Determination of long-term spatial and seasonal distribution of contaminants in an urban river and estuarine system using polarographic techniques.

Ph. D. Research Thesis by
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DECLARATION

I hereby certify that this material, which I now submit for assessment on the programme of study leading to the award of Ph.D. is entirely my own work and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my work.

Signed: Conor Buggy

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Date: **30th September 2006**

This work is dedicated to my family and friends for their unwavering faith and support in me.

But it is especially for three people.

Nan, who is my Rock

Mam, who is my teacher.

Dave, who is my Everything.

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ABSTRACT

Determination of long term spatial and seasonal distribution of contaminants in an urban river and estuarine system using polarographic techniques.

The Tolka River and Estuary, Co. Dublin, Ireland, is a typical Irish urban river and estuarine system. It has significant metal and organometal contaminant loading. A one-month rapid sampling and analysis regime was devised to optimise riverine and estuarine sampling techniques and to determine seasonality of contaminant distribution. Over a thirty-month period contaminant concentrations within the surface sediment of the aquatic system were analysed from twenty sampling points. Six metals (Cd, Cr, Cu, Ni, Pb and Zn) and an organometal (TBT) were analysed using Differential Pulse Polarography for thirty and nineteen months respectively. Organic Matter, Suspended Particulate Matter, pH, Salinity and metal content of the water column were also analysed. This thirty-month assessment created an extensive database to determine spatial and seasonal distributions of contaminants over time and various in situ environmental and anthropogenic parameters that influence these distributions. It was found that contaminant concentrations within surface sediment are highly variable over a twelve-month period and that environmental conditions and anthropogenic sources of contaminants are the key factors affecting spatial and seasonal distributions.

PREFACE

Project Conceptual Formation

The primary focus of this research is aimed at the elucidation of seasonally variable contaminant distributions in aquatic systems. Research into riverine and estuarine seasonality is virtually non-existent and is confined solely to contaminant fluctuations in the water column. However, surface sediment provides the greatest indication of contaminant retention in aquatic systems and seasonal variation of metal contaminants in surface sediment had not been observed previously. The concept of researching a single aquatic system over a period of at least two years on a monthly basis to determine seasonal variation is the main aim of the project. Supplementary to this aim is the utilisation of novel analytical techniques for the determination of metal and organometal contaminants. As the research project covered a broad area of topics and produced a significant dataset it is necessary to provide a roadmap to the thesis.

Chapter 1 Introduction

The first section of Chapter 1 comprises a literature review of the key mechanisms controlling contaminant transportation, retention and dispersion from aquatic systems. It also introduces the key parameters that are assessed during the thirty months of sampling. The second section of Chapter 1 continues the literature review but focuses on contamination of estuarine and riverine ecosystems; origins of metal and organometal contamination and a review of many sites and associated contamination around the globe. Chapter 1 also provides a synopsis of the chosen aquatic system –

the Tolka River and Estuary. The final section of Chapter 1 outlines the aims and objectives of this research project.

Chapter 2 Methodology

Chapter 2 outlines the methods utilised in this research for sampling and analysis. A full account of sampling procedures and sample treatment is provided for future projects that may use this research as a basis for new projects. A significant portion of Chapter 2 is devoted to the novel analytical method used for contaminant determination – Differential Pulse Polarography and the optimisation and validation processes of these analytical techniques.

Chapter 3 Results

Chapter 3 illustrates in tables, 3D and 2D graphics the results from thirty-months sampling and analysis. Both in situ environmental parameters and metal and organometal results are represented in 3D graphics to compress significant quantities of data. These 3D graphics illustrate how both environmental parameters such as Organic Matter and Suspended Particulate Matter along with contamination vary over time and space in both the surface sedimentary matrices and in the water column. 3D graphics are utilised as 2D graphics are indecipherable with twenty sites over thirty months of analysis. However, selected sites are represented in 2D format to observe temporal contaminant distribution along a progressive timescale.

Chapter 4 Discussion

The Discussion chapter outlines in two major sections the key research findings. Initially each environmental parameter is assessed for its impact on contamination both spatially and temporally. Subsequent to this the aquatic system is observed as a whole unit and its complex interactions and relationships between parameters over space and time are discussed. Based on results obtained from thirty-months of sampling, seasonal contaminant variation is observed to be strongly linked with seasonally variable environmental parameters, in situ physical parameters and anthropogenic input. Finally a modelling exercise is undertaken to predict future contaminant concentrations in the aquatic system and this is the final section of this chapter.

Chapters 5 and 6 Conclusion and Future Research

The final two chapters outline the key findings of the research project and areas that could be considered for future research. As seasonal variation in aquatic systems is only explained at a basic level in this project there exist many avenues for future research projects with narrower and a more specialised focus.

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PUBLICATIONS

Buggy, C.J., Tobin, J.M., 2006. Spatial distribution of nine metals in surface sediment of an urban estuary prior to a large scale reclamation project. Marine Pollution Bulletin 52, 8, 969-974. (Located in Appendix E).

Buggy, C.J., Tobin, J.M., 2006. Seasonal and spatial distributions of tributyltin in surface sediment of the Tolka Estuary, Dublin, Ireland. Environmental Pollution 143, 294-303. (Located in Appendix E).

Buggy, C.J., Tobin, J.M., 2003. Polarographic Analysis of Sediment in an Irish Estuary. 2nd International Symposium on Contaminated Sediments, Quebec, Canada. ASTM International Publications, PA, USA. (Located in Appendix E).

POSTERS

Buggy, C.J., Lacey, C., Cheney, J., 2006. Determination of Pharmaceuticals in aqueous samples using Liquid Chromatography Mass Spectrophotometry and Differential Pulse Polarography. ENVIRON 2006 – 16th National Environmental Symposium, Environmental Scientists Association of Ireland. UCD Belfield, Dublin, Ireland.

Buggy, C.J., Tobin, J.M., 2003. Polarographic Analysis of Sediment in an Irish Estuary. 2nd International Symposium on Contaminated Sediments, Quebec, Canada.

PRESENTATIONS

January 2006 - Polarographic Determination of Spatial and Seasonal Distribution of Tributyltin in Surface Sediment of an urban river and estuary. ENVIRON 2006 – 16th National Environmental Symposium, Environmental Scientists Association of Ireland. UCD Belfield, Dublin, Ireland.

December 2004 - Polarographic Determination of Seasonal and Spatial Distribution of Metals and Tributyltin in an Irish River and Estuarine system. Collaborative Research Meeting. The Marine Institute, Dublin, Ireland.

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"Water is sometimes sharp and sometimes strong, sometimes acid and sometimes bitter, sometimes sweet and sometimes thick or thin, sometimes it is seen bringing hurt or pestilence, sometime health-giving, sometimes poisonous. It suffers change into as many natures as are the different places through which it passes. And as the mirror changes with the colour of its subject, so it alters with the nature of the place, becoming noisome, laxative, astringent, sulfurous, salty, incarnadined, mournful, raging, angry, red, yellow, green, black, blue, greasy, fat or slim. Sometimes it starts a conflagration, sometimes it extinguishes one; is warm and is cold, carries away or sets down, hollows out or builds up, tears or establishes, fills or empties, raises itself or burrows down, speeds or is still; is the cause at times of life or death, or increase or privation, nourishes at times and at others does the contrary; at times has a tang, at times is without savor, sometimes submerging the valleys with great floods. In time and with water, everything changes"

Leonardo da Vinci, Summer 1509.

INTRODUCTION

Metal loading in rivers and particularly estuaries is a cause of interest and concern in present society and the fate of metals in estuarine environments has been discussed extensively within the scientific community (Turner, 2000; Griscom et al., 2000). Concern arises because rivers, estuaries and brackish waters are places of extraordinary biological interest and estuarine flats provide vital feeding grounds for flocks of migrant wading birds and nursery grounds for fish. Yet such areas are often perceived as wastelands ripe for industrialisation or for reclamation (Little, 2000). Environmental protection of such sites is important to many bodies including government authorities and especially the public. Hence metal loading assessment is vital for the continual improvement of ecotoxicological methodologies demanded by such bodies (EPA, 2000). An understanding of the general principles governing metal loading in the estuarine environment is often overlooked yet required by all.

To adequately interpret results of any contaminant analysis, it is necessary to know the spatial and temporal variance in the objective area (Chapra, 1997; Birch et al., 2001). Temporal variation at a site includes natural variance associated with physical, chemical and biological processes. Small-scale spatial variations hinder accurate interpretation of temporal contamination. If these are excessive, larger local and regional trends may be obscured. When temporal trends are large, a single synoptic survey may be insufficient to determine contaminant loading, degradation and circulation over time. Multiple repeated sampling over an extended period at each site is required to address seasonal variation (Birch et al., 2001).

Seasonal variation in metal contamination has been observed in aquatic environments (Birch et al., 2001; Caccia et al., 2003). Analysis of metal distributions in intertidal estuarine sediments has frequently been used to investigate chronological inputs (French, 1993), to identify deviations and point sources of inputs (Emmerson et al., 1997) and to investigate metal behaviour (Comber et al., 1995). However, determination of seasonal aspects of contamination in estuarine systems is an area where current research is lacking, and studies concerning seasonal variation in surface sediment are limited. Temporal aspects of riverine and estuarine research mainly focus on the water-column as it is the key transport mechanism. Surface sediment is the site of contaminant retention in the estuarine system but is rarely utilised to determine seasonal trends. When particle-reactive pollutants, such as metals enter riverine and estuarine waters, many are quickly adsorbed on suspended matter and removed to the surface sediment layer at the bottom (Birch & Taylor, 1999; Caccia et al., 2003). Sediments therefore provide a temporally integrated indication of the condition of riverine and estuarine systems, and act as a major reservoir for metals. Concentrations have greater orders of magnitude than the overlying water column (Forstner & Stoffers, 1981). Hence examination and study of sediment quality over extended periods of time can reveal the pollutant variations, degradations and cycles and the effects of water discharges (Fernand-Ferreira et al., 1996).

A range of environmental factors that affect metals is common to all rivers and estuaries (Breslin & Sanudo-Wilhelmy, 1999). In the estuarine environment riverine freshwater encounters marine salt water and geochemical and biogeochemical processes occurring include sediment transport, sedimentation, precipitation and flocculation of particulate substances. These factors affect the fate of metals in estuarine environments. Composition evolution of the particle in the estuarine mixing zones indicates that metals do not behave conservatively and that they are also affected by changing riverine and estuarine conditions such as pH and salinity (Calmano & Hong, 1993; Che et al., 2003).

Estuarine systems are inherently more complex than riverine systems (Herut & Kress, 1997; Hoch et al., 2003). The primary focus of this research is concerned with estuarine systems and associated internal contaminant / sediment dynamics over time. Riverine systems do not magnify temporal variation to an equivalent degree as estuarine systems (Birch et al., 2001), therefore determining seasonal contaminant variability and associated in situ environmental factor dynamics was more viable in an estuary rather than a river. However, researching a contaminated riverine and estuarine system together allowed for a synoptic analysis of spatial and temporal contaminant variation for the entire system with the estuary as the key area for temporal analysis while analysis of contaminant transportation was focused on the riverine system.

1.1 In Situ Physical Features

Estuarine and riverine physical conditions affect the fate of metals in the aquatic environment (Herut & Kress, 1997). Although chemical and biological processes are common to all rivers and estuaries, the distributions of metals and their rates of reactivity vary greatly between estuaries, depending on environmental factors such as hydrodynamic residence times, mixing patterns and transport processes (Hatje et al., 2003b). There is no universal pattern of metal behaviours in aquatic systems, however there are features common to all rivers and estuaries (Camusso et al., 1997). Because of the variety in estuarine behaviour it is important to understand the full range of common features of rivers and estuaries, across the entire spectrum of climates, flow regimes, geological terrains and biological communities. This allows for better assessment of natural variability and provides a basis for differentiating natural from anthropogenic metal loading (Herut & Kress, 1997; Hatje et al., 2003a).

A river at its simplest is a moving conduit of freshwater whereas an estuary at its simplest is a partly enclosed tidal inlet of the sea in which seawater and riverwater mix to some degree (Little, 2000). Estuaries may vary in size from a few square kilometres to hundreds of square kilometres yet most have many similar features and patterns. Their shape is highly variable. In situ physical factors affecting estuaries include freshwater saltwater mixing, tides, wave action, sediment transport, erosion and deposition, biota, and temporal cycles. Generally estuaries can be divided into three sectors: (1) a marine or lower estuary, in free connection with the open sea, (2) a middle estuary, subject to strong salt and freshwater mixing and (3) an upper or fluvial estuary, characterised by freshwater but subject to daily tidal action (Kramer et al., 1995). The Yangtze estuary, China is a good example of this sectioning. The geographical boundaries between these sectors are not fixed. They are subject to the tidal movements, to seasonal variability, river discharge, and may vary according to depth (Zhang et al., 2001).

1.2 The Role of Sediment

The examination and study of sediment quality can reveal pollutant variations, degradations and cycles and the effects of water discharges (Fernand-Ferreira et al., 1996). The role of sediment and its interactions in aquatic systems are very important in pollution assessment and the analysis of metal distributions in intertidal estuarine sediments has frequently been used to investigate chronological inputs (French, 1993). Sediment is used to identify deviations and point sources of inputs (Emmerson et al., 1997) and to investigate metal behaviour (Comber et al., 1995).

Spatial and temporal distributions of metal concentrations in sediments are influenced by so many factors that it is difficult to find the main contributing factor. Some studies have shown that in high turbidity estuaries, biogeochemical exchange processes do not significantly modify the composition of fine-grained detrital fraction of the suspended matter in the mixing zone and sedimentary dynamics dominate the fate of metal contamination (Che et al., 2003). There are three major sources of estuarine sediment: (1) inflowing streams and rivers; (2) the coast; and (3) the margins of the estuarine basin itself. Metal concentrations in riverine sediments are different from those in marine sediments (Feng et al., 2002). Riverine sediments are finer and carry more metals than marine sediments. Most riverine sediments settle in the middle estuary and are mixed and partially diluted with marine sediment (Che et al., 2003). Often there are distinct down estuary gradients and zonations in grain size, sedimentary structures, mineral assemblages and floral and faunal distributions (Carter, 1988). Impact of metal pollutants is greatest in sedimentary deposits where the pollutants are accumulating and where they can enter the marine food chains (Goldberg & Bertine, 2000). Thus sediment analysis provides advantages in the assessment of human impacts on the aquatic environment (Yap et al., 2002).

1.2.1 Sediment Transportation

Sediment transportation is an important factor in the distribution of metals and organometals through riverine and estuarine systems (Spencer, 2002). Assuming there is a local supply of sediment to the estuary, generally from the river, a combination of waves, tides and currents is responsible for determining where sediments are deposited. Sediments and associated contaminants can not only be mixed in a water column due to turbulence, but also transported and redistributed in the lower river and entire estuarine extent depending on the magnitude of currents and the dynamic equilibrium between sediment surface and tidal currents (Feng et al., 2002).

1.2.1.1 Waves

Heavier sediments, like coarse sands and shingle, occur mostly in sheltered river zones and on wave exposed outer coasts, but where tidal currents in estuaries are strong they may form extensive banks in what may be relatively sheltered waters (Kramer et al., 1995). The Slaney Estuary, Ireland, has extensive sand-banks in its outer sections. Two sand spits protect the estuary mouth and strong tidal movements at the mouth allow for the formation of sand banks in the estuary itself (Jeffery et al., 1985). Where the currents and waves are diminished, finer sediments accumulate, so that extensive mudflats occur only where there is some degree of shelter. Estuaries may provide this shelter. Because the Tinto-Odiel Estuary in southwest Spain has a narrow mouth, marine influx is minor and currents and wave action are reduced. Consequently, extensive mudflats in the estuary were formed (Elbaz-Poulichet et al., 2001). Similar sheltering patterns give rise to extensive mudflats in the Shannon

Estuary, Ireland (Jeffrey et al., 1985) and the mudflats of the Tagus Estuary, Portugal which extend across its 300 km^2 area (Cacador et al., 2000).

1.2.1.2 Tides

Because the movement of the tides is slower than that of wind-driven waves, it is less obvious. However, in estuaries tides may be responsible for violent currents and consequently for the movement and sorting of large quantities of sediment. Tidal influence can extend far inland into the riverine system. In the Tagus Estuary, tidal influence can reach 80km inland (Cacador et al., 2000). In the Elbe Estuary, Germany, marine sediment deposits carried by the tide are located as far as 100 km inland (Groengroeft et al., 1998). The strength of a tidal current alone can relocate sediment and their contaminants around the estuary, and also drag it out into the pure marine system. In Dublin Bay, Ireland, the circular rotation of the tide, relocates sediment around the bay and also out to sea (Dublin Bay Project, 2001; Jeffrey et al., 1985).

1.2.1.3 Currents

As currents in an intertidal zone weaken landward, sediments become progressively finer in this direction characterised by coarse silts in low tidal flat, and silts and clay silts in the upper tidal flat areas. Factors affecting currents include the weather, freshwater and saline water mixing and layering, and tidal influx and efflux. In the Tees Estuary, UK, sand and sandy silts occur at the mouth of the estuary with the strongest currents, while further into the estuary sediment becomes finer and the freshwater section of the estuary is composed of silts and muds (Kennish, 1994; Jones & Turki, 1997). When storm events occur in an estuarine area, the intertidal zone is modified by waves. In the Yangtze estuary periodic fair to storm weather patterns cause alternate layers of fine and coarse deposits to occur widely in the intertidal zone (Zhang et al., 2001). In general, erosion occurs in the middle and low tidal flats, and deposition in the upper flats (Birch et al, 2001). In the Hudson Estuary, U.S., during periods of high freshwater flow the distance of up- and down-estuary transport of suspended particles could be up to ~15 km (Feng et al., 2002).

Studies have shown that in high turbidity rivers and estuaries with elevated mixing and internal turbulence, biogeochemical exchange processes did not significantly modify the composition of the fine grained detrital fraction of the Suspended Particulate Matter (SPM) in the mixing zone and that sedimentary dynamics dominated the fate of metals (Zhang et al., 1988; Che et al., 2003). Desorption and remobilization of particle-bound trace elements down estuary, together with the influx of clean marine sediments through the estuarine mouth, account for the gradual seaward decline in the metal content of estuarine sediments (Kennish, 1994). The lower estuary can function as a source of metal contaminants to the upper estuary. Metal contaminants in the lower estuary can be removed and relocated to upper estuary regions and redistributed over the course of a tidal cycle that increases the inner estuary and lower river zone metal concentrations. In the Hudson estuary, fine grained bottom sediments were resuspended by currents and along with associated contaminants were mixed in the water column and transported over a 10 - 20 km distance along the axis of the estuary during a semi-diurnal tidal cycle (Feng et al., 2002). In the Seine estuary, mixing of saltwater and freshwater due to tidal influence allows for remobilization and transport of sediments from the mouth up to 100 kms inland (Cossa et al., 1994).

1.2.2 Sediment Granulometry

Sediment quality has been recognised as an important indicator of water pollution as sediments faithfully record and time-integrate the contaminant status of an aquatic environment (Borgmann, 2000; Birch et al., 2001). The concentration of metals in sediments can be related to physical characteristics e.g. particle size and/or the chemical conditions of the sedimentary environment (Birch et al., 1999). Due to their strong affinity for sedimentary particles, scavenging by suspended particulate matter and subsequent sedimentation exacerbates the environmental impact of metals and sustains the environmental deterioration of estuaries (Ruiz-Fernandez et al., 2003). Metals are mainly concentrated in the fine-grained size fraction of the sediment (Chu et al., 1990; Breslin and Sanudo-Wilhelmy, 1999; Che et al., 2003). Clay minerals present in the fine grained fraction are the main carriers of metals during mobilising and diffusing (Santschi et al., 1997). Accumulation of metals and organometals is not solely dependent on the proximity to contaminant sources, but also on the pattern of sediment transport and sedimentation associated with estuarine hydrodynamics: freshwater and saline water mixing, tidal influx and efflux and internal currents (Zhang et al., 2001). In most estuaries intertidal sediments are predominantly composed of silts and clayey silts. The intertidal sediments of the Yangtze are composed of silts and clayey silts, dominated by fine grained particles, 67 % less than 50 μm (Zhang et al., 2001). This reflects the fact that the suspended materials discharging into an estuarine region are dominated by fine-grained particles carried from the freshwater riverine inputs (Birch et al., 2001; Hoch, 2001; Hoch et al., 2003).

Since specific geomorphic units tend to have a particular sediment particle-size distribution, an evaluation of the spatial variability of metal concentrations, must, therefore, take into account the influence of geomorphic variation in sediment particle size (Zhang et al., 1988). Sediment particle size plays a significant role in determining metal accumulation, and fine-grained sediments often show higher concentrations of metals due to their greater surface to volume ratio and enrichment of organic matter (Zhang et al., 2001).

1.2.3 Organic Matter Content

Distribution, transport and fate of metals in estuarine systems is significantly influenced by Organic Matter (OM) (Singer, 1977) and it is established that OM content of sediment is a controlling factor in the distribution of metals (Rubio et al., 2000). Metals are associated with OM in the fine-grained fraction, such as detritus and organic material coating mineral particles and colloids. Living OM composed of algae, plankton and estuarine meiofauna also influence metal distributions in the fine-grained sedimentary material. Metals bound to faecal pellets, crustacean moults, and dead plant matter and animals are generally responsible for more than 90% of their vertical transport in the water column (Bryan, 1985). Approximately 60% of some metals are mobilised from Rhine River sediments as organometallic complexes by the decomposition of OM prior to reaching the sea (Bryan et al., 1989). The presence of OM concentrates metal accumulation in the substrate (Gerritse & Van Driel, 1984).

However, other studies have found little or no correlation between OM content and metal concentrations (Cacador et al., 2000).

Fine-grained sediments tend to have relatively high metal contents due in part to the high specific surface area of OM content. This enrichment is mainly due to surface adsorption and ionic attraction binding to the organic matter (Wangersky, 1986; Horowitz & Elrick, 1987; Hoch, 2001; Hoch et al., 2003). Sediment bound OM is capable of altering the distribution between oxidised and reduced forms of metals which can affect the impact metals have on the estuarine ecosystem (Yap et al., 2002). Often in sediments where organic matter is not retained metals become immobilised and thus non-bioavailable (El-Rayis et al., 2003). OM particles may be broken up to free the soluble metals in natural waters under oxidised conditions (Tokalioglu et al., 2000). Decomposition of OM results in a lowering of the pH which can affect metal uptake and binding to $CaCO_3$ often present in colloidal particles (Chambers & Odum, 1990; Spencer, 2002). Humic acids common to detrital particles present in OM bind appreciable quantities of free metal ions, making them unavailable for biological uptake (Cabral, 1996).

The organic phase of sediment could also play a dominant role in the transport of metals in natural water systems from several points of view. One of these would be the physical transport of particulate OM, in which the metal and OM would become associated in the form of insoluble complexes (Lee and Bada, 1975). Particulate OM in estuaries will predominantly be riverine in origin (Ruiz-Fernandez et al., 2003). Riverine and marine OM mixing occurs mainly in the mid estuarine mixing zone. OM accumulates in these areas of low turbulence in the mid estuary hence metal OM associations will be most evident in this zone (Rubio et al., 2000; Regnier & Wollast, 1993).

1.2.4 Suspended Particulate Matter

It is well known that estuaries can be efficient filters for SPM and metals, due primarily to particle/solute interactions, flocculation and coagulation, and sedimentation of particle bound metals (Zhou et al., 2003). In non-urban catchments, SPM composition is mainly determined by catchment geology and biology, and SPM is typically composed of quartz, clay and other silicate minerals, hydrous metal oxides, as well as diatoms and other microorganisms, and plant detritus (Bibby & Webster-Brown, 2005). In the urban environment, however, storm-water run-off during high rainfall washes across mainly anthropogenically modified, impermeable surfaces such as roads, car parks, rooftops, construction sites and paved areas. SPM in storm-water may therefore potentially include a variety of anthropogenically derived materials, and unusual components, compared to SPM from an unmodified catchment (Bibby & Webster-Brown, 2005; Williamson & Morrisey, 2000). Urban storm-water run-off has been cited as the largest non-point source of pollution to receiving waters, leading to increased degradation of downstream coastal and stream environments (Characklis & Wiesner, 1997; Morrisey et al., 2000; Parker et al., 2000).

Adsorption onto SPM is an important process controlling dissolved metal concentrations and how they are transported and distributed within an estuary (Comber et al., 1995). Dissolved and particulate matter in the environment generally reduces metal toxicity by complexation and binding (Gadd, 1993). Adsorption behaviour of metals onto SPM in marine and freshwater varies according to slight changes in pH conditions. An increase in pH with increasing salinity will favour the sorption of metals and organometals onto SPM (Hoch, 2001; Hoch et al., 2003). This suggests an increase in association of metals to particles as salinity increases. This favours the retention of metals in the estuary since net transport in a coastal zone is directed landward (Hatje et al., 2003a). It would be expected that metals are trapped in the estuarine environment once the metals are mostly associated with the particulate phase in seawater and the net transport of sediments in the coastal zone (Wen et al., 1997). Significant seasonal variability in metal concentrations could be explained in terms of change in SPM and hence sediment OM composition due to biological processes in the summer months (Hatje et al., 2001). However, SPM is not solely responsible for seasonal variation in metal loading (Hatje et al., 2003a). Understanding the kinetics involved in trace element uptake and release from SPM is an ongoing process and offers new information about metal transportation in estuaries.

1.2.5 Salinity

Salinity also plays a role in the processes in an estuary. Oscillations of salinity with time during the tidal cycle reflect the stage of tides i.e. high salinity corresponds to high tide and low salinity corresponds to low tide (Feng et al., 2002). Seasonal variation in salinity can also have a minor role in metal distribution in estuaries. This is often due to an increase in freshwater input from riverine sources during periods of heavy rainfall (Shiller, 1997). Riverine metal inputs are greater than marine metal inputs in estuaries (Spencer, 2002). A steep gradient in salinity commonly observed in estuaries is a major controlling factor for the partitioning of dissolved and particulate metals. Metal distribution usually show a complex pattern relative to salinity (Hatje et al, 2003a). Complexation of metals by chloride at higher salinities can release metals from particulates into the water column and out of the estuarine system (Comans et al., 1988). The stability and solubility of these chlorocomplexes enhance the mobilisation of metals in estuaries and usually prevents the competing readsorption process from occurring (Elbaz-Poulichet et al., 2001). Salinity can have varying effects on each metal present in an estuary. Dissolved Cd, Cu and Zn will often show a maximum at relatively high salinities with their maximal levels often occurring in the mid estuary as higher salinities desorb the metals from surface sediment matrices to the overlying water column. These dissolved metals can increasingly be complexed by chloride ions as salinity increases (Hatje et al., 2003a). However, these metals in particulate form often show a decrease in relation to salinity. This does not reflect the effect salinity has on the metals but on the mixing of riverine and marine particulates (Tramontano & Bohlen, 1984; Zhou et al., 2003). In comparison, particulate bound Ni and Mn will often show maximum levels in the inner estuary with lower salinity and decreasing seaward with only a slight discernible mid estuarine maximum. Higher salinities desorb particulate metals and allows seawater cation adsorption (Elbaz-Poulichet et al., 2001; Kraepiel et al., 1997; Hatje et al., 2003a).

Salinity affects organometals more so than metals. At high salinity less adsorption is expected due to competition of chloride ions with the particulate matter for the butyltin species and competition for sodium ions with the butyltin compound for carboxylate sites on the particulate matter (Hoch & Schwesig, 2004). Salinity variance can affect the metal spatial distribution in the estuary. Increasing salinity and an increase in water column particulates transported by riverine input into the estuary, contributes to particulate flocculation and deposition in the inner estuary and mid estuarine mixing zone (Tian & Ruiz-Pino, 1995). This decrease in water column particulates leads to metal concentrations in suspended sediments decreasing after the inner and mid estuarine zones (Che et al., 2003).

1.3 Contaminant Input to Aquatic Systems

Input of metal into estuaries arrives from two pathways, riverine and marine (Spencer, 2002). It is possible to discriminate between sources of metals to estuaries and to the oceans. There are two major naturally-occurring metal sources, (1) weathering products of continental rocks transported to the sea by atmospheric and riverine action and (2) the interaction of seawater with newly formed oceanic basalt at ridge-crest spreading centres via hydrothermal activity (Bruland, 1980). This does not include metals and organometals anthropogenically introduced to riverine and estuarine systems. Metals exist in natural waters in dissolved, colloidal, and particulate phases, although the concentration of dissolved forms is generally low: μg / L in comparison to mg / L for particulate metals (Kennish, 1994). When transported in river water, a trace metal may occur in six possible chemical forms: (1) in solution as inorganic ion and both inorganic and organic complexes, (2) adsorbed onto surfaces, (3) in solid organic particles, (4) in coatings on detrital particles after coprecipitation with and sorption onto mainly iron and manganese oxides, (5) in lattice positions of detrital crystalline material and (6) precipitated as pure phase, possible on detrital particles (Duinker et al., 1980). While the uptake of dissolved trace metals onto solid phases already present in riverine and estuarine water is important to the overall concentration of the elements in solution, so is the release of material into solution from particulate phases by dissolution, desorption, and autolytic respiratory biological processes (Burton, 1975). The desorption of certain elements e.g. Ba, from suspended particulate matter results from increasing salinity and the concomitant rise in the concentration of major seawater cations Na and K. The exchange of trace metals between dissolved and particulate phases is a regular phenomenon in estuarine systems (Kennish, 1994). A major pathway through which metal is transported to estuaries is riverine input. During this process, part of the material being transported will be modified through estuarine mixing. As a result, estuaries are referred to as filters for river-derived signals (Morris et al., 1986).

1.3.1 Anthropogenic Sources of Metals and Organometals

Metals reach the estuarine habitat via a range of human activities, including the burning of fossil fuels, use of antifouling paints, smelting, power station corrosion products, sewage-sludge disposal, ash disposal, dredged-material disposal, seed dressings and slimicides, automobile emissions, oil refinery effluent, and other industrial processes (Kennish, 1994). The use of antifouling paints to protect the hulls of ships from boring and fouling organisms has been responsible for the slow release of large amounts of metals and organometals to estuarine and marine waters (Kennish, 1994). Copper oxides have proved to be an effective antifouling agent. Antifouling paints containing copper(I)oxide provide out-of-dock protection for up to three years (Davies & Houghton, 1984). Because of deleterious effects on marine life copper-based antifouling paints became less favourable; and were replaced by organotin based paints (Thomas & Robinson, 1986). Organotins are widespread in the environment. They have diverse industrial and biocidal applications. Their main application is in the thermal and UV stabilisation of rigid and semi-rigid polyvinyl chlorides. Triorganotins are exploited for their fungicidal, bactericidal, algicidal and acaricidal properties. TBT has received the most attention because of its use as antifouling paint (White et al., 1999). Organotins can enter the riverine and estuarine environment through many routes. Leaching and normal weathering of PVC products can lead to release of butyltins and methyltins (White et al., 1999). The effects of the accumulation of organotin based paint in estuarine environments are extreme. Antifouling paints are the main source of organometallic compounds in rivers and estuaries.

1.3.2 Metals and their Sources

A significant source of metals to the estuarine environment in the past has been waste disposal, particularly sewage sludge and dredged materials disposal. Due to the fact the major proportion of metals in disposed wastes is associated with solid phases, which accumulate on the estuarine bottom, the biological effects are manifested most conspicuously among the sediment benthic community. Many commercially and recreationally important fin- and shellfish species, either inhabiting the seafloor or feeding on bottom dwelling organisms, tend to absorb and accumulate the metals. The contamination of these species may have deleterious effects on humans that consume them (Bryan, 1985). The concentrations of metals in the water column does not reflect the metal contamination trapped in sediment (Kennish, 1994). As sediment locks in metals, they can still exist in an estuarine system long after the original source of the contaminant has been depleted (Jeffrey et al., 1985). Often in metal pollution assessment six metals will be analysed: Cd, Cr, Cu, Ni, Pb and Zn. They are considered the most common and dangerous to the estuarine ecosystem (EPA, 2000).

Cd is often associated with the use of zinc in industry. It arises from the fumes, dust and wastewater from lead and zinc mining and quarrying. In the Slaney Estuary, Ireland, levels as high as 5 ppm Cd were recorded in areas considered pristine. These sites were 1 km downstream from a quarry (Buggy, 2001; Jeffrey et al., 1985). Rinsing water from electroplating may contain 100 - 500 ppm Cd (Little, 2000). For example in Port Pirie, Australia, levels as high as 267 ppm Cd have been recorded. This site is near a smelter and electroplating facility (Ward et al., 1984). In the Derwent Estuary, Tasmania, levels as high as 862 ppm Cd were recorded in proximity to a refinery (Kojima & Kagi, 1978). Sewage sludge may contain up to 30 ppm Cd (Gray, 2000). Cd has been increasingly used in Ni-Cd batteries, thus Cd pollution can arise from landfills which leach into groundwater and riverine systems (Clarke, 1997).

Cr is often associated with quarrying and industrial processes (Clarke, 1997), as well as from sewage sludge (Gray, 2000). Sewage accumulating in Venice Lagoon contributed to levels of 106 ppm Cr up to 5 km away from the sewage outfall (Sfriso et al., 1995). The Fraser River Estuary, Canada which also has sewage outfalls has levels greater than 60 ppm Cr (Swain & Walton, 1990). Cr can be attributed to particulate matter washed into the estuarine environment from streets and roads of urban areas, as it is used in automobile manufacture at an increasing rate (Gray, 2000). Urban run-off loading can contain between 10 – 50 µg Cr / L (Shepherd et al., 2006).

Cu enters the estuarine environment from the bedrock and sediment composition of the estuary which may be copper enriched from its bedrock source e.g. limestone and sandstone (GSI, 2005). Anthropogenic sources of Cu include sewage sludge (Gray, 2000), contamination from quarry tailings (Clarke, 1997) and notably from antifouling paints from ships. Some antifouling paints contain up to 50g of copper per litre (Kennish, 1994). Cu levels in Restronguet Sound, UK, exceeding 2500 ppm Cu were close to mining and quarrying facilities (Bryan et al., 1985). Near the previously mentioned Los Angels Outfall, levels reach 940 ppm Cu (Mason & Simkiss, 1982). Urban runoff concentrations can range from 10 - 100 µg Cu / L (Bibby & Webster-Brown, 2005; Shepherd et al., 2006).

Ni is introduced into estuarine ecosystems through various routes, notably from landfills where Ni-Cd batteries accumulate, breakdown and leach into aquatic systems (Gray, 2000). Ni is used in steel and other alloys, electroplating and in batteries, (Ward, 1984). In Cork Harbour, Ireland, levels range from 14 – 20 ppm Ni because of the presence of a steel plant (Berrow, 1991). Fossil fuels are rich in Ni, and combustion of oil and coal results in a significant contribution to atmospheric deposition. Long Island Sound, US, records levels of 33 ppm Ni, This is in direct line from the major air pollution centre of New York, (Larsen et al., 1992). But the major input of Ni to the estuarine environment is by river. Most of the nickel is particulate and there is heavy deposition in estuaries so that dredgings from harbours are often heavily contaminated (Clarke, 1997). Urban run-off loading can contain between 60 – 220 µg Ni / L (Shepherd et al., 2006).

Pb was a major riverine and estuarine contaminant in the 1970's and 80's, but since the introduction of unleaded automobile fuel consumption Pb contamination has reduced dramatically. It enters riverine and estuarine system in particulate form from roads and streets in urban areas (Kennish, 1994). However its retention time in aquatic sediments is becoming more apparent with each new analysis. At certain sites on the Medway Estuary, UK the Pb levels vary greatly, 22 – 1139 ppm Pb (Spencer, 2002). Pb also enters the estuarine environment from sewage sludge (Gray, 2000). The Venice Lagoon, Italy has levels exceeding 300 ppm Pb (Sfriso et al., 1995) while in Los Angeles, US, levels reach 580 ppm Pb near a minor city sewage outlet (Mason & Simkiss, 1982). In the Tagus Estuary, Portugal, levels vary from 0 – 500 ppm Pb in different areas of the estuary. Samples close to the urban centre of Lisbon recorded the highest levels (Cacador et al., 2000). The urban centres around the Ria de Vigo, Spain contribute to the elevated levels in this estuary, as high as 160 ppm Pb has been recorded (Rubio et al., 2000). Most Pb used in compound form is lost to the environment and will enter watercourses and eventually the estuarine ecosystem. Urban runoff Pb concentrations can range from 10 - 100 μg Pb / L (Bibby & Webster-Brown, 2005; Shepherd et al., 2006).

Input of Zn into estuarine systems results from anthropogenic sources as well as from natural background Zn levels from both seawater and bedrock (GSI, 2005). Anthropogenic sources include phosphate fertilisers, automobiles and from quarrying and cement processing (Clarke, 1997). Urban runoff Zn levels from a city of approximately 1 million people can range from 40 - 100 μg Zn / L (Bibby & Webster-Brown, 2005). Zn concentrations in the Restronguet Creek, U.K. reached as high as 2090 ppm Zn. This was in close proximity to a cement quarry and mining region

(Bryan et al., 1989). In Cork Harbour, Ireland, zinc levels reached 120 ppm Zn due to the presence of the Irish Steel Plant (Berrow, 1991). In Port Pirie, Australia levels were extreme, reaching 16,700 ppm Zn. This site is situated near a smelting facility (Ward et al., 1984).

1.4 Research Area – Tolka River and Estuary, Co. Dublin

1.4.1 Geological and Geographical Physicality

The Tolka River originates in north west Co. Meath, its route is primarily over post-glacial tills and gravels, and its subsurface geology is carboniferous limestone and silurian sandstone. This bedrock is rich in metal ores, notably Ni, Pb and Zn (GSI, 2005) and a Pb/Zn mine (Tara Mines, Co. Meath) is located within the Tolka catchment. This bedrock has aquifer properties and is deemed regionally important by the GSI. For a large portion of its course the river is exposed to this bedrock and contributes to recharge of the surrounding aquifer. The quaternary geology of glacial tills and gravels is classified as a locally important aquifer by the GSI (GSI, 2005).

The Tolka River flows south east through Co. Meath and enters north-west Co. Dublin at Blanchardstown. The river then flows through the northern suburbs and inner city and its estuarine zone is on the northern side of Dublin Port, the rivers course is illustrated in Figure 1.1.

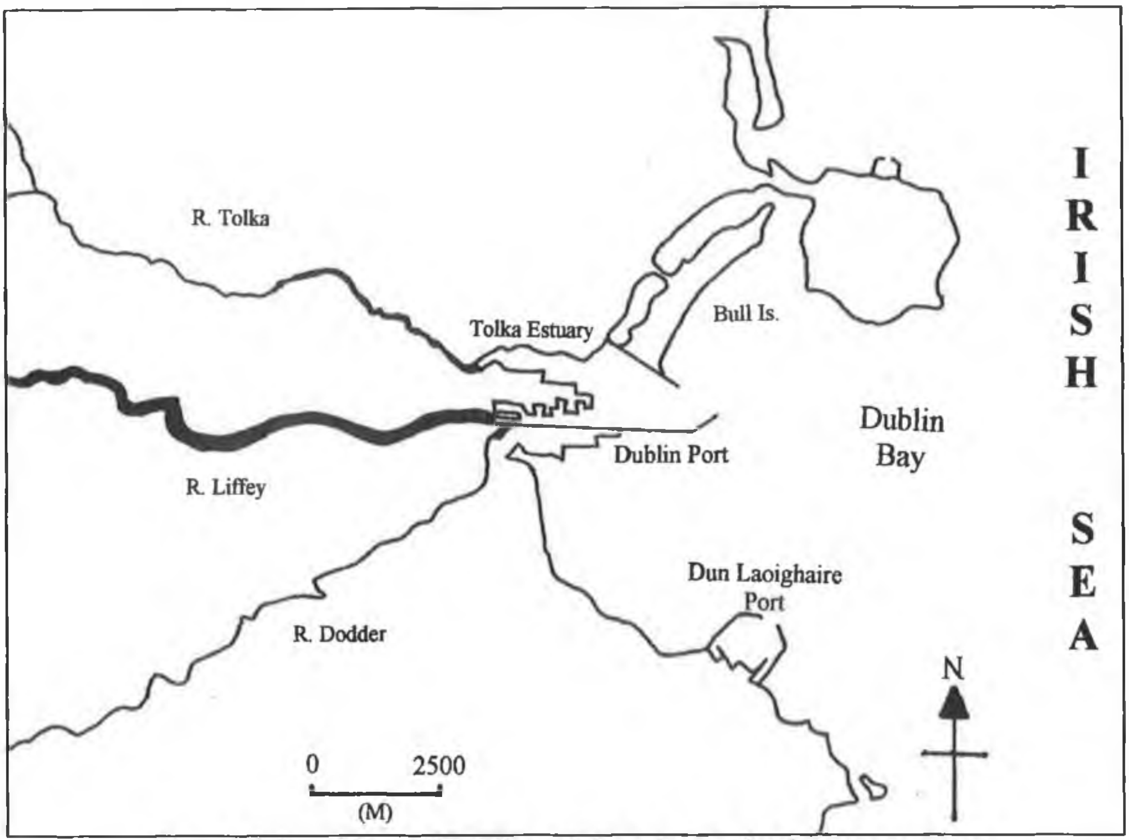


Figure 1.1 Map of Dublin and its primary freshwater sources.

The Tolka catchment is 145.7 km^3, 28.9 km^3 of which is classified as urban. The river course is urban for approximately 12 km. It flows through the suburbs of Tyrrellstown, Blanchardstown, Finglas, Glasnevin, Drumcondra and Fairview before entering the estuary. The estuary is approximately 2 km^2 and has man-made margins. It is located entirely in the urban landscape of Dublin City. It is bounded by the suburbs of Fairview and Clontarf to the west and north, Dublin Port and East Point business park to the south and the Bull Wall and Bull Island to the east. The Tolka River has been noted for its fish kills caused by pollution incidents (Dept. of Environment and Local Government, 1998; Dublin Bay Project, 2001). The Tolka River is prone to flooding and during this project three serious flood events occurred. On the 15th of November 2002 a flood event with a flow rate of 97 m^3 / s (approximately ten times normal flow rate) was recorded at the Botanic Gardens, while on 8th January 2005 a flow rate of 38 m^3 / s was recorded at the Botanic

Gardens (EPA, 2005). Between August 2003 and January 2004 the river regularly recorded flow rates over 30 m^3 / s, and on occasion topped 60 m^3 / s due to a prolonged season of heavy rainfall (EPA, 2005) The Tolka River since early 2003 has been the subject of retaining wall construction and renovation due to these serious flooding events (Dublin City Council, 2005).

The Tolka estuary is subjected to sedimentation from the Tolka River (Jeffrey et al., 1985) but internal circulation between Dublin Ports retaining sea walls also deposits sediment from Dublin's primary river - the Liffey, into the estuary. The enclosed nature of the estuary minimises marine flushing, increases sediment deposition and retention which subsequently lead to metal retention in surface sediment.

1.4.2 Pollution Sources

Dublin is a city of 1.1 million people (Central Statistics Office, 2002) and the urban environment itself is a source of metals to this river system. The latest EPA report on nutrient quality for the Tolka River (EPA, 2003) states that for the sample area the Tolka is seriously polluted, while upstream of the sample area in Co. Meath the Tolka is severely polluted by agricultural run-off. Approximately 65 % of the river course suffers from eutrophication which contributes to fish kills. Dublin Port, the Liffey River and local boating activity on the estuary are also potential sources of various metals to the estuary. According to the Eastern River Basin District Authority (ERBD), the Tolka River and Estuary are at high risk from diffuse pollution through groundwater and urban run-off and from point sources located within its catchment (ERBD, 2005).

1.4.2.1 Dublin Port

The majority of Dublin City's import / exportation occurs through Dublin Port. The port is situated near the city centre between the estuarine zones of two rivers – the Liffey and the Tolka and has an import / export turnover of 23.5 million tonnes, 1.4 million passengers and an estimated 8000 vessels pass through it annually (Dublin Port Authority, 2005). Furthermore, Ni, Pb and Zn ores are exported through Dublin Port and significant concentrations of both Ni, Pb and Zn attributed to ore spillages have been recorded in sediment from the Alexandria Basin (Davoren et al., 2005). Continuous dredging and construction work in estuarine zones has been known to release metals locked in subsurface sediment back into the estuarine aquatic system (Caplat et al, 2005). At Dublin Port, dredging takes place on a continued basis. This potential release of metals may cause deleterious effects on the estuarine ecosystem.

The impact Dublin Port currently has on the estuarine zone of the Liffey River is monitored as it is Dublin's primary river and freshwater source to Dublin Bay. However, the Tolka River is Dublin's secondary river and its estuarine zone to the north of the port is monitored for metal contaminants infrequently: approximately once every five years by Dublin City Council (Dublin Bay Project, 2001). The Tolka estuary has the only significant intertidal mudflats within the combined estuarine zones of the Tolka and Liffey, and it is directly adjacent to a wetland site of international environmental importance, designated by the Ramsar Convention 1971 – Bull Island and its lagoons (Dublin Bay Project, 2001).

1.4.2.2 Sewage Outfalls

Within Co. Meath, the Tolka is utilised by two water treatment plants and has an outfall from a wastewater treatment plant at Dunboyne (ERBD, 2005). Within Co. Dublin, the Tolka catchment area has fourteen sewage overflow outfalls, twelve of which are within the sampling area. Nine of these are located within the river section and three in the estuarine section. On average, these overflow outfalls discharge during periods of rainfall exceeding 2 cm / day (Dublin Bay Project, 2001; ERBD, 2005).

1.4.2.3 Licensed Industrial Discharges

There are seven industrial facilities within Co. Meath licensed to discharge treated effluents to the Tolka River (ERBD, 2005; EPA, 2006). The facilities have Integrated Pollution Prevention and Control Licences authorised by both the EPA and Meath County Council (Meath County Council, 2006). The facilities have licences restricting nutrient loading but allow metal concentrations up to 0.5 mg / L Fe, Al, Mn, Mg and 0.1 mg / L Ag, As, Cd, Co, Cr, Cu, K, Ni, Pb, Se, Sn, Zn and 0.05 mg / L Hg (EPA, 2006). There are fourteen industrial facilities within Co. Dublin licensed to discharge treated effluents to the Tolka River (ERBD, 2005; EPA, 2006). Licences are authorised by the EPA and Dublin City Council (Dublin City Council, 2006). All of these facilities have equivalent licence requirements as facilities in Co. Meath.

1.4.2.4 Unlicensed Discharges

Within the river's urban catchment area there exist fourteen business parks that contain various industrial facilities including metallurgy, electroplating, paintwork and automotive servicing and which are not licensed under IPPC regulations. Surface water discharges from these business parks enter the Tolka River at multiple culverted shore points (ERBD, 2005).

1.4.2.5 Dunsink Landfill

A key source of metals to the Tolka River is caused by groundwater seepage and an inflowing tributary from the closed Dunsink Landfill 200 m north of the river in the north-west of Dublin City. This landfill was opened in the late 1960's in an old gravel quarry and was closed in 2000, however sporadic dumping has taken place on site between 2000 and 2005. Until 1995 no records were kept of what wastes were deposited in this landfill. The landfill has an average depth of 10 m but has a maximum depth of 37 m and is sites directly on limestone bedrock. The landfill has an area of 32 ha. In 2005 the landfill was capped. The landfill currently falls under the jurisdiction of Fingal County Council and Dublin City Council but there are no current environmental sampling procedures set up for the landfill as it did not fall under IPPC licencing agreement with the EPA (Fingal County Council, 2006).

1.5 Sample Area and Sampling Points

Figure 1.1 illustrates the greater Dublin area and its main riverine, estuarine and marine features. Sampling began in August 2002 following an extensive survey of the river and estuary. Initially eighteen sediment sample points were used. Subsequently two more sediment sampling points were added upstream and another point in the Dunsink tributary. Water sampling began in January 2004 initially from five bridges, a further upstream bridge and Dunsink tributary were added to the sampling regime in July and August respectively. A further set of water sampling points for salinity analysis was instigated in September 2004. All sampling points are illustrated in Figures 1.2 to 1.5 (Maps) and Figures 1.6 to 1.36 (Photographs).

🟦	Urban Area
🟦	Industrial Area
🟥	Landfill
🟫	Wetland Area
▭	Bridge
▬	Weir
▬	Sample Bridges 0 - 5
▲	Outfall
○	Sediment Sample Points 1 – 20 & A
●	Salinity Sample Points S1 – S12 & D1 – D4

Key to Figures 1.2 to 1.5

The following four consecutive figures (1.2 to 1.5) illustrate the upper, middle and lower riverine and estuarine zones respectively.

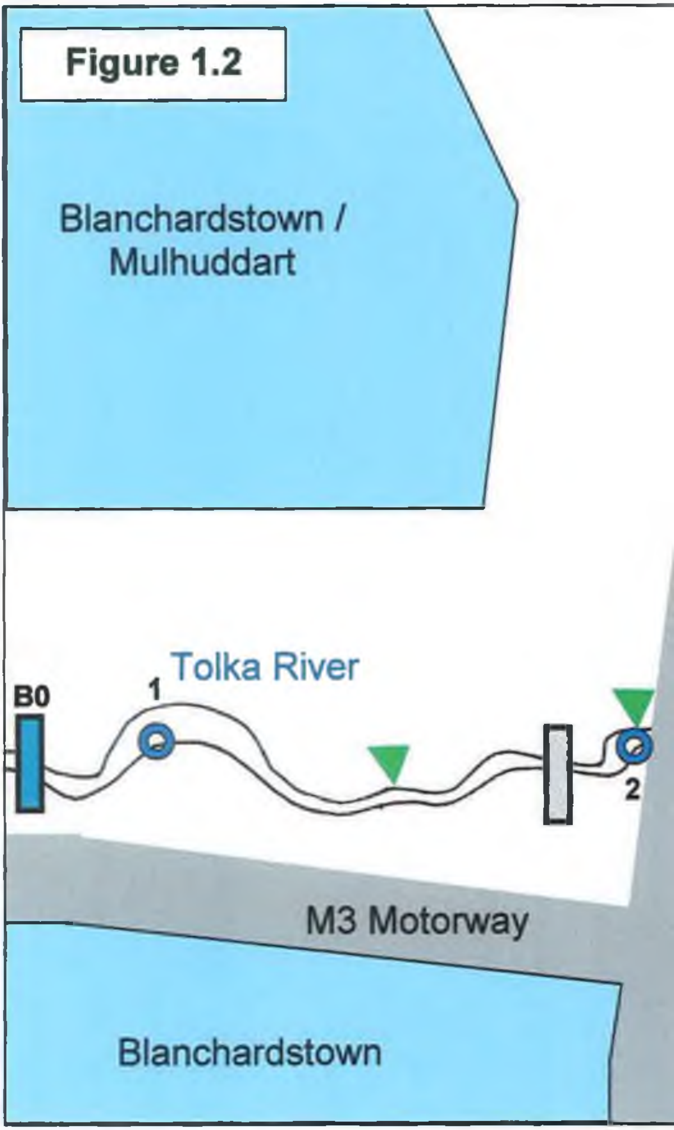
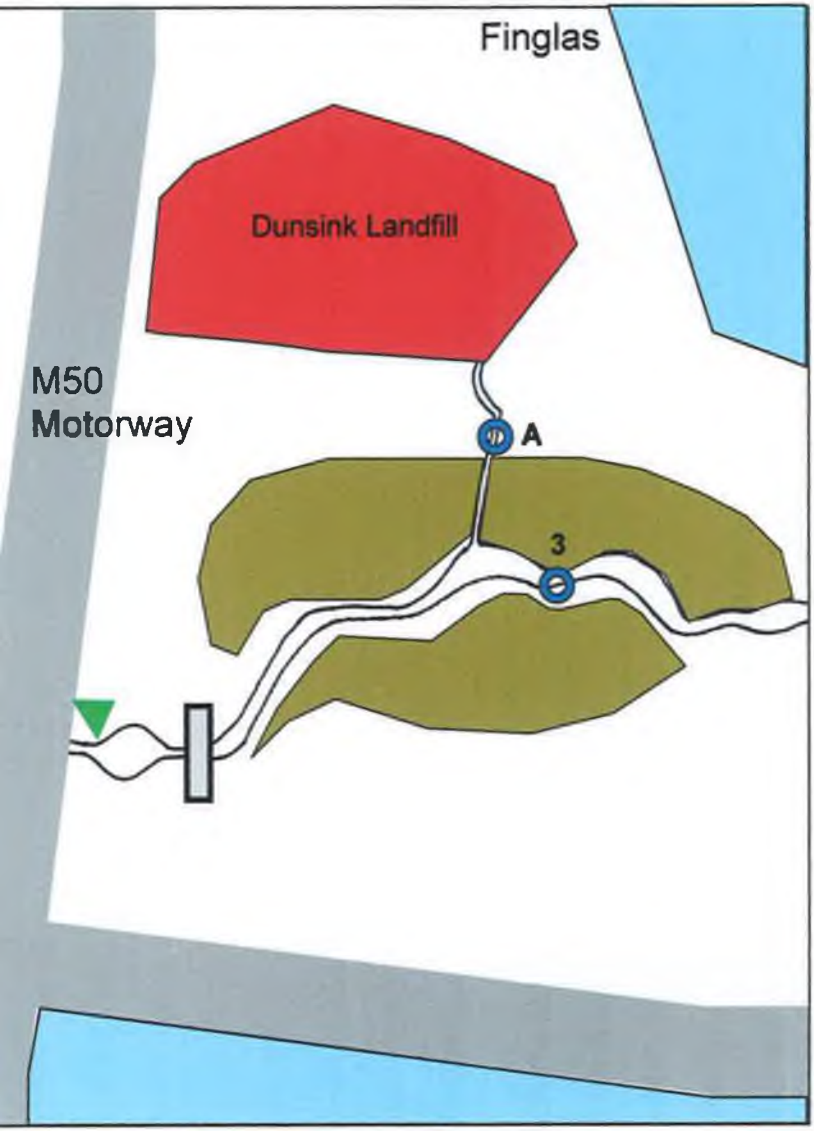


Figure 1.2

Blanchardstown / Mulhuddart
Tolka River
B0
1
2
M3 Motorway
Blanchardstown


Finglas
Dunsink Landfill
M50
Motorway
A
3

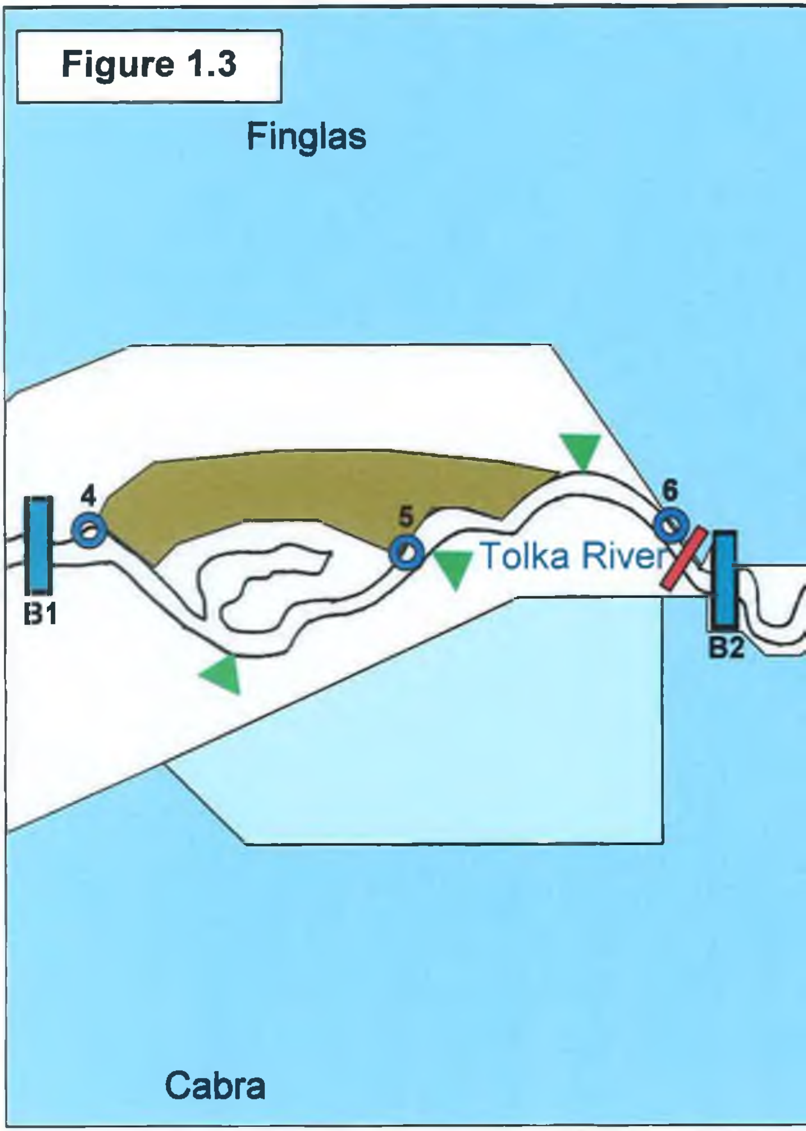


Figure 1.3

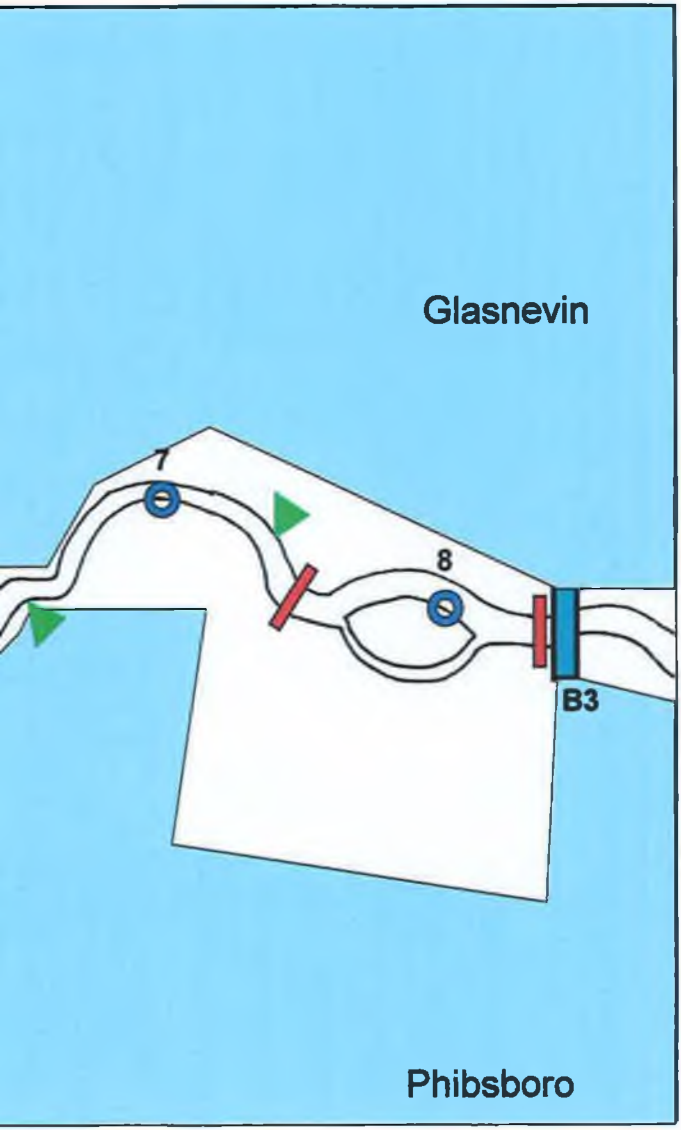
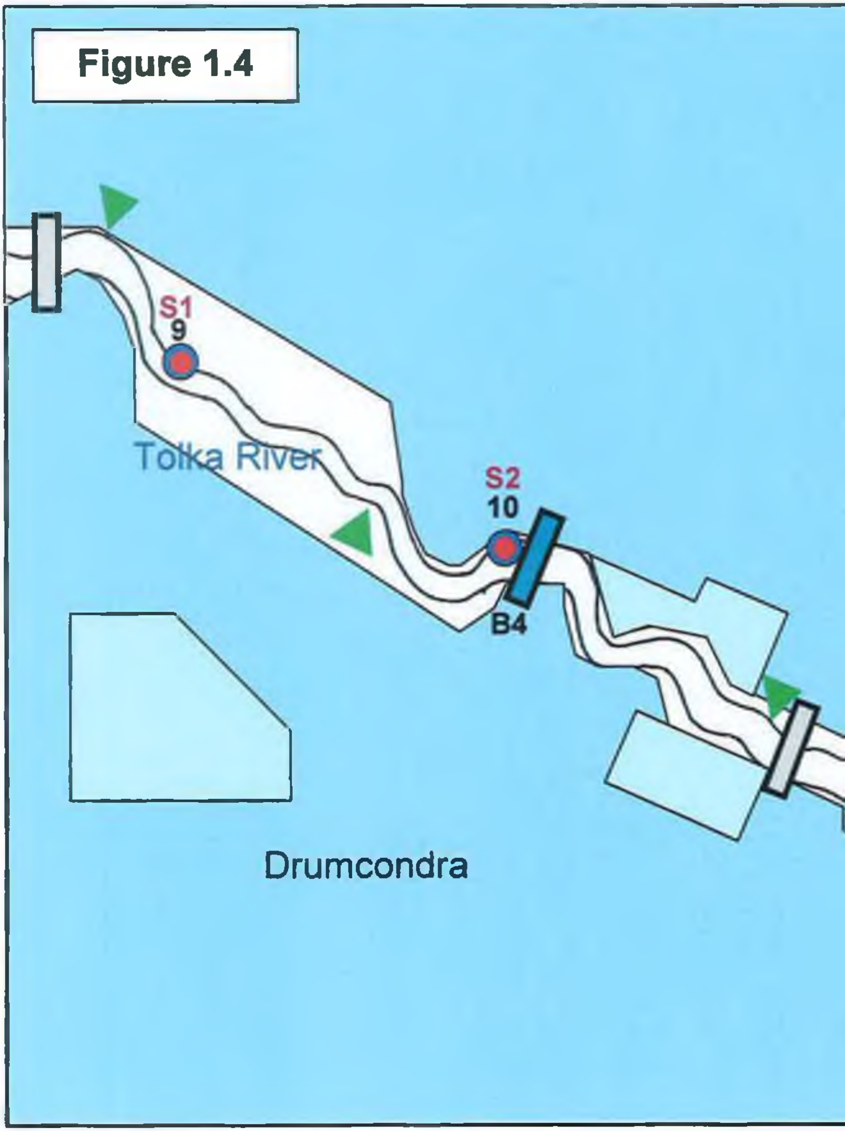

Glasnevin
7
8
B3
Phibsboro

Figure 1.4



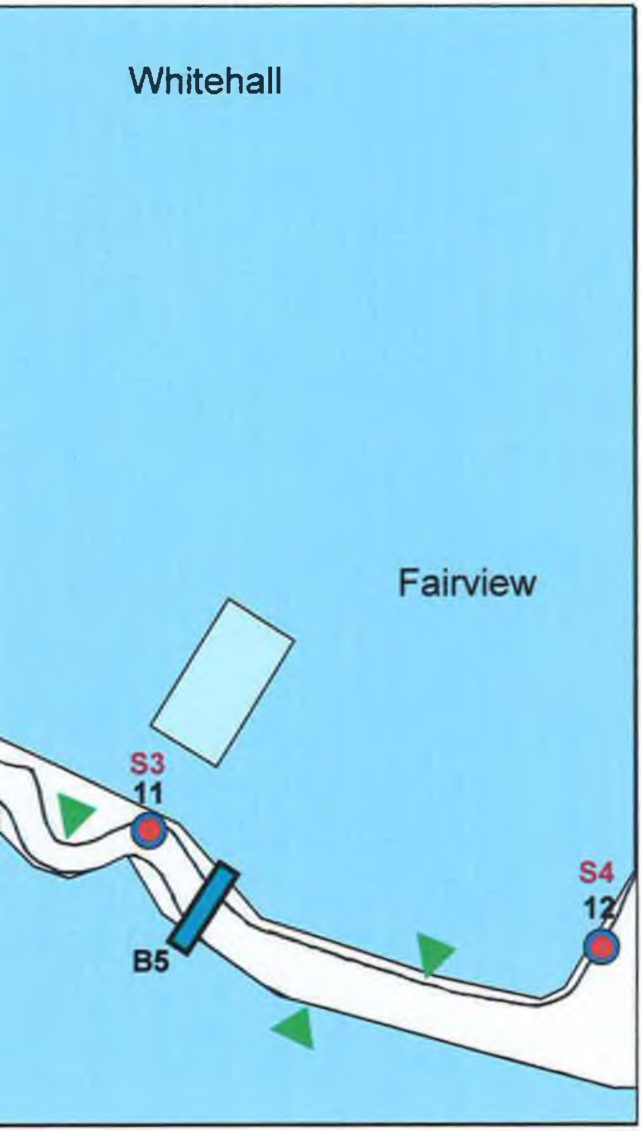

Whitehall
Fairview
S3
11
S4
12
B5

Figure 1.5

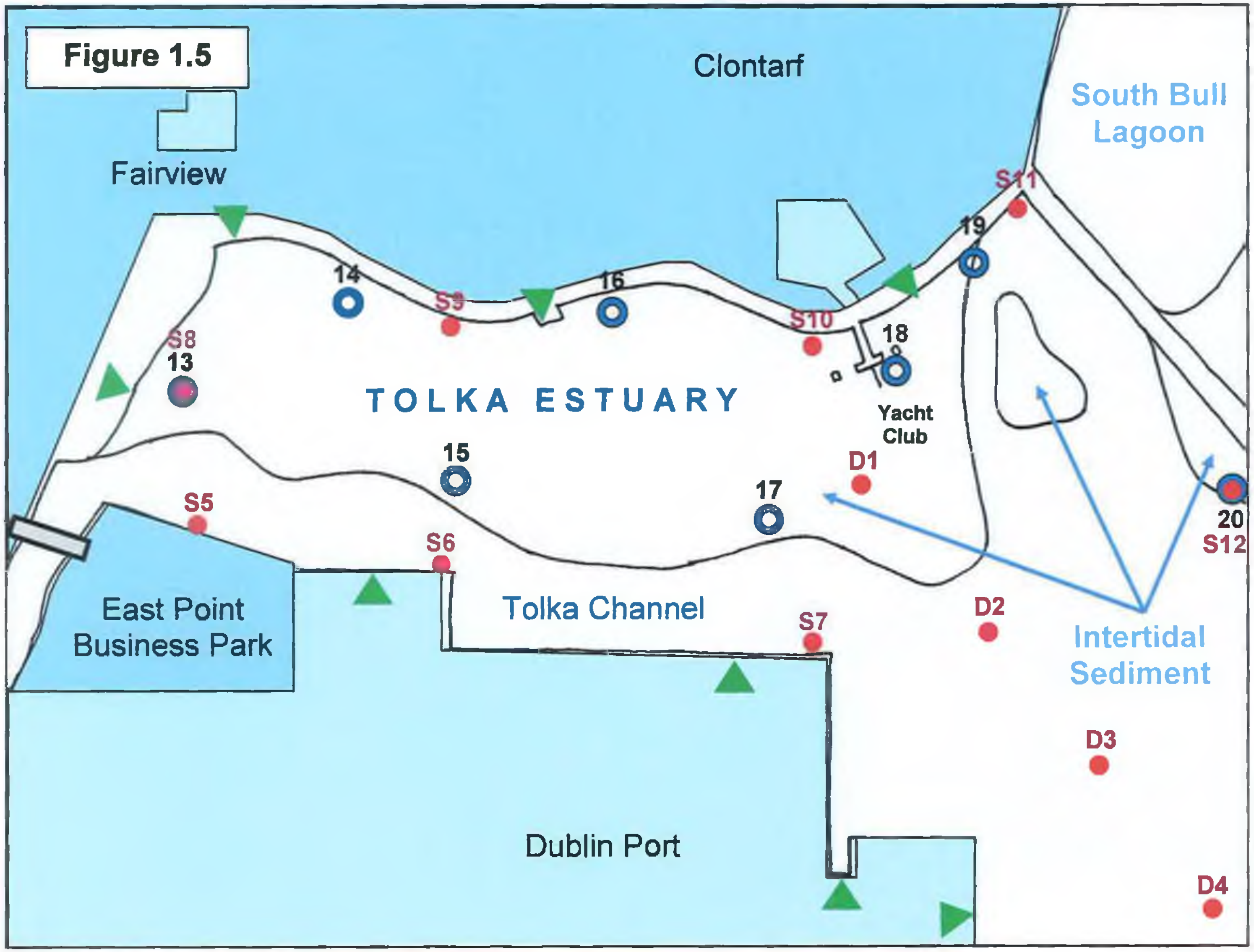

Clontarf
South Bull
Lagoon
Fairview
S11
19
14
S9
16
S10
18
S8
13
TOLKA ESTUARY
Yacht
Club
15
D1
17
S5
S6
20
S12
East Point
Business Park
Tolka Channel
S7
D2
Intertidal
Sediment
D3
Dublin Port
D4

Figure 1.6 River Tolka upstream of Sample Point 1.

Figure 1.7 Sediment Sample Point 1.

Figure 1.8 Bridge 0.

Figure 1.9 Sediment Sample Point 2.

Figure 1.10 River Tolka 10 m upstream of M50 Motorway.

Figure 1.11 Sediment Sample Point 3.

Figure 1.12 Dunsink Stream.

Figure 1.13 Dunsink / Tolka Confluence.

Figure 1.14 Bridge 1 and Sediment Sample Site 4.

Figure 1.15 Sediment Sample Point 5.

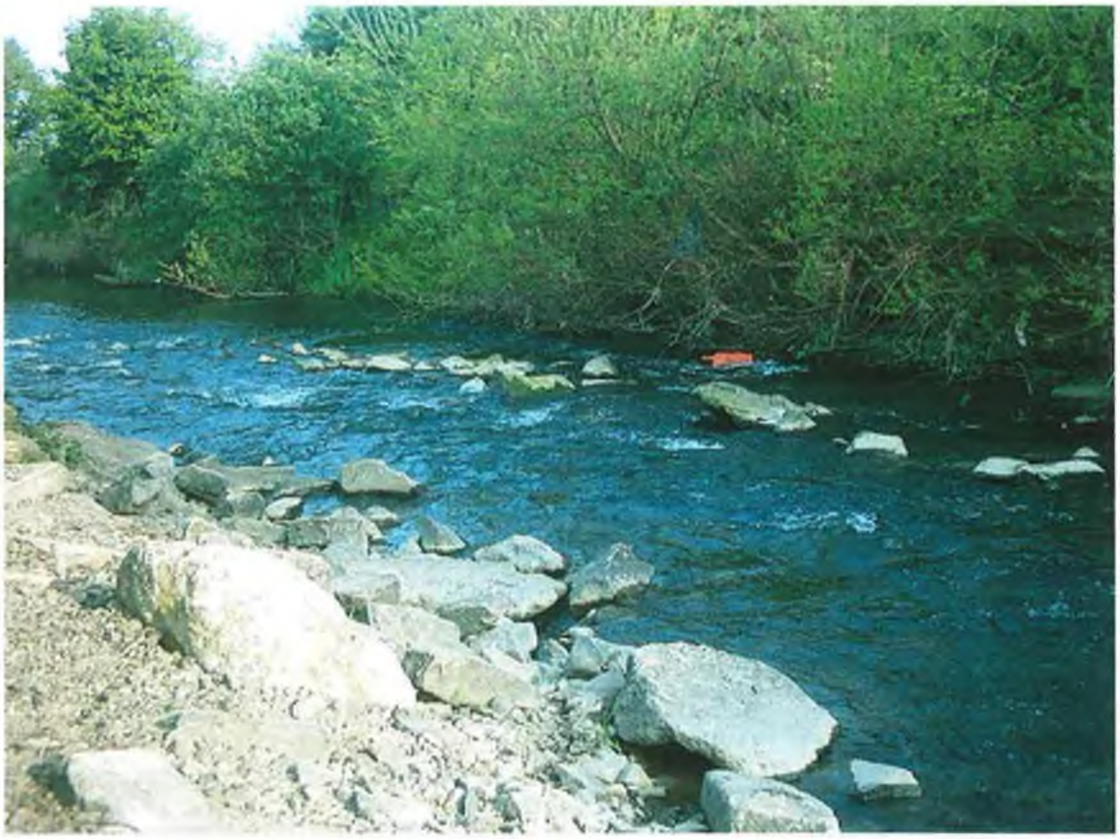


Figure 1.16 Sediment Sample Point 6.

Figure 1.17 Bridge 2.

Figure 1.18 Sediment Sample Point 7.

Figure 1.19 Sediment Sample Point 8.

Figure 1.20 Bridge 3.

Figure 1.21 Sediment Sample Point 9.

Figure 1.22 Sediment Sample Point 10 and Bridge 4.

Figure 1.23 Sediment Sample Point 11 and Bridge 5.

Figure 1.24 River mouth and estuarine silt flats.

Figure 1.25 Sediment Sample Point 12.

Figure 1.26 East Point Business Park and the inner estuarine zone.

Figure 1.27 View of the estuary from its western edge.

Figure 1.28 Sediment Sample Point 13.

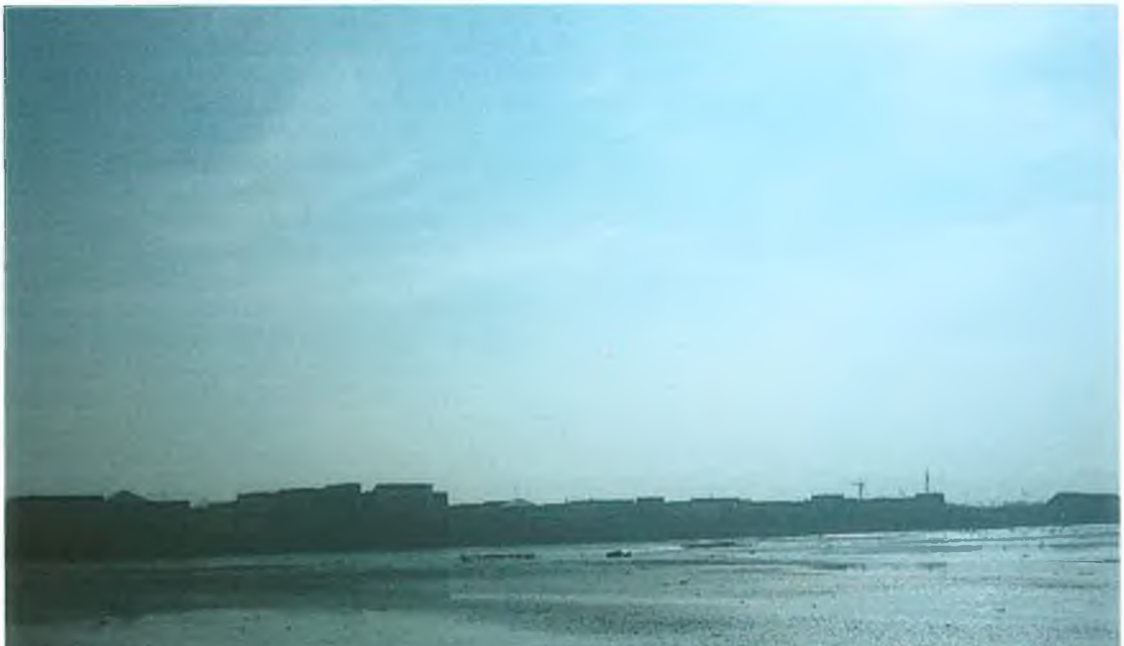


Figure 1.29 Inner Estuary.

Figure 1.30 Sediment Sample Point 14.

Figure 1.31 Sediment Sample Point 15.

Figure 1.32 Sediment Sample Point 16.

Figure 1.33 Sediment Sample Point 17 with Dublin Port in the background.

Figure 1.34 Sediment Sample Point 18 at Clontarf Yacht Club.

Figure 1.35 Sediment Sample Point 19.

Figure 1.36 Sediment Sample Point 20 looking back towards the estuary.

1.5 Statement of Research Objectives

Determination of spatial and seasonal contaminant distribution in riverine and estuarine system is the primary focus of this research. Current research in this area is lacking, and studies concerning seasonal variation in surface sediment are virtually non-existent. Temporal aspects of riverine and estuarine research are predominantly targeted on the water-column as it is the key transport mechanism. Temporal research targeting sediment matrices is generally focused on long time periods and temporality is referred to on an annual basis rather than seasonal or monthly (Kennish, 1994; Little, 2000). However, surface sediment is the site of contaminant retention in riverine and estuarine systems and is rarely utilised to determine seasonal trends. Sampling over thirty months at twenty sediment sample points for contaminants and environmental parameters provides a large database to determine relationships between seasonally variable environmental conditions and introduced anthropogenic contaminants over time. This allows greater understanding of in situ processes affecting contaminants on a short term and long term basis in the riverine and estuarine ecosystem. It also contributes to new understanding of tracking pollution sources and contaminant transportation and retention mechanisms in aquatic ecosystems.

Developing a monthly sampling regime and analytical procedures to be completed by one individual on a limited budget was a supplementary aim to the elucidation of contaminant temporal variation. The EPA provided funding for this research specifically for the development of standard sampling and analytical procedures to regulate riverine and estuarine pollution assessment (EPA, 2000). Polarographic techniques have the potential for cost efficient and fast multi-component analyses compared to expensive gas chromatography analysis or slower atomic adsorption spectrophotometry (Buggy & Tobin, 2003). As an addition to the optimisation of sampling and analytical procedures, creation of a simple predictive model for surface sediment contamination would be utilised as a research aid. This allows for month to month comparison with surface sediment contaminant concentrations predicted by the model and actual sampled results. This can assist in determination of variable pollution loading and pollution incidents.

Ultimately the aim of this research is to contribute greater knowledge regarding seasonally variable aquatic systems through the improvement of temporal sampling, analysis and assessment, and subsequently the elucidation of contaminant introduction, transportation, accumulation, retention and reduction mechanisms within riverine and estuarine aquatic networks.

