic + sedimentary	G1	103	1160
54	Umbiella Creek	rural	L3	siltstone, shale + sandstone	G2	59	330
55	Crown Creek	rural	L3	igneous + sedimentary	G1	56	160
56	Capertee River	rural	L3	sedimentary + coal	G2	101	5160

Table A7. Survey study sites and individual descriptions.

Site number	Site name	Catchment landuse	Landuse category	Catchment geology	Geology category	Water velocity (cm/s)	Discharge (L/s)
57	Megalong Creek	bush/rural	L2	granitic	G1	31	760
58	Beafsteak Creek	bush	L1	sedimentary + lava	G2	112	120
59	Ganbenang Creek	rural	L3	granitic	G1	77	290
60	Kanangra Creek tributary	bush	L1	sedimentary + coal	G2	48	350
61	Blackheath Creek	bush	L1	granitic + sedimentary	G1	56	70
62	Jocks Creek	bush/rural	L2	igneous	G1	49	210
63	Stony Creek	rural	L3	igneous	G1	38	30
64	Mandemar Creek	rural	L3	Hawkesbury sandstone	G4	0	0
65	Cooks River	industrial	L3	shale + some sandstone *	G2	96	50
66	Duck River	urban	L3	shale + some sandstone	G2	0	0
67	Back Creek	bush	L1	shale + some sandstone	G2	0	0
68	Sheehys Creek	bush	L1	shale + sandstone	G2	44	50
69	Drapers Creek tributary	rural/dam	L3	shale + some sandstone	G2	0	0
70	Barracks Creek	rural	L3	shale + some sandstone	G2	0	0
71	Bullio Creek tributary	rural	L3	igneous	G1	0	0
72	Bullio Creek	rural	L3	igneous	G1	0	0
73	Wollondilly River	bush/rural	L2	igneous	G1	upm	upm
74	Luthers Creek	bush	L1	igneous	G1	0	0
75	Boyd River	bush	L1	granitic	G1	38	300
76	Boggy Creek	bush	L1	igneous + sedimentary	G1	52	100
77	Oak Creek	rural/pipe works	L3	granitic	G1	71	70
78	Coxs River	rural/road works	L3	granitic	G1	92	4100
79	Pulpit Hill Creek	bush	L1	sedimentary + coal	G2	44	20
80	Ingar Creek	bush	L1	sandstone + some shale	G4	28	60
81	Edith Falls pool	bush/urban	L2	sandstone + some shale	G4	0	0
82	Peach Tree Creek	urban	L3	shale + some sandstone	G2	0	0
83	South Creek	rural/residential	L3	shale + some sandstone	G2	0	0
84	Bonds Creek	rural/residential	L3	shale + some sandstone	G2	0	0

Table A7. Survey study sites and individual descriptions.

Site number	Site name	Catchment landuse	Landuse category	Catchment geology	Geology category	Water velocity (cm/s)	Discharge (L/s)
85	Harris Creek	urban	L3	shale + some sandstone	G2	0	0
86	Williams Creek	urban	L3	sandstone + shale	G4	0	0
87	Hawkesbury River	bush/residential	L2	sandstone + some shale	G4	upm	upm
88	Mooney Mooney Creek	mangrove bush	L1	sandstone + some shale	G4	upm	upm
89	Salt Pan Creek	industrial	L3	Hawkesbury sandstone	G4	31	1800
90	Thompsons Creek	rural	L3	shale + some sandstone	G2	0	0

* river was a concrete channel at sampling site

upm = unable to perform measurement

Table A8. Survey study analytical chemistry data.

Site number	pH	Turbidity (NTU)	Colour (A440)	Chloride (mg/L)	Sulfate (mg/L)	Alkalinity (mg/L)	Total phosphorus (mg/L)	ortho-Phosphate (mg/L)	Nitrate (mg/L)	Ammonia (mg/L)	Sodium (mg/L)	Potassium (mg/L)	Calcium (mg/L)	Magnesium (mg/L)	Lead (ug/L)	Zinc (ug/L)	Copper (ug/L)
1	6.0	6.7	0.015	13.4	0.8	0.8	0.80	<0.001	0.27	0.01	10.0	1.8	0.8	3.0	<0.4	<0.25	<0.4
2	6.0	8.0	<0.001	170	<0.1	1.8	1.20	<0.001	0.07	0.03	70.1	4.1	12.0	20.2	<0.4	<0.25	<0.4
3	7.4	3.5	<0.001	1781	200	2.2	0.59	<0.001	0.15	0.01	994	36.0	41.0	143	<0.4	<0.25	<0.4
4	6.9	65.0	0.079	36.8	<0.1	1.6	0.69	<0.001	0.07	0.02	21.6	5.9	1.8	4.1	<0.4	<0.25	<0.4
5	7.0	2.0	<0.001	14.2	4.1	0.8	0.91	<0.001	0.20	0.09	11.4	0.9	2.1	2.9	<0.4	<0.25	<0.4
6	7.0	20.0	<0.001	28.3	4.0	1.4	1.11	<0.001	2.79	0.72	22.5	3.5	11.0	3.8	0.5	8.7	0.8
7	7.3	8.2	0.022	36.8	33.6	10.6	0.83	0.01	0.04	0.01	24.5	3.1	37.9	7.8	<0.4	<0.25	1.4
8	6.5	2.0	0.014	25.5	31.2	4.0	1.33	0.52	2.58	<0.009	20.0	4.0	26.9	5.7	1.1	1.0	6.4
9	6.1	1.2	<0.001	29.7	20.0	1.0	1.14	<0.001	0.16	0.01	19.5	1.1	16.1	5.0	<0.4	0.9	0.7
10	7.1	4.0	0.014	58.1	12.4	5.8	0.64	<0.001	0.53	<0.009	41.0	3.0	17.0	10.0	<0.4	0.4	2.1
11	6.9	1.7	0.013	56.6	17.4	2.6	0.51	<0.001	0.18	<0.009	33.4	2.0	16.9	7.3	<0.4	0.8	2.6
12	6.9	22.7	0.038	61.8	12.2	14.4	0.43	<0.001	0.38	4.30	50.5	8.6	30.0	9.2	9.2	100	25.0
13	7.3	23.0	<0.001	40.6	28.6	11.0	0.44	<0.001	1.84	0.07	27.5	3.2	30.6	8.5	150	50.0	11.8
14	7.5	2.2	<0.001	79.3	174	8.0	0.45	<0.001	0.35	0.01	46.0	2.3	39.8	7.3	<0.4	<0.25	<0.4
15	6.6	9.9	0.006	9.0	<0.1	1.8	0.51	<0.001	0.95	<0.009	8.5	0.6	4.1	4.9	<0.4	<0.25	<0.4
16	6.2	11.9	0.008	28.3	9.2	9.0	0.49	0.02	0.38	0.02	15.1	1.2	1.4	3.8	<0.4	0.5	<0.4
17	7.7	2.9	<0.001	119	5.6	14.6	0.46	<0.001	0.01	<0.009	73.7	3.4	22.1	33.1	<0.4	<0.25	<0.4
18	7.7	25.9	<0.001	217	22.4	18.4	0.62	<0.001	0.27	0.03	126	4.5	41.2	42.4	<0.4	<0.25	<0.4
19	6.2	2.1	<0.001	11.3	<0.1	7.5	0.42	<0.001	0.04	<0.009	8.8	0.5	0.7	1.4	<0.4	<0.25	<0.4
20	5.9	1.6	0.011	12.7	13.0	1.0	0.39	<0.001	0.01	<0.009	8.4	0.2	1.5	1.4	<0.4	<0.25	<0.4
21	7.2	6.6	0.031	15.6	12.2	1.6	0.67	<0.001	0.15	<0.009	13.0	1.2	2.8	3.3	<0.4	<0.25	0.7
22	7.0	6.6	0.016	24.1	<0.1	54.0	0.92	0.15	0.17	0.03	17.6	2.6	4.9	5.7	<0.4	<0.25	<0.4
23	7.0	16.9	0.029	29.7	1.8	1.6	0.69	0.03	0.45	<0.009	21.0	2.4	3.3	4.3	<0.4	<0.25	<0.4
24	6.8	1.6	0.015	12.0	2.9	1.0	0.34	<0.001	0.03	<0.009	8.0	0.3	1.2	1.5	<0.4	<0.25	0.5
25	6.9	14.9	0.015	70.3	<0.1	1.8	0.58	<0.001	0.13	0.02	41.4	1.7	4.4	10.0	<0.4	<0.25	0.4

Table A8. Survey study analytical chemistry data.

Site number	pH	Turbidity (NTU)	Colour (A440)	Chloride (mg/L)	Sulfate (mg/L)	Alkalinity (mg/L)	Total phosphorus (mg/L)	ortho-Phosphate (mg/L)	Nitrate (mg/L)	Ammonia (mg/L)	Sodium (mg/L)	Potassium (mg/L)	Calcium (mg/L)	Magnesium (mg/L)	Lead (ug/L)	Zinc (ug/L)	Copper (ug/L)
26	5.3	0.6	<0.001	6.3	1.5	0.6	0.62	<0.001	0.02	0.01	5.3	0.7	0.1	1.3	<0.4	<0.25	<0.4
27	7.1	64.9	0.062	82.1	23.2	6.8	2.48	2.21	0.37	4.78	63.0	6.7	9.9	9.2	3.0	1.2	6.5
28	7.0	6.5	0.031	76.5	15.8	5.6	0.33	<0.001	0.31	0.02	45.8	2.5	20.0	10.2	<0.4	<0.25	<0.4
29	7.1	3.0	<0.001	28.3	0.6	1.0	0.31	<0.001	0.03	<0.009	18.3	0.9	6.2	3.3	<0.4	<0.25	<0.4
30	7.7	9.9	0.024	1153	88.0	21.6	1.16	0.45	1.71	2.46	700	12.0	38.0	114	<0.4	<0.25	2.1
31	7.2	300	0.204	231	<0.1	6.6	0.50	0.07	1.43	0.07	137.5	4.0	16.6	31.8	4.5	50.0	5.4
32	5.1	0.5	0.015	28.3	5.4	0.6	0.38	<0.001	<0.005	<0.009	13.9	0.7	1.0	3.1	<0.4	0.6	0.5
33	6.9	1.7	<0.001	11.3	4.0	0.8	0.22	<0.001	0.22	0.01	10.1	0.7	2.5	2.6	<0.4	<0.25	<0.4
34	7.2	24.9	0.057	32.6	<0.1	3.8	0.54	0.04	0.97	0.36	19.8	6.2	8.1	8.5	4.1	0.9	3.0
35	7.1	4.2	0.022	84.1	19.0	7.8	0.49	0.03	3.43	4.26	67.2	9.0	17.8	7.9	<0.4	1.2	4.7
36	7.3	45.0	<0.001	126	11.5	6.6	0.52	0.01	0.32	0.06	63.0	4.4	27.7	23.4	<0.4	<0.25	<0.4
37	6.2	7.7	0.018	7.1	<0.1	1.0	0.55	<0.001	0.01	0.01	7.7	1.6	0.1	1.2	<0.4	<0.25	<0.4
38	7.4	6.5	<0.001	45.3	2.0	3.6	0.58	<0.001	0.14	0.04	24.7	4.5	3.5	8.1	<0.4	<0.25	<0.4
39	5.9	5.3	<0.001	41.1	3.3	0.6	0.43	<0.001	<0.005	<0.009	22.8	1.4	2.1	4.9	<0.4	<0.25	<0.4
40	7.3	6.5	<0.001	42.5	2.8	3.8	0.27	<0.001	0.12	0.05	24.9	3.5	3.2	8.4	<0.4	<0.25	<0.4
41	6.3	6.2	<0.001	25.5	0.6	1.0	0.52	<0.001	0.04	0.02	14.8	1.1	0.8	3.4	<0.4	<0.25	<0.4
42	6.1	31.9	<0.001	<0.2	<0.1	0.6	0.29	<0.001	<0.005	<0.009	3.5	0.9	0.3	0.4	0.4	0.5	<0.4
43	6.4	12.9	0.080	18.4	6.5	3.0	0.29	<0.001	0.25	0.63	14.9	1.7	6.4	6.6	<0.4	<0.25	<0.4
44	7.1	20.0	<0.001	109	2.2	4.4	0.44	<0.001	0.80	0.47	55.8	3.6	10.6	18.5	<0.4	<0.25	<0.4
45	6.7	14.9	0.041	5.2	<0.1	1.6	0.51	<0.001	<0.005	<0.009	8.6	3.0	0.4	1.3	<0.4	<0.25	<0.4
46	4.9	2.9	<0.001	42.5	18.3	0.2	0.36	<0.001	<0.005	<0.009	24.5	1.2	2.9	6.0	<0.4	<0.25	<0.4
47	6.1	3.7	<0.001	46.7	0.8	0.8	0.49	<0.001	0.01	<0.009	24.8	1.2	1.1	5.1	<0.4	<0.25	<0.4
48	5.1	5.5	<0.001	22.7	0.6	0.4	0.38	<0.001	<0.005	<0.009	13.5	1.0	0.3	2.9	<0.4	<0.25	<0.4
49	8.3	3.0	0.010	91.1	194	23.4	0.40	<0.001	<0.005	<0.009	128	6.0	50.0	86.0	<0.4	<0.25	<0.4
50	7.3	15.0	0.017	7.1	19.0	3.0	0.35	<0.001	0.09	0.02	10.6	0.9	5.1	5.3	<0.4	<0.25	0.7
51	7.8	3.2	0.013	110	276	15.0	0.28	<0.001	0.12	<0.009	120	3.0	74.0	92.0	<0.4	<0.25	<0.4

Table A8. Survey study analytical chemistry data.

Site number	pH	Turbidity (NTU)	Colour (A440)	Chloride (mg/L)	Sulfate (mg/L)	Alkalinity (mg/L)	Total phosphorus (mg/L)	ortho-Phosphate (mg/L)	Nitrate (mg/L)	Ammonia (mg/L)	Sodium (mg/L)	Potassium (mg/L)	Calcium (mg/L)	Magnesium (mg/L)	Lead (ug/L)	Zinc (ug/L)	Copper (ug/L)
52	7.0	2.0	<0.001	<0.2	3.2	1.0	0.39	<0.001	0.01	<0.009	3.8	0.5	1.7	1.9	<0.4	<0.25	<0.4
53	7.6	2.0	<0.001	7.8	11.9	3.6	0.36	<0.001	0.07	0.05	14.9	3.8	17.7	10.2	<0.4	<0.25	2.9
54	7.9	22.5	0.016	77.1	42.8	5.4	0.28	<0.001	0.21	<0.009	66.0	2.2	15.3	17.8	<0.4	<0.25	<0.4
55	8.2	1.0	0.012	23.3	119	26.2	0.43	<0.001	<0.005	<0.009	26.0	1.8	94.0	37.8	<0.4	<0.25	<0.4
56	8.2	3.2	<0.001	114	292	17.2	0.47	<0.001	0.13	<0.009	116	4.3	74.0	84.0	<0.4	<0.25	<0.4
57	6.9	1.7	0.008	4.0	6.3	3.0	0.34	<0.001	0.38	<0.009	4.7	0.6	2.7	2.3	<0.4	<0.25	<0.4
58	7.6	1.7	<0.001	<0.2	0.1	3.8	0.41	0.01	0.04	<0.009	5.3	0.6	7.2	3.7	<0.4	<0.25	<0.4
59	8.1	6.5	<0.001	12.0	3.3	11.8	0.25	0.01	0.02	<0.009	14.5	1.1	24.6	10.5	<0.4	<0.25	0.9
60	6.9	0.5	0.014	<0.2	<0.1	1.2	0.47	<0.001	0.02	<0.009	1.6	0.1	0.6	0.6	<0.4	<0.25	<0.4
61	7.6	3.5	<0.001	23.3	194	3.2	0.29	<0.001	<0.005	<0.009	16.9	4.0	60.0	44.7	<0.4	<0.25	<0.4
62	8.3	0.5	<0.001	17.5	<0.1	28.2	0.27	<0.001	0.04	0.01	37.4	0.9	56.0	21.6	<0.4	<0.25	1.1
63	8.5	4.2	0.005	70.8	0.4	30.4	0.29	<0.001	0.01	<0.009	68.1	0.8	48.0	32.3	<0.4	<0.25	1.0
64	6.4	250	0.685	29.7	<0.1	2.0	0.44	0.01	0.54	0.63	16.1	3.3	4.9	4.8	10.1	1.6	5.8
65	9.1	9.5	0.025	142	38.8	8.6	0.41	0.02	0.46	0.05	103	4.0	25.8	17.5	<0.4	1.3	1.7
66	7.7	14.0	0.017	203	36.6	7.2	0.40	<0.001	0.09	0.16	124	2.9	26.7	21.2	2.5	1.5	1.7
67	5.7	3.2	0.018	56.6	<0.1	0.8	0.25	<0.001	0.02	0.01	24.2	1.7	2.5	6.6	<0.4	0.9	<0.4
68	6.3	2.5	0.021	16.3	<0.1	0.6	<0.03	<0.001	0.02	<0.009	10.8	0.5	0.3	1.5	<0.4	<0.25	<0.4
69	7.2	125	0.200	12.0	<0.1	1.8	<0.03	<0.001	0.04	0.02	10.6	1.3	5.9	1.4	0.7	0.6	2.0
70	7.8	24.0	0.041	7.8	2.5	5.8	0.26	<0.001	<0.005	0.01	9.7	0.7	21.1	3.5	<0.4	<0.25	0.7
71	6.5	18.0	0.062	<0.2	<0.1	6.2	0.68	<0.001	0.27	0.17	9.6	5.7	10.8	6.9	<0.4	0.9	3.6
72	8.0	6.0	0.027	409	2.8	26.2	0.24	<0.001	0.03	0.05	146	2.2	120	86.0	<0.4	<0.25	<0.4
73	8.2	1.0	0.019	45.3	9.6	13.6	0.33	<0.001	0.01	0.01	30.4	1.5	22.1	20.0	<0.4	<0.25	<0.4
74	6.9	2.3	0.033	<0.2	<0.1	1.2	0.24	<0.001	0.02	<0.009	3.0	0.2	1.4	0.8	<0.4	<0.25	<0.4
75	6.5	0.6	0.019	<0.2	<0.1	1.0	0.39	<0.001	<0.005	<0.009	2.2	0.1	0.1	0.3	<0.4	<0.25	<0.4
76	7.0	3.6	0.034	<0.2	<0.1	1.4	0.21	<0.001	0.09	<0.009	4.0	0.5	2.8	1.3	<0.4	<0.25	<0.4
77	8.4	17.0	0.020	21.2	16.0	19.2	0.53	0.02	0.86	0.01	21.6	1.9	33.6	21.8	<0.4	<0.25	3.3

Table A8. Survey study analytical chemistry data.