METHODOLOGY

Standard sampling and analysis methods were utilised to design the initial sampling regime. These methods were subsequently modified to adapt to monthly sampling and a strict month long analysis regime. The introduction of cheaper, faster and less complicated sampling and analytical techniques allowed for rapid sampling and analysis by one person from start to finish rather than separate individuals completing sampling phase, laboratory phase and data interpretation phase. A single individual can thus complete the entire procedure solely, more rapidly and at a minimum cost.

Climatic environmental data was supplied by Met Eireann from their Dublin Airport Weather Station.

2.1 Sediment Sampling

Sediment was sampled at thirty-day intervals at each site over a thirty-month period. Sampling took place over a six-hour period. Standard sampling methods as defined by the Irish Estuarine Research Group (IERP) were utilised (Jeffrey et al., 1985). Sediment from the surface oxygenated layer was sampled. Visual identification of the oxic layer was sufficient for this sampling mode. Rivers and estuaries that exhibit stable sediment assemblages have an upper oxygenated surface layer that has a significantly paler colour than deoxygenated layers below, at the oxic / anoxic interface sediment has a distinctive dark grey / black colour and a strong odour of sulphur dioxide (Loring & Rantala, 1992; Birch & Taylor, 1999; Feng et al., 2002). The time of year determines the depth of oxygenation. Winter layer was approximately 100 mm deep while summer usually varied between 20 - 50 mm. In the riverine system it was not possible to use a quadrate due to river channel walls. Here sediment was sampled at the river edge. The pH of sediment porewater was measured in situ using a Hanna (HI 98127 PHEP 4 WP) pH tester. A 1 m^2 quadrate (semi-rigid polyethylene square boundary frame) was used to mark the boundary of sampling at the site. All surface sediment was sampled within this area using a Teflon coated plastic spatula. Approximately 1 kg wet weight of sediment from each sample point was placed in acid washed polythene vacuum-sealed bags and transported to the laboratory at 4°C.

2.2 Sediment Pre-treatment

Sediment was dried at 105°C for 48 h to remove water content. After drying sediment was disaggregated and sieved (Loring & Rantala, 1992). Sediment was stored at 40°C in acid washed polythene vacuum-sealed bags. Sediment size was graded by sieving with an agitating sieve tower over a six-hour period with the following sieve ranges; >500 µm, 500 - 250 µm, 250 - 125 µm, 125 - 63 µm and <63 µm. Upon consultation with the Marine Institute of Ireland sediment with a grain size of <63 µm sieve was utilised for metal digestion and organotin extraction. Sample variance was substantially reduced by analysing this fine-grained fraction of sediment to minimise the confounding effects of variable grain size (Birch & Taylor, 1999). Assessment of the <63 µm is standard practice in estuarine assessment (Jeffrey et al., 1985; Loring & Rantala, 1992; Yang et al., 1998). While sediment size compartment analysis can reveal contamination that is specific to certain grain sizes, generally 90 – 95 % of metal and organometal contamination is bound to the <63 µm fraction (Thompson et al., 1984; Loring & Rantala, 1992; Yang et al., 1998; Gerringa et al., 2001; Caccia et al., 2003).

2.3 Water and SPM Sampling

A water sampler designed and constructed by technical staff at DCU was utilised for water column sampling. The sampler was lowered from the centre of a bridge into the water column and a 250 ml sample of water was taken at approximately 40 cm below surface level. A dropped weight closed the lid and ensured that the sample remained free of surface debris upon removal from the water column. Four samples were taken at each point and combined as a 1 L sample. Samples were returned to the laboratory at 4°C. Samples were subsequently filtered by vacuum filtration through preweighed Whatman No. 1 filter paper. The filter papers were dried at 40°C and SPM concentrations determined by reweighing.

River speed was assessed by a basic method. A flotation device was introduced to the river and its speed was measured against a 10 m stretch of river bank. River depth was measured from bridges using a graded cable and weight. River width was measured using a tape measure.

SPM deposition rate was assessed utilising a deposition sampler designed and constructed by technical staff at DCU. The sampler measured an area of 30 x 30 cm and had an elevated edge of 3 cm on three sides. The sampler was fixed to the river bed at Site 4 (located in a straight stretch of river downstream from a bridge) for a period of 24 hours, three to four days a month. All sediment trapped by the sampler was dried and weighed to provide an average monthly deposition rates.

Sediment density was measured by volume displacement. Sediment porosity was measured by filtration (Loring & Rantala, 1992).

2.4 Porewater Sampling

Porewater was extracted from a second saturated sediment sample of 1 kg. Sediment porewater was removed from the sediment matrices by vacuum filtration.

2.5 Organic Matter Titration

A Walkey-Black titration was utilised for readily oxidizable organic carbon (Jackson, 1958; Loring & Rantala, 1992). This method differentiates humic matter with anthropogenic sources of organic carbon such as coal and graphite. This titration provides excellent agreement with a LECO elemental analyser combustion method for organic matter (Gaudette et al., 1974). All reagents were supplied by Sigma-Aldrich Ireland Ltd.

2.6 Salinity

A standard salinity testing kit ($AgNO_3$ titration to determine chlorinity and subsequently salinity) was utilised for all salinity results (Loring & Rantala, 1992). Salinity testing kit and standard seawater reference samples were supplied by Sigma-Aldrich Ireland Ltd.

2.7 Metal Acid Digestion

A HNO_3 digestion was used for the metal analysis (Jeffrey et al., 1985; Kramer et al., 1995; Groengroeft et al., 1998). This was a cost effective digestion in comparison to the more expensive aqua regia and HF digestions (Groengroeft et al., 1998). 0.1 g of sediment was placed in a digestion tube with 20 ml 65% HNO_3 and contacted for 48 h at room temperature. Samples were subsequently heated to 100° C for 2 h. Another 10 ml 65% HNO_3 was then added at 150° C for 1 h to reduce the volume to approximately 1 ml. Samples were cooled for 24 h at room temperature, filtered through Whatman No. 1 filter paper and made up to 25 ml with deionised water from an Analyst HP, Purite Select Deioniser (Purite Ltd., Leeds, UK). For SPM, the filter paper and associated desiccated SPM particles were digested together under the same conditions. Control samples including procedural blanks, matrix spikes (5 samples of contaminant free estuarine sediment spiked with 10 ppm Cd, Cr, Cu, Ni, Pb and Zn) and certified reference materials supplied by the Marine Institute of Ireland, were analysed to establish that the methods used were providing valid results. All samples were run in triplicate and the results given in the study are mean values. Mean recovery rates and SD's for the six metals were; Cd - 94% ± 2.8% (*n*=5); Cr – 92% ± 3.1% (n=5); Cu - 97% ± 2.5% (*n*=5); Ni – 94% ± 2.5%; Pb - 95% ± 3.2% (*n*=5) and Zn - 97% ± 2.3% (*n*=5).

2.8 Tributyltin Extraction

A recently developed organotin extraction was utilised for tributyltin (Bancon-Montigny et al., 2003; de Mora et al., 2003; Munoz et al., 2004). 10 g of dried sediment was contacted with 10 ml glacial acetic acid, 30 ml of methanol and 60 ml of sodium acetate buffer 0.2 M, adjusted to pH 5.3. Samples were agitated for 24 h followed by 180 min in an ultra-sonic bath and centrifuged at 3000 rpm for 30 min. Control samples including procedural blanks, matrix spikes (10 samples of contaminant free estuarine sediment spiked with 10 ppb TBT) and certified reference materials supplied by the Marine Institute of Ireland, were analysed to establish that the methods used were providing valid results. All samples were run in triplicate and the results given in the study are mean values. The mean recovery rate for TBT (91% with an SD of ± 3.2% (n=10)) was similar to rates reported by Munoz et al., 2004 (94% with an SD of ± 4.8% (n=6)).

2.9 Polarography

2.9.1 Introduction to Polarography

Voltammetry refers to the measurement of current that results from the application of potential. Unlike potentiometry measurement which employs only two electrodes, voltammetric measurements utilize a three electrode electrochemical cell. The use of three electrodes (working, auxiliary and reference) along with the potentiostat instrument allow accurate application of potential functions and the measurement of the resultant current. The different voltammetric techniques that are used are distinguished from each other primarily by the potential function that is applied to the working electrode to drive the reaction, and by the material used as the working electrode (Smyth & Vos, 1992; Ghoneim et al., 2000).

Polarography is a voltammetric measurement whose response is determined by combined diffusion/convection mass transport. Polarography is a specific type of measurement that falls into the general category of linear-sweep voltammetry where the electrode potential is altered in a linear fashion from the initial potential to the final potential. As a linear sweep method controlled by convection/diffusion mass transport, the current vs. potential response of a polarograph experiment has the typical sigmoidal curve (Smyth & Vos, 1992; Achterberg et al., 2003).

Polarography is a voltammetric technique that uses a dropping mercury electrode (DME) as the cathode. The DME is a narrow silica glass tube through which mercury passes and drops are dislodged from the end. The polarographic cell consists of the DME as the cathode, a large non-polarisable anode and a solution sample for analysis. A potential is applied to the DME, ions or molecules in the sample exchange electrons at the electrode. Oxidation or reduction occurs at the electrode resulting in current consumption or production at the indicator electrode. The greatest advantage of mercury electrodes is the fact that new drops can be readily formed and this cleaning process removes problems that could be caused by contamination as a result of previous analysis. The extensive cathodic potential range of mercury electrodes (from +0.4 V to -2.5 V according to specific electrolyte solution) is also an advantage. Plotting a graph of current versus potential produces a sigmoid curve (Crow, 1969; Ghoneim et al., 2000; Achterberg et al., 2003).

There are a number of limitations to the polarography experiment for quantitative analytical measurements. Because the current is continuously measured during the growth of the Hg drop, there is a substantial contribution from capacitive current. As the Hg flows from the capillary end, there is initially a large increase in the surface area. As a consequence, the initial current is dominated by capacitive effects as charging of the rapidly increasing interface occurs. Toward the end of the drop life, there is little change in the surface area which diminishes the contribution of capacitance changes to the total current. At the same time, any redox process which occurs will result in faradaic current that decays approximately as the square root of time (due to the increasing dimensions of the Nernst diffusion layer). The exponential decay of the capacitive current is much more rapid than the decay of the faradaic current; hence, the faradaic current is proportionally larger at the end of the drop life (Smyth & Vos, 1992).

Polarography is a significantly cheaper form of analysis for environmental samples. Equipment costs in the region of €10 – 20 K in comparison to more expensive Graphite Furnace Atomic Adsorption Spectrophotomoters and Liquid Chromatography Mass Spectrometers ranging from € 50 – 250 K (Princeton Applied Research, 2005). There are three overhead costs – nitrogen, mercury and electrolyte solutions. Electrolyte solutions can be bought in bulk and are inexpensive. All electrolyte solutions utilised in this project cost less than €0.50 per litre (Sigma-Aldrich, 2005).

2.9.2 Differential Pulse Polarography

Pulse polarographic techniques are chronoamperometric and are based in a sampled current potential step experiment (Mann & Barness, 1970). After the potential is stepped, the charging current decreases rapidly (exponentially), while the faradaic current decays more slowly. Differential Pulse Polarography is a polarographic technique that uses a series of discrete potential steps rather than a linear potential ramp to obtain the experimental polarogram. Many of the experimental parameters for differential pulse polarography are the same as with normal pulse polarography including accurately timed drop lifetimes, potential step durations of 50 – 200 ms at the end of the drop lifetime. Unlike Normal Pulse Polarography, however, each potential step has the same amplitude, and the return potential after each pulse is slightly negative of the potential prior to the step (Ghoneim et al., 2000; Achterberg et al., 2003).

The Differential Pulse Polarogram is obtained by measuring the current immediately before the potential step, and then again just before the end of the drop lifetime. The analytical current in this case is the difference between the current at the end of the step and the current before the step (the differential current). This differential current is then plotted vs. the average potential (average of the potential before the step and the step potential) to obtain the differential pulse polarogram. Because this is a differential current, the polarogram obtained is peak shaped. Differential Pulse Polarography has even better ability to discriminate against capacitive current because it measures a difference current (helping to subtract any residual capacitive current that remains prior to each step). Limits of detection with Differential Pulse Polarography are 10^{-8} – 10^{-9} M while AAS is 10^{-5} – 10^{-7} M and HPLC 10^{-8} – 10^{-10} M (Smyth & Vos, 1992; Ghoneim et al., 2000).

2.9.3 Polarograph Optimisation

In this project optimisation of the polarograph took approximately six-months for the determination of a solution containing four metals (Cd, Cu, Pb and Zn). The original recommended electrolyte solution was 2M HCl. However, when more than two metals were combined in solution the interference decreased the sensitivity of the method. Upon further consultation with Princeton University (http://www.princetonappliedresearch.com) a new electrolyte solution was devised for multi-metal samples.

AAS was used to validate the polarographic methods of metal analysis. Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn were analysed by AAS to ensure the accuracy and precision of the Polarograph. The metals were analysed using a Perkin Elmer 3100 Atomic Adsorption Spectrophotometer (Perkin Elmer, Nerwalk, Ct., USA), fitted with a single slot burner head, with an air-acetylene flame. Concentrations were determined, after dilution to a suitable concentration, by reference to appropriate standard solutions. No significant difference (> 5 %) was recorded between standard solution concentrations analysed by AAS and by DPP. All comparative tests used metal standards obtained from Sigma-Aldrich Ireland Ltd.

Metal and TBT concentrations were determined using an EG&G model 394 electrochemical trace analyser with a 303A static mercury drop electrode (EG&G Instruments, Princeton Applied Research, CA, USA). Differential Pulse Polarography (pulse amplitude 50 mV) and a hanging mercury electrode (HMDE) were employed for analysis. Standard addition testing was utilised to determine polarograph accuracy. Table 2.1 indicates standard addition analysis. An initial sample of 2 ppm metal was measured followed by four sequential additions of 2 ppm metal to the existing electrolyte solution sample in the polarographic cell. This process took approximately thirty minutes per metal. A final sample of 10 ppm metal was measured in comparison to the cumulative sample. Each standard addition test was completed five times. Standard addition testing revealed that the cumulative additional process had a mean (10 ppm) result of 95.1 ± 2.5 % compared to the singular (10 ppm) sample. This implied that degradation of the sample over time was minimal and that the polarograph had good accuracy. All standard addition tests used metal standards obtained from Sigma-Aldrich Ireland Ltd.

Metal mg / L	**Cumulative Standard Addition Samples (nA)**					**Singular Samples (nA)**
	2 ± SD	**4 ± SD**	**6 ± SD**	**8 ± SD**	**10 ± SD**	**10 ± SD**
Cd	96 ± 4	198 ± 8	326 ± 8	436 ± 7	556 ± 12	572 ± 6
Cr	125 ± 8	243 ± 4	372 ± 10	509 ± 5	622 ± 9	635 ± 4
Cu	136 ± 4	287 ± 10	402 ± 34	518 ± 26	656 ± 8	676 ± 14
Ni	84 ± 6	162 ± 4	232 ± 4	312 ± 14	398 ± 12	441 ± 8
Pb	56 ± 7	96 ± 8	142 ± 13	173 ± 24	206 ± 22	220 ± 5
Zn	66 ± 3	95 ± 4	146 ± 24	176 ± 21	201 ± 24	211 ± 4

Table 2.1 Standard Addition Testing – Cumulative Addition vs. Singular Sample, SD = Standard Deviation of multiple samples (n = 5).

2.9.4 Metal Analysis

Samples were purged with N_2 for 240 s. The solutions were then scanned from 0.0 to -2.0 V with a scan rate of 4 mV/s and scan increment of 4 mV (Ghoneim et al., 2000). The metal electrolyte solutions, recommended peak wavelengths and actual peak wavelengths used are shown in Table 2.2. Acid digested samples required minor variations on electrolyte solution pH for clear peak definition and this is responsible for shifts in peak wavelength (Buggy & Tobin, 2003). Figure 2.1 illustrates standard curves obtained from multiple metals in one solution. All reagents were supplied by Sigma-Aldrich Ireland.

Metal	**Supporting Electrolyte**	**pH**	**Princeton E ½ V**	**DCU E ½ V**
As(III)	1 M HCl	1.8	-0.430	-0.392
Cd(II)	0.2 M NH_4 Citrate	3.2	-0.620	-0.560
Co(II)	1 M NH_3 – 1 M NH_4Cl	2.5	-1.220	-1.410
Cr(III)	0.2 M KSCN	2.9	-0.850	-0.786
Cu(II)	0.2 M NH_4 Citrate	3.2	-0.070	-0.008
Mn(II)	1 M NH_3 – 1 M NH_4Cl	2.5	-1.660	-1.086
Ni(II)	I M NH_3 – I M NH_4Cl	2.5	-1.000	-1.212
Pb(II)	0.2 M NH_4 Citrate	3.2	-0.450	-0.404
Zn(II)	0.2 M NH_4 Citrate	3.2	-1.040	-1.020

Table 2.2 Electrolyte solution guideline wavelengths (Princeton Applied Research, 2005) and operating wavelengths.

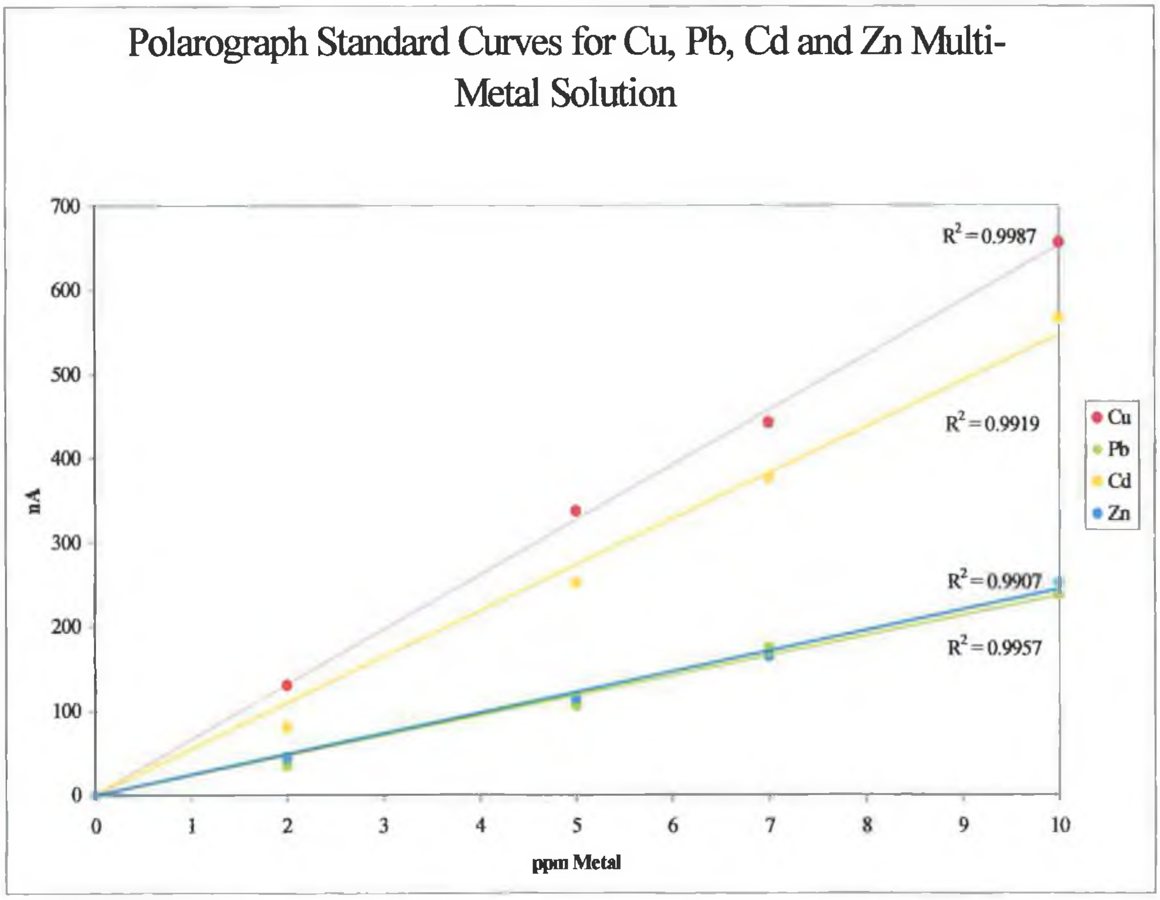


Figure 2.1 Standard Curves for Cu, Pb, Cd and Zn in Ammonium Citrate at pH 3.2 utilising Differential Pulse Polarography.

Polarographic analysis precision was determined using metal and TBT standards supplied by Sigma-Aldrich Ireland and standard reference procedural sediments supplied by the Marine Institute of Ireland. The Marine Institute utilises QUASIMEME (Quality Assurance of Information of Marine Environmental Monitoring) materials for laboratory proficiency testing. The Marine Institute provided a standard sediment sample for determination. Digestions, extractions and polarographic determination were completed and results returned for verification. The mean precision was 95.3% with an SD of ±1.8%. Table 2.3 indicates polarographic determination results compared to the official QUASIMEME standards.

Metal	QUASIMEME Value mg/Kg	DCU Value mg/Kg	DCU SD mg/kg
As	17.19	16.85	0.9
Cd	0.38	0.32	0.7
Cr	89.36	86.9	1.8
Cu	17.50	16.9	2.1
Mn	1003.16	979.2	10.6
Ni	27.81	26.2	3.5
Pb	48.07	47.8	1.7
Zn	148.00	145.3	4.2

Table 2.3 Comparative analysis of QUASIMEME Standards to DCU results, SD = standard deviation of multiple samples (n = 10).

2.9.2 TBT Analysis

A 0.16 M ammonium chloride in 40% ethanol at pH 2.5 electrolyte solution was utilised for TBT determination (White, 2002). Samples were purged with N_2 for 240 s. Solutions were scanned from -0.2 to -1.0 V with a scan rate of 6 mV/s and scan increment of 6 mV. Optimisation of the polarograph resulted in a TBT peak at a half-wave potential of -0.788 mV, a typical TBT polarogram is illustrated in Figure 2.2. TBT polarographic analysis precision was determined using standard reference procedural sediments supplied by the Marine Institute of Ireland. The mean precision was 93.5% with an SD of ± 2.9%.

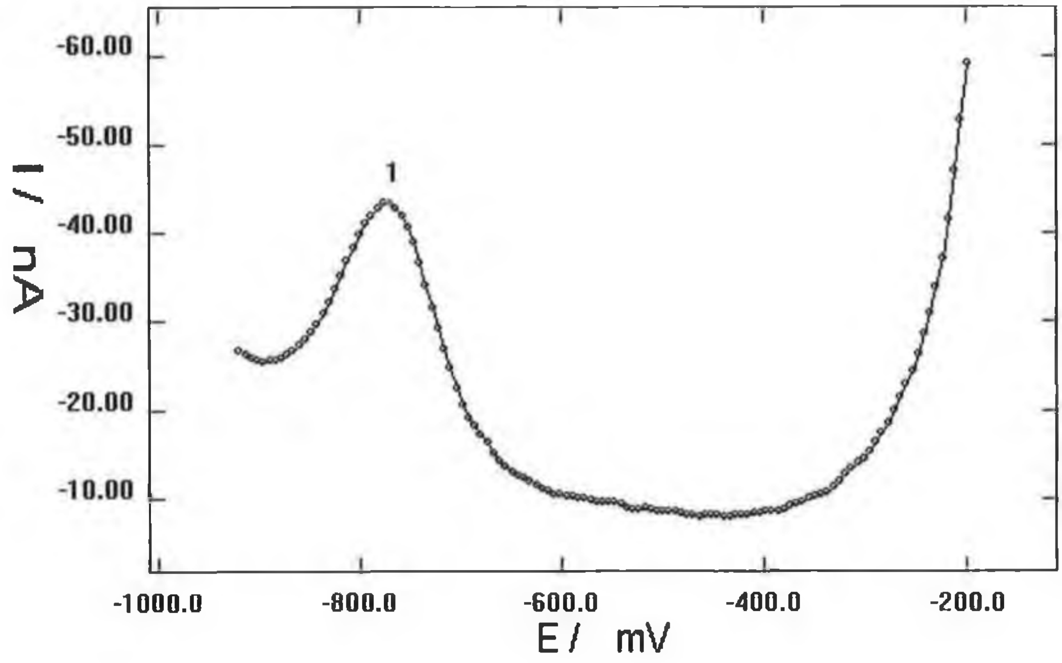


Figure 2.2 Differential Pulse Polarogram of TBT (50 ppb) in 0.16 M Ammonium Chloride in 40 % Ethanol at pH 2.5.

RESULTS

3.1 Sediment Analysis

Sediment was graded each month following drying into three size fractions; 250 - 125 µm, 125 – 63 µm and < 63 µm. Variance from month to month was minimal and did not display seasonal variability in granulometry. For the final sampling in January 2005 a full dry sediment granulometric analysis was completed. Table 3.1.1 indicates the resulting sediment size variation for each site. The riverine section (Sites 1 – 10) sediment was primarily composed of sediment ranging between 500 and 125 µm in diameter, with finer sediments of 63 µm or less forming less than 10% of sediment composition. Estuarine sediment (Sites 11 - 20) was composed primarily of sediment less than 250 µm in diameter, with portions between 125 and 16 µm ranging from 14 % to 50 %.

Site	>500 µm	500 - 250 µm	250 - 125 µm	125 - 63 µm	63 - 32 µm	32 - 16 µm
1	25	18	50	4	2	1
2	26	16	52	3	1	2
3	21	20	53	4	1	1
4	22	23	49	3	2	1
5	28	23	45	2	1	1
6	27	21	46	2	1	3
7	26	20	46	2	2	4
8	25	29	41	3	1	1
9	25	31	37	5	1	1
10	29	32	27	8	1	3
11	22	30	30	12	4	2
12	16	26	40	16	1	1
13	6	28	42	18	4	2
14	4	22	48	17	6	3
15	8	18	34	30	6	4
16	6	16	28	36	9	5
17	2	15	36	36	6	5
18	3	16	40	31	7	3
19	12	22	48	16	1	1
20	16	24	46	10	3	1

Table 3.1.1 Sediment Granulometric Analysis, size distribution as %.

3.2 pH

pH was measured in situ at each site during sampling. pH of the pore water of surface sediment was measured. Spatially there was a distinct pattern of pH levels: riverine sections of the sample network were lower than estuarine levels. pH levels of the river ranged from approximately pH 6.0 – 7.5 while the estuary ranged from pH 7.0 – 8.4, see Figures 3.2.1 to 3.2.5. pH levels in Dunsink Tributary at Site ranged from pH 5.0 to 6.2, see Figure 3.2.6.

pH levels exhibited a minimal temporal distribution over the thirty months of sampling. Generally pH levels were slightly higher in summer months than in winter months in both river and estuary e.g. at Site 7 (Riverine) the following seasonal distribution was observed: October 2002 pH 6.60, March 2003 pH 6.38, August 2003 pH 6.74, November 2003 pH 6.14, June 2004 pH 7.10 and January 2005 pH 6.03, while at Site 16 (Estuarine) the following seasonal distribution was observed: August 2002 pH 7.91, October 2002 pH 6.74, August 2003 pH 8.25, November 2003 pH 7.38, July 2004 pH 8.25 and October 2004 pH 7.81.

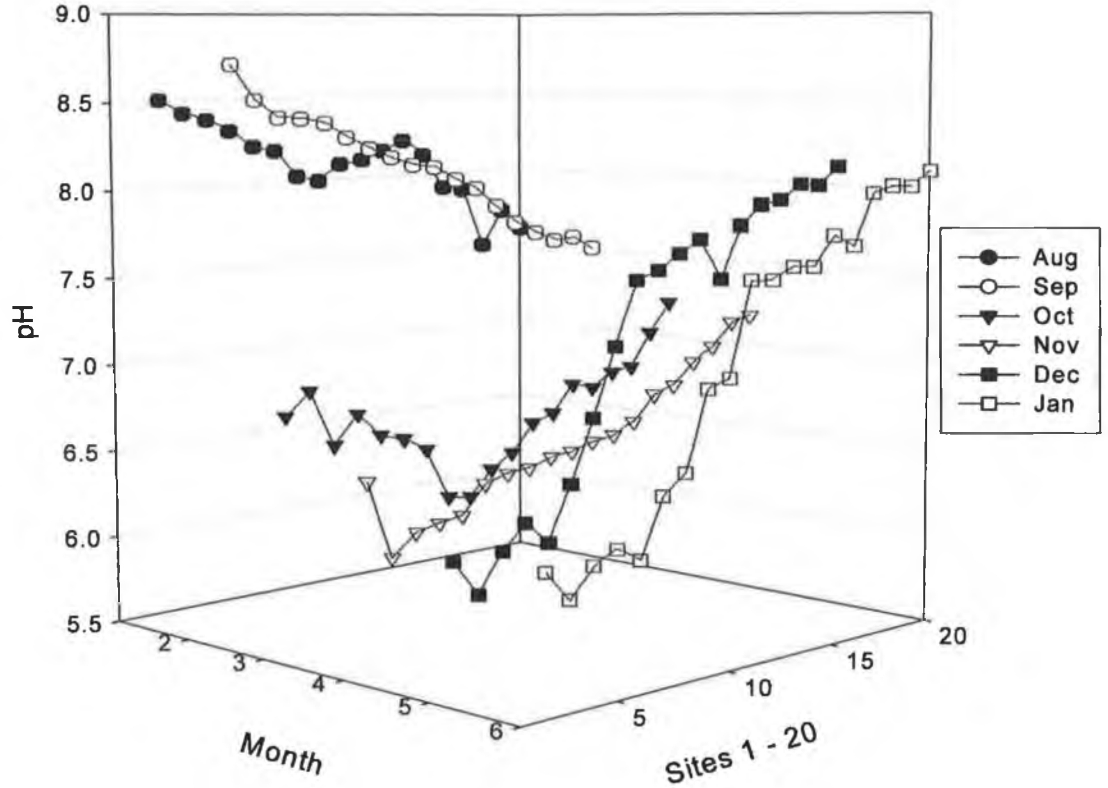


Figure 3.2.1 pH, Sites 1 – 20, August '02 to January '03.

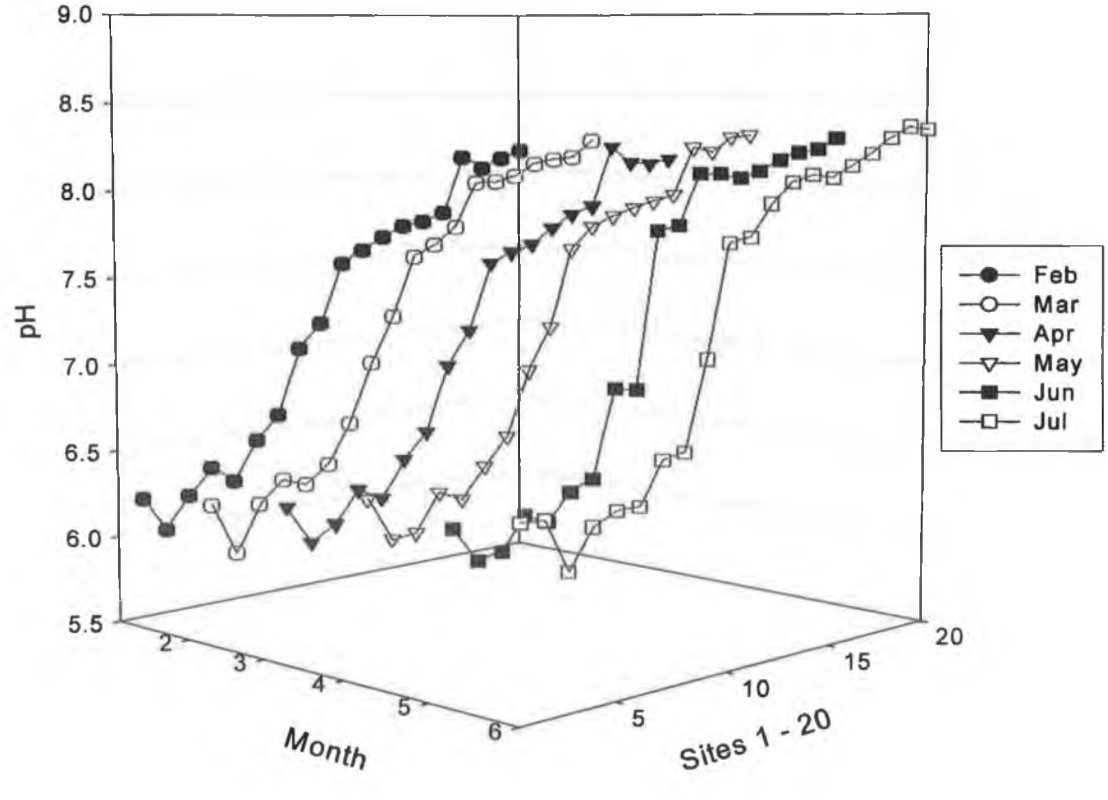


Figure 3.2.2 pH, Sites 1 – 20, February to July '03.

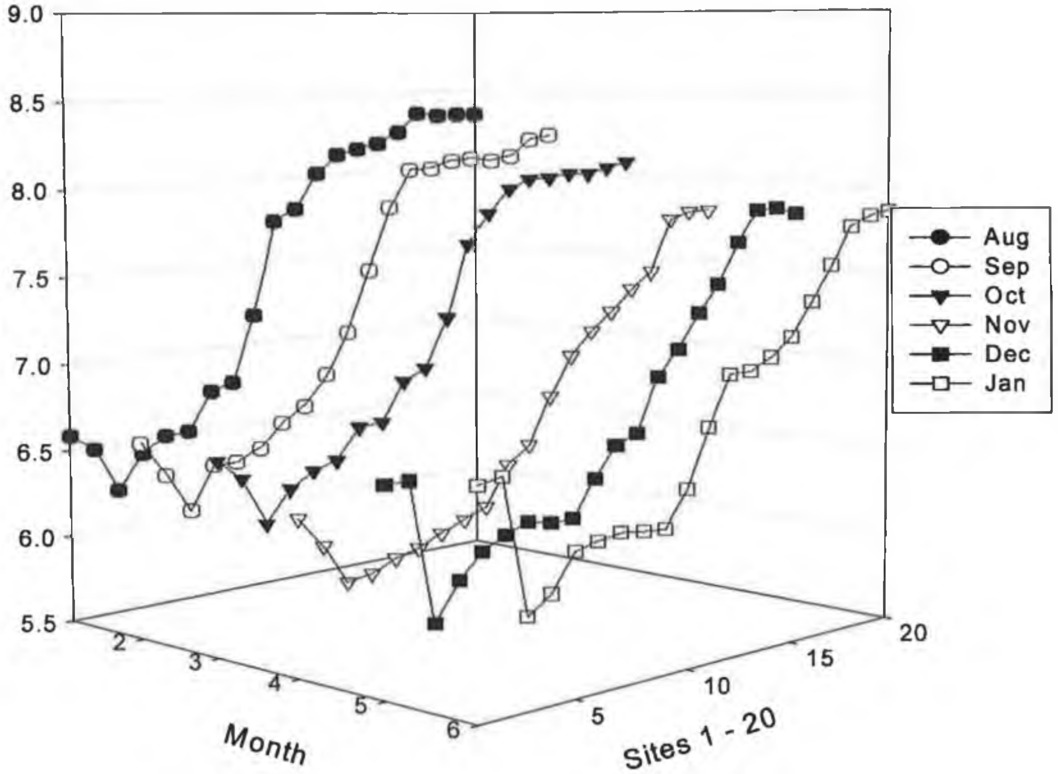


Figure 3.2.3 pH, Sites 1 – 20, August '03 to January '04.

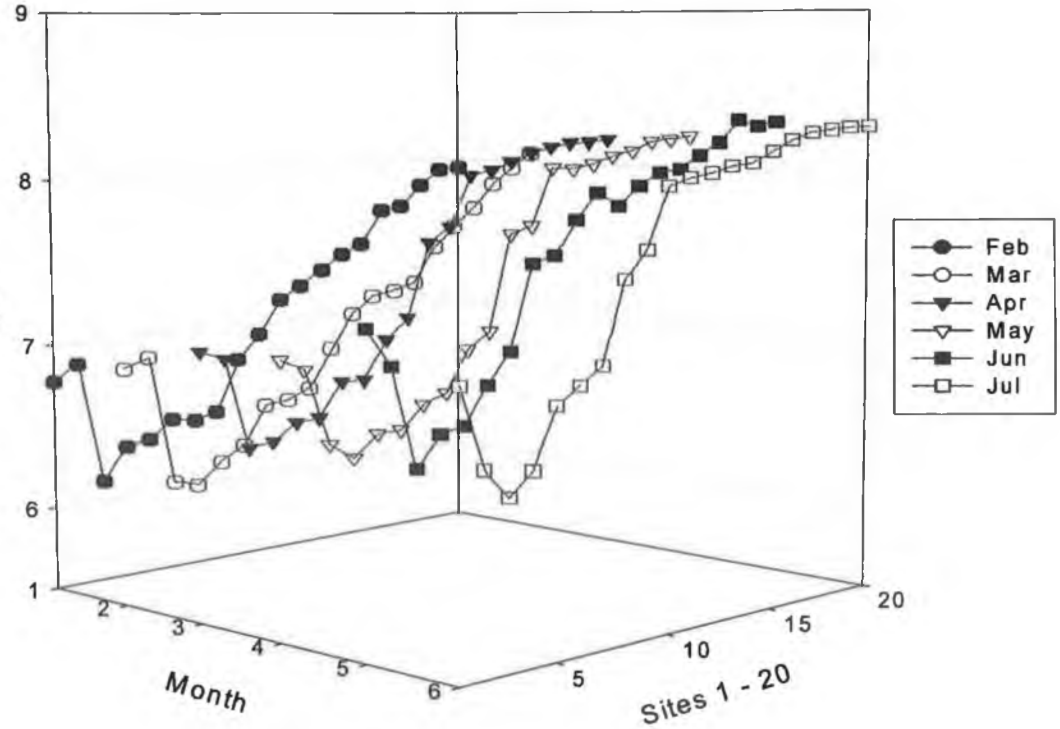


Figure 3.2.4 pH, Sites 1 – 20, February to July '04.

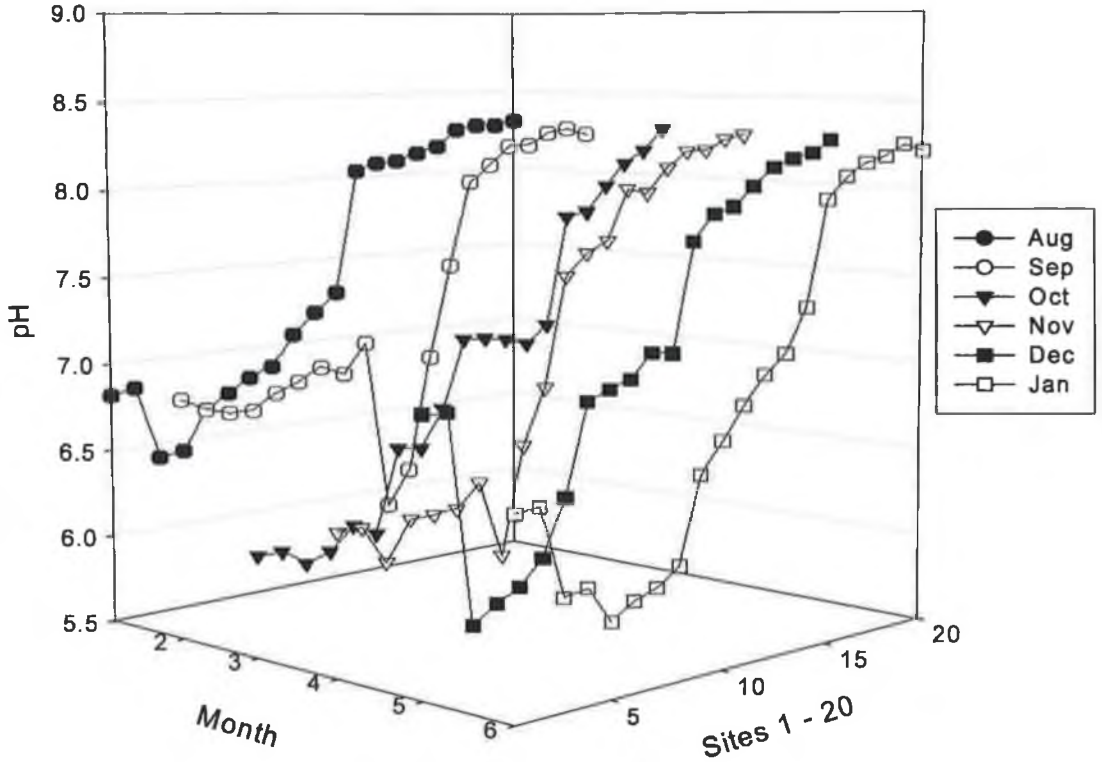


Figure 3.2.5 pH, Sites 1 – 20, August '04 to January '05.

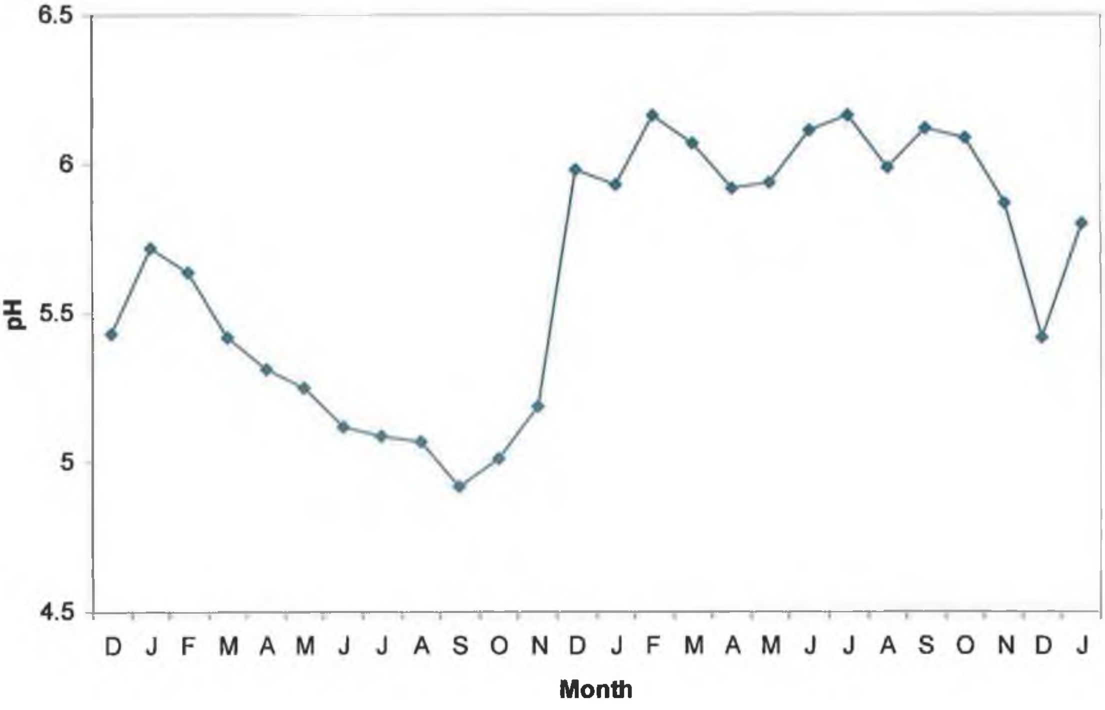


Figure 3.2.6 pH, Site A, Dunsink Tributary, December '02 to January '05.

3.3 Salinity

Salinity was measured over the final five months of sampling at twelve sampling points, nine of which were sampled over low and high tide, while the other three were located on intertidal sediment that had no surface water at low tide. Surface water samples were utilised. Temporal salinity variation showed no specific distribution. Table 3.3.1 provides the data gathered in the five months. Spatially the estuary exhibited a well mixed salinity at high tide. At low tide, the freshwater influence of the Tolka river extended into the estuary and created brackish conditions (~10 - 15 ‰) rather than purely marine (35 ‰). At high tide, saline intrusion extended as far as Drumcondra (Site 10).

Month	**September**		**October**		**November**		**December**		**January**	
Tide Sample Point	**High**	**Low**	**High**	**Low**	**High**	**Low**	**High**	**Low**	**High**	**Low**
S1	1.6	1.9	1.5	1.4	1.8	1.0	1.6	1.2	1.7	0.9
S2	15.9	1.1	11.2	1.3	16.1	1.6	12.2	1.4	13.1	1.0
S3	27.2	1.2	19.7	1.6	26.3	1.7	20.1	2.0	22.6	1.6
S4	30.1	15.2	26.2	9.8	30.2	16.1	29.8	20.1	30.1	16.7
S5	33.8	26.9	30.1	18.6	34.1	26.2	33.6	28.9	34.8	20.1
S6	33.9	27.8	33.1	22.7	33.8	26.6	34.8	29.6	33.1	27.7
S7	35.2	30.2	34.9	31.2	34.6	27.9	33.2	31.3	33.6	29.8
S8	34.2	N/A	29.6	N/A	33.9	N/A	31.6	N/A	34.8	N/A
S9	32.8	N/A	31.9	N/A	32.9	N/A	33.1	N/A	36.7	N/A
S10	34.9	N/A	35.7	N/A	33.9	N/A	34.2	N/A	35.1	N/A
S11	34.9	35.1	33.8	34.6	35.2	32.1	36.1	31.9	36.2	29.8
S12	35.7	34.2	34.5	33.9	34.9	33.1	35.2	32.1	36.8	32.1

Table 3.3.1 Salinity Measurements Sites S1 – S12, September '04 to January '05.

A single salinity profile of the estuary at depth over a tidal cycle was completed during the Spring Tide in September 2004 to determine saline intrusion on the estuary. Salinity measurements revealed a well mixed estuary with minor saline stratification, Table 3.3.2 provides salinity measurements at four equidistant points in the middle and outer estuarine zones, at surface level, -2.5 m, -5.0 m and -10.0 m depths. During low tide salinity reduced to slightly lower than marine normal (35‰) at the surface and closer to the river.

Sample Point	Depth (m)	High Tide Salinity (‰)	Low Tide Salinity (‰)
D1	**0.0**	33.8	25.6
	-2.5	34.9	29.8
	-5.0	34.6	33.1
	-10.0	35.8	34.5
D2	**0.0**	33.6	26.0
	-2.5	33.9	29.7
	-5.0	35.8	32.9
	-10.0	35.9	33.8
D3	**0.0**	35.4	29.0
	-2.5	35.4	32.6
	-5.0	35.9	33.8
	-10.0	35.8	34.2
D4	**0.0**	35.8	30.2
	-2.5	35.7	31.0
	-5.0	34.3	33.7
	-10.0	35.0	33.9

Table 3.3.2 Salinity Measurements at Sites D1 – 4, Spring Tide, September 2004.

3.4 Organic Matter

Organic matter (OM) was sampled over a seventeen month period between September 2003 and January 2005. OM concentrations in river and estuarine surface sediment displayed variable spatial and temporal distributions, see Figures 3.4.1 to 3.4.3. Spatially OM concentrations were low in the river compared with the estuary, where highest concentrations were recorded in the inner and mid estuarine sections. Results of sampling in September '03 indicated riverine OM concentrations increasing towards the estuary from 1.4 % at Site 1 to 5.2 % at Site 10, while estuarine OM concentrations ranged from 7.5 % at site 11 to 10.2% at sites 14 to 15. OM concentrations decreased from 8.9 to 2.6 % between site 16 in the mid-estuary and site 20 at the estuarine margin. This pattern of spatial distribution was observed every month for the seventeen-month period.

OM concentrations also exhibited a seasonal temporal distribution. Concentrations were elevated in autumn 2003, and subsequently decreased during winter months to lowest concentrations in February and March 2004. Concentrations increased from April to October 2004 and subsequently decreased again to lower levels in January 2005. Site 16 provided a good example of this temporal distribution. Between September 2003 and March 2004 concentrations decreased from 8.9 ± 0.12 to 6.6 ± 0.06%. Concentrations then increased from 6.7 ± 0.09 to 8.9 ± 0.04% between April and October 2004. Subsequent OM concentrations then decreased by 1.7 % to 7.2 ± 0.07% in January 2005. OM concentrations displayed moderate temporal distribution in surface sediment of the Dunsink Tributary, ranging from a 2.0 ± 0.29% minimum and a 3.3 ± 0.12% maximum, see Figure 3.4.4.

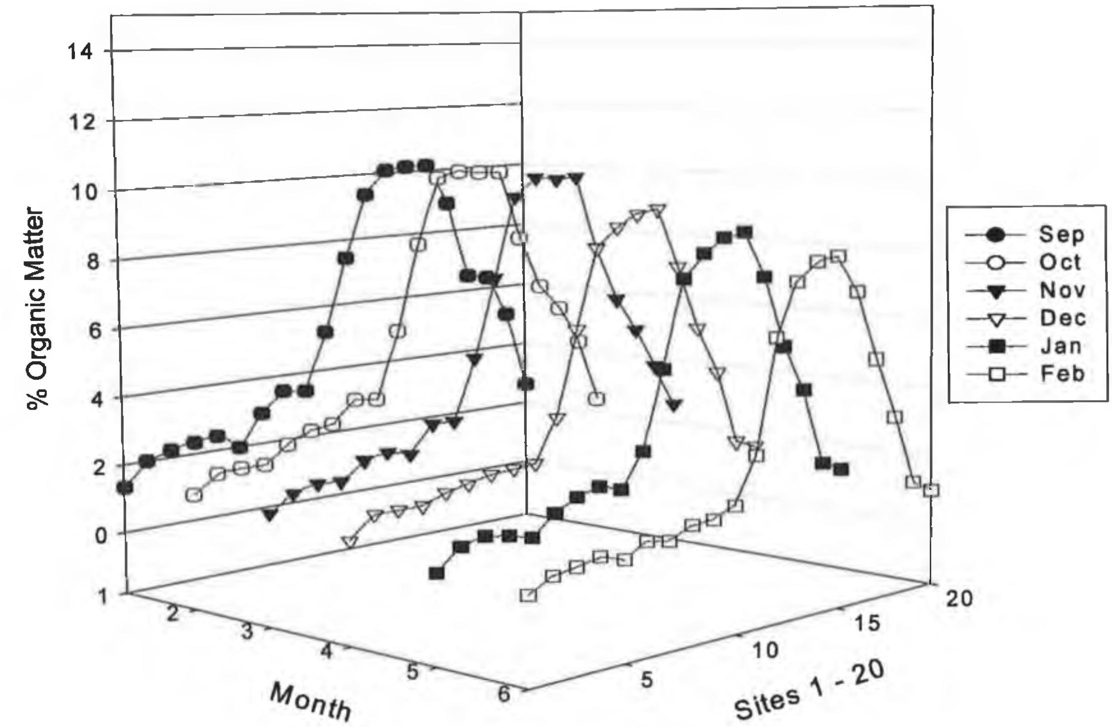


Figure 3.4.1 Organic Matter %, Sites 1 - 20 September '03 to February '04

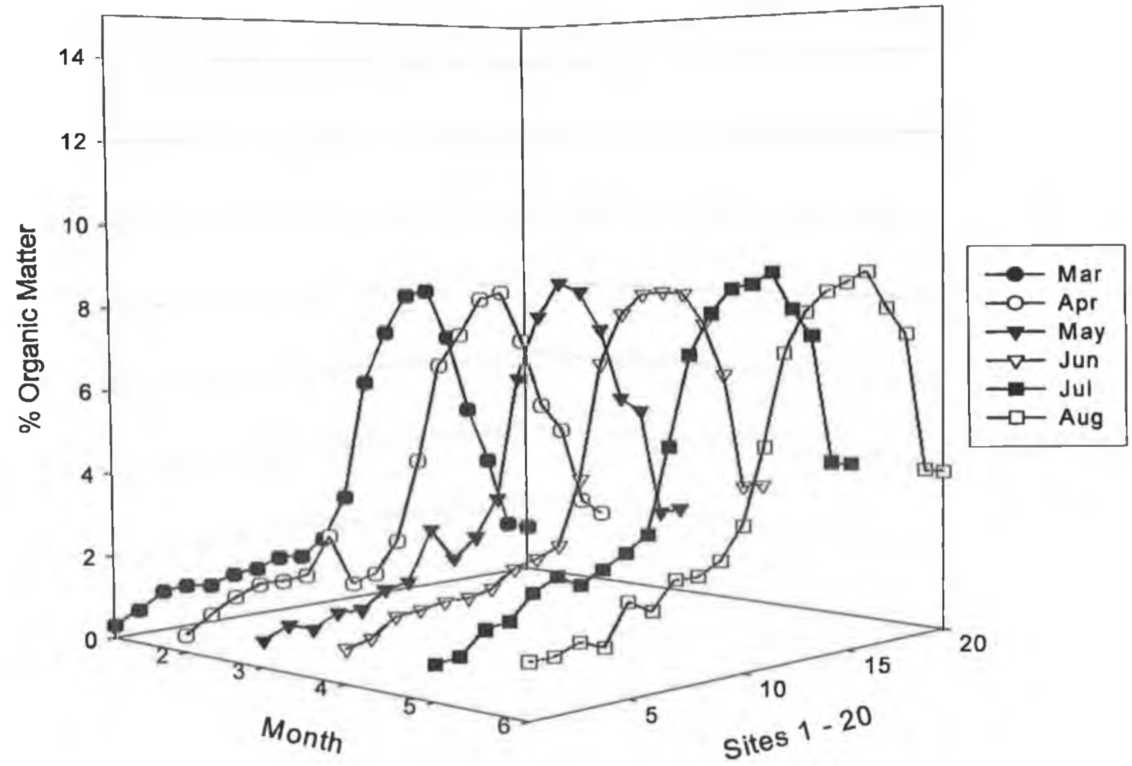


Figure 3.4.2 Organic Matter % Sites 1 - 20 March to August '04

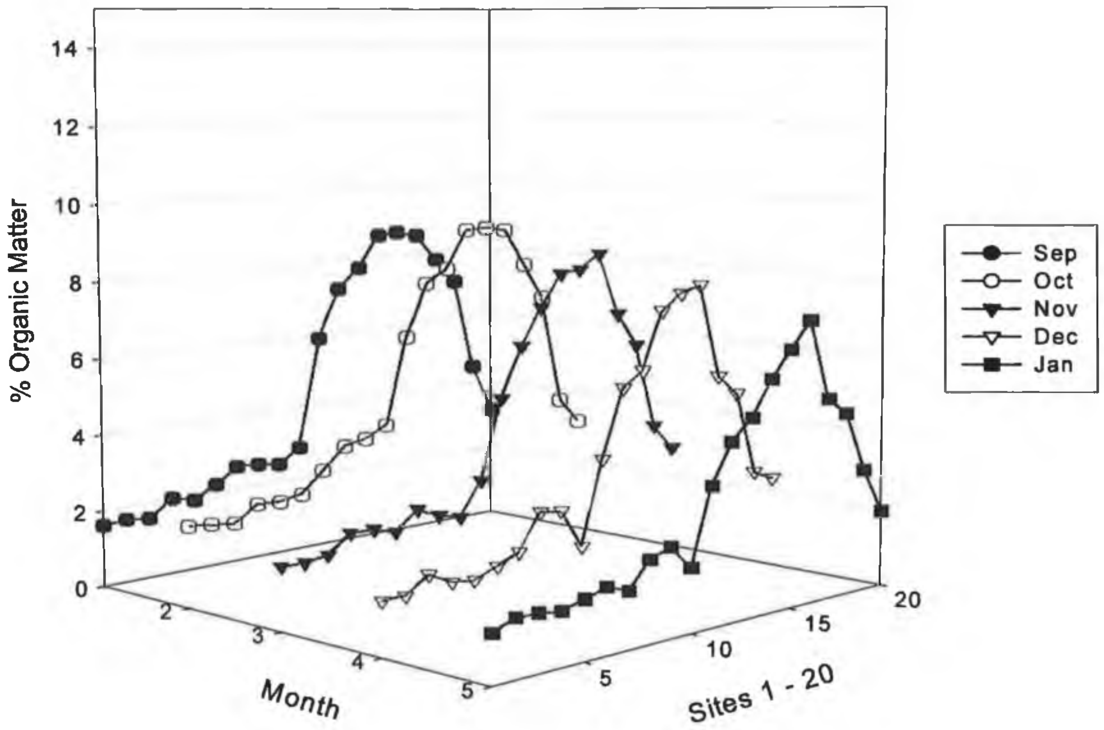


Figure 3.4.3 Organic Matter % Sites 1 - 20, September '04 to January '05

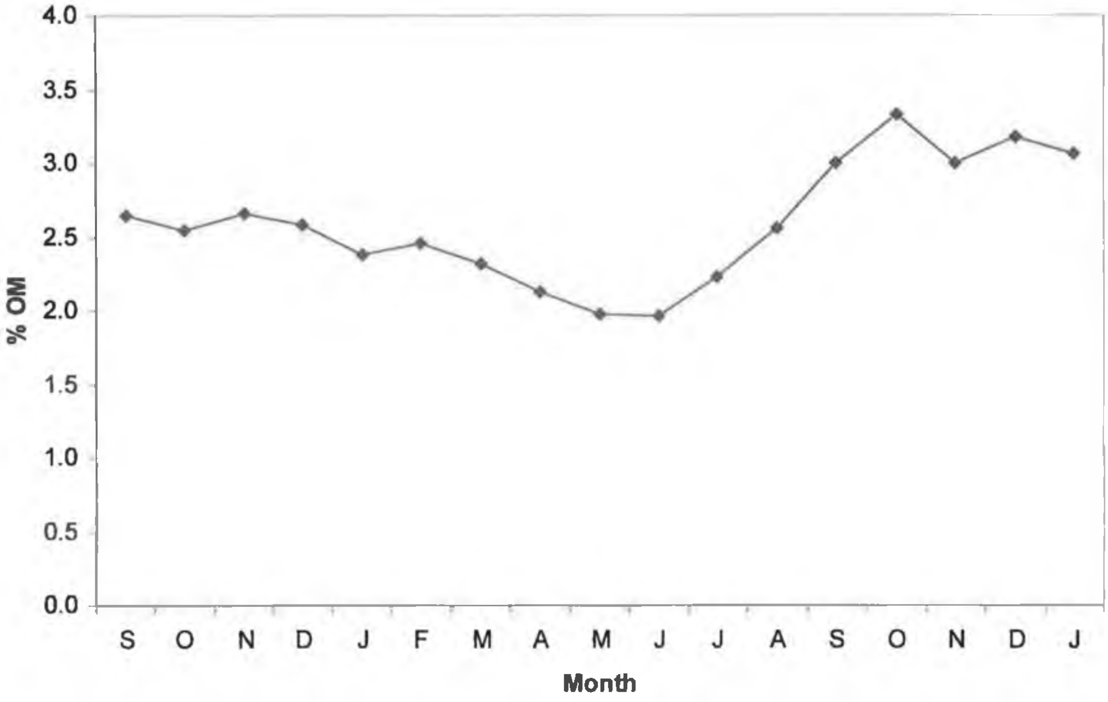


Figure 3.4.4 Organic Matter %, Site A, Dunsink Tributary, September ’03 to January ’05.

3.5 Surface Sediment Metal Concentrations

Metal concentrations in surface sediment varied spatially between river and estuary. Initial sampling did not include sites 1, 2 and A. Initial sampling indicated diminishing metal concentrations from Site 3 towards the estuary. Riverine metal concentrations generally had a lower range than estuarine metal concentrations except in vicinity of the confluence with the Dunsink Tributary. Estuarine metal concentrations were lower in the inner and outer estuarine zones while maximum metal concentrations were recorded in the middle estuarine zones. By December 2002 the sampling regime was expanded further upstream and the influence of the Dunsink Tributary on metal concentrations in surface sediment of upper riverine sampling locations, notably Sites 3 – 5, was observed. Initial metal concentrations recorded in the Dunsink Tributary indicated that surface sediment of this stream was severely contaminated.

Over the thirty month period surface sediment metal concentrations spatial distribution for the river and estuary remained relatively constant. Sites 1 and 2 were low in comparison to Site 3 which was directly downstream of the confluence with the Dunsink Tributary. Metal concentrations subsequently diminished towards the estuary. In the estuary, inner and outer estuarine zones recorded the lowest estuarine metal concentrations while maximum concentrations were recorded in the middle estuarine zone. Temporally, metal concentrations ranged from moderately elevated (Cd, Cr, Cu and Ni) in late summer and autumn months to significantly elevated (Pb and Zn) compared to winter and spring months. Minimum and maximum metal concentrations observed for the river and estuary are indicated in Table 3.5.1.

Metal	River						Estuary					
	Minimum			Maximum			Minimum			Maximum		
	ppm	Site	Month	ppm	Site	Month	ppm	Site	Month	ppm	Site	Month
Cd	0.06	1	Feb '04	2.77	3	Oct '02	0.24	11	Feb '04	2.38	18	Oct '03
Cr	7.22	1	Jan '05	19.2	3	Aug '02	8.74	11	Jan '05	29.3	17	Aug '02
Cu	13.5	1	Jan '05	83.2	3	Sep '02	22.2	11	Feb '04	72.7	16	Aug '02
Ni	11.1	1	Jan '05	44.0	3	Aug '02	13.4	12	Jan '05	47.8	15	Aug '02
Pb	31.1	1	Jan '05	300.5	3	Jul '04	30.3	13	Feb '03	318.2	17	Jul '04
Zn	15.1	2	Jan '03	139.4	3	Jul '03	14.8	11	Dec '02	133.5	17	Aug '04

Table 3.5.1 Minimum and Maximum metal concentrations recorded for Riverine and Estuarine Sites between August '02 and January '05.

3.5.1 Cadmium

Cd surface sediment concentrations are illustrated in Figures 3.5.1 to 3.5.5. Cd surface sediment concentrations for Dunsink Tributary is illustrated in Figure 3.5.6. As indicated, Cd concentrations exhibited moderate spatial variation between the river and estuary. Seasonal variation was evident at all sites over the thirty month period, however the estuarine sites had a broader temporal range. A typical thirty month temporal distribution for the system can be illustrated at Site 17: October 2002 – 2.07 ppm Cd, December 2002 – 1.52 ppm Cd, August 2003 – 2.15 ppm Cd, February 2004 – 0.38 ppm Cd, July 2004 – 0.99 ppm Cd and January 2005 – 0.55 ppm Cd. Figure 3.5.7 illustrates seasonal Cd variation at two riverine sites (3 and 5) and two estuarine sites (13 and 18).

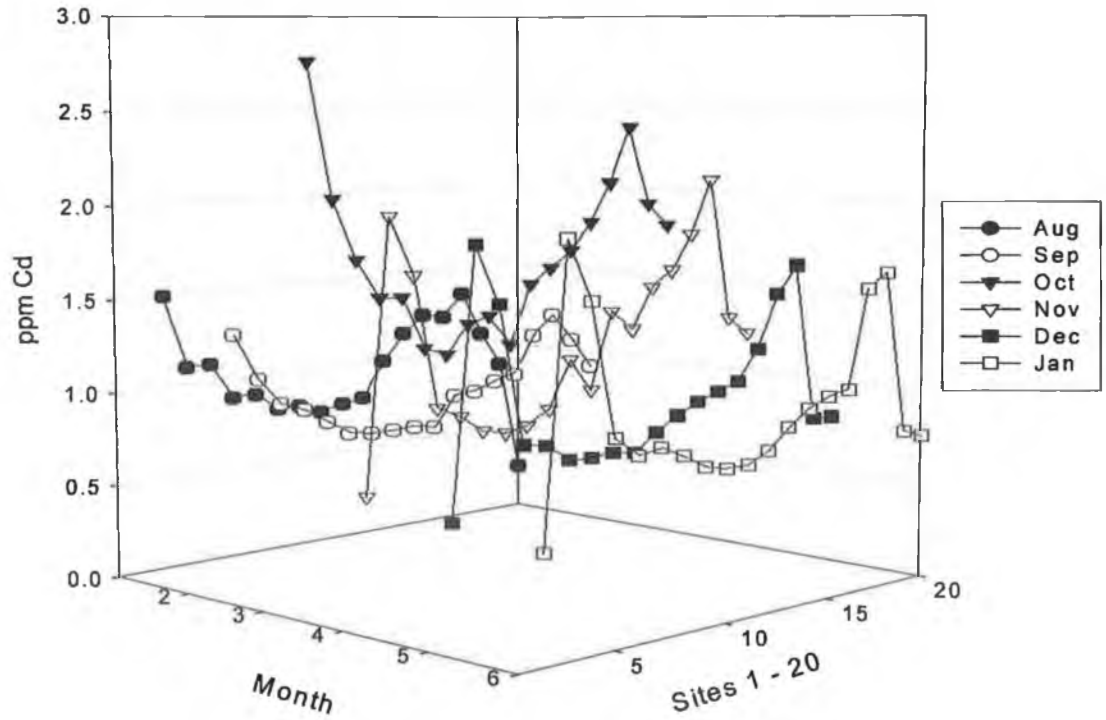


Figure 3.5.1 Cd surface sediment concentrations, Sites 1 – 20, August '02 to January '03.

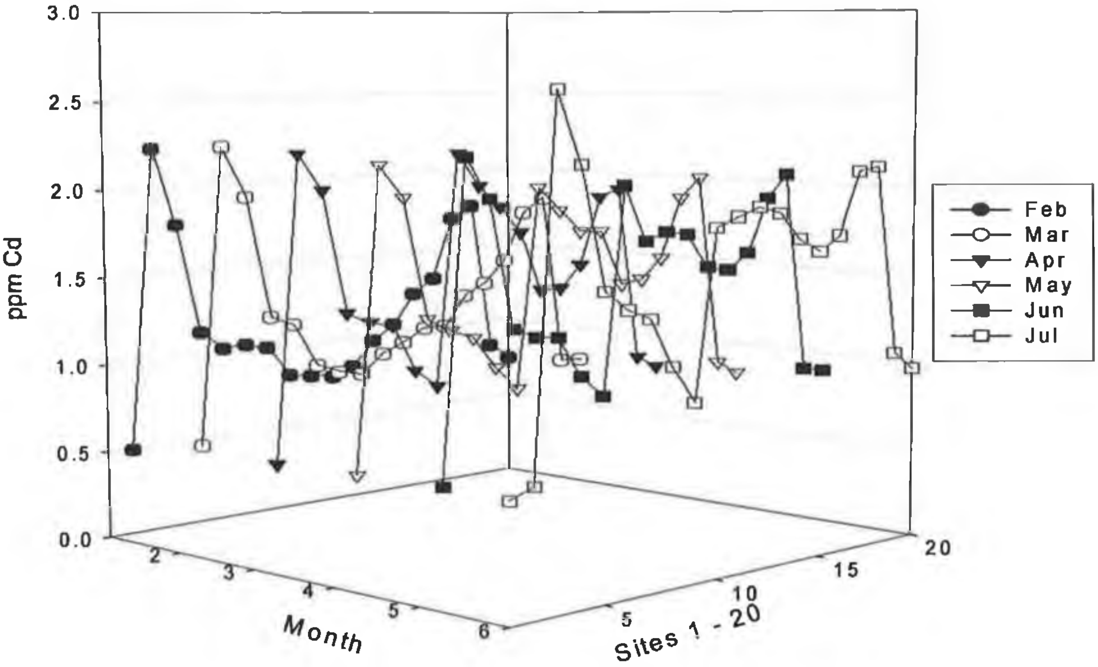


Figure 3.5.2 Cd surface sediment concentrations, Sites 1 – 20, February to July '03

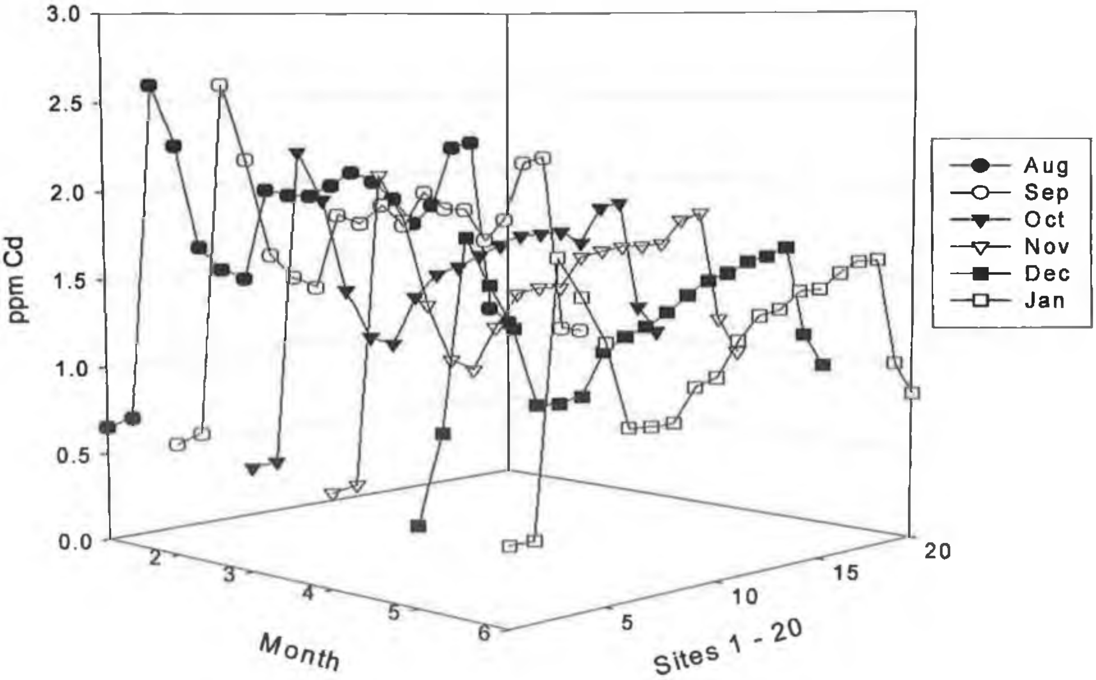


Figure 3.5.3 Cd surface sediment concentrations, Sites 1 – 20, August '03 to January '04

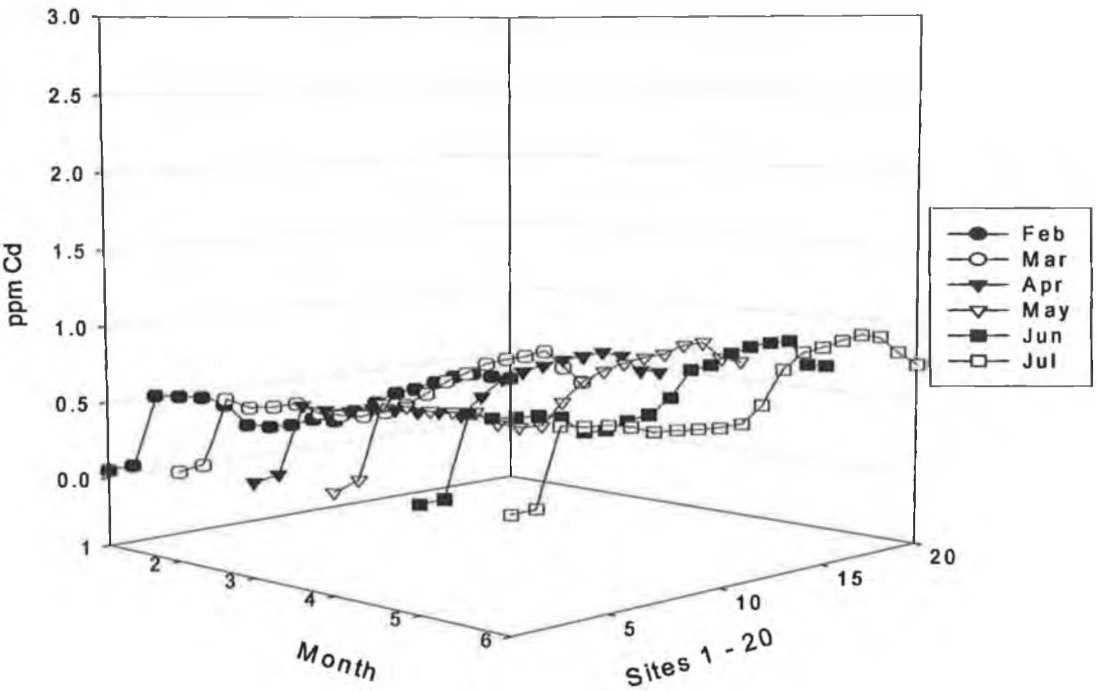


Figure 3.5.3 Cd surface sediment concentrations, Sites 1 – 20, February to July '04.

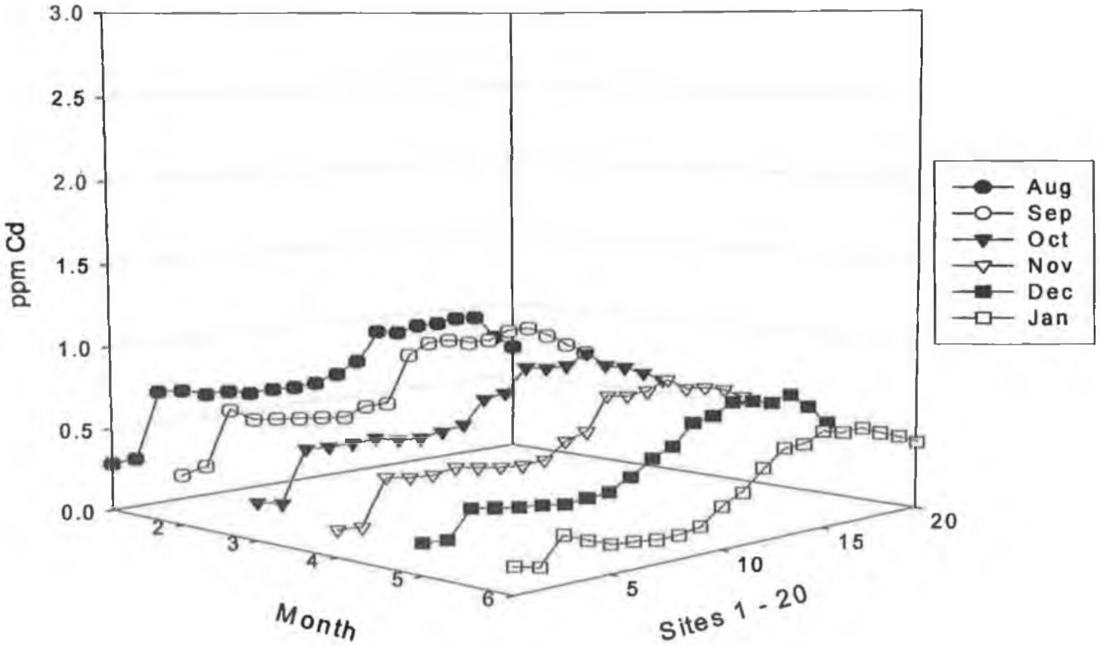


Figure 3.5.5 Cd surface sediment concentrations, Sites 1 – 20, August '04 to January '05.

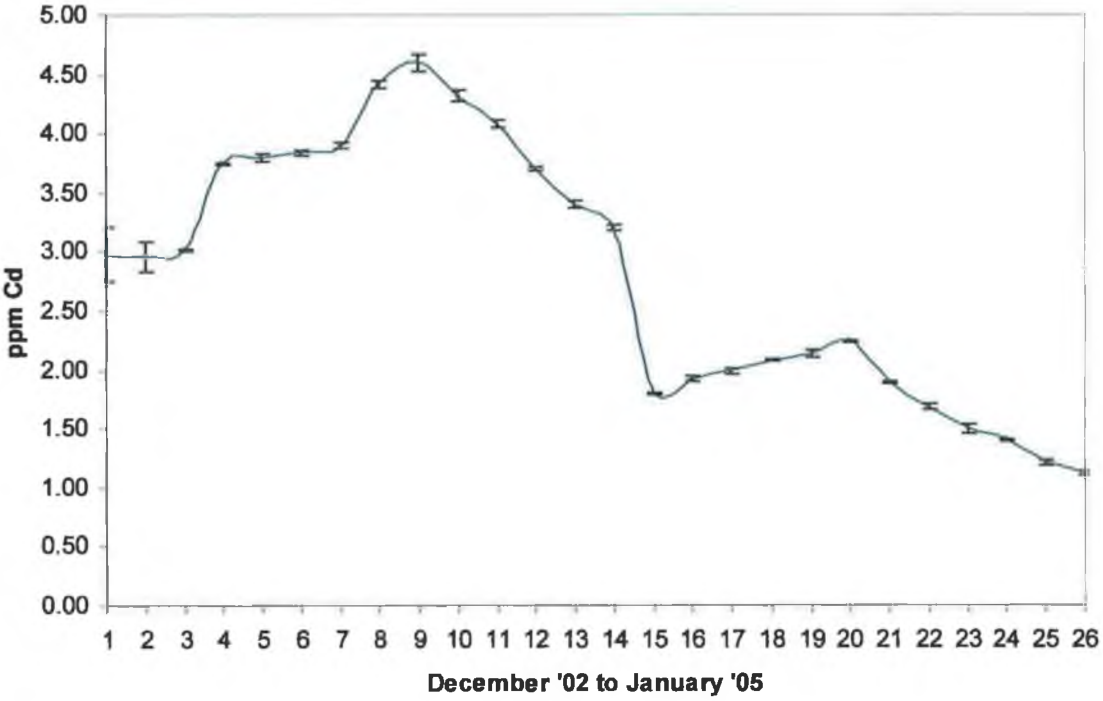


Figure 3.5.6 Cd surface sediment concentrations, Site A, Dunsink Tributary.

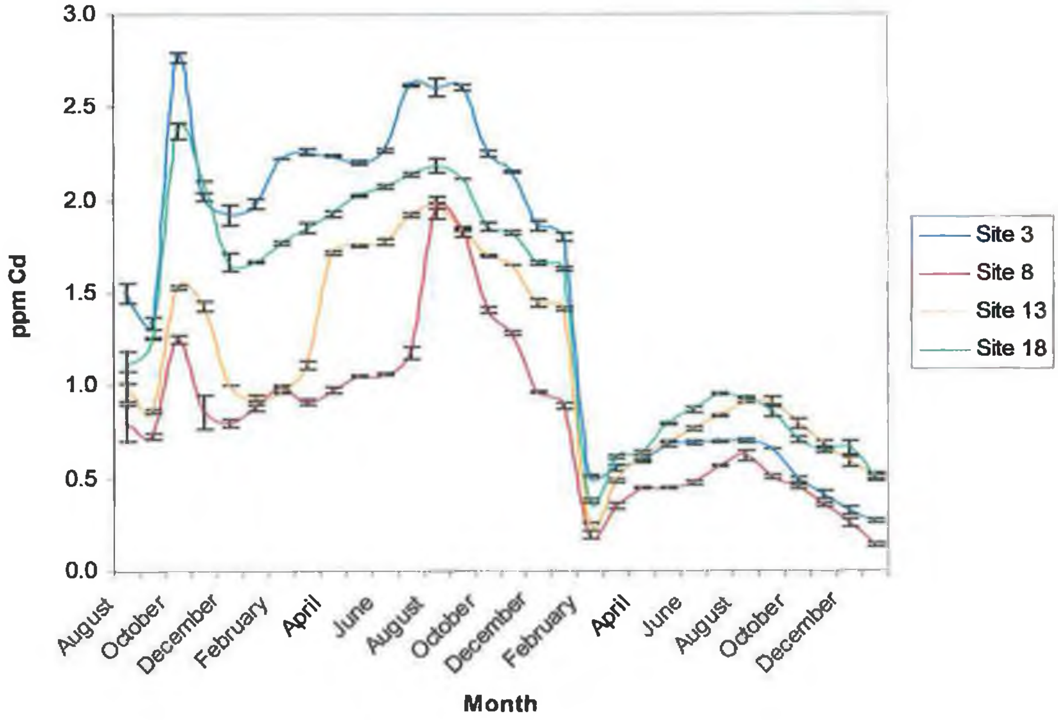


Figure 3.5.7 Cd surface sediment concentrations, Sites 3, 8, 13 & 18, August 2002 to January 2005.

3.5.2 Chromium

Cr concentrations in surface sediment also varied spatially between river and estuary, see Figures 3.5.8 to 3.5.12. Cr surface sediment concentrations for Dunsink Tributary are illustrated in Figure 3.5.13. Over the thirty month period, the spatial pattern for the river and estuary remained relatively constant. Cr surface sediment concentrations were higher than levels recorded for Cd but were substantially lower than the other four metals. In the river, Cr concentrations reduced downstream of Site 3 to the estuary. In the estuary, inner and outer estuarine zones recorded the lowest estuarine Cr concentrations while maximum concentrations were recorded in the middle estuarine zone. A typical thirty month temporal distribution for the system can be illustrated at Site 13: August 2002 – 27.3 ppm Cr, February 2003 – 10.7 ppm Cr, August 2003 – 12.7 ppm Cr, February 2004 – 11.1 ppm Cr, October 2004 – 13.2 ppm Cr and January 2005 – 8.7 ppm Cr. However, as the thirty months progressed, overall Cr concentrations throughout estuarine and riverine zones reduced. For example at Site 17, Cr concentrations ranged from 29.3 ppm in August 2002, to 17.0 ppm in August 2003 and finally to 14.6 ppm in August 2004. Figure 3.5.14 illustrates seasonal Cr variation at two riverine sites (3 and 5) and two estuarine sites (13 and 18).

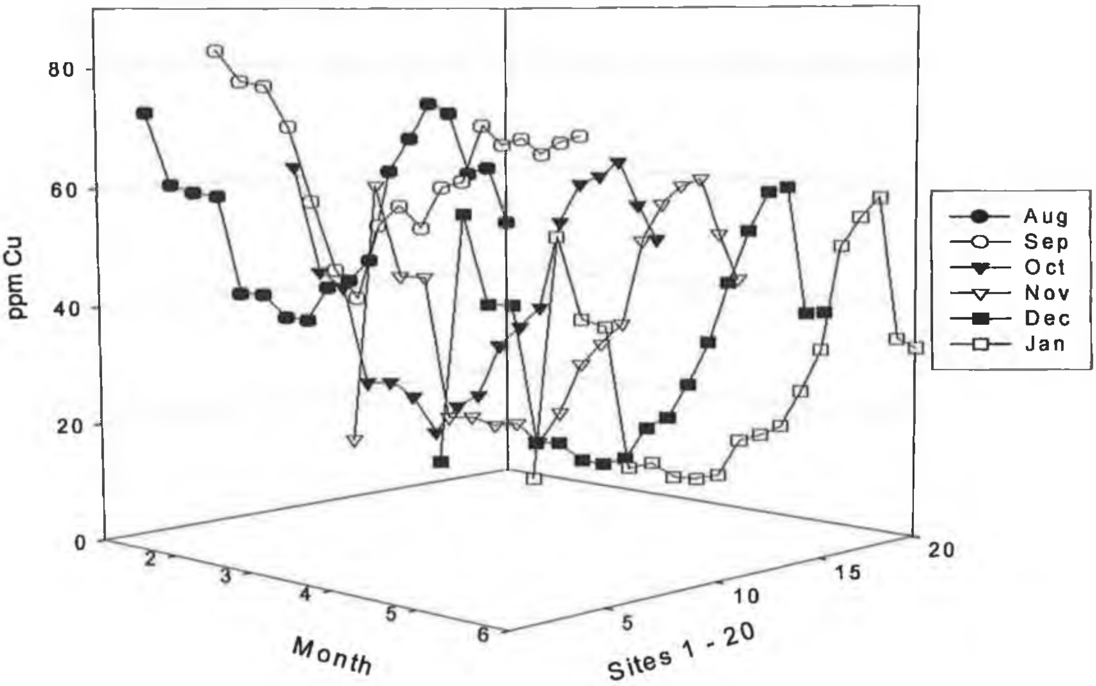


Figure 3.5.8 Cr surface sediment concentrations, Sites 1 – 20, August '02 to January '03.

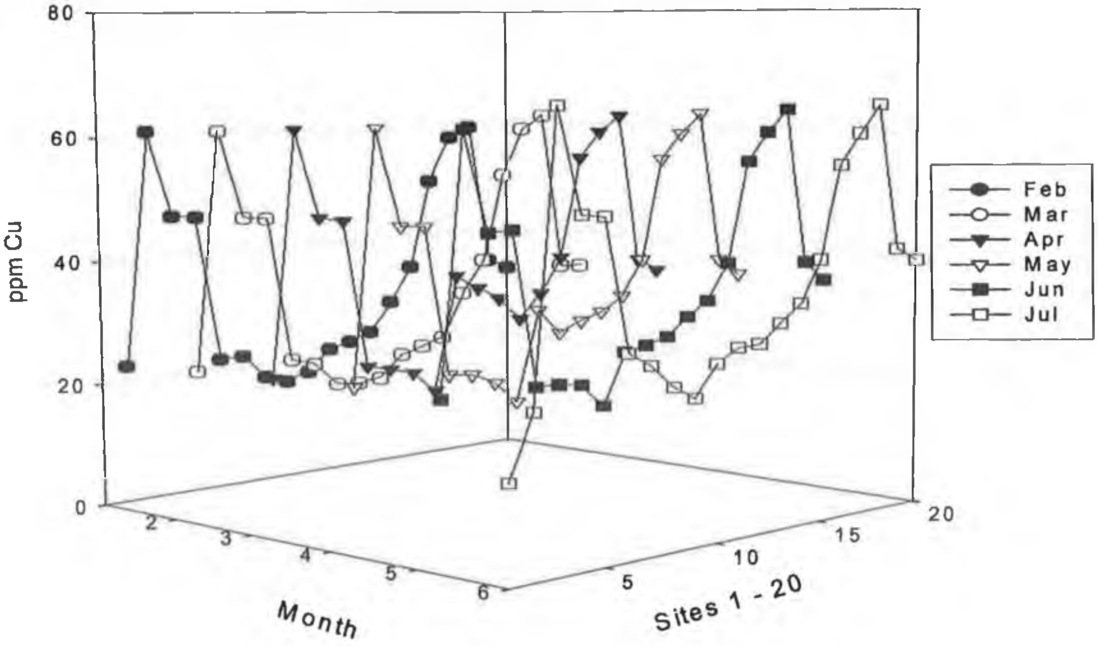


Figure 3.5.9 Cr surface sediment concentrations, Sites 1 – 20, February to July '03.

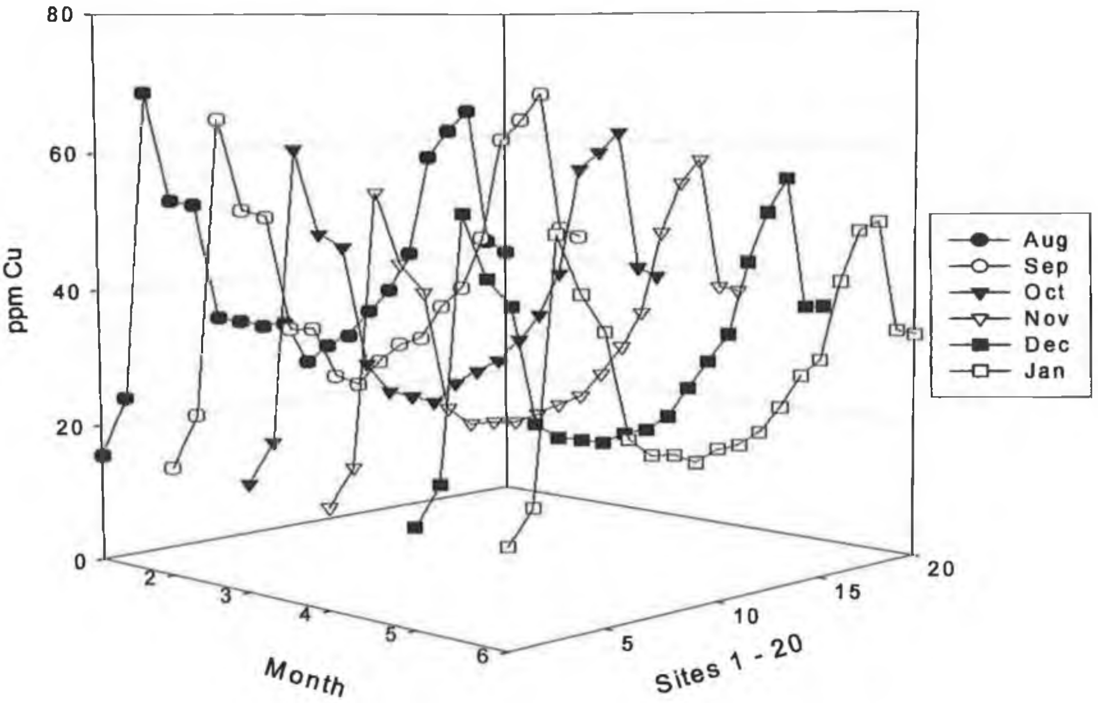


Figure 3.5.10 Cr surface sediment concentrations, Sites 1 – 20, August '03 to January '04.

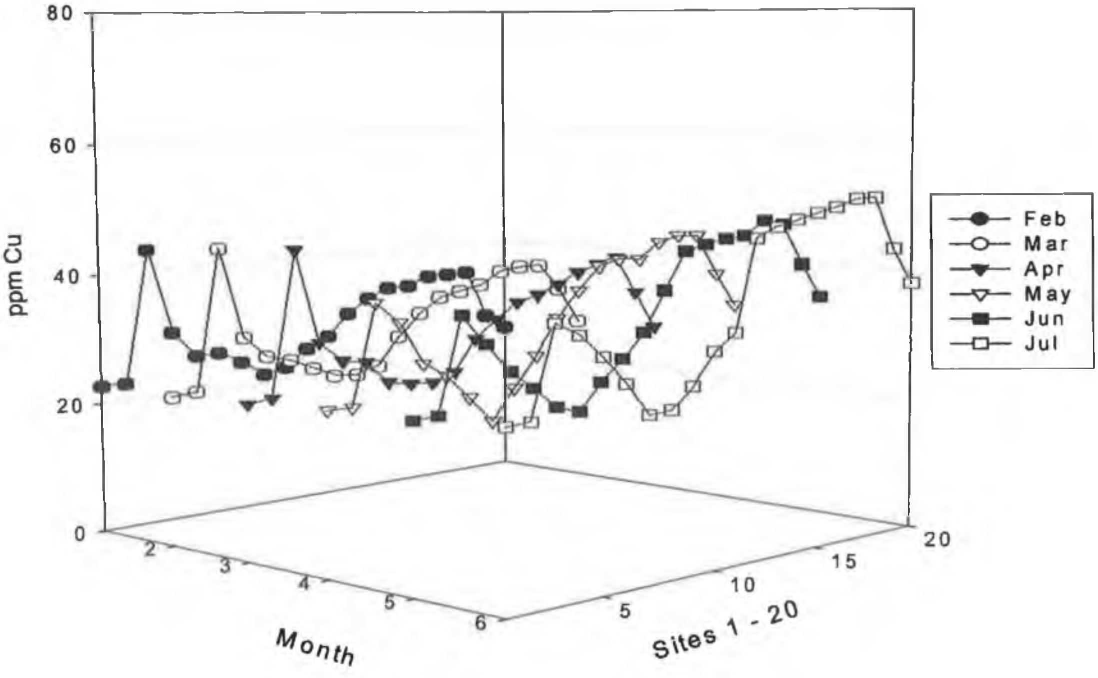


Figure 3.5.11 Cr surface sediment concentrations, Sites 1 – 20, February to July '04.

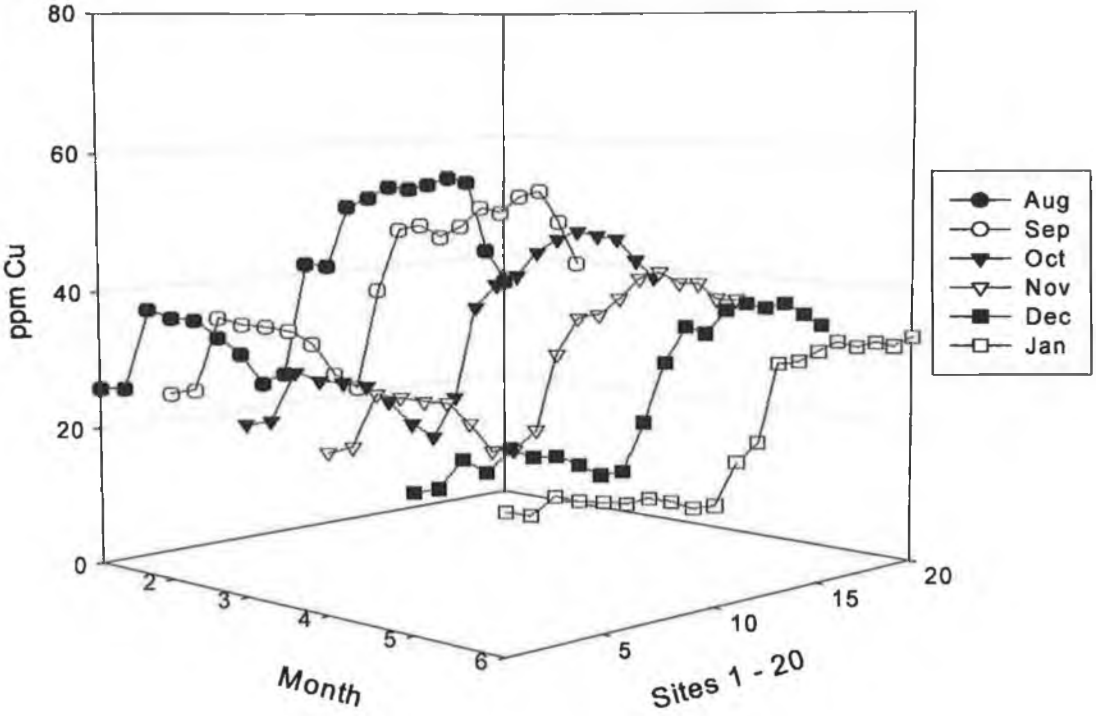


Figure 3.5.12 Cr surface sediment concentrations, Sites 1 – 20, August '04 to January '05.

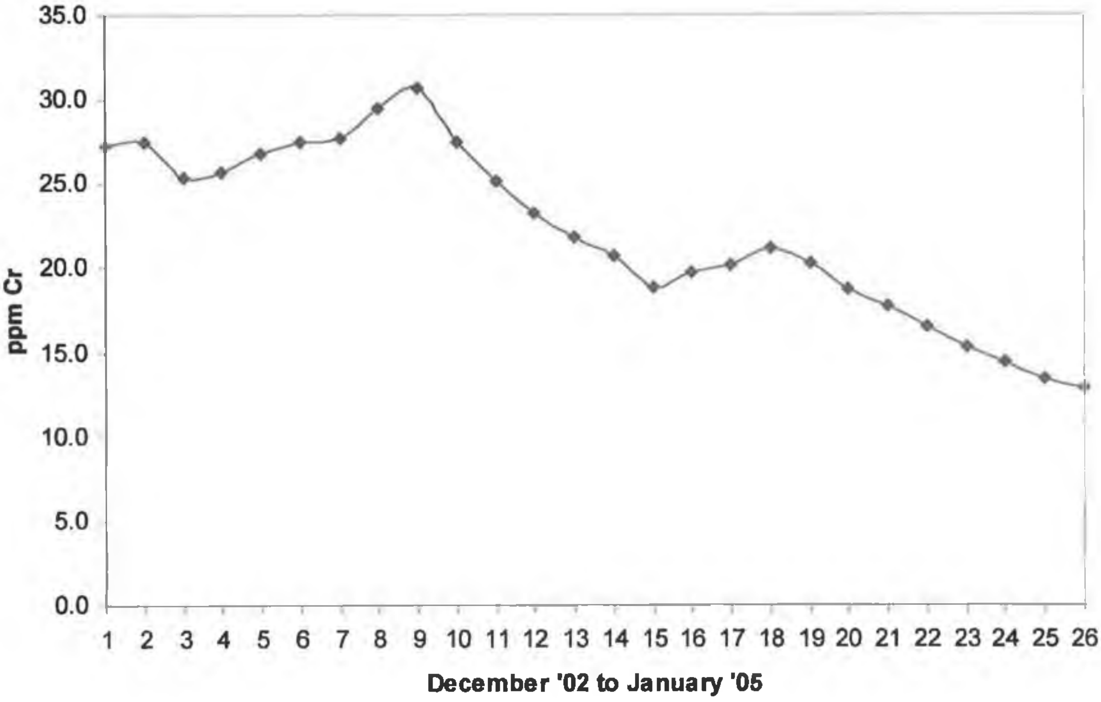


Figure 3.5.13 Cr surface sediment concentrations, Site A, Dunsink Tributary.

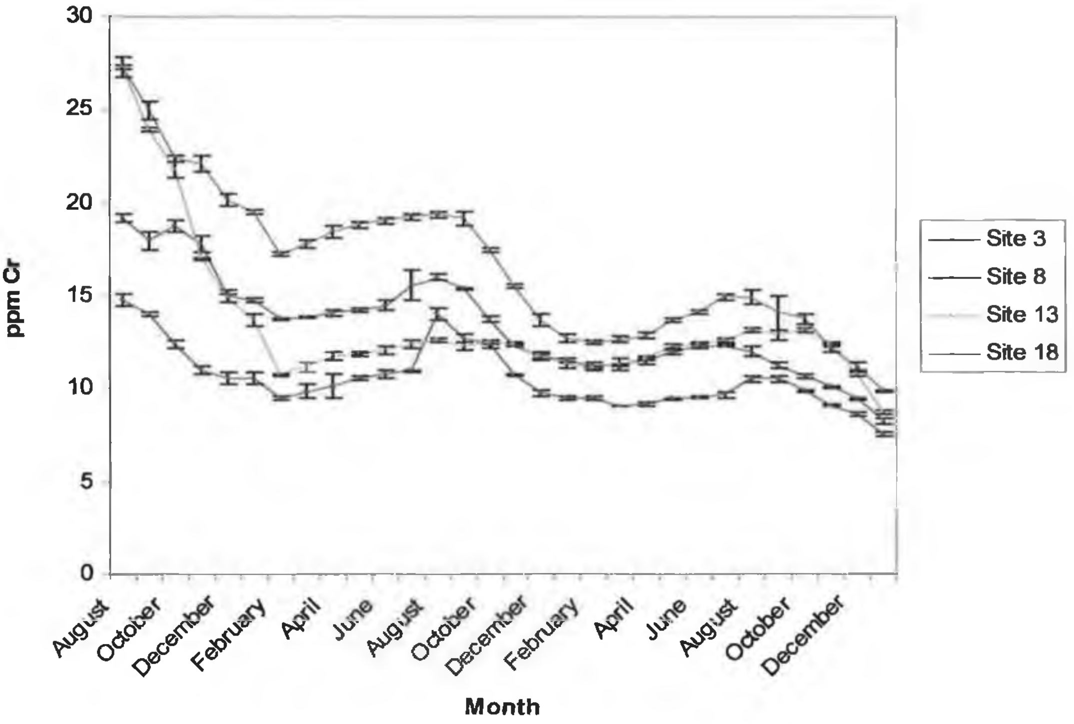


Figure 3.5.14 Cr surface sediment concentrations, Sites 3, 8, 13 & 18, August 2002 to January 2005.

3.5.3 Copper

Cu concentrations in surface sediment had a greater spatial and temporal range between river and estuary than Cd and Cr, see Figures 3.5.15 to 3.5.19. An initial Cu surface sediment concentration of 89.2 ppm was recorded in the Dunsink Tributary; however Cu concentrations had a variable range in the tributary: from 88.9 ppm to 183.4 ppm during the research period, see Figure 3.5.20. Temporally, Cu concentrations were moderately elevated in late summer and autumn months compared to winter and spring months, however the estuary exhibited a broader range in surface sediment concentrations. A typical thirty month temporal distribution for the system can be illustrated at Site 15: September 2002 – 69.0 ppm Cu, February

2003 – 34.5 ppm Cu, September 2003 – 45.0 ppm Cu, January 2004 – 31.4 ppm Cu, August 2004 – 52.1 ppm Cu and January 2005 – 33.0 ppm Cu. However as the thirty months progressed as with Cr, overall Cu concentrations throughout estuarine and riverine zones reduced, for example at Site 12 - the confluence of the river and estuary Cu concentrations ranged from 51.2 ppm in September 2002, to 30.2 ppm in September 2003 and finally to 36.2 ppm in September 2004. Figure 3.5.21 illustrates seasonal Cu variation at two riverine sites (3 and 5) and two estuarine sites (13 and 18).

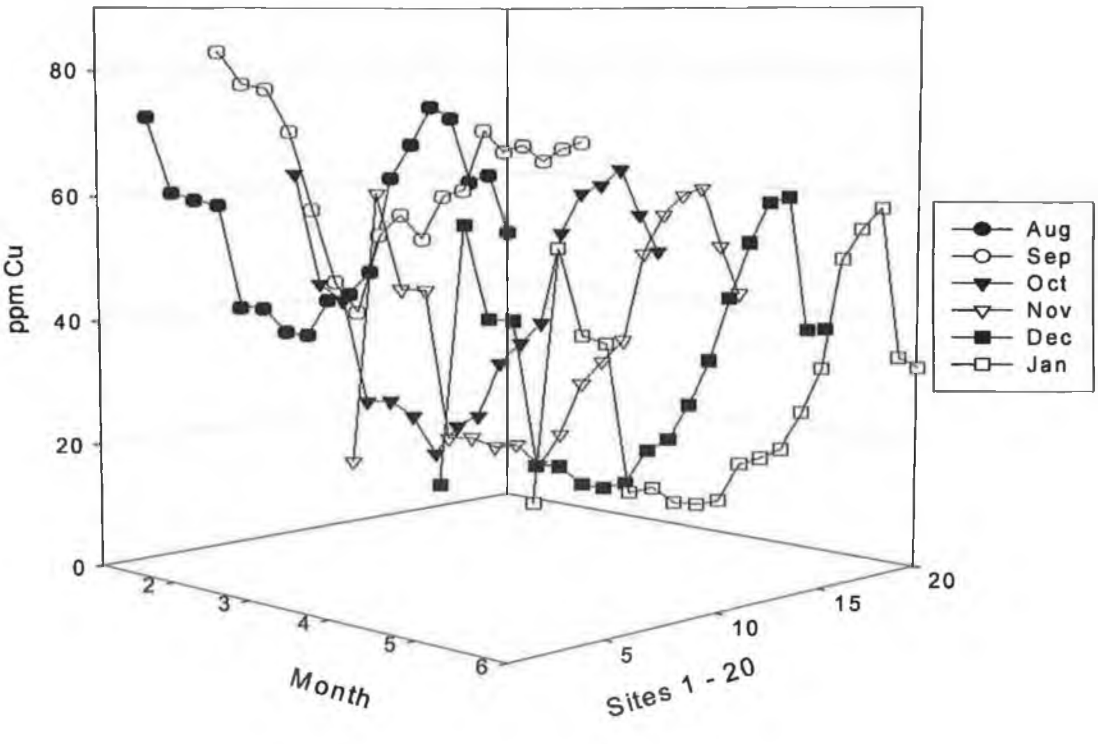


Figure 3.5.15 Cu surface sediment concentrations, Sites 1 – 20, August '02 to January '03.

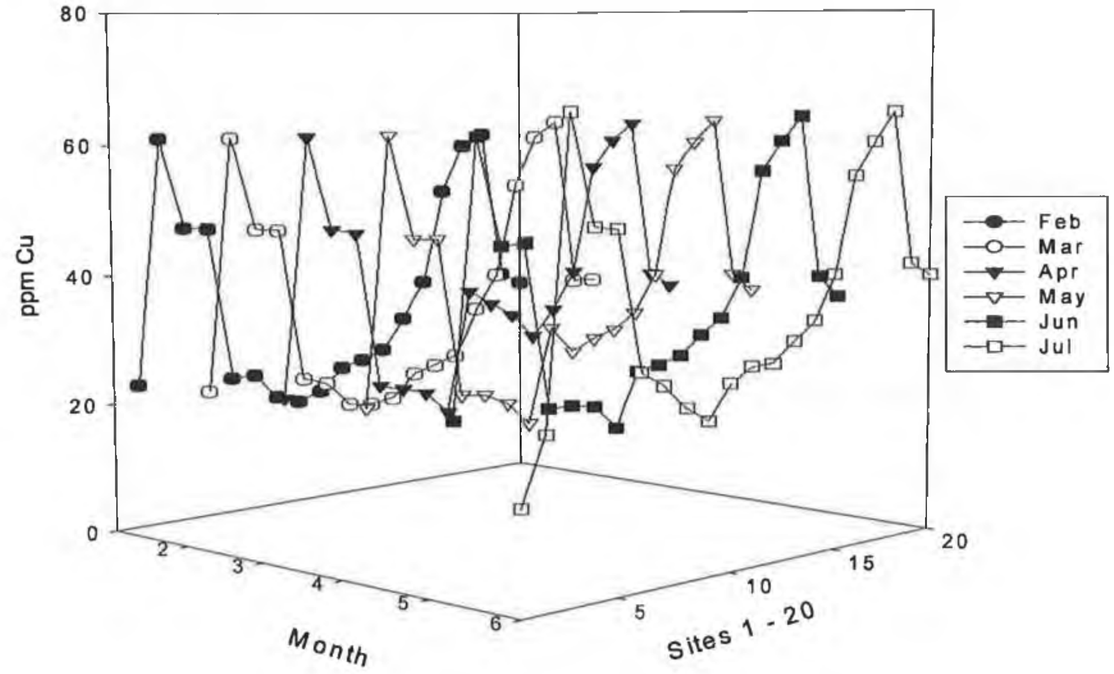


Figure 3.5.16 Cu surface sediment concentrations, Sites 1 – 20, February to July '03.

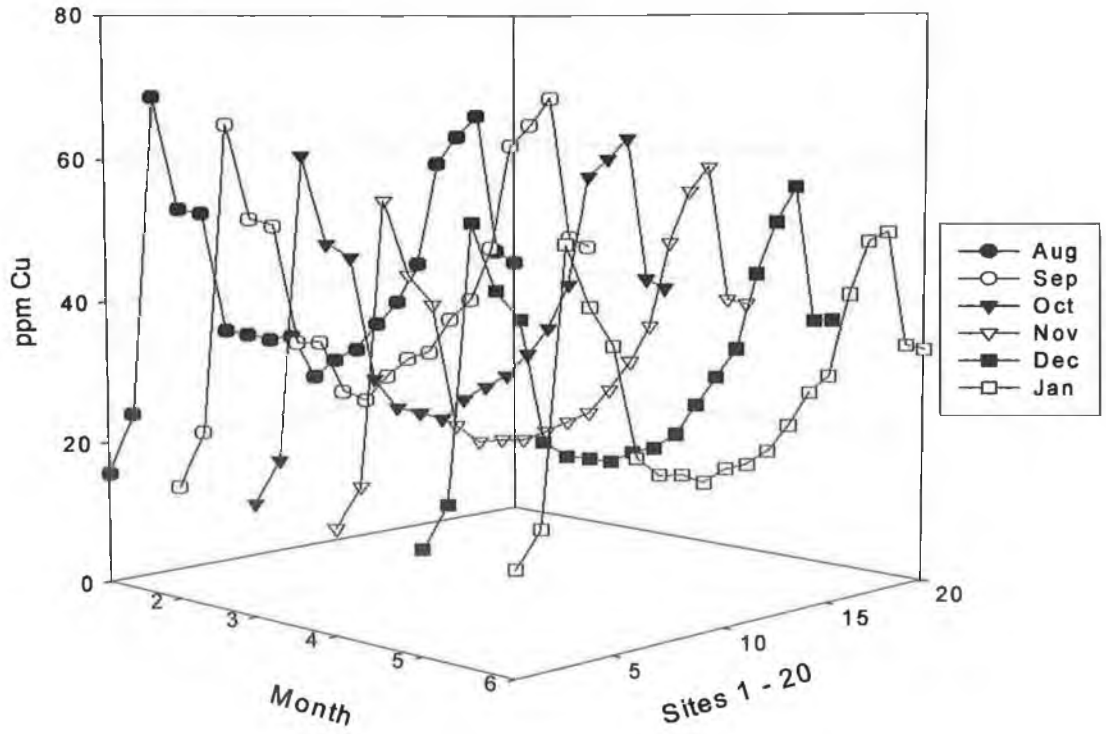


Figure 3.5.17 Cu surface sediment concentrations, Sites 1 – 20, August '03 to January '04.

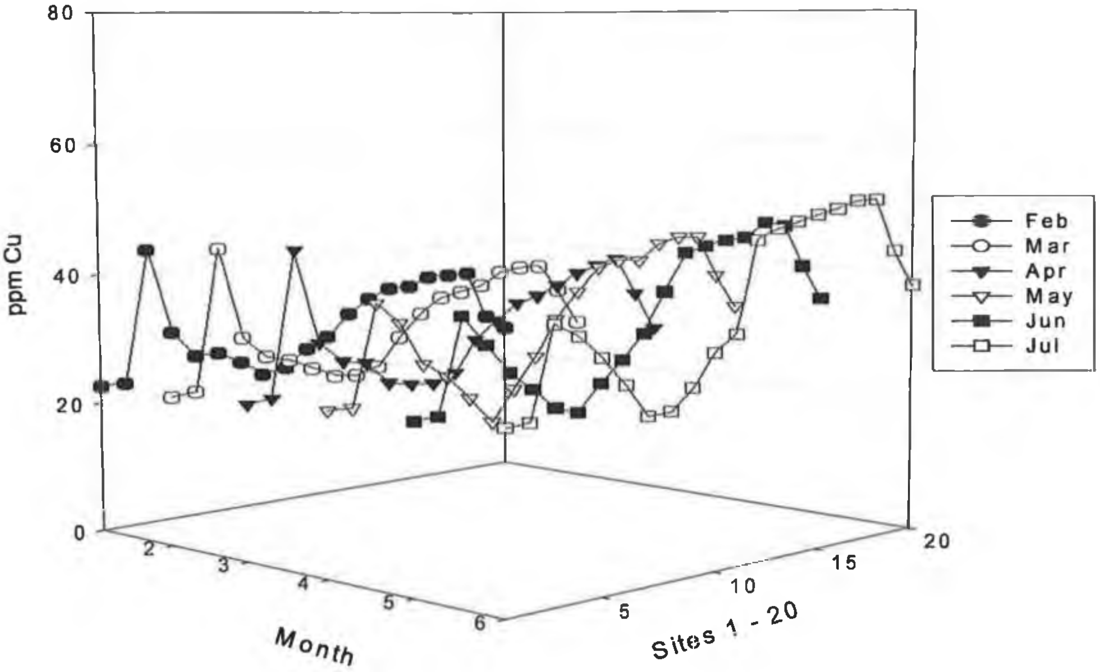


Figure 3.5.18 Cu surface sediment concentrations, Sites 1 – 20, February to July '04.

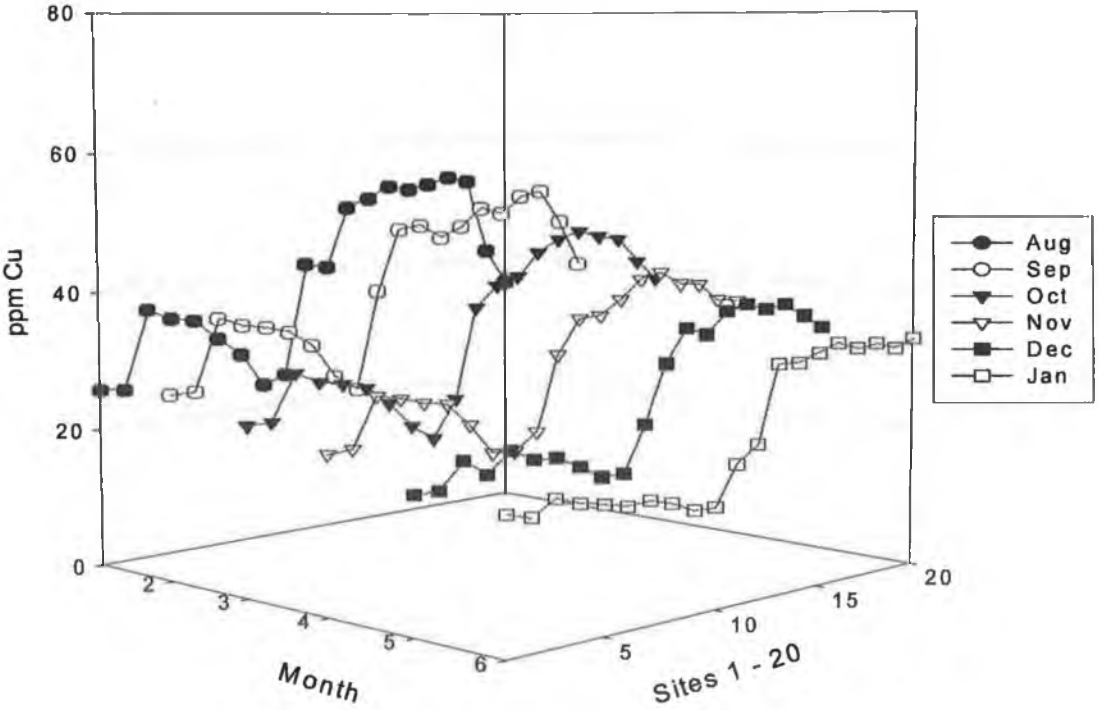


Figure 3.5.19 Cu surface sediment concentrations, Sites 1 – 20, August '04 to January '05.

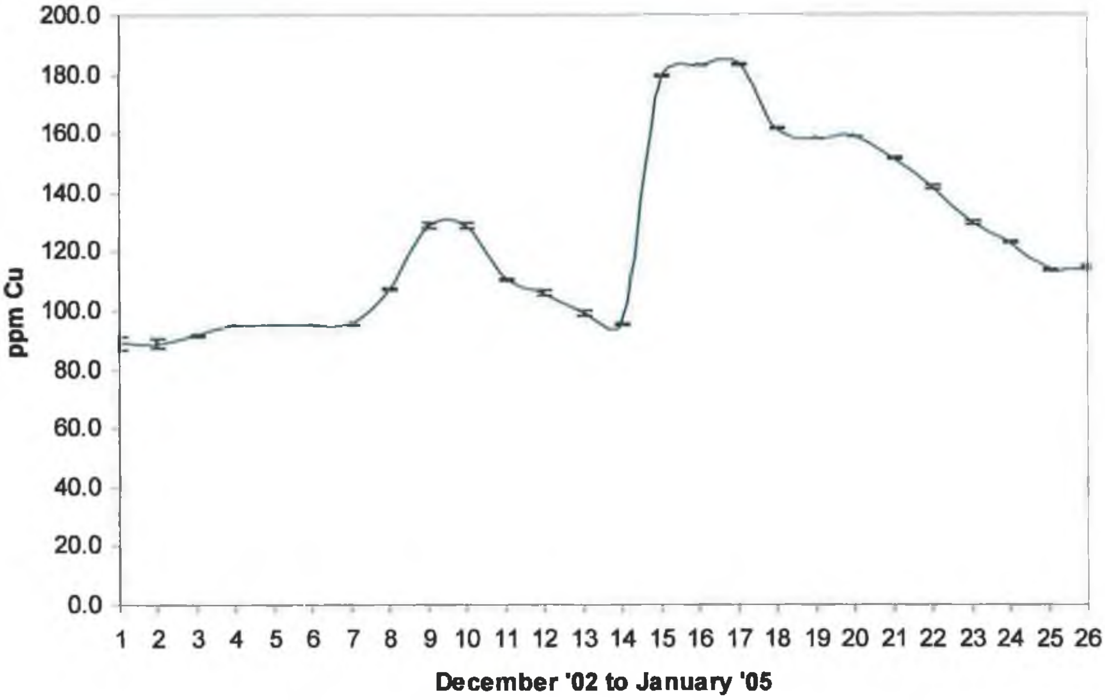


Figure 3.5.20 Cu surface sediment concentrations, Site A, Dunsink Tributary.

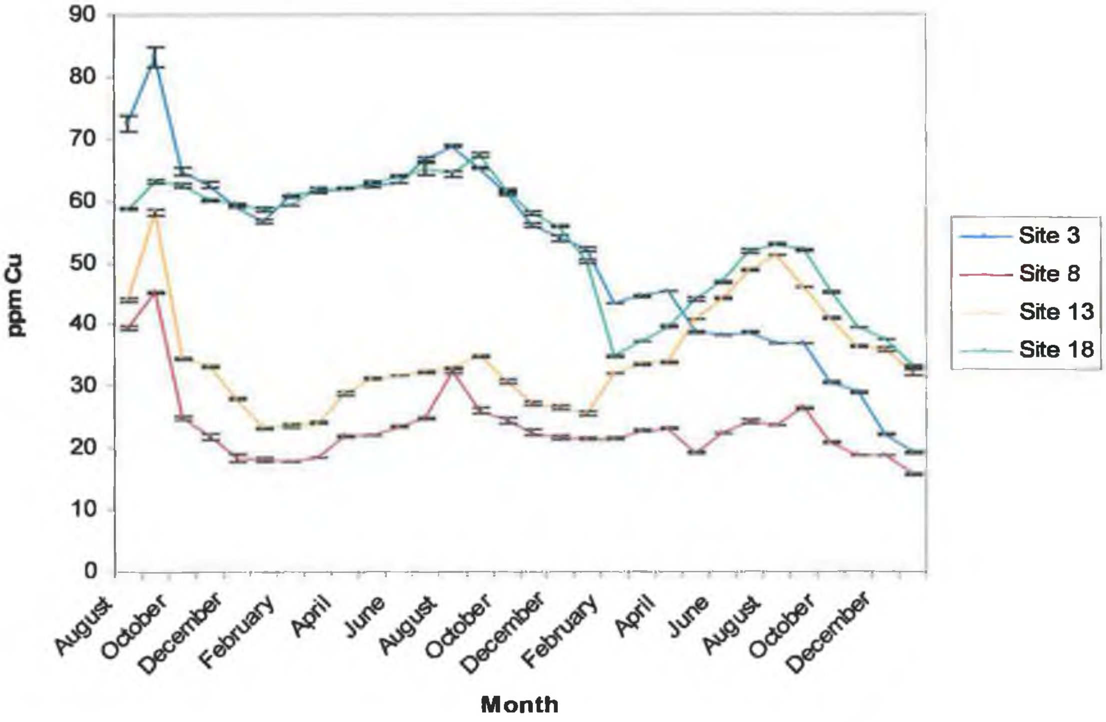


Figure 3.5.21 Cu surface sediment concentrations, Sites 3, 8, 13 & 18, August 2002 to January 2005.

3.5.4 Lead

Pb concentrations in surface sediment had the greatest spatial and temporal range between river and estuary, see Figures 3.5.22 to 3.5.26. Initial sampling indicated elevated concentrations of Pb in both river and estuary. Riverine surface sediment Pb concentrations ranged from a minimum of 33.3 ppm to a maximum of 220.0 ppm, diminishing in concentration towards the estuary. Estuarine surface sediment had ranged from 120.0 to 190.0 ppm Pb. As with Cd, Cr, and Cu maximum concentrations occurred in the middle estuary. An initial Pb surface sediment concentration of 220.0 ppm was recorded in the Dunsink Tributary, however Pb concentrations had a variable range in the tributary: from 165.9 ppm to 354.5 ppm during the research period, indicating the landfill was a significant source of Pb, see Figure 3.5.27. Temporally, Pb concentrations were similar but with a greater range than other metals - elevated in late summer and autumn months compared to much lower concentrations in winter and spring months. A typical thirty month temporal distribution for the system can be illustrated at Site 16: August 2002 – 183.3 ppm Pb, February 2003 – 81.8 ppm Pb, September 2003 – 193.9 ppm Pb, February 2004 – 148.5 ppm Pb, July 2004 – 312.1 ppm Pb and January 2005 – 131.1 ppm Pb. However, unlike Cd, Cr and Cu, Pb concentrations over the thirty months did not diminish significantly overall. Figure 3.5.28 illustrates seasonal Pb variation at two riverine sites (3 and 5) and two estuarine sites (13 and 18).

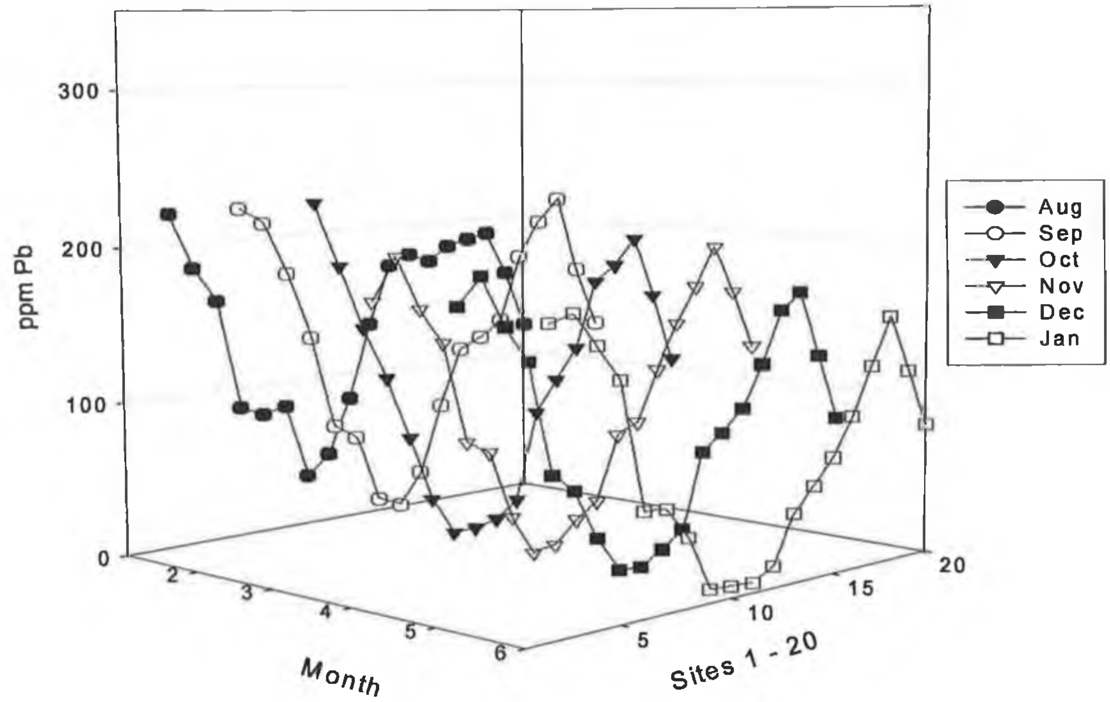


Figure 3.5.22 Pb surface sediment concentrations, Sites 1 – 20, August '02 to January '03.

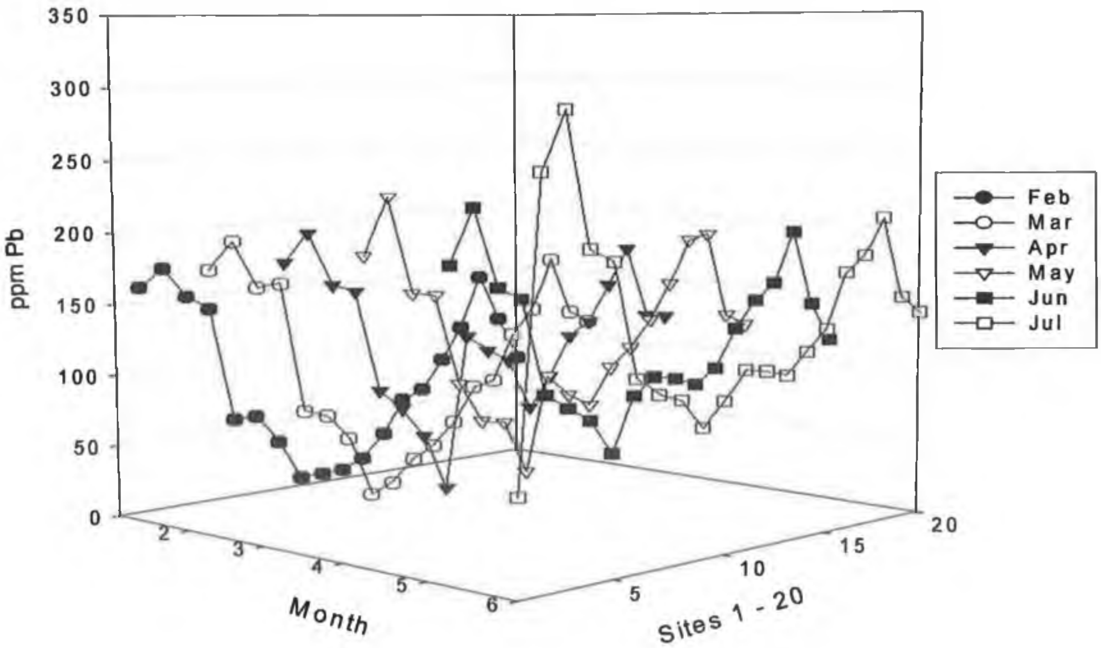


Figure 3.5.23 Pb surface sediment concentrations, Sites 1 – 20, February to July '03.

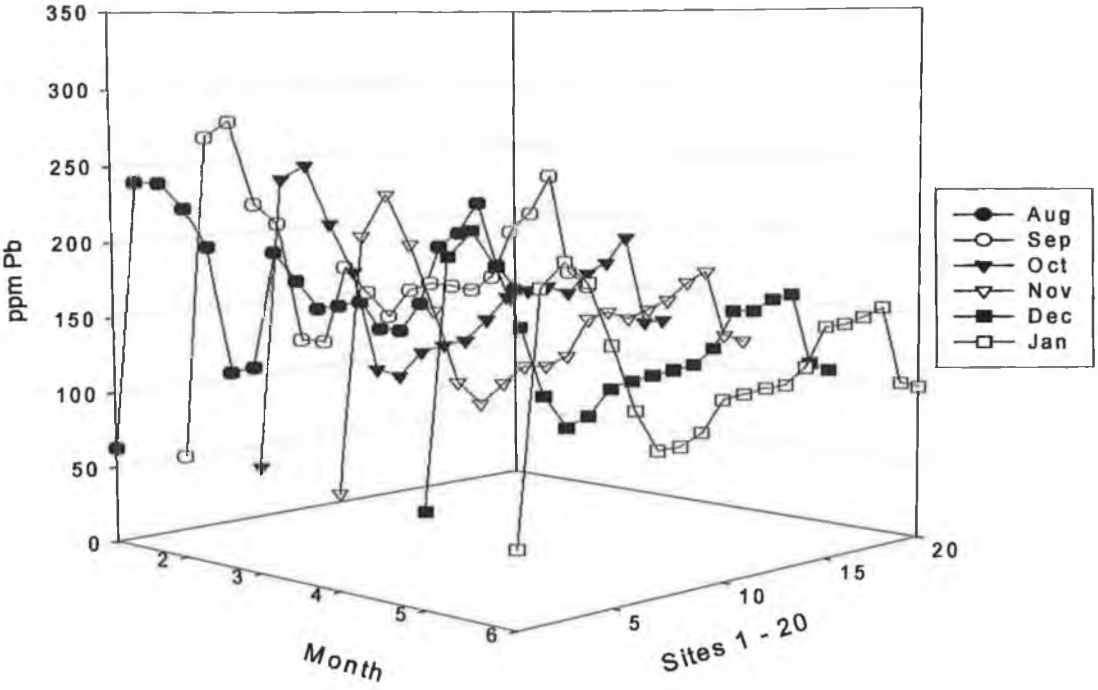


Figure 3.5.24 Pb surface sediment concentrations, Sites 1 – 20, August '03 to January '04.

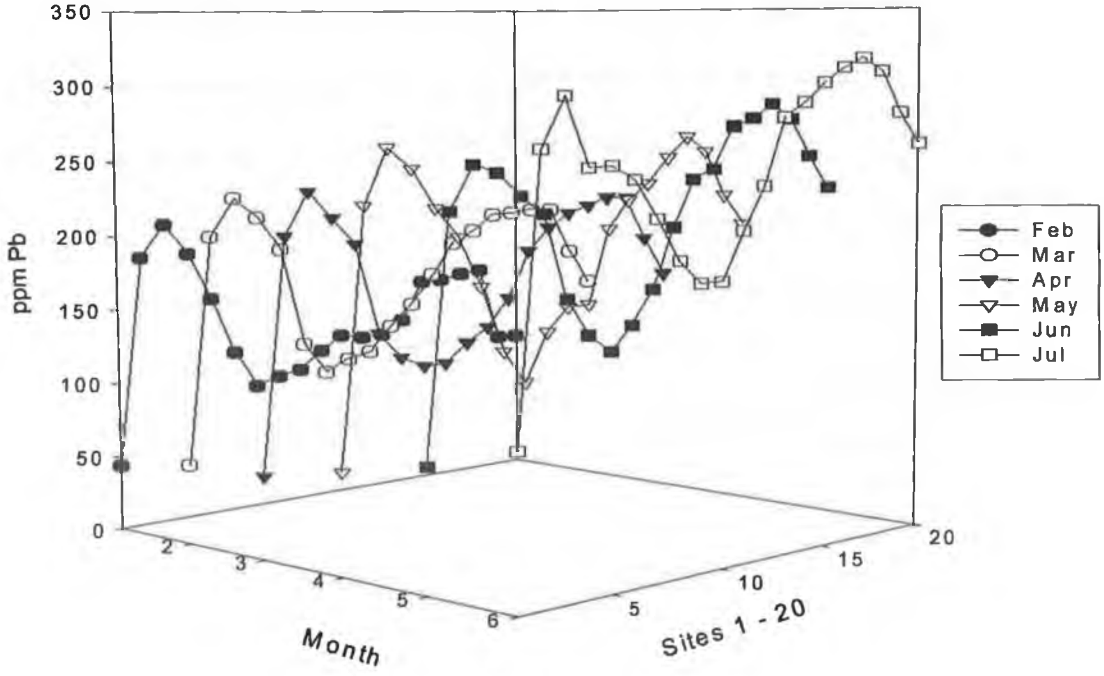


Figure 3.5.25 Pb surface sediment concentrations, Sites 1 – 20, February to July '04.

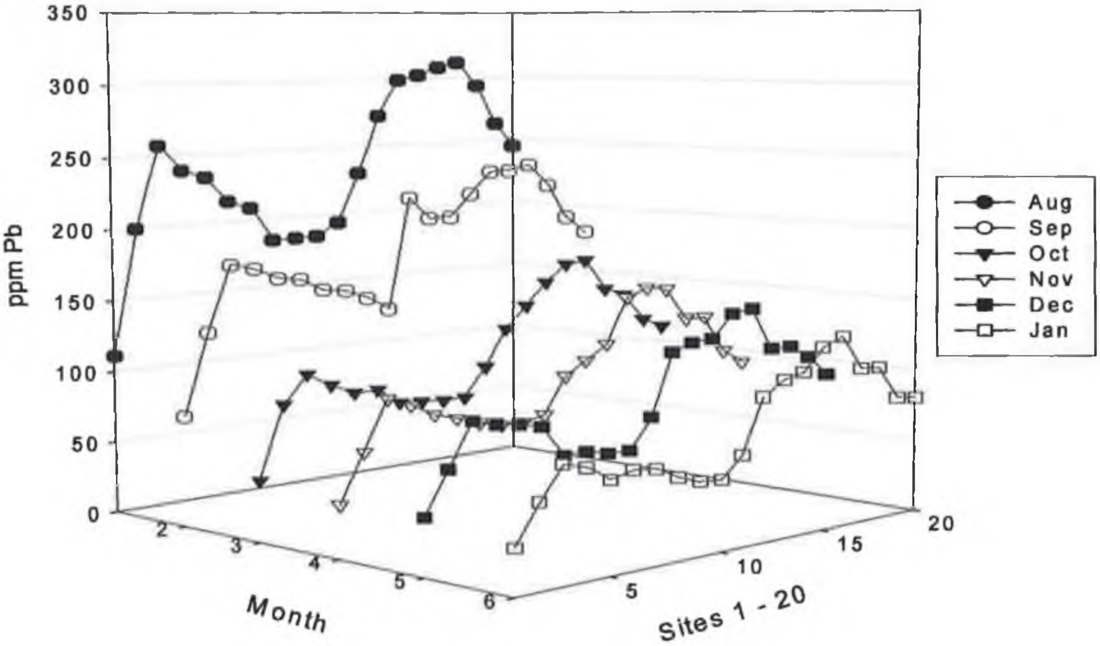


Figure 3.5.26 Pb surface sediment concentrations, Sites 1 – 20, August '04 to January '05.

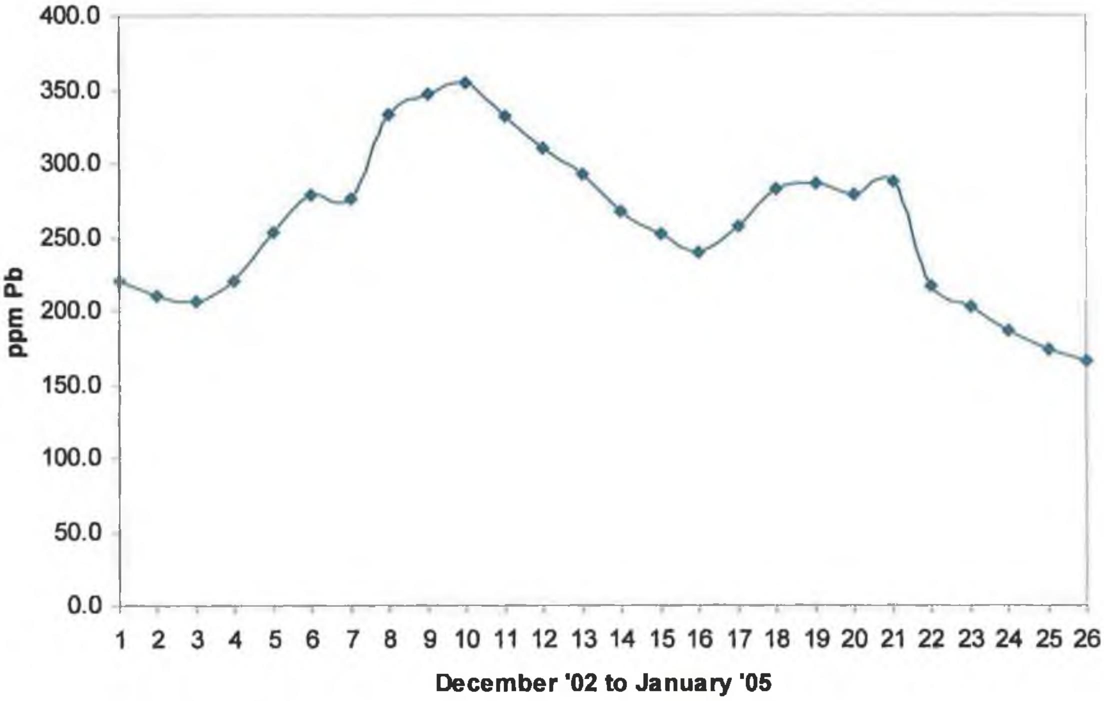


Figure 3.5.27 Pb surface sediment concentrations, Site A, Dunsink Tributary.

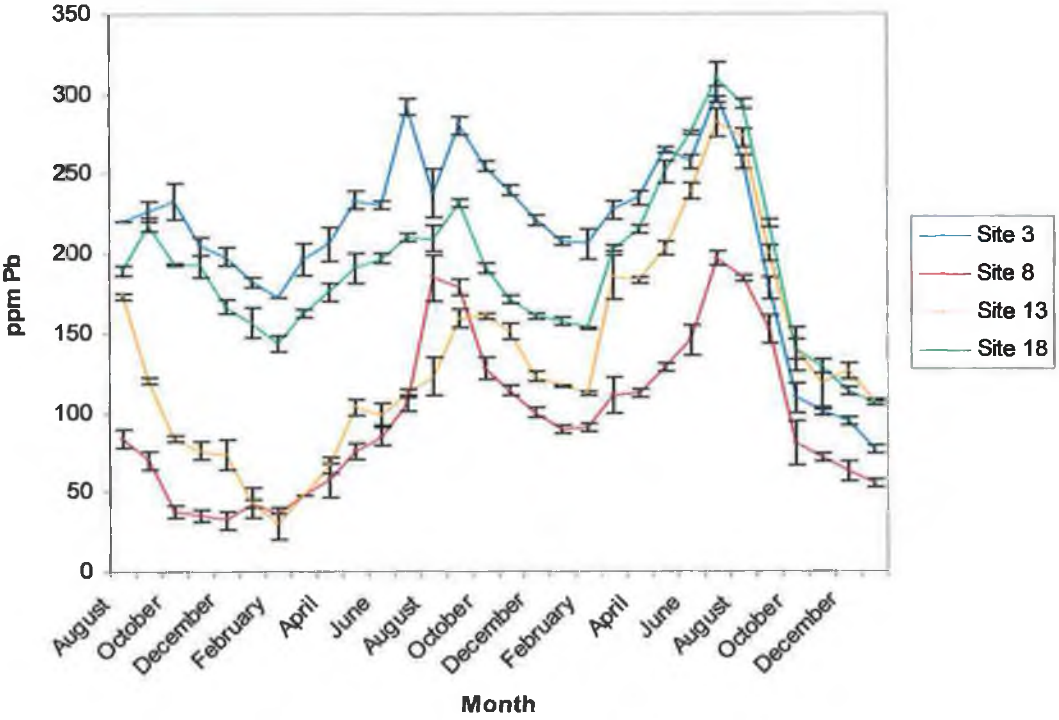


Figure 3.5.28 Pb surface sediment concentrations, Sites 3, 8, 13 & 18, August 2002 to January 2005.

3.5.5 Nickel

Ni surface sediment concentrations are illustrated in Figures 3.5.29 to 3.5.33. Ni surface sediment concentrations for Dunsink Tributary is illustrated in Figure 3.5.34. Ni concentrations exhibited moderate spatial variation between the river and estuary: mid estuarine Ni concentrations were generally higher than the highest riverine concentrations. Seasonal variation was evident at all sites over the thirty month period, however the estuarine sites had a slightly broader temporal range. Temporally, Ni concentrations were moderately elevated in late summer and autumn months compared to winter and spring months. A typical thirty month temporal distribution for the system can be illustrated at Site 16: August 2002 – 47.8 ppm Ni, February

2003 – 22.8 ppm Ni, August 2003 – 30.0 ppm Ni, February 2004 – 21.2 ppm Ni, August 2004 – 38.0 ppm Ni and January 2005 – 23.8 ppm Ni. However as with Cr and Cu, overall Ni concentrations throughout estuarine and riverine zones reduced during the sampling period, for example at Site 12 - the confluence of the river and estuary, Ni concentrations ranged from 45.7 ppm in August 2002, to 26.5 ppm in August 2003 and finally to 31.3 ppm in August 2004. Figure 3.5.35 illustrates seasonal Ni variation at two riverine sites (3 and 5) and two estuarine sites (13 and 18).

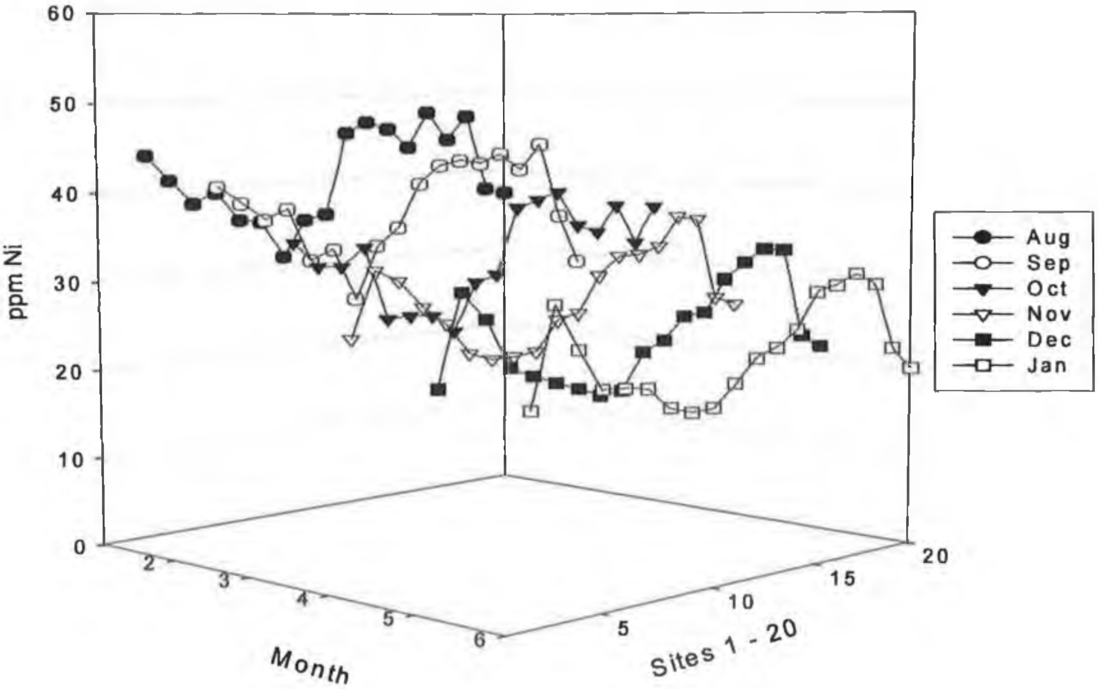


Figure 3.5.29 Ni surface sediment concentrations, Sites 1 – 20, August '02 to January '03.

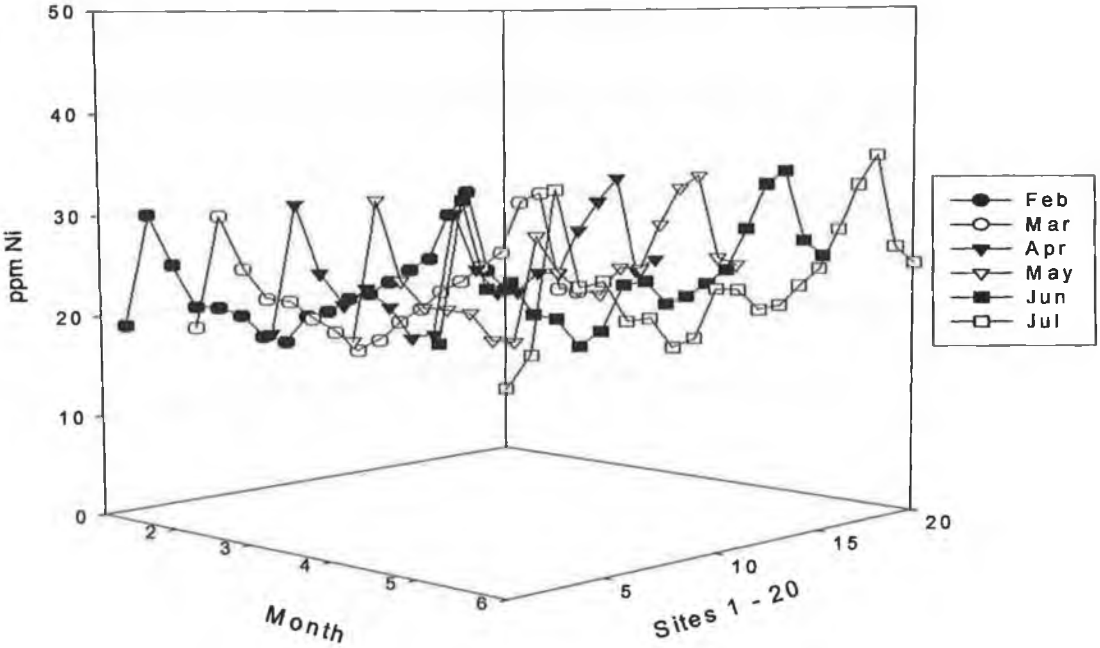


Figure 3.5.30 Ni surface sediment concentrations, Sites 1 – 20, February to July '03.

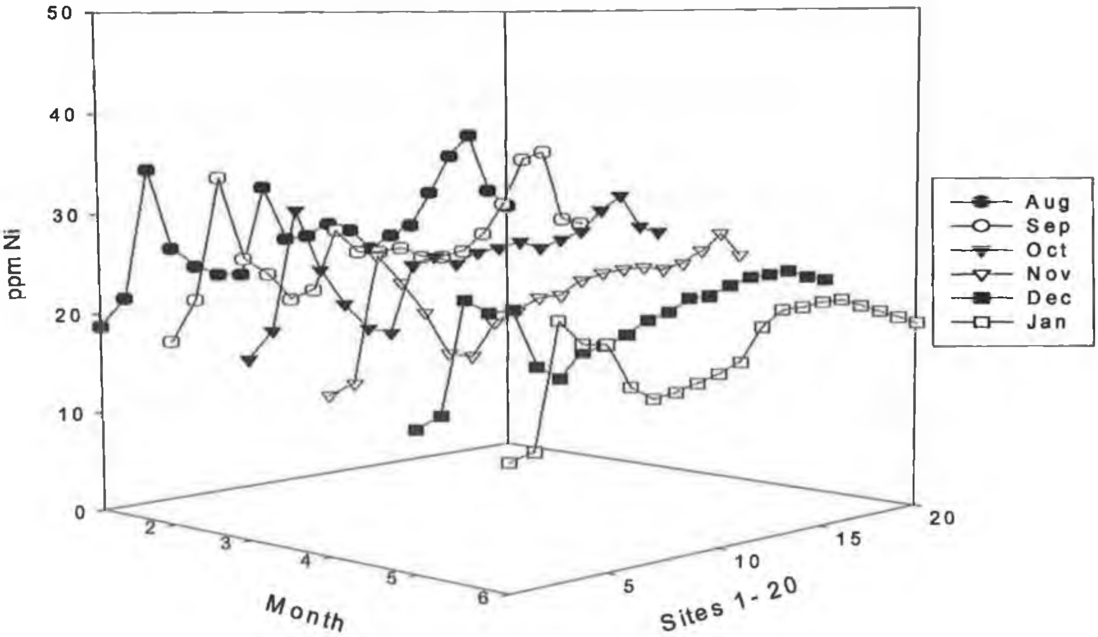


Figure 3.5.31 Ni surface sediment concentrations, Sites 1 – 20, August '03 to January '04.

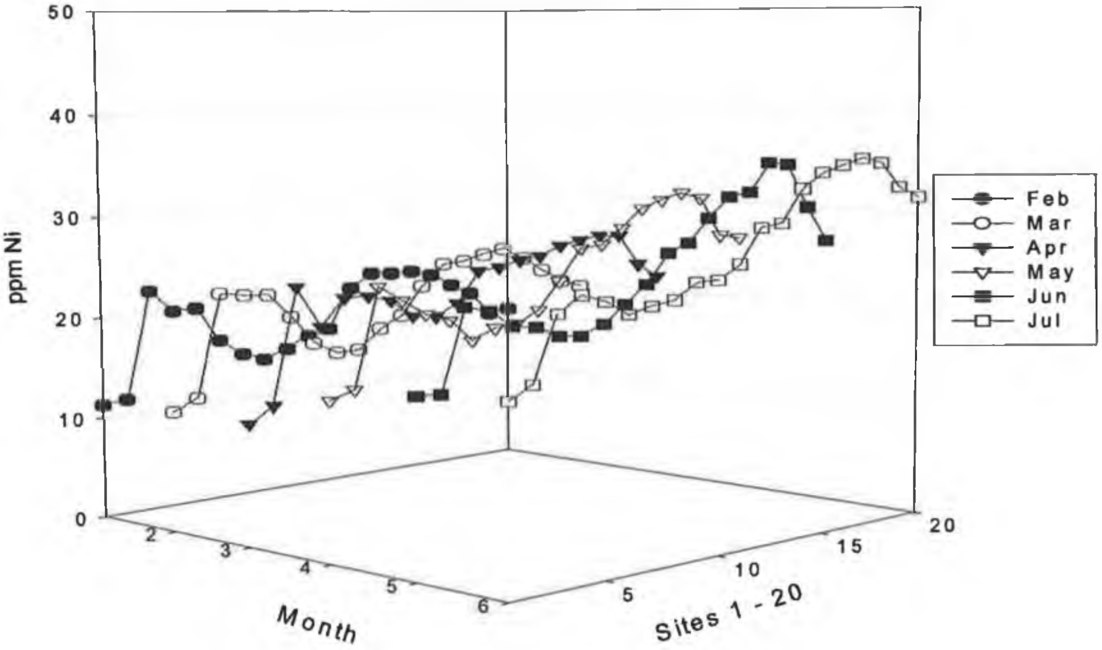


Figure 3.5.32 Ni surface sediment concentrations, Sites 1 – 20, February to July '04.

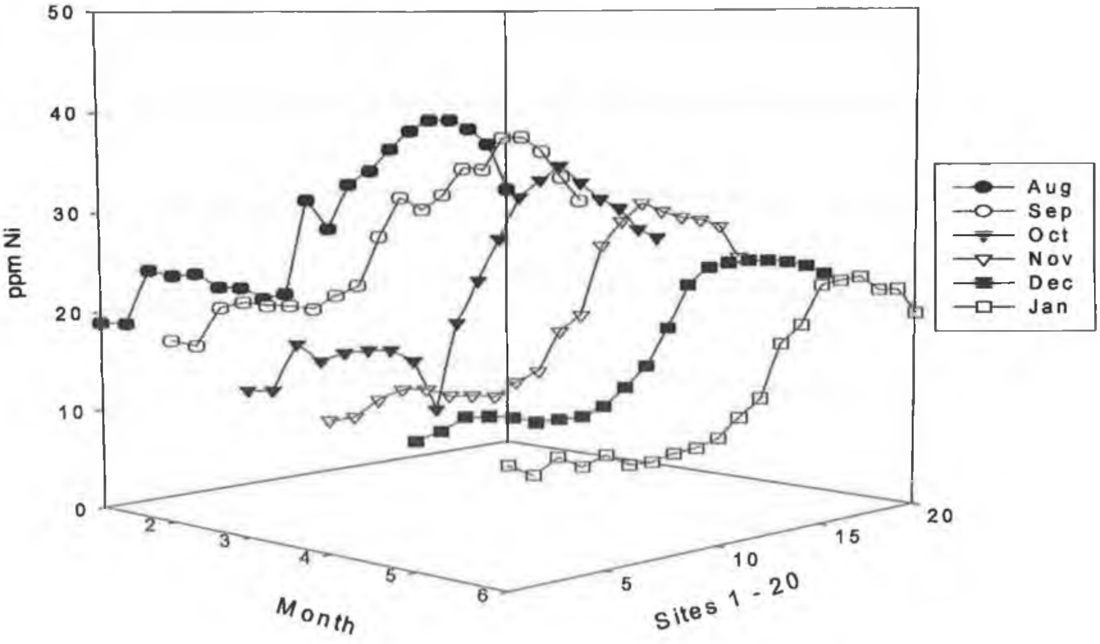


Figure 3.5.33 Ni surface sediment concentrations, Sites 1 – 20, August '04 to January '05.

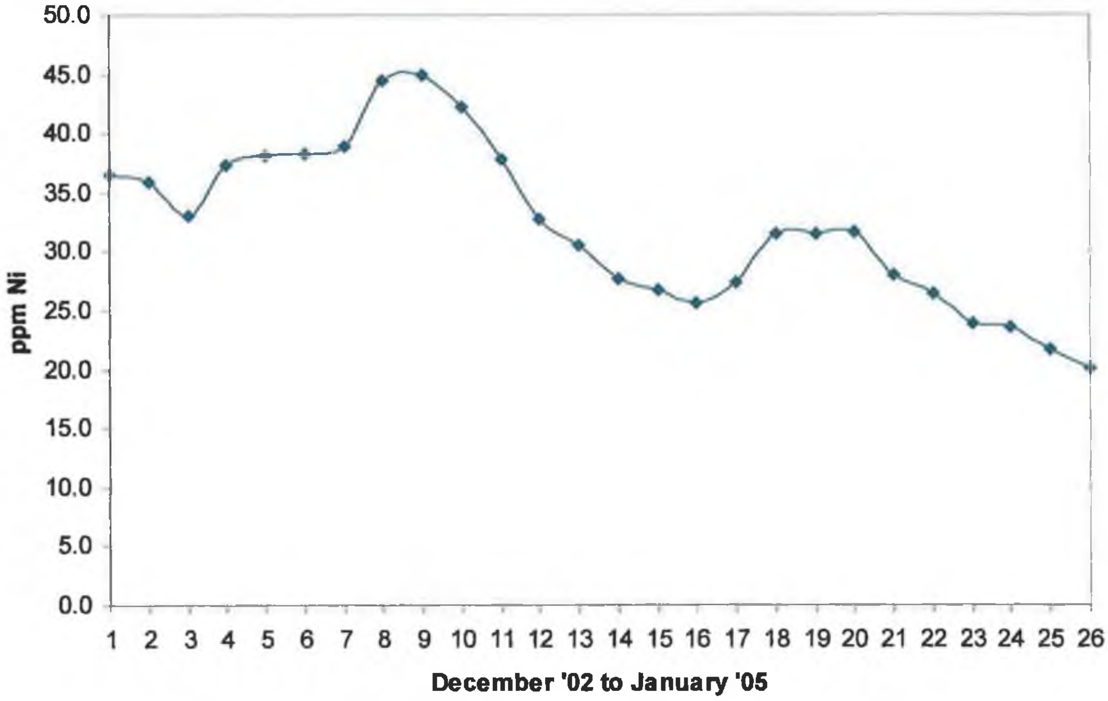


Figure 3.5.34 Ni surface sediment concentrations, Site A, Dunsink Tributary.

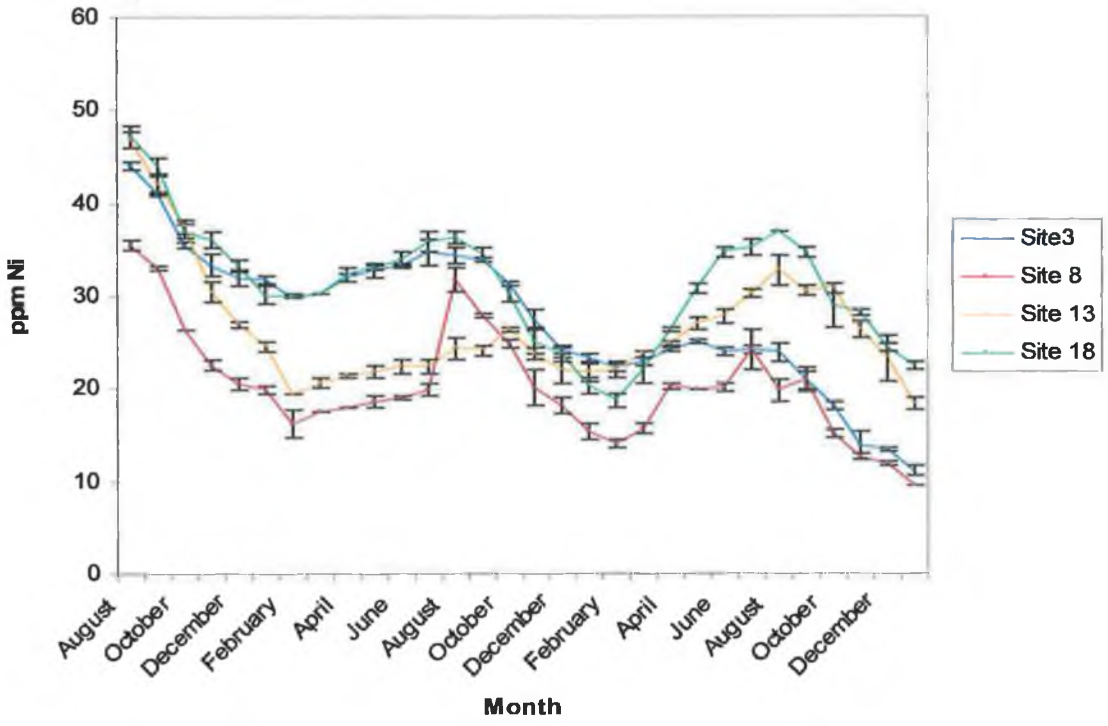


Figure 3.5.35 Ni surface sediment concentrations, Sites 3, 8, 13 & 18, August 2002 to January 2005.