Site number	pH	Turbidity (NTU)	Colour (A440)	Chloride (mg/L)	Sulfate (mg/L)	Alkalinity (mg/L)	Total phosphorus (mg/L)	ortho-Phosphate (mg/L)	Nitrate (mg/L)	Ammonia (mg/L)	Sodium (mg/L)	Potassium (mg/L)	Calcium (mg/L)	Magnesium (mg/L)	Lead (ug/L)	Zinc (ug/L)	Copper (ug/L)
78	7.9	3.1	0.033	8.5	26.2	8.2	0.26	<0.001	0.09	0.02	10.7	2.4	17.6	9.2	<0.4	<0.25	1.0
79	6.0	2.5	0.015	<0.2	<0.1	0.6	0.75	<0.001	0.01	<0.009	4.0	0.2	<0.05	0.4	<0.4	<0.25	<0.4
80	5.7	2.5	0.032	6.6	<0.1	0.8	0.39	<0.001	<0.005	<0.009	4.9	0.1	<0.05	0.5	<0.4	<0.25	<0.4
81	6.8	3.9	0.027	7.8	<0.1	1.0	0.22	<0.001	0.04	0.02	5.8	0.4	0.6	0.8	<0.4	<0.25	<0.4
82	7.6	12.0	0.029	301	33.8	7.8	0.33	0.02	0.08	0.08	165	2.4	31.7	39.0	<0.4	<0.25	<0.4
83	8.3	31.0	0.039	956	16.8	18.0	0.45	<0.001	<0.005	0.01	578	4.0	34.0	100	<0.4	<0.25	2.3
84	8.4	4.0	0.054	1234	123	18.0	1.05	0.49	0.77	0.18	800	20.0	34.0	166	<0.4	<0.25	5.6
85	7.4	12.0	0.033	126	0.2	5.4	0.36	<0.001	<0.005	0.15	69.3	3.2	14.5	22.8	0.9	9.8	<0.4
86	6.9	35.0	0.025	70.8	2.6	1.4	0.35	<0.001	0.01	<0.009	40.3	1.4	3.3	7.6	<0.4	0.7	<0.4
87	7.5	5.0	<0.001	2969	404	3.0	0.57	0.01	0.30	0.01	1650	60.0	73.0	261	0.9	<0.25	2.4
88	7.4	1.0	<0.001	8091	890	7.2	<0.03	0.03	0.08	0.01	4576	172	192	780	<0.4	<0.25	<0.4
89	6.7	6.3	0.010	5670	730	12.4	0.77	0.04	0.02	<0.009	3280	110	142	520	2.4	100	13.8
90	8.3	7.5	0.010	2619	198	47.8	0.25	<0.001	0.04	0.01	1624	2.4	66.0	286	<0.4	<0.25	2.9

Table A9. Survey study calculated relative percentages.

Site number	Anion chloride	relative sulfate	percentages carbonate (alkal.)	Major sodium	cation potassium	relative calcium	percentages magnesium
1	92	4.1	3.9	55.8	6	5.2	32.5
2	99.2	0	0.7	56.3	1.8	11.1	30.8
3	92.3	7.7	0.1	75.6	0.2	3.6	20.6
4	97	0	3	61.8	9.9	5.9	22.4
5	79.8	17	3.2	57.6	2.6	12.1	27.6
6	87.8	9.1	3.1	50.8	4.6	28.5	16.1
7	53.3	35.9	10.9	28.8	2.1	51.6	17.4
8	49.7	44.8	5.5	31.3	3.6	48.2	16.9
9	65.6	32.8	1.6	40.6	1.3	38.5	19.6
10	81.3	12.9	5.7	50.3	2.2	24	23.5
11	79.5	17.9	2.6	49.3	1.7	28.6	20.4
12	76.4	11	12.6	47	4.7	32	16.2
13	58.2	30.6	11.2	34.2	2.3	43.6	19.9
14	37.2	60.1	2.7	43	1.3	42.8	12.9
15	87.4	0	12.6	37.4	1.5	20.7	40.4
16	68.4	16.2	15.4	61.6	2.9	6.5	28.9
17	89.1	3.2	7.7	44.9	1.2	15.5	38.4
18	87.9	6.7	5.3	49.1	1	18.5	31.4
19	68.1	0	31.9	69.3	2.4	6.4	21.9
20	55.4	41.5	3.1	64.3	0.9	13.4	21.4
21	60.9	34.6	4.4	55.9	3.1	14	27
22	38.6	0	61.4	49.3	4.3	15.9	30.5
23	89.2	4	6.8	61.2	4.1	11.1	23.5
24	80.9	14.3	4.8	65.1	1.5	11.1	22.3
25	98.2	0	1.8	62.3	1.5	7.6	28.7
26	80.7	13.9	5.4	63.4	5	1.4	30.3
27	79	16.3	4.6	65.9	4.1	11.8	18.3
28	83	12.7	4.3	51.1	1.6	25.7	21.6
29	96.1	1.4	2.4	57.1	1.6	22.1	19.3
30	93.5	5.3	1.2	72.3	0.7	4.5	22.4
31	98	0	2	62.7	1	8.7	27.6
32	86.8	11.9	1.3	64.7	1.9	5.4	28
33	76.9	19.9	3.8	55.5	2.3	15.8	26.5
34	92.4	0	7.6	40.5	7.5	19.1	32.9
35	81	13.7	5.3	62.3	4.9	19	13.9
36	90.4	6.2	3.4	44.4	1.8	22.5	31.3
37	90.9	0	9.1	69.5	8.6	1	20.8
38	91.8	3	5.2	52.8	5.4	8.6	33.1
39	93.5	5.6	1	64.4	2.3	6.8	26.4
40	90	4.3	5.7	53.5	4.4	7.9	34.2
41	95.7	1.7	2.6	64.8	2.8	4	28.3
42	0	0	100	67.9	10.4	6.8	14.9
43	73.2	18.3	8.4	41.8	2.8	20.6	34.8
44	95.8	1.4	2.7	53.1	2	11.6	33.4
45	82.4	0	17.6	64.1	13.3	3.5	19.1
46	82.8	17	0.2	61.1	1.8	8.3	28.8
47	97.6	1.3	1.2	68.1	1.9	3.5	26.5

Table A9. Survey study calculated relative percentages.

Site number	Anion chloride	relative sulfate	percentages carbonate (alkal.)	Major sodium	cation potassium	relative calcium	percentages magnesium
48	97	1.8	1.2	67.8	3	1.7	27.6
49	36.3	57.1	6.6	36	1.7	16.2	46.1
50	30.3	60.6	9.1	39	1.9	21.6	37.3
51	33.9	62.8	3.3	31.4	0.5	22.3	45.8
52	0	77	23	38.3	3.1	20.3	38.3
53	40.6	46.1	13.3	26.3	3.9	35.8	34
54	68.5	28.1	3.4	55.6	1.1	14.8	28.5
55	18	67.7	14.3	12.6	0.5	52.2	34.7
56	33.4	63	3.6	31.9	0.7	23.4	43.9
57	36.7	43.3	20	37	2.8	25	35.2
58	0	2.6	97.4	25.3	1.6	39.6	34.1
59	52.7	10.7	36.6	22.8	1	44.6	31.5
60	0	0	100	45.7	2	19.6	32.7
61	13.8	84.8	1.3	9.7	1.3	39.8	49.1
62	46.5	0	53.5	26.2	0.4	44.9	28.6
63	76.4	0.3	23.2	36.8	0.2	29.8	33.2
64	95.4	0	4.5	49.3	5.9	16.9	28.2
65	80.3	16.2	3.4	61.2	1.4	17.6	19.8
66	86.3	11.5	2.2	63	0.9	15.6	20.5
67	99	0	1	60	2.5	6.9	30.9
68	97.5	0	2.5	75.6	2.1	2.4	19.9
69	90.4	0	9.6	50.7	3.6	32.5	13.2
70	56.7	13.4	29.9	23.6	1	59.2	16.3
71	0	0	100	25	8.9	32.1	33.9
72	95.2	0.5	4.4	32.5	0.3	30.7	36.4
73	73.1	11.4	15.5	32.1	0.9	26.9	40.1
74	0	0	100	48.1	1.8	25.9	24.4
75	0	0	100	75.9	2.4	2	19.8
76	0	0	100	39.3	3	32.3	25.4
77	45.7	25.1	29.2	21	1.1	37.6	40.3
78	25.2	57.6	17.2	21.3	2.8	40.7	35.2
79	0	0	100	81.7	2.4	0	15.9
80	92.2	0	7.8	82.7	1.2	0	16.1
81	91.7	0	8.3	70.2	2.8	8.4	18.5
82	90.8	7.5	1.7	59.7	0.5	13.2	26.8
83	97.4	1.3	1.3	71.4	0.3	4.8	23.5
84	92.3	6.8	0.9	68.6	1	3.3	27
85	96.9	0.1	2.9	52.8	1.4	12.7	33
86	96.1	2.6	1.3	67.8	1.4	6.4	24.4
87	90.8	9.1	0.1	72.8	1.5	3.7	21.9
88	92.4	7.5	0.1	71.7	1.6	3.5	23.2
89	91.2	8.7	0.1	72.9	1.4	3.6	22
90	93.6	5.2	1.2	74.6	0.1	0.3	25

Anion relative %s based on
equivalent weights of
Cl, SO₄ & CO₃ alkalinity only

Cation relative %s
based on equiv. weights
of Na, K, Ca & Mg only

Table A10(i). Monitoring study sampling dates and flow data for Gwawley Creek.

Sample collection	Date	Width SS1 (m)	Depth SS1 (cm)	Water velocity SS1 (cm/s)	Flow group	Discharge SS1 (m ³ /s)	Width SS2 (m)	Depth SS2 (cm)	Water velocity SS2 (cm/s)	Flow group	Discharge SS2 (m ³ /s)	Width SS3 (m)	Depth SS3 (cm)	Water velocity SS3 (cm/s)	Flow group	Discharge SS3 (m ³ /s)
1	21/3/91	3.20	8.2	<31.3	F1	bdl	1.80	8.5	<31.3	F1	bdl	3.20	16.7	<31.3	F1	bdl
2	5/6/91	4.10	19.0	<31.3	F1	bdl	4.00	36.0	104	F2	1.5	2.30	13.5	92.9	F2	0.29
3	23/10/91	2.30	15.8	<31.3	F1	bdl	6.50	55.0	<31.3	F1	bdl	2.50	5.2	36	F2	0.047
4	14/11/91			<31.3	F1	bdl	6.50	55.0	31.3	F2	1.12	2.50	5.2	36	F2	0.047
5	16/12/91	2.85	25.2	<31.3	F1	bdl	4.80	46.7	<31.3	F1	bdl	2.30	8.8	52.4	F2	0.11
6	2/4/92	2.20	10.2	<31.3	F1	bdl			<31.3	F1	bdl	1.97	5.4	<31.3	F1	bdl
7	2/5/92	2.30	15.3	<31.3	F1	bdl			<31.3	F1	bdl	2.05	7.4	34.8	F2	0.058
8	3/7/92	2.20	15.5	<31.3	F1	bdl	4.90	18.7	<31.3	F1	bdl	1.90	9.9	38.3	F2	0.072
9	27/8/92			<31.3	F1	bdl			<31.3	F1	bdl	1.85	6.3	<31.3	F1	bdl
10	10/9/92	2.10	25.6	<31.3	F1	bdl	3.70	25.1	<31.3	F1	bdl	3.00	11.4	<31.3	F1	bdl
11	19/11/93	5.80	51.8	<31.3	F1	bdl	4.50	21.7	<31.3	F1	bdl	1.83	12.7	<31.3	F1	bdl
12	17/2/93			flood flow	F2	flood flow			flood flow	F2	flood flow			flood flow	F2	flood flow

Table A10(ii). Monitoring study sampling dates and flow data for Savilles Creek.

Sample collection	Date	Width SS1 (m)	Depth SS1 (cm)	Water velocity SS1 (cm/s)	Flow group	Discharge SS1 (m ³ /s)	Width SS2 (m)	Depth SS2 (cm)	Water velocity SS2 (cm/s)	Flow group	Discharge SS2 (m ³ /s)	Width SS3 (m)	Depth SS3 (cm)	Water velocity SS3 (cm/s)	Flow group	Discharge SS3 (m ³ /s)
1	5/4/91	5.50	60.0	<31.3	F1	bdl	6.50	55.0	<31.3	F1	bdl	7.50	30.4	<31.3	F1	bdl
2	5/6/91	4.70	32.2	<31.3	F1	bdl	4.50	13.4	64.2	F2	0.39	3.00	39.6	<31.3	F1	bdl
3	23/10/91			<31.3	F1	bdl			<31.3	F1	bdl			<31.3	F1	bdl
4	14/11/91	6.60	32.0	<31.3	F1	bdl			<31.3	F1	bdl			<31.3	F1	bdl
5	16/12/91	6.35	50.3	31.3	F2	1	5.75	40.6	44.3	F2	1	3.37	54.5	56.4	F2	1
6	21/3/92	6.80	38.8	<31.3	F1	bdl	5.23	50.4	<31.3	F1	bdl	3.20	39.1	<31.3	F1	bdl
7	7/5/92			<31.3	F1	bdl	4.20	44.8	<31.3	F1	bdl	4.50	36.9	<31.3	F1	bdl
8	3/7/92	4.60	18.7	<31.3	F1	bdl	3.80	35.7	<31.3	F1	bdl	3.00	32.8	<31.3	F1	bdl
9	28/8/92			<31.3	F1	bdl			<31.3	F1	bdl			<31.3	F1	bdl
10	10/9/92	6.10	23.3	<31.3	F1	bdl	6.00	17.8	<31.3	F1	bdl	4.80	24.6	<31.3	F1	bdl
11	19/11/93	5.05	20.1	<31.3	F1	bdl	4.30	55.0	<31.3	F1	bdl	3.45	32.9	<31.3	F1	bdl
12	17/2/93			flood flow	F2	flood flow			flood flow	F2	flood flow			flood flow	F2	flood flow

Table A10(iii). Monitoring study sampling dates and flow data for Temptation Creek.

Sample collection	Date	Width SS1 (m)	Depth SS1 (cm)	Water velocity SS1 (cm/s)	Flow group	Discharge SS1 (m ³ /s)	Width SS2 (m)	Depth SS2 (cm)	Water velocity SS2 (cm/s)	Flow group	Discharge SS2 (m ³ /s)	Width SS3 (m)	Depth SS3 (cm)	Water velocity SS3 (cm/s)	Flow group	Discharge SS3 (m ³ /s)
1	5/4/91	3.50	30.0	<31.3	F1	bdl	0.75	9.2	<31.3	F1	bdl	7.50	36.2	<31.3	F1	bdl
2	5/6/91	3.70	22.5	<31.3	F1	bdl	5.00	34.0	<31.3	F1	bdl	7.00	37.7	<31.3	F1	bdl
3	23/10/91			<31.3	F1	bdl			<31.3	F1	bdl			<31.3	F1	bdl
4	14/11/91			<31.3	F1	bdl			<31.3	F1	bdl			<31.3	F1	bdl
5	16/12/91	3.00	30.2	54.9	F2	0.5	5.05	76.1	<31.3	F1	bdl	8.70	81.5	<31.3	F1	bdl
6	21/3/92	4.50	21.0	<31.3	F1	bdl			<31.3	F1	bdl	7.60	25.4	<31.3	F1	bdl
7	2/5/92	2.83	20.6	33.1	F2	0.19			<31.3	F1	bdl			<31.3	F1	bdl
8	3/7/92	2.20	20.7	44.3	F2	0.2	2.45	40.3	<31.3	F1	bdl			<31.3	F1	bdl
9	28/8/92			<31.3	F1	bdl			<31.3	F1	bdl			<31.3	F1	bdl
10	10/9/92	4.00	22.7	<31.3	F1	bdl	4.90	26.4	<31.3	F1	bdl	9.00	35.9	<31.3	F1	bdl
11	19/1/93	4.00	23.1	<31.3	F1	bdl	5.30	38.1	<31.3	F1	bdl	7.80	25.3	<31.3	F1	bdl
12	17/2/93			flood flow	F2	flood flow			flood flow	F2	flood flow			flood flow	F2	flood flow

Table A11(i). Monitoring study surface and interstitial water chemistry for Gwawley Creek.