3.5.6 Zinc

Zn concentrations in surface sediment had the second greatest spatial and temporal range between river and estuary, see Figures 3.5.36 to 3.5.40. Zn surface sediment concentration recorded in the Dunsink Tributary are illustrated in Figure 3.5.41. Zn concentrations had a broad range in the tributary: from 52.6 ppm to 184.2 ppm during the research period, indicating that the landfill was a significant source of Zn. Over the thirty month period the spatial pattern for the river and estuary remained relatively constant. Zn spatial and temporal variations exhibited equivalent distributions to the other five metals but with a greater range than all metals except Pb. A typical thirty month temporal distribution for the system can be illustrated at Site 18: September 2002 – 86.4 ppm Zn, November 2002 – 41.2 ppm Zn, October 2003 – 115.3 ppm Zn, March 2004 – 101.5 ppm Zn, August 2004 – 130.4 ppm Zn and January 2005 – 93.7 ppm Zn. Unlike Cd, Cr and Cu, and similar to Pb concentrations, Zn concentrations over the thirty months did not diminish, but increased overall. Figure 3.5.42 illustrates seasonal Zn variation at two riverine sites (3 and 5) and two estuarine sites (13 and 18).

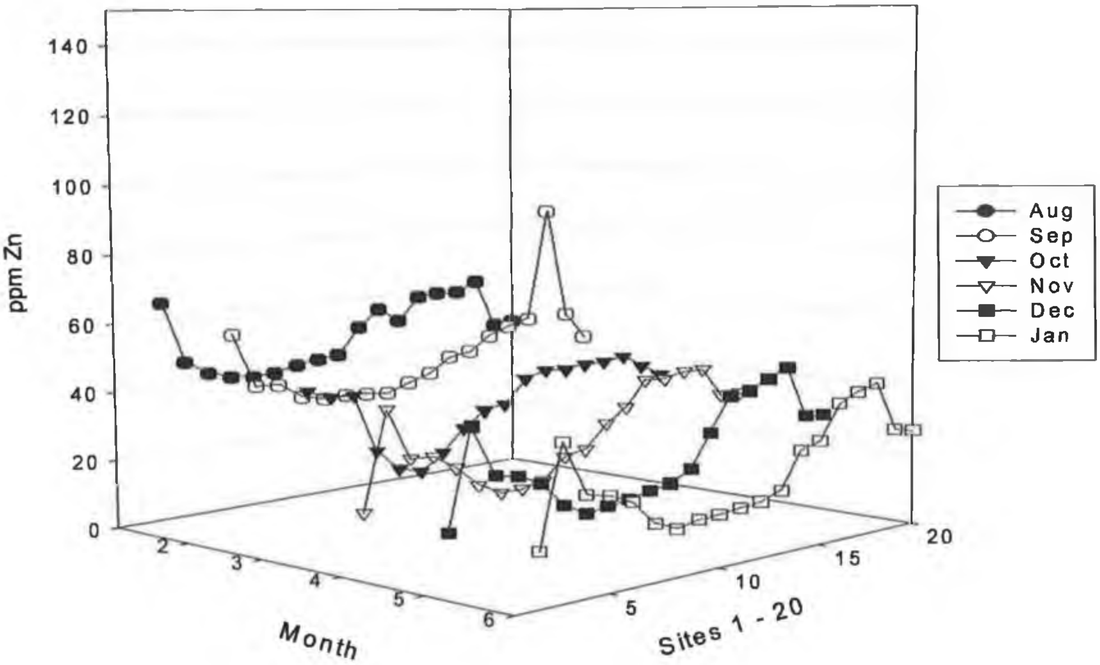


Figure 3.5.36 Zn surface sediment concentrations, Sites 1 – 20, August '02 to January '03.

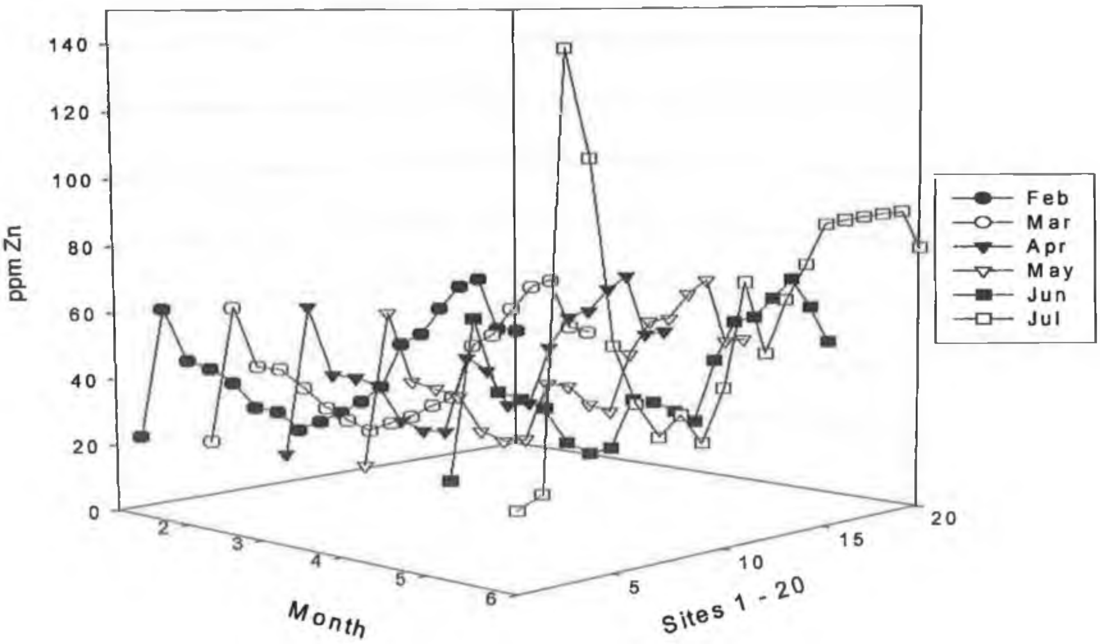


Figure 3.5.37 Zn surface sediment concentrations, Sites 1 – 20, February to July '03.

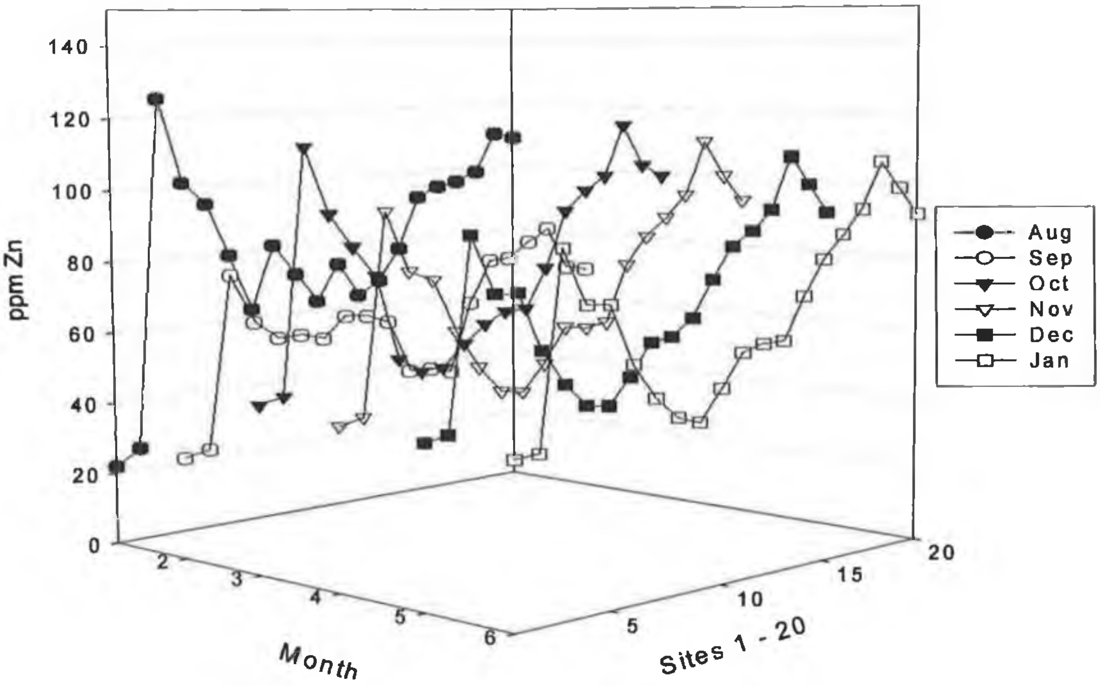


Figure 3.5.38 Zn surface sediment concentrations, Sites 1 – 20, August '03 to January '04.

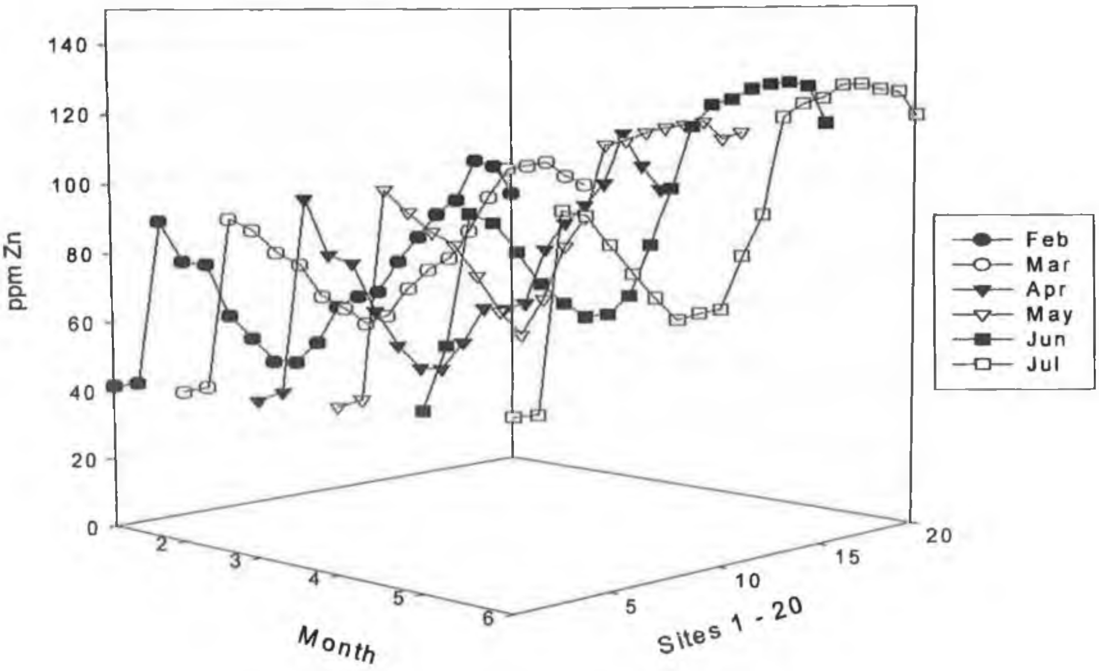


Figure 3.5.39 Zn surface sediment concentrations, Sites 1 – 20, February to July '04.

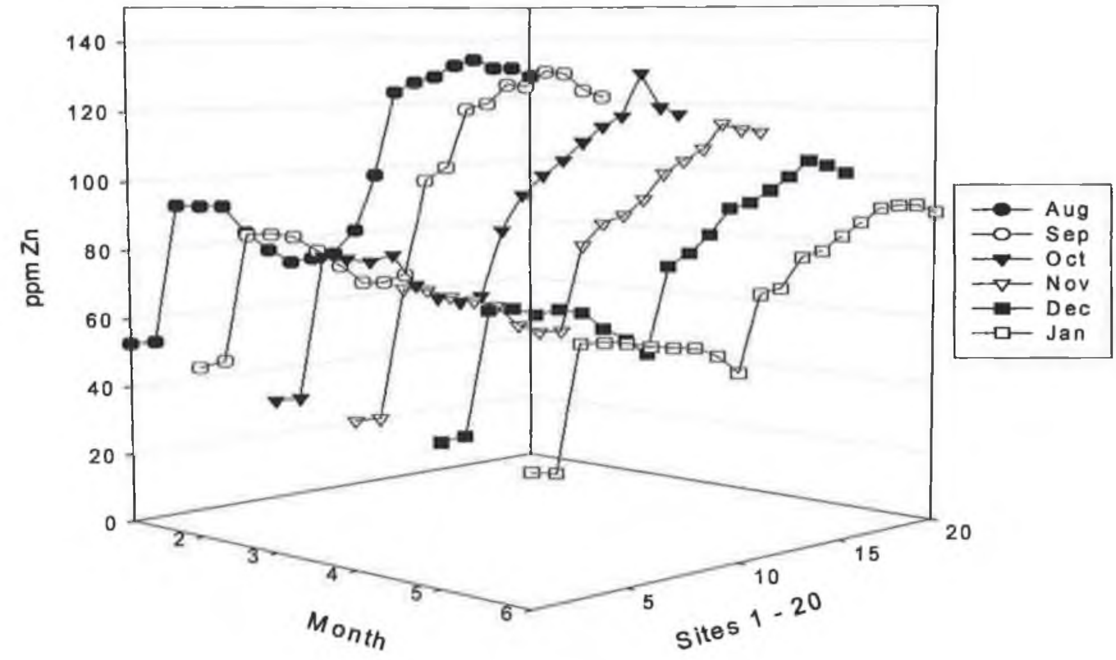


Figure 3.5.40 Zn surface sediment concentrations, Sites 1 – 20, August '04 to January '05.

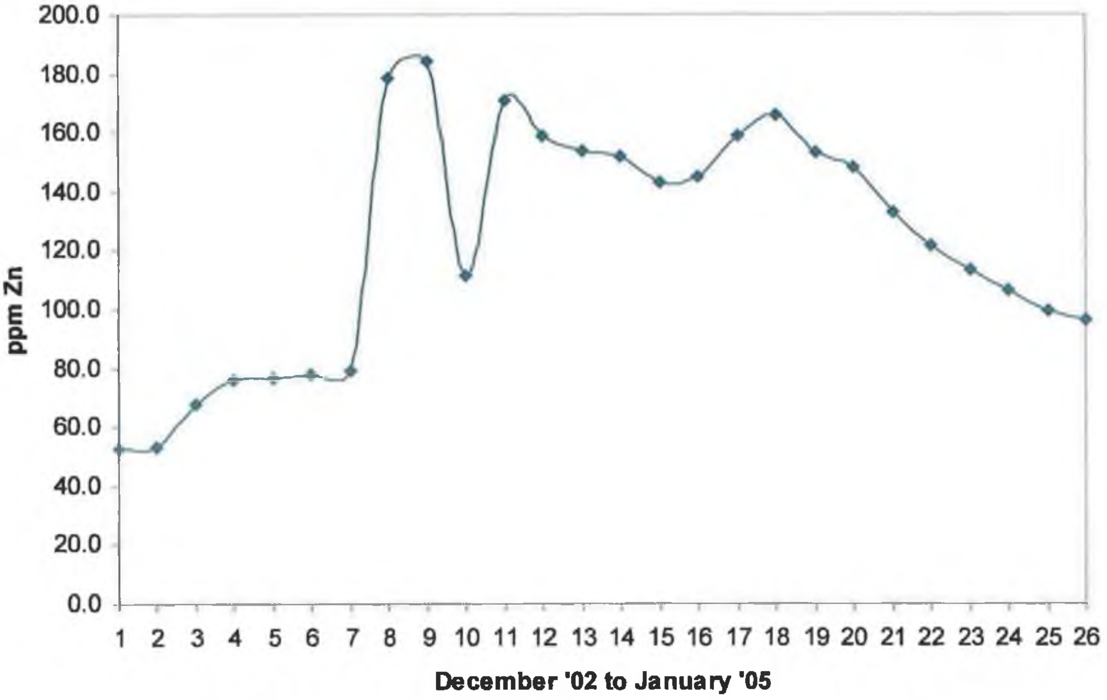


Figure 3.5.41 Zn surface sediment concentrations, Site A, Dunsink Tributary.

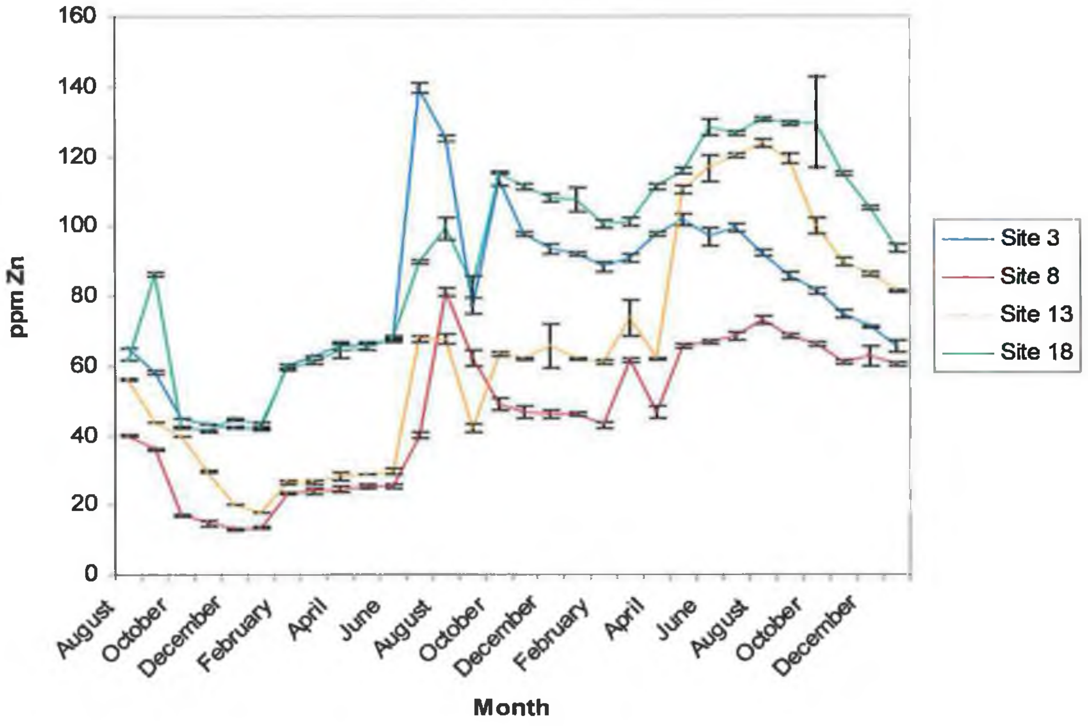


Figure 3.5.42 Zn surface sediment concentrations, Sites 3, 8, 13 & 18, August 2002 to January 2005.

3.5.7 Arsenic, Manganese and Cobalt

As, Mn and Co were analysed in January 2005, see Figures 3.5.43 to 3.5.45. Surface sediment concentrations of these three metals exhibited a similar spatial range as the other six metals. Maximum riverine concentration was recorded in the vicinity of Site 3 – 89.2 ppm As, 41.1 ppm Mn and 56.0 ppm Co. Concentrations in Dunsink Tributary surface sediment were 110.0 ppm As, 45.3 ppm Mn and 76.8 ppm Co. These results indicate that the stream had higher metal contamination concentrations than the river and was a source of these metals to the system. Estuarine metal concentrations were higher than riverine and had a broader range. As surface sediment concentrations ranged from a minimum of 55.9 ppm at Site 11 to a maximum of 111.5 ppm at Site 18. Mn surface sediment concentrations ranged from a minimum of 43.0 ppm at Site 11 to a maximum of 67.9 ppm at Site 15. Co surface sediment concentrations ranged from a minimum of 55.8 ppm at Site 11 to a maximum of 90.3 ppm at Site 17.

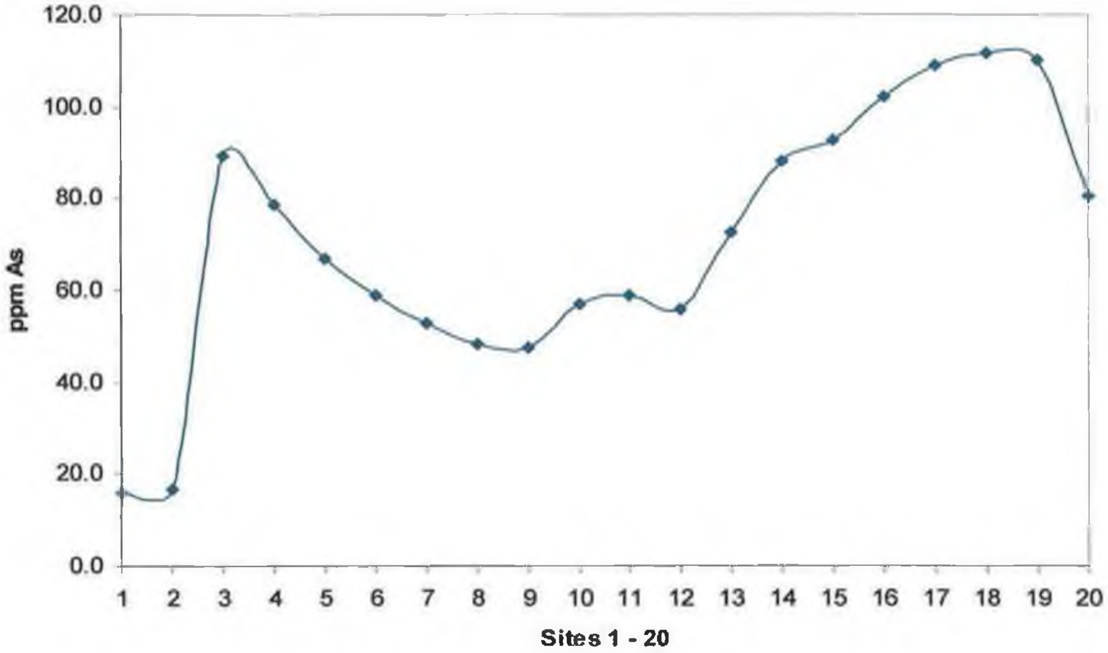


Figure 3.5.43 As surface sediment concentrations, Sites 1 – 20, January '05.

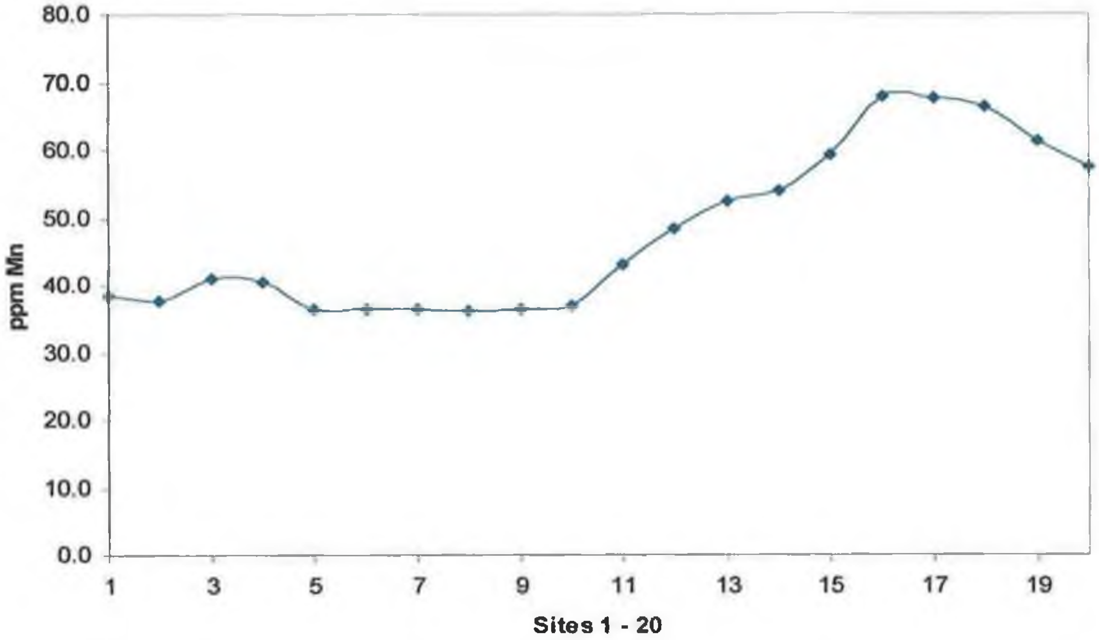


Figure 3.5.44 Mn surface sediment concentrations, Sites 1 – 20, January '05.

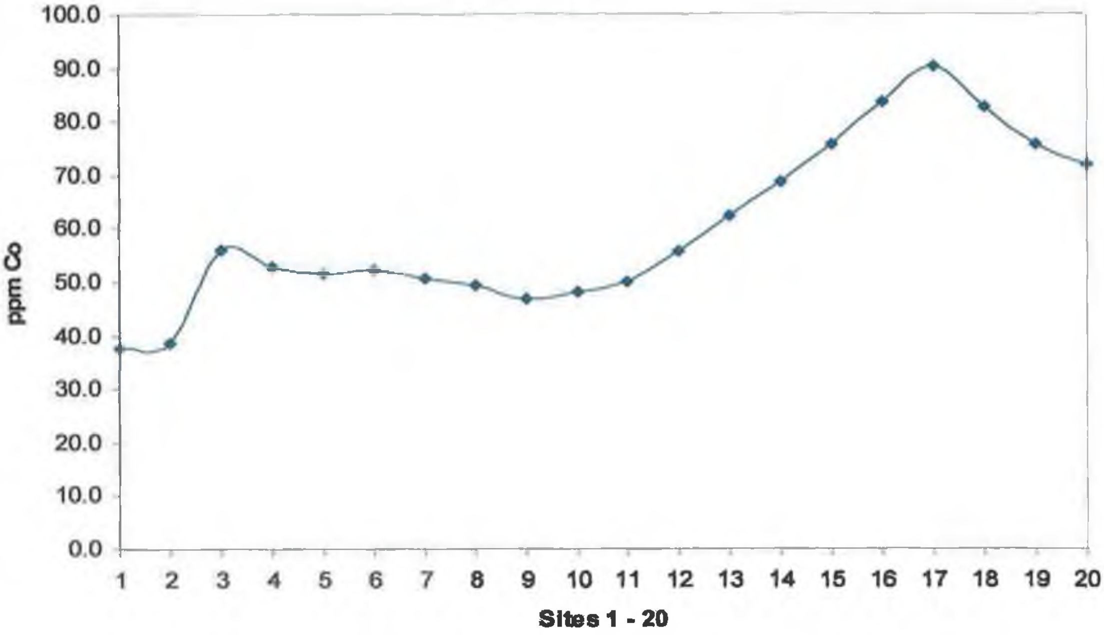


Figure 3.5.45 Co surface sediment concentrations, Sites 1 – 20, January '05.

3.6 Suspended Particulate Matter and Associated Metal Concentrations

Suspended particulate matter (SPM) was sampled from seven separate points. Sampling initially took place in January 2004 from Bridges 1 – 5, and from July 2004, Bridge 0 farther upstream and the Dunsink Tributary. Initial results indicated a highly turbid river that has high SPM load and moderate deposition rate due to a turbulent river channel with many rapids and weirs. Spatially SPM showed a moderate variation: higher at both ends of the river sampling regime with lowest concentrations in the middle section, Figures 3.6.1 and 3.6.2. indicate the spatial and temporal variation. Figure 3.6.3 indicates SPM levels in the Dunsink Tributary. Temporally SPM was higher in winter months than in summer months, e.g. Bridge 3: January 2004 – 221 mg / L, reducing to 134 mg / L in June 2004 and subsequently increasing to 321 mg / L in January 2005.

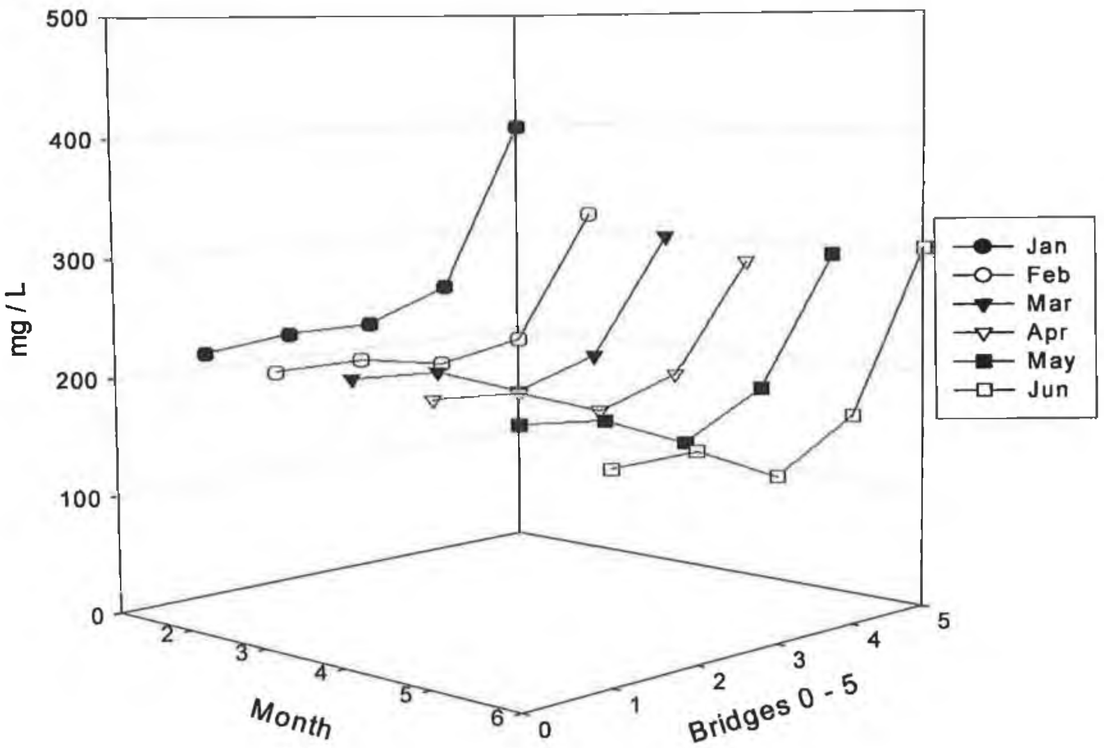


Figure 3.6.1 SPM, Bridges 0 - 5, January to July '04

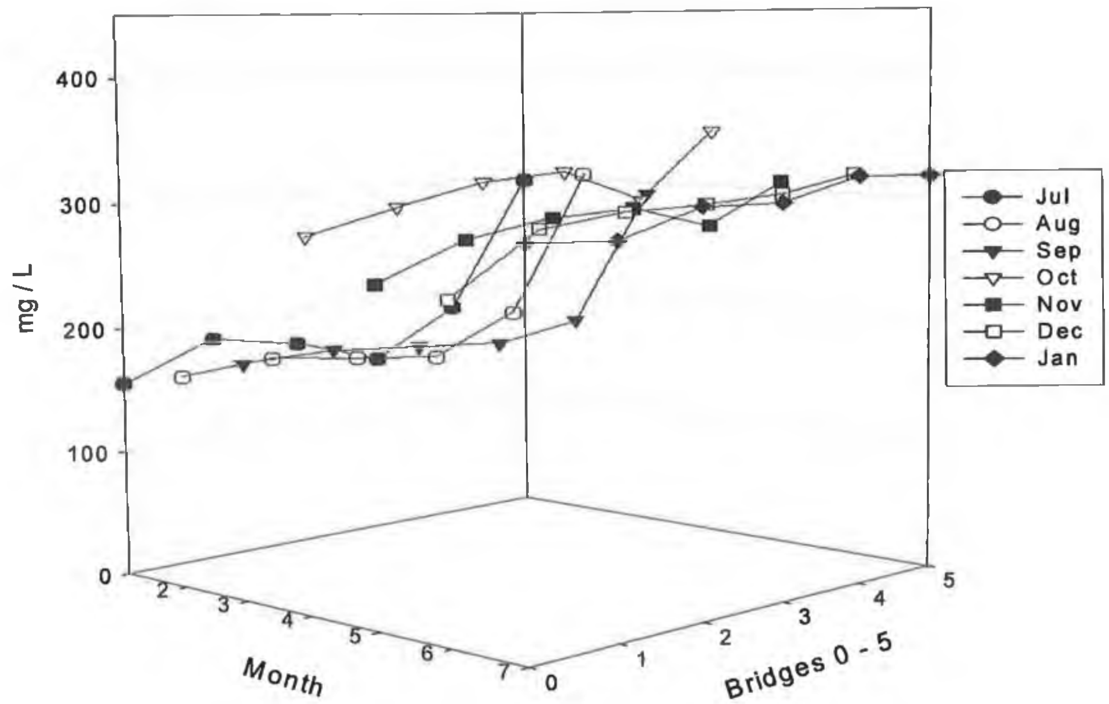


Figure 3.6.2 SPM, Bridges 0 - 5, July '04 to January '05

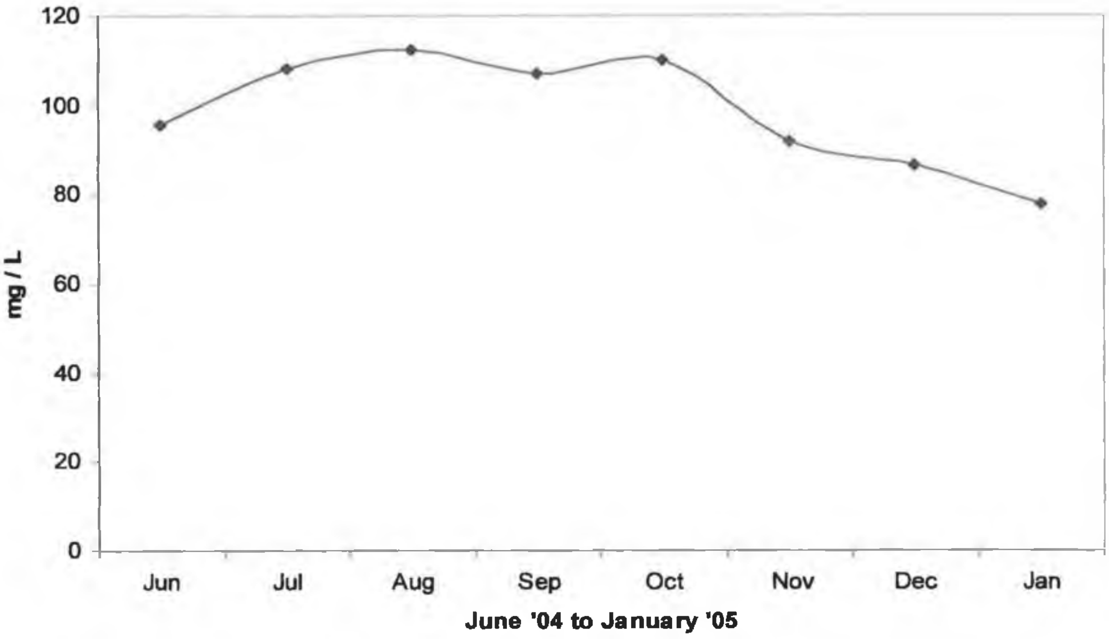


Figure 3.6.3 Suspended Particulate Matter, Dunsink Tributary, June '04 to January '05.

3.6.1 SPM bound Cadmium

SPM bound Cd was analysed from June 2004 to January 2005, see Figure 3.6.4. Spatially Cd content of SPM was lower at Bridge 0 and moderately increased at Bridge 1 downstream of Dunsink Tributary. Subsequently, Cd concentrations decreased towards the end of the river but at Bridge 5 increased again to levels similar to Bridge 1. This can be associated with inflowing SPM from the estuary rather than purely riverine SPM. Temporally, Cd content of SPM was lower in the summer than in winter but as there were only seven months of sampling, a complete seasonal distribution was not observed. Bridge 5 provided the greatest temporal range: 3.48 ppm Cd in June 2004 and 4.84 ppm Cd in January 2005. Cd concentrations of SPM in

Dunsink Tributary also had a similar temporal distribution but at lower levels: 0.12 ppm Cd in August 2004 to 0.5 ppm Cd in January 2005.

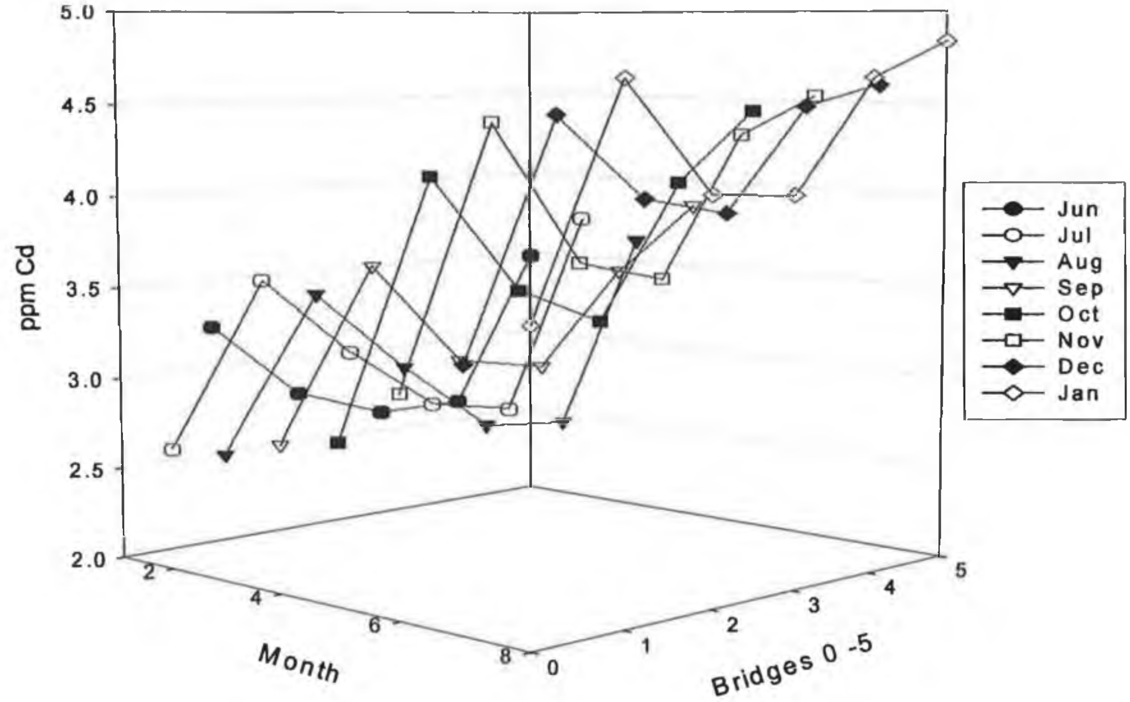


Figure 3.6.4 SPM Cadmium, Bridges 0 - 5 June '04 to January '05

3.6.2 SPM bound Chromium

SPM bound Cr concentrations are illustrated in Figure 3.6.5. Spatially Cr content of SPM was similar to Cd distributions but significantly lower. Temporal variation of Cr concentrations was similar to Cd, i.e. lower in the summer than in winter. As with Cd, Bridge 5 provided the greatest temporal range: 1.06 ppm Cr in June 2004 and 1.83 ppm Cr in January 2005. Cr concentrations of SPM in Dunsink Tributary also had a similar temporal distribution but at low levels similar to Cd concentrations: 0.18 ppm Cr in August 2004 to 0.81 ppm Cr in January 2005.

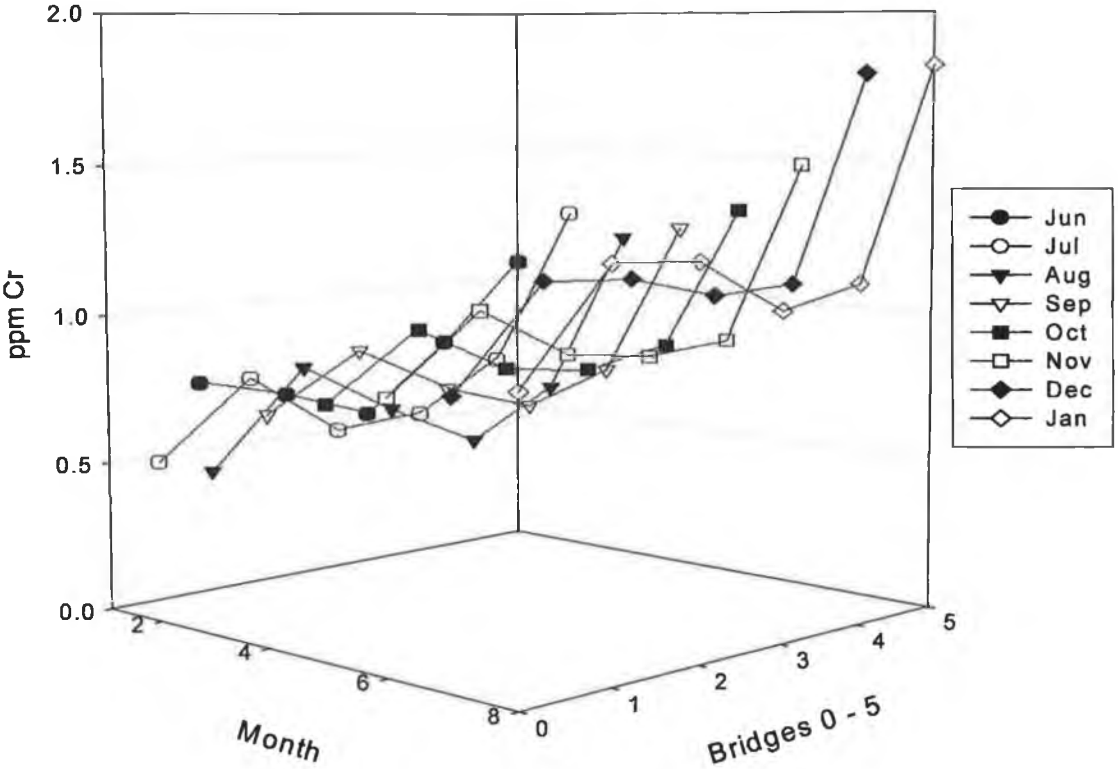


Figure 3.6.5 SPM Chromium, Bridges 0 - 5, June '04 to January '05

3.6.3 SPM bound Copper

SPM bound Cu concentrations are illustrated in Figure 3.6.6. Spatially Cu content of SPM had a distribution similar to both Cd and Cr. Seasonal variation of Cu content of SPM had a similar distribution to Cd and Cr. As with Cd and Cr, Bridge 5 provided the greatest temporal range: 26.9 ppm Cd in June 2004 and 33.4 ppm Cd in January 2005. Cu concentrations of SPM in Dunsink Tributary also had a similar temporal distribution but at lower levels than the river: 4.0 ppm Cu in August 2004 to 10.1 ppm Cu in January 2005.

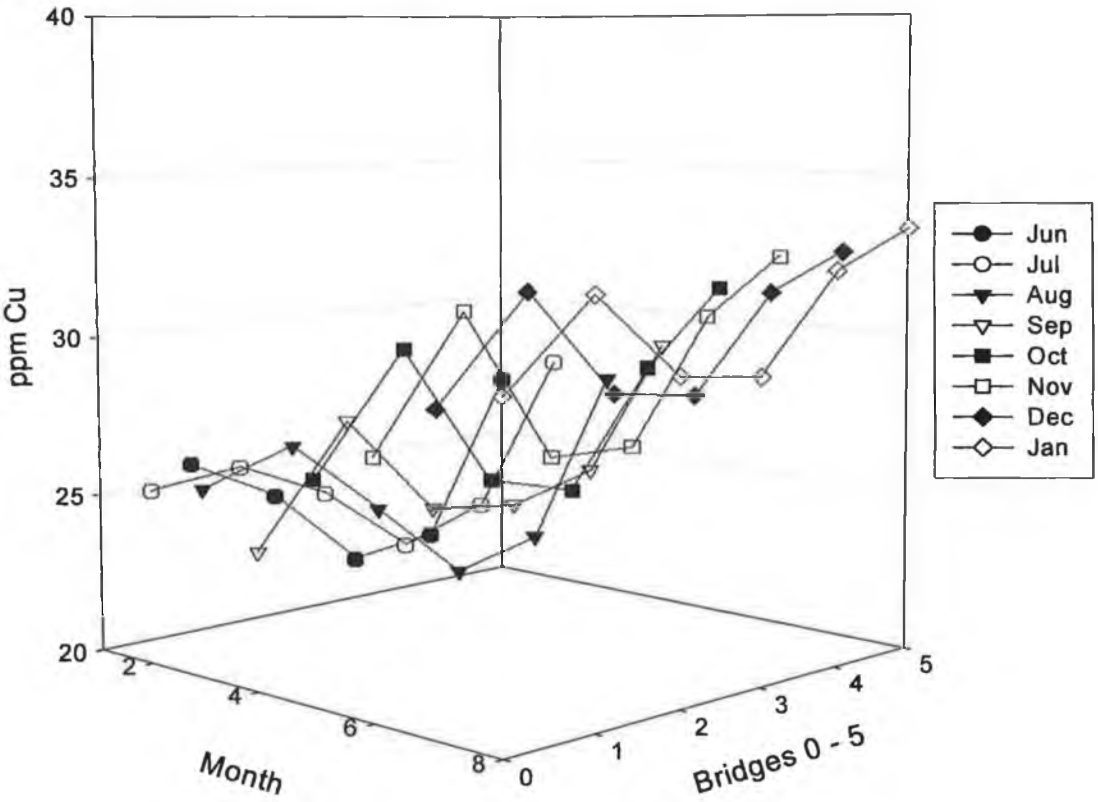


Figure 3.6.6 SPM Copper, Bridges 0 - 5, June '04 to January '05

3.6.4 SPM bound Lead

SPM bound Pb concentrations are illustrated in Figure 3.6.7. Spatially, Pb content of SPM was similar to the previous metal distributions with low concentrations at Bridge 0 and a subsequent moderate increase at Bridge 1 downstream of Dunsink Tributary. Pb concentrations then decreased towards the end of the river but at Bridge 5 increased again to levels similar to Bridge 1. Temporally, Pb content of SPM had a similar distribution to the other metals: lower in the summer than in winter. However, it had the highest concentrations of any metal bound to SPM. As with the other metals, Bridge 5 provided the greatest temporal range: 24.9 ppm Pb in June 2004 and

44.9 ppm Pb in January 2005. Pb concentrations of SPM in Dunsink Tributary also had a similar temporal distribution but at higher levels than the previous metals: 3.8 ppm Pb in August 2004 to 12.5 ppm Pb in January 2005.

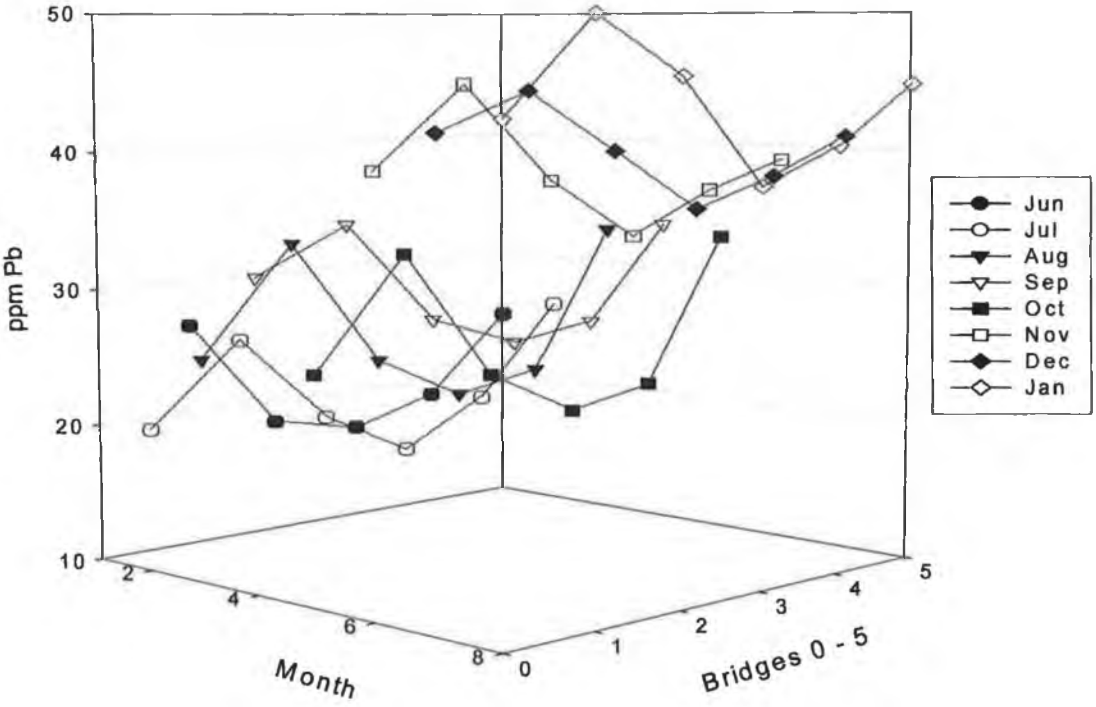


Figure 3.6.7 SPM Lead, Bridges 0 - 5, June '04 to January '05

3.6.5 SPM bound Nickel

Ni concentrations bound to SPM are illustrated in Figure 3.6.8. SPM bound Ni concentrations exhibited equivalent spatial and temporal distributions as the other metals. As with all metals, Bridge 5 provided the greatest temporal range of Ni concentrations: 18.2 ppm Ni in June 2004 and 30.2 ppm Ni in January 2005. Ni concentrations of SPM in Dunsink Tributary were the highest for any metal bound to SPM at this point and also had a similar temporal distribution to Ni in the river but at lower levels: 5.8 ppm Ni in August 2004 to 13.4 ppm Ni in January 2005.

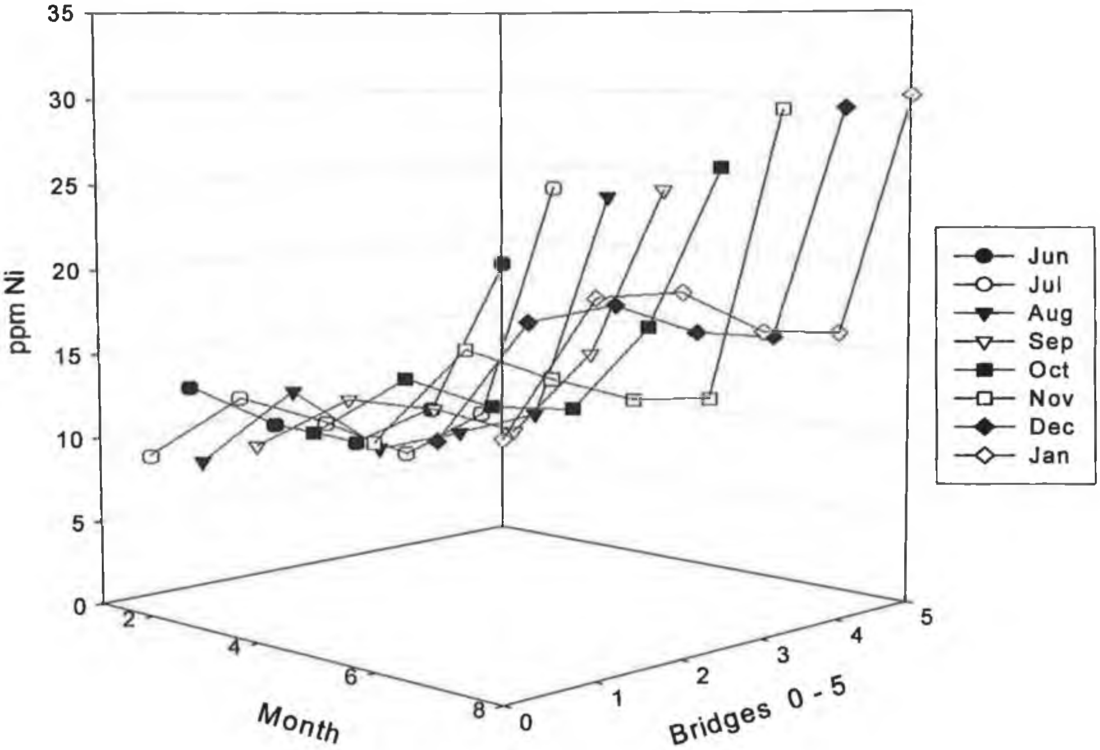


Figure 3.6.8 SPM, Nickel, Bridges 0 - 5, June '04 to January '05

3.6.6 SPM bound Zinc

Spatially, Zn content of SPM was similar to all the other metals distributions but was significantly lower than Cu, Ni and Pb and was similar to levels observed for Cr as shown in Figure 3.6.9. Temporally, Zn content of SPM had a similar distribution to the other metals: lower in the summer than in winter. Bridge 5 provided the greatest temporal range of Zn concentrations bound to SPM: 5.6 ppm Zn in July 2004 and 10.6 ppm Zn in January 2005. SPM bound Zn concentrations in Dunsink Tributary had an equivalent temporal distribution to the other metals but at lower levels similar to Cd concentrations: 0.4 ppm Zn in August 2004 to a maximum of 2. 45 ppm Zn in November 2004 and a decrease to 2.25 ppm Zn in January 2005.

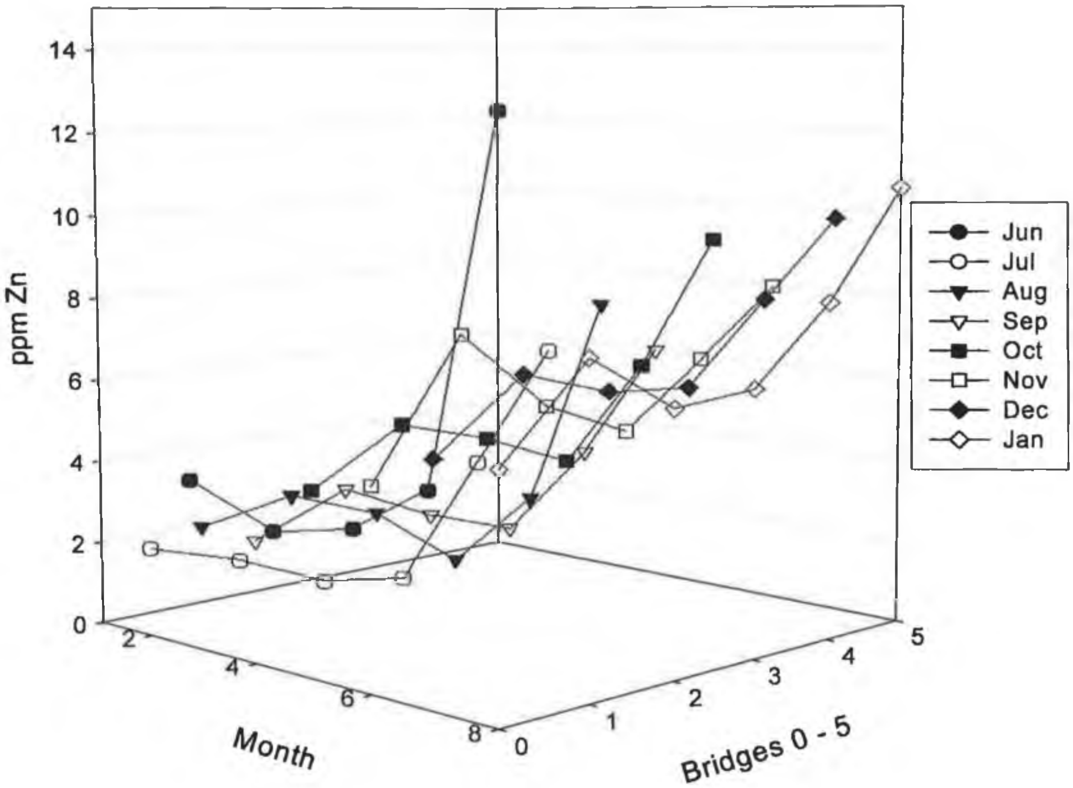


Figure 3.6.9 SPM Zinc, Bridges 0 - 5, June '04 to January '05.

3.6.7 SPM Depositional Rate

Table 3.6.1 indicates sediment deposition rates recorded between Sites 3 and 4 between June 2004 and January 2005. Depositional rates dropped significantly during winter months. Summer deposition rates were significantly higher than winter months: deposition in July was 22 times higher than deposition in January. Deposition rates decreased by 50 % between August and September and 90 % between September and October.

Month / Year	Average Deposition g / m^2
June 2004	37.6
July	38.6
August	37.9
September	19.8
October	2.8
November	1.8
December	2.7
January 2005	1.7

Table 3.6.1 Average suspended sediment deposition, sampled between Sites 3 and 4 of the river.

3.7 Water Column Dissolved Metal Concentrations

The dissolved metal fraction of the water column was analysed between January 2004 and January 2005 between Bridges 1 and 5 while Bridge 0 and Site A (Dunsink Tributary) were subsequently added in July and August respectively. Dissolved metal concentrations increased towards the estuary, indicating dissolved metal load was elevated by passing through the urban area. Minimum and maximum dissolved metal loadings are shown in Table 3.7.1. Over the course of thirteen months sampling, dissolved metal concentrations generally increased overall in the water column but a seasonal distribution was also observed, i.e. dissolved metal concentrations reduced in summer months and were significantly higher in winter months.

Metal	Minimum			Maximum		
	ppm	Bridge	Month	ppm	Bridge	Month
Cd	0.01	3	Jun ‘04	1.28	5	Jan ‘05
Cr	0.06	4	Mar ‘04	1.49	5	Jan ‘05
Cu	0.31	3	Jun’04	2.09	5	Jan ‘05
Ni	0.50	3	Apr ‘04	6.98	5	Jan ‘05
Pb	0.05	1	Jul ‘04	38.35	5	Dec ‘04
Zn	2.08	2	Jun ‘04	7.87	5	Jan ‘05

Table 3.7.1 Minimum and maximum dissolved metal concentrations between Bridge 0 and Bridge 5.

3.7.1 Dissolved Cadmium

Initial sampling indicated elevated Cd concentrations closer to the estuary, see Figures 3.7.1 and 3.7.2. Cd levels diminished slightly from Bridge 1 – 0.14 ppm Cd to Bridge 3 – 0.06 ppm Cd, and then increased to Bridge 5 – 0.31 ppm Cd. Over the course of thirteen months sampling, Cd concentrations increased overall in the water column but a seasonal distribution was also observed, for example at Bridge 1 Cd concentrations ranged from 0.14 ppm Cd in January 2004 to 0.09 ppm Cd in June 2004, subsequently Cd concentrations increased through winter to a maximum of 0.83 ppm Cd in January 2005. Dunsink Tributary water column Cd concentrations ranged from 0.32 to 0.51 ppm Cd and had a similar temporal distribution to the river for the final six months of sampling.

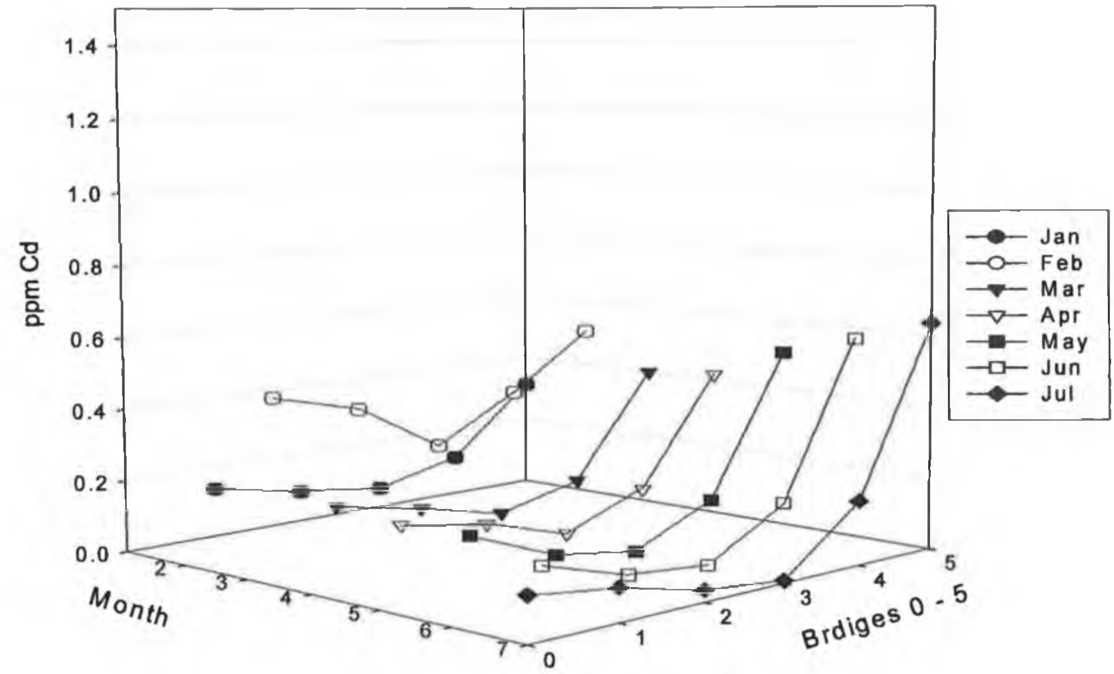


Figure 3.7.1 Water Column Cadmium, Brdiges 0 - 5, January to July '04

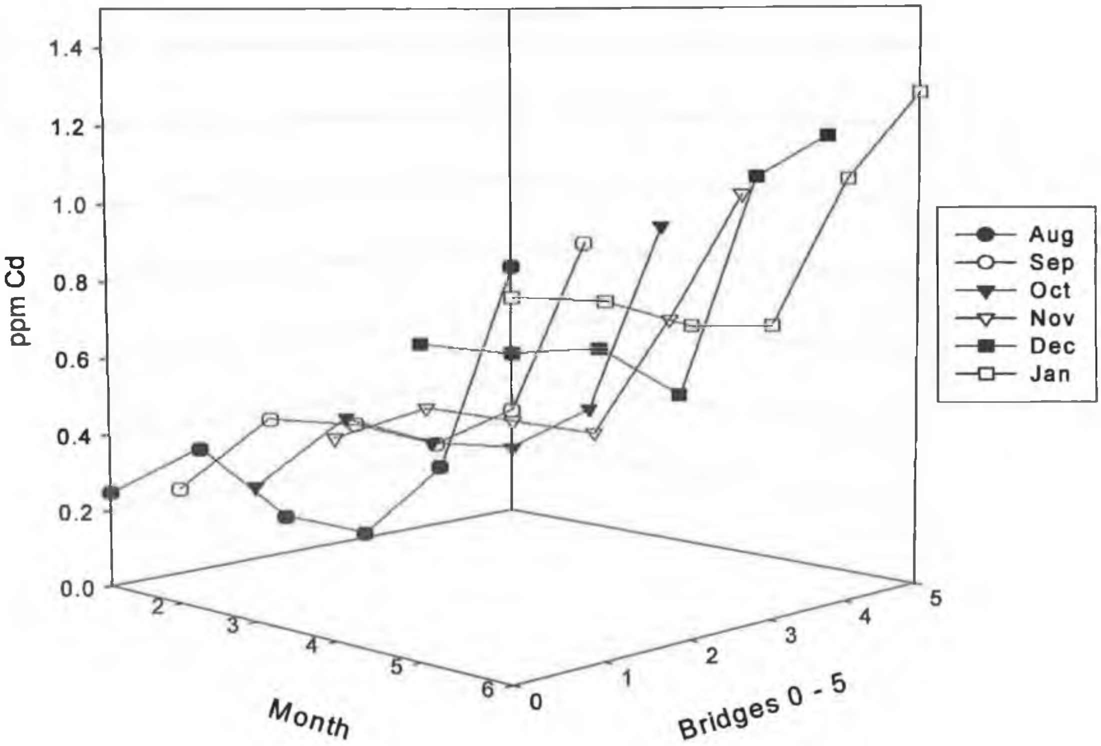


Figure 3.7.2 Water Column Cadmium, Bridges 0 - 5, August '04 to January '05

3.7.2 Dissolved Chromium

Dissolved Cr concentrations are shown in Figures 3.7.3 and 3.7.4. During the thirteen months of sampling, Cr concentrations increased substantially overall in the water column and exhibited the previously mentioned seasonal distribution: for example at Bridge 5 Cr concentrations ranged from 0.5 ppm Cr in January 2004 to 0.38 ppm Cr in April 2004, subsequently Cr concentrations increased through winter to a maximum of 1.49 ppm Cr in January 2005. Dunsink Tributary water column Cr concentrations ranged from 0.09 to 0.40 ppm Cr and also had a similar temporal distribution to the river for the final six months of sampling.

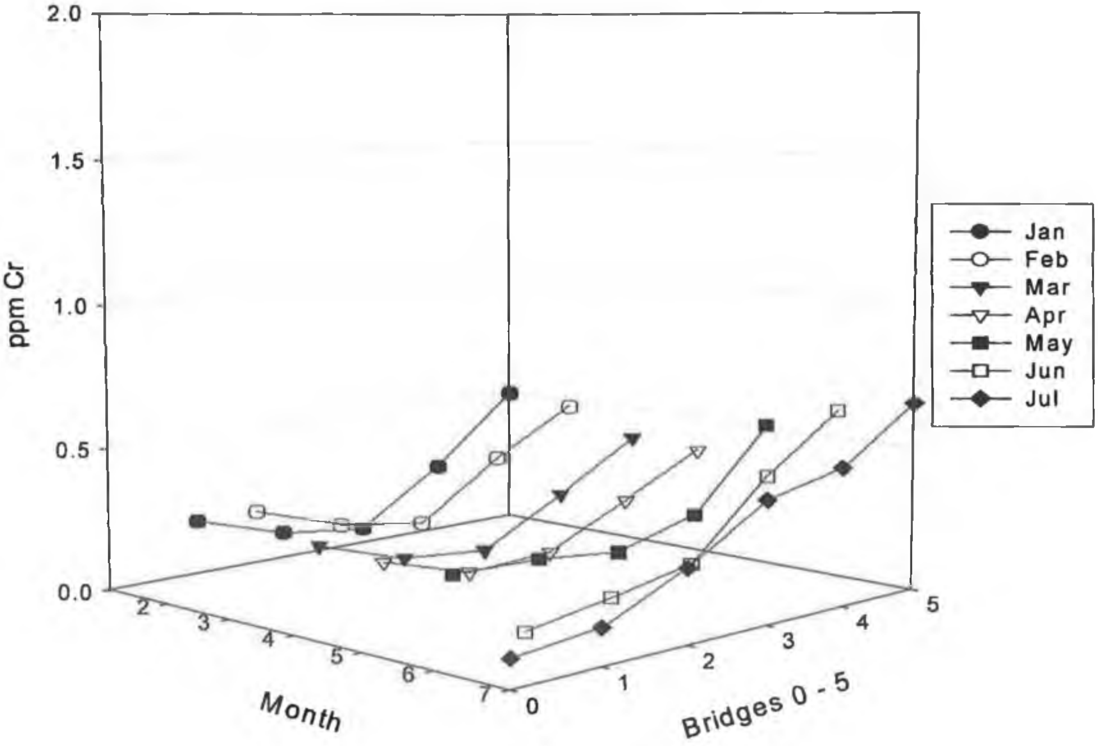


Figure 3.7.3 Water Column Chromium, Bridges 0 - 5, January to July '04

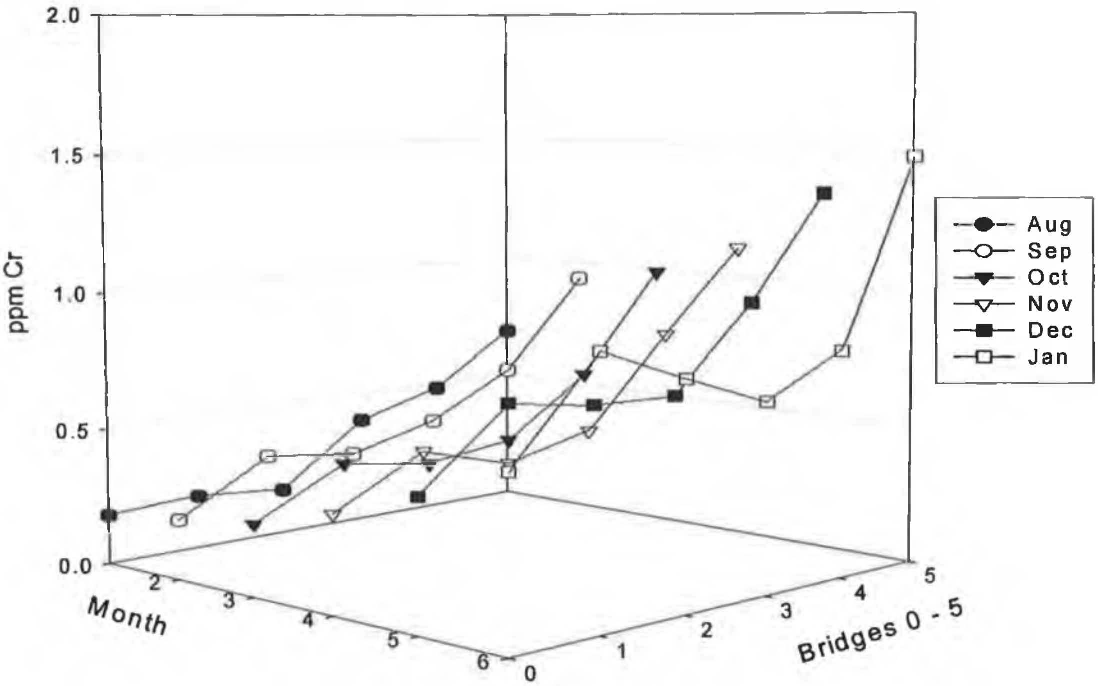


Figure 3.7.4 Water Column Chromium, Bridges 0 - 5, August '04 to January '05

3.7.3 Dissolved Copper

Initial sampling indicated higher Cu concentrations than both Cd and Cr with elevated Cu concentrations closer to the estuary, see Figures 3.7.5 and 3.7.6. Cu levels diminished significantly from Bridge 1 – 0.69 ppm Cu to Bridge 3 – 0.37 ppm Cu, and then increased to Bridge 5 – 0.8 ppm Cu. During the thirteen months sampling, dissolved Cu concentrations like Cr, increased substantially overall in the water column. But Cu concentrations had a greater temporal distribution than Cd and Cr. For example at Bridge 2 dissolved Cu concentrations ranged from 0.68 ppm Cu in February 2004 to 0.34 ppm Cu in July 2004, subsequently Cu concentrations increased through winter to a maximum of 1.67 ppm Cu in January 2005. Dunsink

Tributary water column Cu concentrations ranged from 0.72 to 1.21 ppm Cu and had a similar temporal distribution to the river for the final six months of sampling.

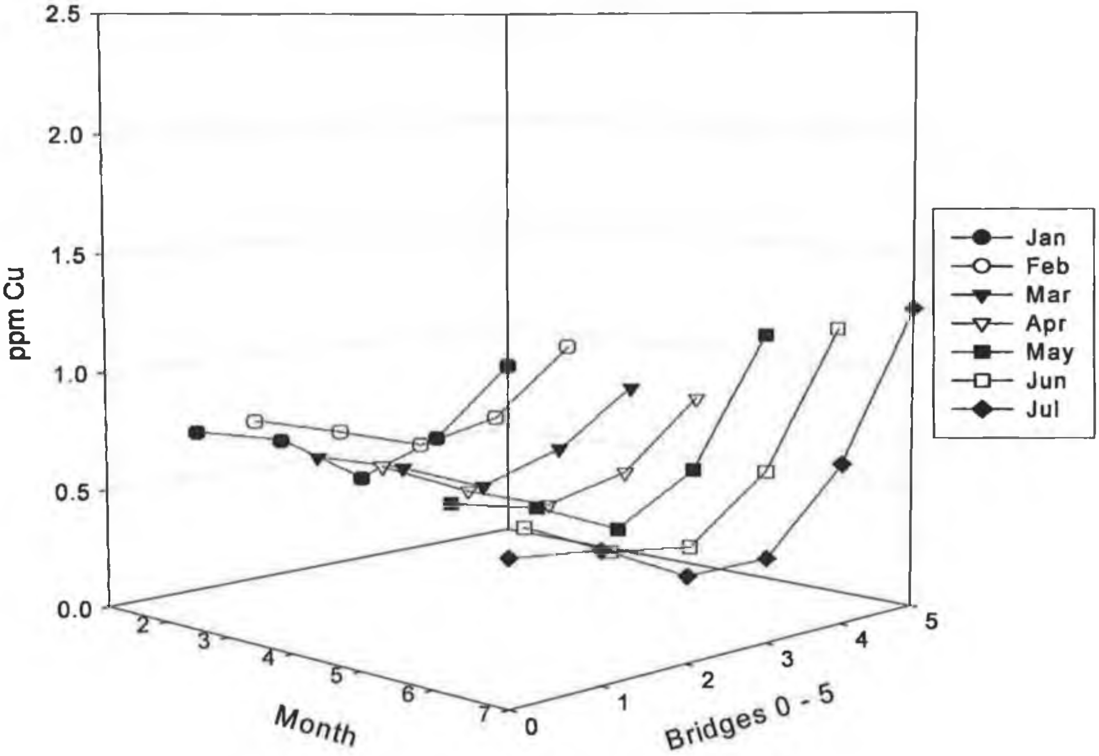


Figure 3.7.5 Water Column Copper, Bridges 0 - 5, January to July '04.

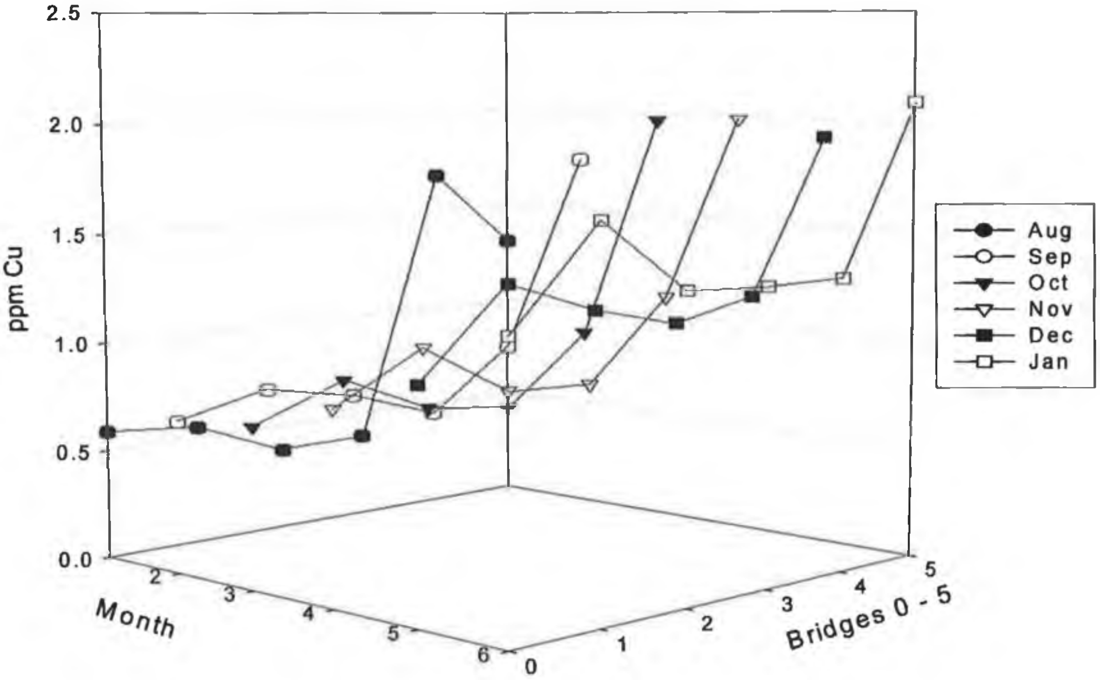


Figure 3.7.6 Water Column Copper, Bridges 0 - 5, August '04 to January '05

3.7.4 Dissolved Lead

Dissolved Pb concentrations in the water column were significantly higher than all the other metals sampled. Similar to the other metals Pb concentrations increased closer to the estuary as shown in Figures 3.7.7 and 3.7.8. For example in August 2004, Pb levels increased from Bridge 0 – 2.19 ppm Pb to Bridge 1 – 6.32 ppm Pb, and then decreased to Bridge 3 – 4.26 ppm Pb and subsequently increased to Bridge 5 – 16.65 ppm Pb. Dissolved Pb concentrations increased overall in the water column. However, Pb concentrations also reduced slightly in spring/ summer months and were significantly higher in winter months. For example at Bridge 2 Pb concentrations ranged from 6.32 ppm Pb in January 2004 to 1.16 ppm Pb in June 2004. Subsequently Pb concentrations increased through winter to a maximum of 22.38 ppm

Pb in January 2005. Dunsink Tributary water column Pb concentrations ranged from 4.26 to 12.52 ppm Pb and had an equivalent temporal distribution to the river for the final six months of sampling.

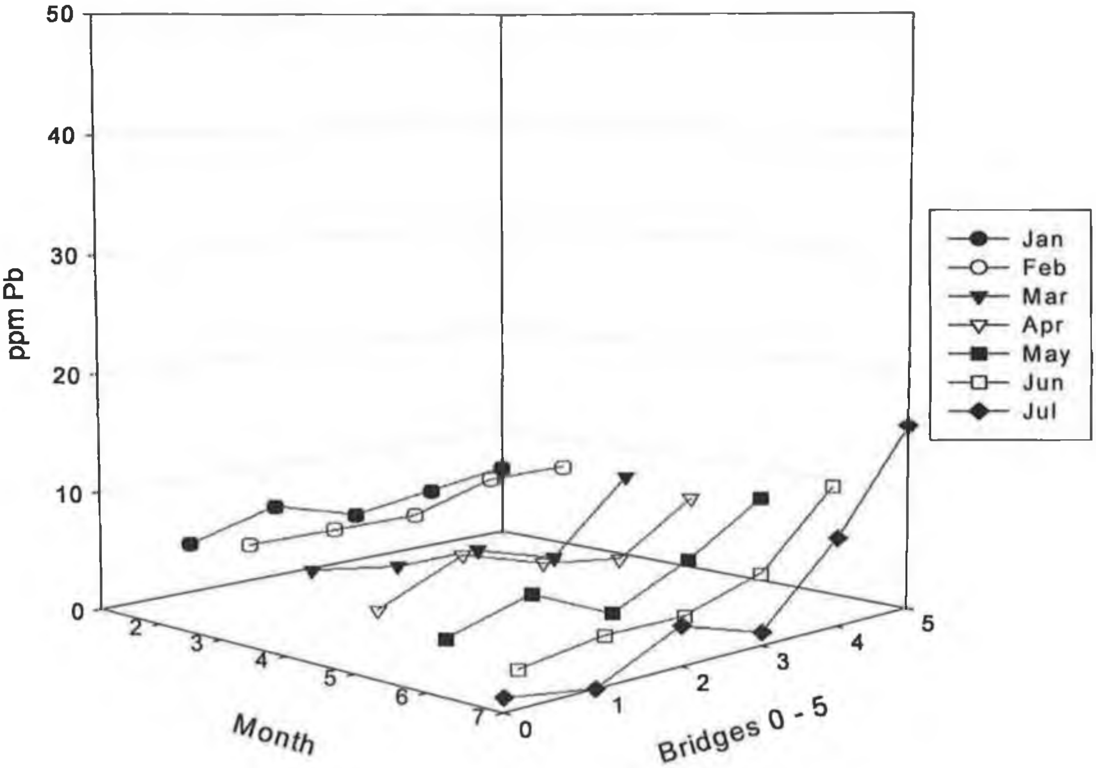


Figure 3.7.7 Water Column Lead, Bridges 0 - 5, January to July '04.

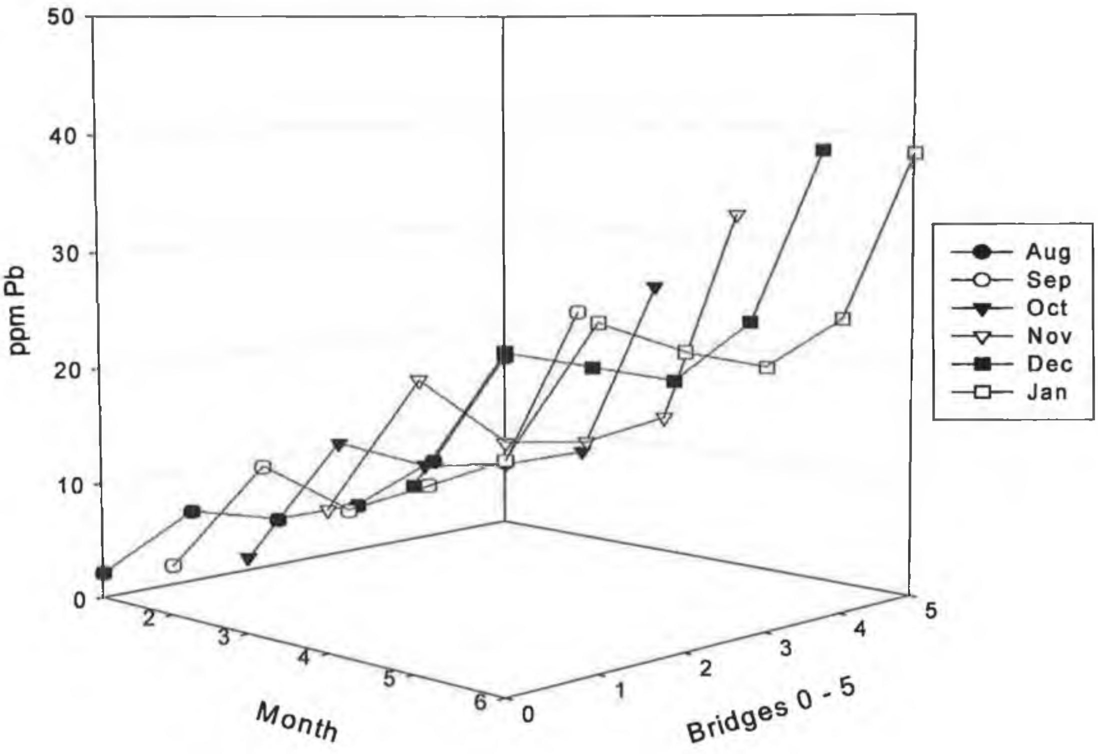


Figure 3.7.8 Water Column Lead, Bridges 0 - 5, August '04 to January '05

3.7.5 Dissolved Nickel

Dissolved Ni concentrations for the water column are illustrated in Figures 3.7.9 and 3.7.10. Dissolved Ni concentrations increased substantially overall in the water column but with a moderately greater seasonal distribution than Cd and Cr. A typical temporal distribution for dissolved Ni can be observed at Bridge 1 where Ni concentrations ranged from 1.07 ppm Ni in January 2004 to 0.74 ppm Ni in July 2004, subsequently Ni concentrations increased through winter to a maximum of 3.67 ppm Ni in January 2005. Dunsink Tributary water column Ni concentrations displayed similar temporal distributions to the other metals and had a minor range from 1.86 to 1.98 ppm Ni. This minor range indicated that the landfill was a relatively consistent source of Ni.

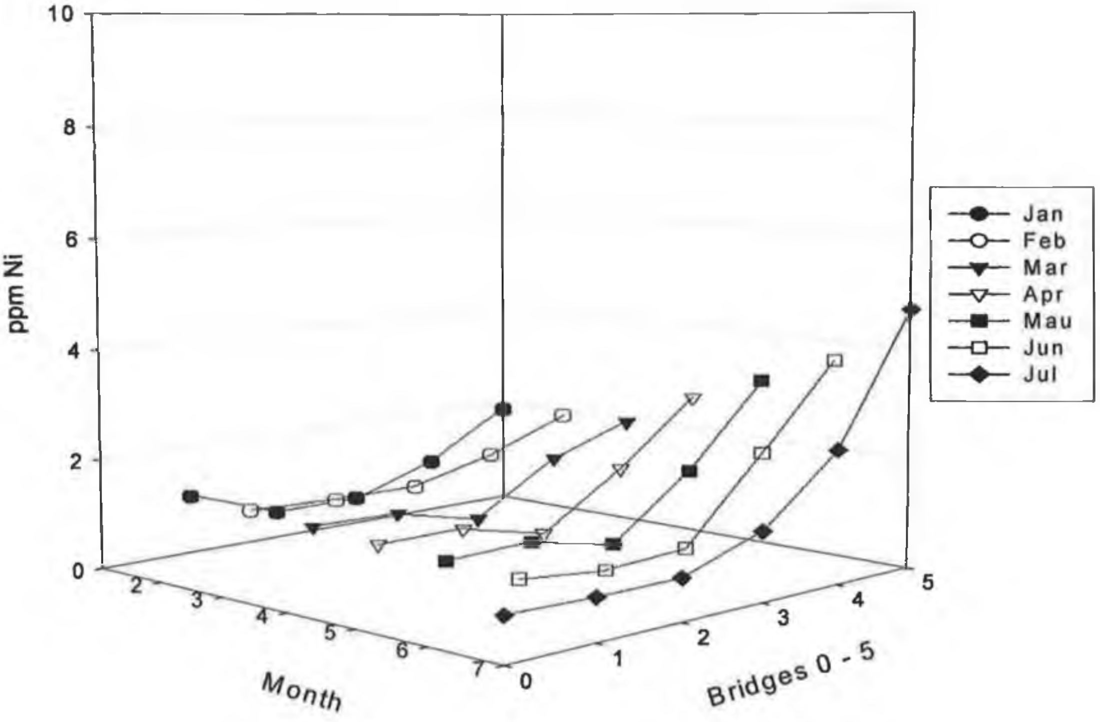


Figure 3.7.9 Water Column Nickel, Bridges 0 - 5, January to July '04

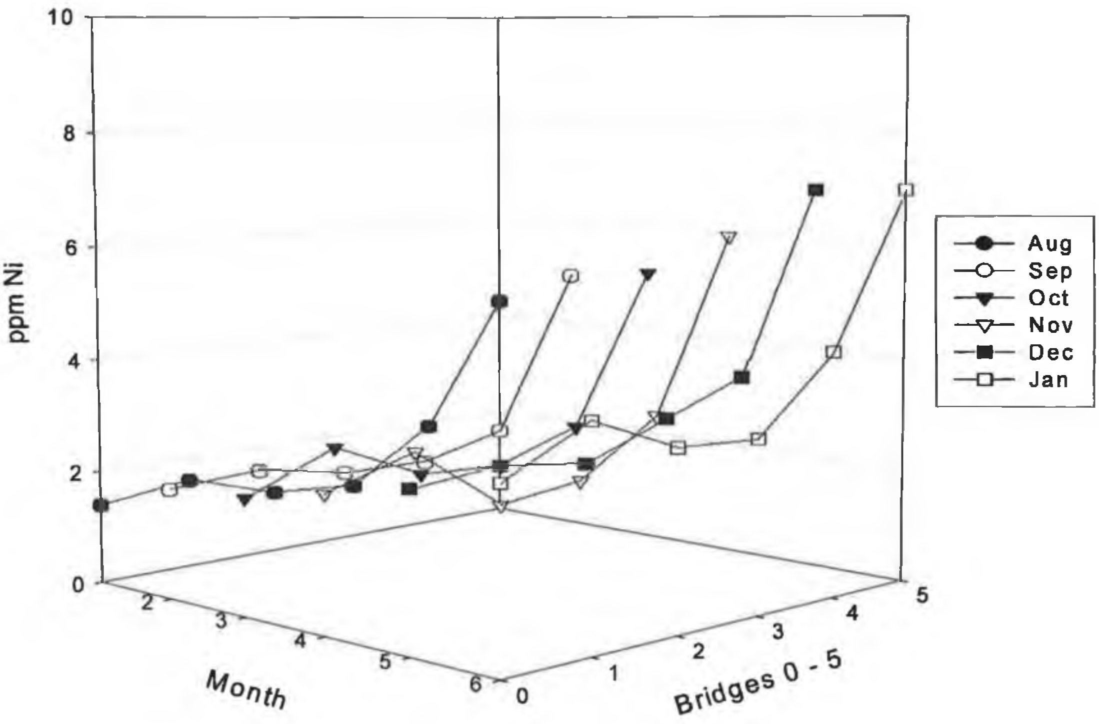


Figure 3.7.10 Water Column Nickel, Bridges 0 - 5, August '04 to January '05

3.7.6 Dissolved Zinc

Initial sampling indicated elevated dissolved Zn concentrations but not as high as Pb, concentrations. Dissolved Zn concentrations had a similar spatial range to the other metals as shown in Figures 3.7.11 and 3.7.12. A typical seasonal distribution can be observed at Bridge 1 where dissolved Zn concentrations ranged from 3.44 ppm Zn in February 2004 to 2.57 ppm Zn in July 2004 and subsequently increased through winter to a maximum of 4.61 ppm Zn in January 2005. Dissolved Zn concentrations in the water column of Dunsink Tributary displayed a similar temporal distribution as the other five metals and ranged from 3.06 to 4.22 ppm Zn.

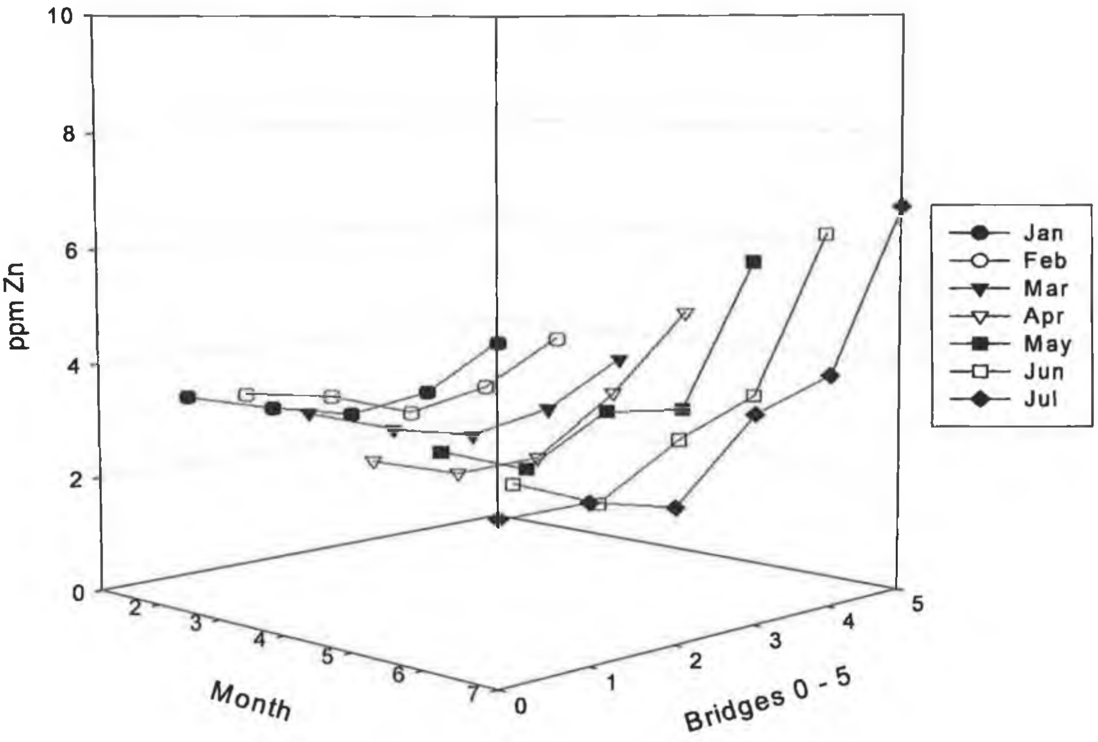


Figure 3.7.11 Water Column Zinc, Bridges 0 - 5, January to July '04

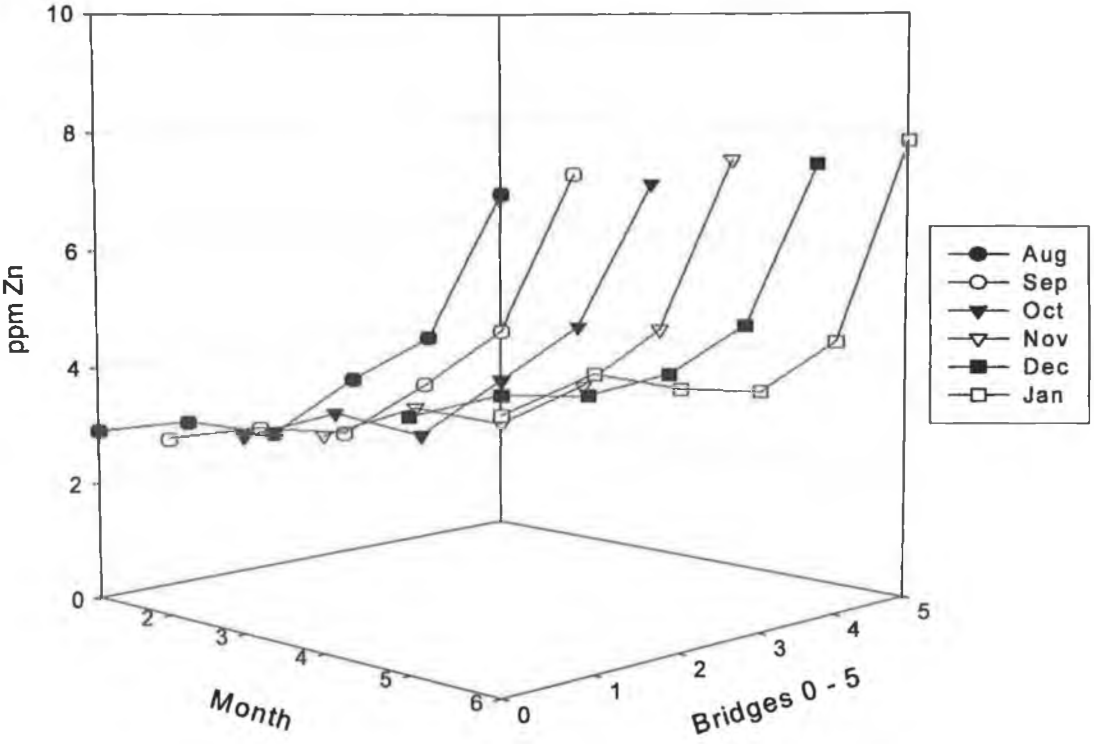


Figure 3.7.12 Water Column Zinc, Bridges 0 - 5, August '04 to January '05

3.8 Surface Sediment Tributyltin Concentrations

Spatial and temporal distributions of TBT were monitored in the river and estuary over a twenty month period, from June 2003 to January 2005 (Figures 3.8.1 to 3.8.3). Sites 1 and 2 in the upper river channel exhibited no TBT during the sample period. Site 3 however, had significant TBT concentrations, ranging from a minimum measured level of 1.0 ppb to a maximum of 7.8 ppb. Spatially TBT concentrations diminished to non detectable concentrations at Site 6 and were not detected between this point and Site 11 over the twenty months. A key source of TBT contamination was the Dunsink landfill tributary. This was located just upstream of Site 3. This tributary had an annual average of 4.5 ppb TBT in its surface sediment. It had a fluctuating temporal distribution but remained a constant source of TBT contamination (Figure 3.8.4).

Spatially, TBT distribution exhibited maximum concentrations in the mid-estuary with lower concentrations in the inner and outer estuaries. The highest TBT concentrations were observed between sites 16 and 20, specifically at site 18. At this site TBT concentrations decreased from 14.1 ppb in July 2003 to 2.0 ppb in April 2004 and subsequently increased to 8.6 ppb TBT for May 2004 and decreased to a concentration of 2 ppb in January 2005. This distinct temporal distribution of concentrations was observed throughout the estuary, while in the river temporal distribution was dominated by fluctuating input from Dunsink Tributary.

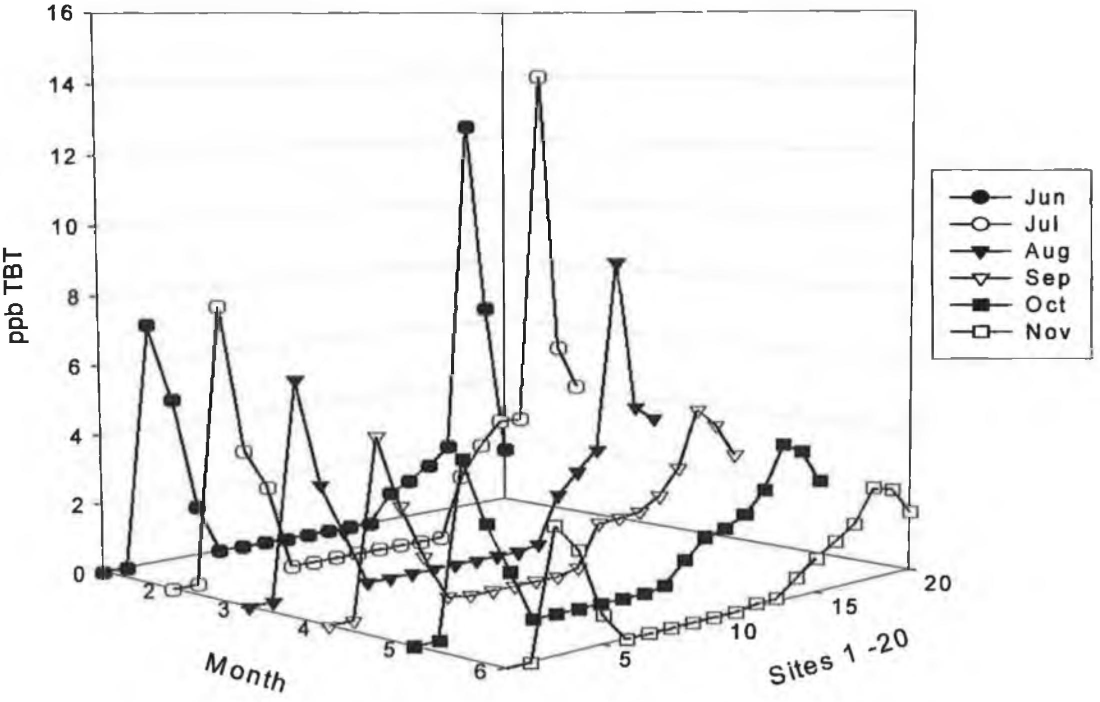


Figure 3.8.1 TBT, Sites 1 - 20 June to November '03

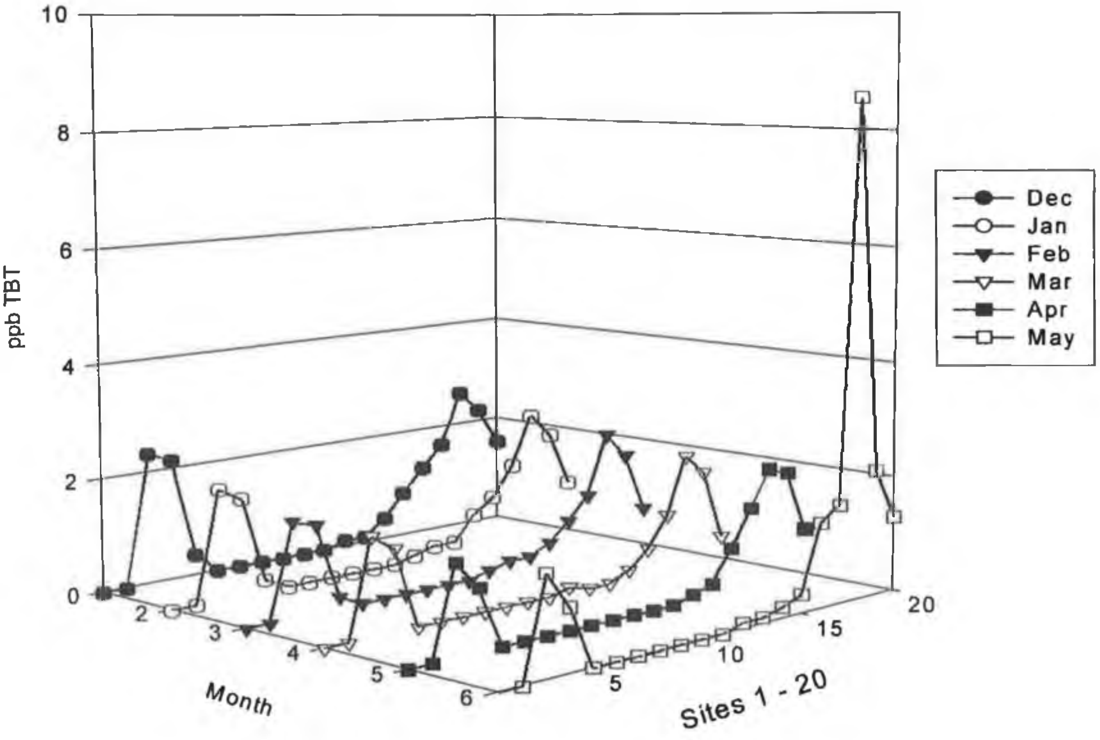


Figure 3.8.2 TBT, Sites 1 - 20, December '03 to May '04

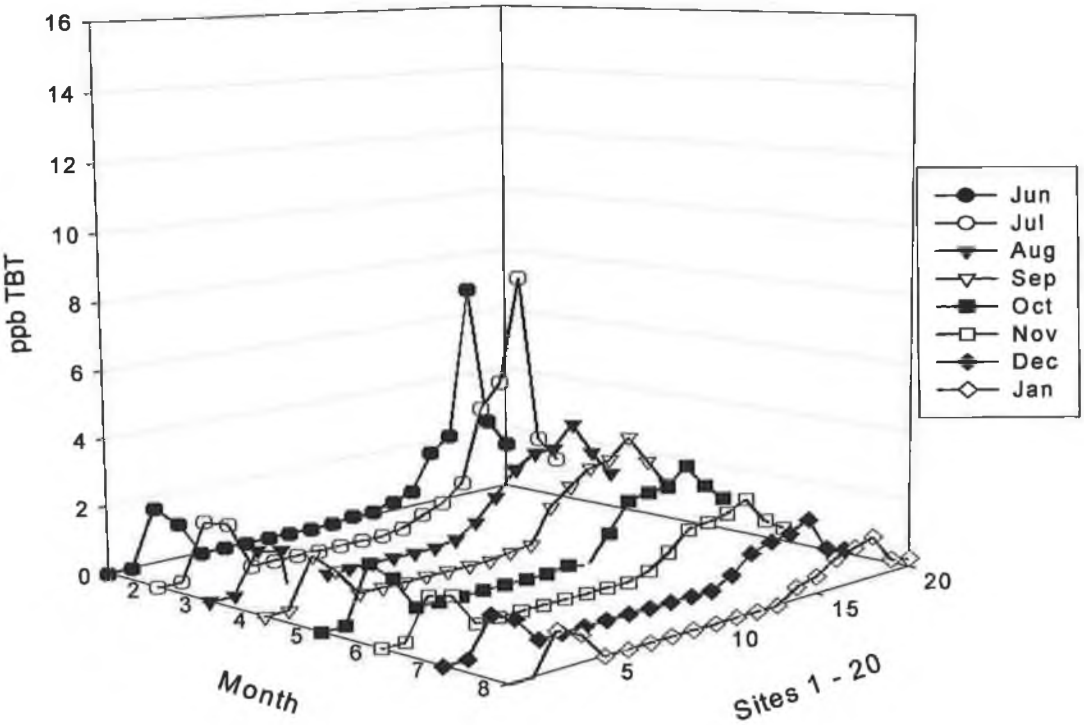


Figure 3.8.3 TBT, Sites 1 - 20, June '04 to January '05.

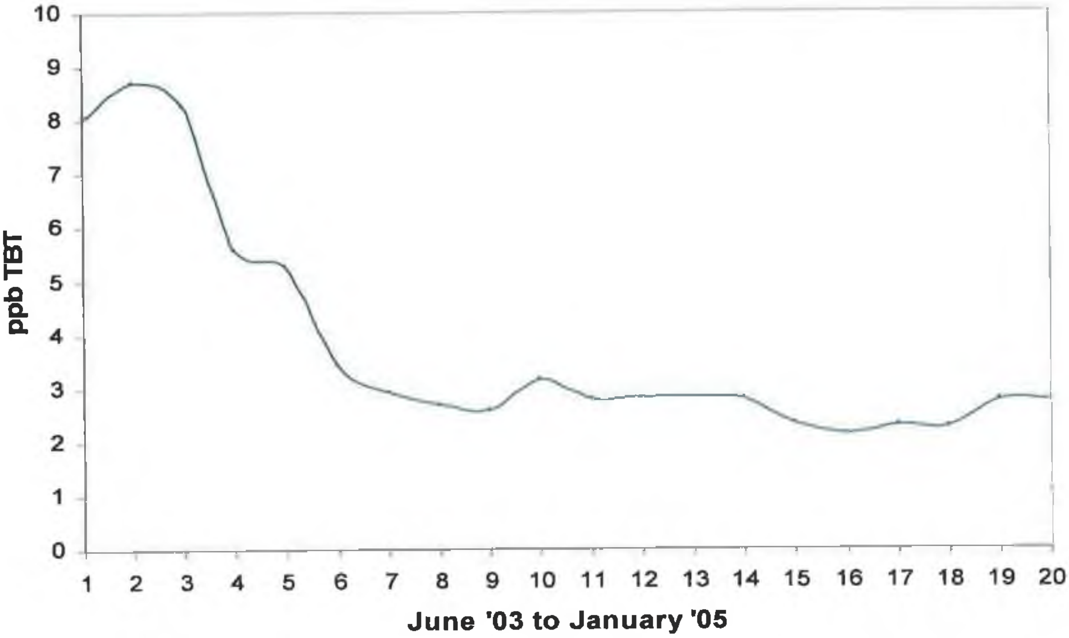


Figure 3.8.4 TBT, Sites 1 - 20, June '04 to January '05.

DISCUSSION

When particle-reactive pollutants, such as metals and organometals, enter riverine and estuarine waters, many are quickly adsorbed on suspended particulate matter and organic matter and removed to the surface sediment layer (Birch & Taylor, 1999; Caccia et al., 2003). Sediments therefore provide a temporally integrated indication of the condition of the estuary, and act as a major reservoir for metals and organometals. As concentrations have greater orders of magnitude than the overlying water column (Forstner & Stoffers, 1981), assessment of surface sediment contaminant concentrations provides a broader synoptic perspective of the environmental status of aquatic systems.

To adequately interpret results of any contaminant analysis, it is necessary to know the spatial and temporal variance in the objective area (Birch et al., 2001). Long term assessment of the complexities of contaminant circulation in an estuarine system was the primary aim of this project. The thirty-month long term investigation of the Tolka transitional aquatic system provided in depth spatial and temporal data, allowing for greater interpretation of many aspects of contaminant transportation and retention.

4.1 Surface Sediment Contamination Levels

Some metal concentrations observed in this project may be considered deleterious to the estuarine ecosystem as indicated by IERP (Irish Estuarine Research Programme) guideline threshold levels (Table 4.1). IERP Guidelines were designed for estuarine systems and not riverine; however for continuity they were applied for riverine sampling in this project also. In particular As, Co, Ni and Pb surface sediment concentrations were above the threshold level at certain sites of the middle estuary. In contrast, Norwegian guidelines (the most stringent in Europe – currently no EU wide guidelines) classify the Tolka estuary as in a fair condition, Cr, Ni and Zn concentrations were good, Cd and Cu were fair and only As and Pb concentrations fall into the poor classification (Table 4.2).

Metal	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
Baseline	5	0.5	5	5	5	150	5	10	20
Threshold	100	1.5	10	50	50	500	20	100	100

Table 4.1 Irish Estuarine Research Programme Guideline Metal Concentrations – all data in mg / kg (Jeffrey et al, 1985). Baseline = Natural Background Level, Threshold = Concentration at which deleterious affects to the aquatic environment occur.

Metal	Good	Fair	Poor	Bad	Very Bad
Arsenic	<20	20 - 80	80 - 400	400 - 1000	>1000
Cadmium	<0.25	0.25 - 1	1 - 5	5 - 10	>10
Chromium	<70	70 - 300	300 - 1500	1500 - 5000	>5000
Copper	<35	35 - 150	150 - 700	700 - 1500	>1500
Lead	<30	30 - 120	120 - 600	600 - 1500	>1500
Nickel	<30	30 - 130	130 - 600	600 - 1500	>1500
Zinc	<150	150 - 650	650 - 3000	3000- 10000	>10000

Table 4.2 Norwegian Classification of Environmental Quality and Degree of Pollution - all data in mg / kg (IADC/CEDA 1997).

4.1.1 Metal Concentrations

During the thirty-month sample period metal levels fluctuated seasonally and at certain periods exceeded respective IERP threshold guideline level. Table 4.3 indicates maximum metal levels recorded for each metal and at which site and month the concentrations were recorded. Concentrations highlighted in blue indicate an exceedence of IERP guideline threshold levels.

Metal	Concentration (ppm)	Site	Month /Year
As*	111.5	18	January 2005
Cd	2.7	3	October 2003
Co*	60.3	18	January 2005
Cr	29.3	17	August 2002
Cu	72.5	16	August 2002
Mn*	67.9	16	January 2005
Ni	47.8	16	August 2002
Pb	318.2	17	July 2004
Zn	133.5	17	August 2004

Table 4.3 Maximum metal concentrations observed in the Tolka aquatic system. * Metals analysed only in January 2005.

Metal levels in the Dunsink Tributary far exceed IERP guidelines. Table 4.4 indicates the maximum metal levels at Site A and month recorded. This tributary clearly contributed significant metal contamination to the Tolka fluvial network. Concentrations highlighted in blue indicate an exceedence of IERP guideline threshold levels.

Metal	Concentration (ppm)	Month /Year
As*	110.0	January 2005
Cd	4.4	July 2003
Co*	76.8	January 2005
Cr	30.7	August 2003
Cu	183.4	April 2004
Mn*	45.3	January 2005
Ni	45.0	August 2003
Pb	354.5	September 2003
Zn	184.2	August 2003

Table 4.4 Maximum metal concentrations observed at Site A in Dunsink Tributary. * Metals analysed only in January 2005.

Metal concentrations in the estuary were a cause for concern at certain periods of the sampling regime. However, as noted previously in Chapter 3, metal concentrations were diminishing overall in the aquatic system and the final sampling in January 2005 indicated only relatively minor metal contamination in comparison to other periods during the project. Table 4.5 indicates maximum metal concentrations observed in the riverine and estuarine sections and Dunsink Tributary at the final sampling. Concentrations highlighted in blue indicate an exceedence of IERP guideline threshold levels.

Metal	**Riverine (ppm)**	**Estuarine (ppm)**	**Dunsink Tributary (ppm)**
As	**(3)** 89.2	**(18)** 111.5	110.0
Cd	**(3)** 0.3	**(15)** 0.6	1.1
Co	**(3)** 56.0	**(17)** 90.3	76.8
Cr	**(3)** 8.3	**(18)** 9.9	13.0
Cu	**(3)** 19.3	**(16)** 34.0	114.5
Mn	**(3)** 41.0	**(16)** 67.9	45.3
Ni	**(3)** 11.1	**(17)** 23.9	20.1
Pb	**(3)** 76.5	**(16)** 131.9	165.9
Zn	**(3)** 56.8	**(18)** 93.7	96.5

Table 4.5 January 2005 Surface Sediment Sites of maximum metal concentration – all data in ppm (Sites in parentheses).

In comparison to another Irish estuary, contamination of the Tolka is still a cause for concern. The Slaney Estuary in the south east of Ireland is approximately 9 km^2. It is similar to the Tolka in that it is contaminated by landfill leachate from one active and one abandoned landfill. Metal levels were recorded over 15 points in the Slaney in 2001. Maximum values were lower than those found in the Tolka: 1.3 ppm Cd, 31.9 ppm Cu, 43.6 ppm Pb, 121.7 ppm Zn, 32.5 ppm Ni and 38.2 ppm Cr (Buggy, 2001).

Compared to another aquatic system influenced by urban run-off and proximity to port facilities the Tolka shows moderate metal contamination. The Tees Estuary, UK is considered seriously contaminated from the urban environment (Teeside is an urban agglomeration of approximately 400,000 people) and from port facilities (including the largest petrochemical refinery outside the US). Metal concentrations were generally higher than those recorded on the Tolka and were approximately double levels of Cd, Cu, Pb and Zn, and ten times that of Cr. Sediment samples exhibited the following metal levels: 5.9 ppm Cd, 103 ppm Cu, 307 ppm Pb, 392 ppm Zn, 41 ppm Ni and 224 ppm Cr (Jones & Turki, 1997).

4.1.2 Tributyltin Concentrations

As indicated by Figures 3.8.2 to 3.8.3 there are two distinct areas of TBT contamination: the upper riverine section and the estuary. The upper riverine section contamination is a direct input from the Dunsink tributary. Site A recorded a maximum of 8.7 ppb in July 2003. Site 3 directly downstream from the entry point records 7.8 ppb in that month. Estuarine TBT contamination is most likely from local boating in the outer estuary and from backwash from Dublin Port and Liffey River. A maximum TBT concentration of 14.1 ppb was recorded in July 2003 at Site 18.

TBT concentrations of the Tolka are relatively minor compared to larger Irish estuaries: reported values elsewhere include 35 ppb in surface sediment of the Boyne Estuary at Drogheda Port (Drogheda Port Company, 2001) and 78 ppb in surface sediment of the Liffey Estuary at Dublin Port (Davoren et al., 2005). In comparison to a similar urbanised estuary the Tolka can be noted as having minor TBT contamination. In Mobile Bay, Alabama, USA, TBT concentrations ranged from 3 to 54 ppb with a 12 ppb average (Peachey, 2003) whereas the Tolka ranged from 0 to 14.1 ppb with a 0.9 ppb average. According to guidelines set by the Department of the Environment, Australia, (internationally recognised TBT guidelines; currently no EU wide guidelines exist) acceptable TBT levels in estuarine sediment range from 0.5 to 7 ppb (DoE, Australia, 2002). At Site 18 this level is doubled, however in general the

Tolka fell within this acceptable range. Continuous TBT contamination of the Tolka indicated that anthropogenic input is an ongoing issue that has not been completely resolved despite regulation of TBT use in the 1980's (Alzieu, 1998).

4.1.3 Organic Matter

There are currently no definitive EU or Irish guidelines on OM content of surface sediment. IERP guidelines state that 2.0 % OM is considered normal for an estuary (Jeffrey et al., 1985). Dutch, Norwegian and NOAA (National Oceanographic and Atmospheric Administration) guidelines for sediment contamination normalisation assessment state that above 0.2 %, OM dominated metal partitioning in surface sediment and should therefore be considered the normal level for an estuary. However, some studies (Luthy et al. 1991, Le Boeuf & Weber, 2000) have challenged the concept of "normal" river and estuarine OM concentrations.

In the Tolka system, OM concentrations ranged from 0.3 to 10.2 % with an average of 2.6 % over the seventeen-month sampling period. In comparison to other similar aquatic systems, the Tolka is not considered especially different or of interest, for example the Nahr-Ibrahim aquatic system in the Lebanon displayed a lesser range of concentrations but similar OM average concentrations; ranging from 0.8 to 2.5 % with an average of 2.1 % (Korfali & Davies, 2004).

4.2 Water Column Concentrations

There are currently no guidelines regarding metal concentrations bound to SPM within the water column. Relevant international guidelines are solely concerned with dissolved metals at present. Moreover, there are no Irish guidelines regarding metal content of the water column although river quality guidelines are under review by the Environmental Protection Agency of Ireland based on Dutch guideline levels. Current practice is in line with Australian guidelines which are considered some of the most stringent international river water metal guidelines. Table 4.6 indicates current general river water (not utilised for agriculture or recreation) guidelines (ANZAC, 2000).

Metal	Recommended Maximum Concentration (ppm)
Cd	0.01
Cr	0.1
Cu	0.2
Ni	0.2
Pb	2.0
Zn	2.0

Table 4.6 Australian River Water Quality Guidelines (ANZAC, 2000).

Metal concentrations in the water column of the Tolka River indicated a river with significant metal contamination. Both dissolved fraction and SPM bound metals were analysed from five points on the river. Tables 4.7 and 4.8 indicate maximum metal levels recorded in the river.

Metal	Concentration (ppm)	Site	Month / Year
Cd	4.84	B5	January 2005
Cr	1.83	B5	January 2005
Cu	33.4	B5	January 2005
Ni	30.2	B5	January 2005
Pb	49.9	B1	January 2005
Zn	12.2	B5	July 2004

Table 4.7 Maximum metal concentrations of SPM (µg of metal per g of SPM) in the water column.

Metal	Concentration (ppm)	Site	Month / Year
Cd	1.28	B5	January 2005
Cr	1.49	B5	January 2005
Cu	2.09	B5	January 2005
Ni	6.98	B5	January 2005
Pb	38.3	B5	December 2005
Zn	7.87	B5	January 2005

Table 4.8 Maximum dissolved metal concentrations in the water column.

Site B5 (Bridge 5) was located directly adjacent to the estuarine mouth and records significantly higher concentrations of SPM, SPM bound metal and dissolved metal than the other water column sampling sites, as indicated in Figures 3.6.4 to 3.7.10. However, in general metal concentrations of the water column of the Tolka were a cause of concern. Results indicated that the dissolved portion of metals in the water column greatly exceeded international guidelines. As there are no current guidelines for metals bound to SPM, the Tolka's SPM bound metal cannot be classified as either normal or deleterious to the environment for a river of its size. However the Tolka's SPM bound metal concentrations were comparable to other major rivers: in the upper reaches of the Danube SPM bound metal concentrations were similar to the maximum concentrations recorded in the Tolka – 0.4 ppm Cd; 34.9 ppm Cr; 21.9 ppm Cu; 35.4

ppm Ni; 11.9 ppm Pb; and 59.9 ppm Zn (Woitke et al., 2003). SPM bound metal concentrations of the Severn had a broader range than concentrations observed in the Tolka, however the Severn River has an average flow rate equivalent to three times the Tolka's maximum flow rate. Concentrations in the Severn ranged from 0.26 – 0.4 ppm Cd, 67 – 81 ppm Cr, 25 – 37 ppm Cu, 31 – 37 ppm Ni, 51 – 77 ppm Pb and 194 – 238 ppm Zn (Duquesne et al., 2006).

4.3 Spatial Distribution

Over the thirty month assessment, the Tolka aquatic system displayed two distinct spatial trends of contaminant distribution: riverine and estuarine. As well as seasonality effects, spatial trends must be analysed to adequately interpret how contaminants move through the aquatic system, how they are retained and how they are transported out of the system. Interpretation of the spatial trend over time also allows determination of anthropogenic inputs from temporally sporadic point sources. Environmental factors that influenced spatial trends will be discussed in greater depth in relation to their role in seasonal distribution in section 4.4.

The two trends observed were associated with radically different physicalities and environmental factors. Spatially the Tolka river and the Tolka estuary are two different physical systems as described in Chapter 1. The Tolka River while located in an urban area displays river valley characteristics. Its v-shaped valley drains a significant portion of north Dublin's urban landscape, particularly the built up suburbs of Blanchardstown, Finglas, Phibsboro/Cabra, Glasnevin, Drumcondra, the north inner City and Fairview. The river channel drops approximately 30 m between the first sampling point and the estuary mouth. It has three weirs and a number of small river braided islands. The river is deep (upper river 1 – 3 m, lower river at high tide 2 – 4 m) but has shallow sediment banks where deposition and erosion occur.

The estuary is broad and shallow with significant intertidal mudflats. The estuarine channel hugs the southern boundary of the estuary along Dublin Port's northern wall. Training walls bound the estuaries extent which has no means of expansion. The estuaries continued sediment deposition and a lack of dredging are leading to extensive mudflat expansion in the inner and middle estuarine sections as only the outer estuary is subject to tidal wave force (Dublin Bay Project, 2001).

4.3.1 Environmental Factors affecting Spatial Contaminant Distribution

As outlined in Chapter 1, spatial trends in aquatic systems include natural variance associated with physical (wind, tide, freshwater input, etc.), biological (bioturbation) and chemical (OM breakdown, pH) processes (Birch et al., 2001). Both physical and chemical environmental factors influence spatial contaminant trends in the Tolka aquatic system.

4.3.1.1 Sediment Characteristics

As indicated by Table 3.1.1, sediment characteristics of the system displayed two distinct physicalities. Sediment composition at riverine sampling sites had a higher proportion of larger particle sizes. At these points, sediment particles ranging from

125 – 250 μm were in the majority and fine-grained sediments <63 μm predominantly made up less than 10% of total sediment. This level of fine-grained particle composition does not favour extensive retention of contaminants in the riverine system as sediment matrices have greater interstitial voids (Jones & Turki, 1997). As deposition of fine-grained particles in the riverine section is substantially reduced, the deposition that does occur is primarily of larger particles and particle clumps that contain detrital material bound with contaminants (Miles & Tome, 1997). Fine grained particles remain in the water column and are transported out of the riverine system and into the estuary (see section 4.3.1.2). This is indicated by the minor increase of fine grained particles at the lower riverine sampling sites closest to the estuary, e.g. Site 8 – 5 % <63 μm; Site 9 – 7 % <63 μm; and Site 10 – 12 % <63 μm.

The estuary displays a sedimentary distribution that is commonly found in many estuaries: fine grained sediments in the inner and middle estuarine sections and coarser grained sediments in the outer estuary. Appendix A, Figure 1 illustrates a complete sediment particle size distribution from January 2005. Table 3.1.1 illustrates that estuarine sediment was composed primarily of grains <125 μm and that in the middle estuary, grains <63 μm were the highest in the whole aquatic system. This distribution is associated with physical forces in the water column. Fine grained sediments i.e. <125 μm are deposited in the inner estuary as the river water column reduces in speed as it spreads over a wider channel area. While in the outer estuary fine grained sediments are carried from the surface sediment by tidal wave action and transported to the middle estuary. This contributes to the phenomenon known as the mid-estuarine maximum (Duquesne et al., 2006; Miles & Tome, 1997; Caccia et al., 2003) which is discussed further in section 4.3.3.

4.3.1.2 Suspended Particulate Matter

SPM analysis provided an overview of contaminant transportation within the system and how SPM affects the spatial distribution of contaminants. It has been established that SPM is a significant transport agent for metal contaminants in river and stream environments (Characklis & Wiesner, 1997; Neal et al., 1997; Pettine et al., 1994; Webster et al., 2000). It is well known that aquatic systems are efficient filters for SPM, due primarily to particle/solute interactions, flocculation and coagulation, and sedimentation of particle bound metals (Zhou et al., 2003). Adsorption onto SPM is an important process controlling dissolved metal concentrations and how they are transported and distributed within any aquatic system (Comber et al., 1995).

SPM distribution in the water column of the Tolka river was an indicator of turbulence and areas of deposition. Figures 3.6.1 and 3.6.2 illustrate spatial SPM distribution in the Tolka River from Bridges 0 to 5. In the upper riverine sections between Bridges 0 – 2, high SPM loads in the water column often > 200 mg / L indicated a river affected by high runoff rates from the surrounding urban environment but also a turbulent river with only minor in situ deposition influenced by a moderate slope and the positioning of weirs and rapids in the channel. Further downstream between Bridges 3 and 4, the channel had a gentler slope, smoother bed surface and a wider channel. At this stage, SPM levels reduced indicating a greater depositional rate attributed to alteration of river bedform. Highest SPM levels were recorded adjacent to the estuary at Bridge 5. High levels of SPM at this point were attributed to the influx of marine SPM by tidal action and does not imply that this area was a low depositional environment. This area likely had the highest depositional rate in the river as indicated by higher fine grained sediment deposits and higher contaminant concentrations than the river in general.

4.3.1.3 pH

pH plays a minor role in adsorption of contaminants, particularly metals and organometals to colloidal particles (Woitke et al., 2003; Hoch & Schwesig, 2004). pH levels are significantly influenced by OM content of the sediment; generally higher OM content leads to more acidic porewater, while the influence of seawater increases alkalinity. pH trends were typical for a river and estuary. pH increased from a moderately acidic river to slightly lower than normal seawater in the estuary. The pH of seawater at the centre of Dublin Bay is 8 - 8.3 (Costello et al., 1999). The physical nature of the Tolka contributes to this slight reduction of estuarine pH. Marine influx is minimised due to a narrow zone of entry and the Liffey freshwater backwash at the mouth of the Tolka. The outer estuarine zone had an average of pH 7.9 that was still somewhat below that of Dublin Bay. The pH of inner and middle estuarine sections are slightly reduced but remain close to typical seawater levels.

The riverine section is generally typical of a river flowing through an area of acidic limestone bedrock: ranging between pH 6 and 7 (GSI, 2005). Just as parent material of the river floor contributes to metal levels in the river and estuary, it can also affect pH levels (Liu et al., 2002). As the upper sediment layer of the Tolka is composed mainly of limestone silts (GSI, 2005; Buggy & Tobin, 2003), $CaCO_3$ will be released into the overlying mixed salinity water and will lower pH, to a greater extent in the river as limestone bedrock is exposed in many sections whereas in the estuary it is not.

In the vicinity of Dunsink tributary, riverine pH is lowered to below 6 and approached 5 on a number of occasions between Sites 3 and 5. The Dunsink tributary had an average pH of 5.1. Landfill leachate is generally acidic (EPA, 2000). During periods of heavy rainfall, pH can fluctuate with an influx of urban run-off and increased leaching from the landfill. This alteration of riverine pH by an anthropogenic source illustrates how the pH balance of an aquatic system can easily be disrupted and how it can affect spatial trends in pH. Subsequent effects of pH alteration can include variable contaminant concentration of contaminants bound to SPM in the water column and porewater and in surface sediment.

4.3.1.4 Organic Matter

Distribution, retention, resuspension, transportation and eventual fate of contaminants in estuarine systems are primarily controlled by OM distribution within aquatic systems (Singer, 1977; Wheatcroft & Butman, 1997). The hypothesis is well established that OM content of surface sediment is a controlling factor in the spatial distribution of contaminants (Rubio et al., 2000). Fine-grained sediments tend to have relatively high contaminant concentrations due in part to the high specific surface area of the OM content. This enrichment is mainly due to surface adsorption and ionic attraction binding to OM (Wangersky, 1986; Horowitz & Elrick, 1987). The spatial distribution of OM in the Tolka aquatic system had a noticeable correlation with the distribution of contaminants in the system. OM was transported through the system as

SPM and riverine sections with higher levels of water column SPM displayed moderately positive correlations (r^2 values ranging from 0.583 – 0.657) with lower OM content of surface sediment.

Higher OM content of the estuary indicated the retention of OM in surface sediment of a high depositional area compared to lower retention levels in the channelled river where OM can be removed through increased turbulence. Elevated concentrations of fine grained sediment particles in the estuary also allowed for greater retention of OM and associated bound contaminants in these sections. The major role of OM in contaminant distribution will be discussed further in section 4.4.

4.3.2 Riverine Contaminant Spatial Distribution

Generally contaminant levels were lower in the riverine section compared to the estuarine sections due to its constant flushing of contaminants downstream into the estuary. As previously stated the physicality of the river and its influence on channel deposition and river flow and the environmental influences of sediment composition, SPM, pH and OM all contributed to lower contaminant concentrations in the river compared to the estuary.

Due to the influence of the point pollution source of the Dunsink Tributary, the riverine section of sample regime did not reflect other typical river systems. If this point source had not been present it is likely that contaminant levels observed at Sites 1 and 2 would have been observed throughout the upper and middle sections of the

Tolka River with a moderate increase in contaminant concentrations in the lower riverine section from tidal influx from the heavily contaminated estuary.

The influence of the inactive landfill point source provided an indication of anthropogenic impact on contaminant levels in the fluvial system (Ward et al., 1984). The Tolka River is located 200 m from the 32 ha Dunsink landfill. Surface water flow in the area is directed to the Tolka river and the landfill is situated the northern rim of the river valley. The inactive landfill had a stream exiting its base that enters the Tolka River in the upper riverine stage above sample Site 3 as illustrated in Figure 1.2. The stream passes through a broad wetland area before entering the river. As the stream ran through the landfill, leachate contamination entered the water course and contamination of tributary surface sediment was evident. Elevated contaminant levels in the water column, bound to SPM and in the surface sediment, significantly higher than the river, were observed in this tributary upstream of its confluence with the Tolka River. The presence of TBT in riverine surface sediment directly downstream of the confluence at Sites 3, 4 and 5 and in the tributary sediments (Figures 3.8.1 to 3.8.4) provided clear indication of anthropogenic contamination from this point source. Sample sites directly downstream of this tributary demonstrated the effects this anthropogenic source had on the spatial distribution of contaminants in the system. Sites 1 and 2 located upstream of the confluence point had much lower levels of contamination than sites located downstream. Site 3, directly downstream of the tributary had the highest contaminant concentrations making it the most contaminated site in the sample network.

In spite of the elevated concentrations of contaminants in the water column of the tributary, it does not account for the significant levels of metal loading downstream of the site. Tables 4.9 to 4.14 illustrate a metal loading analysis of the Tolka River from August 2004 to January 2005. These results indicate that contaminants transported in the water column of Dunsink Tributary constituted minor levels of contaminants to the Tolka itself (generally between 0.5 to 2.5 % of total metal loading entering the estuary) and can only be attributed as a moderate point source. However, evidence from surface sediment results indicated elevated concentrations of metals and TBT in the river directly downstream of the tributary confluence and in the tributary itself. It has been previously observed that landfill leachate can move through groundwater into aquatic systems (Denton et al., 2006; Buggy, 2001; Gray, 2000) and it is likely that landfill leachate from Dunsink has contaminated the regionally important aquifer, and through groundwater flow has entered the Tolka through the wetland area that surrounds the tributary upstream of Site 3. It is also likely that metal contaminants are bound to heavy particles in the leachate (Fan et al., 2006; Kjeldsen et al., 2002; Kjeldsen & Spokas, 2004) and are transported in the tributary via river bottom sediment traction and saltation rather than bound to SPM (Kjeldsen et al., 2002; Kjeldsen & Spokas 2004; Abu-Rukah & Al-Kofahi, 2001). It can also be noted that both metal and TBT concentrations in surface sediment of Dunsink Tributary were in decline towards the end of the sampling regime and the effect the tributary had on the upper stages of the river was likely diminishing.

Tables 4.9 to 4.14 – Key to River Loading.

A - Loading from Dunsink Stream at River Confluence (Upstream of Site 3), % of total loading at that point.

B - Loading from Dunsink Stream, % of total loading at River / Estuary Interface.

C - Loading from catchment upstream of Tolka / Dunsink Stream Confluence, % of total river load at River / Estuary Interface.

D - Loading from Urban Environment between Tolka / Dunsink Stream confluence and River / Estuary Interface, % of total river load at that point.

Metal	A	B	C	D
Cd	9.3	1.72	5.9	92.3
Cr	9.1	1.63	10.8	87.6
Cu	8.9	1.42	8.3	90.3
Ni	11.8	2.65	6.1	91.2
Pb	9.7	2.48	7.7	89.9
Zn	10.2	2.61	11.8	85.6

Table 4.9 River metal loading (as % of total flow) August 2004.

Metal	A	B	C	D
Cd	7.9	1.71	5.5	92.8
Cr	6.9	1.66	9.9	88.5
Cu	6.3	1.47	8.2	90.3
Ni	9.9	2.59	6.9	90.6
Pb	7.5	2.49	9.1	88.4
Zn	7.3	2.64	11.3	85.9

Table 4.10 River metal loading (as % of total flow) September 2004.

Metal	A	B	C	D
Cd	7.7	1.38	5.6	93.0
Cr	6.1	1.47	10.0	88.5
Cu	6.2	1.44	9.1	89.5
Ni	8.6	1.61	7.9	90.5
Pb	7.7	1.42	11.1	87.5
Zn	7.5	1.63	12.0	86.4

Table 4.11 River metal loading (as % of total flow) October 2004.

Metal	A	B	C	D
Cd	6.9	0.70	6.1	93.2
Cr	5.6	0.64	9.9	89.5
Cu	5.9	0.48	9.7	89.8
Ni	7.8	0.63	9.1	90.3
Pb	6.8	0.49	12.8	86.7
Zn	5.4	0.58	13.3	86.1

Table 4.12 River metal loading (as % of total flow) November 2004.

etal	A	B	C	D
Cd	6.9	0.69	6.1	93.2
Cr	5.9	0.70	10.3	89.0
Cu	6.1	0.46	9.6	89.9
Ni	7.9	0.59	8.1	91.3
Pb	7.4	0.44	12.9	86.6
Zn	5.9	0.60	12.2	87.2

Table 4.13 River metal loading (as % of total flow) December 2004.

Metal	A	B	C	D
Cd	6.8	0.70	6.2	93.1
Cr	5.7	0.61	9.7	89.7
Cu	6.2	0.49	9.9	89.6
Ni	8.1	0.61	8.9	90.5
Pb	7.5	0.52	13.1	86.4
Zn	5.2	0.63	11.9	87.5

Table 4.14 River metal loading (as % of total flow) January 2005.

From observations on river metal loading in Tables 4.9 to 4.14 it can be seen that the greatest source of metals to the river was the urban environment. The environs of Dublin City comprise a significant portion of the river catchment area, and entirely enclosed the sample area. As previously described in Section 1.4.2, sewage storm outfalls, gullies, shores and pipes as well as surface water streams are located at various points along the river course (see Figures 1.2 to 1.5), and during periods of rainfall were observed to discharge significant volumes of urban run-off to the river. The urban environment intensified in road network and structure closer to the estuary. Contribution of urban run-off in this area was the primary source of contamination in the lower stages of the river and led to the elevation of contaminant levels as the river approached the estuarine mouth. As discussed in Section 1.2.4, urban run-off is considered the greatest non-point source of pollution to aquatic systems in urban environments (Characklis & Wiesner, 1997; Morrisey et al., 2000; Parker et al., 2000). Previous studies have indicated that urban run-off can contain significant concentrations of metals (Bibby & Webster-Brown, 2005; Shepherd et al., 2006). In Wolverhampton, UK, urban run-off metal concentrations ranged from 13 – 75 μg Cu / L, 61 – 224 μg Ni / L, 4 – 54 μg Cr / L, 25 – 101 μg Zn / L, 2- 42 μg Pb / L and 0.1 – 0.5 μg Cd / L (Shepherd et al., 2006). Urban run-off sampling did not fall under the scope of this research, however it can be assumed that similar metal concentrations would have been observed in Dublin's urban run-off and would have contributed significant quantities of metals to the Tolka system.

4.3.3 Estuarine Contaminant Spatial Distribution

Spatially the six metals and TBT concentrations in the estuarine surface sediment exhibited distinct and similar trends. However, while the metal spatial distribution reflected environmental influences, TBT distribution was anthropogenically influenced. Sediment homogeneity and OM content influenced contaminant distribution in the estuary significantly.

4.3.3.1 Metal Distribution

Generally, the inner estuary metal concentrations in surface sediments were low and increased through the middle section of the estuary, and reached a plateau before dropping in the outer section of the estuary. The middle estuary is a convergence zone between marine and freshwaters. This phenomenon known as the mid-estuarine maximum has been observed in other estuaries in relation to metal concentrations (Caccia et al., 2003; Gerringa et al., 2001; Thompson et al., 1984; Yang et al., 1998). Sediment homogeneity and estuarine stability are key factors in the occurrence of this estuarine feature. As previously stated surface sediment in the Tolka estuary does not have significant granulometric variation: fine-grained sediments dominate the estuarine intertidal areas. Fine-grained sediment across the estuary's extent provided a stable environment for contaminant retention. Contaminant loss from fine-grained sediment is dependent on in situ physical factors such as marine influx with tides, turbulence associated with adverse weather conditions and freshwater influx from riverine systems. Contaminant loss occurs at estuarine margins because of these factors whereas contaminant concentrations at the middle of the estuary are relatively unaffected (Miles & Tome, 1997). While SPM was not sampled in the estuary it can be assumed that remobilization of SPM bound metals from the Tolka outer estuary, together with the influx of clean marine sediments through Dublin Ports entraining walls, account for the gradual seaward decline in contaminant concentrations of estuarine sediments in the Tolka (Kennish, 1994).

The outer estuary can also function as a source of metal to the mid-estuary. Metal in the outer estuary can be removed and relocated to the middle and inner estuary regions and redistributed over the course of a tidal cycle that increases mid-estuary concentrations. In the Tolka estuary the local yachting channel runs directly from the edge of the middle estuary at Site 18 to the Liffey Channel and pollutant backwash in this channel may have contributed metals to this zone. Influx of marine water through the ports retaining walls forces the Liffey riverine water up the yachting channel to mix with the Tolka riverine water in the middle estuary. Deposition of the Liffey's suspended load occurs in this section due to its anticlockwise rotational gyre and contributes to elevated metal concentrations in the middle estuary.

As illustrated in Chapter 3 Figures 3.5.1 to 3.5.45, the outer estuary exhibited lower metal concentrations than the inner and middle estuary. The influx of seawater from Dublin Bay and freshwater from the Liffey River carried metal contamination further into the Tolka estuary in solute form and bound to SPM. Turbulence in the outer estuary would resuspend contaminated surface sediment and as contaminated SPM transport it towards the middle and inner estuarine zones. Dublin Port, located at the mouth of the Liffey River has significant metal contamination from the exportation of Ni, Pb and Zn ores through Alexandria Dock (Davoren et al., 2005; Dublin Port, 2005). Metal trapped in the matrices of colloidal particles and in solute form in the water column is likely to be transported on the tide up the estuary from the outer margins and deposited as the tide recedes (Luoma, 1990).

It is likely that local boating in the estuary contributes appreciable quantities of metal and TBT from yacht antifouling paints to this site and subsequently to the mid-estuary. Boats are cleaned and launched in April. Old antifouling paint scraped from the boats is likely washed into the estuary at this point. As, Cd, Cr, Cu, Pb and Zn have been used in antifouling paints in recent years as an alternative to TBT (Bryan & Langston 1992; Yebra et al 2004). Up to seventy boats remain in the estuary in proximity to sites 18, 19 and 20 each summer till the end of September. In particular, As and Zn concentrations were elevated at Site 18 and adjacent sites and were likely associated with antifouling paint residues arising from boat maintenance and cleaning in the site vicinity. Generally the influence of boating activity on metal and TBT concentrations at sites of the middle estuary may be seen in the elevated metal and TBT concentrations between Sites 15 – 18.

4.3.3.2 TBT and OM Distribution

Spatially TBT and OM concentrations in the estuarine surface sediment exhibit similar trends to metal distribution. Generally, the inner estuary TBT and OM concentrations were lower and increased through the middle section of the estuary, and reached a plateau before dropping in the outer section of the estuary, an equivalent pattern to metal distribution. While the distribution of OM in the estuary is largely dependent on sediment granulometry and on tidal forces, the distribution of TBT in the estuary is dominated by anthropogenic input but influenced by OM and sediment granulometric distribution.

A large proportion of organotin contaminants such as TBT is found to be associated with the clay fraction of particulate matter (Hoch, 2001; Hoch et al., 2002). Adsorption and concentration onto this fraction are important controlling mechanisms concerning distribution and fate of TBT in the estuarine environment (Hall et al., 1987; Hoch, 2001; Hoch et al., 2003; Hoch & Schwesig 2004). Sample sites with elevated levels of this fine fraction would also be expected to have a higher association with TBT concentrations (Langston & Pope, 1995; Hoch & Schwesig 2004). As previously stated fine-grained sediments dominated the inner and middle Tolka estuarine zones. Sites 15 to 18 in the mid-estuary had the highest levels of fine-grained sediment and the corresponding TBT concentrations were the highest in the estuary.

In the aquatic environment, TBT has low aqueous solubility and low mobility, and is easily adsorbed onto SPM. This is an important process in the fate of TBT in the aquatic system (Hoch, 2001; Hoch et al., 2003). In the Tolka, the outer estuary exhibited lower TBT concentrations. The influx of seawater from Dublin Bay and freshwater from the Liffey River carried TBT further into the Tolka estuary. Dublin Port located at the mouth of the Liffey River has significant TBT contamination and levels of 78 ppb were measured in surface sediment from Alexandria Dock in 2004 (Davoren et al., 2005). TBT trapped in the matrices of colloidal particles and in solute form in the water column is likely transported on the tide up the estuary from the outer margins and deposited as the tide receded (Luoma, 1990). OM is transported to the mid-estuary by the same tidal force. This appears to account for a reduction in TBT and OM concentrations at sites 19 and 20.

4.4 Seasonal Distribution

The ability to detect temporal change is dependent on the nature of the site. Temporal variance can be demonstrated in low energy, depositional environments of rivers and estuaries by repeat sampling (Birch et al., 2001). The Tolka river and estuary due to their enclosed nature offered potential in observing temporal trends. Distinct seasonal distributions were observed over the thirty-month period. Generally a reduction for all contaminants in the surface sediment occurred from autumn into winter, and lowest concentrations were observed in February/March. Metal concentrations increased gradually in spring and generally reached a maximum in July/August. TBT concentrations were anthropogenically introduced during the summer months. The initial twelve months of sampling provided distinct seasonal distributions for all six metals. The following eighteen months of sampling mirrored the initial twelve months with some minor fluctuations.

4.4.1 Environmental Factors influencing Seasonal Contaminant Distribution

Understanding the causes of temporal variability in contaminant concentrations in estuaries can be complicated by interrelationships among potential controlling factors and anthropogenic inputs (Hatje et al., 2003). Seasonally variable environmental factors can include rainfall, temperature, pH, salinity, OM content and SPM, and flow rate of the river.

4.4.1.1 Sediment Homogeneity

Sediment homogeneity is a key factor in the occurrence of distinct seasonal variation in contaminant concentration of surface sediment in aquatic systems. As discussed in Section 3.1, surface sediment had a relatively constant granulometry. Appendix A, Table 1 illustrates the percentage of relatively constant fine grained sediment fraction (<63 μm) observed at each site throughout the thirty months of sampling. Stability of surface sediment deposits is determined by the local hydrodynamic and sediment transport processes and the transportation of sediment during a storm event is dependent on the physiographic conditions of the surrounding watershed. Entraining walls, weirs, bridges and dams within aquatic systems create impoundments that retain sediment stability and minimise storm event turbulence (Crane, 2003). The sample area of the Tolka River and estuary was almost entirely entrained by man made river and estuary walls in the urban environment, and these were likely to influence surface sediment stability. This stability contributed to the distinct spatial distribution that was evident over the thirty month period. This sediment spatial pattern remained relatively constant over time in spite of contaminant concentration fluctuations.

4.4.1.2 Rainfall

Rainfall influences OM and contaminant transportation and retention time significantly in aquatic systems by inducing turbulence within the water column and so removing OM from the surface sediment layer by resuspension (Hatje et al., 2001). As OM retention and transportation plays a key role in contaminant distribution within aquatic systems, rainfall can be considered to play a subsidiary role in contaminant seasonal distribution. In Dublin rainfall was highest in winter months (Figure 4.1).

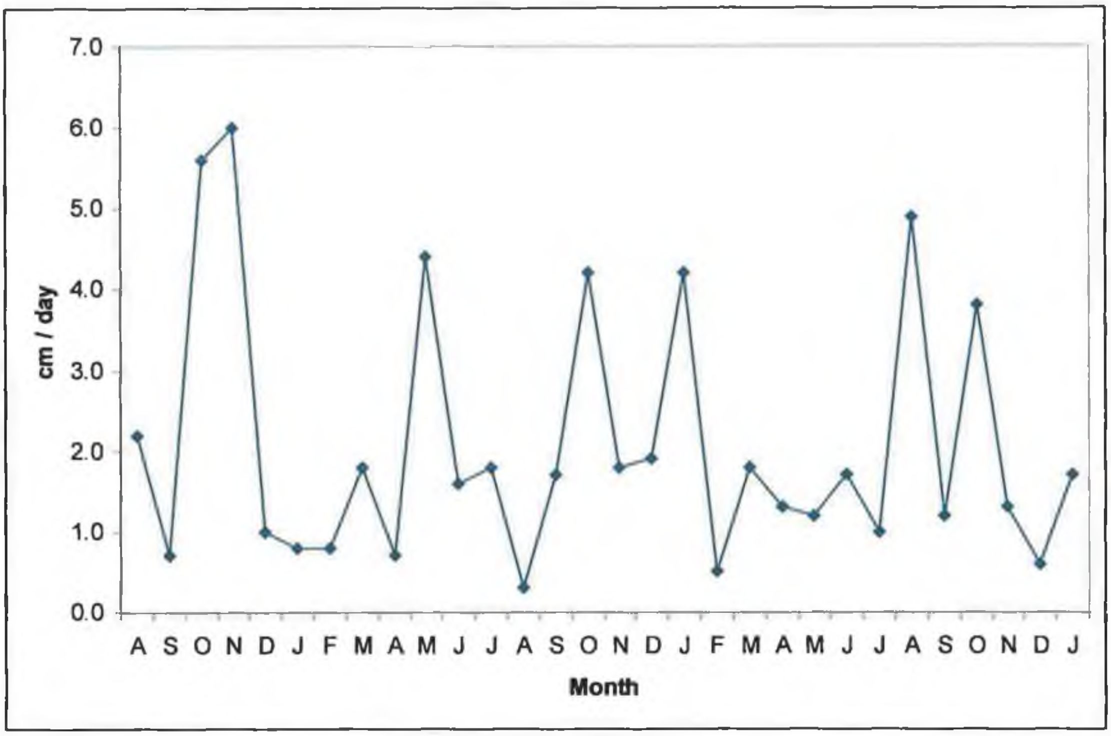


Figure 4.1 Average monthly rainfall (cm / day) recorded at Dublin Airport, August 2002 to January 2005.

Increased rainfall leads to increased flow rates and variable deposition rates in the river over time. As discussed in Section 1.4.1 flood events coincided with prolonged periods of rainfall. In November 2002 a flow rate of 97 m^3 / s was recorded after a sustained period of time. Figures 4.2 and 4.3 illustrate river speed over time at Sites 3 and 9 in the upper and lower riverine zones respectively (river speeds for Sites 1 to 12 from December 2002 to January 2003 are reported in Appendix B).

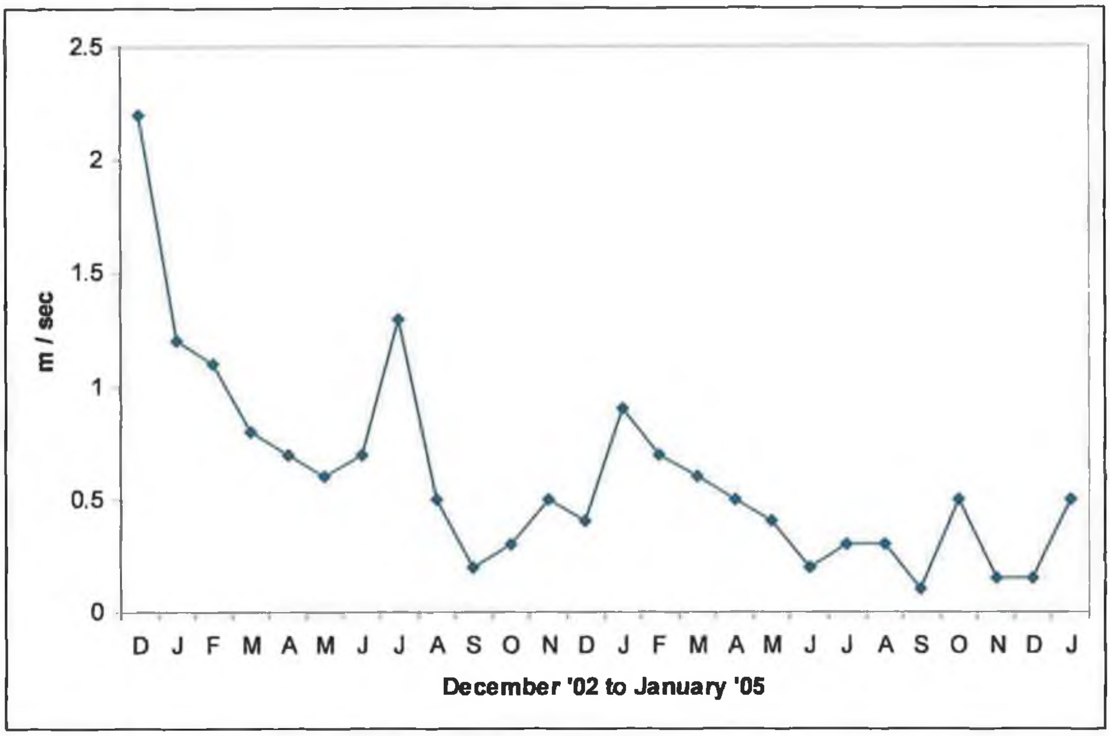


Figure 4.2 Site 3 River speed (m / sec), December 2002 to January 2005.

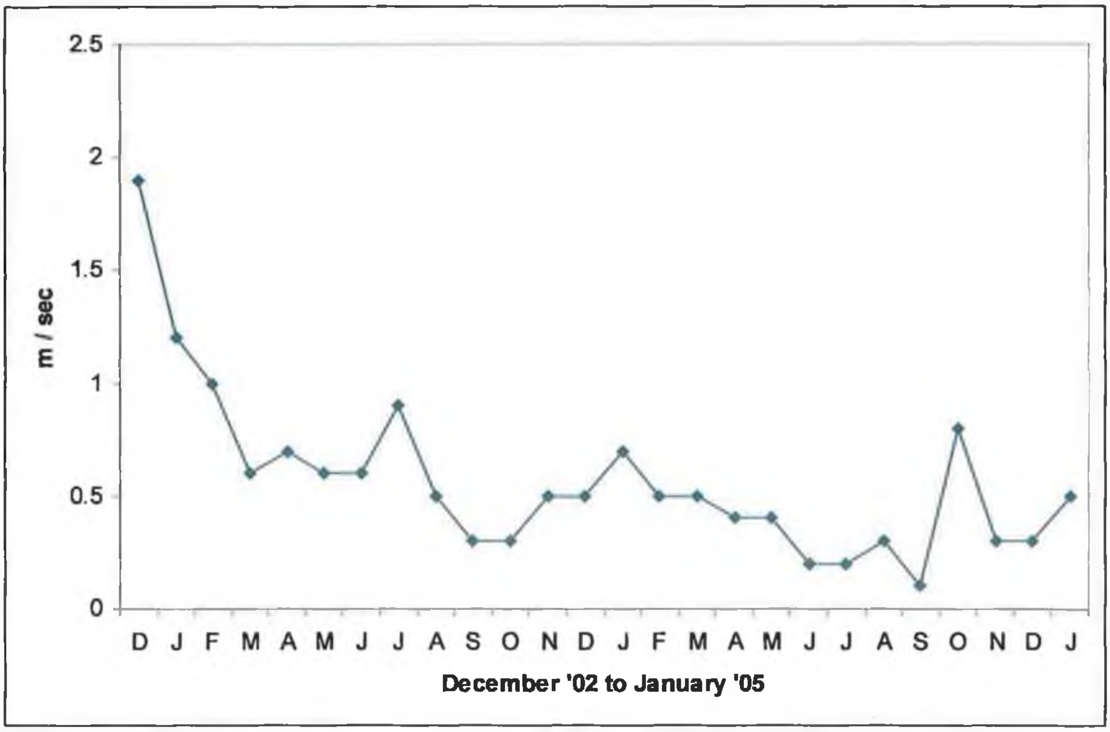


Figure 4.3 Site 9 River speed (m / sec), December 2002 to January 2005.

Table 3.6.1 indicates average monthly deposition rates recorded between Sites 3 and 4 in the upper riverine zone for the final eight months of sampling. While deposition rate sampling was completed only for one site on the river, it can be assumed that similar depositional rates were observed across the upper and middle sections of the river (Morrisey et al., 2000; Parker et al., 2000), while higher deposition rates would be observed in the lower stages of the river as the channel broadened and tidal influx increased deposition rates (Bibby & Webster-Brown, 2005). A minor positive correlation was observed between river speed and deposition rate (r^2 0.2725) during this time period. Ideally, as river speed increased, deposition rate should have decreased (see Figure 4.4), which was observed during the sample period, however low deposition rates were also evident during periods of lower river speed indicating that SPM loading river speed to not behave uniformly. Other studies have shown that during periods of elevated river speed, SPM loading displayed an equivalent increase for a period of time but then decreased as all fine grained particles had effectively been removed from the river and only heavier particles remained on the bottom (Parker et al., 2000; Characklis & Wiesner, 1997; Bibby & Webster-Brown, 2005). Seasonal variation in rainfall would also have an effect on SPM levels in the river, i.e. as rainfall increased, urban run off to the river from the surrounding catchment increased and as volume was elevated, river speed increased which further elevated channel turbulence and increased resuspension of surface sediment thus increasing total SPM of the water column.

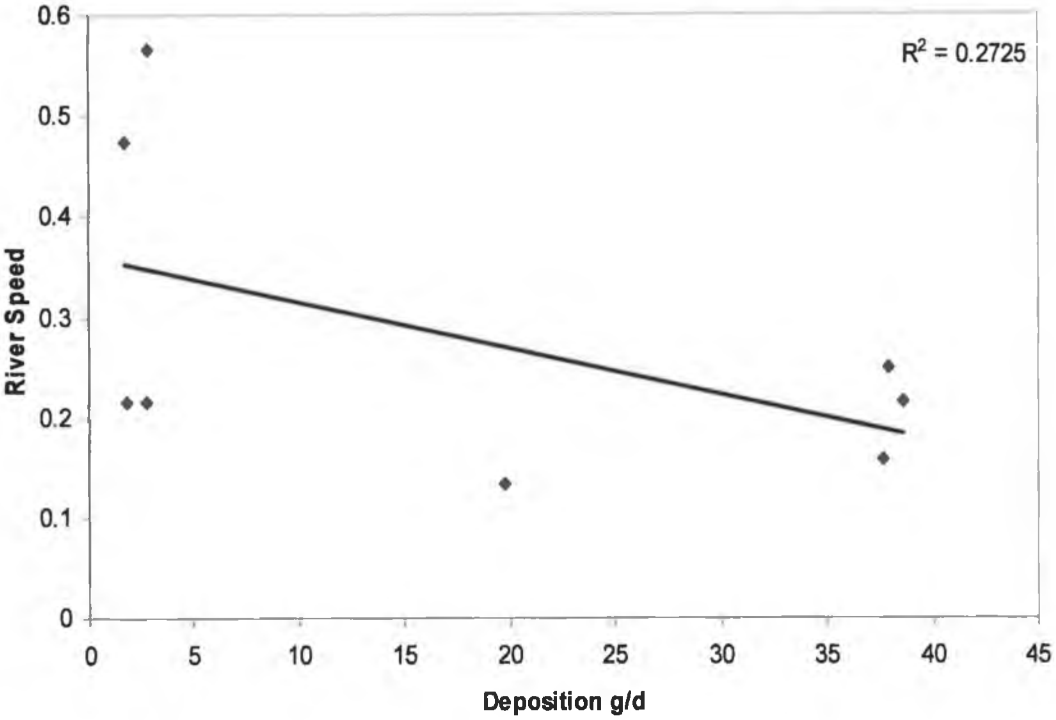


Figure 4.4 River Speed versus Depositional Rate (June 2004 to January 2005) Correlation Scatter Plot.

Due to increased freshwater-seawater mixing induced by higher rainfall, rougher seas, higher tides and increased wind effects, turbulence in the estuary itself was higher in winter than summer months. Resuspension of surface sediment by this increased turbulence in winter months contributed to sediment bound contaminants re-entering the water column and either leaving the estuarine system as SPM into the marine zone or to a much lesser extent pushed back into the inner and middle estuarine zones (Wheatcroft & Butman, 1997). As a result, the estuarine system is flushed during winter. Significant storm events occurred in Dublin in the early winters of 2002, 2003 and 2004. Each year the Tolka River reached record 100-year flood levels (50 m^3 / s) and in combination with high tides and easterly prevailing winds caused turbulent floods in the river and estuary (EPA, 2005). Significant quantities of surface sediment were removed from the estuary and lost to the marine zone.

4.4.1.3 Salinity and pH

The adsorption behaviour of contaminants in both estuarine and freshwater varies according to moderate changes in pH conditions (Hatje et al., 2003b) and has important implications on transportation and retention of contaminants in aquatic systems over time where physicochemical variable such as salinity, pH and SPM vary greatly seasonally. It has been observed in previous studies (Hatje et al, 2001; Hatje et al 2003a, Hoch & Schwesig 2004) that the metals investigated in this assessment and TBT are strongly adsorbed to sediment particles both in the water column and on surface sediment between pH 6 and 8.