Surface water

Sample collection	Temperature SS1 (oC)	Temperature SS2 (oC)	Temperature SS3 (oC)	Conductivity SS1 (mS/m)	Conductivity SS2 (mS/m)	Conductivity SS3 (mS/m)	Dissolved oxygen SS1 (mg/L)	Dissolved oxygen SS2 (mg/L)	Dissolved oxygen SS3 (mg/L)	pH SS1	pH SS2	pH SS3
1	22.5	21.2	20.9	31.5	25.5	25.0	8.7	9.2	7.2	6.60	7.40	6.90
2	15.0	13.8	14.1	29.0	25.0	31.0	9.2	9.9	9.7	7.30	7.20	7.20
3	18.0	16.5	17.0	27.0	14.0	28.0	7.2	8.8	8.8	7.20	7.60	6.40
4	21.4	18.1	18.5	31.5	29.0	28.0	8.5	9.7	9.5	6.90	7.70	7.10
5	23.0	24.6	23.7	49.5	50.0	46.0	6.2	6.0	7.7	6.84	7.21	6.98
6	21.2	20.4	20.5	38.0	38.5	39.0	6.5	8.4	7.6	7.21	7.14	7.26
7	18.5	16.7	16.6	36.5	37.0	36.0	5.2	6.7	6.4	7.06	7.33	6.82
8	14.7	12.6	13.1	37.5	41.5	38.0	12.0	11.6	13.6	7.12	7.01	7.06
9	14.3	12.2	14.3	26.0	26.0	25.5	9.2	11.3	12.3	6.24	6.41	6.92
10	15.5	14.8	14.8	30.0	25.0	24.0	8.2	9.1	10.6	6.54	6.95	7.12
11	21.5	21.7	21.6	45.0	22.0	20.0	5.0	5.3	4.7	6.95	7.35	7.10
12				4.0	5.0	5.0				7.35	7.62	7.53
Mean	18.7	17.5	17.7	32.1	28.2	28.8	7.8	8.7	8.9	6.90	7.20	7.00
Standard error	1.0	1.2	1.1	3.3	3.5	3.1	0.6	0.6	0.8	0.10	0.10	0.10

Interstitial water

Sample collection	Temperature SS1 (oC)	Temperature SS2 (oC)	Temperature SS3 (oC)	Conductivity SS1 (mS/m)	Conductivity SS2 (mS/m)	Conductivity SS3 (mS/m)	Dissolved Oxygen SS1 (mg/L)	Dissolved Oxygen SS2 (mg/L)	Dissolved Oxygen SS3 (mg/L)	pH SS1	pH SS2	pH SS3
1		21.2	21.0		28.0	35.0		6.1	3.0	6.70	7.00	6.90
3	17.0	17.0	17.0	65.0	65.0	21.0	2.2	3.3	4.7	6.80	6.30	6.70
4	19.5	17.3	17.8	44.0	60.0	40.0	1.6	1.8	3.6	6.60	6.10	5.90
5	21.1	21.3	20.6	55.0	55.0	29.0	1.4	1.7	2.7	6.30	6.38	6.60
6	21.1	20.4	20.5	50.0	45.0	43.0	3.3	5.8	6.1	6.50	7.02	7.18
7	18.4	16.9	16.7	37.0	45.0	35.0	3.2	2.4	3.5	6.95	6.84	6.93
9	14.0	12.3	14.3	44.0	55.0	22.5	4.8	3.4	5.7	6.63	6.65	6.20
10	15.2	14.4	15.3	44.0	60.0	25.0	2.7	3.5	5.4	6.36	6.65	6.93
11	22.1	22.0	21.8	75.0	70.0	34.0	1.8	1.6	2.4	7.75	7.45	7.40
Mean	18.5	18.1	18.3	51.7	53.7	31.6	2.6	3.3	4.1	6.70	6.70	6.70
Standard error	1.0	1.1	0.9	4.5	4.2	2.6	0.4	0.6	0.5	0.10	0.10	0.10

Table A11(i). Monitoring study surface and interstitial water chemistry for Gwawley Creek.

Surface water

Sample collection	Redox SS1 (mV)	Redox SS2 (mV)	Redox SS3 (mV)	Alkalinity SS1 (mg/L)	Alkalinity SS2 (mg/L)	Alkalinity SS3 (mg/L)	Acidity SS1 (mg/L)	Acidity SS2 (mg/L)	Acidity SS3 (mg/L)	Hardness SS1 (mg/L)	Hardness SS2 (mg/L)	Hardness SS3 (mg/L)
1	80	140	140	6.2	7.4	7.6	1.05	0.90	1.70	84.0	104	86.0
2	153	200	158	17.8	10.7	11.0	0.50	0.40	0.40	32.0	20.0	18.0
3	45	180	209	53.5	54.5	54.0				71.8	65.7	64.6
4	55	157	125	60.0	70.0	63.0	0.60	0.30	0.45	60.0	72.0	64.0
5	-13	7	56	100	108	102	1.15	0.55	0.65	108	104	98.0
6	-30	-27	-34	85.5	94.5	86.0	1.95	1.00	1.40	106	96.0	84.0
7	-25	-41	-28	95.5	104	97.5	1.70	1.60	1.70	90.0	92.0	88.0
8	-6	-2	-2	103	108	103	3.30	3.35	3.50	150	144	148
9	21	13	-13	66.0	70.5	60.0	4.80	3.45	3.10	92.0	104	92.0
10	6	-25	-32	63.0	60.5	57.5	2.85	2.00	1.80	106	88.0	88.0
11				71.0	49.5	49.5	15.3	5.55	6.05	104	64.0	64.0
12	158	151	167	9.0	10.5	10.0	1.00	1.45	1.10	16.0	14.0	12.0
Mean	40	69	68	60.9	62.3	58.4	3.10	1.90	2.00	85.0	80.6	75.5
Standard error	20	29	28	9.9	10.9	10.1	1.30	0.50	0.50	10.5	10.6	10.4

Interstitial water

Sample collection	Redox SS1 (mV)	Redox SS2 (mV)	Redox SS3 (mV)	Alkalinity SS1 (mg/L)	Alkalinity SS2 (mg/L)	Alkalinity SS3 (mg/L)	Acidity SS1 (mg/L)	Acidity SS2 (mg/L)	Acidity SS3 (mg/L)	Hardness SS1 (mg/L)	Hardness SS2 (mg/L)	Hardness SS3 (mg/L)
1	60	-12	-60	8.0	9.0	8.4	2.00	1.75	2.15	84.0	104	114
3	-63	169	254		86.5	22.5				230	114	51.3
4	39	215	260	226	17.0	50.0	1.50	2.20	4.75	146	52.0	70.0
5	13	-64	137	132	62.0	36.0	4.10	3.75	1.10	96.0	82.0	64.0
6	6	-22	-30	169	199	97.2	5.82	4.80	0.90	104	134	84.0
7	-14	-17	-16	84.0	208	108	1.90	3.00	1.40	90.0	114	90.0
9	0	-4	26	211	222	31.5	8.95	9.80	2.65	220	258	76.0
10	20	-7	1	115	119	29.0	15.3	9.05	2.00	140	182	68.0
11				294	177	79.0	35.4	25.0	12.3	296	228	104
Mean	8	32	72	155	122	51.3	9.40	7.40	3.40	156	141	80.1
Standard error	13	36	45	32	28	11.7	4.10	2.70	1.30	25	23	6.6

Table A11(i). Monitoring study surface and interstitial water chemistry for Gwawley Creek.

Surface water													
Sample collection	ortho-Phosphate SS1 (ug/L)	ortho-Phosphate SS2 (ug/L)	ortho-Phosphate SS3 (ug/L)	Copper SS1 (ug/L)	Copper SS2 (ug/L)	Copper SS3 (ug/L)	Zinc SS1 (mg/L)	Zinc SS2 (mg/L)	Zinc SS3 (mg/L)	Cadmium SS1 (ug/L)	Cadmium SS2 (ug/L)	Cadmium SS3 (ug/L)	
1	7.1	47.3	25.7	<10.5	<10.5	11.7	0.03	0.05	0.07	<0.75	0.83	2.42	
2	56.0	46.0	46.0	<10.5	<10.5	<10.5	0.13	0.11	0.11	<0.75	<0.75	<0.75	
3	4.7	6.5	6.1	26.0	<10.5	22.4	0.03	<0.01	<0.01	<0.75	<0.75	<0.75	
4	3.4	5.6	5.1	<10.5	<10.5	<10.5	0.02	<0.01	<0.01	<0.75	<0.75	<0.75	
5	16.9	15.0	16.4	<10.5	<10.5	<10.5	0.02	<0.01	0.02	<0.75	<0.75	<0.75	
6	6.7	3.5	6.7	<10.5	<10.5	<10.5	<0.01	0.02	<0.01	<0.75	<0.75	<0.75	
7	2.2	1.8	2.2	<10.5	166	18.4	0.03	0.03	0.04	<0.75	<0.75	<0.75	
8	1.2	1.6	2.1	15.7	35.6	32.9	0.03	0.04	0.03	<0.75	<0.75	<0.75	
9	2.9	2.9	3.4	<10.5	<10.5	<10.5	0.05	0.07	0.05	<0.75	<0.75	<0.75	
10	5.6	4.2	3.8	<10.5	10.9	<10.5	0.04	0.05	0.06	<0.75	<0.75	<0.75	
11	4.2	14.8	12.8	<10.5	<10.5	<10.5	0.04	0.10	0.08	<0.75	0.98	1.12	
12	172	160	160	<10.5	<10.5	<10.5	0.02	0.03	0.02	<0.75	<0.75	<0.75	
Mean	23.6	25.8	24.2	3.5	17.7	7.1	0.04	0.04	0.04		0.15	0.29	
Standard error	14.2	13.1	12.9	2.4	13.8	3.3	0.01	0.01	0.01		0.10	0.21	
Interstitial water													
Sample collection	ortho-Phosphate SS1 (ug/L)	ortho-Phosphate SS2 (ug/L)	ortho-Phosphate SS3 (ug/L)	Copper SS1 (ug/L)	Copper SS2 (ug/L)	Copper SS3 (ug/L)	Zinc SS1 (mg/L)	Zinc SS2 (mg/L)	Zinc SS3 (mg/L)	Cadmium SS1 (ug/L)	Cadmium SS2 (ug/L)	Cadmium SS3 (ug/L)	
1	4.0	5.3	7.9	22.6	<10.5	17.6	0.21	0.12	0.25	<0.75	<0.75	<0.75	
3	2.0	5.4	2.0	27.8	24.6	28.6	<0.01	0.38	0.43	<0.75	<0.75	<0.75	
4	2.0	4.2	6.7	<10.5	<10.5	<10.5	0.02	0.07	0.15	<0.75	<0.75	<0.75	
5	7.2	380	315	<10.5	<10.5	<10.5	0.08	0.05	0.04	<0.75	<0.75	<0.75	
6	4.9	3.5	11.8	<10.5	<10.5	33.6	<0.01	<0.01	0.02	<0.75	<0.75	<0.75	
7	<1.0	8.2	4.5	10.8	17.2	<10.5	0.11	0.03	0.04	<0.75	<0.75	<0.75	
9	1.5	<1.0	3.4	<10.5	<10.5	<10.5	0.08	0.06	0.11	<0.75	<0.75	<0.75	
10	<1.0	1.0	2.0	26.2	<10.5	<10.5	0.06	0.11	0.06	<0.75	<0.75	<0.75	
11	<1.0	<1.0	3.0	<10.5	<10.5	<10.5	0.03	0.03	<0.01	<0.75	<0.75	2.83	
Mean	2.4	45.3	39.6	9.7	4.6	8.9	0.07	0.09	0.11			0.31	
Standard error	0.8	41.8	34.4	4.1	2.9	4.6	0.02	0.04	0.05			0.31	

Table A11(i). Monitoring study surface and interstitial water chemistry for Gwawley Creek.

Surface water									
Sample collection	Lead SS1 (ug/L)	Lead SS2 (ug/L)	Lead SS3 (ug/L)	Suspended solids SS1 (mg/L)	Suspended solids SS2 (mg/L)	Suspended solids SS3 (mg/L)	Total phosphorus SS1 (ug/L)	Total phosphorus SS2 (ug/L)	Total phosphorus SS3 (ug/L)
1	<4.75	7.85	14.4	3.2	4.0	1.6	100	180	70.0
2	24.4	31.8	30.4	13.6	19.2	19.2	70.0	140	280
3	14.4	13.6	24.2	28.2	71.2	3.0	29.3	61.6	17.6
4	<4.75	<4.75	<4.75	124	14.6	34.0	147	56.1	51.6
5	<4.75	<4.75	<4.75	8.4	2.4	1.2	130	130	<1.3
6	6.10	<4.75	<4.75	15.2	34.0	1.8	22.9	32.0	39.9
7	<4.75	4.90	11.8	14.8	14.8	0.6	40.2	21.8	9.1
8	5.80	<4.75	<4.75	2.0	10.4	1.2	7.3	8.8	11.2
9	<4.75	<4.75	<4.75	10.6	5.0	4.0	40.0	18.4	12.0
10	<4.75	<4.75	<4.75	33.6	37.4	13.2	267	304	125
11	<4.75	9.60	7.40	67.4	13.6	1.8	168	81.0	50.0
12	<4.75	<4.75	<4.75	88.2	119	145	316	376	364
Mean	4.20	5.60	7.30	34.1	28.8	18.9	111	117	85.9
Standard error	2.20	2.70	3.10	11.2	9.9	11.8	29	34	33.7

Interstitial water			
Sample collection	Lead SS1 (ug/L)	Lead SS2 (ug/L)	Lead SS3 (ug/L)
1	176	44.8	88.0
3	15.0	12.8	6.80
4	5.00	7.80	<4.75
5	<4.75	<4.75	<4.75
6	<4.75	8.20	23.8
7	5.80	<4.75	<4.75
9	<4.75	<4.75	<4.75
10	<4.75	<4.75	<4.75
11	<4.75	<4.75	12.4
Mean	22.4	8.20	14.5
Standard error	19.3	4.90	9.6

Table A11(ii). Monitoring study surface and interstitial water chemistry for Savilles Creek.

Surface water

Sample collection	Temperature SS1 (oC)	Temperature SS2 (oC)	Temperature SS3 (oC)	Conductivity SS1 (mS/m)	Conductivity SS2 (mS/m)	Conductivity SS3 (mS/m)	Dissolved oxygen SS1 (mg/L)	Dissolved oxygen SS2 (mg/L)	Dissolved oxygen SS3 (mg/L)	pH SS1	pH SS2	pH SS3
1	16.9	18.9	18.2	100	33.5	22.0	8.6	7.9	7.7	6.00	9.00	8.90
2	12.8	12.3	12.4	90.0	75.0	75.0	10.1	9.7	9.8	7.00	7.10	7.10
3	16.5	16.0	16.0	90.0	90.0	90.0	8.6	8.3	5.1	7.50	7.20	7.40
4	17.7	17.1	16.8	46.5	46.0	55.0	6.4	4.7	4.5	7.70	6.50	7.50
5	20.8	19.5	19.2	28.0	23.0	22.0	8.2	7.9	6.9	6.95	6.90	6.32
6	19.6	19.5	19.8	48.5	36.5	37.0				7.51	6.93	7.40
7	16.1	15.8	15.7	29.5	24.5	24.0	6.2	6.4	8.2	7.10	6.73	6.61
8	10.7	10.5	10.7	47.0	30.5	26.5	15.0	15.9	14.4	7.84	7.79	7.77
9	10.4	10.6	10.6	32.0	25.5	22.5	12.5	12.8	12.5	6.43	6.79	6.71
10	12.1	13.3	12.6	28.0	28.0	34.0	12.0	11.8	9.6	6.49	6.97	7.12
11	22.0	22.2	22.1	47.0	43.5	42.5	4.7	6.0	6.8	7.35	7.40	7.50
12				5.5	6.0	6.0				7.48	7.00	7.18
Mean	16.0	16.0	15.8	49.3	38.5	38.0	9.2	9.1	8.5	7.10	7.20	7.30
Standard error	1.2	1.2	1.2	8.4	6.7	7.0	1.0	1.1	1.0	0.20	0.20	0.20

Interstitial water

Sample collection	Temperature SS1 (oC)	Temperature SS2 (oC)	Temperature SS3 (oC)	Conductivity SS1 (mS/m)	Conductivity SS2 (mS/m)	Conductivity SS3 (mS/m)	Dissolved oxygen SS1 (mg/L)	Dissolved oxygen SS2 (mg/L)	Dissolved oxygen SS3 (mg/L)	pH SS1	pH SS2	pH SS3
1	18.1	19.1	16.9	82.5	34.5	21.5	6.4	6.2	3.2	7.40	8.30	8.50
3	16.5	16.0	16.0	90.0	46.5	70.0	2.1	2.6	2.1	7.30	7.10	7.30
4	18.3	17.0	16.7	70.0	85.0	70.0	1.8	1.9	1.7	7.50	7.10	7.30
5	20.7	19.5	19.2	51.0	26.5	80.0	1.4	5.2	2.0	6.71	7.06	6.07
6	21.0	19.6	19.7	48.0	38.5	39.0				7.02	6.87	7.03
7	16.2	16.1	15.9	31.0	24.0	25.0	5.3	4.7	5.0	7.31	6.91	6.86
9	10.6	11.0	10.7	35.0	23.0	24.5	7.4	3.3	4.4	6.59	6.55	6.87
10	12.2	12.7	12.6	37.0	34.5	47.5	5.5	4.8	5.3	6.58	6.78	6.97
11	22.7	22.2	22.3	49.0	40.0	44.5	2.0	2.6	2.9	7.70	7.70	7.85
Mean	17.4	17.0	16.7	54.8	39.2	46.9	4.0	3.9	3.3	7.00	7.10	7.20
Standard error	1.3	1.2	1.2	7.1	6.3	7.3	0.8	0.5	0.5	0.10	0.20	0.20

Table A11(ii). Monitoring study surface and interstitial water chemistry for Savilles Creek.