As previously described in section 4.3.1.3 and illustrated in Figures 3.2.1 to 3.2.5, porewater pH of the river and estuary maintained a distinct spatial trend over time. pH levels exhibited minimal temporal variation to this spatial trend over the thirty months of sampling. Generally pH levels were slightly higher in summer months in both river and estuary compared to winter pH levels. In free flowing rivers and estuaries that have an adequate flushing mechanism excessive humic acids cannot accumulate in the system as OM degrades (Kennish, 1994; Little, 2000). This is the primary reason for elevated acidity in summer months. There were no radical alterations of pH observed within the system that would have severely affected metal sorptive processes (Characklis & Wiesner, 1997). pH variation was too minor to have any significant effect on metal distribution as both river and estuary exhibited optimal pH conditions throughout the thirty month assessment for metal adsorption to sedimentary particles (Bibby & Webster-Brown, 2005; Morrisey et al., 2000; Parker et al., 2000).

TBT adsorption to OM is dependent both on pH and on the mineral constituents of the sediment. Optimal adsorption to fine grained clay rich sediments similar to surface sediment in the Tolka occurs between pH 6 and 7, while optimal adsorption to OM occurs between pH 6 and 8 (Hoch & Schwesig, 2004). The average annual pH range of the Tolka estuarine porewater is 7.3 to 8.0 which clearly correlates with optimal conditions for TBT adsorption to the estuarine sediment over the twelve-month period. While pH levels had only minimal seasonal variation, it is considered that pH played a negligible role in TBT temporal distribution after the primary role of organic matter distribution and secondary role of anthropogenic seasonal input, discussed further in Section 4.4.2.

The common increase in pH associated with increasing salinity favours the greater sorption of contaminants to SPM in the water column. This would suggest an increased association of contaminants to SPM particles towards the estuary mouth (Hatje et al., 2003a). This favours retention of metals in the estuary. The transportation of SPM from the outer estuary to middle and inner estuarine zones has previously been attributed to the spatial mid-estuarine maximum trend that was observed throughout the estuarine thirty-month assessment. Studies elsewhere have shown that desorption of contaminants from SPM during transition from freshwater to saline conditions is determined by "saline shock factor" i.e. an abrupt change in salinity will allow almost total desorption of contaminants from SPM to the water column (Achterberg et al., 2003; Boyes & Elliott, 2006). However, as salinity increased gradually seaward in the Tolka rather than an abrupt change between river and estuary, metals bound to SPM will remain bound even against consequent competition for SPM binding sites by major seawater cations such as Zn (Glegg et al., 1999; Boyes & Elliott, 2006; Duquesne et al., 2006). Table 3.3.1 in the results section indicates salinity variation observed within the estuary between September 2004 and January 2005. Salinity variation between tides shows the effect the Tolka freshwater source had on the inner estuary: the Tolka freshwater plume extended brackish water as far as the middle estuary at low tide as indicated by salinities <20 ‰. At high tide virtually the entire estuary was at normal marine salinity (35 ‰) except at the confluence of the river and estuary where brackish waters dominated, see Table 3.3.1. A full seasonal assessment was not completed however during salinity sampling variation was minimal and was likely to have made a negligible contribution to seasonal variation of contaminant temporal distribution. The temporally limited seasonal assessment of salinity did not allow for a correlation assessment between salinity and SPM metal content or with surface sediment metals. However, future interpretation of salinity correlation utilising partitioning coefficients is discussed in the future research chapter.

4.4.1.4 Suspended Particulate Matter

Adsorption onto SPM and OM in surface sediments is an important process controlling contaminant concentrations, bioavailability, and toxicity to biota, and both the fate and transport of contaminants (Jannasch et al., 1988). As discussed in Section 1.2.4, the role of aquatic systems, particularly estuaries, as filters for SPM, is due primarily to particle/solute interactions and sedimentation of particle bound metals (Zhou et al., 2003). Adsorption onto SPM is an important process controlling dissolved metal concentrations and a reduction in metal toxicity is a frequent consequence (Gadd, 1993). In a system with high SPM loading, metals are more likely to be SPM bound and eventually become locked into surface sediment matrices upon deposition (Gee & Bruland, 2002; Hatje et al., 2003a).

SPM particles present in aquatic systems comprise a diverse array of components, ranging from clays to metal oxides to organic detritus. A mixture of such materials would be expected to have a wide range of surface chemical properties and contaminant adsorption characteristics (Ciffroy et al., 2001; Tang et al., 2002). A number of studies have shown that metal concentrations in aquatic systems are buffered by organic complexation with SPM (Kozelka & Bruland, 1998; Muller, 1999) and that this complexation controls bioavailability (Tang et al., 2002). SPM particles can contain highly variable organic components locked within colloidal matrices of larger particles including sulfhydryl organic ligands, carbohydrates, uronic and humic acids and metal sulfides, all of which play significant roles in the sorptive properties of SPM particles (Santschi et al., 1997; Wells et al., 1998; Tang et al, 2002; Achterberg et al., 2003). These properties vary temporally throughout the year as decomposition rates within the aquatic system and within the system catchment vary over time. It can be hypothesised that as the quantity and composition of SPM vary seasonally, this variation plays a role in contaminant seasonal distribution within aquatic systems (Achterberg et al., 2003; Woitke et al., 2003; Hatje et al., 2001; Tang et al., 2002). Significant seasonal variability in contaminant concentrations may be explained in terms of change in SPM and hence sediment organic matter composition due to biological processes in the summer months (Santschi et al., 1997; Hatje et al., 2001).

4.4.1.4.1 Tolka Riverine SPM

While it was not logistically possible to determine SPM in the water column of the estuary (due to lack of access to a boat on a continuous basis), analysis of SPM of the Tolka River water column over a thirteen-month period revealed significant seasonal variation in total SPM loading. The Tolka is a highly turbid river due to a turbulent river channel with many rapids and weirs that contribute to a generally low deposition rate even during periods of moderate river flow. As illustrated in Table 4.9 deposition rates were significantly reduced in winter months compared to summer months. However, the deposition rate of the Tolka is similar to much larger rivers due to its high SPM load (Woitke et al., 2003; Robert et al., 2004). Figures 3.6.1 and 3.6.2 indicate the spatial and temporal variation of SPM loading in the riverine water column over time. Temporally SPM was significantly higher in winter months than in summer months due to rainfall levels having a direct influence on river speed which in turn increased river turbulence. Riverine turbulence reduced deposition rates and retained SPM in the water column and also increased sediment resuspension. High rainfall increased run-off from the watershed and contributed higher SPM loading to the river (Bibby & Webster-Brown, 2005). Thus the prolonged rainfall of winter was a significant factor in elevating the SPM load of the water column in winter months. A positive correlation was observed between rainfall levels and the final SPM loading of the river recorded at Bridge 5 (see Figure 4.5).

A typical seasonal variation was observed at Bridge 3, located in the middle riverine section: in January 2004 levels were 221 mg SPM / L, subsequently reduced to 134 mg SPM / L in June 2004 and increased in winter months to a maximum recorded level of 321 mg SPM / L in January 2005. These levels are similar to the rural upper stages of other major rivers including the Danube (SPM levels in its upper reaches regularly above 350 mg SPM / L and in its lower reaches over 1000 mg SPM / L), Gironde (SPM levels regularly above 300 mg SPM / L) and rivers of a similar size such as Bells Creek, Queensland which recorded levels of 123 – 357 mg SPM / L (Liaghati et al., 2003; Woitke et al., 2003; Robert et al., 2004) and to the urban stages of the Pakuranga and Puhini Rivers in Auckland, New Zealand which recorded SPM levels as high as 260 mg SPM / L (Bibby & Webster-Brown, 2005).

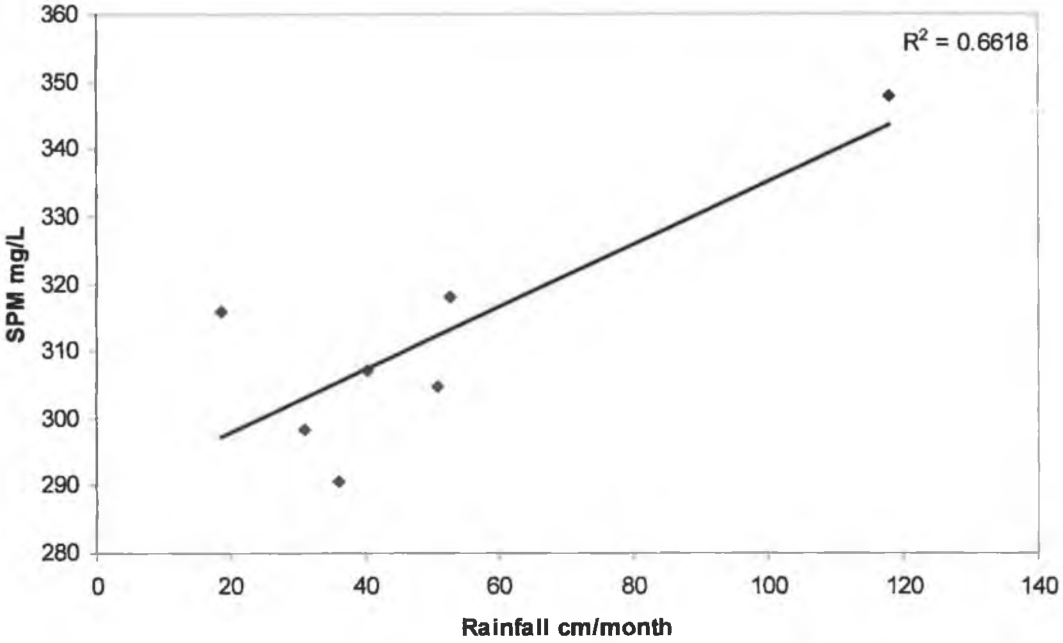


Figure 4.5 SPM Load (Bridge 5) versus monthly rainfall (January 2004 to January 2005) Correlation Scatter Plot.

4.4.1.4.2 SPM Bound Metal

SPM bound metal concentrations displayed a similar seasonal variation as SPM loading. As illustrated in Figures 3.6.4 to 3.6.9, all metals noticeably increased in proportion to SPM loading, however, mg metal per kg of SPM also increased. This implies that as SPM loading increased, total metal binding to SPM from the dissolved fraction in the water column also increased. Metal loading of SPM was not significantly different to other rivers but had a more moderate range of concentrations (Bibby & Webster-Brown, 2005; Morrisey et al., 2000; Parker et al., 2000). The east Tanaki River, New Zealand had metal levels ranging from 63 – 83460 mg Cu / kg SPM and 40 – 2180 mg Pb / kg SPM (Bibby & Webster-Brown, 2005). SPM bound Cr and Zn had relatively low concentrations in comparison to Cd, Ni and Pb concentrations. This implies that this is the primary mode of transportation for these metals within the system. Notably Cd concentrations bound to SPM were higher than concentrations within surface sediment for the same time period, at some points by a factor of 10: e.g. in January 2005 at Site 3, 0.27 ppm Cd was recorded in surface sediment, while in the water column 4.68 ppm Cd bound to SPM was recorded at Bridge 1 directly upstream, while for Pb the equivalent levels were 76.5 ppm Pb and 49.9 ppm Pb respectively. Significant temporal variation of metal concentrations bound to SPM was observed for all metals at all sampling points. Bridge 5 displayed the greatest ranges in concentration over time, though this was influenced by an influx of estuarine SPM at this point. Table 4.15 illustrates a comparison of SPM bound metal loadings at Bridge 5 between June 2004 and January 2005.

Metal	June 2004 (ppm)	January 2005 (ppm)
Cd	3.5	4.8
Cr	1.1	1.8
Cu	27.0	33.4
Ni	18.2	30.2
Pb	24.9	44.9
Zn	12.2	10.7

Table 4.15 SPM bound metal concentrations (µg metal / g SPM), June 2004 versus January 2005.

The increase in dissolved metal loading of the river during winter months (see Section 4.4.1.5) coupled with an equivalent increase in SPM loading contributed to the reduction of metals in the surface sediment. SPM bound metal and dissolved metal in the porewater were resuspended. Quantities of dissolved metal became bound to the elevated SPM load and transported out of the riverine system and into the estuarine and subsequent marine zones. While it was not possible to determine TBT loading of SPM, it can be assumed that SPM played a significant role in transportation of TBT in a similar manner as it did for metals (Hall et al., 1987; Hoch, 2001; Hoch et al., 2003; Hoch & Schwesig 2004). From observations made on figures 3.6.1 to 3.6.9 it can be hypothesised that SPM played the primary role in contaminant transport within the riverine system and subsequently estuarine and marine systems (Characklis & Wiesner, 1997; Neal et al., 1997; Pettine et al., 1994; Webster et al., 2000; Duquesne et al., 2006). Within the estuarine zone, SPM was reported to be the primary mechanism for removal of contaminants from the surface sediment during winter months (Duquesne et al., 2006; Martino et al., 2004; Town & Filella, 2002; Turner & Millward, 2002; Warren & Haack, 2001; Price et al., 1991). The resuspension of surface sediments during turbulent winter months would elevate SPM loading and subsequently carried significant quantities of SPM bound contaminants out of the estuarine zone and into the greater marine zone of Dublin Bay.

4.4.1.5 Water Column - dissolved contaminant transportation

Temporal variability in dissolved metal concentration within the water column of the Tolka was observed over a thirteen month period for all six metals, as seen in Figures 3.7.1 to 3.7.13. Dissolved metal concentrations were generally higher in winter than summer months. This is likely due to a combination of higher in situ riverine flow rates and turbulence in the river channel leading to dissolved metals previously trapped in surface sediment porewater being released to the water column and transported out of the system (Hatje et al., 2003; Hoch & Schwesig, 2001). This contributed to a loss in total metal concentrations of surface sediment. Metal concentrations within the water column were high. As seen in Section 4.2, the dissolved portion of metals in the water column greatly exceeded international guidelines and these concentrations are attributable to the urban environment, particularly the urban road network in the rivers vicinity. A source of metals from an industry located within the urban catchment (as discussed in Section 1.4.2) may account for the elevated concentrations, or the often metal rich limestone bedrock contributed higher metal concentrations to the river. Table 4.16 indicates the basic temporal variation for dissolved metal loading at Bridge 4 which reflects the final stage of the river before entry to the estuary. Bridge 5 where temporal variation though greatest, was influenced by tidal influx. While not all metals reduced in summer months at Bridge 4, overall metal concentrations throughout the river over the course of thirteen months displayed the temporal trend previously described, and illustrated in Figures 3.7.1 to 3.7.13. Metal concentrations of porewater were analysed for the final seven months of sampling to determine free metal concentrations within surface sediment matrices that could readily diffuse to the water column. Concentrations were generally lower than water column dissolved metal concentrations. There was a slight temporal variation. Porewater metal concentrations increased in winter months (Appendix C, Figures 1 – 12).

Metal	February 2004 (ppm)	June 2004 (ppm)	January 2005 (ppm)
Cd	0.4	0.1	1.1
Cr	0.3	0.4	0.8
Cu	0.7	0.6	1.3
Ni	3.0	3.4	4.6
Pb	7.3	3.2	24.9
Zn	3.5	6.2	7.9

Table 4.16 Metal concentrations (ppm) of the water column at Bridge 4 between February 2004 and January 2005.

While TBT concentrations were not analysed from water column samples due to unavailability of analytical methods, new techniques are now available for TBT solid phase extraction of SPM, (Prasad & Schafran, 2006; Diez et al., 2005). It is likely that TBT loading of the river would not have been similar as TBT loading of the water column was dependent on contamination from the point source of Dunsink landfill. It is more probable that TBT concentrations within the water column diminished with distance from this point source. It is likely that only a reduced temporal variation would have been observed as leachate flow from landfills is entirely dependent on rainfall levels (Christensen & Christensen, 2000). On this basis it can be hypothesised that dissolved metal loading of the water column was a secondary mode of transportation for contaminants within the system.

4.4.1.6 Organic Matter

Distribution, transport and fate of contaminants in estuarine systems are significantly influenced by OM (Hoch, 2001; Rubio et al., 2000; Bryan et al., 1989; Wangersky, 1986; Horowitz & Elrick, 1987; Singer, 1977). As discussed, living OM influences contaminant distributions spatially and temporally in fine-grained surface sedimentary material. Contaminants bound to larger SPM particles (faecal pellets, crustacean moults, and dead plant and animal matter) are generally responsible for more than 90% of their vertical transport in the water column (Bryan, 1976). OM content of surface sediment is capable of altering the distribution between oxidised and reduced forms of metals which can affect the impact metals have on the estuarine ecosystem (Yap et al., 2002). Often in sediments where OM is not retained metals become immobilised within colloidal particles through binding with Fe, Mn and Al oxides and thus non-bioavailable (El-Rayis et al., 2003).

4.4.1.6.1 OM Distribution in the Tolka Aquatic System

OM content of surface sediment had a distinct spatial trend that was maintained throughout the sampling but with variable seasonal fluctuations (Figures 3.4.1 to 3.4.3). Spatially, OM concentrations were low in the river compared with the estuary. In the estuarine zone highest concentrations were recorded in the inner and mid estuarine sections with lower concentrations in the outer estuary. The initial sampling results in September 2003 indicated riverine OM concentrations increased towards the estuary from 1.4 % at Site 1 in the upper river to 5.2 % at Site 10 at the estuarine confluence. This indicated that OM concentrations increased as river speed reduced and riverine channel broadened allowing for greater deposition and retention, and less turbulence to the surface sedimentary layer.

Estuarine OM concentrations ranged from 7.5 % at site 11 to 10.2% at sites 14 to 15. OM concentrations decreased from 8.9 to 2.6 % between site 16 in the mid-estuary and site 20 at the estuarine margin. The middle estuary is a central assimilative zone between marine and freshwaters (Caccia et al., 2003; Gerringa et al., 2001; Thompson et al., 1984; Yang et al., 1998). Greatest accumulation of OM and associated contaminants occurs at this point as SPM loading from the river and from the outer estuary and marine zone combine in this area during high tide and are deposited on the surface sedimentary layer as tides recede (Bally et al., 2004; Robert et al., 2004). Mudflats within the Tolka estuary are most extensive in the inner and middle estuarine zones, and are the most biologically productive areas in the estuary (Jeffrey et al., 1985). The in situ production of OM in the inner and middle estuarine zones also contributed to the formation of this mid-estuarine maximum, particularly in summer and autumn months when higher levels of biological activity occur.

In situ turbulence in the river and estuary during winter months resuspends surface sediment to the water column, resulting in elevated SPM levels for that time, as was observed in the Tolka River. OM locked into surface sediment matrices was subsequently released through resuspension along with mineralic particles and becomes water column SPM. SPM was transported out of the aquatic system to the marine zone. In summer and autumn months, high biological activity – growth and decomposition, in the aquatic system and the greater catchment contributed to greater OM concentrations to the aquatic system. As river and estuarine conditions were less turbulent from reduced river flow and marine influx, elevated deposition of particulate OM occurred and increased surface sediment OM concentrations, particularly in the high deposition and high biological activity environment of the estuary. This seasonal distribution had a significant effect on contaminant distribution in the aquatic system.

4.4.1.6.2 OM and Metals

Generally, a reduction of all metals and OM in the surface sediment occurred from autumn into winter, and lowest concentrations were observed in February/March. Both metals and OM increased gradually in spring and generally reached a maximum in July/August. Table 4.17 indicates correlations at each site between OM and specific metal for the final twelve months of sampling. Positive correlations were observed for all metals at all sites in the estuarine zone illustrating the clear relationship between OM and metal over time in this environment. Some metals displayed less positive correlations than others: Pb correlations in the estuary ranged from 0.285 to 0.591 in comparison to Cd which ranged from 0.483 to 0.905.

In the riverine zones, lower positive correlations and negative correlations were observed at a significant proportion of the sites for each metal. This implies that OM did not play the primary role for metal retention within surface sediment of the riverine system. OM concentrations were lower in the river than in the estuary indicating that retention of OM in surface sediment is dependant on the differing physical environments (Caccia et al., 2003; Gerringa et al., 2001). As the river is a low depositional environment due to its artificial boundaries and constant flushing, retention of OM in its surface sediment is reduced (Feng et al., 2001). Elevated depositional rates occur in the estuary due to its broad expanse and lower turbulence. This allows greater concentrations of OM to accumulate in estuarine surface sediment and for OM production by organisms within estuarine sediment. This greater concentration of OM retains higher concentrations of contaminants than in the river.

From the results and correlation coefficients, OM can be seen as the major mechanism for metal accumulation, retention and dispersal in a system that has a relatively constant source of metals, more so in the estuary than in the river. Dunsink landfill and the urban environment introduced a steady supply of metal to the Tolka river and consequently the estuarine aquatic system. As OM concentrations in the sediment vary seasonally, metal concentrations adsorbed to OM within surface sediment fluctuate in parallel. An OM seasonal cycle of production, retention and loss within the system was observed over the course of a year (Regnier & Wollast, 1993), and associated metals adsorbed to the OM were also gained and lost within the system. The implication that OM content controls metal retention in an estuarine system also implies that nutrient content of an estuary plays a role in metal retention. Greater nutrient loading of an estuary leads to elevated OM production in the system which in turn will elevate metal retention in the estuary.

Site	Cd (r^2)	Cr (r^2)	Cu (r^2)	Ni (r^2)	Pb (r^2)	Zn (r^2)
1	0.514	-0.360	-0.014	0.228	-0.153	-0.077
2	0.192	-0.558	-0.113	-0.079	-0.770	-0.269
3	-0.392	-0.434	-0.642	-0.607	-0.648	-0.622
4	-0.171	-0.043	-0.069	-0.359	-0.549	-0.261
5	0.150	0.305	0.385	-0.123	-0.163	0.127
6	0.190	0.469	0.354	-0.012	0.057	0.378
7	0.411	0.621	0.491	0.245	0.093	0.347
8	0.232	0.270	-0.150	-0.058	-0.031	0.666
9	0.382	0.337	-0.201	-0.218	0.028	0.688
10	0.763	0.435	0.548	0.537	0.294	0.692
11	0.778	0.512	0.714	0.549	0.285	0.713
12	0.652	0.940	0.856	0.860	0.557	0.608
13	0.483	0.918	0.650	0.827	0.580	0.496
14	0.524	0.952	0.669	0.769	0.522	0.514
15	0.490	0.889	0.723	0.698	0.504	0.589
16	0.752	0.546	0.813	0.768	0.337	0.731
17	0.770	0.674	0.862	0.833	0.456	0.868
18	0.798	0.616	0.857	0.870	0.407	0.872
19	0.799	0.204	0.854	0.825	0.284	0.752
20	0.905	0.379	0.889	0.919	0.591	0.917

Table 4.17 OM v Metal correlation coefficients, Sites 1 – 20 over the final twelve months of sampling; February 2004 to January 2005. (Green = Negative Correlation, White = 0 – 0.5 Positive Correlation, Red = 0.5 – 0.75 Positive Correlation, Blue = 0.75 – 1.0 Positive Correlation).

4.4.1.6.3 OM and TBT

OM concentrations greater than 0.2 % of estuarine and riverine surface sediment appear to be a major controlling factor for sediment-water partitioning of TBT (Di Toro et al., 1991; Langston & Pope, 1995; Meador, 2000) as OM associated humic acids contribute to optimal TBT adsorption conditions between pH 6 and 8 in surface sediment layers (Hoch & Schwesig, 2004). Lowest OM concentrations in the Tolka estuary were 1.0 %. The proportion of OM in surface sediment is considered to be the most important parameter controlling TBT distribution (Poerschmann et al., 1997; Arnold et al., 1998; Hoch & Schwesig, 2004). TBT is more strongly adsorbed to fine grained sediments containing OM than to sediments without. Positive correlations between OM and TBT distributions at each site for the final twelve months are indicated in Table 4.18 with higher r^2 values noted in the mid-estuary. Positive correlation between OM and TBT underscores the relationship between the two parameters. TBT in the water column, in solute form and bound to SPM is retained in surface sediment porewater or deposited to surface sediment and retained by OM during calm summer conditions in the estuary. As with metal contaminants, the seasonal OM cycle was the primary factor controlling TBT retention in surface sediment. As OM content increased during this period, TBT accumulation in surface sediment increased. During winter months as OM was lost due increased turbulence in the estuary, TBT was released into the water column and transported out of the estuary.

Site	**r^2**
1	N/A
2	N/A
3	0.389
4	0.256
5	0.119
6	0.105
7	N/A
8	N/A
9	N/A
10	N/A
11	N/A
12	0.376
13	0.634
14	0.724
15	0.643
16	0.829
17	0.811
18	0.508
19	0.763
20	0.406

Table 4.18 OM v TBT correlation coefficients, Sites 1 – 20 over the final twelve months of sampling; February 2004 to January 2005. (Green = Negative Correlation, White = 0 – 0.5 Positive Correlation, Red = 0.5 – 0.75 Positive Correlation, Blue = 0.75 – 1.0 Positive Correlation).

4.4.2 Surface Sediment Seasonal Metal Distribution

Distinct seasonal distributions were observed for metal contaminants in surface sediment over the thirty-month period (Figures 3.5.1 to 3.5.42). The initial twelve months of sampling provided surface sediment seasonal distributions for all six metals. The following eighteen months of sampling mirrored the initial twelve months with some minor fluctuations that provided data regarding pollution incidents and point source influence on temporal variability of metal concentrations within surface sediment matrices. All metal spatial distributions within the system were maintained over time but also exhibited temporal fluctuations. The distinct spatial pattern of the mid-estuarine maximum was evident throughout the thirty months but the concentrations that constituted this pattern increased in summer and decreased in winter. The previous sections described the primary factors influencing the variable seasonal trends of contaminants within the aquatic system: climatic conditions contributing to variable system physical conditions and water column turbulence, seasonal water column volume/flow variation and associated variable SPM loading and OM accumulation and loss from surface sediment.

In situ environmental factors affecting variability in contaminant concentrations of surface sediment layers can be further complicated by interrelationships with anthropogenic inputs (Bibby & Webster-Brown, 2005, Duquesne et al., 2006; Hatje et al., 2003a). If anthropogenic inputs were relatively constant, temporal variation would be dictated by in situ environmental factors. However if anthropogenic inputs were sporadic and / or extreme, contaminant input would determine both spatial and seasonal distribution (Boyes & Elliott, 2006; Shepherd et al., 2006; Relic et al., 2005).

Anthropogenically induced pollution incidents strongly affect the delicate balance within aquatic systems by altering internal spatial and temporal distributions of trace contaminants over space and time (Kennish, 1994).

During the thirty-month sampling period, anthropogenic input of metals remained relatively constant. However, there were sporadic pollution incidents that altered spatial and temporal distributions for short periods of time. The general seasonal distribution in the river and estuary was a concentration reduction for all metals in surface sediment from autumn into winter, with lowest concentrations observed in February/March. Metal concentrations subsequently increased gradually in spring and generally reached a maximum in July/August. This temporal variation was observed in river and estuarine zones, although to a lesser extent in the river. The previous sections described mechanisms for contaminant accumulation, retention, and removal from surface sediment in the Tolka aquatic system. In brief, physical and chemical in situ parameters vary seasonally and induce seasonal contaminant distribution. As both metal transportation and retention mechanisms varied seasonally, metal concentrations associated with these mechanisms were effectively accumulated, retained and lost from surface sediment matrices accordingly.

4.4.2.1 Winter

To summarise, the mechanisms for the loss of metals from surface sediment in winter month were initiated by climatic conditions. Higher rainfall in winter months elevated river volume and speed which induced greater water column turbulence. This rainfall also contributed significant volumes of urban river and sewage overflow to the Tolka system. However, as river volume increased, water column turbulence also increased. Turbulence in the estuary also increased as a result of higher riverine volume entering its western end and stronger wave action induced by winter climate conditions, entering its eastern mouth. Turbulence in the river and estuary reduced SPM deposition to surface sediment and increased surface sediment resuspension and porewater dissolution, essentially removing metals from surface sedimentary layers and retaining introduced metals from urban run-off in the water column. Elevated SPM loading of the water column during winter months can be attributed to these mechanisms. OM production within surface sediment layer is low during winter months and it is also removed from surface sediment matrices by turbulent resuspension. Subsequently metals associated with OM particles were removed from the surface sediment layer to become SPM bound metals within the water column. Metals were then transported in solute form and bound to SPM via the water column out of the riverine system, through the estuarine system and into the marine zone. Figure 4.6 illustrates the basic physical mechanisms for contaminant removal during winter months.

4.4.2.2 Summer

In summer months, reduced rainfall induced lower river volume and speed. This lowered water column turbulence which in turn would induce greater deposition of particulates from the water column to surface sediment. As observed, SPM deposition to surface sediment increased in summer months (Table 3.6.1). Surface sediment resuspension and porewater dissolution would have decreased in proportion to decreasing flow rates and associated internal turbulence, which can be observed by the lower SPM loading of the water column for summer months (Characklis & Wiesner, 1997). The summer water column as a low turbulent environment induced dissolved metal retention in surface sediment porewater and SPM bound metals accumulation within surface sediment as SPM was deposited at an increased rate. Urban run-off while not as high in summer as in winter months, upon joining the river would have a greater opportunity for deposition to surface sediment (Bibby & Webster-Brown, 2005). OM production in aquatic systems, especially estuaries, is higher in summer months, due to increased temperature and calmer water column conditions (Tokalioglu et al., 2000). OM concentrations within surface sediment layer were higher during summer months in the Tolka system, especially in the estuary. Metal contaminants were retained in the Tolka bound to OM within surface sediment matrices and the lack of water column turbulence reduced the loss of OM and associated metals from surface sediment. Metals were thus retained in surface sediment through a variety of linked mechanisms that were induced by variation in climatic conditions. Figure 4.7 illustrates the basic physical mechanisms for contaminant accumulation during summer months.

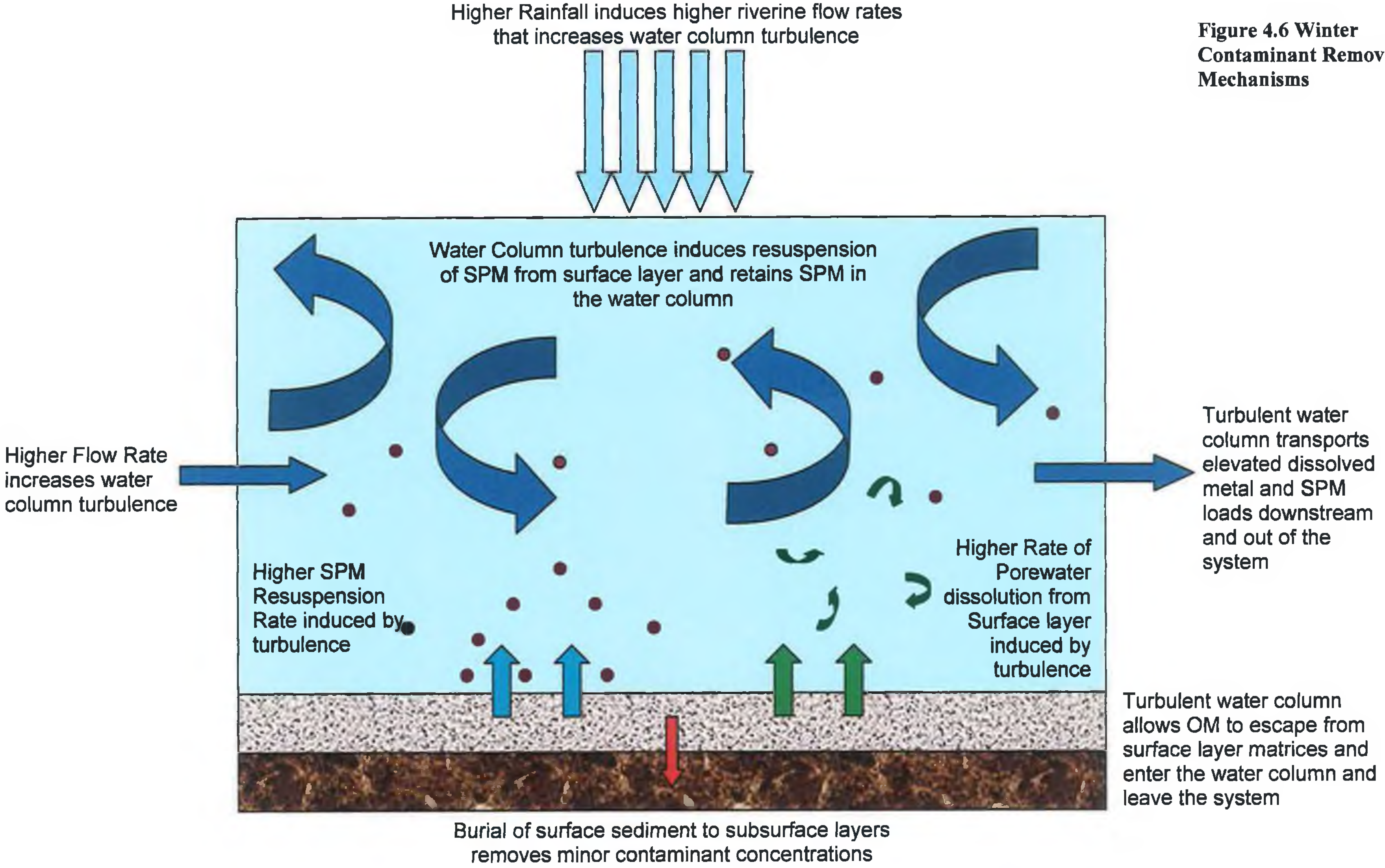


Figure 4.6 Winter Contaminant Removal Mechanisms

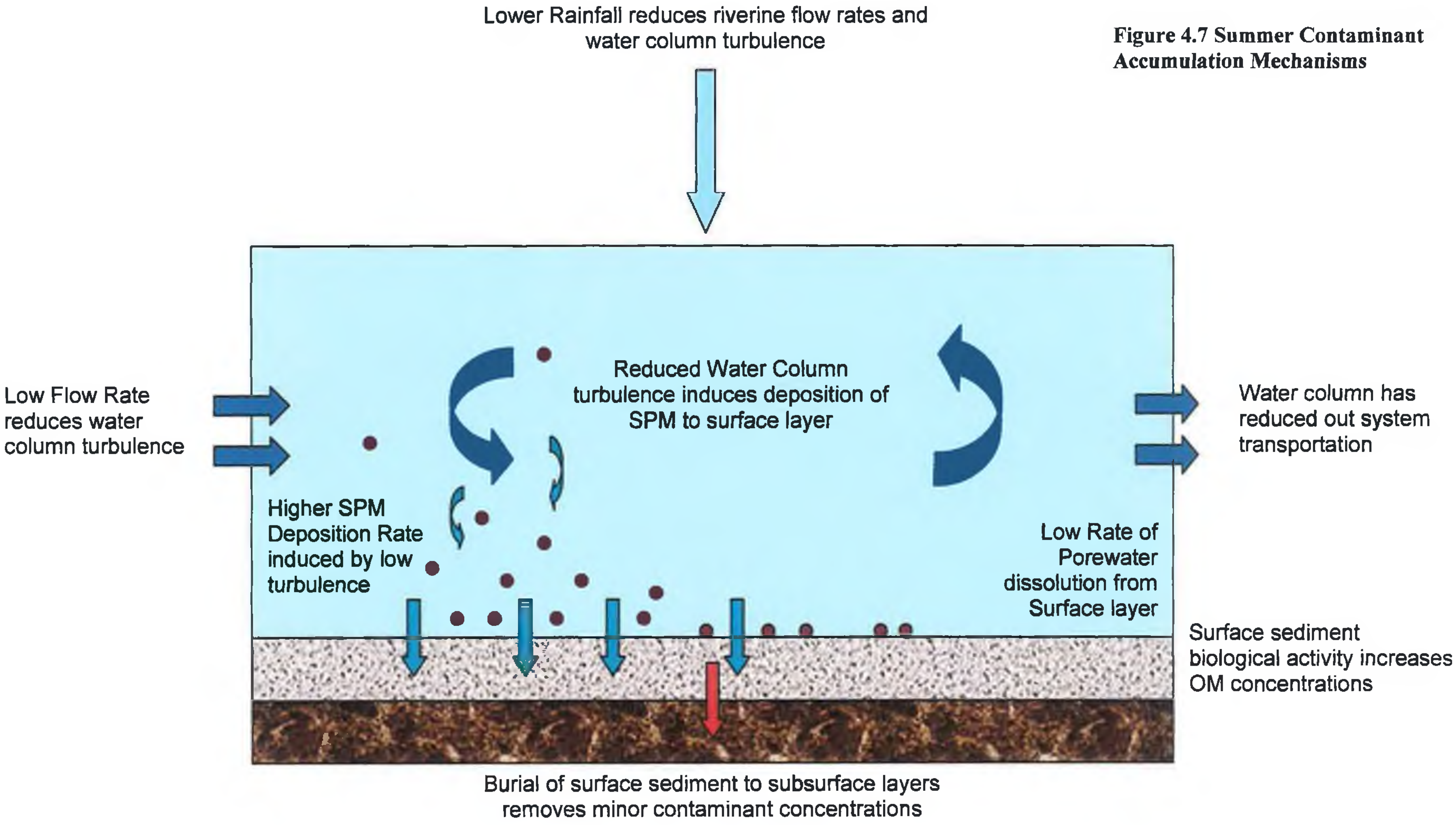


Figure 4.7 Summer Contaminant Accumulation Mechanisms

This seasonal distribution applied to all metals with varying concentrations ranges. Cd concentrations displayed minimal seasonal variation, as illustrated in Figures 3.5.1 to 3.5.5. In comparison, fluctuating Pb concentrations provided the greatest range of concentrations but also the widest seasonal range (Figures 3.5.19 to 3.5.23). Site 7 in the middle riverine zone provides a typical seasonal variation from the river. An initial Pb concentration of 80 ppm Pb was recorded in August 2002 that reduced over winter to 57 ppm Pb in February 2003. Pb concentrations subsequently increased through spring and summer months to 130 ppm Pb in September 2003. Pb concentrations then decreased again during winter months to a level of 86 ppm Pb in February 2004. Concentrations then increased by 138 ppm Pb over five months to 224 ppm Pb in July 2004, which was followed by the final decrease of 161 ppm over eight months to 63 ppm Pb in January 2005.

While Pb concentrations offered the greatest seasonal fluctuations, similar seasonal distributions were observed for all metals. Figures 4.8 to 4.13 illustrate seasonal variation at two sites for each metal: Site 5 located in the middle riverine zone and Site 15 located in the middle estuarine zone. It can be observed from these temporal distributions that while seasonal variation was observed in both the river and estuary, the ideal summer / winter seasonal variation of a progressive increase and decrease in metal concentrations over a twelve month period rarely occurred. It can be seen that Cu and Ni had a more symmetrical seasonal variation with a gradual summer increase and winter decrease of metal concentrations in estuarine surface sediments. Cr concentrations in the riverine section provided the smoothest seasonal variation despite a narrow range of seasonal concentrations. Metal concentrations did not conform to a perfect seasonal variation but all metals did display basic seasonal variation with an increase in summer months and a decrease in winter months in spite of an overall metal concentration decrease towards the end of the thirty month sampling regime.

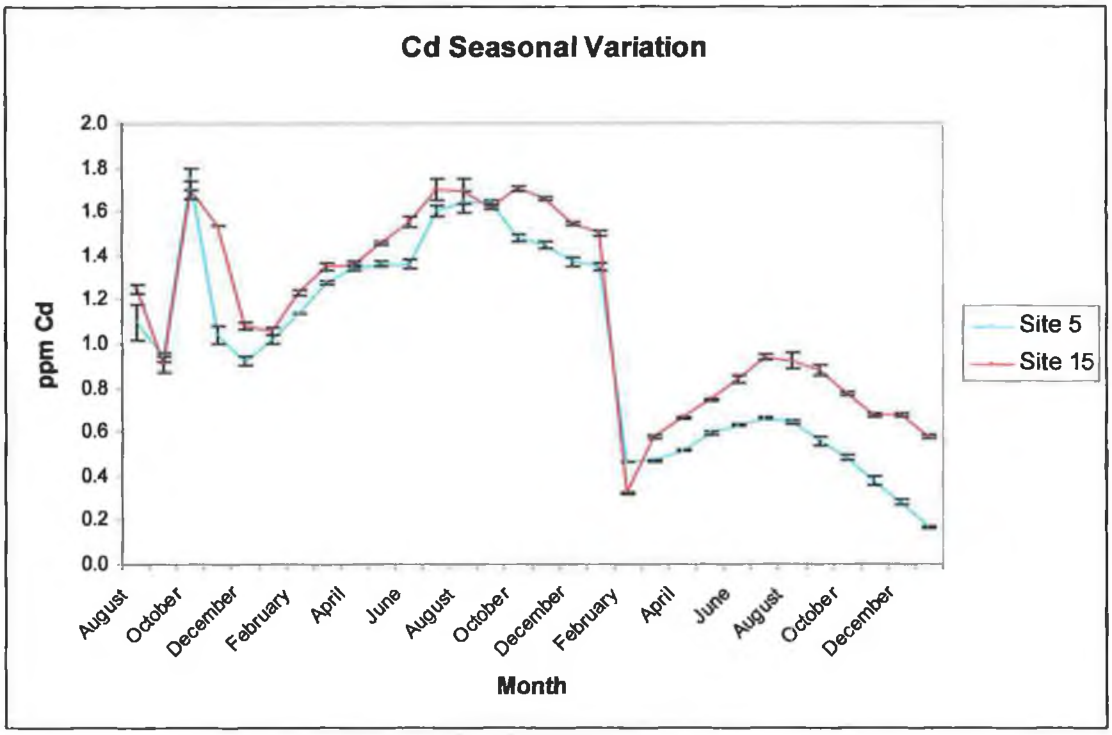


Figure 4.8 Cd seasonal variation at Sites 5 and 15, August 2002 to January 2005, error bars indicate standard deviation (n=3).

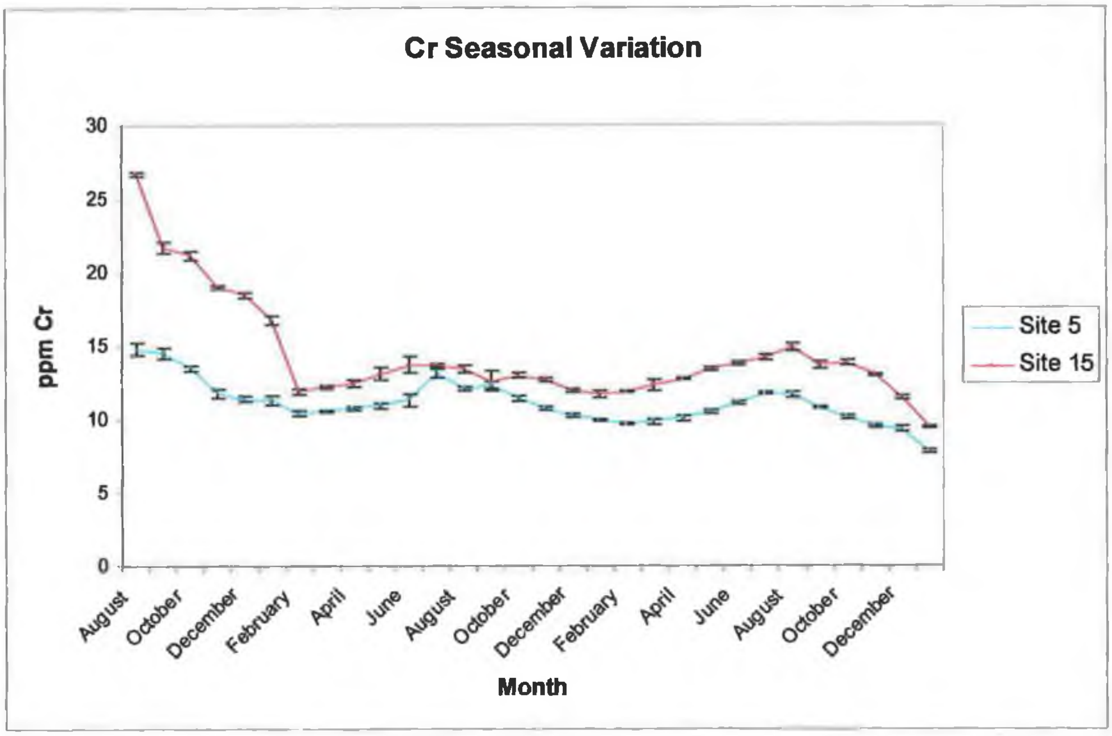


Figure 4.9 Cr seasonal variation at Sites 5 and 15, August 2002 to January 2005, error bars indicate standard deviation (n=3).

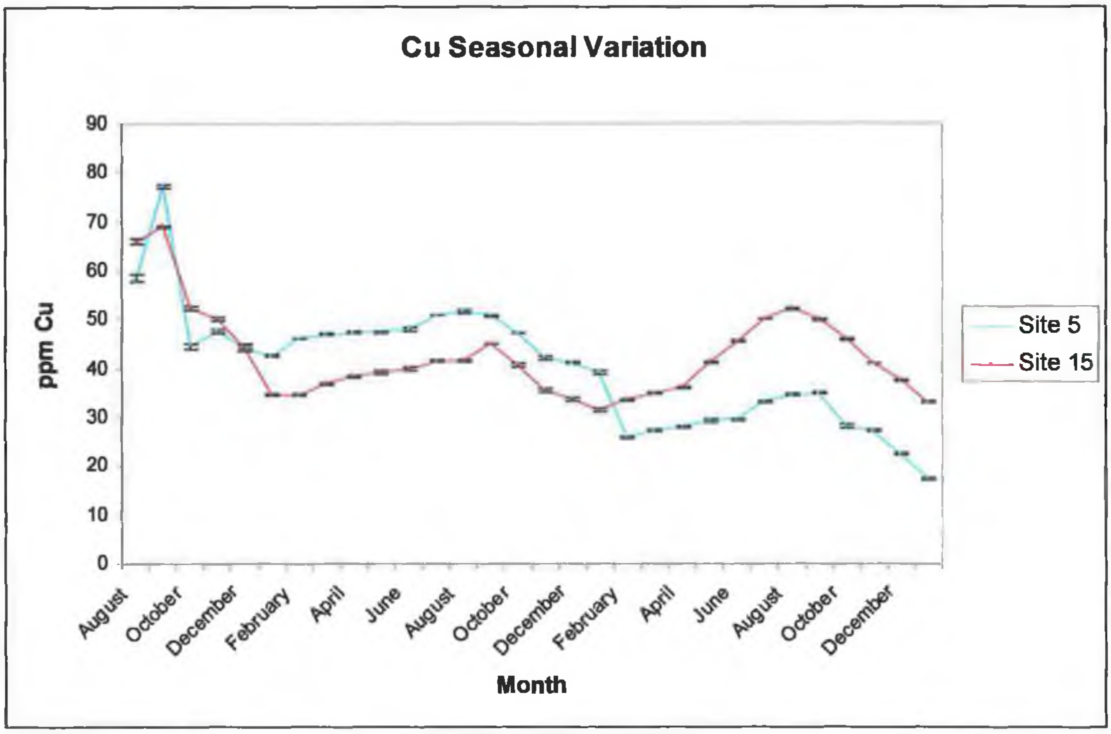


Figure 4.10 Cu seasonal variation at Sites 5 and 15, August 2002 to January 2005, error bars indicate standard deviation (n=3).

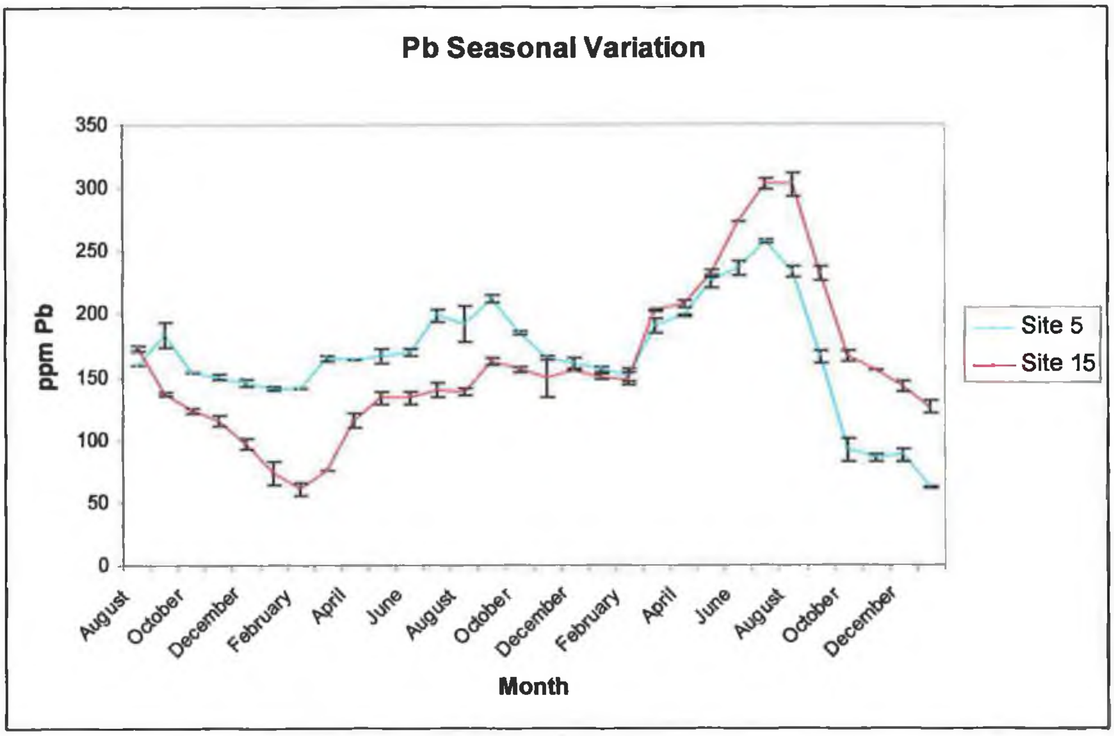


Figure 4.11 Pb seasonal variation at Sites 5 and 15, August 2002 to January 2005, error bars indicate standard deviation (n=3).

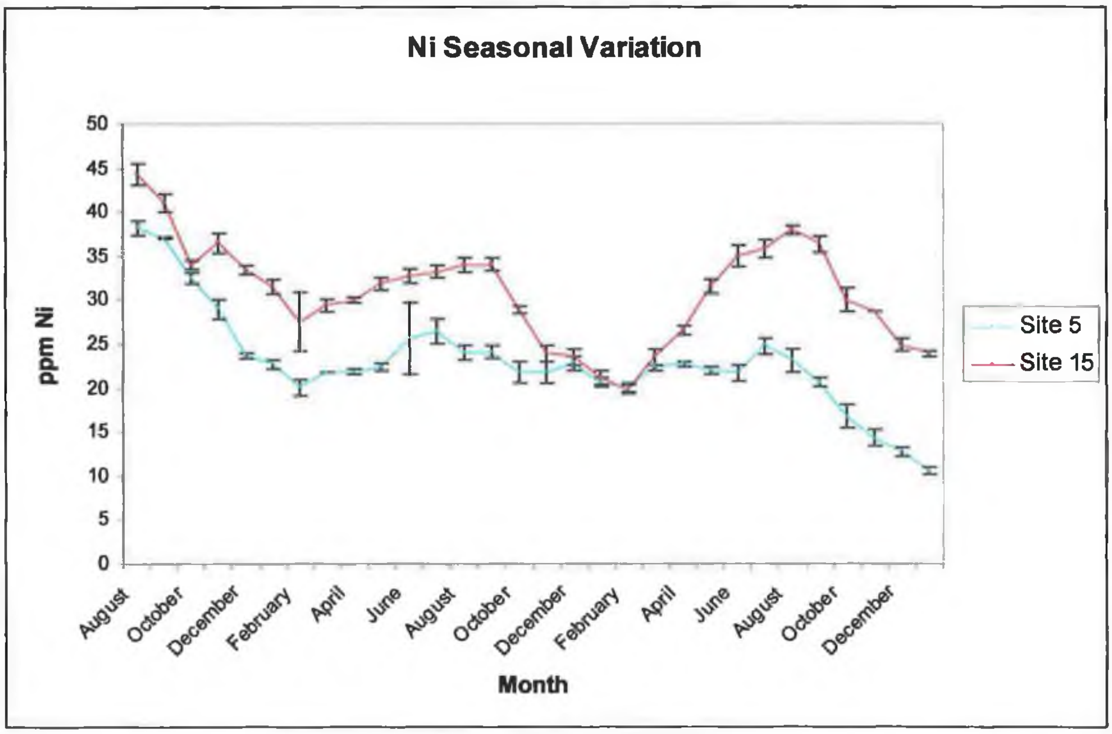


Figure 4.12 Ni seasonal variation at Sites 5 and 15, August 2002 to January 2005, error bars indicate standard deviation (n=3).

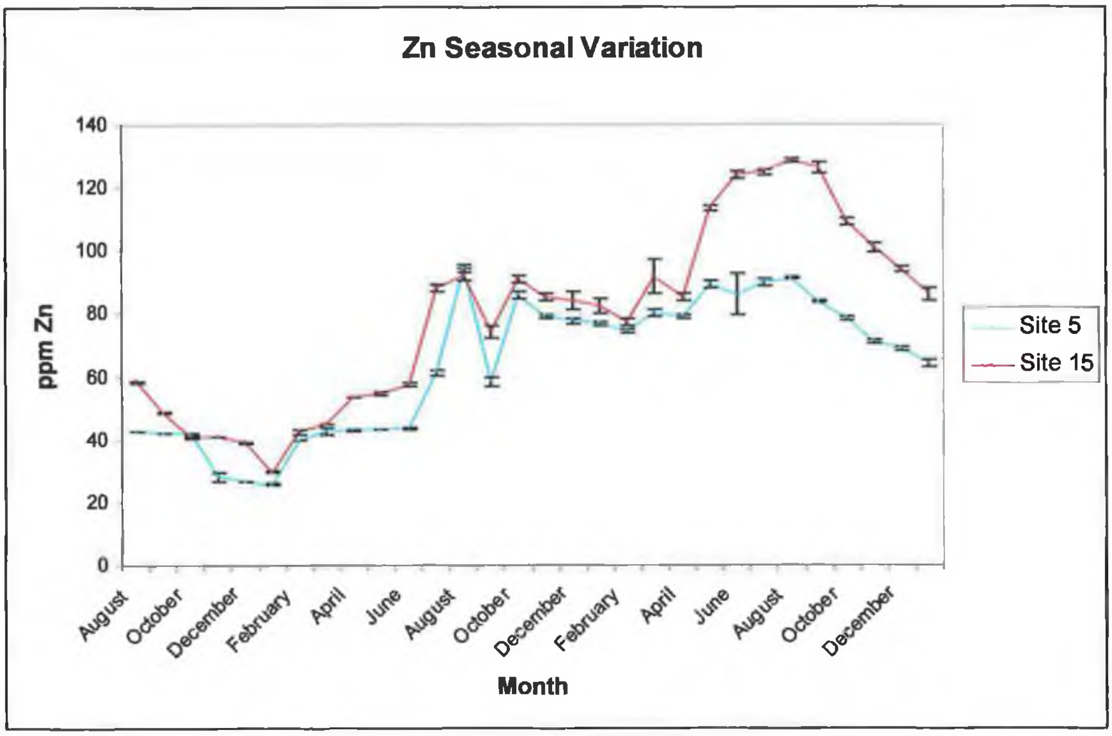


Figure 4.13 Zn seasonal variation at Sites 5 and 15, August 2002 to January 2005, error bars indicate standard deviation (n=3).

4.4.2.3 Pollution Incidents

During the initial twelve-month period a pollution incident was observed in the riverine section of the Tolka in April 2003. The resulting effects on spatial and seasonal trends of the Tolka were evident over the next four months directly downstream of the point source. As discussed in the introduction the Tolka is prone to flooding, and in the past five years flooding on the Tolka has caused serious damage to property in the rivers vicinity. Construction work on the retaining walls of the Tolka river in Drumcondra and Glasnevin (between Sites 8 and 11) was deemed an effective method for flood retention (Dublin City Council, 2005; EPA, 2005). New sediment banks were created in the river channel to support heavy construction vehicles. This sediment was contaminated and the effects of the input of this sediment into the river can be observed in Figures 4.14 to 4.19. A noticeable increase in all metal concentrations at Site 10 in April 2003 was followed by further contamination of downstream sites in subsequent months. This illustrates how direct anthropogenic input can alter both spatial and seasonal metal distributions in surficial sediment.

This demonstrates that there is a delicate natural balance for spatial and temporal variation of metal concentrations in surface sediment of aquatic systems. This balance is determined by in situ environmental factors but is altered by anthropogenic influence. However it can also be seen that once the anthropogenic input has ceased the aquatic system does return to its natural balance after a period of time. The concentration of contaminants in the initial anthropogenic impact determines how long the system will take to reach an equilibrium.

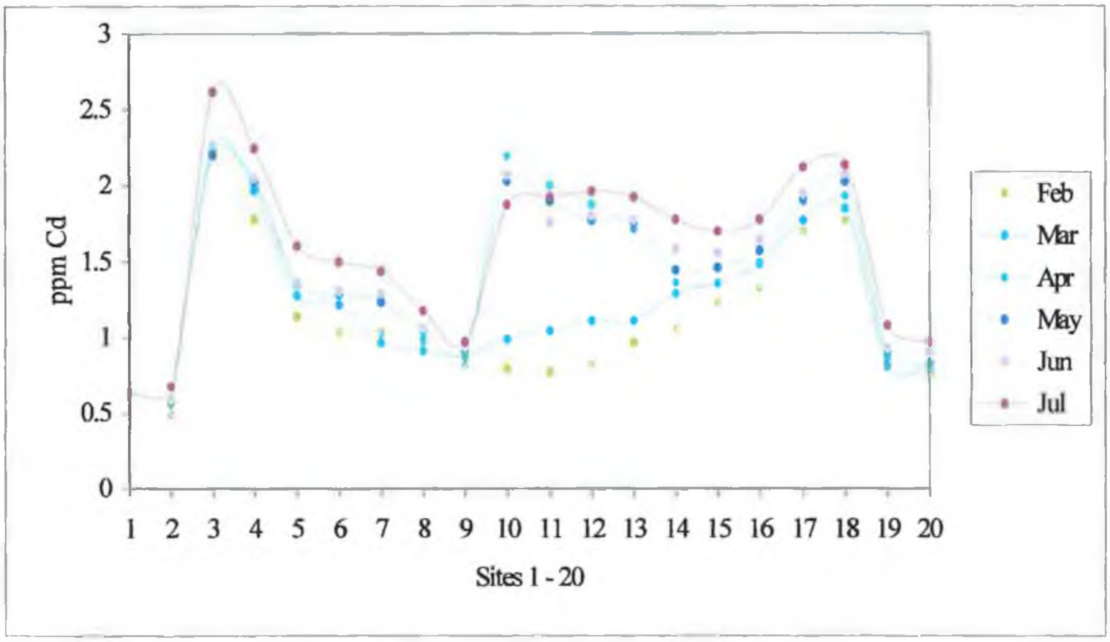


Figure 4.14 Cd distribution, Sites 1 – 20, February to July 2003.

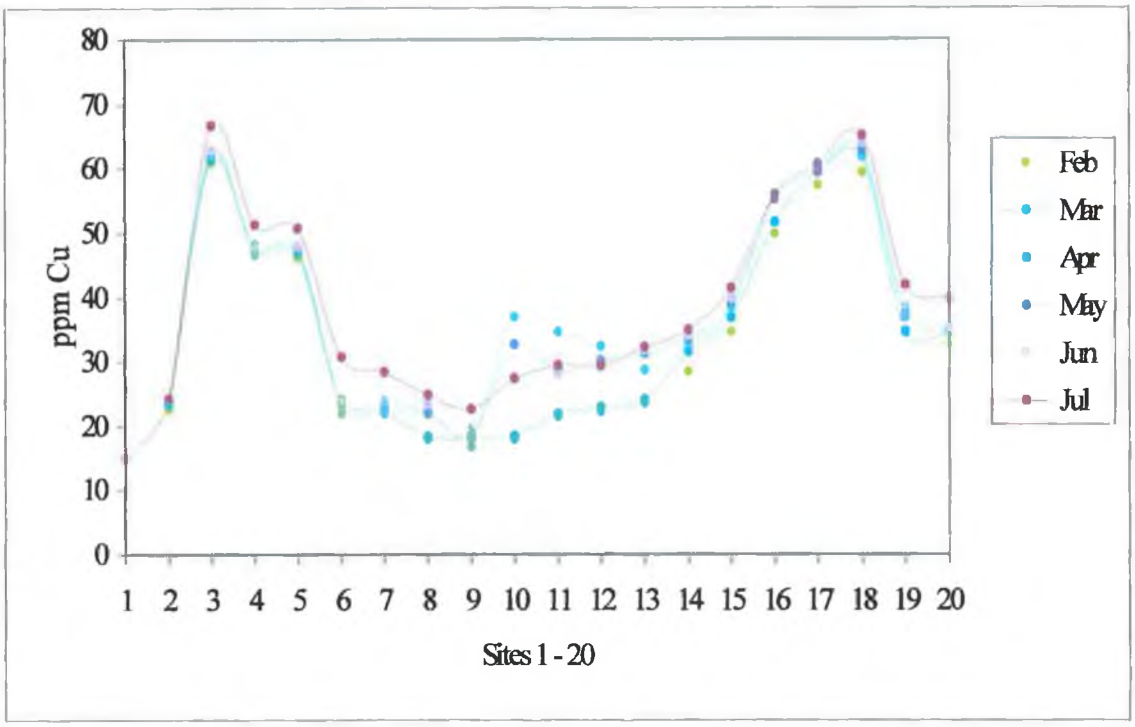


Figure 4.15 Cr distribution, Sites 1 – 20, February to July 2003.

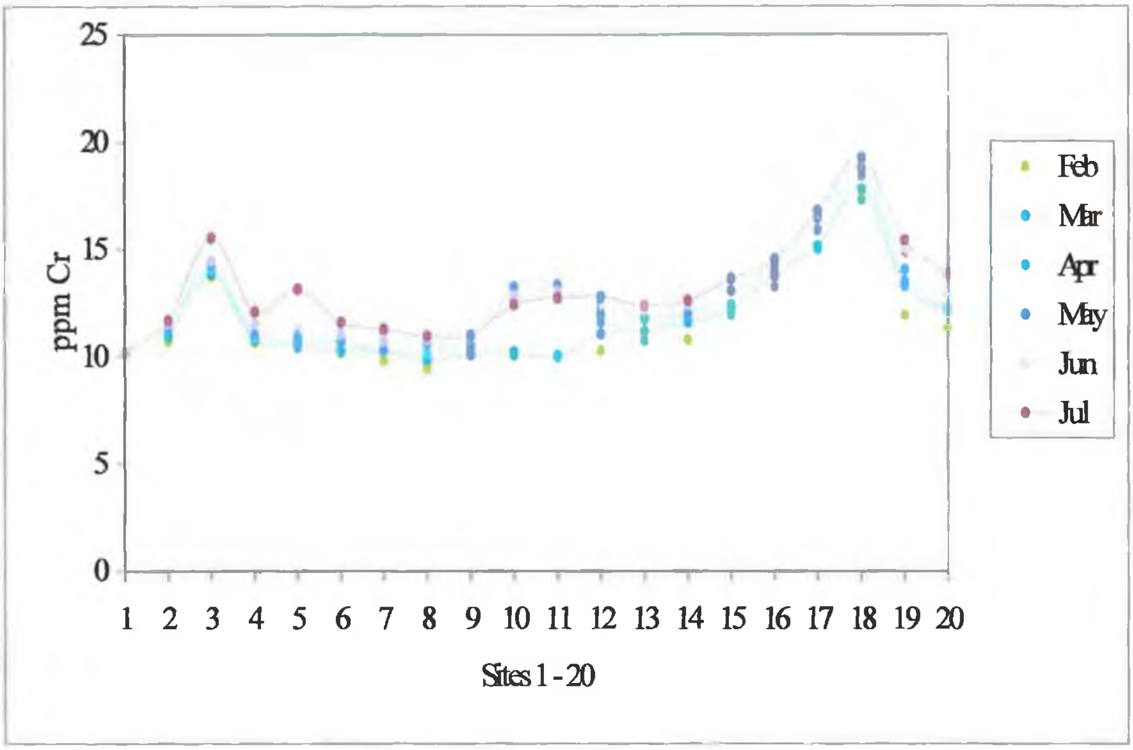


Figure 4.16 Cu distribution, Sites 1 – 20, February to July 2003.

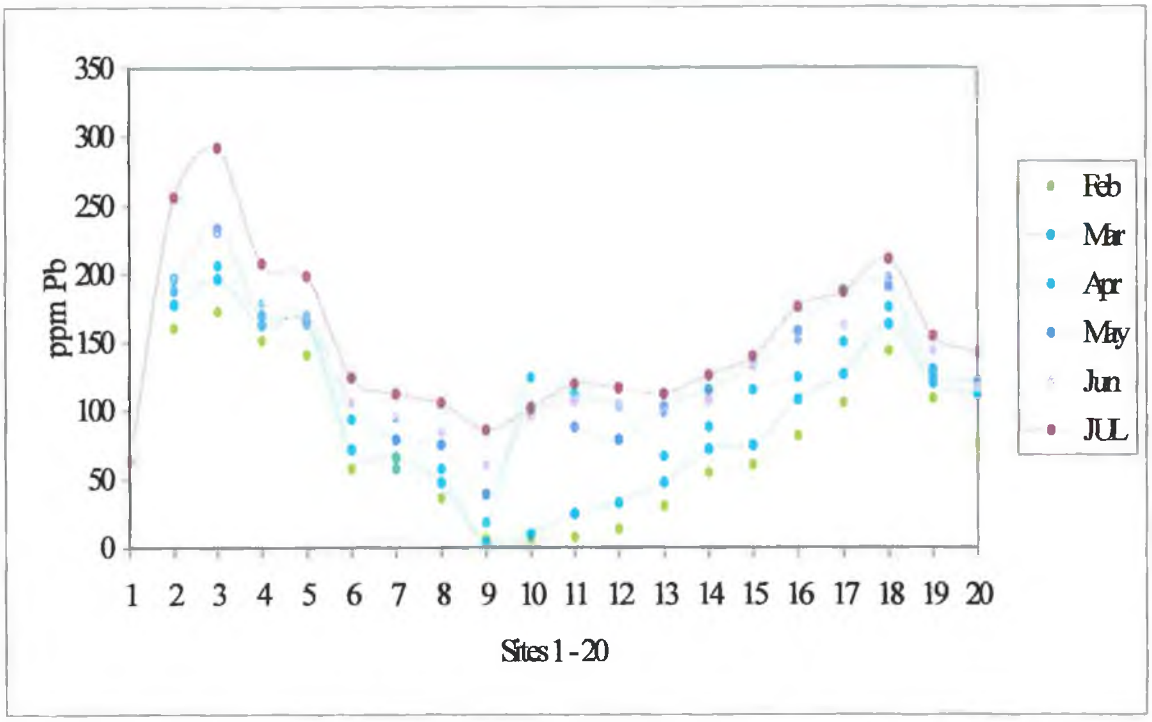


Figure 4.17 Pb distribution, Sites 1 – 20, February to July 2003.

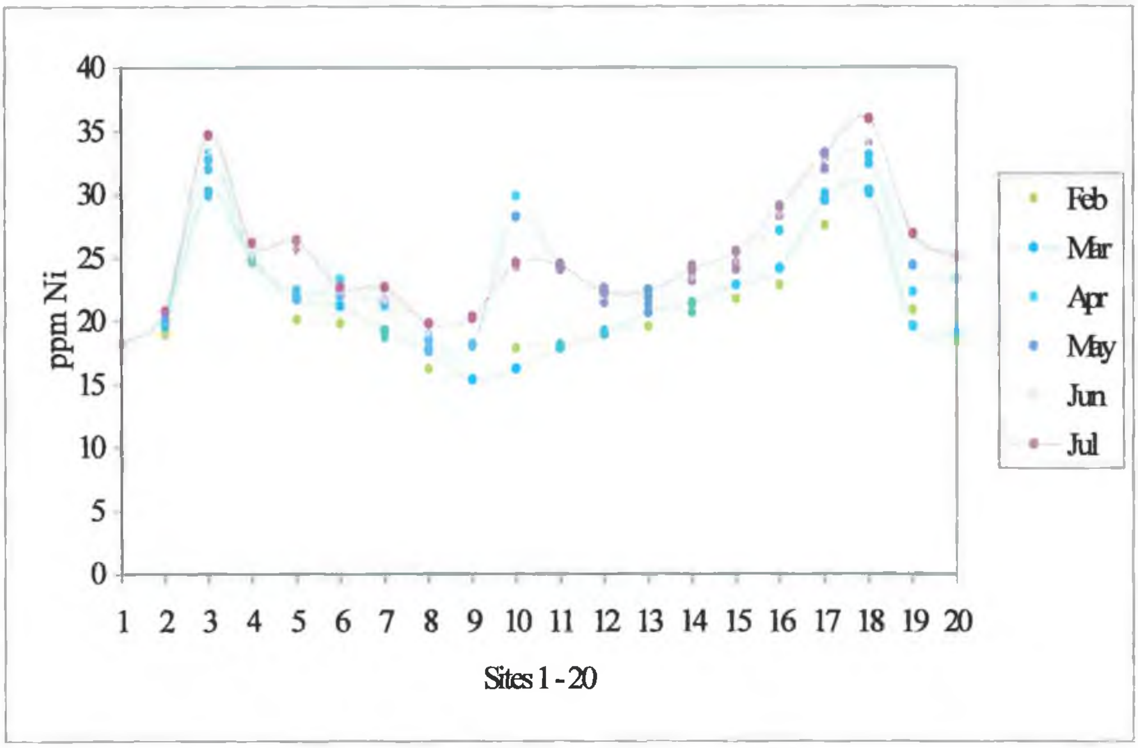


Figure 4.18 Ni distribution, Sites 1 – 20, February to July 2003.

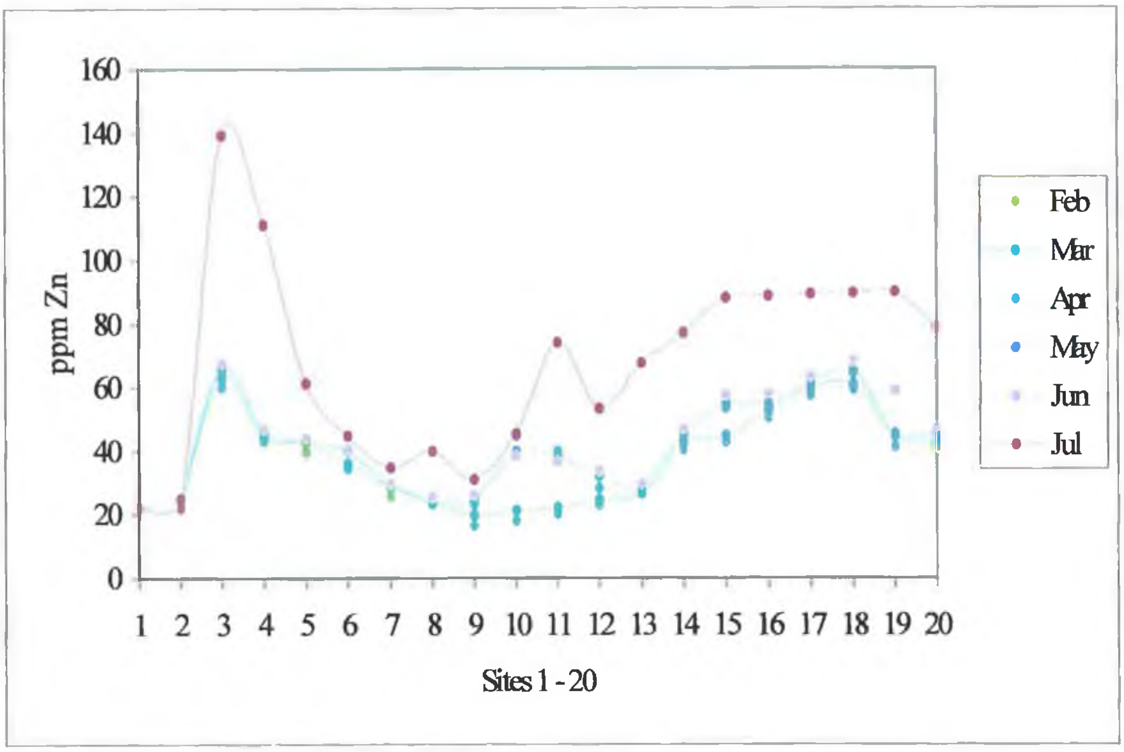


Figure 4.19 Zn distribution, Sites 1 – 20, February to July 2003.

4.4.3 Surface Sediment Seasonal TBT Distribution

TBT concentrations within surface sediment displayed similar seasonal distributions to metals and to in situ environmental factors. However, the seasonal trend is primarily induced by anthropogenic inputs while environmental parameters were factors in retention within the system once the variable anthropogenic input ceased. Section 3.8 and Figures 3.8.1 to 3.8.3 describe and illustrate TBT seasonal variation in the riverine and estuarine systems. The riverine system displayed minimal seasonal variation in the sites where TBT was detected. These sites were directly downstream of Dunsink Tributary which was a constant source of TBT contamination to the upper riverine sampling sites. Surface sediment TBT concentrations ranged from 2.1 to 8.7 ppb in the tributary.

It is likely that local boating activity and mooring facilities closeby contribute quantities of TBT from antifouling paints to this site and subsequently to the mid-estuary. It can clearly be seen that this source impacted on spatial and temporal TBT distribution in the estuary. The increased levels of TBT at Sites 18, 19 and 20 in May 2004 and the following months are consistent with increased boating activity that lasts over the summer months till September. Seasonal distribution of TBT in the estuary however is primarily anthropogenically induced rather than influenced by in situ environmental factors. TBT was introduced to the system in summer months, and input ceased in autumn, TBT then reduced in concentration gradually over winter months. TBT concentrations were likely maintained by secondary input from Dublin Port and from the river. TBT was retained in the system by surface sediment OM concentrations, and as OM was resuspended and removed from surface sediment in winter months there was an equivalent associated OM bound TBT removal. TBT subsequently increased in late spring upon resumption of local boating activity. It is likely that if the source of TBT contamination was removed from the system, surface sediment TBT concentrations would diminish and become non detectable within a short period.

4.5 Modelling Riverine Surface Sediment Metal Concentrations

Section 4.3 highlighted the variability of sediment contaminant spatial distribution, and significantly how the loading of the river water column altered over time. Section 4.4 illustrated the temporal variability of contaminants in surface sediments that are utilised to provide a synoptic overview of the pollution status of aquatic systems. The elucidation of temporally variable loading and its effects on surface sediment contaminant concentrations indicated the inherent complexities of a river system in an urban environment. It has been recognised that there is a growing need to address issues of this complexity in the modelling of aquatic systems. Up to the point of entering the urban zone, the Tolka displayed moderate metal contamination in surface sediment. However, the effects of the urban environment on the river were indicated by the sourcing of water column contamination: between 85 – 93 % of contaminant loading entering the estuary from the river was sourced from the urban catchment between Sites 3 and 12. While this is quite high, other urban rivers displayed similar loading patterns including the Hudson in New York, USA (Feng et al., 2002) and the fluvial network in Auckland, New Zealand (Bibby & Webster-Brown, 2005). Continuous contamination of the river and subsequently the estuary from the urban environment directed research to undertake an assessment of riverine systems to predict eventual loading of surface sediment over time. Consequently, it was decided to supplement the synoptic river/estuarine assessment protocol for observations on seasonal contaminant variability with an effective model predicting future seasonally variable surface sediment contaminant concentrations.

4.5.1 Introduction to River Modelling

Despite the ability of computers to solve numerical approximations to various aquatic parameters, simple models are still unable to estimate river loads of various contaminants in real channels to a consistently high level of accuracy. Recent studies (Uncles et al., 2003; Lindenschmidt, 2006) have highlighted the need to address interactions between elements in the aquatic system to provide a more complete understanding of fluvial transportation and loading process.

Integrative management of river basins has become an important research focus in Europe since the implementation of the European Unions Water Framework Directive (ERBD, 2005). A key component of such management systems is the depiction of the river sediment quality, which is directly or indirectly affected by activities within the basin. The primary question in choosing or developing a river sediment quality model is how complex the model structure should be to suit the needs in evaluating the management measures to be implemented. Increased complexity means that more processes will be represented in the system potentially reducing the model error (deviations between measurement samples and simulation results). The downside is that increasing the model complexity increases the number of degrees of freedom within the model (more parameters and variables) which can be expressed as the total increase in model sensitivity (the change in output results due to a percentage change in input data such as parameter settings and initial and boundary conditions).

Model sensitivity increases with model complexity due to the larger number of degrees of freedom and the structure of the interactions between parameters and state variables. Modelling error decreases with increasing model complexity as the more complex models are able to better simulate reality with more processes included and fewer simplifying assumptions (Snowling & Kramer, 2001). Inspite of the trend increasing model complexity to increase sensitivity, modelling should be designed to be as straight forward as possible so that one does not have to rely on complicated computer model programmes and instead can do one in a relatively fast and methodical fashion without specific training.

4.5.1.1 Mass Balance Modelling

Mass balance equations account for all material entering and leaving model segments through direct and diffuse loading, advective and dispersive transport, and any physical or chemical transformations, hence they have many benefits for river modelling (Carroll et al., 2000). A variety of mass balances has been developed to address water and sediment quality issues in lakes, estuaries and slow flowing water bodies (Chapra & Reckhow, 1983). These range from a single water compartment, such as EQuilibrium Criterion (EQC) Model (Mackay et al., 1996) and SimpleBox (van der Kooij, 1991), to multi-segment models simulating spatial heterogeneity. Multiple-segment models are preferred for faster flowing water bodies, such as rivers, since they better characterise the faster advective processes that determine spatial concentration patterns. For river basins, spatial distributions can be determined from concentrations based on parameters, such as emission sources, flow characteristics and sediment types.