Surface water													
Sample collection	Redox SS1 (mV)	Redox SS2 (mV)	Redox SS3 (mV)	Alkalinity SS1 (mg/L)	Alkalinity SS2 (mg/L)	Alkalinity SS3 (mg/L)	Acidity SS1 (mg/L)	Acidity SS2 (mg/L)	Acidity SS3 (mg/L)	Hardness SS1 (mg/L)	Hardness SS2 (mg/L)	Hardness SS3 (mg/L)	Hardness
1	275	60	77	13.4	7.7	5.0	0.80	0.70	0.50	144	44.0	44.0	44.0
2	118	85	97	62.5	54.2	54.2	1.70	1.25	1.25	176	144	160	160
3	36	39	101	82.5	73.0	73.0				92.3	98.5	102	102
4	-30	141	-30	79.0	86.0	83.0	0.35	0.95	0.85	68.0	66.0	70.0	70.0
5	92	96	51	43.0	30.0	31.0	0.40	0.20	0.25	56.0	44.0	46.0	46.0
6	-42	-20	-38	58.0	42.0	45.0	0.60	0.30	0.30	60.0	56.0	52.0	52.0
7	-35	-6	0	57.0	38.5	36.5	0.80	0.60	0.55	68.0	46.0	44.0	44.0
8	-45	-44	-43	44.5	34.5	35.0	1.40	2.00	1.35	76.0	58.0	60.0	60.0
9	10	-8	-10	62.5	35.0	36.0	1.95	1.70	1.05	82.0	62.0	64.0	64.0
10	3	-24	-32	52.0	46.0	51.5	2.15	1.40	1.80	94.0	88.0	80.0	80.0
11				56.0	57.5	55.5	9.00	3.45	3.00	84.0	88.0	82.0	82.0
12	156	179	169	12.0	15.0	12.0	2.00	1.10	1.00	12.0	16.0	14.0	14.0
Mean	49	45	31	51.9	43.3	43.1	1.90	1.20	1.10	84.4	67.5	68.2	68.2
Standard error	31	22	22	6.3	6.4	6.5	0.70	0.30	0.20	12.1	9.6	10.6	10.6
Interstitial water													
Sample collection	Redox SS1 (mV)	Redox SS2 (mV)	Redox SS3 (mV)	Alkalinity SS1 (mg/L)	Alkalinity SS2 (mg/L)	Alkalinity SS3 (mg/L)	Acidity SS1 (mg/L)	Acidity SS2 (mg/L)	Acidity SS3 (mg/L)	Hardness SS1 (mg/L)	Hardness SS2 (mg/L)	Hardness SS3 (mg/L)	Hardness
1	-83	-105	-93	21.4	16.2	8.0	5.90	2.30	0.90	320	148	124	124
3	-50	-56	-28	87.0	148	128				94.4	127	138	138
4	-260	-198	-150	100	106	132	0.90	2.55	0.85	88.0	98.0	106	106
5	-104	120	-53	214	57.5	137	0.95	0.40	1.40	118	64.0	90.0	90.0
6	-14	-11	-17	73.5	69.0	92.0	0.30	0.30	1.40	68.0	62.0	68.0	68.0
7	-39	-16	-14	55.5	50.5	45.0	0.70	1.05	0.65	52.0	48.0	52.0	52.0
9	1	5	-13	65.5	105	83.0	1.70	2.90	3.05	94.0	124	97.2	97.2
10	-3	-13	-25	56.5	124	113	2.40	4.55	2.30	110	156	138	138
11				110	139	106	12.50	9.30	8.60	118	152	128	128
Mean	-69	-34	-49	87.0	90.6	93.8	3.20	2.90	2.40	118	109	105	105
Standard error	30	32	17	18.1	14.9	14.4	1.50	1.00	0.90	26	14	10	10

Table A11(ii). Monitoring study surface and interstitial water chemistry for Savilles Creek.**Surface water**

Sample collection	ortho-Phosphate SS1 (ug/L)	ortho-Phosphate SS2 (ug/L)	ortho-Phosphate SS3 (ug/L)	Copper SS1 (ug/L)	Copper SS2 (ug/L)	Copper SS3 (ug/L)	Zinc SS1 (mg/L)	Zinc SS2 (mg/L)	Zinc SS3 (mg/L)	Cadmium SS1 (ug/L)	Cadmium SS2 (ug/L)	Cadmium SS3 (ug/L)
1	<1.0	47.3	26.2	<10.5	<10.5	<10.5	0.50	0.08	0.06	10.5	25.8	20.0
2	7.1	3.0	3.4	<10.5	<10.5	<10.5	<0.01	0.02	<0.01	<0.75	<0.75	<0.75
3	1.6	1.1	1.1	<10.5	<10.5	<10.5	<0.01	<0.01	<0.01	<0.75	<0.75	<0.75
4	4.7	2.0	2.0	<10.5	<10.5	<10.5	<0.01	<0.01	<0.01	<0.75	<0.75	<0.75
5	12.8	9.5	12.8	<10.5	<10.5	<10.5	<0.01	<0.01	<0.01	<0.75	<0.75	<0.75
6	6.0	3.3	3.3	<10.5	<10.5	23.6	<0.01	<0.01	<0.01	<0.75	<0.75	<0.75
7	3.1	9.5	2.7	<10.5	82.0	40.9	0.02	0.03	<0.01	<0.75	<0.75	<0.75
8	2.6	2.1	2.1	12.8	<10.5	10.9	<0.01	0.04	0.02	<0.75	<0.75	<0.75
9	2.4	1.0	1.0	<10.5	<10.5	<10.5	0.03	0.03	0.02	<0.75	<0.75	<0.75
10	2.0	2.0	1.0	<10.5	<10.5	<10.5	<0.01	0.02	0.02	<0.75	0.99	<0.75
11	2.0	1.0	8.8	<10.5	<10.5	<10.5	<0.01	<0.01	0.03	3.02	<0.75	0.93
12	80.0	70.4	61.6	<10.5	<10.5	<10.5	<0.01	0.02	0.02	<0.75	<0.75	<0.75
Mean	10.4	12.7	10.5	1.1	6.8	6.3	0.05	0.02	0.01	1.10	2.20	1.70
Standard error	6.4	6.4	5.1	1.1	6.8	3.8	0.04	0.01	0.01	0.90	2.10	1.70

Interstitial water

Sample collection	ortho-Phosphate SS1 (ug/L)	ortho-Phosphate SS2 (ug/L)	ortho-Phosphate SS3 (ug/L)	Copper SS1 (ug/L)	Copper SS2 (ug/L)	Copper SS3 (ug/L)	Zinc SS1 (mg/L)	Zinc SS2 (mg/L)	Zinc SS3 (mg/L)	Cadmium SS1 (ug/L)	Cadmium SS2 (ug/L)	Cadmium SS3 (ug/L)
1	1.3	4.4	6.2	99.2	<10.5	30.4	1.74	0.05	0.37	93.8	<0.75	<0.75
3	2.0	<1.0	8.9	<10.5	<10.5	<10.5	<0.01	<0.01	<0.01	<0.75	<0.75	<0.75
4	8.4	8.0	5.0	<10.5	<10.5	<10.5	0.02	<0.01	<0.01	<0.75	<0.75	<0.75
5	14.4	27.3	8.3	<10.5	66	<10.5	<0.01	<0.01	<0.01	<0.75	<0.75	<0.75
6	8.8	18.8	6.9	<10.5	21	20.6	<0.01	<0.01	<0.01	<0.75	0.95	1.00
7	3.1	2.2	2.2	101	16.8	20	0.03	0.02	0.02	<0.75	<0.75	<0.75
9	1.0	<1.0	<1.0	<10.5	<10.5	<10.5	0.04	0.07	0.07	<0.75	<0.75	<0.75
10	5.6	10.2	3.4	<10.5	<10.5	<10.5	0.06	0.08	0.06	<0.75	<0.75	<0.75
11	2.0	<1.0	2.4	<10.5	<10.5	<10.5	0.03	0.03	0.03	6.03	<0.75	<0.75
Mean	5.2	7.9	4.8	22.2	11.5	7.9	0.21	0.03	0.06	11.1	0.11	0.11
Standard error	1.5	3.2	1.0	14.7	7.3	4.1	0.19	0.01	0.04	10.4	0.11	0.11

Table A11(ii). Monitoring study surface and interstitial water chemistry for Savilles Creek.

Surface water

Sample collection	Lead SS1 (ug/L)	Lead SS2 (ug/L)	Lead SS3 (ug/L)	Suspended solids SS1 (mg/L)	Suspended solids SS2 (mg/L)	Suspended solids SS3 (mg/L)	Total phosphorus SS1 (ug/L)	Total phosphorus SS2 (ug/L)	Total phosphorus SS3 (ug/L)
1	<4.75	<4.75	<4.75	14.4	2.4	14.2	40.0	50.0	90.0
2	<4.75	<4.75	<4.75	8.8	5.2	4.8	60.0	160	50.0
3	6.20	<4.75	7.20	35.2			44.5	114	142
4	<4.75	<4.75	<4.75	47.2	4.0	31.6	37.1	14.5	56.1
5	<4.75	<4.75	<4.75		0.4	2.0	<1.3	<1.3	<1.3
6	17.0	<4.75	15.9	25.8	6.6	12.4	6.9	7.8	6.0
7	<4.75	<4.75	7.40	68.0	42.2	349	22.2	118	66.3
8	<4.75	<4.75	<4.75	1.8	<0.4	<0.4	19.3	2.1	2.6
9	<4.75	<4.75	<4.75	39.0	32.2	67.4	58.3	330	20.2
10	<4.75	<4.75	<4.75	114	10.0	268	8.8	1.5	20.7
11	<4.75	<4.75	<4.75	10.4	2.2	951	34.4	9.2	10.0
12	<4.75	<4.75	<4.75	311	291	339	372	364	392
Mean	1.90		2.50	61.4	36.0	185	58.6	97.6	71.3
Standard error	1.50		1.50	26.8	25.8	87	29.0	37.2	31.6

Interstitial water

Sample collection	Lead SS1 (ug/L)	Lead SS2 (ug/L)	Lead SS3 (ug/L)
1	350	8.50	206
3	10.2	9.60	<4.75
4	<4.75	17.6	<4.75
5	<4.75	5.80	<4.75
6	19.7	16.2	<4.75
7	5.40	<4.75	<4.75
9	<4.75	<4.75	<4.75
10	<4.75	16.7	<4.75
11	10.4	<4.75	<4.75
Mean	44.0	8.30	22.9
Standard error	38.3	2.50	22.9

Table A11(iii). Monitoring study surface and interstitial water chemistry for Temptation Creek.

Surface water

Sample collection	Temperature SS1 (oC)	Temperature SS2 (oC)	Temperature SS3 (oC)	Conductivity SS1 (mS/m)	Conductivity SS2 (mS/m)	Conductivity SS3 (mS/m)	Dissolved oxygen SS1 (mg/L)	Dissolved oxygen SS2 (mg/L)	Dissolved oxygen SS3 (mg/L)	pH SS1	pH SS2	pH SS3
1	17.5	18.2	19.0	47.0	26.5	22.5	7.8	7.0	7.6	8.50	7.60	8.80
2	12.8	13.0	13.0	46.0	60.0	49.0	6.5	5.7	7.5	7.30	7.40	8.10
3	17.0	17.0	18.0	70.0	19.0	10.0	8.0	5.2	6.0	7.80	7.20	7.30
4	18.7	19.4	20.1	47.0	28.5	23.0	5.8	6.5	7.3	7.80	7.70	8.00
5	22.2	21.3	20.3	14.0	14.0	14.0	7.8	6.0	5.8	6.73	7.13	7.25
6	21.3	21.6	22.1	16.5	16.5	16.0				5.92	5.94	6.20
7	15.7	15.7	15.6	12.0	13.0	13.0	7.1	7.1	7.2	5.73	6.17	6.31
8	10.7	10.8	11.3	21.5	19.5	14.0	14.6	14.7	14.2	6.60	6.48	6.39
9	11.0	11.0	11.6	18.0	19.0	15.5	11.9	12.0	12.4	5.66	5.76	6.04
10	12.9	12.7	13.7	16.5	16.5	14.0	10.9	9.2	9.5	5.64	5.40	5.45
11	23.5	23.7	24.4	18.0	18.0	18.0	5.6	4.5	4.1	6.55	6.30	6.20
12				5.0	7.0	6.0				7.29	7.32	7.01
Mean	16.7	16.8	17.2	27.6	21.5	17.9	8.6	7.8	8.2	6.80	6.70	6.90
Standard error	1.3	1.3	1.3	5.7	3.9	3.1	0.9	1.0	1.0	0.30	0.20	0.30

Interstitial water

Sample collection	Temperature SS1 (oC)	Temperature SS2 (oC)	Temperature SS3 (oC)	Conductivity SS1 (mS/m)	Conductivity SS2 (mS/m)	Conductivity SS3 (mS/m)	Dissolved oxygen SS1 (mg/L)	Dissolved oxygen SS2 (mg/L)	Dissolved oxygen SS3 (mg/L)	pH SS1	pH SS2	pH SS3
1	18.3	18.0	19.8	47.5	25.0	24.5	7.2	9.0	5.2	7.80	6.40	8.00
3	17.5	17.0	18.0	80.0	19.0	18.5	2.0	2.2	2.4	7.30	6.90	7.10
4	18.3	19.3	20.8	90.0	22.5	26.0	2.1	2.0	1.7	7.50	7.25	6.60
5	21.3	21.7	18.3	29.5	14.0	18.0	1.8	9.5	1.9	6.60	7.10	6.72
6	22.5	23.1	23.6	23.0	21.0	30.0				6.00	6.31	6.41
7	15.8	15.9	15.9	13.0	12.5	14.5	5.7	5.2	6.0	5.63	6.02	6.69
9	11.8	11.5	11.3	20.5	19.0	18.0	4.6	5.3	3.7	5.62	6.12	5.95
10	12.9	12.8	13.4	17.5	22.5	19.0	3.5	2.4	2.9	5.99	5.52	5.99
11	23.3	23.3	24.8	21.0	24.0	25.5	2.0	2.4	2.6	6.65	6.50	6.65
Mean	18.0	18.1	18.4	38.0	19.9	21.6	3.6	4.7	3.3	6.60	6.50	6.70
Standard error	1.3	1.4	1.5	9.5	1.4	1.7	0.7	1.1	0.5	0.30	0.20	0.20

Table A11(iii). Monitoring study surface and interstitial water chemistry for Temptation Creek.

Surface water

Sample collection	Redox SS1 (mV)	Redox SS2 (mV)	Redox SS3 (mV)	Alkalinity SS1 (mg/L)	Alkalinity SS2 (mg/L)	Alkalinity SS3 (mg/L)	Acidity SS1 (mg/L)	Acidity SS2 (mg/L)	Acidity SS3 (mg/L)	Hardness SS1 (mg/L)	Hardness SS2 (mg/L)	Hardness SS3 (mg/L)
1	81	130	101	7.5	2.4	1.8	0.65	0.60	0.35	74.0	26.0	20.0
2	80	177	226	10.2	3.3	4.0	0.75	0.95	0.60	42.0	32.0	24.0
3	68	165	130	52.0	6.5	7.0				75.9	39.0	38.0
4	46	180	74	73.0	5.5	7.0	0.55	0.45	0.40	64.0	38.0	40.0
5	110	151	119	5.5	5.0	5.0	0.25	0.20	0.15	30.0	28.0	32.0
6	45	44	29	5.0	6.0	6.0	0.50	0.50	0.35	32.0	28.0	30.0
7	52	29	19	4.0	3.5	3.0	0.55	0.60	0.35	30.0	30.0	32.0
8	21	30	34	7.5	7.0	7.0	0.70	0.80	0.75	22.0	24.0	20.0
9	50	49	37	5.0	4.5	3.5	1.20	1.50	2.00	32.0	32.0	30.0
10	53	67	62	2.0	3.5	3.5	0.70	0.75	0.55	30.0	30.0	32.0
11				6.0	4.5	4.5	3.00	1.85	1.80	26.0	18.0	22.0
12	180	202	180	13.0	11.5	12.0	2.20	2.40	2.80	16.0	14.0	12.0
Mean	71	111	92	15.9	5.3	5.4	1.00	0.96	0.92	39.5	28.2	27.7
Standard error	13	20	20	6.5	0.7	0.8	0.20	0.20	0.26	5.9	2.1	2.4

Interstitial water

Sample collection	Redox SS1 (mV)	Redox SS2 (mV)	Redox SS3 (mV)	Alkalinity SS1 (mg/L)	Alkalinity SS2 (mg/L)	Alkalinity SS3 (mg/L)	Acidity SS1 (mg/L)	Acidity SS2 (mg/L)	Acidity SS3 (mg/L)	Hardness SS1 (mg/L)	Hardness SS2 (mg/L)	Hardness SS3 (mg/L)
1	-45	-18	-30	7.0	1.3	2.2	2.00	2.20	0.90	120	40.0	48.0
3	-89	-80	-110	26.0	18.5	19.0				57.5	41.0	38.0
4	-265	160	-127	73.0	10.0		0.50	0.25		74.0	36.0	40.0
5	-72	160	-32	44.5	10.0	30.5	0.60	0.40	0.75	40.0	28.0	40.0
6	35	23	16							48.0	36.0	57.5
7	55	35	-4	6.5	4.5	12.0	0.50	0.40	0.90	30.0	32.0	34.0
9	56	28	32	10.0	44.0	30.0	1.71	3.90	3.80	36.0	40.0	38.0
10	31	38	29	45.0	45.0	27.1	4.25	4.10	2.80	50.0	48.0	46.0
11				39.0	23.0	35.0	9.50	8.40	8.00	34.0	26.0	42.0
Mean	-37	43	-28	31.4	19.5	22.3	2.70	2.80	2.90	54.4	36.3	42.6
Standard error	39	29	22	8.3	6.0	4.4	1.20	1.10	1.10	9.4	3.3	2.3

Table A11(iii). Monitoring study surface and interstitial water chemistry for Temptation Creek.