For relatively complex systems, higher resolution models provide more accurate simulations of contaminant fate, particularly if their spatial resolutions can provide information from locally elevated pollution centres. Models such as GREAT-ER (Geography-Referenced Regional Exposure Assessment Tool for European Rivers – Feijtel et al., 1997) and BASINS (Better Assessment Science Integrating Point and Non-point Sources – Whittemore, 1998), have successfully simulated point-source pollutant behaviour on river water and sediment quality. These more complex models incorporate detailed hydrological data (e.g. flow gauging records for a number of years at several stations), and the location and size of wastewater effluents (at treatment facilities or direct discharges). They may use Geographical Information Systems to present and display key inputs and outputs, such as predicted concentrations. Although the information required to run these models is usually readily available in many highly developed countries, this is not the case everywhere. Incompatibilities between the resolution of hydrological or GIS data required and that which is available (in terms of quality and/or quality) may be a result of economic factors, or in the case of some countries like Canada, the size and complexity of the river systems. As a result more sophisticated mass balance models may not always be easily applied, and it may be more practical to use models with an intermediate level of spatial and temporal resolution and complexity.

4.5.2 Model Development

The development of a simple mass balance approach to determine temporal distribution of contaminants in river sediment as a supplement to temporal research was a supplementary section to the primary focus on seasonal contaminant distributions of this research project. The environmental model would allow further research on the mechanisms of contaminant temporal variability. Ideally the model developed would be simple to use once research into the specific river system in question is completed. The preliminary formulation of this model was based on 24 months of monitoring the metal concentrations in the Tolka River, their distributions over time and space in the river, and tracking of incidents of metal pollution from point sources and consequent effects on both seasonal and spatial patterns. From experience gained in the initial 24 months it was decided to increase the level of monitoring for the final six months to include parameters for the model. Thus a comparative analysis of modelled data versus six months of data would determine the viability of any mass balance model developed.

4.5.2.1 Model Parameters

The highest level of model complexity which can be applied in any evaluation will be limited by the availability of data and time and expertise constraints imposed by the user. It will also be limited on the assumptions made regarding model parameters. Many parameters can be utilised in mass balance equations. Inputs and outputs of many environmental factors influence river systems. However, including all factors would be a statistical impossibility and make the model a futile exercise (Diamond, 1995; Abrahamsson & Hakanson, 1998). When applying a particular method for mass balance computation, primary consideration should be given to the characteristics of the solute, the size of the watershed, the magnitude of the input and output fluxes, and perhaps most importantly, the hydrologic residence time and related importance of hydrologic pathways contributing to river water (Cerny et al., 1994).

The objective of this model is to predict metal concentrations in surface sediment of a river segment at any time in the future based on current inputs and outputs measured physically. However, river systems are complex with highly variable environmental parameters that are in a constant state of flux. Many of the model parameters are assumed to have constant values for specific periods of time for model prediction (Pontier et al., 2004; Bowes et al., 2005). Probably the most important individual characteristics affecting interpretation of the mass balance is the time scale during which the solute and suspended inputs are transported though one segment to be exported to another (Tipping et al., 1998). Therefore timescale plays a primary role in determining a mass balance model effectiveness in accurate prediction (Zeng et al., 2001; Lindenshmidt, 2005). The shorter the time scale the less error involved but also less practical. Greater time scales are often desired but fluxing environmental parameters introduce error into any prediction. Hence it may be more suitable to base models on moderate time scales (Abrahamsson & Hakanson, 1998). Utilising the initial time period prediction in the process of predicting the next time period concentration, would introduce error with every increasing prediction. However, this would be more accurate than large time scales. For example using data gathered for a river in January to predict metal concentrations the following January based on annual averages would not be as accurate as utilising Januarys data to predict March, some minimal in situ river analysis coupled with March's prediction to predict June, and so on through the twelve months.

The following variable river physical parameters were utilised for this model. Each parameter was averaged and assumed to remain constant for the specific time frame of prediction:

- Average River Depth (m)
- Average River Speed (m/s)
- Surface Sediment Layer Depth (cm)
- Suspended Sediment Deposition (g/Day)

The following parameters for metal transportation and retention in river systems were utilised for this model. Each parameter was averaged and assumed to remain constant for the specific time frame of prediction:

- Dissolved Metal Load (mg/L)
- Suspended Sediment Load (mg/L)
- Suspended Sediment Metal Concentrations (mg/Kg)
- Surface Sediment Metal Concentrations (mg/Kg)
- Surface Sediment Porewater Metal Concentrations (mg/L)

The following assumptions were also made about the physical environment based upon various literature sources (Zeng et al., 2001; Lindenshmidt, 2005; Bowes et al., 2005; Warren et al., 2005; Tipping et al., 1998; Pontier et al., 2004; Peters et al., 2005; Abrahamsson & Hakanson, 1998):

- Sediment Burial from surface sediment to subsurface is negligible due to bedrock layer close to river bed.
- Groundwater impact on the river system is negligible. While the Tolka does have a source of groundwater contamination from Dunsink Landfill in its upper sections, it was not possible to obtain groundwater flow and recharge data or samples for analysis. Groundwater contamination from the landfill enters the Tolka primarily through quaternary sediments layered above bedrock and was not from the bedrock aquifer which is uncontaminated (GSI, 2005). As the Tolka flows through urban areas, incidence of groundwater entering the river is significantly diminished by entraining walls constructed

on bedrock. Subsequently, incorporation of groundwater parameters into the Tolka model was not feasible for the entire river and would have been restricted to the initial upper sections if groundwater data had been available. However, other groundwater systems significantly impact on riverine systems and may have data that could be utilised in a temporal model based on the Tolka model.

- River flow was constant over specific time periods.
- Rates of deposition were constant for the whole river and over specific time periods.
- Sediment density, sediment porosity, the depth of the surface sediment layer and the amount of suspended sediment contained within each model segment remained constant over time.
- The water compartment in each model is assumed to be completely mixed.
- Surface sediments are also assumed to be completely mixed to a depth of 10 cm to account for bioturbation by benthic riverine invertebrates (Diamond, 1995). Bioturbation can occur to greater depths in rivers with broad flat channels and deep sedimentary layers above bedrock (Chapra, 1997; Elbaz-Poulichet et al., 2001; Davoren et al., 2005). However, the Tolka river is narrow with shallow surface sediment layers and a depth of 10 cm is considered standard for similar river physicalities (Chapra, 1997).
- Evaporation and precipitation would only be significant in large open water areas with relatively still waters. The Tolka River does not have physical parameters similar to this. The gain or loss of water through evaporation and precipitation represented a small fraction of the water flowing through each segment and the inclusion of net precipitation would not substantially alter the

conclusions of this model (Interlandi & Crockett, 2003). Therefore these parameters were not included.

4.5.2.2 Existing Model

Utilising an existing model as a guideline provided this model with certain advantages. As this model is designed to reflect short to medium term changes in metal concentration in surface sediment of a river channel i.e. seasonal variations, using a long term prediction model and modifying it to suit short term was considered a viable way to create a mass balance model based on a tested methodology.

Various models were researched to assess which river system most closely resembled the Tolka River System for physical parameters (river speed, flow volume, channel depth and width, catchment size and urban environment). The Moira River Model developed for the Government of Ontario, Canada provided an adequate methodology to base the Tolka River Mass Balance Model on. The Moira River Model (MRM) was developed to simulate long-term water and sediment quality in the Moira River system (OME, 2001). The model was based on average, long-term monthly water flows (WSC, 2001; Diamond, 1995). The model incorporated sediment-water interaction and was calibrated to reflect general, long-term, water quality trends observed over the last ten years. The model was not designed to adequately reflect the effects of short-term, sporadic events, such as flooding or dry spells. However this model did include all of the most important processes that control average metal concentrations in a river system (OME, 2001).

The MRM was spread over a significant river catchment with numerous tributaries, many similar in physical parameters to the Tolka River. The model was segmentalised and each model segment incorporated advective transport, chemical partitioning, sediment deposition and resuspension, sediment bioturbation and burial as the primary factors determining metal concentrations in each segment (Cornette & Chant, 1986). Youngs Creek is a tributary of the Moira River and its physical parameters closely matched the Tolka for volume and flow rate, river depth and channel width (OME, 2001; Diamond, 1990; Diamond, 1995; WSC, 2000). It was used as a reference for comparison to variable resuspension, diffusion and deposition rates for the Tolka River.

4.5.2.3 Tolka River Mass Balance

For any linearly connected river mass balance models divide the river into segments. The numbering of segments is arbitrary, although for this model it has adopted the convention of numbering segments such that flow is always in the direction of increasing segment number. The Tolka was divided into five segments each with slightly different physical dimensions. Some segments had more sediment sample points than others; however this was due to standardising each segment to have relatively the same length. Each segment had one bridge sample point for water column sampling. The width of each segment was averaged based on five width measurements in each segment.

Segment	Length (km)	Average Width (m)	Sediment Sample Points	Bridge Sample Points
1	3.0	5.0	2, 3 & 4	B1
2	2.5	4.0	5& 6	B2
3	2.5	4.0	7 & 8	B3
4	2.0	3.5	9 & 10	B4
5	3.0	6.0	11	B5

Table 4.19 Model River Segment Physical Dimensions.

Each model segment was subdivided into three compartments: water, surface sediment (the uppermost sediment layer) and deep sediment (below the surface sediment, mostly bedrock). Each segment was treated as a static waterbody within a fluvial system, essentially a static box with an inflow and an outflow but with no internal laminar flow. A box system version of the in situ river transportation process is illustrated in Figure 4.20.

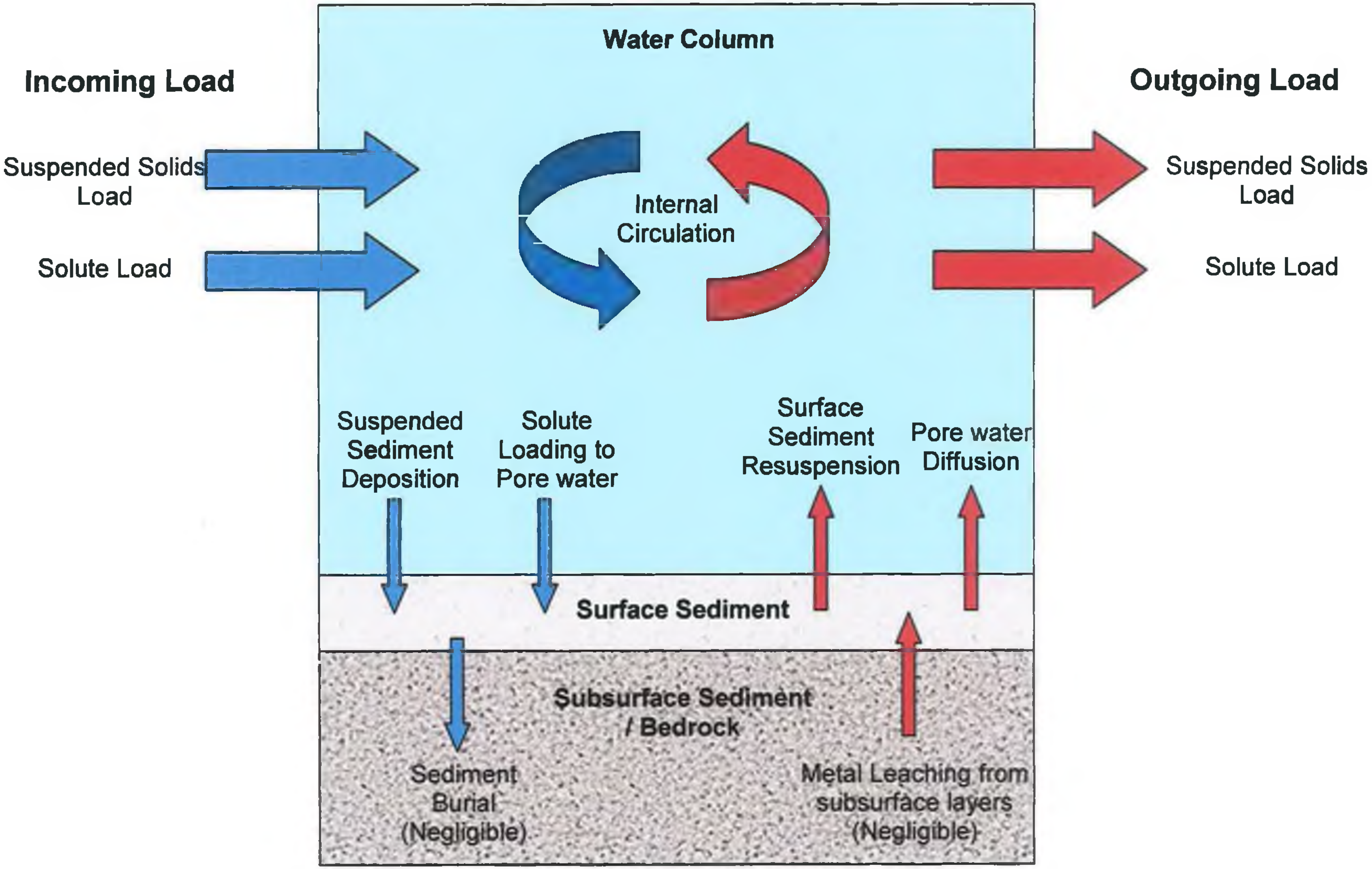


Figure 4.20 Riverine Metal Transportation Mechanisms.

The Tolka Mass Balance Model has as its basis the following concept;

Equation 1

$$V_x = V_a - V_r - V_d - V_b\ *$$

Where V_X = Metal accumulation or loss to/from surface sediment, V_a = Metal Deposited, V_r = Metal Resuspended, V_d = Metal Diffused and V_b = Metal Buried.

*Metal burial is considered insignificant in the mass balance as the subsurface layer of the Tolka is predominantly bedrock.

The model has four separate components as inputs and outputs within the river system Metal Deposited constitutes the metal concentrations deposited to surface sediment via SPM and associated metals deposition: Metal Resuspended is the concentration of metals bound to SPM that are resuspended through water column turbulence. Metal Diffused constitutes the metal concentrations lost from surface sediment porewater to the overlying water column via porewater diffusion. Metal Buried constitutes the metal lost from surface layers to subsurface layers via sediment burial, however for the Tolka system this has been discounted as bedrock is sufficiently near surface sediments to eliminate sediment burial.

Predicting short to medium term accumulation or loss of metal contamination in river systems is not as accurate as long term prediction. This model facilitates predicting metal concentrations based on current in situ river analysis for short term analysis but it can also be applied for adequate long term continuous monitoring without extensive data accumulation for the river in question. This simplifies the model for general use by users who do not have an extensive knowledge of river systems and without the need for extensive computer programmes.

Deposition rates were assessed for one section of the river (see Section 2.3) and assumed to be spatially constant throughout the river. Resuspension rates can be determined based on estimated from literature however Resuspension Velocity (V_r) was determined from river and lake modelling equations devised by Chapra (Chapra, 1997; Mulder & Alexander, 2001) which are based on settling velocities of particulate matter in the water column. A sediment density greater >2 g cm^3 and <2.25 g cm^3 indicates that SPM deposition to the surface sediment is primarily composed of large particulate OM with a diameter of > 64 µm (Burns & Rosa, 1980; Stow & Bowen, 1980; Mulder & Alexander, 2001). Assuming that SPM is composed primarily of OM (Characklis & Wiesner, 1997), particulate OM has a setting velocity (V_s) of 0.2 m/d (Burns & Rosa, 1980; Stow & Bowen, 1980; Chapra, 1997). Subsequently V_r can be determined from this parameter and from burial velocity V_b. However as V_b is negligible in the Tolka it can be removed from the following equation;

Equation 2

$$V_r = \{(V_s \times M) \div ((1 - \Phi) \times \rho)\} - V_b$$

Where **M** is the Suspended Load (SPM / L) of the water column, **Φ** = surface sediment porosity (Unitless; 0 = non porous, 1 = maximum porosity) and **ρ** = sediment density (g / cm^3).

Diffusion rates were determined using the following formula for Diffusion Velocity (Di Toro et al., 1991; Chapra 1997; Mulder & Alexander, 2001; OME, 2001; Diamond, 1995; Jahnke et al., 2005):

Equation 3

$$V_d = 69.35 \times \Phi \times MW_{ion}^{-2/3}$$

Where **69.35** = Sediment Porewater Diffusion Coefficient, **Φ** = Sediment Porosity (Unitless), $\mathbf{MW_{ion}}$ = Molecular Weight of the dominant metal ion.

4.5.2.3.1 Example Application of Tolka Mass Balance Model

Parameter	July	November
Depth m	1.5	2.5
Speed m/s	0.1	0.25
Water Surface Width m	8	12
Deposition g/m^2	601.6	28.8
Surface Sediment Area m^2	15000	15000
Inflow m^3/s	1.2	7.5
Surface Sediment Density kg/m^3	2200	2200
Porewater ml/kg	98	102

Table 4.20 Tolka Segment 1 Physical Parameters utilised in the mass balance equation.

Metal Concentrations	July	November
Surface Sediment mg Pb /kg	271.3	87.9
Porewater mg Pb/L	1.16	11.49
Suspended Sediment mg Pb/kg	26.09	39.77

Table 4.21 Pb concentrations observed in the Tolka River.

The model can predict both accumulation and loss of metal in river surface sediment. From the 30 month spatial and seasonal distributions observed in the Tolka, metal concentrations increase in summer months and decrease in winter months. Therefore to illustrate the effectiveness of the model at predicting accumulation and loss two examples will be outlined for Segment 1 of the river. The first showing Pb fluctuations over two 30 day periods between July and August 2004 and November and December 2004. The second showing Cu fluctuations over the same two time periods. Pb was used for the first model example as it was the most abundant metal in the river system. Cu was used to demonstrate fluctuations in a less abundant metal.

Example 1

Pb Resuspension (V_r)

July
For the Tolka the inflowing SPM in July was 168.4 mg /L and the outflowing was 173.6 mg / L, implying a loading of 5.2 mg /L for Segment 1. Particulate OM $V_s = 0.2$ m / day.

P (Density) = 2200 kg / m^3

Φ (Porosity) = 0.97

$V_r = \{(0.2 \times 5.2) \div ((1 - 0.97) \times (2.2 \times 10^6))\} - 0 = 0.00001576$ m / day
= 0.471 mm / month

November
For the Tolka the inflowing SPM in November was 284.8 mg /L and the outflowing was 302.6 mg / L, implying a loading of 17.8 mg /L for Segment 1.

P (Density) = 2200 kg / m^3

Φ (Porosity) = 0.97

$V_r = \{(0.2 \times 17.8) \div ((1 - 0.97) \times (2.2 \times 10^6))\} - 0 = 0.0000539$ m / day
= 1.62 mm / month

⇒ **July V_r** = 0.471 mm / month over 15000 m^2

= 7.06 m^3 of sediment resuspended per month

As sediment density = 2200 kg / m^3

⇒ 15, 532 kg of surface sediment resuspended

Average Pb concentration of surface sediment in July = 271.3 mg/kg

⇒ 4.2 × 10^6 mg Pb resuspended.

⇒ **November V_r** = 1.62 mm / month over 15000 m^2

= 24.3 m^3 of sediment resuspended per month

As sediment density = 2200 kg / m^3

⇒ 53,460 kg of surface sediment resuspended

Average Pb concentration of surface sediment in November = 87.9 mg/kg

⇒ 4.7 × 10^6 mg Pb resuspended.

Pb Diffusion (V_d)

Metal diffusion plays a secondary role in metal loss for a river segment. Metal from the porewater is lost without alteration of the surface sediment and can occur even during periods of low flow and stagnancy. Diffusion rates were determined using Equation 3 (Di Toro et al., 1981; Chapra 1997; MRM, 2001)

Pb $V_d = 69.35 \times 0.97 \times 207.2^{-2/3}$
$= 1.917$ m / yr
$= 0.16$ m / month

Assuming that porewater diffusion was constant over the surface sediment area (15000 m^2) ⇒ 2394.6 m^3 / month of porewater diffused to the water column from the surface sediment (2.39 x 10^6 L).

⇒ **July V_d** = Metal concentration of 1.16 mg Pb/ L Porewater

⇒ 2.77 × 10^6 mg Pb diffused

⇒ **November V_d** = Metal concentration of 11.49 mg Pb/ L Porewater

⇒ 27.51 × 10^6 mg Pb diffused

Pb Deposition (V_a)

Deposition of suspended sediment is the primary input of metal to the surface sediment. Assuming suspended sediment deposition was constant over the entire segment surface sediment area (15000 m^2) and constant over time then

⇒ **July V_a** = 601.6 g/m^2/day suspended sediment deposited
=18048 g/m^2/month
Over an area of 15000 m^2
<u>= 270720 kg suspended sediment deposited</u>
Metal Concentration of 26.09 mg Pb/kg of suspended sediment

<u>⇒ 7.06 × 10^6 mg Pb deposited</u>

⇒ **November V_a** = 28.8 g/m^2/day suspended sediment deposited
= 864 g/m^2/month
Over an area of 15000 m^2
<u>= 12960 kg suspended sediment deposited</u>
Metal Concentration of 39.77 mg Pb/kg of suspended sediment

<u>⇒ 5.15 × 10^5 mg Pb deposited</u>

From the initial Tolka Mass Balance Model (Accumulation / Loss = Deposition – (Resuspension + Diffusion)) the following applied for each month;

⇒ **July** = {7.06×10^6 mg Pb (Deposited Metal)} - {4.2×10^6 mg Pb (Resuspended Metal)} - {2.77×10^6 mg Pb (Diffused Metal)}

= 0.09×10^6 mg Pb in 9.9×10^5 kg of surface sediment

⇒ 0.3 mg Pb/kg increase in metal concentration of surface sediment after 30 days. (Pb decreased by 28 mg between July and August).

⇒ **November** = {5.15×10^5 mg Pb (Deposited Metal)} - {4.7×10^6 mg Pb (Resuspended Metal)} - {27.51×10^6 mg Pb (Diffused Metal)}

= -31.7×10^6 mg Pb in 9.9×10^5 kg of surface sediment

⇒ 32.0 mg Pb/kg decrease in metal concentration of surface sediment after 30 days. (Pb decreased by 3 mg between November and December).

Example 2

Metal Concentrations	July	November
Surface Sediment mg Cu/kg	36.6	28.1
Porewater mg Cu/L	0.06	1.07
Suspended Sediment mg Cu/kg	25.75	31.49

Table 4.22 Cu concentrations observed in the Tolka River.

Cu Resuspension (V_r)

Utilising previous V_r for Cu resuspension:

⇒ **July V_r** = 0.471 mm / month over 15000 m^2

= 7.06 m^3 of sediment resuspended per month

As sediment density = 2200 kg / m^3

= 15,532 kg of surface sediment resuspended

Average Cu concentration of surface sediment in July = 36.6 mg/kg

⇒ 5.68 × 10^5 mg Cu resuspended.

⇒ **November V_r** = 1.62 mm / month over 15000 m^2

= 12.0 m^3 of sediment resuspended per month

As sediment density = 2200 kg / m^3

= 53,460 kg of surface sediment resuspended

Average Cu concentration of surface sediment in November = 28.1 mg/kg

⇒ 1.5 × 10^6 mg Cu resuspended.

Cu Diffusion (V_d)

Utilising Equation 3:

$$\text{Cu } V_d = 69.35 \times 0.97 \times 63.54^{-2/3}$$
$$= 4.34 \text{ m / yr}$$
$$= 0.36 \text{ m / month}$$

Assuming that porewater diffusion was constant over the surface sediment area (15000 m^2) ⇒ 5425 m^3 / month of porewater diffused to the water column from the surface sediment (5.42×10^6 L).

⇒ **July V_d** = Metal concentration of 0.06 mg Cu/ L Porewater

⇒ 0.33×10^6 mg Cu diffused

⇒ **November V_d** = Metal concentration of 1.07 mg Cu/ L Porewater

⇒ 5.81×10^6 mg Cu diffused

Cu Deposition (V_a)

⇒ **July V_a** = 601.6 g/m^2/day suspended sediment deposited

=18048 g/m^2/month

Over an area of 15000 m^2

= 270720 kg suspended sediment deposited

Metal Concentration of 25.75 mg Cu/kg of suspended sediment

⇒ 6.97 × 10^6 mg Cu deposited

⇒ **November V_a** = 28.8 g/m^2/day suspended sediment deposited

= 864 g/m^2/month

Over an area of 15000 m^2

= 12960 kg suspended sediment deposited

Metal Concentration of 31.49 mg Cu/kg of suspended sediment

⇒ 4.08 × 10^5 mg Cu deposited

From the initial Tolka Mass Balance Model (Accumulation / Loss = In Situ Concentration + Deposition – (Resuspension + Diffusion)) the following applied for each month;

⇒ **July** = {6.97×10^6 mg Cu (Deposited Metal)} - {0.57×10^6 mg Cu (Resuspended Metal)} - {0.33×10^6 mg Cu (Diffused Metal)}
= 6.07×10^6 mg Cu in 9.9×10^5 kg of surface sediment

⇒ 6.1 mg Cu/kg increase in metal concentration of surface sediment after 30 days. (Cu decreased by 0.8 mg between July and August).

⇒ **November** = {4.08×10^5 mg Cu (Deposited Metal)} - {1.5×10^6 mg Cu (Resuspended Metal)} - {5.81×10^6 mg Cu (Diffused Metal)}
= -6.9×10^6 mg Cu in 9.9×10^5 kg of surface sediment

⇒ 7.0 mg Cu/kg decrease in metal concentration of surface sediment after 30 days. (Cu decreased by 6.5 mg between November and December).

From these two examples using Segment 1, it can clearly be observed that the mass balance model is only moderately effective in predicting substantial accumulation or loss of metal from surface sediment. The model is inherently dependent on observation of chemical parameters that change over time. While it may be impractical to make predictions for 30 days, the model may be useful for short term effects such as pollution incidents. The model can be adapted for longer periods i.e. 3 month periods to observe seasonal variation or 12 month periods to observe annual variation.

Over the river system as a whole, generally the model performed adequately for each metal, however it did predict loss of metal from surface sediment with greater accuracy than for metal accumulation, see Figures 4.21 to 4.32. It can be seen that in some instances the model predicted with greater accuracy in certain segments of the river and for certain metals. This may be due to extended stable periods for various physical parameters in those segments or the fact that these segments as single units readily integrate and disseminate metals into surface sediment over shorter periods of time. Segment 5 continuously displayed the best fit between model prediction and the actual concentration observed. This is likely due to its physical stability, with a broad flat uniform channel and its greater capacity to assimilate larger volumes of water before entering the estuary.

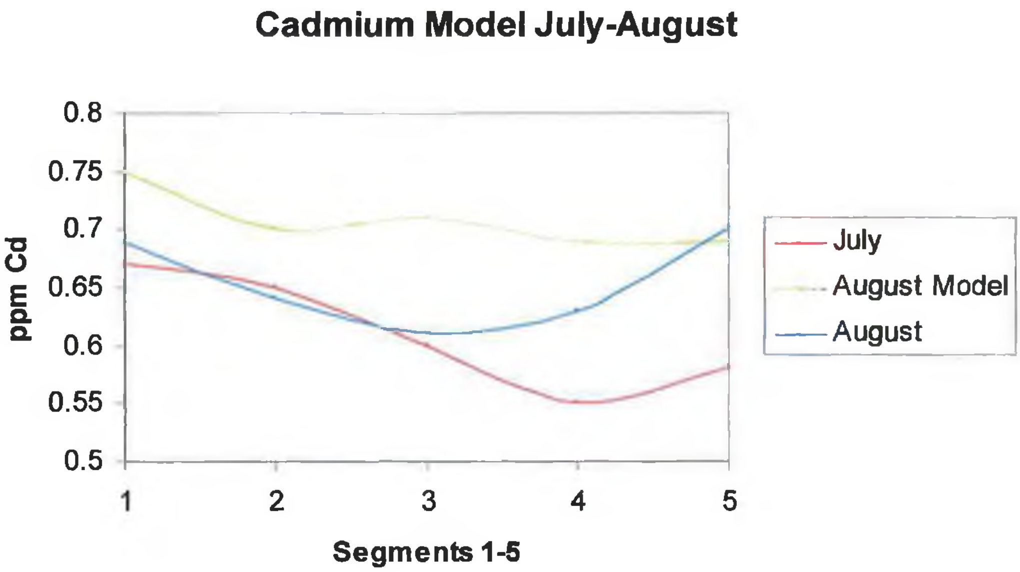


Figure 4.21 Cadmium Model V Recorded Concentration for August 2004.

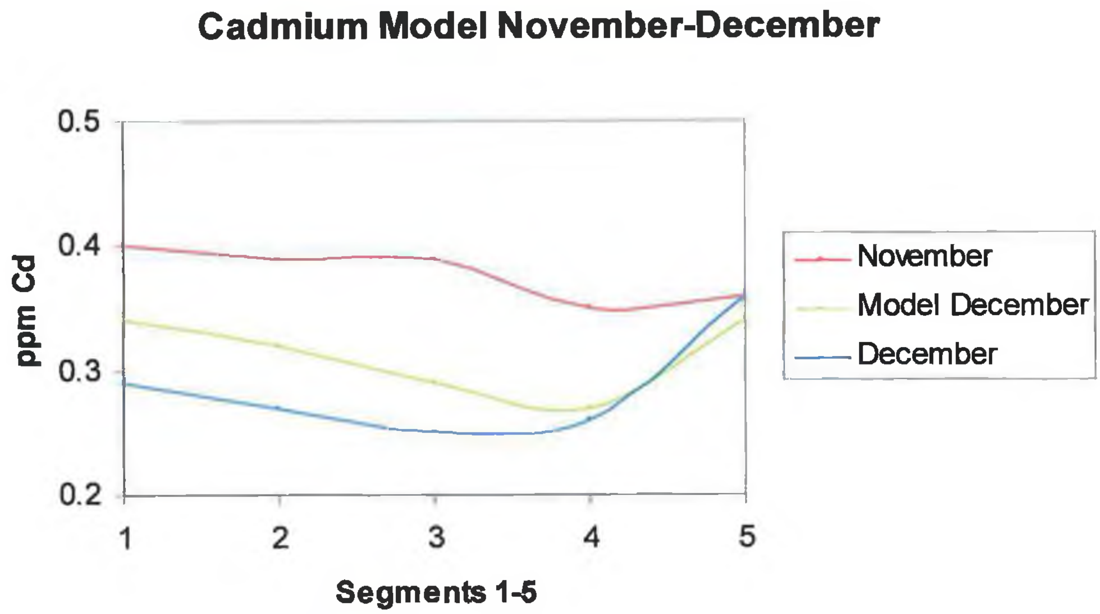


Figure 4.22 Cadmium Model V Recorded Concentration for December 2004.

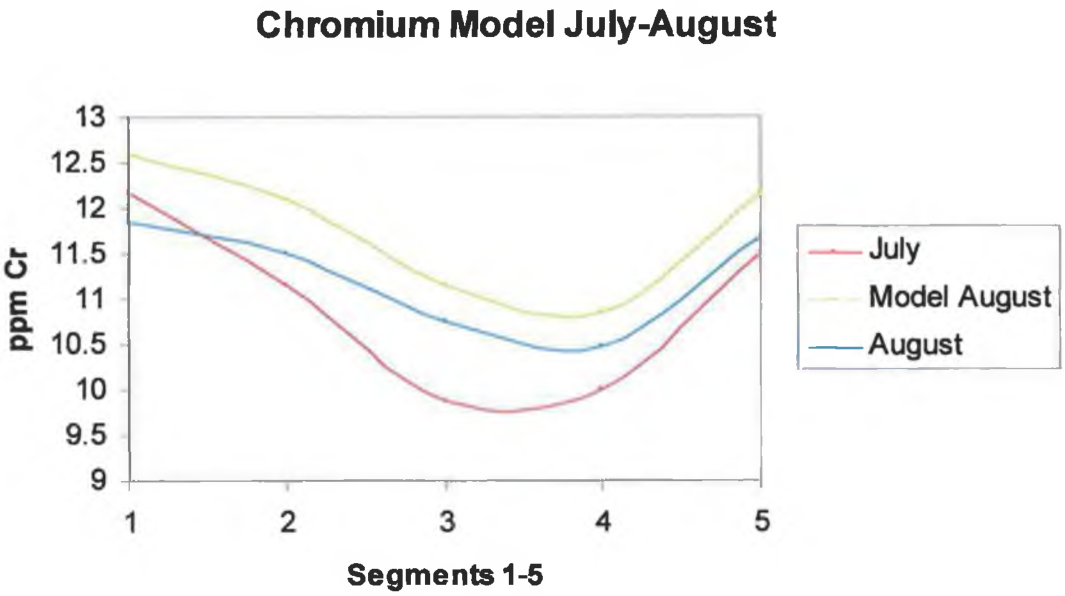


Figure 4.23 Chromium Model V Recorded Concentration for August 2004.

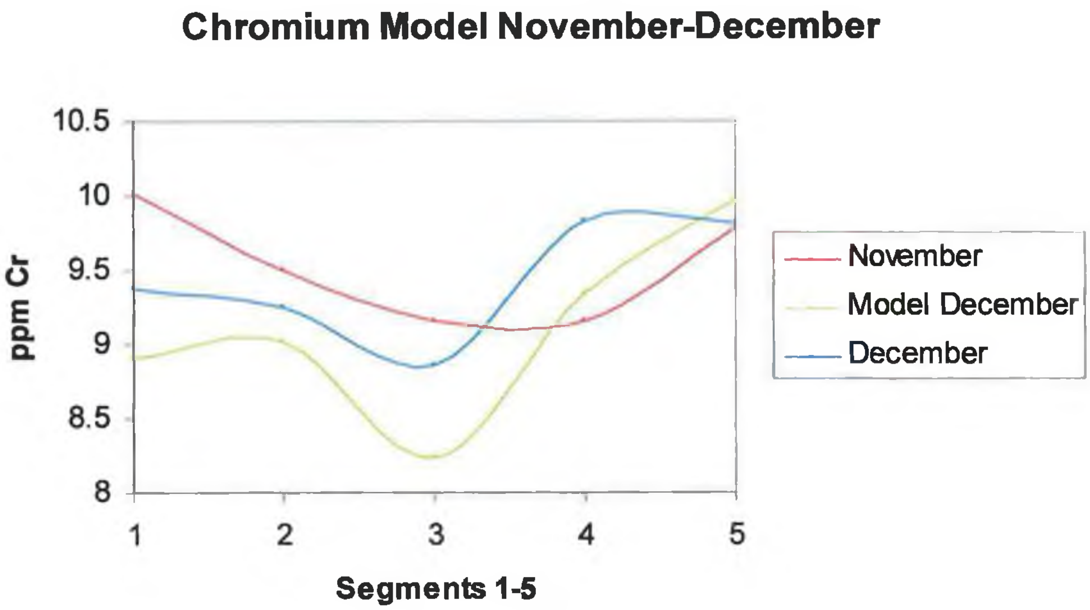


Figure 4.24 Chromium Model V Recorded Concentration for December 2004.

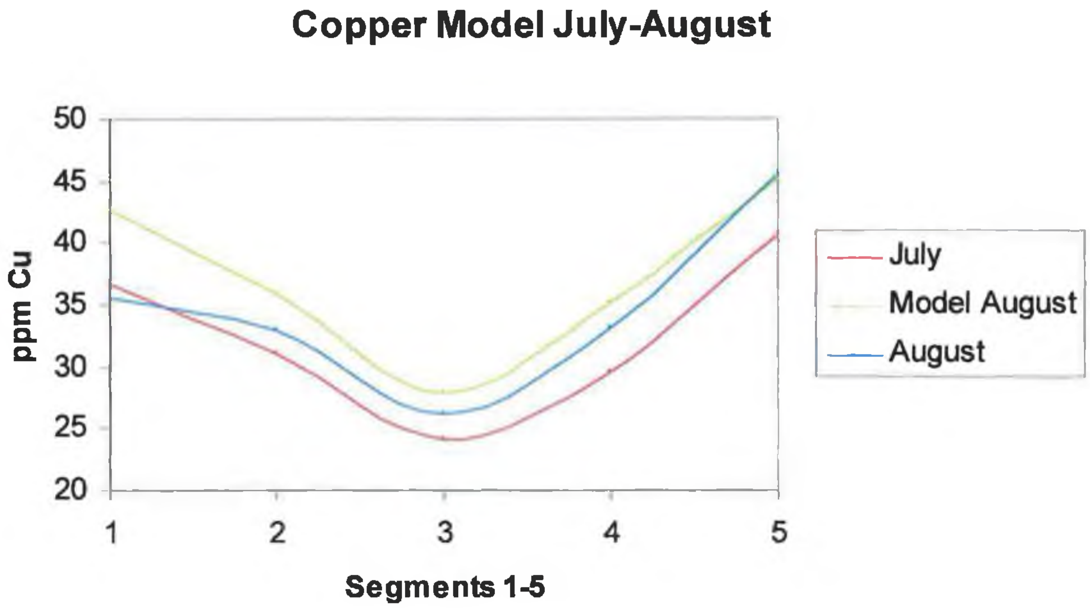


Figure 4.25 Copper Model V Recorded Concentration for August 2004.

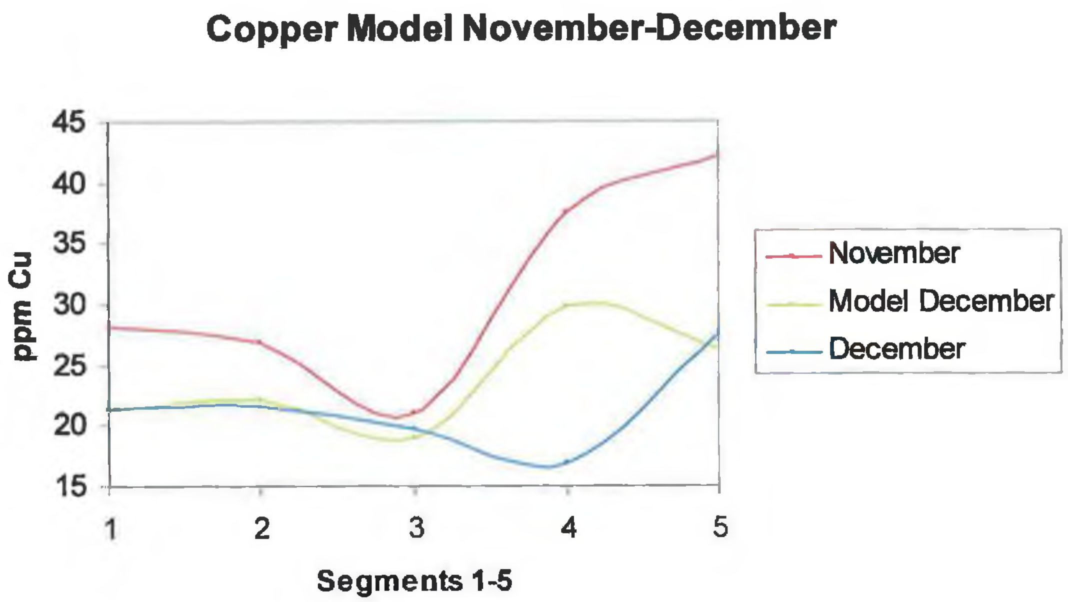


Figure 4.26 Copper Model V Recorded Concentration for December 2004.

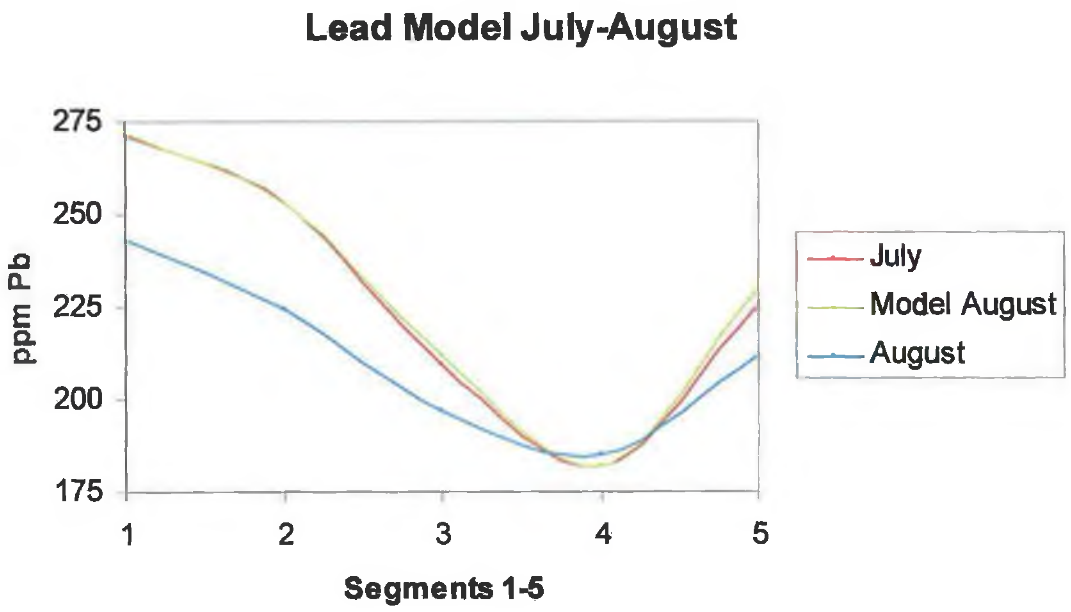


Figure 4.27 Lead Model V Recorded Concentration for August 2004.

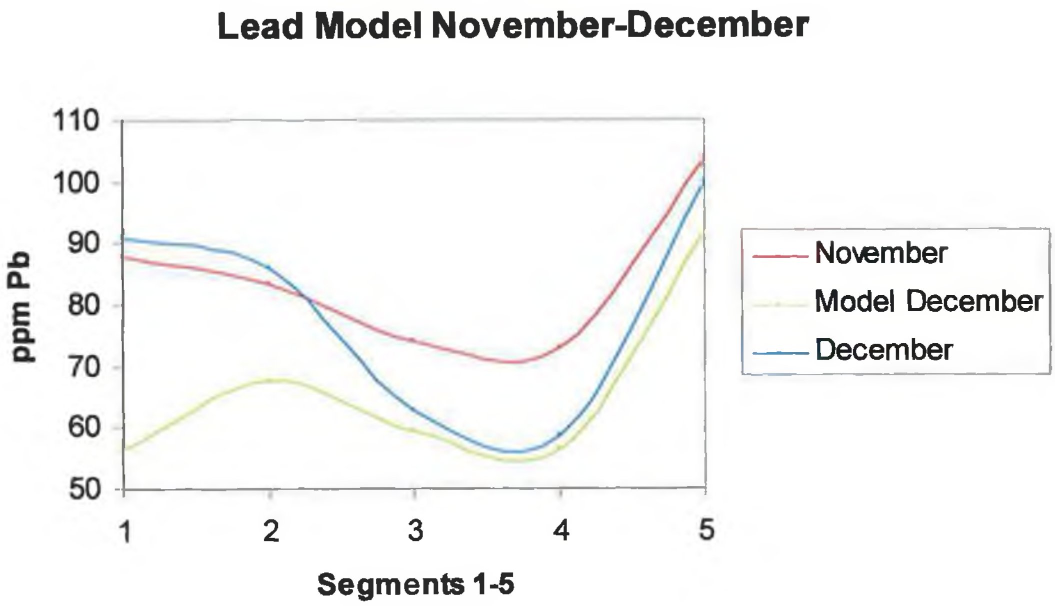


Figure 4.28 Lead Model V Recorded Concentration for December 2004.

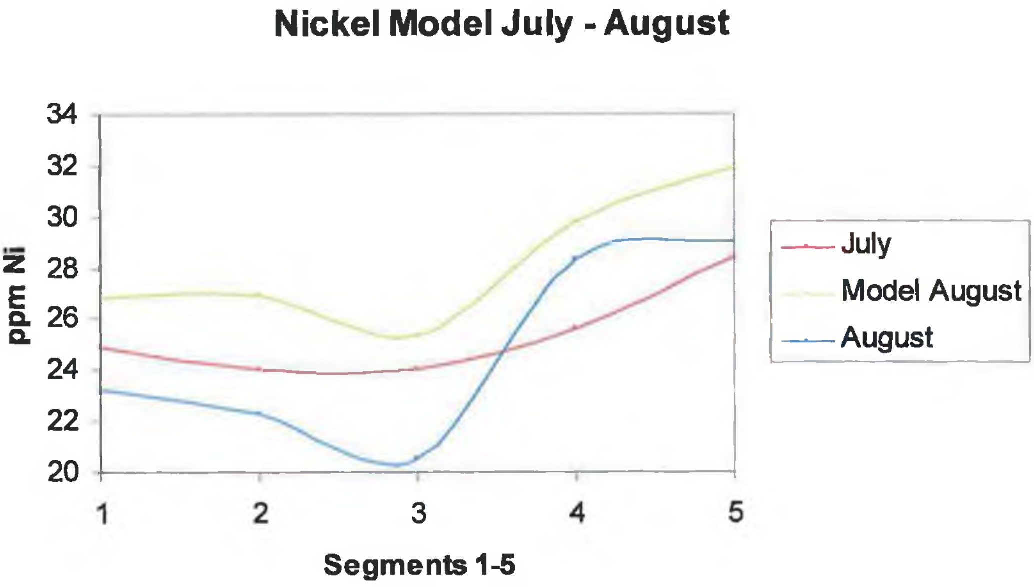


Figure 4.29 Nickel Model V Recorded Concentration for August 2004.

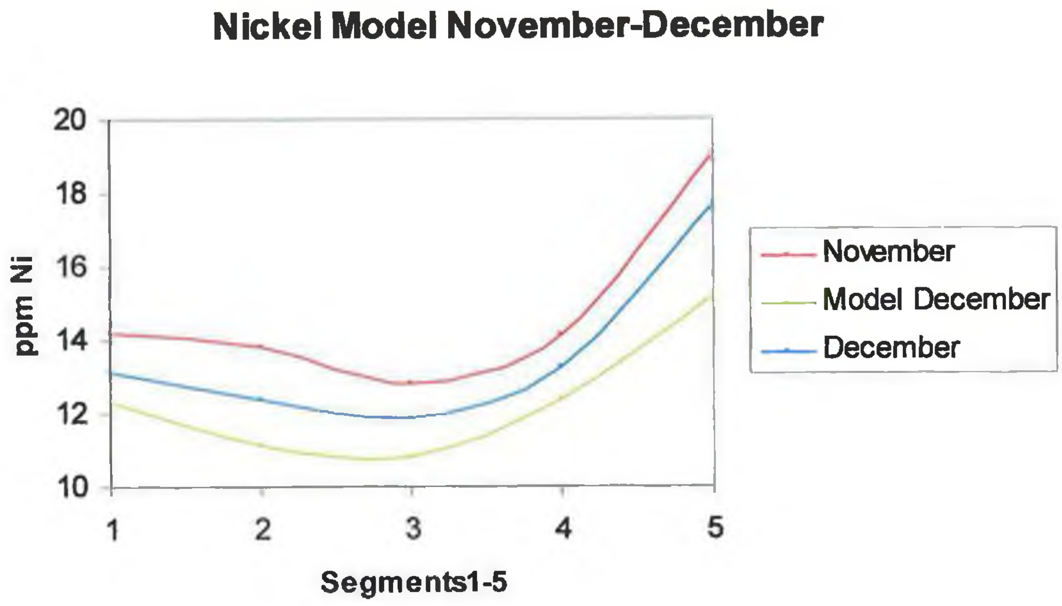


Figure 4.30 Nickel Model V Recorded Concentration for December 2004.

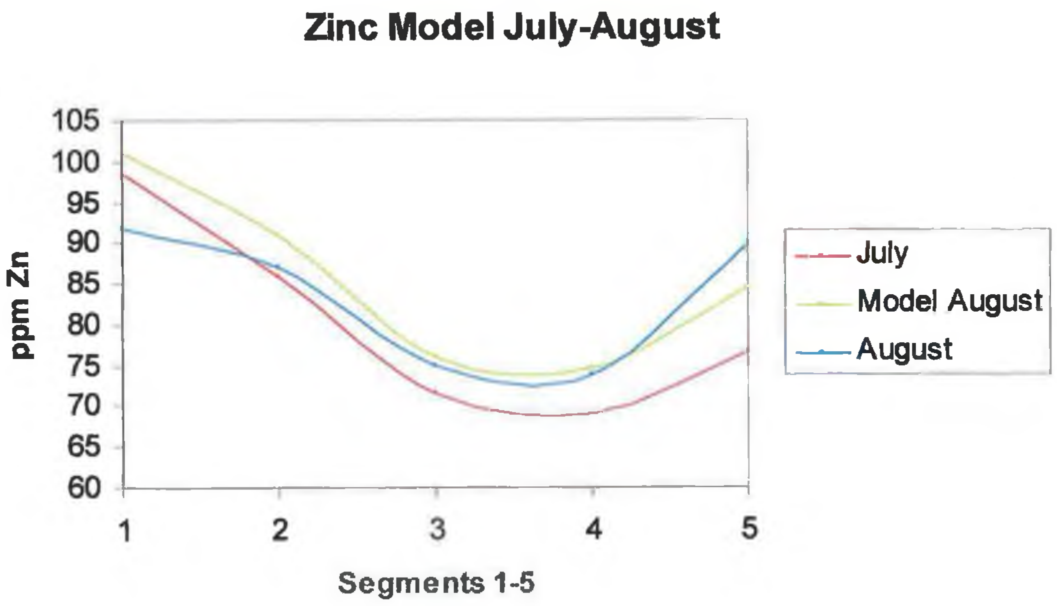


Figure 4.31 Zinc Model V Recorded Concentration for August 2004.

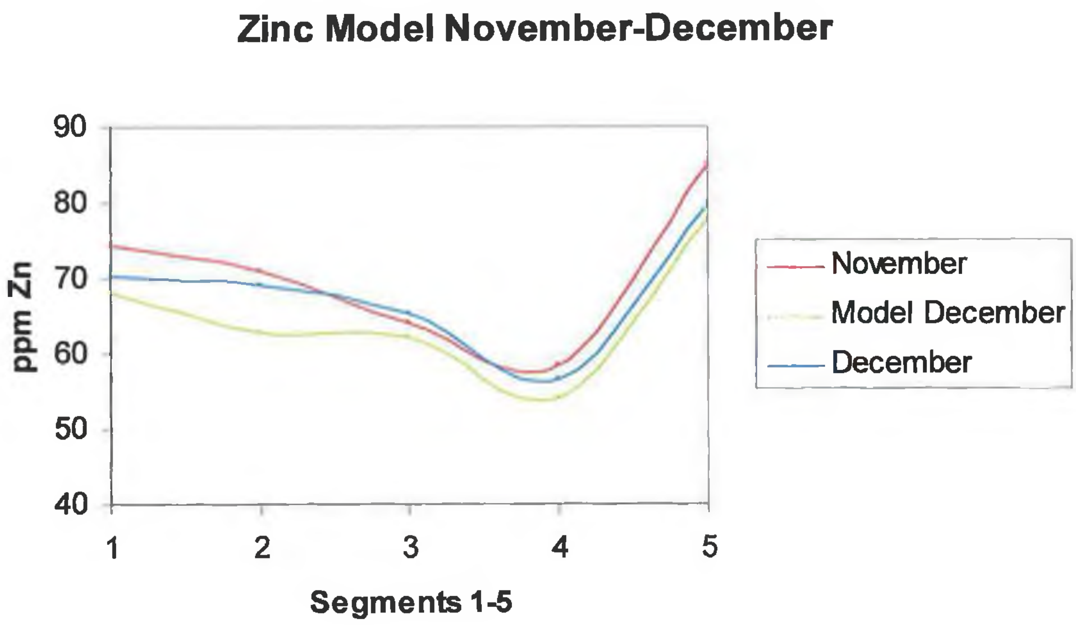


Figure 4.32 Zinc Model V Recorded Concentration for December 2004.

For sufficient applicability to predict metal concentrations in surface sediment over time this is an adequate concept model (Diamond, 1990; Lindenshmidt, 2005; Bowes et al., 2005; Chapra, 1997). The model is limited by the reduced number of parameters assessed. This was a measure to simplify the model to a basic mass balance model based on the assumptions previously made. While simplifying the process so that the model could be applied for any river system, accuracy was reduced by limiting the number of parameters involved; deposition, diffusion and resuspension. In other riverine systems groundwater and sediment burial would need to be incorporated into the model, as would any additional static water compartments such as lakes and ponds. The Tolka model could be used in any river system to predict temporal variation provided a broad riverine physical and chemical analysis was completed beforehand. Variable environmental conditions such as river height, speed and volume would need to be assessed on a regular basis so that the model could be used in all river conditions including flooding and low flow periods. However, all riverine systems are different (e.g. groundwater infiltration, different physical and chemical conditions, urban and rural environments) and each river would need slight modification of the model for accurate predictions.

Model sensitivity testing was completed by altering deposition, resuspension and diffusion rates and the results are located in Appendix D. Inherent seasonal variability of in situ physical and chemical parameters in the river make predicting short term and seasonal metal concentrations in surface sediment difficult. In comparison, predicting concentrations on an annual basis and utilising annual average deposition, resuspension and diffusion rates is a simpler process. While the surface sediment layer is a relatively stable physical feature of the river, the river itself is constantly in a state of flux. While monitoring of metals on a monthly basis is valuable in determining seasonal distribution in the river, modelling on a month to month basis in tandem with sampling is not overly practical. It does however provide a useful tool for predicting the eventual fate of contaminants that may have been introduced during a pollution incident. This short-term model would indicate a short term pollution incident and how its contaminants were integrated into surface sediment, residence and diffusion times of the contaminant. This would not be possible in a model designed to determine long-term predictions.

CONCLUSION

The continual assessment of metal contamination of estuarine ecosystems is a goal of many environmental agencies. The United Nations and the European Union have initiated many agreements to protect these coastal environments. The Ospar and Ramsar Conventions secured that these zones of extraordinary biological diversity will be protected (Little, 2000). However, pollution of these sites is still ongoing and remediation of polluted sites once contamination has ceased is slow. The continued analysis of estuaries for metal contamination is essential for understanding and protection of the marine environment as a whole as estuaries are the pathways by which pollutants enter the marine ecosystem.

This study has formulated a rapid aquatic system assessment procedure that allows for multiple repeat sampling throughout the course of a year. This provides a complete synoptic assessment of temporal contaminant distributions within an aquatic system and serves as an aid tracking pollution incidents. While the assessment was completed on a month to month basis by one person to determine complete seasonal contaminant variability, the procedures could be modified for shorter time periods to assess a rapid impact by a pollution incident or longer time periods to provide a more basic overview of the aquatic system while still determining seasonality.

5.1 Spatial and Temporal Variation

This research has categorically shown that contaminants have distinct spatial trends and variable temporal distributions in a river and estuarine system over a twelve-month period. Contaminant concentrations in surface sediment are heavily influenced by environmental factors including aquatic system physical features, the water column contaminant load including SPM bound contaminants and dissolved contaminant loading, OM content of surface sediment and by fluctuating anthropogenic inputs. The river and estuary displayed different spatial distributions. The river was primarily influenced by an inflowing pollution source, while the estuary was influenced by its broad flat physicality that induced the mid estuarine maximum phenomenon. Seasonality in the Tolka aquatic system was evident but is highly variable and not uniform. Ideally surface sediment contaminants would be expected to increase in summer and reduce in winter. While this was observed in the river and estuary, each year the trends were different. Spatial and seasonal distributions were disrupted by pollution incidents and variable environmental factors.

From this research it can clearly be observed that seasonal variation of surface sediment contaminant concentrations is evident on a month to month basis in aquatic systems. Estuaries display a greater range of seasonally variable contaminant concentrations compared to rivers. However, pollution incidents and extreme environmental fluctuations such as storms or flooding can severely effect seasonal distributions. Contaminant concentrations generally increase in summer months and decrease in winter months. At a basic level this seasonal distribution of contaminants in surface sediment can be described as a flushing and retention mechanism induced by seasonally fluctuating environmental conditions. While this research took place using an urban river and estuary, an equivalent seasonal distribution would likely occur in non-urban systems with a lower concentration range. Future temporal research should include the parameters utilised in this project but vary the temporal sampling and also extend research to non urban aquatic systems including canals and estuaries with different physical and chemical conditions.

5.2 Metals

Metal concentrations in sediment of the Tolka River are not of a significant level except in close proximity to the landfill leachate stream. However, metal concentrations in the estuary can be categorised as potentially harmful to the benthic community of this system. Metal concentrations displayed seasonal variation within surface sediments. Metal seasonal variability had strong correlations with OM seasonal variation indicating that metals became bound to increasing OM concentrations and were subsequently retained in surface sediment during summer months. As OM was degraded in winter months and lost from surface sediment, metals were released from surface sediment matrices and were resuspended to the water column bound to SPM in winter months during periods of high water column turbulence.

Indications from the last six months of sampling indicate that metal loading of surface sediment is in decline and that the Tolka aquatic system is slowly removing contaminants. However, the possibility exists for the Tolka estuary to change from a fair to a poor or bad condition. This will depend largely on the management and future impact of the Dublin Port reclamation project.

5.3 TBT

This study has also shown that TBT has a similar variable temporal distribution to that of metals. However, TBT concentrations in surface sediment are influenced significantly by fluctuating anthropogenic inputs, and TBT seasonal variability can be described as anthropogenically induced. Continued TBT contamination of the Tolka indicates that anthropogenic input is an ongoing issue that has not been completely resolved despite regulation of TBT use in the 1980's (Alzieu, 1998). The Tolka sediment TBT levels range from 0 to 8.6 ppb with a 1.5 ppb annual average. According to recent Australian guidelines, acceptable TBT levels in estuarine sediment range from 0.5 to 7 ppb (DoE, Australia, 2002). In general, the Tolka falls within this range.

5.4 River Modelling

The mass balance model devised for the Tolka River was ultimately a basic tool to aid the research on elucidating seasonality. It highlighted the effects of deposition, resuspension and particularly diffusion mechanisms had on surface sediment metal concentration temporal flux. Porewater diffusion rates were observed to have a strong influence on surface sediment metal concentration temporal variability. While the model did provide moderately accurate metal predictions after a thirty day period, this was not a practical use of mass balance modelling. However, the model could be further adapted for longer periods of time and to incorporate variable flow rates to assess climatic influence on surface sediment metal concentrations.

The full analysis of seasonal variation of surface sediment contamination completed by this research provided a more in depth knowledge of short term variability and pollution incident effects in aquatic systems. Aquatic systems were observed to be much more complex and temporally variable than previously thought. Aquatic systems are linked together in various seasonal cycles influenced by in situ physical, chemical and biological parameters as well as anthropogenic inputs. However, further research on elucidating the transportation, circulation, retention and persistence of metals and organometals in riverine and estuarine environments is required. Research into the transportation mechanisms of pollutants through aquatic ecosystems will assist in determining riverine and estuarine quality which can no longer be justified by a simple assessment of nutrients on a biannual basis and metals and complex contaminants on a five year basis.

FUTURE RESEARCH

A number of avenues of research can be pursued based on the conclusions of this research project. Through the polarographic optimisation process, new techniques were applied primarily for analysis of simple environmental contaminants. Differential Pulse Polarography provided an efficient, fast, reliable and cost effective form of analysis for metal contaminants as well as the organometal TBT. DPP offers the potential for analysis of more complicated chemical contaminants in the aquatic environment including organic pesticides (organochlorines, organophosphates and organometals) as well as pharmaceutical residues. Minimal research has been carried out on the potential of DPP for metal contaminant speciation in such environmental matrices. From this research it can be seen that polarographic techniques offer a broad scope for environmental analysis and should be pursued.

The primary focus of this research was directed at seasonal variation of contaminants in aquatic systems. The mechanisms for detection of seasonal variability developed in this project should be enhanced further in an optimisation process. New sampling techniques, variation to temporal sampling regimes and sample point networks would increase the efficiency of temporal analysis. The creation of a temporal sampling network in a watershed would be an invaluable tool for research on catchment hydrology over time and how catchment processes that vary over time influence contaminant transportation, retention and diffusion in aquatic systems.

Seasonal variation was observed for both metals and TBT contamination. The former was influenced primarily by variable environmental factors while the latter had a seasonal variation that was anthropogenically induced. Through the extensive sampling regime a distribution relationship was observed between organic matter content of surface sediment and metal contamination both spatially and over time. However, this relationship was one of many that influenced contaminant seasonal variability. Seasonal and spatial variability of dissolved solute loading, suspended particulate matter, salinity and pH of the water column also indicate relationships with metal and organometal contamination. Salinity plays a significant role at the saltwater / freshwater interface through adsorption and sorption of contaminants from SPM to and from the water column and SPM coagulation. These processes subsequently affect contaminant concentrations within surface sediment matrices. Assessing the role of salinity using partition coefficients over extended periods of time would provide information on the role salinity has on contaminant diffusion mechanisms particularly at the freshwater/saltwater interface. While limited salinity assessment was completed in this research, it will be incorporated into the next research paper focusing on minor aspects of this research. The next phase of research on contaminant seasonal variability within aquatic systems should be directed towards these environmental parameters. The estuarine water column offers a complex aquatic system that has had limited research relating to seasonal variation. A complex interrelationship between SPM concentration and composition, salinity and pH plays a fundamental role in metal contaminant distribution spatially but has yet to be researched on a long-term basis. Directing research into this area may indicate new contaminant temporal transportation phenomena and could be utilised to aid determination of pollution plumes, and contaminant retention times in aquatic systems.

This research generated an extensive dataset of information regarding physical and chemical parameters of a moderately sized aquatic system. Creating a basic mass balance model to predict future contaminant concentrations based on this data provided insight into in situ physical mechanisms that played a role in transportation, retention and dispersal of contaminants. However, inputting the data gathered by this research into a pre-existing computer model would provide a far greater interpretation on these in situ transportation mechanisms. Seasonally variable parameters assessed by this research could also be included in the development of a computerised model to predict temporal variation, spatial variation and pollution plumes. As the research was completed under variable environmental conditions (weather and aquatic physico-chemical conditions) and fluctuating contaminant concentrations there exists a viable basis for a computerised prediction model for temporal contaminant variability based on this data.

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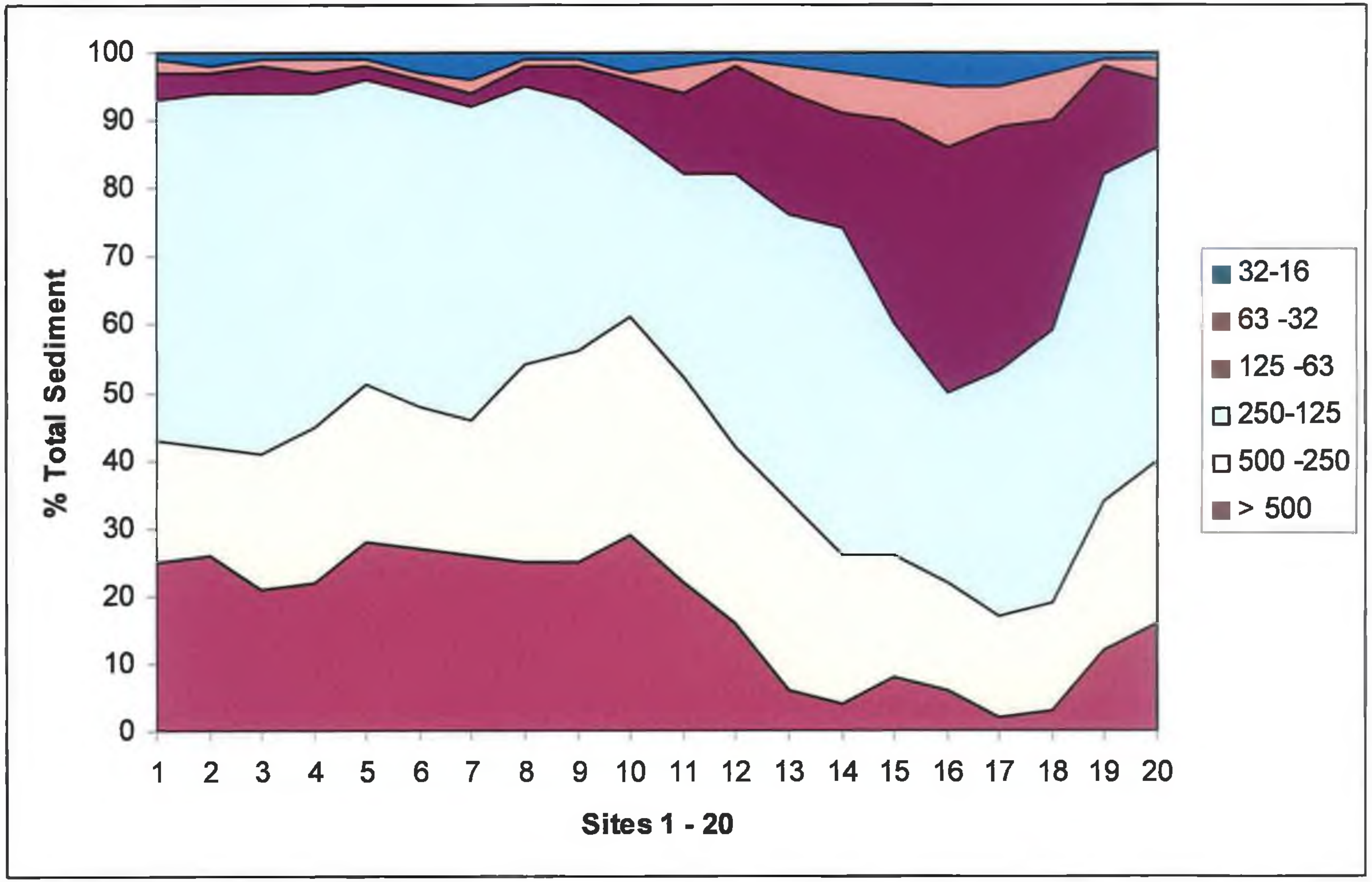
APPENDIX A
Sediment Granulometry

	Month																												
Site	**A**	**S**	**O**	**N**	**D**	**J**	**F**	**M**	**A**	**M**	**J**	**J**	**A**	**S**	**O**	**N**	**D**	**J**	**F**	**M**	**A**	**M**	**J**	**J**	**A**	**S**	**O**	**N**	**D**	**J**
1											2	3	3	2	3	3	4	2	3	2	3	4	5	3	3	4	5	3	2	3
2				4	3	3	3	1	2	3	3	2	3	3	3	2	3	4	3	3	3	4	2	3	4	3	3	2	2	3
3	2	4	2	3	4	2	4	2	3	2	2	2	2	3	3	3	2	3	4	3	5	3	3	3	2	1	1	2	3	2
4	4	2	4	4	5	3	2	2	3	2	2	4	3	4	2	4	4	2	2	3	2	4	3	2	3	4	2	3	2	3
5	4	3	5	5	3	2	2	4	4	4	4	4	5	3	4	3	4	3	4	5	4	2	2	3	4	5	4	3	4	2
6	2	3	6	2	3	3	3	4	5	3	3	3	3	3	3	3	4	4	2	3	4	3	2	3	4	2	3	2	3	4
7	3	3	5	4	3	4	3	3	6	5	5	5	5	5	4	3	4	5	6	5	4	5	4	6	5	4	5	5	5	6
8	5	4	5	4	4	4	4	4	5	6	6	6	5	6	5	4	5	6	5	5	5	4	5	6	6	5	4	5	6	2
9	6	5	4	5	4	5	6	6	9	10	12	9	8	6	6	6	6	5	4	5	6	6	6	5	6	7	6	6	6	2
10	9	8	6	8	7	6	7	6	12	12	13	11	11	9	9	8	8	8	5	7	8	6	8	6	6	8	9	6	6	4
11	10	9	8	9	9	8	9	10	11	9	9	8	11	12	12	11	11	11	10	9	10	12	12	11	11	10	9	8	9	4
12	9	10	9	9	9	10	9	12	13	11	12	13	13	13	12	11	11	9	9	8	9	11	11	11	12	14	12	11	11	2
13	10	10	10	9	10	9	11	12	13	11	12	13	13	14	11	10	10	9	9	9	11	8	9	11	13	13	14	11	10	5
14	11	11	10	10	11	10	11	11	13	12	13	14	15	11	9	10	8	9	10	11	12	14	14	13	12	11	11	11	9	9
15	10	11	12	11	11	11	11	12	12	12	14	14	13	12	11	11	13	11	10	13	14	14	15	12	13	13	14	11	11	110
16	10	11	12	11	12	10	12	12	11	14	15	14	11	13	14	15	16	13	14	12	11	13	14	15	11	11	10	11	11	14
17	12	13	11	12	12	12	13	11	11	13	13	12	11	11	11	10	10	9	10	11	11	12	13	14	14	11	10	9	9	11
18	13	11	11	11	14	13	13	13	12	14	13	13	14	15	12	11	12	10	9	10	10	10	11	13	14	14	11	11	11	10
19	5	5	4	5	6	6	5	8	8	9	9	4	5	6	6	5	5	3	2	3	4	5	7	8	9	6	4	4	3	2
20	6	7	6	6	7	6	5	8	9	9	9	9	8	7	7	7	7	5	5	4	7	7	9	9	8	8	6	5	5	4

Appendix A, Table 1. Sediment Composition % < 63 μm.



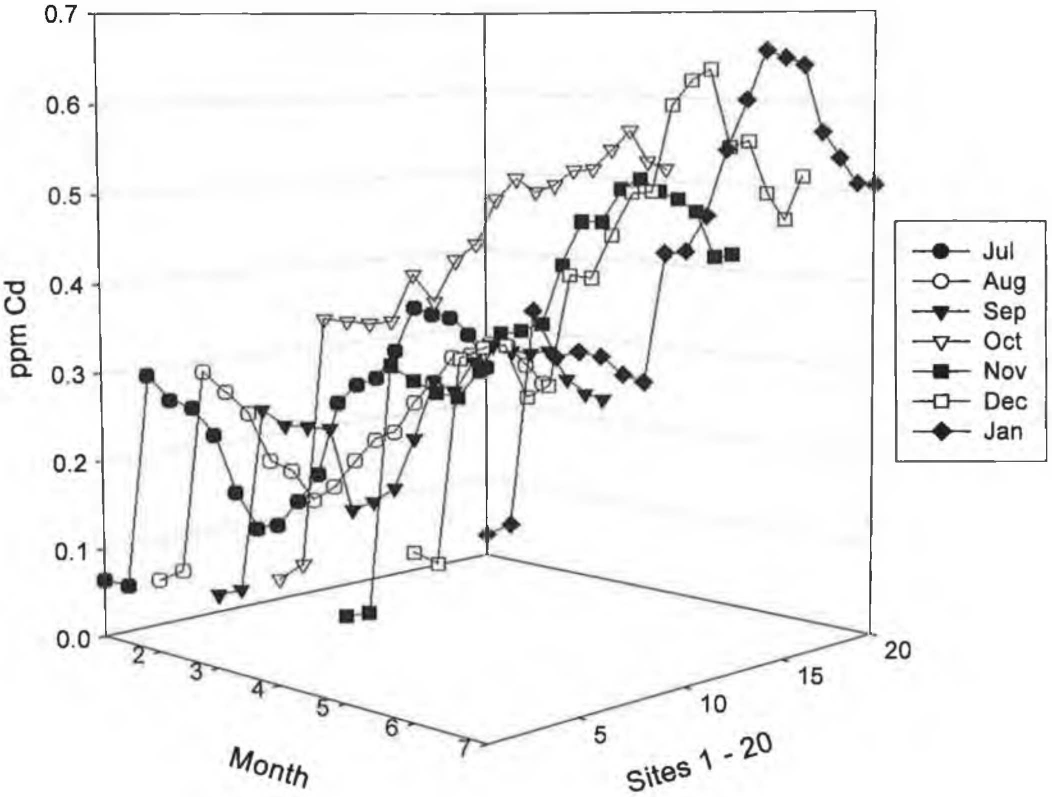
Appendix A, Figure 2. Grain Size Distribution, January 2005, % of total surface sediment, sediment size measured in µm.

APPENDIX B
River Speed

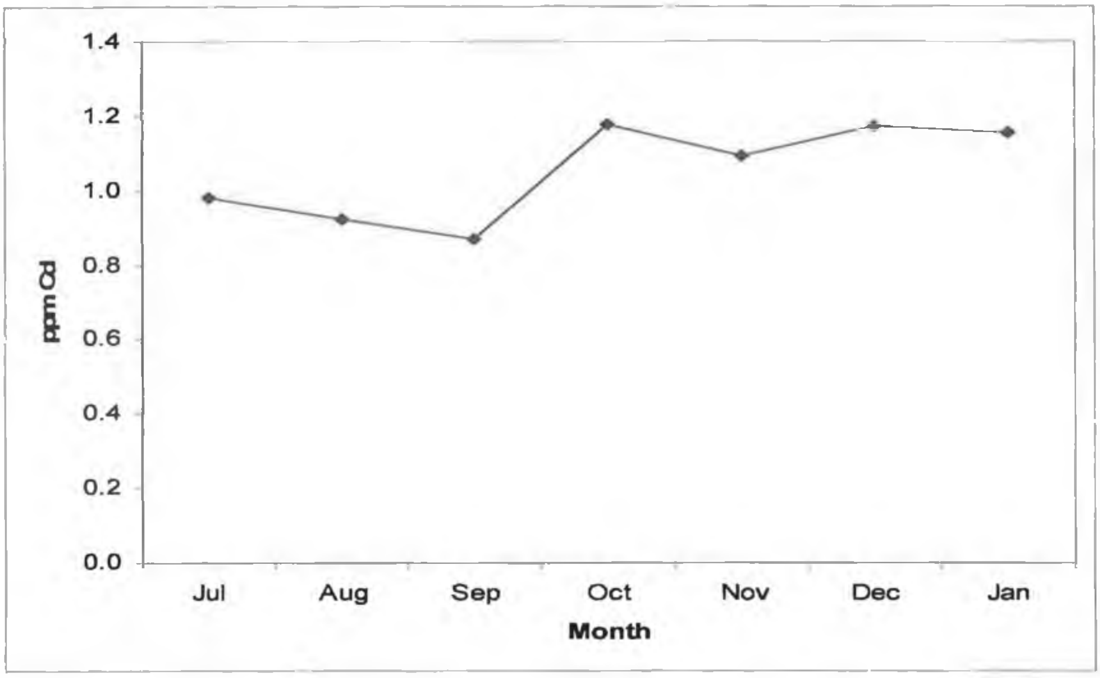
	Month																									
Site	**D**	**J**	**F**	**M**	**A**	**M**	**J**	**J**	**A**	**S**	**O**	**N**	**D**	**J**	**F**	**M**	**A**	**M**	**J**	**J**	**A**	**S**	**O**	**N**	**D**	**J**
1								1.2	0.4	0.2	0.3	0.5	0.5	0.6	0.4	0.3	0.4	0.3	0.2	0.3	0.3	0.2	0.4	0.2	0.2	0.4
2	2.5	1.2	1.0	0.8	0.7	0.6	0.7	1.1	0.4	0.2	0.3	0.5	0.5	0.8	0.6	0.5	0.5	0.4	0.2	0.2	0.3	0.2	0.4	0.2	0.2	0.4
3	2.2	1.2	1.1	0.8	0.7	0.6	0.7	1.3	0.5	0.2	0.3	0.5	0.4	0.9	0.7	0.6	0.5	0.4	0.2	0.3	0.3	0.1	0.5	0.2	0.2	0.5
4	2.4	1.1	1.0	0.8	0.7	0.6	0.8	1.3	0.4	0.2	0.4	0.7	0.4	0.8	0.6	0.5	0.5	0.3	0.1	0.2	0.3	0.2	0.4	0.2	0.1	0.5
5	2.3	1.3	0.8	0.6	0.6	0.4	0.5	1.1	0.4	0.2	0.4	0.7	0.6	0.8	0.7	0.4	0.4	0.3	0.1	0.2	0.2	0.1	0.5	0.2	0.2	0.5
6	2.2	1.1	0.8	0.6	0.6	0.4	0.6	1.0	0.3	0.1	0.3	0.6	0.6	0.9	0.6	0.4	0.3	0.1	0.1	0.1	0.2	0.1	0.6	0.2	0.2	0.4
7	2.1	1.1	0.9	0.5	0.5	0.5	0.5	1.0	0.5	0.1	0.2	0.6	0.6	0.9	0.6	0.3	0.3	0.3	0.2	0.1	0.2	0.2	0.7	0.2	0.3	0.4
8	1.9	1.0	0.8	0.5	0.5	0.5	0.5	0.9	0.5	0.3	0.3	0.5	0.5	0.8	0.6	0.4	0.3	0.3	0.1	0.2	0.3	0.1	0.7	0.3	0.3	0.5
9	1.9	1.2	1.0	0.6	0.7	0.6	0.6	0.9	0.5	0.3	0.3	0.5	0.5	0.7	0.5	0.5	0.4	0.4	0.2	0.2	0.3	0.1	0.8	0.3	0.3	0.5
10	2.2	1.2	1.0	0.7	0.8	0.6	0.6	1.0	0.5	0.3	0.4	0.6	0.6	0.8	0.5	0.4	0.4	0.4	0.1	0.3	0.2	0.1	0.7	0.3	0.3	0.6
11	2.2	1.3	0.9	0.8	0.9	0.6	0.6	1.1	0.6	0.3	0.4	0.6	0.6	0.7	0.5	0.3	0.3	0.4	0.2	0.2	0.2	0.1	0.6	0.3	0.3	0.5
12	2.1	1.3	1.1	0.9	0.9	0.7	0.8	1.0	0.6	0.4	0.5	0.6	0.5	0.7	0.4	0.3	0.2	0.3	0.2	0.3	0.2	0.1	0.5	0.3	0.3	0.5

Appendix B. Table 1. Tolka River Speed m / s, December 2002 to January 2005, Sites 1 – 12.