Surface water													
Sample collection	ortho-Phosphate SS1 (ug/L)	ortho-Phosphate SS2 (ug/L)	ortho-Phosphate SS3 (ug/L)	Copper SS1 (ug/L)	Copper SS2 (ug/L)	Copper SS3 (ug/L)	Zinc SS1 (mg/L)	Zinc SS2 (mg/L)	Zinc SS3 (mg/L)	Cadmium SS1 (ug/L)	Cadmium SS2 (ug/L)	Cadmium SS3 (ug/L)	
1	<1.0	<1.0	1.4	<10.5	<10.5	<10.5	0.05	0.05	0.67	2.34	2.88	10.8	
2	3.0	<1.0	<1.0	<10.5	<10.5	16.4	0.06	<0.01	0.07	<0.75	<0.75	2.46	
3	1.6	1.6	1.1	<10.5	<10.5	<10.5	<0.01	<0.01	<0.01	<0.75	<0.75	<0.75	
4	2.9	<1.0	<1.0	<10.5	<10.5	<10.5	<0.01	<0.01	<0.01	<0.75	<0.75	<0.75	
5	9.1	7.2	7.2	<10.5	<10.5	<10.5	<0.01	<0.01	<0.01	<0.75	<0.75	<0.75	
6	2.4	1.4	1.4	<10.5	<10.5	<10.5	<0.01	<0.01	<0.01	<0.75	<0.75	<0.75	
7	<1.0	<1.0	<1.0	46.0	35.3	52.0	0.02	0.02	<0.01	<0.75	<0.75	<0.75	
8	<1.0	<1.0	<1.0	25.4	<10.5	27.9	<0.01	<0.01	0.02	<0.75	<0.75	<0.75	
9	<1.0	1.0	<1.0	<10.5	<10.5	<10.5	<0.01	<0.01	<0.01	<0.75	<0.75	<0.75	
10	<1.0	<1.0	<1.0	<10.5	<10.5	<10.5	0.02	0.04	0.02	<0.75	<0.75	<0.75	
11	<1.0	<1.0	<1.0	<10.5	<10.5	<10.5	<0.01	<0.01	<0.01	<0.75	<0.75	<0.75	
12	71.6	76.8	84.4	<10.5	<10.5	<10.5	0.02	0.02	0.02	<0.75	<0.75	<0.75	
Mean	7.5	7.3	8.0	5.9	2.9	8.0	0.01	0.01	0.07	0.19	0.24	1.10	
Standard error	5.9	6.3	7.0	4.2	2.9	4.7	0.01	0.01	0.06	0.19	0.24	0.90	
Interstitial water													
Sample collection	ortho-Phosphate SS1 (ug/L)	ortho-Phosphate SS2 (ug/L)	ortho-Phosphate SS3 (ug/L)	Copper SS1 (ug/L)	Copper SS2 (ug/L)	Copper SS3 (ug/L)	Zinc SS1 (mg/L)	Zinc SS2 (mg/L)	Zinc SS3 (mg/L)	Cadmium SS1 (ug/L)	Cadmium SS2 (ug/L)	Cadmium SS3 (ug/L)	
1	<1.0	<1.0	1.3	<10.5	<10.5	<10.5	0.07	0.45	0.24	1.75	18.6	0.78	
3	<1.0	1.5	1.1	<10.5	<10.5	<10.5	<0.01	<0.01	0.03	<0.75	<0.75	<0.75	
4	3.3	1.1	<1.0	<10.5	<10.5	21.2	<0.01	<0.01	0.02	<0.75	<0.75	<0.75	
5	11.0	6.4	9.5	<10.5	<10.5	<10.5	0.03	0.03	0.02	<0.75	<0.75	<0.75	
6	5.0	3.3	7.3	<10.5	<10.5	<10.5	<0.01	<0.01	0.02	<0.75	<0.75	<0.75	
7	<1.0	1.3	<1.0	<10.5	<10.5	15.2	0.02	0.02	0.02	<0.75	<0.75	<0.75	
9	<1.0	1.5	1.0	<10.5	<10.5	<10.5	0.04	0.05	0.05	<0.75	<0.75	<0.75	
10	1.5	1.0	2.0	<10.5	<10.5	<10.5	0.04	0.04	0.03	<0.75	<0.75	<0.75	
11	<1.0	<1.0	<1.0	<10.5	<10.5	<10.5	0.02	0.03	0.03	<0.75	<0.75	<0.75	
Mean	2.3	1.8	2.5			4.0	0.02	0.07	0.05	0.19	2.10	0.09	
Standard error	1.2	0.7	1.2			2.7	0.01	0.05	0.02	0.19	2.10	0.09	

Table A11(iii). Monitoring study surface and interstitial water chemistry for Temptation Creek.

Surface water										
Sample collection	Lead SS1 (ug/L)	Lead SS2 (ug/L)	Lead SS3 (ug/L)	Suspended solids SS1 (mg/L)	Suspended solids SS2 (mg/L)	Suspended solids SS3 (mg/L)	Total phosphorus SS1 (ug/L)	Total phosphorus SS2 (ug/L)	Total phosphorus SS3 (ug/L)	
1	<4.75	<4.75	<4.75	10.8	6.8	6.2	90.0	190	30.0	
2	23.0	<4.75	<4.75	2.4	4.8	17.6	130	20.0	50.0	
3	<4.75	<4.75	<4.75	32.0	18.4	5.6	42.8	8.9	20.5	
4	<4.75	<4.75	<4.75	6.8	17.6	11.8	47.1	18.7	20.1	
5	<4.75	<4.75	<4.75	2.0	7.6	9.2	<1.3	<1.3	<1.3	
6	<4.75	19.2	5.70	1.2	11.8	2.0	1.9	4.2	1.9	
7	<4.75	<4.75	11.1	1.6	5.4	12.6	6.8	4.1	4.1	
8	<4.75	<4.75	<4.75	<0.4	<0.4	59.8	<1.3	<1.3	3.6	
9	<4.75	<4.75	<4.75	33.0	10.6	9.2	12.0	<1.3	<1.3	
10	<4.75	<4.75	<4.75	14.4	9.4	20.6	1.5	<1.3	7.9	
11	<4.75	<4.75	<4.75	14.4	168	34.8	4.8	7.2	5.2	
12	<4.75	<4.75	<4.75	239	407	322	320	360	400	
Mean	2.60	1.60	1.40	29.8	55.6	42.6	54.7	51.1	45.3	
Standard error	2.00	1.60	1.00	19.3	34.6	25.8	26.9	32.0	32.5	

Interstitial water				
Sample collection	Lead SS1 (ug/L)	Lead SS2 (ug/L)	Lead SS3 (ug/L)	
1	<4.75	<4.75	24.8	
3	<4.75	<4.75	<4.75	
4	5.00	6.80	<4.75	
5	<4.75	<4.75	<4.75	
6	<4.75	15.2	<4.75	
7	<4.75	<4.75	8.40	
9	<4.75	<4.75	<4.75	
10	<4.75	<4.75	<4.75	
11	<4.75	<4.75	<4.75	
Mean	0.56	2.40	3.70	
Standard error	0.56	1.80	2.80	

Table A12(i). Monitoring study additional surface water chemistry for Gwawley Creek.

Sample collection	Turbidity SS1 (NTU)	Turbidity SS2 (NTU)	Turbidity SS3 (NTU)	Colour SS1 (A440)	Colour SS2 (A440)	Colour SS3 (A440)	Ammonia SS1 (ug/L)	Ammonia SS2 (ug/L)	Ammonia SS3 (ug/L)	Nitrate SS1 (ug/L)	Nitrate SS2 (ug/L)	Nitrate SS3 (ug/L)
1	1.0	2.0	1.0	0.038	0.031	0.013	25.2	7.8	9.1	1100	450	490
2	13.0	14.0	13.0	0.016	0.022	0.011	176	136	124	1190	5800	860
8	4.4	3.2	6.0	0.011	0.003	0.001	121	106	81.7	1710	1610	1610
12	20.0	36.0	33.0	0.048	0.079	0.063	85.2	89.0	86.7	500	400	360
Mean	9.6	13.8	13.2	0.028	0.034	0.022	102	84.7	75.4	1125	2065	830
Standard error	4.3	7.9	7.0	0.009	0.016	0.014	32	27.4	24.0	248	1276	281

Table A12(ii). Monitoring study additional surface water chemistry for Savilles Creek.

Sample collection	Turbidity SS1 (NTU)	Turbidity SS2 (NTU)	Turbidity SS3 (NTU)	Colour SS1 (A440)	Colour SS2 (A440)	Colour SS3 (A440)	Ammonia SS1 (ug/L)	Ammonia SS2 (ug/L)	Ammonia SS3 (ug/L)	Nitrate SS1 (ug/L)	Nitrate SS2 (ug/L)	Nitrate SS3 (ug/L)
1	5.5	1.0	1.0	0.010	0.024	0.041	29.8	24.6	13.0	9.4	13.0	17.1
2	8.0	7.0	6.0	0.011	0.012	0.017	21.4	18.8	24.6	1230	660	1190
8	4.5	3.0	2.8	0.025	0.025	0.026	14.2	12.0	13.0	622	405	188
12	78.0	77.0	77.0	0.121	0.143	0.154	30.5	36.5	32.0	360	325	500
Mean	24.0	22.0	21.7	0.042	0.051	0.060	24.0	23.0	20.6	555	351	474
Standard error	18.0	18.4	18.5	0.026	0.031	0.032	3.9	5.2	4.7	257	133	259

Table A12(iii). Monitoring study additional surface water chemistry for Temptation Creek.

Sample collection	Turbidity SS1 (NTU)	Turbidity SS2 (NTU)	Turbidity SS3 (NTU)	Colour SS1 (A440)	Colour SS2 (A440)	Colour SS3 (A440)	Ammonia SS1 (ug/L)	Ammonia SS2 (ug/L)	Ammonia SS3 (ug/L)	Nitrate SS1 (ug/L)	Nitrate SS2 (ug/L)	Nitrate SS3 (ug/L)
1	1.2	1.5	1.5	0.012	0.019	0.040	23.3	195	11.0	8.2	10.2	7.4
2	2.2	2.0	3.0	0.010	0.006	0.014	31.6	7.8	15.6	17.1	19.6	25.6
8	1.1	1.3	6.0	0.005	0.006	0.007	8.2	7.2	8.2	29.5	28.0	25.2
12	80.0	83.0	83.0	0.090	0.120	0.144	30.5	28.2	29.5	387	337	337
Mean	21.1	21.9	23.4	0.029	0.038	0.051	23.4	59.5	16.1	110	98.7	98.8
Standard error	19.6	20.3	19.9	0.020	0.027	0.031	5.4	45.4	4.7	92	79.5	79.5

Table A12(i). Monitoring study additional surface water chemistry for Gwawley Creek.

Sample collection	Chloride SS1 (mg/L)	Relative %	Chloride SS2 (mg/L)	Relative %	Chloride SS3 (mg/L)	Relative %	Sulfate SS1 (mg/L)	Relative %	Sulfate SS2 (mg/L)	Relative %	Sulfate SS3 (mg/L)	Relative %	Carbonate SS1 (mg/L)	Relative %	Carbonate SS2 (mg/L)	Relative %	Carbonate SS3 (mg/L)	Relative %
1	35.4	69.7	38.3	69.5	39.7	63.8	14.8	21.6	15.6	20.9	23.2	27.5	3.7	8.6	4.4	9.5	4.6	8.7
2	5.9	28.9	<0.2	0	<0.2	0	3.0	10.6	2.2	17.7	<0.1	0	10.7	60.5	6.4	82.3	6.6	100
8	47.5	32.9	50.3	30.8	89.3	47.2	32.0	16.5	49.3	22.3	36.5	14.2	61.7	50.6	64.7	46.8	61.7	38.6
12	<0.2	0	<0.2	0	7.8	29.7	12.0	58.1	12.2	54.7	15.4	43.3	5.4	41.9	6.3	45.3	6.0	27.0
Mean	22.2	32.9	22.1	25.1	34.2	35.2	15.4	26.7	19.8	28.9	18.8	21.2	20.4	40.4	20.4	46.0	19.7	43.6
Standard error	11.4	14.3	13.0	16.5	20.3	13.6	6.1	10.7	10.2	8.6	7.6	9.2	13.9	11.3	14.8	14.9	14.0	19.8

Table A12(ii). Monitoring study additional surface water chemistry for Savilles Creek.

Sample collection	Chloride SS1 (mg/L)	Relative %	Chloride SS2 (mg/L)	Relative %	Chloride SS3 (mg/L)	Relative %	Sulfate SS1 (mg/L)	Relative %	Sulfate SS2 (mg/L)	Relative %	Sulfate SS3 (mg/L)	Relative %	Carbonate SS1 (mg/L)	Relative %	Carbonate SS2 (mg/L)	Relative %	Carbonate SS3 (mg/L)	Relative %
1	241	88.5	56.7	91.2	49.6	79.2	29.6	8.0	<0.1	0	12.8	15.1	8.0	3.5	4.6	8.8	3.0	5.7
2	149	63.4	106	58.1	113	60.7	56.0	17.7	51.6	20.9	47.2	18.7	37.5	18.9	32.5	21.0	32.5	20.6
8	50.3	50.1	41.1	50.2	40.4	50.7	25.2	18.5	22.2	20.0	19.6	18.1	26.7	31.4	20.7	29.8	21.0	31.1
12	9.9	27.2	7.1	19.2	7.8	25.7	24.5	49.5	26.0	52.0	19.0	46.3	7.2	23.3	9.0	28.8	7.2	28.0
Mean	113	57.3	52.7	54.7	52.7	54.1	33.8	23.4	24.9	23.2	24.6	24.5	19.8	19.3	16.7	22.1	15.9	21.3
Standard error	52	12.8	20.6	14.8	22.0	11.1	7.5	9.0	10.6	10.7	7.7	7.3	7.4	5.9	6.3	4.8	6.7	5.7

Table A12(iii). Monitoring study additional surface water chemistry for Temptation Creek.

Sample collection	Chloride SS1 (mg/L)	Relative %	Chloride SS2 (mg/L)	Relative %	Chloride SS3 (mg/L)	Relative %	Sulfate SS1 (mg/L)	Relative %	Sulfate SS2 (mg/L)	Relative %	Sulfate SS3 (mg/L)	Relative %	Carbonate SS1 (mg/L)	Relative %	Carbonate SS2 (mg/L)	Relative %	Carbonate SS3 (mg/L)	Relative %
1	120	95.7	80.0	92.9	63.8	91.4	<0.1	0	6.0	5.1	6.4	6.7	4.5	4.2	1.4	2.0	1.1	1.8
2	53.2	70.5	49.6	75.0	42.5	74.9	20.4	20.0	19.2	21.4	15.4	20.0	6.1	9.6	2.0	3.5	2.4	5.0
8	32.6	71.7	31.9	71.1	34.0	72.1	10.2	16.6	10.8	17.8	11.1	17.4	4.5	11.7	4.2	11.1	4.2	10.5
12	9.2	22.6	9.2	29.3	10.6	32.0	30.2	54.7	19.0	44.7	19.0	42.3	7.8	22.6	6.9	26.0	7.2	25.6
Mean	53.8	65.1	42.7	67.1	37.7	67.6	15.2	22.8	13.7	22.2	13.0	21.6	5.7	12.0	3.6	10.6	3.7	10.7
Standard error	23.8	15.3	14.9	13.5	11.0	12.6	6.5	11.5	3.2	8.3	2.7	7.5	0.8	3.9	1.2	5.5	1.3	5.3

Table A12(i). Monitoring study additional surface water chemistry for Gwawley Creek.

Sample collection	Sodium SS1 (mg/L)	Relative %	Sodium SS2 (mg/L)	Relative %	Sodium SS3 (mg/L)	Relative %	Potassium SS1 (mg/L)	Relative %	Potassium SS2 (mg/L)	Relative %	Potassium SS3 (mg/L)	Relative %	Calcium SS1 (mg/L)	Relative %	Calcium SS2 (mg/L)	Relative %	Calcium SS3 (mg/L)	Relative %
1	24.4	38.2	25.7	34.9	25.0	37.9	2.80	2.6	4.10	3.3	3.50	3.1	21.1	38.0	28.5	44.4	23.1	40.2
2	6.3	33.9	2.6	25.7	2.1	22.6	1.50	4.7	1.30	7.5	1.30	8.2	7.3	45.1	4.4	50.0	4.4	54.7
8	26.8	37.4	26.3	35.1	38.8	38.2	2.54	2.1	2.49	2.0	2.45	1.4	25.5	41.1	29.0	44.6	41.5	46.9
12	0.9	22.8	2.2	35.0	1.8	31.1	1.24	18.7	1.70	15.7	1.69	17.1	1.5	43.9	2.2	40.1	2.1	41.8
Mean	14.6	33.1	14.2	32.7	16.9	32.4	2.02	7.0	2.40	7.1	2.23	7.4	13.8	42.0	16.0	44.8	17.7	45.9
Standard error	6.5	3.5	6.8	2.3	9.1	3.7	0.38	3.9	0.62	3.1	0.48	3.5	5.6	1.6	7.4	2.0	9.2	3.3

Table A12(ii). Monitoring study additional surface water chemistry for Savilles Creek.

Sample collection	Sodium SS1 (mg/L)	Relative %	Sodium SS2 (mg/L)	Relative %	Sodium SS3 (mg/L)	Relative %	Potassium SS1 (mg/L)	Relative %	Potassium SS2 (mg/L)	Relative %	Potassium SS3 (mg/L)	Relative %	Calcium SS1 (mg/L)	Relative %	Calcium SS2 (mg/L)	Relative %	Calcium SS3 (mg/L)	Relative %
1	165	69.9	41.2	60.3	33.4	59.5	3.90	1.0	1.65	1.4	1.50	1.6	42.3	20.6	16.4	27.6	14.0	28.7
2	93.9	51.0	73.5	49.6	74.2	50.6	3.50	1.1	3.30	1.3	3.00	1.2	57.8	36.2	46.0	35.7	43.9	34.4
8	23.4	58.1	22.7	62.3	21.3	60.6	1.14	1.6	1.04	1.7	1.01	1.7	8.2	23.3	7.1	22.4	7.2	23.6
12	4.7	51.8	5.5	53.9	5.5	53.5	1.53	9.9	1.48	8.6	1.55	8.9	2.5	31.9	2.5	28.2	2.7	30.2
Mean	71.7	57.7	35.7	56.5	33.6	56.0	2.52	3.4	1.87	3.2	1.76	3.3	27.7	28.0	18.0	28.5	16.9	29.2
Standard error	36.5	4.4	14.5	2.9	14.7	2.4	0.69	2.2	0.49	1.8	0.43	1.8	13.3	3.6	9.8	2.7	9.3	2.2

Table A12(iii). Monitoring study additional surface water chemistry for Temptation Creek.

Sample collection	Sodium SS1 (mg/L)	Relative %	Sodium SS2 (mg/L)	Relative %	Sodium SS3 (mg/L)	Relative %	Potassium SS1 (mg/L)	Relative %	Potassium SS2 (mg/L)	Relative %	Potassium SS3 (mg/L)	Relative %	Calcium SS1 (mg/L)	Relative %	Calcium SS2 (mg/L)	Relative %	Calcium SS3 (mg/L)	Relative %
1	90.3	64.4	49.5	77.2	41.7	73.6	3.10	1.3	1.30	1.2	2.30	2.4	28.7	23.5	1.6	2.9	1.4	2.8
2	36.3	62.2	28.0	63.4	24.2	65.3	1.60	1.6	1.30	1.7	1.30	2.0	7.3	14.4	2.0	5.2	1.4	4.4
8	16.3	78.9	16.2	80.5	16.5	81.7	0.61	1.7	0.61	1.8	0.65	1.9	0.5	2.8	0.3	1.7	0.4	2.3
12	3.9	46.8	4.1	49.9	4.5	52.0	1.52	10.8	1.50	10.8	1.50	10.1	2.4	33.2	2.3	32.3	2.2	29.2
Mean	36.7	63.1	24.4	67.7	21.7	68.1	1.71	3.8	1.18	3.9	1.44	4.1	9.7	18.5	1.5	10.5	1.3	9.7
Standard error	19.1	6.6	9.7	7.0	7.8	6.3	0.52	2.3	0.19	2.3	0.34	2.0	6.5	6.5	0.4	7.3	0.4	6.5

Table A12(i). Gwawley Creek.

Sample collection	Magnesium SS1 (mg/L)	Relative %	Magnesium SS2 (mg/L)	Relative %	Magnesium SS3 (mg/L)	Relative %
1	7.1	21.2	6.8	17.5	6.5	18.7
2	1.6	16.3	0.9	16.8	0.7	14.4
8	7.3	19.4	7.2	18.3	7.2	13.4
12	0.3	14.6	0.3	9.1	0.3	10.0
Mean	4.1	17.9	3.8	15.4	3.7	14.1
Standard error	1.8	1.5	1.8	2.1	1.8	1.8

Table A12(ii). Savilles Creek.

Sample collection	Magnesium SS1 (mg/L)	Relative %	Magnesium SS2 (mg/L)	Relative %	Magnesium SS3 (mg/L)	Relative %
1	10.6	8.5	3.8	10.6	3.0	10.2
2	11.3	11.7	10.4	13.3	10.7	13.8
8	3.6	16.9	2.6	13.6	2.6	14.1
12	0.3	6.4	0.5	9.3	0.4	7.4
Mean	6.4	10.9	4.3	11.7	4.2	11.4
Standard error	2.7	2.3	2.1	1.0	2.2	1.6

Table A12(iii). Temptation Creek.

Sample collection	Magnesium SS1 (mg/L)	Relative %	Magnesium SS2 (mg/L)	Relative %	Magnesium SS3 (mg/L)	Relative %
1	8.0	10.8	6.3	18.7	6.3	21.1
2	6.7	21.8	6.9	29.6	5.5	28.2
8	1.8	16.6	1.7	16.0	1.5	14.1
12	0.4	9.1	0.3	7.0	0.4	8.7
Mean	4.2	14.6	3.8	17.8	3.4	18.0
Standard error	1.8	2.9	1.6	4.6	1.5	4.2

Table A13(i). Monitoring study sediment chemistry for Gwawley Creek.

Sample collection	Organic carbon SS1 (g/100g)	Organic carbon SS2 (g/100g)	Organic carbon SS3 (g/100g)	Total phosphorus SS1 (ug/g)	Total phosphorus SS2 (ug/g)	Total phosphorus SS3 (ug/g)	Organic phosphorus SS1 (ug/g)	Organic phosphorus SS2 (ug/g)	Organic phosphorus SS3 (ug/g)
1	0.217	0.075	0.112	210	93.2	119	<1.5	<1.5	<1.5
3	0.435	0.274	0.299	245	185	192	<1.5	23.0	16.0
4	0.479	0.213		413	160		32.0	9.0	
5	0.376	0.290	0.395	165	155	94.6	73.0	82.0	42.9
6	0.439	0.430	0.181	376	92.0	87.4	76.8	9.7	34.3
7	0.517	0.229	0.095	694	183	188	<0.74	<0.74	<0.74
9	0.492	0.874	1.83	545	178	156	84.9	21.0	14.0
10	0.843	1.56	0.459	509	138	394	34.8	16.0	<0.74
11	1.57	0.815	0.931	1195	853	2212	<0.71	9.0	430
Mean	0.596	0.529	0.538	484	226	430	33.5	18.8	67.1
Standard error	0.133	0.158	0.207	106	79	257	12.1	8.3	52.1

Table A13(ii). Monitoring study sediment chemistry for Savilles Creek.

Sample collection	Organic carbon SS1 (g/100g)	Organic carbon SS2 (g/100g)	Organic carbon SS3 (g/100g)	Total phosphorus SS1 (ug/g)	Total phosphorus SS2 (ug/g)	Total phosphorus SS3 (ug/g)	Organic phosphorus SS1 (ug/g)	Organic phosphorus SS2 (ug/g)	Organic phosphorus SS3 (ug/g)
1	0.510	0.810	0.375	76.8	172	152	<1.5	4.5	4.5
3	0.118	0.208	0.255	159	124	84.7	13.0	12.0	4.2
4	0.148	0.195	0.210	112	151	175	2.0	89.0	9.0
5	0.155	0.057	0.042	73.9	126	76.2	51.0	77.0	60.0
6	0.761	0.153	0.189	24.2	85.4	110	22.3	22.6	35.4
7	0.367	0.238	0.429	30.6	55.4	43.7	<0.71	<0.75	4.3
9	0.713	0.398	0.146	106	68.7	176	14.4	10.0	7.5
10	1.01	0.702	0.930	102	86.1	67.6	25.9	13.5	10.0
11	0.471	0.563	0.649	210	148	211	6.0	<0.66	13.0
Mean	0.473	0.369	0.358	99.4	113	122	15.0	25.4	16.4
Standard error	0.104	0.088	0.093	19.6	13	19	5.5	11.2	6.3

Table A13(iii). Monitoring study sediment chemistry for Temptation Creek.

Sample collection	Organic carbon SS1 (g/100g)	Organic carbon SS2 (g/100g)	Organic carbon SS3 (g/100g)	Total phosphorus SS1 (ug/g)	Total phosphorus SS2 (ug/g)	Total phosphorus SS3 (ug/g)	Organic phosphorus SS1 (ug/g)	Organic phosphorus SS2 (ug/g)	Organic phosphorus SS3 (ug/g)
1	0.045	0.180	0.120	35.2	33.6	40.0	<1.5	11.5	<1.5
3	0.133	<0.015	0.059	37.1	29.8	32.6	2.0	<1.5	<1.5
4	0.045	0.060	<0.015	32.6	31.3	31.3	<1.5	<1.4	2.5
5	0.057	0.058	0.042	24.9	21.3	28.5	13.5	<0.73	<0.76
6	0.193	0.073	0.087	6.1	4.8	6.6	<0.74	<0.74	<0.75
7	0.111	0.200	0.189	15.5	11.1	27.2	<0.75	<0.75	<0.74
9	0.230	0.218	0.170	12.8	10.2	10.2	<0.75	<0.75	<0.75
10	0.484	1.79	0.217	18.7	38.7	19.4	<0.75	3.5	<0.75
11	0.176	0.445	0.353	29.6	32.8	41.8	<0.72	<0.72	<0.72
Mean	0.164	0.336	0.137	23.6	23.7	26.4	1.7	1.7	0.3
Standard error	0.046	0.187	0.036	3.6	4.1	4.1	1.5	1.3	0.3

Table A13(i). Monitoring study sediment chemistry for Gwawley Creek.

Sample collection	Total copper SS1 (ug/g)	RE copper SS1 (ug/g)	HMO copper SS1 (ug/g)	OMS copper SS1 (ug/g)	R copper SS1 (ug/g)	Total copper SS2 (ug/g)	RE copper SS2 (ug/g)	HMO copper SS2 (ug/g)	OMS copper SS2 (ug/g)	R copper SS2 (ug/g)	Total copper SS3 (ug/g)	RE copper SS3 (ug/g)	HMO copper SS3 (ug/g)	OMS copper SS3 (ug/g)	R copper SS3 (ug/g)
1	15.0	2.50	1.60	7.40	1.80	6.50	0.70	0.80	1.20	<0.40	9.00	3.30	1.40	1.20	0.60
3	9.80	<0.20	<0.40	4.75	<0.40	6.40	<0.20	<0.40	3.39	<0.40	13.0	<0.20	<0.40	7.40	5.40
4	24.3	<0.20	<0.40	7.11	10.5	6.02	<0.20	<0.40	5.41	<0.40					
5	27.1	<0.20	2.59	10.3	6.95	9.99	<0.20	<0.40	3.38	<0.40	12.9	<0.20	<0.40	4.75	<0.40
6	21.2	<0.20	3.39	11.8	4.38	6.68	<0.20	1.80	6.40	3.20	10.5	<0.20	2.06	5.44	4.88
7	42.9	<0.20	5.60	15.0	11.2	13.7	<0.20	5.39	8.39	5.60	19.6	<0.20	5.59	9.19	7.59
9	35.1	<0.20	4.58	16.9	15.5	10.6	<0.20	2.56	3.35	1.57	25.2	<0.20	6.35	12.3	11.0
10	35.9	<0.20	3.98	27.1	6.78	14.9	<0.20	3.19	9.98	1.99	23.5	<0.20	3.39	12.8	5.98
11	85.5	0.30	8.68	53.7	30.3	24.8	<0.20	3.37	13.1	7.94	15.3	<0.20	2.99	7.78	5.18
Mean	33.0	0.31	3.38	17.1	9.71	11.1	0.08	1.90	6.07	2.26	16.1	0.41	2.71	7.61	5.08
Standard error	7.4	0.28	0.92	5.1	3.03	2.0	0.08	0.63	1.27	0.95	2.1	0.41	0.83	1.37	1.25

Table A13(ii). Monitoring study sediment chemistry for Savilles Creek.

Sample collection	Total copper SS1 (ug/g)	RE copper SS1 (ug/g)	HMO copper SS1 (ug/g)	OMS copper SS1 (ug/g)	R copper SS1 (ug/g)	Total copper SS2 (ug/g)	RE copper SS2 (ug/g)	HMO copper SS2 (ug/g)	OMS copper SS2 (ug/g)	R copper SS2 (ug/g)	Total copper SS3 (ug/g)	RE copper SS3 (ug/g)	HMO copper SS3 (ug/g)	OMS copper SS3 (ug/g)	R copper SS3 (ug/g)
1	6.00	1.20	<0.40	0.60	<0.40	8.00	2.30	0.80	2.00	0.80	7.00	1.20	0.80	2.00	0.60
3	3.10	<0.20	<0.40	3.16	<0.40	<2.00	<0.20	<0.40	<0.40	<0.40	<2.00	<0.20	<0.40	<0.40	<0.40
4	<2.00	<0.20	<0.40	<0.40	<0.40	<2.00	<0.20	<0.40	<0.40	<0.40	2.80	<0.20	<0.40	1.99	<0.40
5	5.98	<0.20	<0.40	2.35	<0.40	3.81	<0.20	<0.40	2.18	<0.40	9.97	<0.20	<0.40	1.59	<0.40
6	<2.00	<0.20	<0.40	<0.40	<0.40	7.39	<0.20	0.99	2.39	1.19	10.4	<0.20	0.99	3.58	2.78
7	5.09	<0.20	1.19	2.39	1.59	3.90	<0.20	0.79	1.59	1.59	7.10	<0.20	1.19	2.78	1.99
9	7.06	<0.20	0.99	4.77	1.59	6.28	<0.20	1.20	4.58	1.99	11.5	<0.20	2.97	7.53	3.17
10	11.2	<0.20	0.80	3.19	6.58	11.0	<0.20	2.75	3.15	6.30	7.17	<0.20	0.79	1.18	3.15
11	11.0	<0.20	1.98	5.15	3.96	8.79	<0.20	1.78	4.95	3.16	14.4	<0.20	1.41	4.62	3.22
Mean	5.49	0.13	0.55	2.40	1.52	5.46	0.26	0.92	2.32	1.67	7.82	0.13	0.91	2.81	1.66
Standard error	1.35	0.13	0.24	0.64	0.77	1.28	0.26	0.31	0.58	0.68	1.47	0.13	0.31	0.74	0.50

Table A13(iii). Monitoring study sediment chemistry for Temptation Creek.

Sample collection	Total copper SS1 (ug/g)	RE copper SS1 (ug/g)	HMO copper SS1 (ug/g)	OMS copper SS1 (ug/g)	R copper SS1 (ug/g)	Total copper SS2 (ug/g)	RE copper SS2 (ug/g)	HMO copper SS2 (ug/g)	OMS copper SS2 (ug/g)	R copper SS2 (ug/g)	Total copper SS3 (ug/g)	RE copper SS3 (ug/g)	HMO copper SS3 (ug/g)	OMS copper SS3 (ug/g)	R copper SS3 (ug/g)
1	<2.00	<0.20	<0.40	<0.40	<0.40	<2.00	<0.20	<0.40	<0.40	<0.40	<2.00	<0.20	<0.40	<0.40	<0.40
3	<2.00	<0.20	<0.40	<0.40	<0.40	<2.00	<0.20	<0.40	<0.40	<0.40	<2.00	<0.20	<0.40	<0.40	<0.40
4	<2.00	<0.20	<0.40	<0.40	<0.40	<2.00	<0.20	<0.40	<0.40	<0.40	<2.00	<0.20	<0.40	<0.40	<0.40
5	<2.00	<0.20	<0.40	<0.40	<0.40	<2.00	<0.20	<0.40	<0.40	<0.40	<2.00	<0.20	<0.40	<0.40	<0.40
6	<2.00	<0.20	<0.40	<0.40	<0.40	<2.00	<0.20	<0.40	<0.40	<0.40	<2.00	<0.20	<0.40	<0.40	<0.40
7	<2.00	<0.20	<0.40	<0.40	<0.40	<2.00	<0.20	<0.40	<0.40	<0.40	<2.00	<0.20	<0.40	<0.40	<0.40
9	2.00	<0.20	<0.40	<0.40	<0.40	1.81	<0.20	<0.40	1.18	<0.40	2.00	<0.20	<0.40	1.18	<0.40
10	2.98	<0.20	<0.40	1.00	1.20	5.11	<0.20	<0.40	2.20	1.60	1.92	<0.20	<0.40	0.80	<0.40
11	2.20	<0.20	1.64	2.05	0.00	2.51	<0.20	<0.40	0.98	1.18	2.05	<0.20	<0.40	0.59	<0.40
Mean	0.80		0.18	0.47	0.13	1.05			0.48	0.31	0.66			0.29	
Standard error	0.41		0.18	0.25	0.13	0.60			0.27	0.21	0.33			0.15	

Table A13(i). Monitoring study sediment chemistry for Gwawley Creek.

Sample collection	Total zinc SS1 (ug/g)	RE zinc SS1 (ug/g)	HMO zinc SS1 (ug/g)	OMS zinc SS1 (ug/g)	R zinc SS1 (ug/g)	Total zinc SS2 (ug/g)	RE zinc SS2 (ug/g)	HMO zinc SS2 (ug/g)	OMS zinc SS2 (ug/g)	R zinc SS2 (ug/g)	Total zinc SS3 (ug/g)	RE zinc SS3 (ug/g)	HMO zinc SS3 (ug/g)	OMS zinc SS3 (ug/g)	R zinc SS3 (ug/g)
1	69.0	24.6	27.4	2.20	2.80	27.0	10.0	8.60	0.60	0.40	30.0	12.8	10.4	1.20	1.00
3	42.9	<0.10	26.9	9.10	4.76	14.6	<0.10	15.6	8.90	<0.20	45.4	<0.10	27.2	10.8	11.2
4	107	<0.10	36.7	16.0	20.0	60.2	<0.10	27.9	13.0	7.61					
5	126	<0.10	51.4	36.2	78.4	45.0	<0.10	26.0	10.0	2.79	49.5	<0.10	26.4	11.3	<0.20
6	57.1	0.20	54.2	9.57	15.1	49.0	<0.10	40.8	6.00	18.8	72.5	<0.10	15.4	4.32	19.1
7	128	<0.10	57.5	15.0	28.0	39.8	<0.10	34.0	6.79	11.2	55.8	<0.10	30.6	5.79	15.6
9	137	0.30	79.5	11.0	53.0	65.0	9.15	15.5	1.77	6.30	46.0	1.59	33.0	4.87	19.1
10	173	6.18	125	21.3	25.9	25.2	<0.10	14.8	2.19	6.38	63.7	1.10	41.1	6.38	26.3
11	203	<0.10	124	14.9	47.6	68.3	<0.10	48.4	6.95	19.4	55.6	<0.10	37.7	4.79	14.4
Mean	116	3.48	64.7	15.0	30.6	43.8	2.13	25.7	6.24	8.10	52.3	1.94	27.7	6.18	13.3
Standard error	18	2.72	12.5	3.2	8.2	6.3	1.41	4.5	1.37	2.39	4.5	1.57	3.7	1.19	3.2

Table A13(ii). Monitoring study sediment chemistry for Savilles Creek.

Sample collection	Total zinc SS1 (ug/g)	RE zinc SS1 (ug/g)	HMO zinc SS1 (ug/g)	OMS zinc SS1 (ug/g)	R zinc SS1 (ug/g)	Total zinc SS2 (ug/g)	RE zinc SS2 (ug/g)	HMO zinc SS2 (ug/g)	OMS zinc SS2 (ug/g)	R zinc SS2 (ug/g)	Total zinc SS3 (ug/g)	RE zinc SS3 (ug/g)	HMO zinc SS3 (ug/g)	OMS zinc SS3 (ug/g)	R zinc SS3 (ug/g)
1	18.0	8.20	5.20	0.60	<0.20	24.0	9.10	6.00	1.00	1.60	21.2	8.20	6.80	0.80	1.60
3	24.8	0.59	9.11	4.45	4.75	17.2	0.70	10.3	3.48	1.99	15.5	0.40	8.18	4.69	<0.20
4	17.6	<0.10	13.7	6.08	3.39	13.9	<0.10	13.0	5.93	4.93	14.2	<0.10	14.2	5.29	4.59
5	21.4	<0.10	11.4	5.52	5.12	21.0	<0.10	12.7	6.56	5.57	23.9	0.65	11.2	5.28	4.58
6	12.9	<0.10	10.9	3.38	3.38	16.5	<0.10	11.7	2.19	7.16	29.2	<0.10	12.1	3.77	11.9
7	23.8	<0.10	11.6	2.19	7.57	23.1	0.20	10.7	2.18	4.77	26.7	<0.10	16.5	4.17	6.36
9	49.4	0.40	32.4	4.58	10.7	48.8	0.40	25.9	3.99	8.37	42.2	1.49	52.3	11.5	1.58
10	57.3	0.50	36.7	8.77	6.38	44.7	0.59	37.2	11.0	5.31	30.6	1.28	16.1	7.48	3.54
11	41.7	<0.10	26.7	4.36	12.3	33.7	<0.10	24.1	3.96	7.91	37.4	<0.10	21.5	3.62	12.9
Mean	29.7	1.08	17.5	4.44	5.95	27.0	1.22	16.8	4.48	5.29	26.8	1.34	17.6	5.18	5.23
Standard error	5.2	0.89	3.8	0.78	1.27	4.2	0.99	3.3	1.01	0.79	3.1	0.88	4.6	0.99	1.50

Table A13(iii). Monitoring study sediment chemistry for Temptation Creek.

Sample collection	Total zinc SS1 (ug/g)	RE zinc SS1 (ug/g)	HMO zinc SS1 (ug/g)	OMS zinc SS1 (ug/g)	R zinc SS1 (ug/g)	Total zinc SS2 (ug/g)	RE zinc SS2 (ug/g)	HMO zinc SS2 (ug/g)	OMS zinc SS2 (ug/g)	R zinc SS2 (ug/g)	Total zinc SS3 (ug/g)	RE zinc SS3 (ug/g)	HMO zinc SS3 (ug/g)	OMS zinc SS3 (ug/g)	R zinc SS3 (ug/g)
1	3.00	0.40	0.80	<0.20	<0.20	4.00	0.60	0.80	<0.20	<0.20	5.00	0.70	1.00	<0.20	<0.20
3	2.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
4	1.80	<0.10	1.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
5	3.46	<0.10	<0.20	<0.20	<0.20	2.00	<0.10	<0.20	<0.20	<0.20	1.99	<0.10	<0.20	0.99	<0.20
6	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
7	2.87	<0.10	1.40	<0.20	1.20	3.05	<0.10	1.20	<0.20	1.20	4.41	<0.10	1.20	<0.20	2.39
9	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
10	1.19	<0.10	1.80	<0.20	<0.20	6.39	<0.10	4.00	1.00	2.00	1.92	<0.10	1.60	0.40	1.20
11	2.83	<0.10	3.49	<0.20	<0.20	4.08	<0.10	2.94	0.59	1.18	6.16	<0.10	3.77	0.59	1.59
Mean	1.91	0.04	0.97		0.13	2.17	0.07	0.99	0.18	0.49	2.16	0.08	0.84	0.22	0.58
Standard error	0.43	0.04	0.39		0.13	0.79	0.07	0.50	0.12	0.26	0.81	0.08	0.42	0.12	0.30

Table A13(i). Monitoring study sediment chemistry for Gwawley Creek.

Sample collection	Total cadmium SS1 (ug/g)	RE Cd SS1 (ug/g)	HMO Cd SS1 (ug/g)	OMS Cd SS1 (ug/g)	R Cd SS1 (ug/g)	Total cadmium SS2 (ug/g)	RE Cd SS2 (ug/g)	HMO Cd SS2 (ug/g)	OMS Cd SS2 (ug/g)	R Cd SS2 (ug/g)	Total cadmium SS3 (ug/g)	RE Cd SS3 (ug/g)	HMO Cd SS3 (ug/g)	OMS Cd SS3 (ug/g)	R Cd SS3 (ug/g)
1	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
3	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
4	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
5	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
6	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
7	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
9	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
10	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
11	<1.00	<0.10	<0.20	<0.20	<0.20	1.74	<0.10	<0.20	<0.20	<0.20	1.33	<0.10	<0.20	<0.20	<0.20
Mean						0.19					0.17				
Standard error						0.19					0.17				

Table A13(ii). Monitoring study sediment chemistry for Savilles Creek.

Sample collection	Total cadmium SS1 (ug/g)	RE Cd SS1 (ug/g)	HMO Cd SS1 (ug/g)	OMS Cd SS1 (ug/g)	R Cd SS1 (ug/g)	Total cadmium SS2 (ug/g)	RE Cd SS2 (ug/g)	HMO Cd SS2 (ug/g)	OMS Cd SS2 (ug/g)	R Cd SS2 (ug/g)	Total cadmium SS3 (ug/g)	RE Cd SS3 (ug/g)	HMO Cd SS3 (ug/g)	OMS Cd SS3 (ug/g)	R Cd SS3 (ug/g)
1	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
3	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
4	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
5	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
6	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
7	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
9	1.41	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
10	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
11	1.53	<0.10	<0.20	<0.20	<0.20	1.17	<0.10	<0.20	<0.20	<0.20	1.00	<0.10	<0.20	<0.20	<0.20
Mean	0.33					0.13					0.11				
Standard error	0.22					0.13					0.11				

Table A13(iii). Monitoring study sediment chemistry for Temptation Creek.

Sample collection	Total cadmium SS1 (ug/g)	RE Cd SS1 (ug/g)	HMO Cd SS1 (ug/g)	OMS Cd SS1 (ug/g)	R Cd SS1 (ug/g)	Total cadmium SS2 (ug/g)	RE Cd SS2 (ug/g)	HMO Cd SS2 (ug/g)	OMS Cd SS2 (ug/g)	R Cd SS2 (ug/g)	Total cadmium SS3 (ug/g)	RE Cd SS3 (ug/g)	HMO Cd SS3 (ug/g)	OMS Cd SS3 (ug/g)	R Cd SS3 (ug/g)
1	<1.00	<0.10	<0.20	<0.20	<0.20	2.00	<0.10	0.40	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
3	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
4	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
5	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
6	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
7	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
9	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
10	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
11	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20	<1.00	<0.10	<0.20	<0.20	<0.20
Mean						0.22		0.04							
Standard error						0.22		0.04							

Table A13(i). Monitoring study sediment chemistry for Gwawley Creek.

Sample collection	Total lead SS1 (ug/g)	RE lead SS1 (ug/g)	HMO lead SS1 (ug/g)	OMS lead SS1 (ug/g)	R lead SS1 (ug/g)	Total lead SS2 (ug/g)	RE lead SS2 (ug/g)	HMO lead SS2 (ug/g)	OMS lead SS2 (ug/g)	R lead SS2 (ug/g)	Total lead SS3 (ug/g)	RE lead SS3 (ug/g)	HMO lead SS3 (ug/g)	OMS lead SS3 (ug/g)	R lead SS3 (ug/g)
1	70.0	30.3	11.0	2.80	<2.00	12.5	6.90	<2.00	<2.00	<2.00	17.5	14.6	4.00	<2.00	<2.00
3	32.1	1.14	29.9	4.35	<2.00	49.4	1.15	34.6	4.99	5.59	35.2	<1.00	23.2	8.60	9.20
4	51.4	<1.00	28.9	7.13	11.5	56.2	<1.00	32.1	9.60	6.81					
5	87.8	1.39	81.0	19.5	13.1	35.0	<1.00	29.2	10.5	4.78	39.6	<1.00	23.2	8.44	<2.00
6	124	1.59	117	14.7	9.17	60.8	<1.00	46.0	8.80	9.20	48.6	2.44	37.2	7.51	9.20
7	109	<1.00	64.7	8.59	9.99	30.9	<1.00	38.0	8.59	7.19	54.0	<1.00	30.2	6.19	<2.00
9	209	2.29	195	16.1	21.1	27.8	11.7	9.45	<2.00	<2.00	67.5	13.7	53.8	3.18	8.47
10	148	13.8	104	15.5	13.1	51.7	1.00	29.9	3.99	4.39	69.9	3.39	29.7	4.19	9.17
11	128	<1.00	113	10.9	27.1	37.9	<1.00	26.6	4.37	8.34	29.0	<1.00	21.3	4.39	4.79
Mean	107	5.61	82.7	11.1	11.7	40.2	2.31	27.3	5.65	5.14	45.2	4.27	27.8	5.31	5.10
Standard error	18	3.41	19.1	1.9	2.9	5.2	1.39	4.7	1.32	1.10	6.5	2.21	5.0	1.04	1.58

Table A13(ii). Monitoring study sediment chemistry for Savilles Creek.

Sample collection	Total lead SS1 (ug/g)	RE lead SS1 (ug/g)	HMO lead SS1 (ug/g)	OMS lead SS1 (ug/g)	R lead SS1 (ug/g)	Total lead SS2 (ug/g)	RE lead SS2 (ug/g)	HMO lead SS2 (ug/g)	OMS lead SS2 (ug/g)	R lead SS2 (ug/g)	Total lead SS3 (ug/g)	RE lead SS3 (ug/g)	HMO lead SS3 (ug/g)	OMS lead SS3 (ug/g)	R lead SS3 (ug/g)
1	18.0	5.60	<2.00	<2.00	<2.00	29.7	10.8	<2.00	<2.00	<2.00	13.0	5.50	<2.00	<2.00	<2.00
3	20.9	1.53	13.9	<2.00	<2.00	14.5	1.14	10.7	<2.00	<2.00	10.1	1.55	5.59	<2.00	<2.00
4	11.8	<1.00	8.36	<2.00	<2.00	13.9	<1.00	8.70	1.76	<2.00	12.7	<1.00	8.58	<2.00	<2.00
5	17.0	<1.00	25.6	3.74	<2.00	15.2	<1.00	9.73	<2.00	<2.00	18.9	<1.00	8.58	1.59	<2.00
6	12.9	<1.00	8.26	4.90	4.50	<10.0	<1.00	<2.00	<2.00	<2.00	<10.0	<1.00	<2.00	<2.00	<2.00
7	15.2	<1.00	7.57	<2.00	<2.00	19.0	<1.00	8.14	<2.00	<2.00	30.0	<1.00	19.9	5.76	<2.00
9	26.1	<1.00	20.7	2.19	<2.00	106	1.99	54.8	6.78	<2.00	26.1	4.65	17.4	1.98	<2.00
10	34.9	<1.00	19.1	5.58	6.58	80.4	1.47	58.4	5.51	12.6	75.6	4.04	32.1	5.91	17.5
11	24.8	0.99	18.4	3.56	<2.00	52.1	1.88	42.1	6.92	5.14	39.4	<1.00	33.8	5.43	4.82
Mean	20.2	0.90	13.5	2.22	1.23	36.8	1.92	21.4	2.33	1.97	25.1	1.75	14.0	2.30	2.48
Standard error	2.5	0.62	2.7	0.77	0.83	11.9	1.14	7.8	1.04	1.44	7.4	0.77	4.2	0.89	1.95

Table A13(iii). Monitoring study sediment chemistry for Temptation Creek.

Sample collection	Total lead SS1 (ug/g)	RE lead SS1 (ug/g)	HMO lead SS1 (ug/g)	OMS lead SS1 (ug/g)	R lead SS1 (ug/g)	Total lead SS2 (ug/g)	RE lead SS2 (ug/g)	HMO lead SS2 (ug/g)	OMS lead SS2 (ug/g)	R lead SS2 (ug/g)	Total lead SS3 (ug/g)	RE lead SS3 (ug/g)	HMO lead SS3 (ug/g)	OMS lead SS3 (ug/g)	R lead SS3 (ug/g)
1	<10.0	<1.00	<2.00	<2.00	<2.00	<10.0	<1.00	<2.00	<2.00	<2.00	<10.0	<1.00	<2.00	<2.00	<2.00
3	<10.0	<1.00	<2.00	<2.00	<2.00	<10.0	<1.00	<2.00	<2.00	<2.00	<10.0	<1.00	<2.00	<2.00	<2.00
4	<10.0	<1.00	<2.00	<2.00	<2.00	<10.0	<1.00	<2.00	<2.00	<2.00	<10.0	<1.00	<2.00	<2.00	<2.00
5	<10.0	<1.00	<2.00	<2.00	<2.00	<10.0	<1.00	<2.00	<2.00	<2.00	<10.0	<1.00	<2.00	<2.00	<2.00
6	<10.0	<1.00	<2.00	<2.00	<2.00	<10.0	<1.00	<2.00	<2.00	<2.00	<10.0	<1.00	<2.00	<2.00	<2.00
7	<10.0	<1.00	<2.00	<2.00	<2.00	<10.0	<1.00	<2.00	<2.00	<2.00	<10.0	<1.00	<2.00	<2.00	<2.00
9	<10.0	<1.00	<2.00	<2.00	<2.00	<10.0	<1.00	<2.00	<2.00	<2.00	<10.0	<1.00	<2.00	<2.00	<2.00
10	7.16	<1.00	<2.00	<2.00	<2.00	10.2	<1.00	4.00	4.20	<2.00	<10.0	<1.00	<2.00	<2.00	<2.00
11	<10.0	<1.00	<2.00	<2.00	<2.00	4.39	<1.00	1.18	<2.00	<2.00	<10.0	<1.00	<2.00	<2.00	<2.00
Mean	0.80					1.62		0.58	0.47						
Standard error	0.80					1.18		0.45	0.47						

Table A14(i). Monitoring study sediment particle size and cation exchange capacity for Gwawley Creek.

Sample collection	Coarse sand SS1 (g/100g)	Fine sand SS1 (g/100g)	Silt + clay SS1 (g/100g)	Coarse sand SS2 (g/100g)	Fine sand SS2 (g/100g)	Silt + clay SS2 (g/100g)	Coarse sand SS3 (g/100g)	Fine sand SS3 (g/100g)	Silt + clay SS3 (g/100g)	CEC (mmolNa/100g)	CEC (mmolNa/100g)	CEC (mmolNa/100g)
1	86.3	8.44	4.33	98.3	0.69	0.72	95.3	2.88	1.44	2.85	2.04	2.20
6	96.4	1.10	1.34	98.0	0.66	0.98	95.9	2.26	1.14	3.14	3.24	3.13
9	93.2	4.76	2.00	98.6	0.56	0.83	97.3	1.30	1.39	2.33	1.45	1.92
11	96.7	1.75	1.65	98.0	0.85	1.18	97.6	0.71	1.77	4.01	1.02	2.66
Mean	93.1	4.01	2.33	98.2	0.69	0.93	96.5	1.79	1.43	3.08	1.93	2.48
Standard error	2.4	1.68	0.68	0.1	0.06	0.10	0.5	0.48	0.13	0.35	0.48	0.27

Table A14(ii). Monitoring study sediment particle size and cation exchange capacity for Savilles Creek.

Sample collection	Coarse sand SS1 (g/100g)	Fine sand SS1 (g/100g)	Silt + clay SS1 (g/100g)	Coarse sand SS2 (g/100g)	Fine sand SS2 (g/100g)	Silt + clay SS2 (g/100g)	Coarse sand SS3 (g/100g)	Fine sand SS3 (g/100g)	Silt + clay SS3 (g/100g)	CEC (mmolNa/100g)	CEC (mmolNa/100g)	CEC (mmolNa/100g)
1	90.2	5.79	2.74	91.4	5.95	1.94	94.6	3.69	0.74	2.98	2.75	1.83
6	90.8	5.30	2.94	96.4	1.82	0.71	94.1	3.48	0.87	4.25	2.41	2.50
9	90.3	5.51	4.12	90.8	7.40	1.60	98.0	1.12	0.93	3.09	1.99	1.54
11	97.8	1.22	0.93	91.3	7.29	1.30	87.3	7.56	5.09	1.55	1.21	1.49
Mean	92.3	4.45	2.68	92.5	5.61	1.39	93.5	3.96	1.91	2.97	2.09	1.84
Standard error	1.8	1.08	0.66	1.3	1.31	0.26	2.2	1.33	1.06	0.55	0.33	0.23

Table A14(iii). Monitoring study sediment particle size and cation exchange capacity for Temptation Creek.

Sample collection	Coarse sand SS1 (g/100g)	Fine sand SS1 (g/100g)	Silt + clay SS1 (g/100g)	Coarse sand SS2 (g/100g)	Fine sand SS2 (g/100g)	Silt + clay SS2 (g/100g)	Coarse sand SS3 (g/100g)	Fine sand SS3 (g/100g)	Silt + clay SS3 (g/100g)	CEC (mmolNa/100g)	CEC (mmolNa/100g)	CEC (mmolNa/100g)
1	96.8	1.52	0.61	98.0	0.55	0.71	96.5	1.37	1.14	1.89	1.43	1.30
6	96.1	1.83	1.01	92.3	4.77	1.49	95.2	2.77	1.21	2.49	2.58	1.97
9	98.8	0.51	0.69	97.5	1.41	1.06	98.5	0.59	0.89	0.58	1.07	0.91
11	99.3	0.11	0.62	98.6	0.61	0.83	98.9	0.49	0.66	0.39	0.72	0.38
Mean	97.7	0.99	0.73	96.6	1.83	1.02	97.3	1.30	0.97	1.34	1.45	1.14
Standard error	0.8	0.41	0.09	1.4	1.00	0.17	0.9	0.53	0.13	0.51	0.40	0.34

Appendix 5. Sample Station Photographs for the Three Sutherland Shire Creeks



Plate 1. Gwawley Creek Sample Station 1



Plate 2. Gwawley Creek Sample Station 2

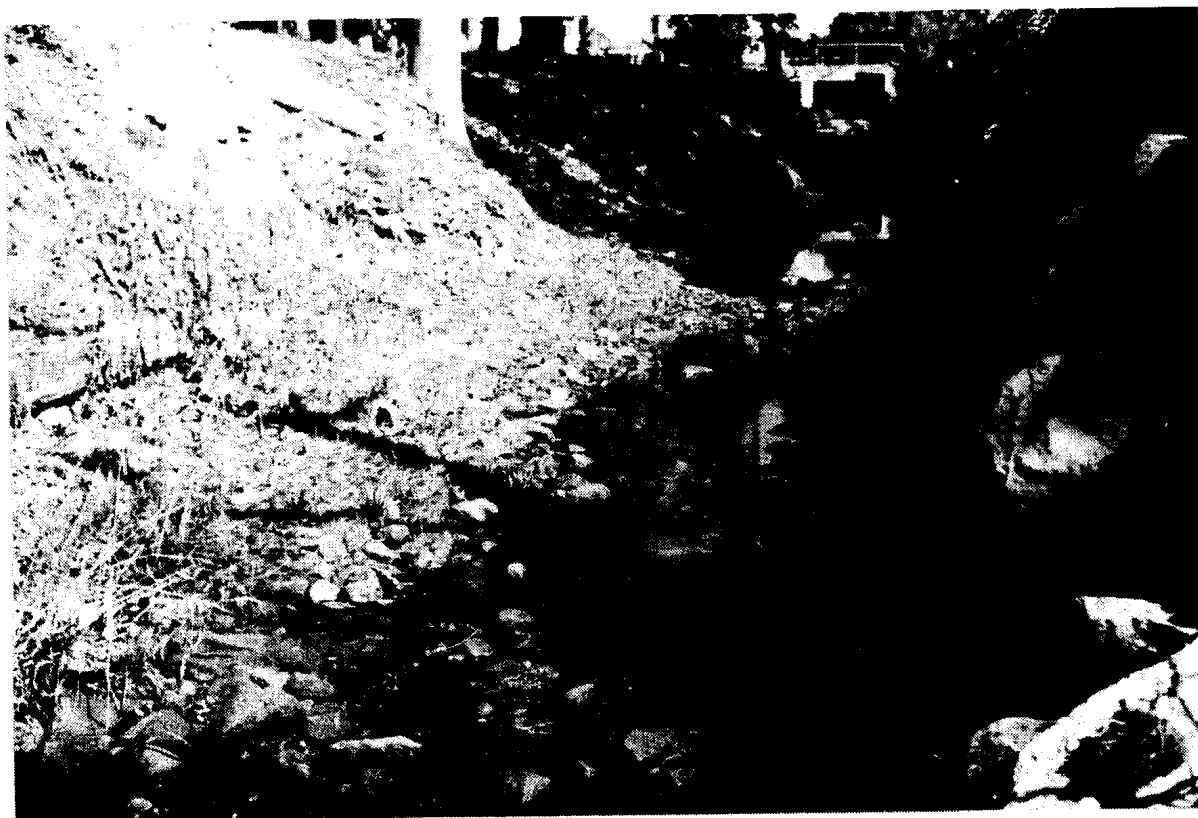


Plate 3. Gwawley Creek Sample Station 3

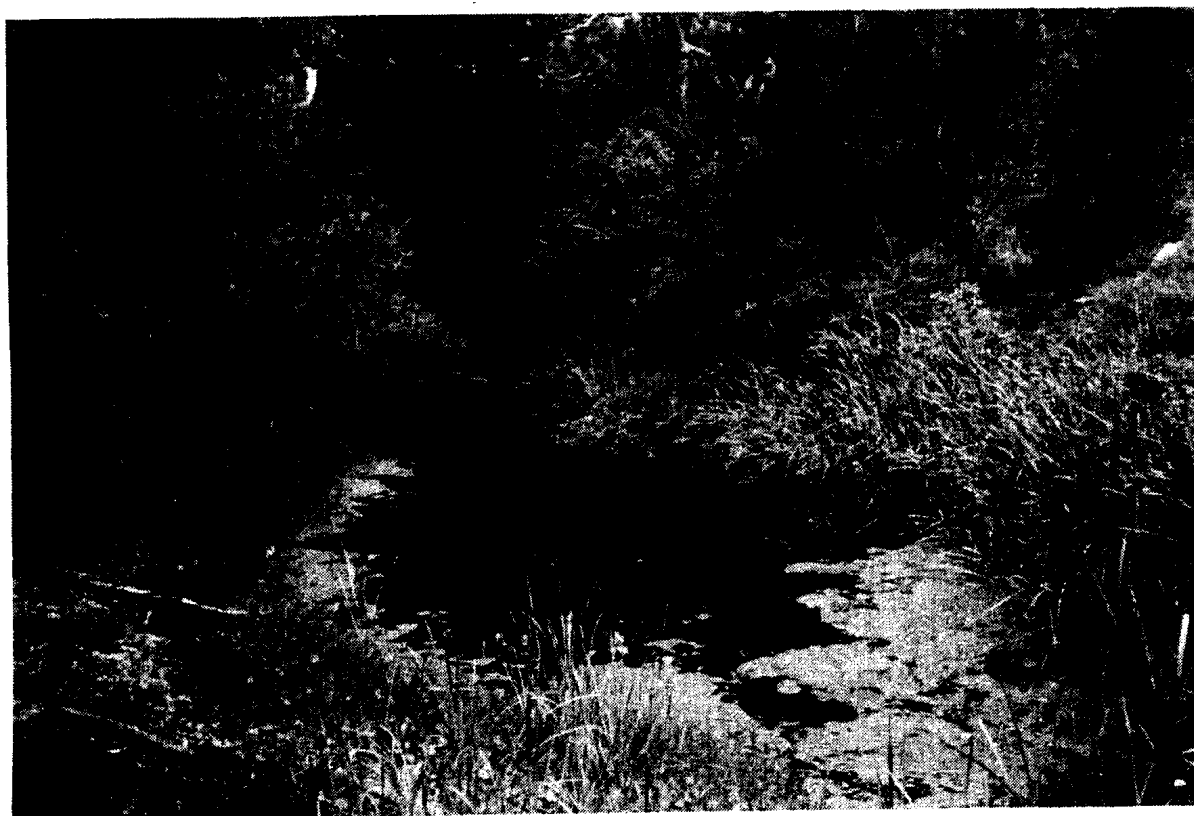


Plate 4. Savilles Creek Sample Station 1



Plate 5. Savilles Creek Sample Station 2

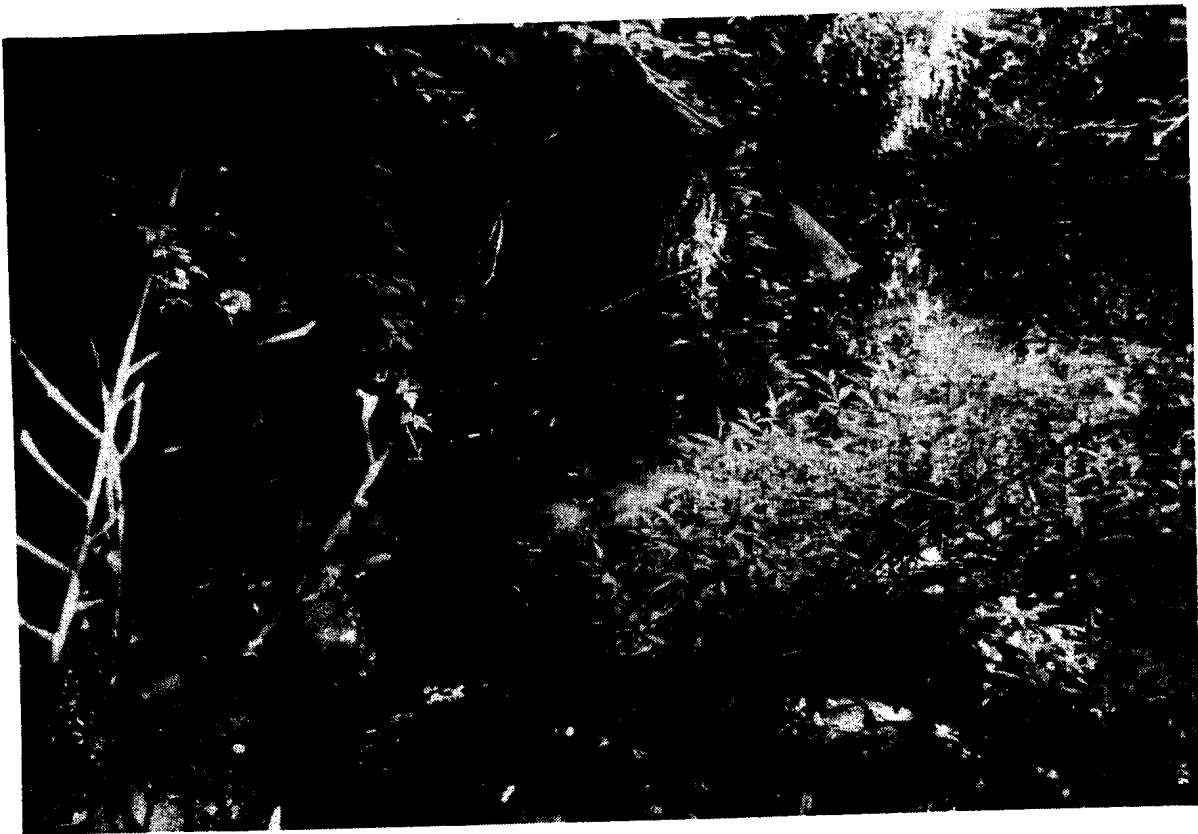


Plate 6. Savilles Creek Sample Station 3



Plate 7. Temptation Creek Sample Station 1



Plate 8. Temptation Creek Sample Station 2



Plate 9. Temptation Creek Sample Station 3

Appendix 6. Calculated Values (Set 1) for Differences in Surface Water Loading and Diffusional Fluxes for the Three Shire Creeks

Table A15(i). Comparison of surface water loads and interstitial water diffusional fluxes of heavy metals and phosphorus for Gwawley Ck. 75mm sample separation.

Constituent/ Sample collection	Difference (2-1) in surface water load (mg h ⁻¹)	Flux (2-1) (mg h ⁻¹)	Difference (3-2) in surface water load (mg h ⁻¹)	Flux (3-2) (mg h ⁻¹)
o-phosphate				
1	911	-0.14	936	-0.09
3	3403	-0.01	-2642	-0.01
4			-21716	0.00
5	3399	1.12	1148	1.05
10	136	-0.03	-415	-0.01
11	276	-0.06	-1830	-0.04
copper				
1	0	0.08	969	0.02
3	-1498	0.07	3790	0.04
4			0	0.00
5	0	0.00	0	0.00
10	1609	0.04	-1609	-0.01
11	0	0.00	0	0.00
zinc				
1	72	0.63	4536	0.32
3	-1728	0.89	0	1.02
4			0	0.28
5	-2304	0.28	7920	0.09
10	3924	0.20	-4140	0.08
11	-3528	-0.20	-12600	-0.19
cadmium				
1	21	0.00	179	0.00
3	0	0.00	0	0.00
4			0	0.00
5	0	0.00	0	0.00
10	0	0.00	0	0.00
11	152	0.00	-111	0.00
lead				
1	198	0.72	995	0.19
3	6857	0.00	-3592	-0.03
4			0	0.01
5	0	0.00	0	0.00
10	0	0.00	0	0.00
11	1486	-0.03	-1220	-0.01

Note : (2-1) indicates 'between GC stations 1 and 2'; (3-2) indicates 'between GC stations 2 and 3'

Table A15(ii). Comparison of surface water loads and interstitial water diffusional fluxes of heavy metals and phosphorus for Savilles Ck. 75mm sample separation.

Constituent/ Sample collection	Difference (2-1) in surface water load (mg h ⁻¹)	Flux (2-1) (mg h ⁻¹)	Difference (3-2) in surface water load (mg h ⁻¹)	Flux (3-2) (mg h ⁻¹)
o-phosphate				
1	26734	-0.27	-17019	-0.08
5	-11880	0.13	11880	0.02
6	-1128	0.12	-725	0.03
7			-2129	-0.01
10	-108	0.08	-151	0.01
11	50	-0.01	1210	-0.01
copper				
1	0	0.53	0	0.03
5	0	0.35	0	0.07
6	0	0.11	4673	0.02
7			-13753	-0.09
10	0	0.00	0	0.00
11	0	0.00	0	0.00
zinc				
1	-215784	6.38	-22968	0.30
5	0	0.00	0	0.00
6	0	0.00	0	0.00
7			-8964	0.01
10	3384	0.63	360	0.11
11	0	0.32	5400	0.03
cadmium				
1	9101	0.31	-7166	-0.05
5	0	0.00	0	0.00
6	0	0.01	0	0.00
7			0	0.00
10	168	-0.01	-168	0.00
11	-489	0.02	167	0.00
lead				
1	0	2.54	0	0.30
5	0	0.04	0	0.01
6	-7099	0.13	3148	0.00
7			1945	-0.01
10	0	0.12	0	0.02
11	0	0.07	0	0.00

Note : (2-1) indicates 'between SC stations 1 and 2'; (3-2) indicates 'between SC stations 2 and 3'

Table A15(iii). Comparison of surface water loads and interstitial water diffusional fluxes of heavy metals and phosphorus for Temptation Ck. 75mm sample separation.

Constituent/ Sample collection	Difference (2-1) in surface water load (mg h ⁻¹)	Flux (2-1) (mg h ⁻¹)	Difference (3-2) in surface water load (mg h ⁻¹)	Flux (3-2) (mg h ⁻¹)
o-phosphate				
1	0	0.00	600	0.00
5	-12000	0.00	3707	0.00
10	0	0.01	0	0.01
11	0	0.00	0	0.00
copper				
1	0	0.00	0	0.00
5	0	0.00	0	0.00
10	0	0.00	0	0.00
11	0	0.00	0	0.00
zinc				
1	-7740	0.89	286488	-0.06
5	0	0.13	0	0.11
10	5328	0.04	2016	0.02
11	0	0.11	0	0.13
cadmium				
1	-356	0.03	4596	0.01
5	0	0.00	0	0.00
10	0	0.00	0	0.00
11	0	0.00	0	0.00
lead				
1	0	0.00	0	0.07
5	0	0.00	0	0.00
10	0	0.00	0	0.00
11	0	0.00	0	0.00

Note : (2-1) indicates 'between TC stations 1 and 2'; (3-2) indicates 'between TC stations 2 and 3'

Appendix 7. Calculated Values (Set 2) for Differences in Surface Water Loading and Diffusional Fluxes for the Three Shire Creeks

Table A16(i). Comparison of surface water loads and interstitial water diffusional fluxes of heavy metals and phosphorus for Gwawley Ck. 0.5mm sample separation.

Constituent/ Sample collection	Difference (2-1) in surface water load (mg h ⁻¹)	Flux (2-1) (mg h ⁻¹)	Difference (3-2) in surface water load (mg h ⁻¹)	Flux (3-2) (mg h ⁻¹)
o-phosphate				
1	911	-21.41	936	-14.19
3	3403	-1.80	-2642	-1.23
4			-21716	0.05
5	3399	168.65	1148	157.49
10	136	-4.18	-415	-1.19
11	276	-9.04	-1830	-5.84
copper				
1	0	11.41	969	2.49
3	-1498	10.18	3790	5.94
4			0	0.00
5	0	0.00	0	0.00
10	1609	5.90	-1609	-2.10
11	0	0.00	0	0.00
zinc				
1	72	94.90	4536	47.45
3	-1728	132.87	0	153.75
4			0	41.76
5	-2304	41.76	7920	13.29
10	3924	30.37	-4140	11.39
11	-3528	-30.37	-12600	-28.47
cadmium				
1	21	-0.32	179	-0.63
3	0	0.00	0	0.00
4			0	0.00
5	0	0.00	0	0.00
10	0	0.00	0	0.00
11	152	-0.38	-111	0.14
lead				
1	198	108.67	995	28.21
3	6857	-0.10	-3592	-4.64
4			0	1.99
5	0	0.00	0	0.00
10	0	0.00	0	0.00
11	1486	-4.90	-1220	-1.17

Note : (2-1) indicates 'between GC stations 1 and 2'; (3-2) indicates 'between GC stations 2 and 3'

Table A16(ii). Comparison of surface water loads and interstitial water diffusional fluxes of heavy metals and phosphorus for Savilles Ck. 0.5mm sample separation.

Constituent/ Sample collection	Difference (2-1) in surface water load (mg h ⁻¹)	Flux (2-1) (mg h ⁻¹)	Difference (3-2) in surface water load (mg h ⁻¹)	Flux (3-2) (mg h ⁻¹)
o-phosphate				
1	26734	-41.14	-17019	-12.44
5	-11880	19.18	11880	2.63
6	-1128	18.10	-725	3.78
7			-2129	-1.54
10	-108	11.67	-151	2.10
11	50	-0.99	1210	-1.46
copper				
1	0	79.68	0	4.88
5	0	53.01	0	10.60
6	0	16.87	4673	2.89
7			-13753	-13.83
10	0	0.00	0	0.00
11	0	0.00	0	0.00
zinc				
1	-215784	956.96	-22968	44.29
5	0	0.00	0	0.00
6	0	0.00	0	0.00
7			-8964	1.58
10	3384	94.91	360	15.82
11	0	47.45	5400	4.75
cadmium				
1	9101	46.51	-7166	-7.41
5	0	0.00	0	0.00
6	0	0.77	0	0.32
7			0	0.00
10	168	-0.80	-168	-0.16
11	-489	2.43	167	-0.15
lead				
1	0	381.13	0	45.61
5	0	6.17	0	1.23
6	-7099	20.09	3148	0.06
7			1945	-1.57
10	0	17.75	0	3.55
11	0	11.06	0	0.00

Note : (2-1) indicates 'between SC stations 1 and 2'; (3-2) indicates 'between SC stations 2 and 3'

Table A16(iii). Comparison of surface water loads and interstitial water diffusional fluxes of heavy metals and phosphorus for Temptation Ck. 0.5mm sample separation.

Constituent/ Sample collection	Difference (2-1) in surface water load (mg h ⁻¹)	Flux (2-1) (mg h ⁻¹)	Difference (3-2) in surface water load (mg h ⁻¹)	Flux (3-2) (mg h ⁻¹)
o-phosphate				
1	0	0.00	600	-0.04
5	-12000	0.44	3707	0.59
10	0	0.99	0	1.19
11	0	0.00	0	0.00
copper				
1	0	0.00	0	0.00
5	0	0.00	0	0.00
10	0	0.00	0	0.00
11	0	0.00	0	0.00
zinc				
1	-7740	132.87	286488	-9.49
5	0	18.98	0	15.82
10	5328	6.33	2016	3.16
11	0	15.82	0	18.98
cadmium				
1	-356	4.90	4596	1.84
5	0	0.00	0	0.00
10	0	0.00	0	0.00
11	0	0.00	0	0.00
lead				
1	0	0.00	0	10.55
5	0	0.00	0	0.00
10	0	0.00	0	0.00
11	0	0.00	0	0.00

Note : (2-1) indicates 'between TC stations 1 and 2'; (3-2) indicates 'between TC stations 2 and 3'