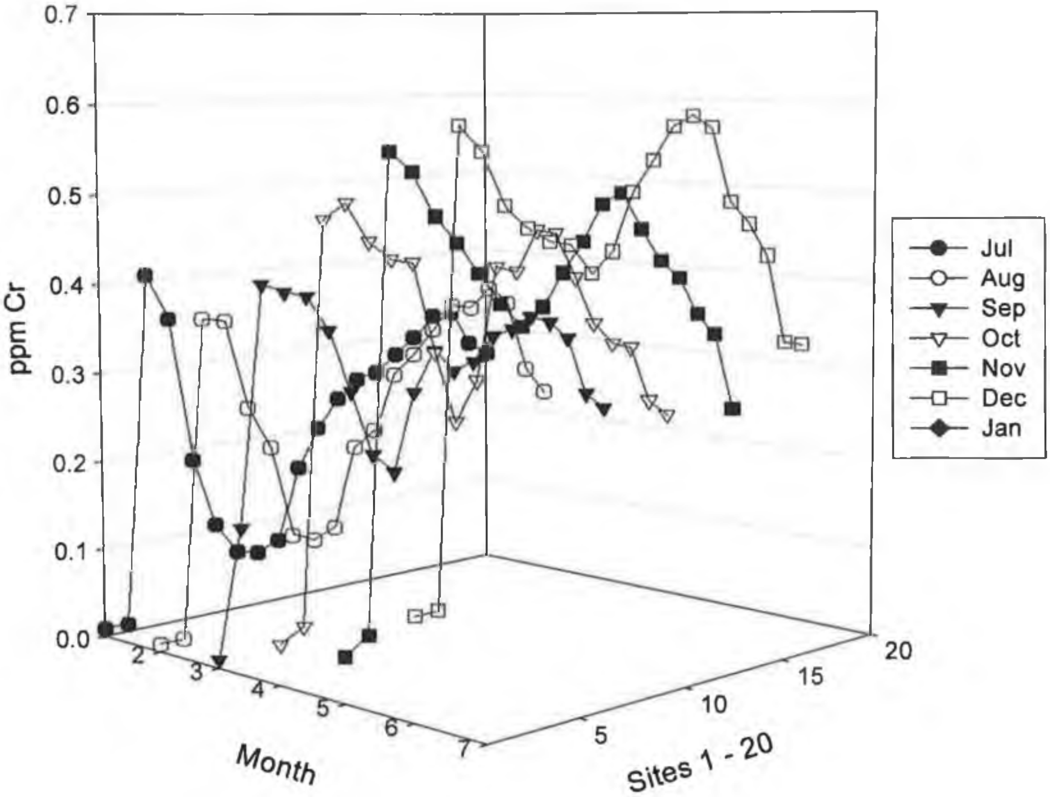
APPENDIX C
Porewater Results



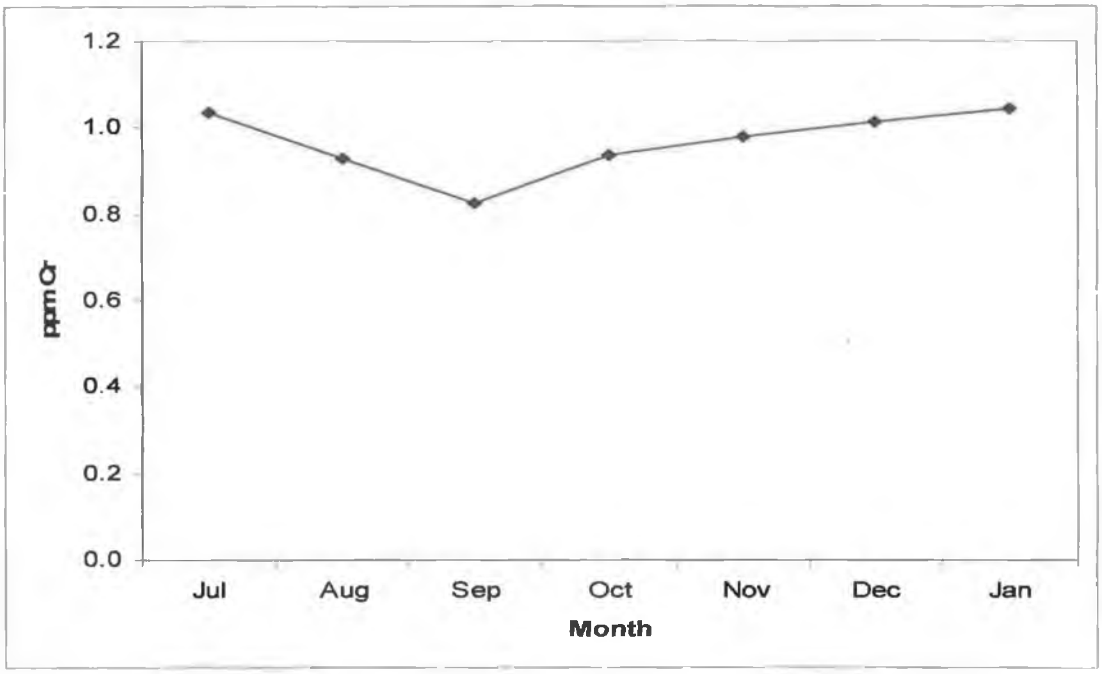
Appendix C, Figure 1. Cadmium Porewater Concentrations (ppm), Sites 1 – 20, July 2004 – January 2005.



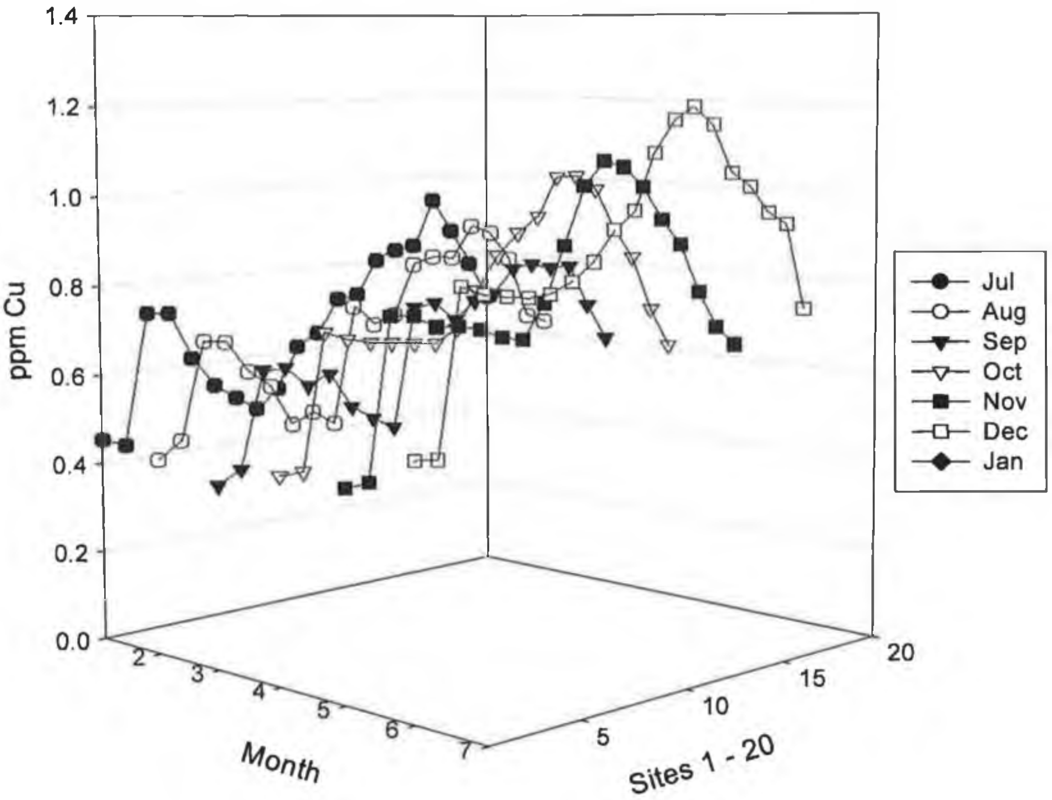
Appendix C, Figure 2. Cadmium Porewater Concentrations (ppm), Site A- Dunsink Tributary, July 2004 – January 2005.



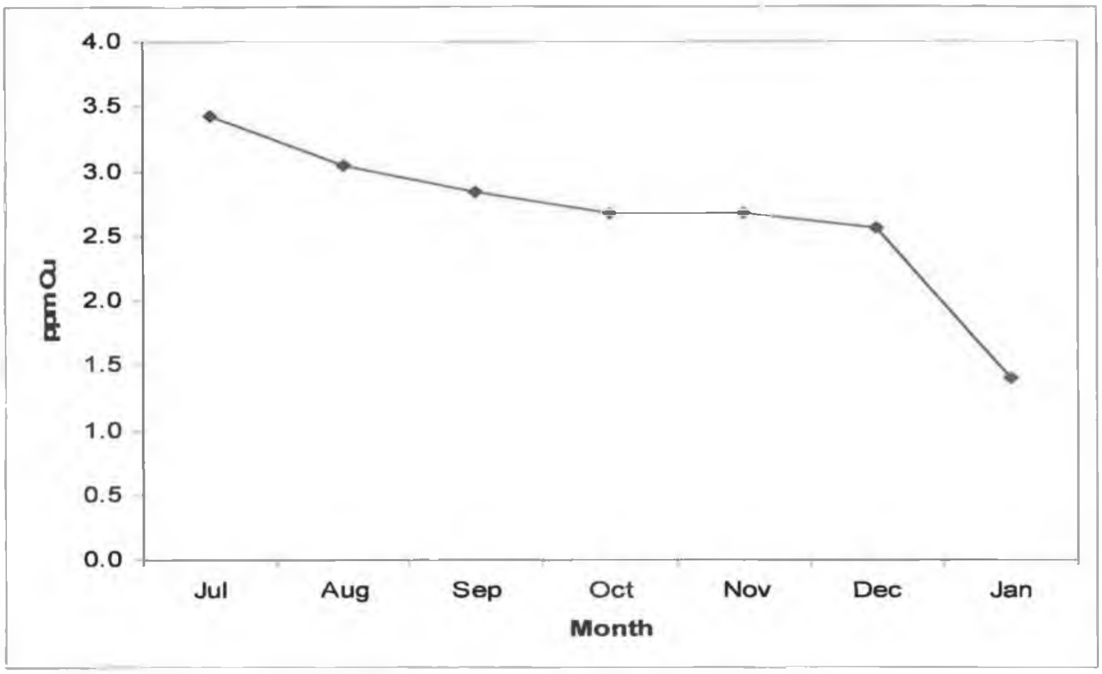
Appendix C, Figure 3. Chromium Porewater Concentrations (ppm), Sites 1 – 20, July 2004 – January 2005.



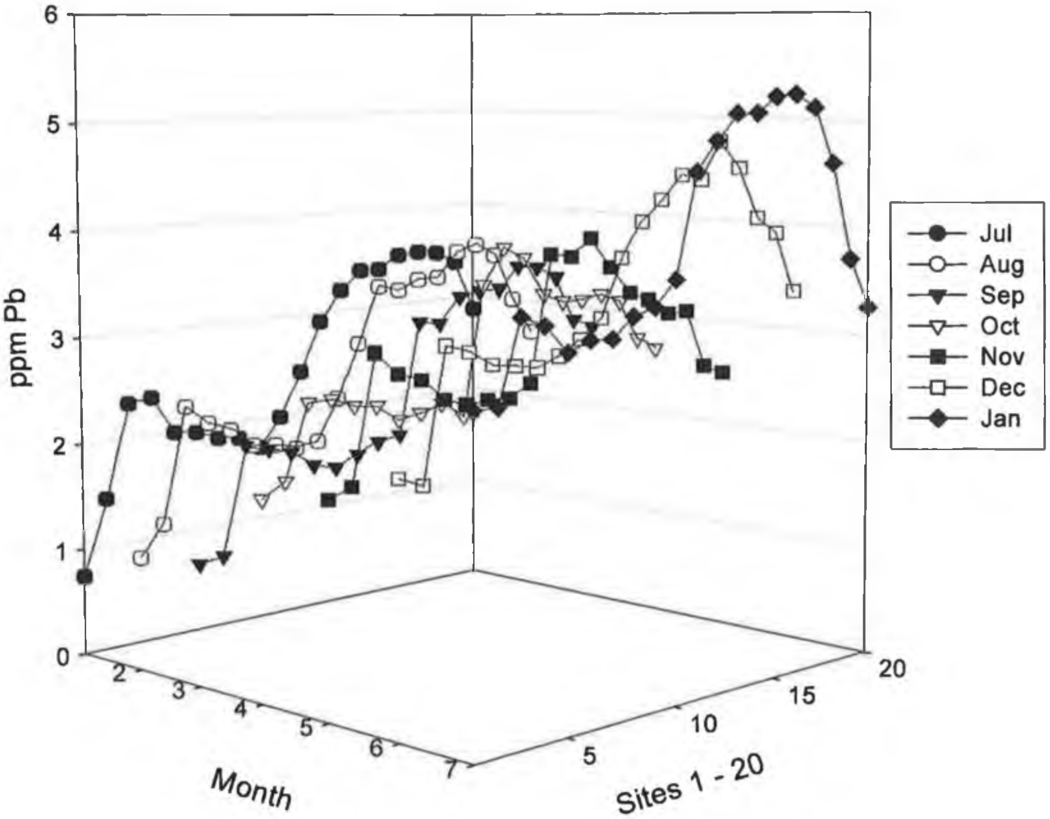
Appendix C, Figure 4. Chromium Porewater Concentrations (ppm), Site A- Dunsink Tributary, July 2004 – January 2005.



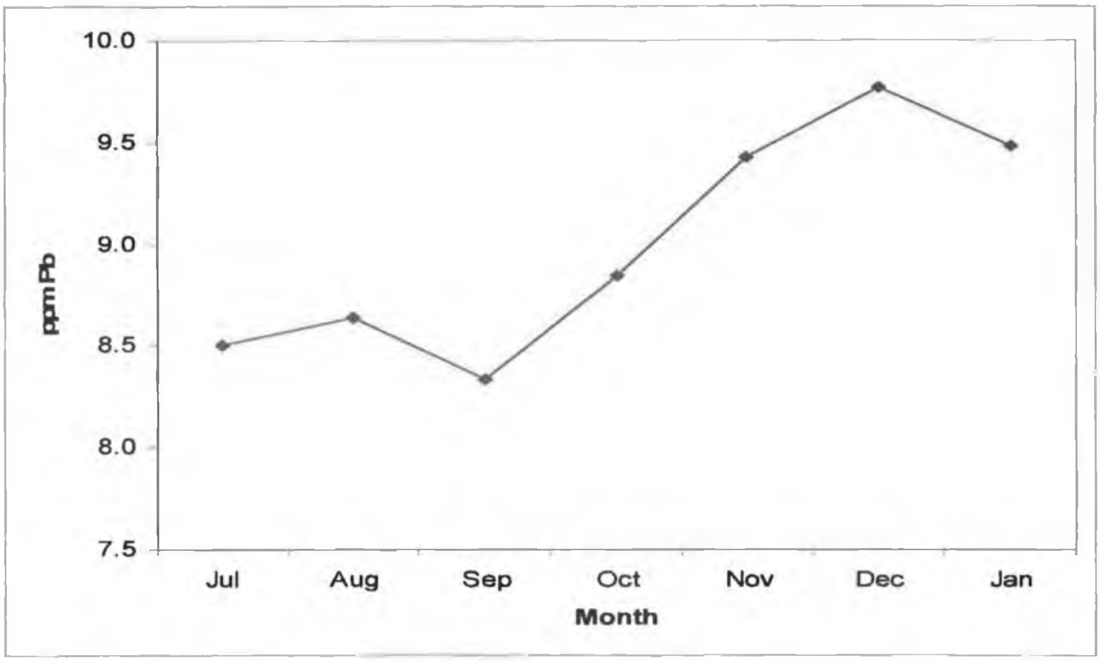
Appendix C, Figure 5. Copper Porewater Concentrations (ppm), Sites 1 – 20, July 2004 – January 2005.



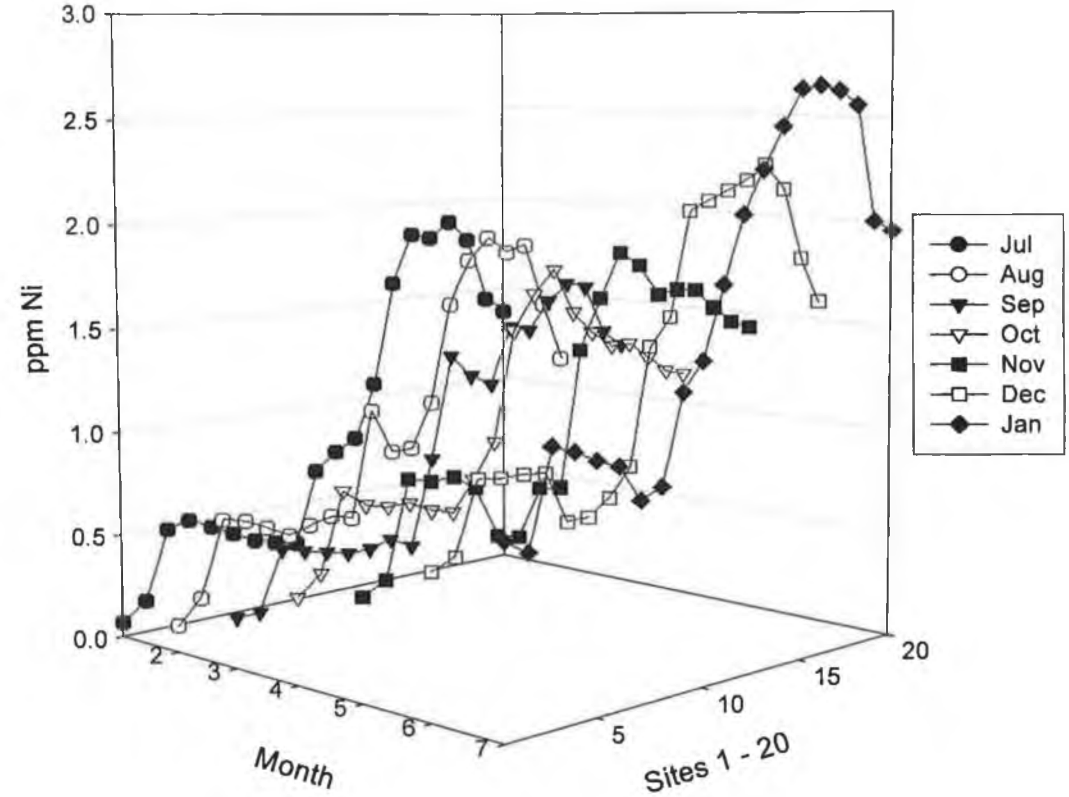
Appendix C, Figure 6. Copper Porewater Concentrations (ppm), Site A- Dunsink Tributary, July 2004 – January 2005.



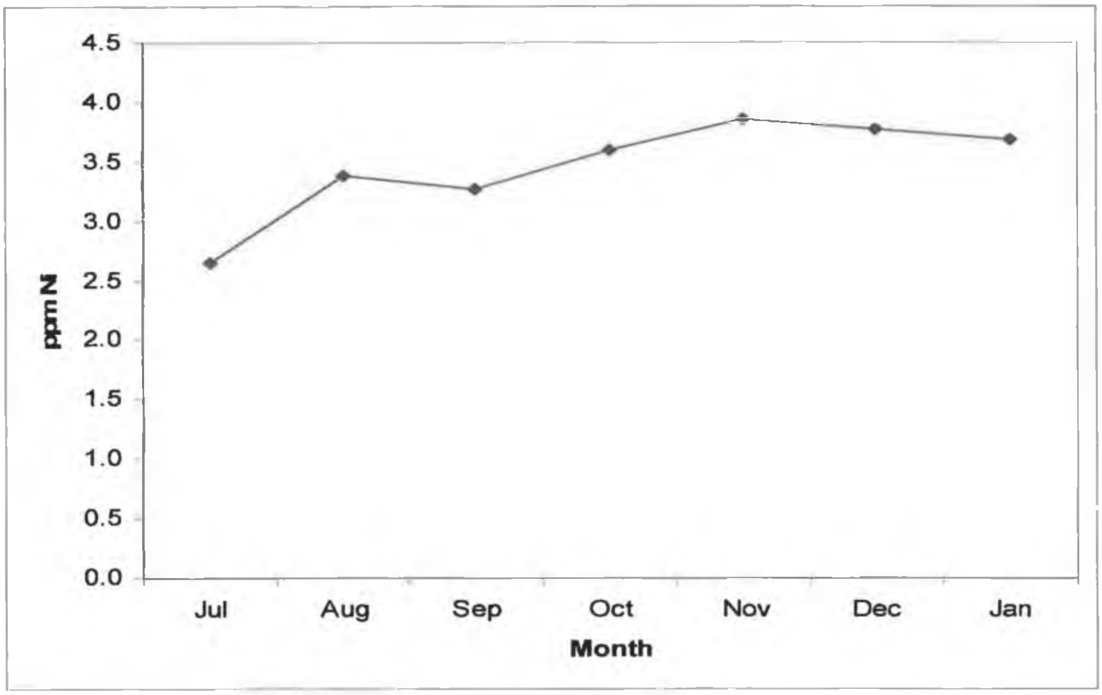
Appendix C, Figure 7. Lead Porewater Concentrations (ppm), Sites 1 – 20, July 2004 – January 2005.



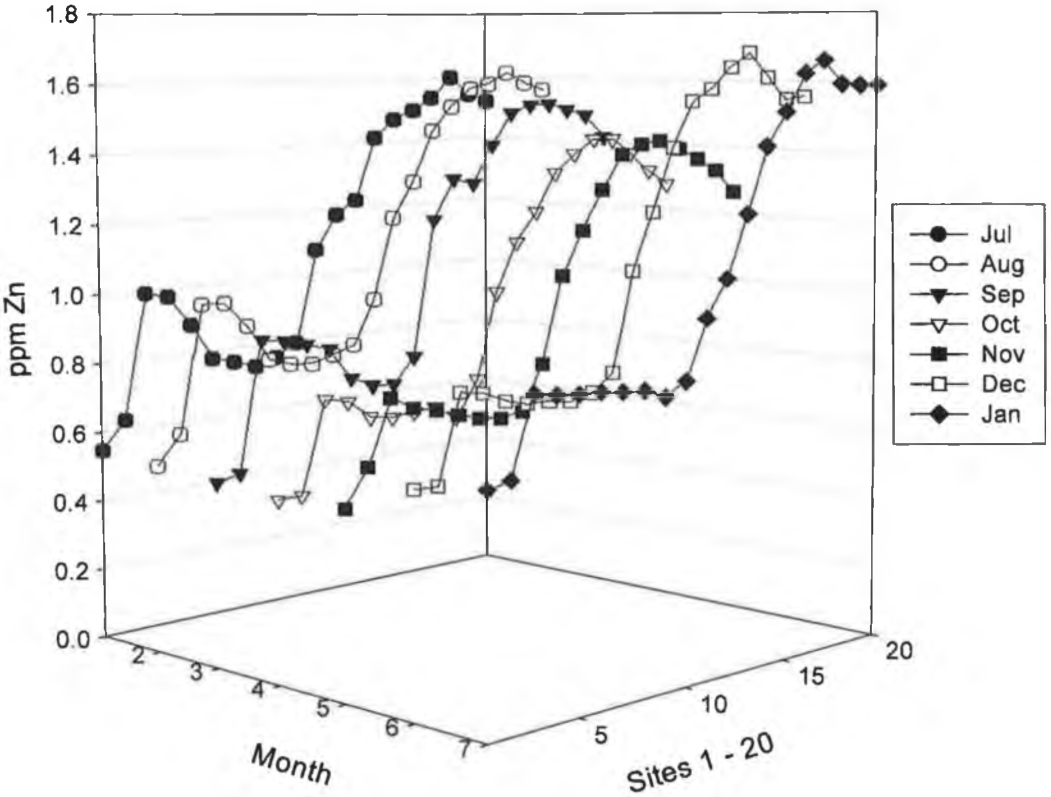
Appendix C, Figure 8. Lead Porewater Concentrations (ppm), Site A- Dunsink Tributary, July 2004 – January 2005.



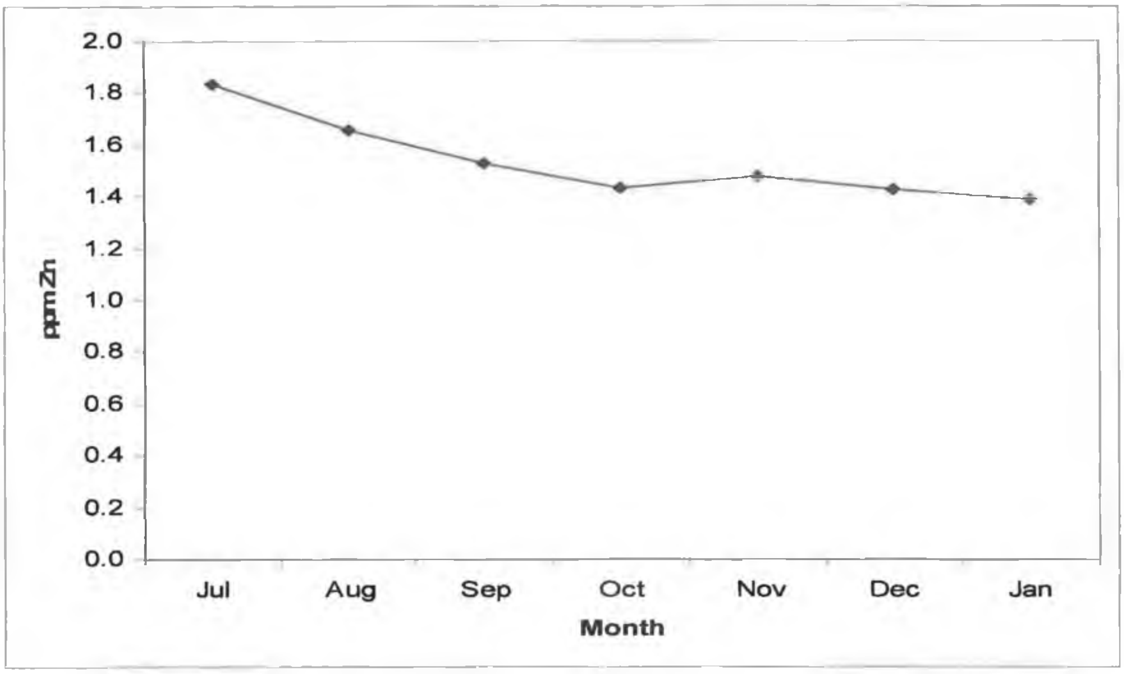
Appendix C, Figure 9. Nickel Porewater Concentrations (ppm), Sites 1 – 20, July 2004 – January 2005.



Appendix C, Figure 10. Nickel Porewater Concentrations (ppm), Site A- Dunsink Tributary, July 2004 – January 2005.



Appendix C, Figure 11. Zinc Porewater Concentrations (ppm), Sites 1 – 20, July 2004 – January 2005.



Appendix C, Figure 12. Zinc Porewater Concentrations (ppm), Site A- Dunsink Tributary, July 2004 – January 2005.

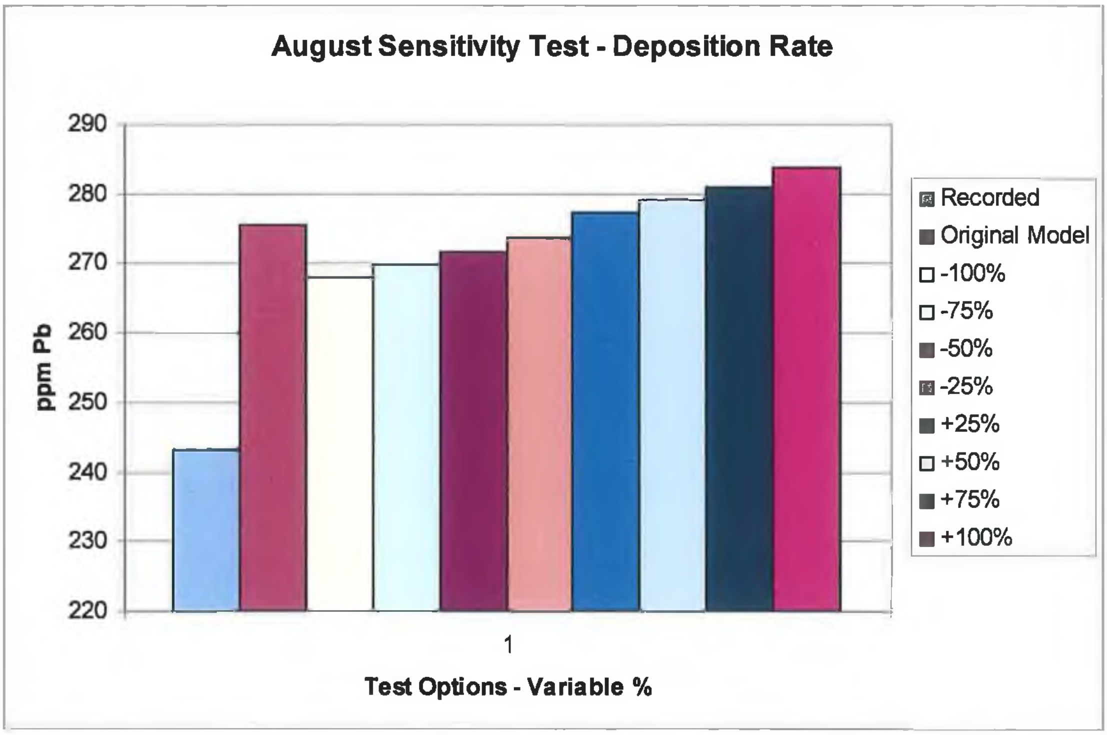
APPENDIX D
Model Sensitivity Testing

Model Sensitivity Testing

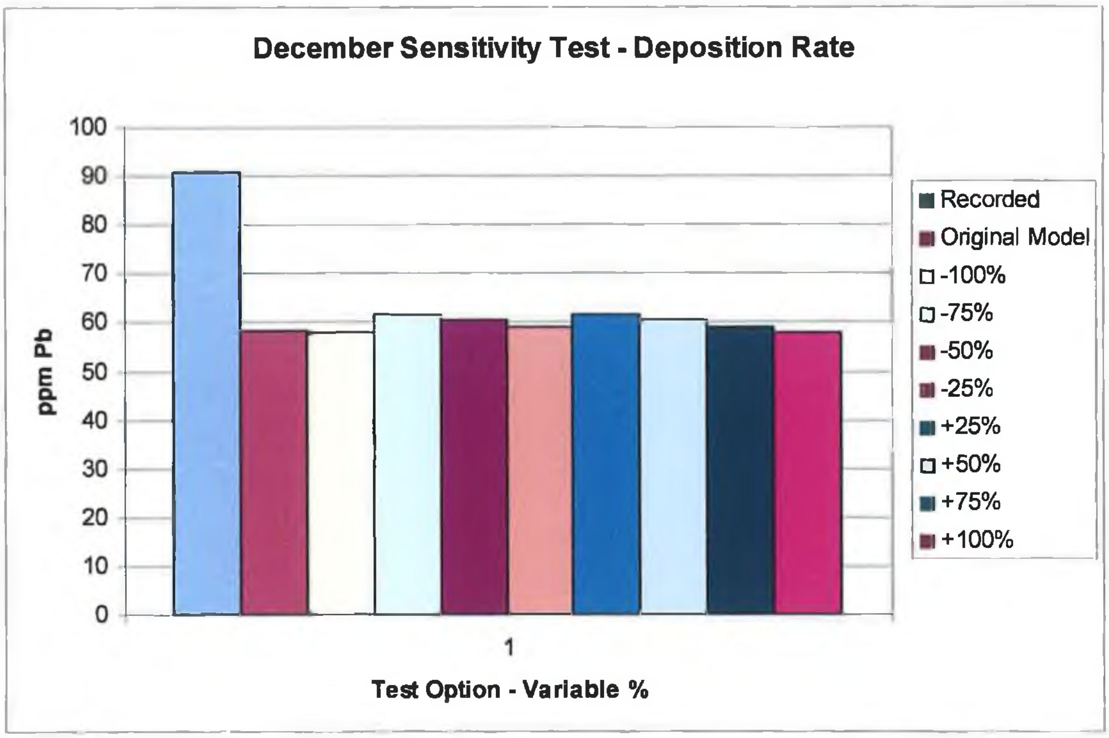
The three mechanisms used in the model were subject to sensitivity testing to determine which mechanism was the primary influence on surface sediment metal concentration change over time. Parameter sensitivity was arbitrarily assessed by increasing and decreasing deposition, resuspension and diffusion rates by ± 25 %, ± 50 %, ±75 % and ± 100 % respectively and comparing it to original model predictions (Stow & Bowen, 1980; Chapra, 1997; Characklis & Wiesner, 1997; Mulder & Alexander, 2001; Jahnke et al., 2005). Figures 1 to 12 illustrate these modified rates for Pb and Cu in August and December in comparison to original model predictions.

It was observed that deposition and resuspension of solid material to and from surface sediment layers played a secondary role to diffusion of dissolved metal to and from this layer. Based on modelling predictions seasonal summer accumulation of metals in surface sediment is not dependent on greater SPM deposition rates at that time but on lower resuspension and diffusion rates. It is clearly illustrated that elevating the diffusion rate in summer and winter months increased the accuracy of the model. Varying summer resuspension rates had little effect on model accuracy. However, elevating resuspension rates in winter months did increase model accuracy: a resuspension rate increase of 50 % predicted the measured Cu surface sediment concentration for December.

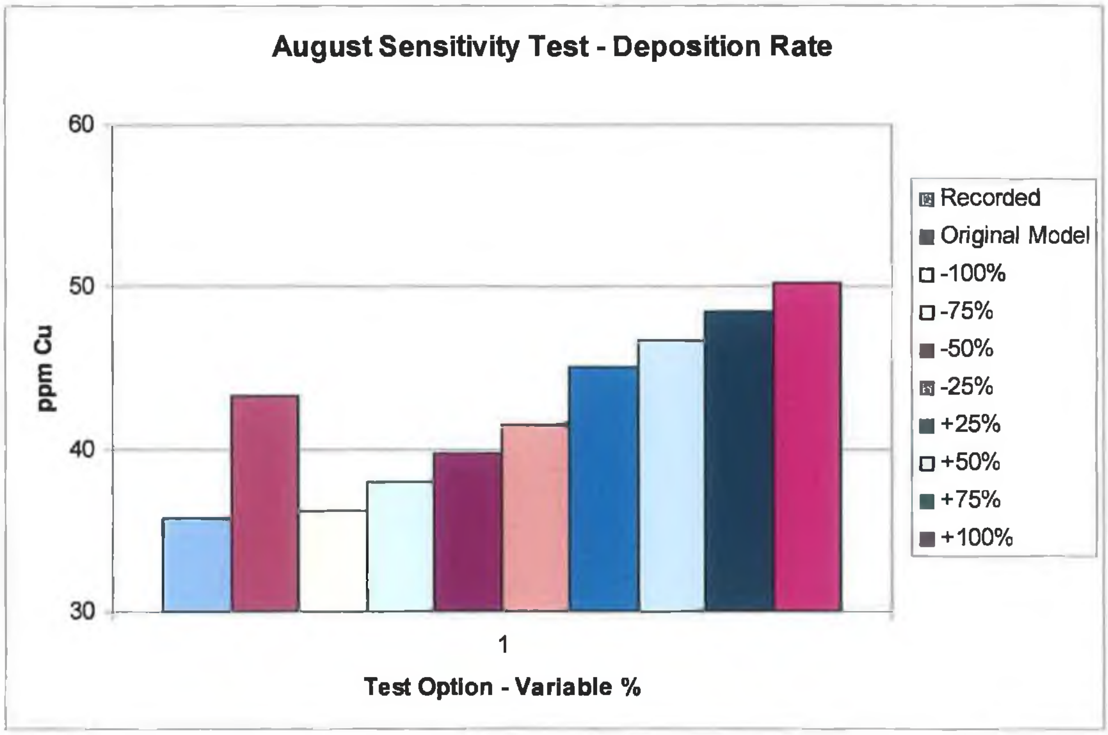
Generally, lowering the diffusion rate increased model accuracy. However, the Pb model predicted a decrease in concentration between November and December while there was an actual increase. Reducing the Pb diffusion rate to non-existent provided a relatively accurate prediction: 86.9 mg Pb/ kg in comparison to the measured concentration of 90.9 mg Pb/ kg. Increasing or decreasing diffusion rates greater than ± 25 % reduced model accuracy, implying that the diffusion rates utilised in the original model are the most viable. Based on model sensitivity testing porewater diffusion between surface sediment and the overlying water column is the primary mechanism for metal accumulation and loss from surface sediment. In summer months lower diffusion and resuspension rates in combination with greater deposition increase surface sediment metal concentration. It is also likely that metal diffusion from the water column down into surface sediment porewater contributes to summer metal accumulation (Chapra, 1997). In comparison, winter month deposition rates play an insignificant role in surface sediment metal dynamics. Metals accumulated by deposition are removed by higher rates of diffusion and resuspension that remove metal from this layer in both dissolved and particulate form.



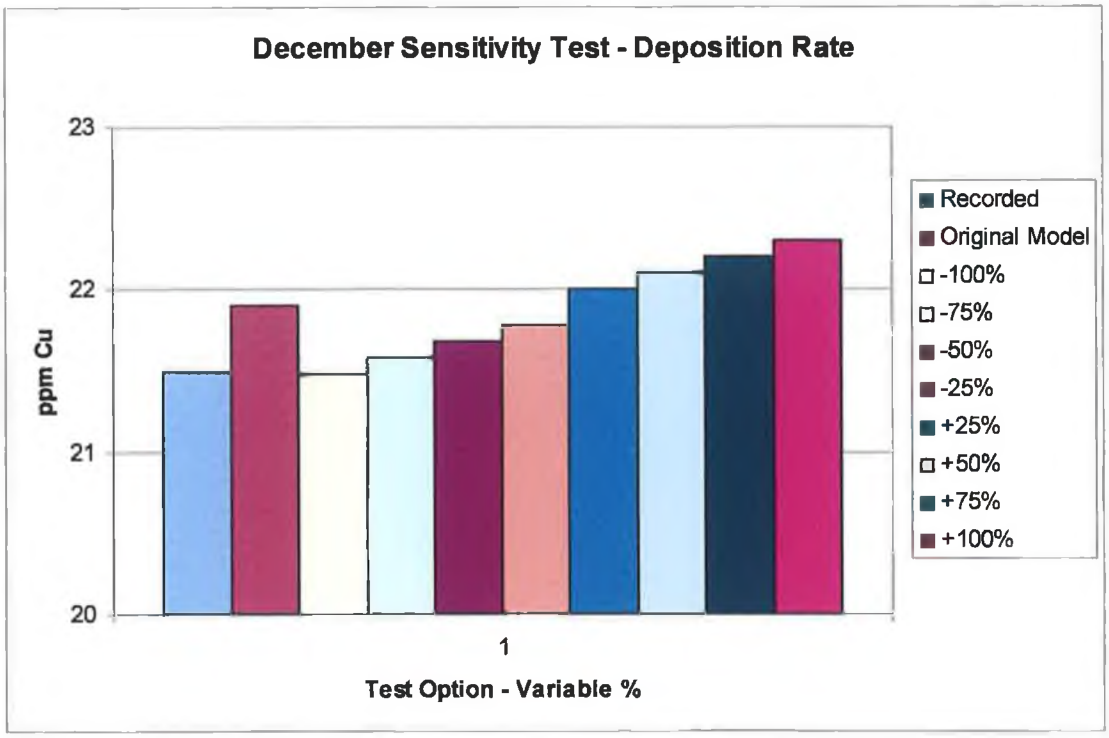
Appendix D Figure 1 Lead Deposition Sensitivity Test, August Model.



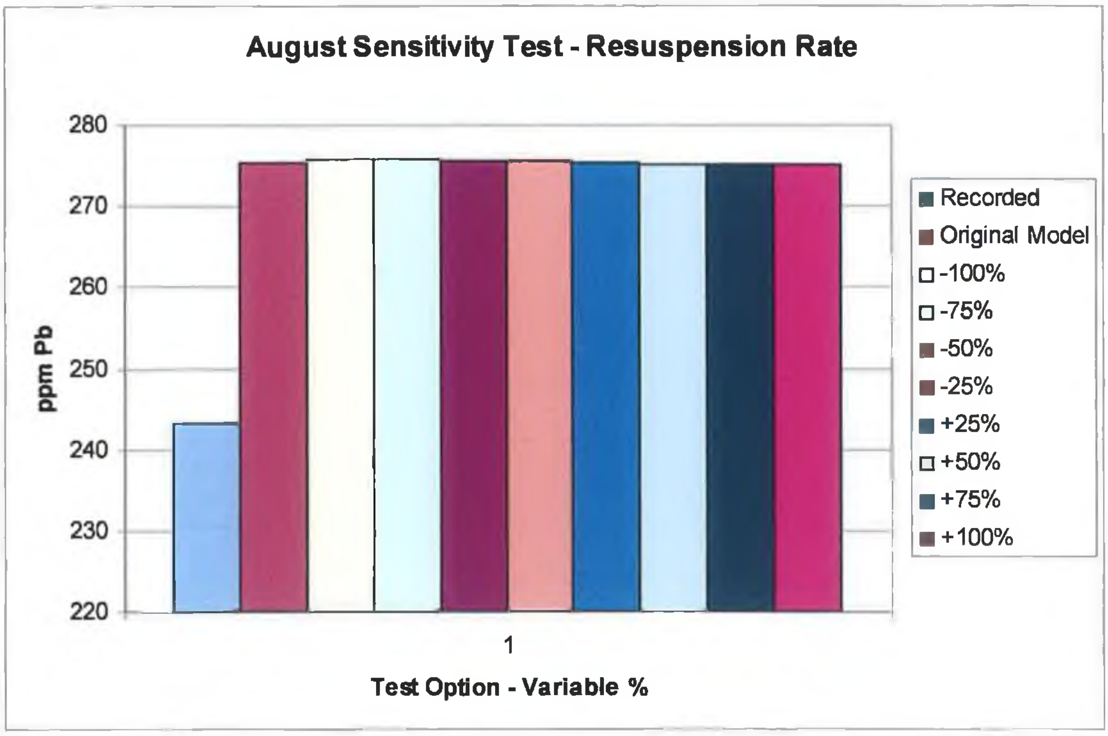
Appendix D Figure 2 Lead Deposition Sensitivity Test, December Model.



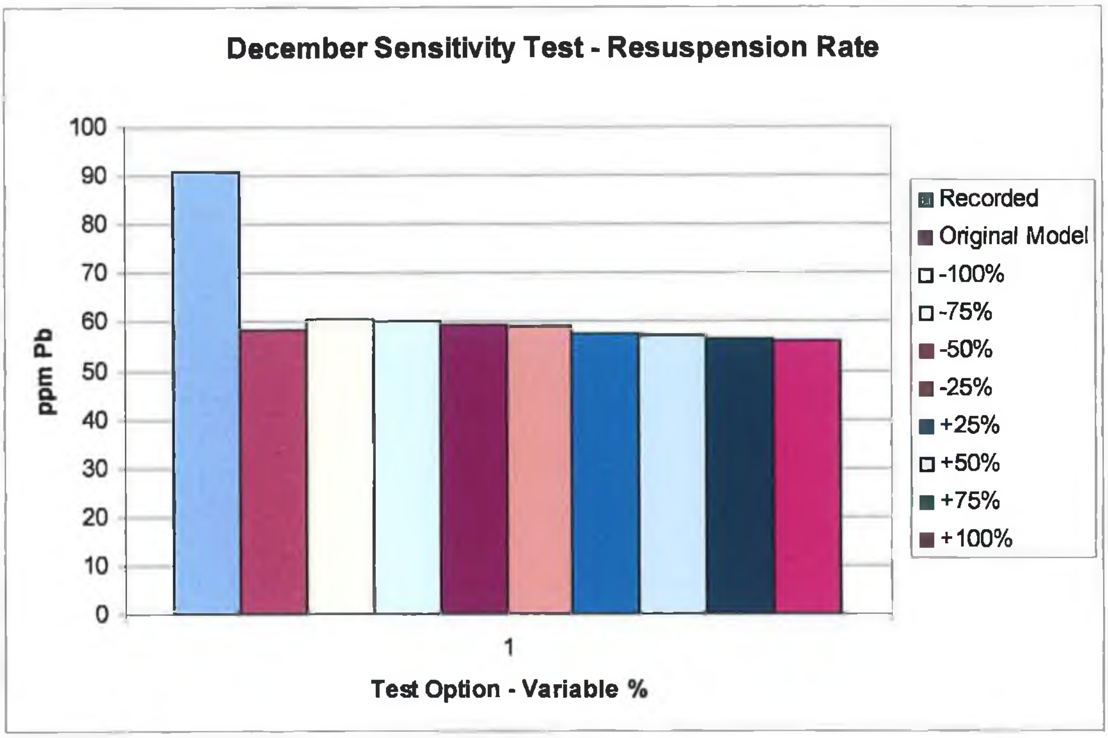
Appendix D Figure 3 Copper Deposition Sensitivity Test, August Model.



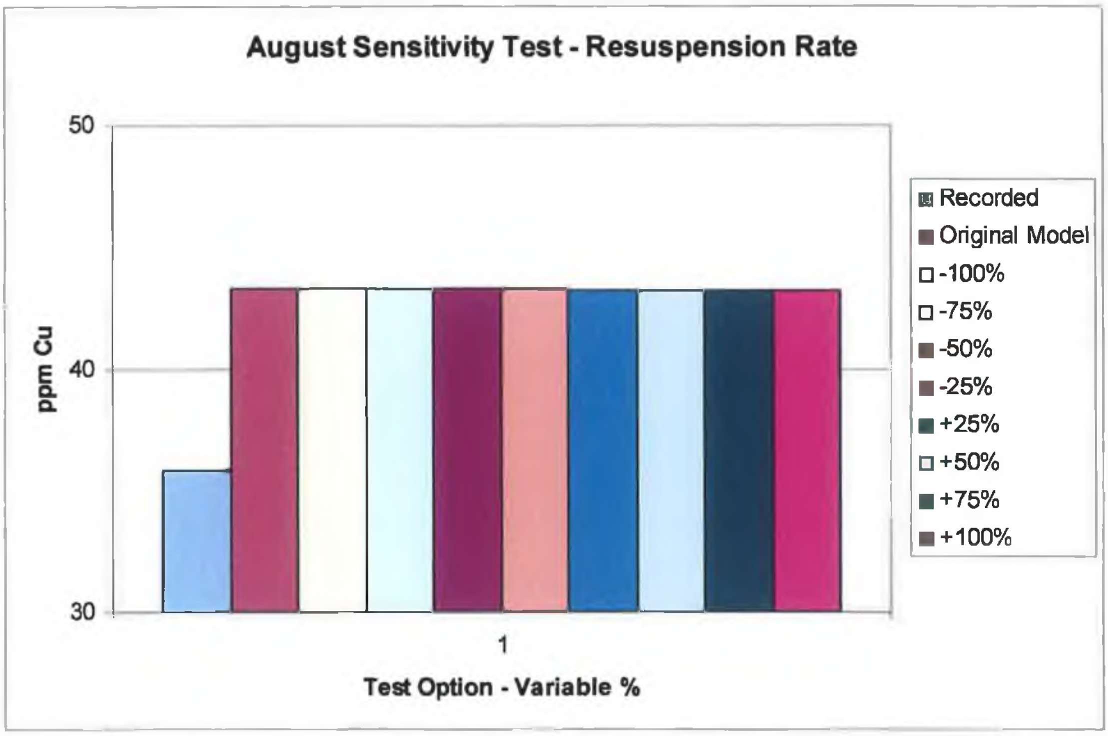
Appendix D Figure 4 Copper Deposition Sensitivity Test, December Model.



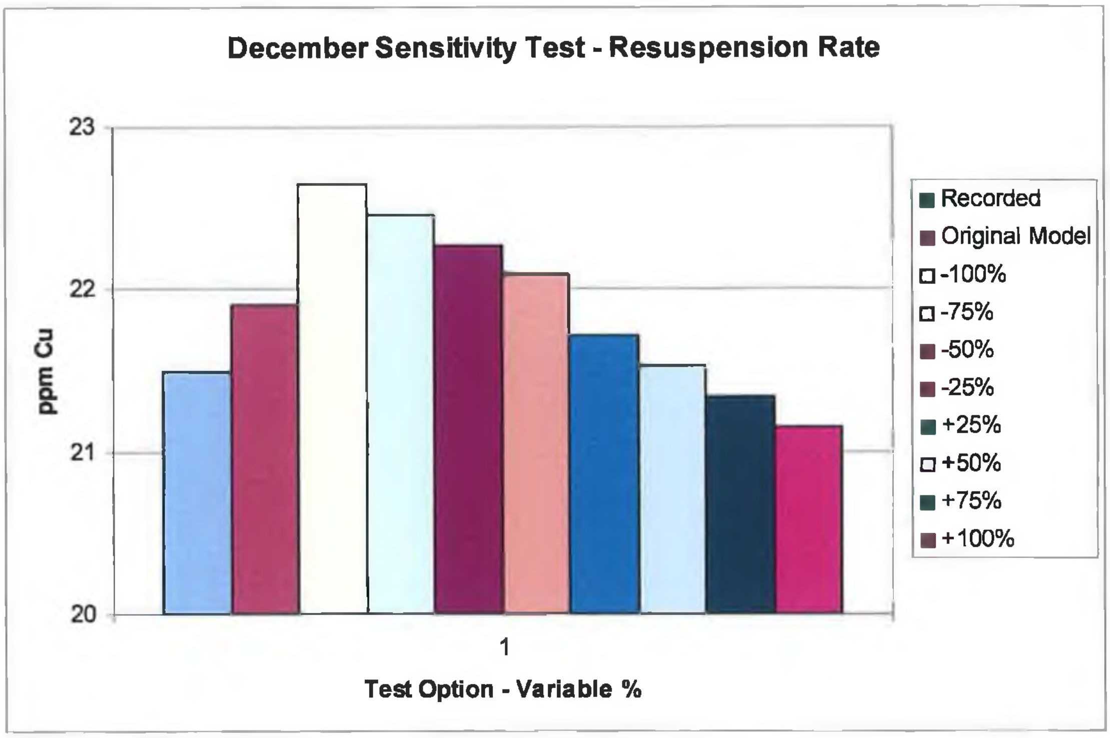
Appendix D Figure 5 Lead Resuspension Sensitivity Test, August Model.



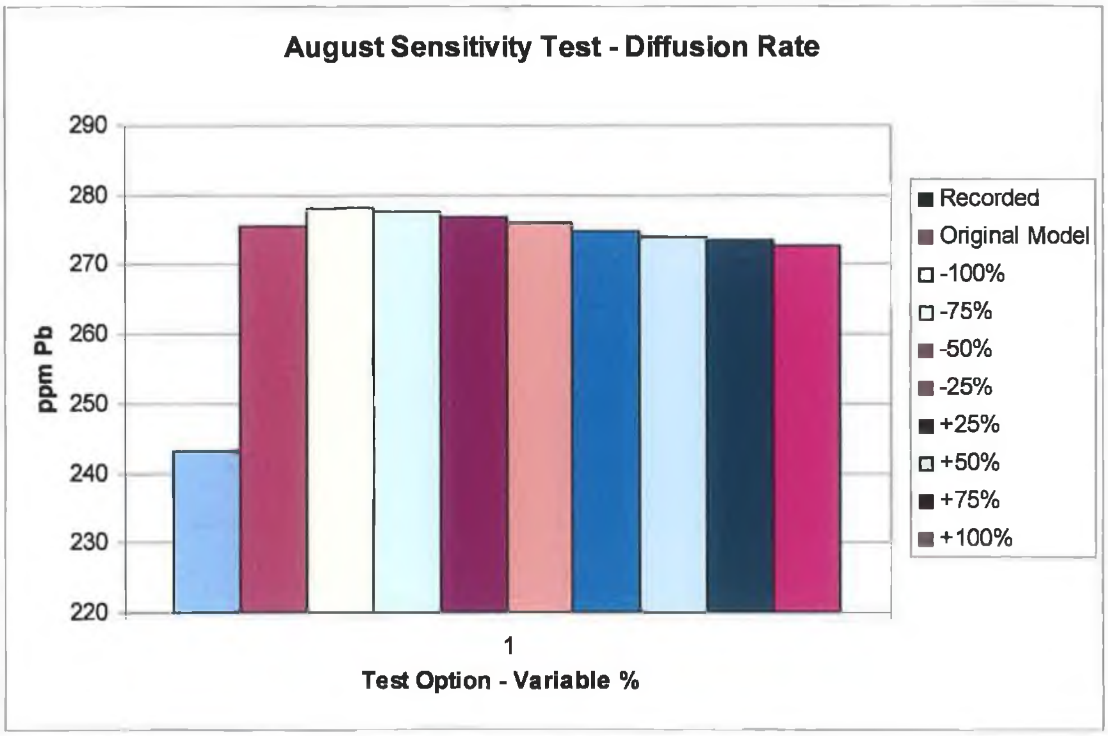
Appendix D Figure 6 Lead Resuspension Sensitivity Test, December Model.



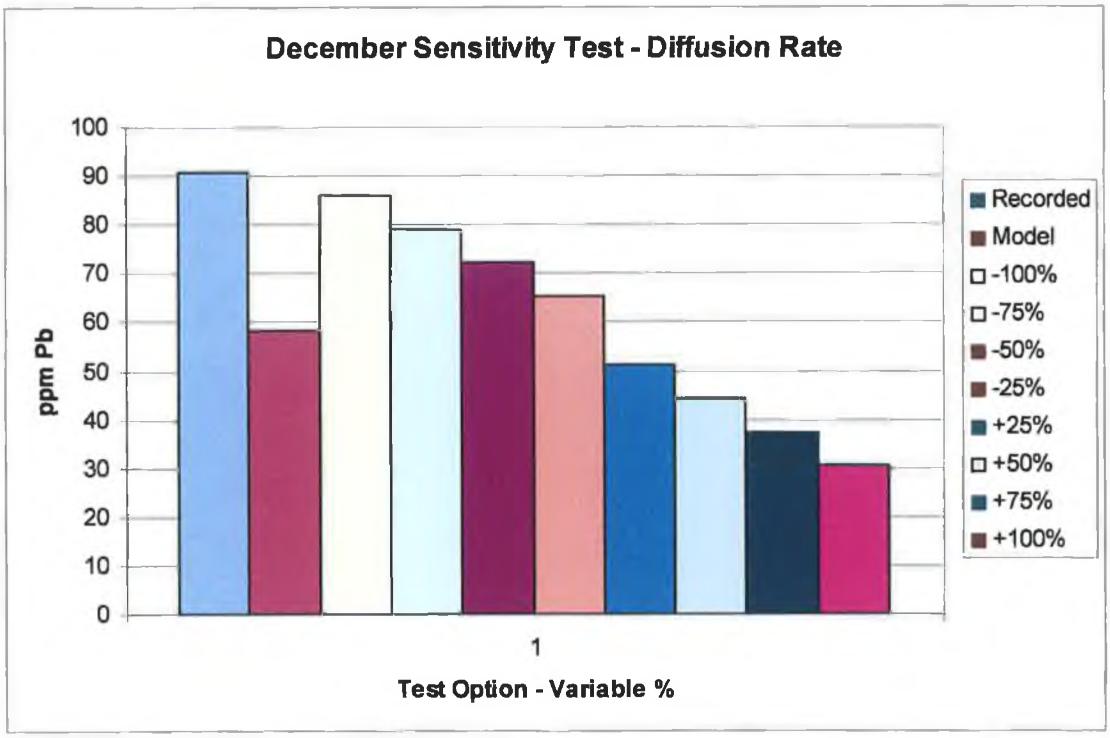
Appendix D Figure 7 Copper Resuspension Sensitivity Test, August Model.



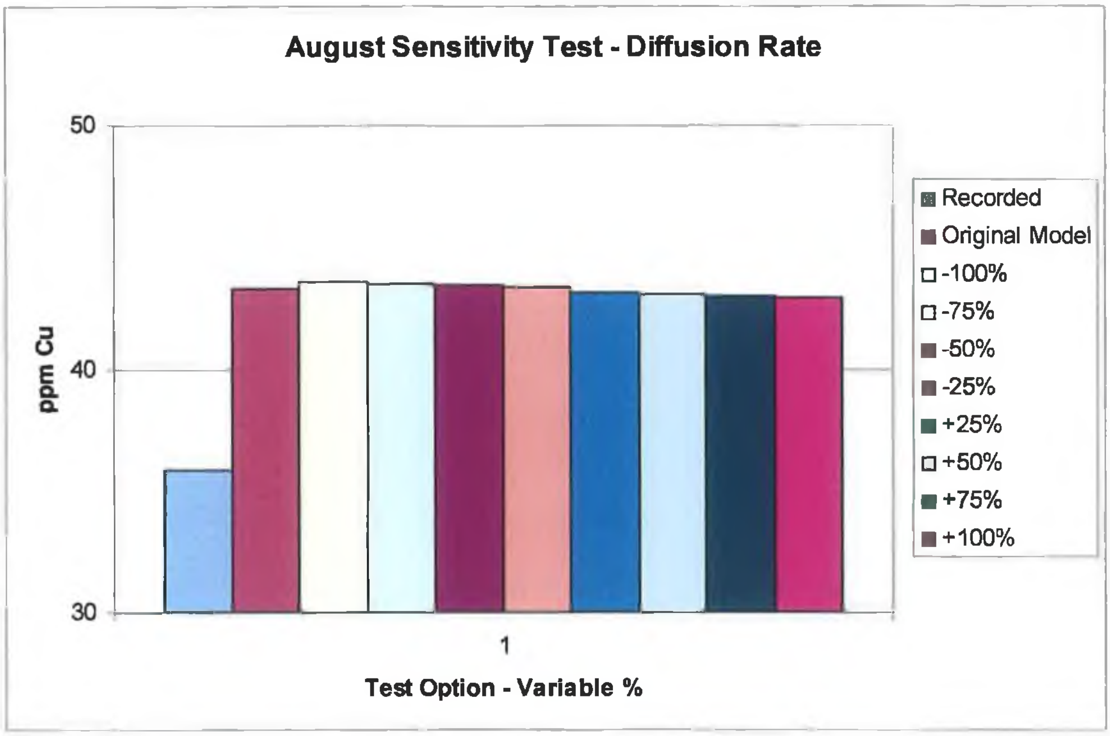
Appendix D Figure 8 Copper Resuspension Sensitivity Test, December Model.



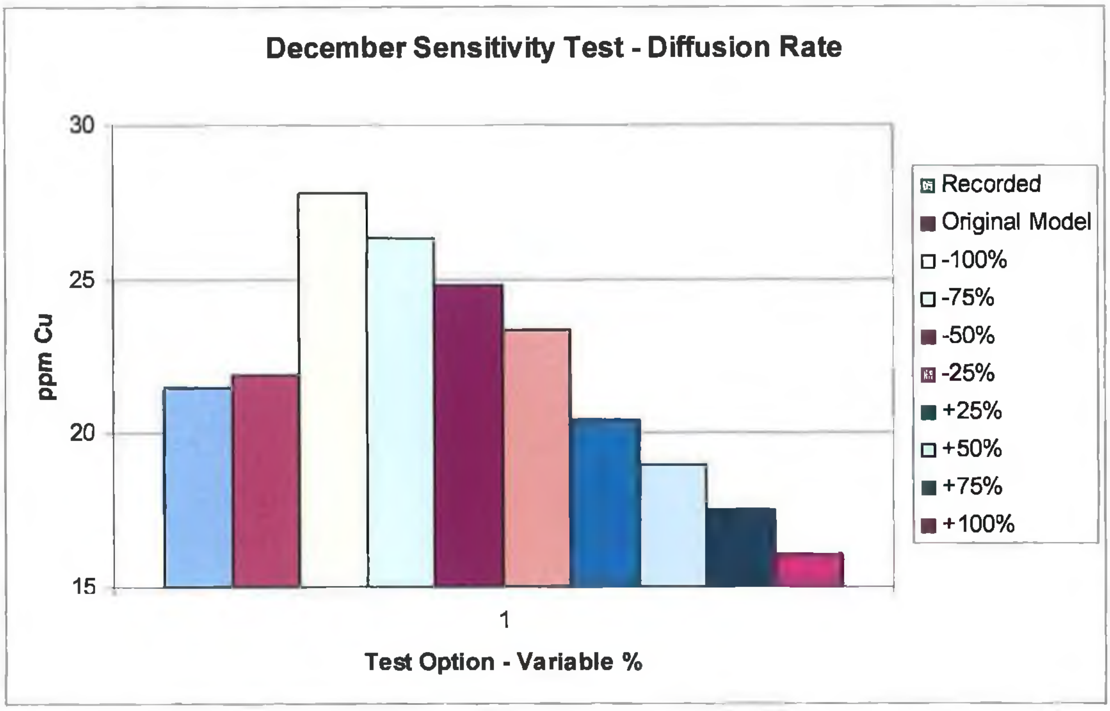
Appendix D Figure 9 Lead Diffusion Sensitivity Test, August Model.



Appendix D Figure 10 Lead Diffusion Sensitivity Test, December Model.



Appendix D Figure 11 Copper Diffusion Sensitivity Test, August Model.

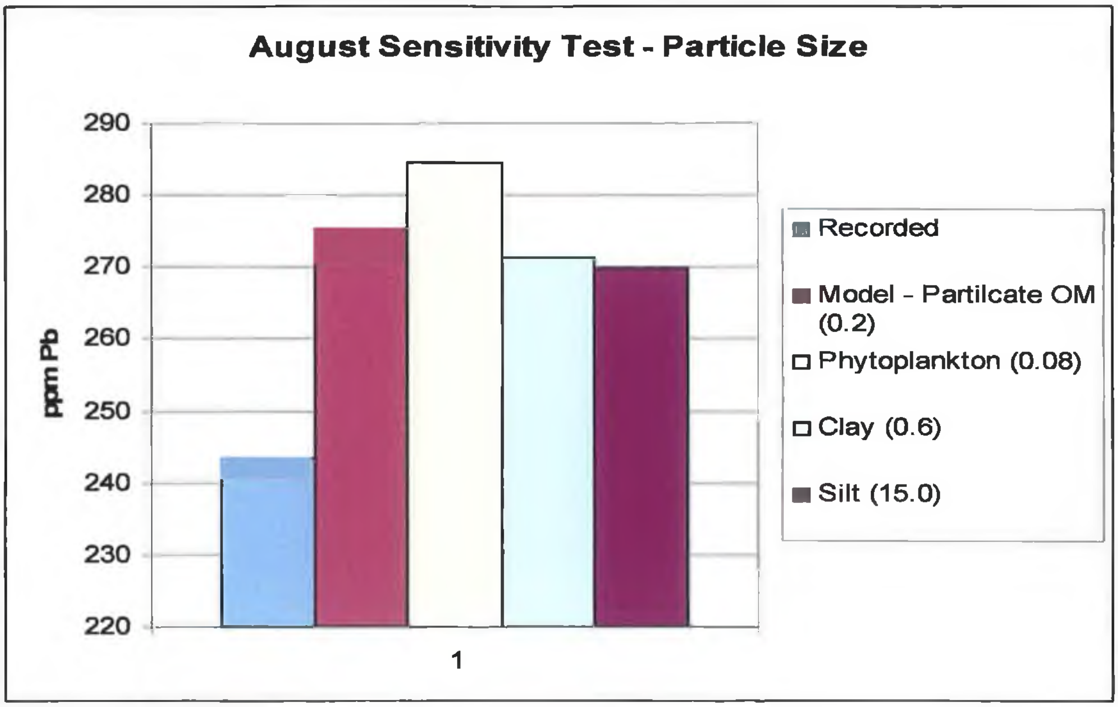


Appendix D Figure 12 Copper Diffusion Sensitivity Test, December Model.

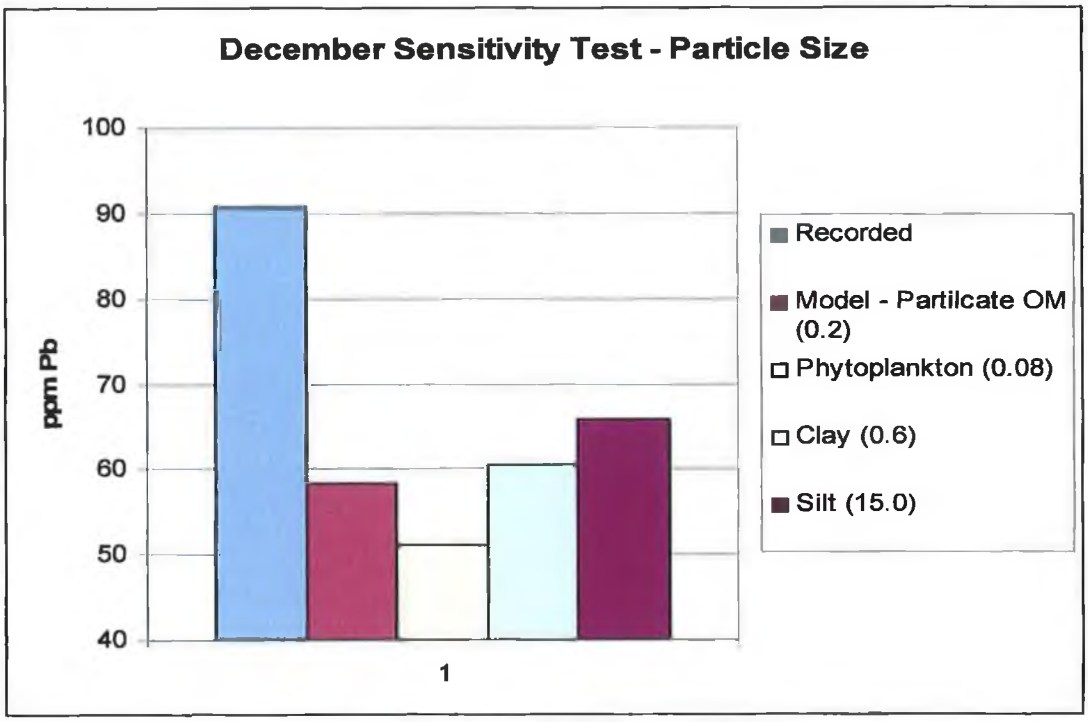
Supplementary to modifying resuspension rate by increasing and decreasing as a percentage, resuspension rates were also modified by altering initial formulation of V_r. This was achieved through utilisation of different particle sizes and associated settling velocities in the V_r equation (Equation 2, page 207). Table 1 indicates particles settling velocities. Altering settling velocities produced minor variations to V_r which were then introduced into the larger mass balance equation. Figures 13 to 16 illustrate the effect particle size has on the mass balance. It can be seen that particle size does play a significant role in determining resuspension rate and subsequently in the mass balance model. While surface sediment densities indicated that SPM was primarily composed of particulate OM (Burns & Rosa, 1980; Stow & Bowen, 1980; Mulder & Alexander, 2001), it has been observed that silt with a faster settling velocity produced modelled results closer to the actual recorded concentrations. This implies that larger inorganic particles play a greater role than particulate OM in metal transportation in aquatic systems. However, it should be noted that particulate OM is primarily bound to larger particles in the water column (Chapra, 1997). Further research into particle/ metal interaction and particle settling velocities would add to the accuracy of this mass balance model.

Particle Type	Average Settling Velocity (m / day)
Phytoplankton	0.08
Particulate 0M	0.2
Clay	0.6
Silt	15.0

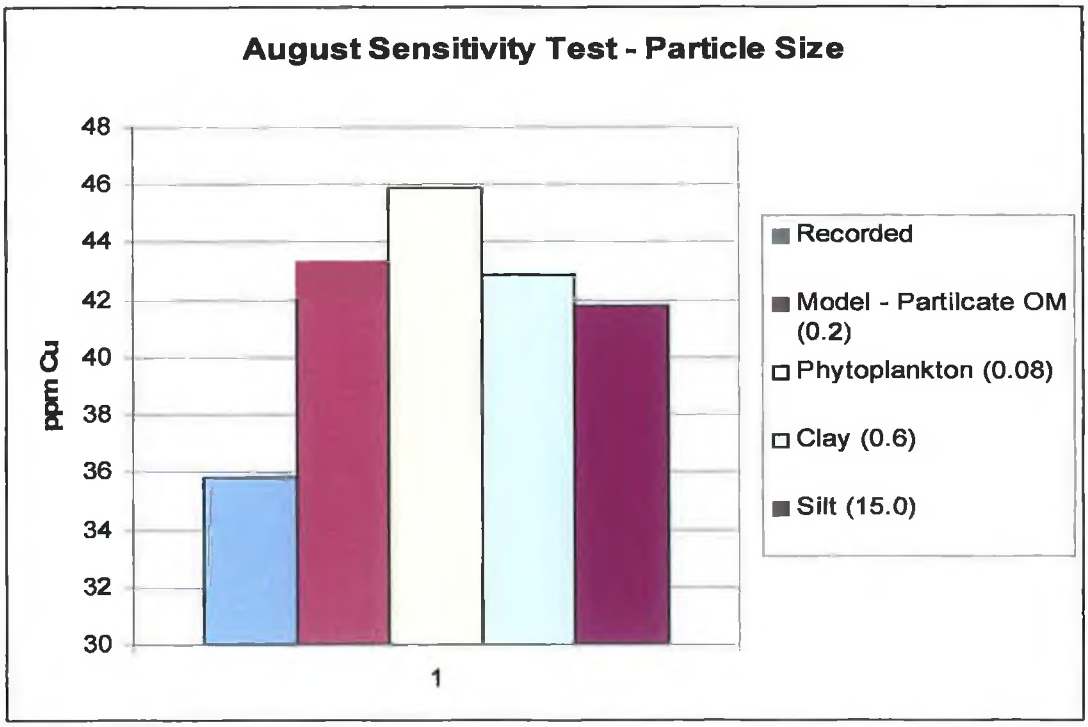
Appendix D Table 1. Particle Average Settling Velocities (m / day) (Burns & Rosa, 1980).



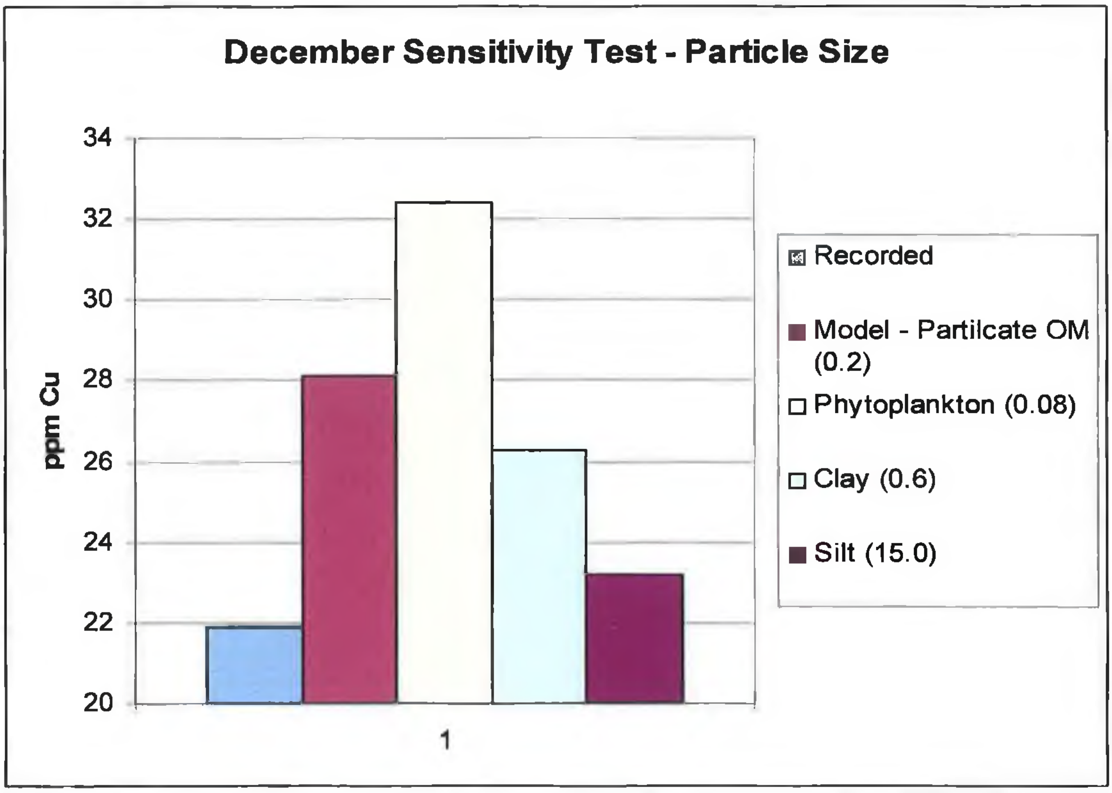
Appendix D Figure 13 Lead Particle Size Sensitivity Test, August Model.



Appendix D Figure 14 Lead Particle Size Sensitivity Test, December Model.



Appendix D Figure 15 Copper Particle Size Sensitivity Test, August Model.



Appendix D Figure 16 Copper Particle Size Sensitivity Test, December Model.

APPENDIX E
Publications

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MARINE POLLUTION BULLETIN
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Baseline

Spatial distribution of nine metals in surface sediment of an urban estuary prior to a large scale reclamation project

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Dublin is a city of 1.1 million people (Central Statistics Office, 2002). The majority of its import/exportation occurs through Dublin Port. The port is situated near the city centre between the estuarine zones of two rivers—the Liffey and the Tolka and has an import/export turnover of 23.5 million tonnes, 1.4 million passengers and an estimated 8000 vessels pass through it annually (Dublin Port Authority, 2005). To facilitate expansion of the port Dublin Port Authority plans to reclaim 21 ha of the estuarine zone between the retaining walls of the port to the north of the Liffey channel and south of the Tolka estuary. The impact this reclamation will have on the estuarine zone has been documented in an environmental impact statement (Dublin Port Authority, 2002). However, dredging and construction work in estuarine zones has been known to release metals locked in subsurface sediment back into the estuarine aquatic system (Caplat et al., 2005). This potential release of metals may cause deleterious effects on the estuarine ecosystem.

The impact Dublin Port currently has and will have on the estuarine zone of the Liffey River is monitored as it is Dublin's primary river and freshwater source to Dublin Bay. However, the Tolka River is Dublin's secondary river and its estuarine zone to the north of the port is monitored for metal contaminants infrequently. The Tolka estuary has the only significant intertidal mudflats within the combined estuarine zones of the Tolka and Liffey (Fig. 1), and it is directly adjacent to a wetland site of international environmental importance, designated by the Ramsar Convention 1971—Bull Island and its lagoons (Dublin Bay Project, 2001). Assessment of metal concentrations in surface sediment prior to reclamation provides a baseline survey to ascertain future impacts this project may have on pollution levels in the estuarine zone.

The Tolka River flows through the northern suburbs and inner city and its estuarine zone is on the northern side of Dublin Port. The estuary is approximately 2 km^2 and has man-made margins. It is located entirely in the urban landscape of Dublin City. It is bounded by the suburbs of Fairview and Clontarf to the west and north, Dublin Port and East Point business park to the south and the Bull Wall and Bull Island to the east. The river course is urban for 12 km. It flows through the suburbs of Tyrrellstown, Blanchardstown, Finglas, Glasnevin, Drumcondra and Fairview before entering the estuary. The Tolka River has been noted for its fish kills caused by pollution incidents (Department of Environment and Local Government, 1998; Dublin Bay Project, 2001). The enclosed nature of the estuary minimises marine flushing, increases sediment deposition and retention which subsequently lead to metal retention in surface sediment. The urban environment itself is a source of metals to this river system. A key source of metals to the Tolka River is caused by groundwater seepage and an inflowing tributary from the closed Dunsink Landfill 200 m north of the river in the north-west of Dublin City. Dublin Port, the Liffey River and local boating activity on the estuary are also potential sources of various metals to the estuary. Furthermore, Pb and Zn ores are exported through Dublin Port and significant concentrations of both Pb and Zn attributed to ore spillages have been recorded in sediment from the Alexandria Basin (Davoren et al., 2005).

Sampling took place over a 6-h period on February 6th 2005. A 20 point sample network was established, 10 points in the Tolka River and 10 points in the estuary (Figs. 2–4). Standard sampling methods as defined by the Irish Estuarine Research Group (IERP) were employed (Jeffrey et al., 1985). Sediment from the surface oxygenated layer which was identified visually was sampled. The oxic layer was approximately 100 mm deep. A 1 m^2 quadrate was used to mark the boundary of sampling at the site. All surface

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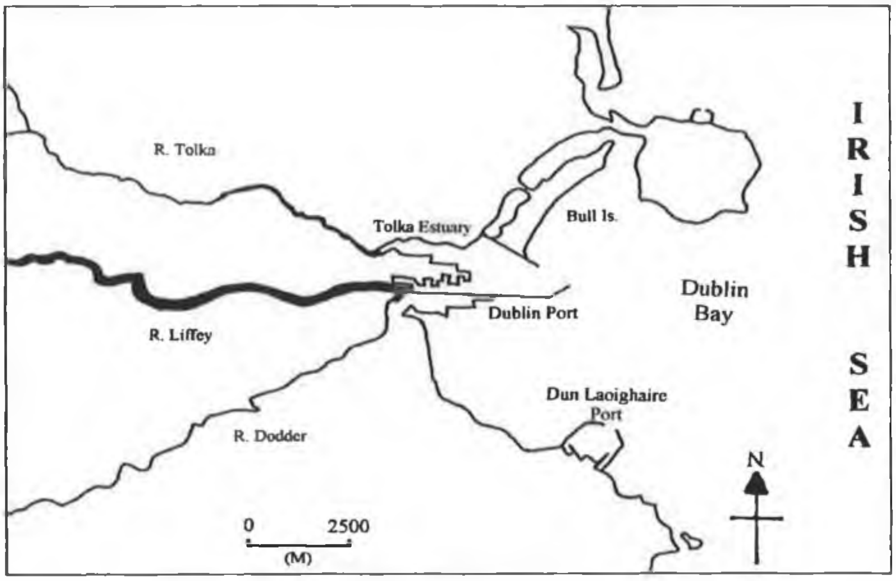

Fig. 1. Map of Dublin Bay and its freshwater inputs.

sediment was sampled within this area using a Teflon coated plastic spatula. Approximately 1 kg wet weight of sediment from each sample point was collected and stored in acid washed polythene vacuum-sealed bags and transported to the laboratory at 4 °C. Sediment was dried at 105 °C for 48 h to remove water content. After drying sediment was disaggregated and sieved (Loring and Rantala, 1992). Sediment was stored at 40 °C in acid washed polythene vacuum-sealed bags. Sediment size was graded by sieving into the following sieve ranges; >500 μm, 500–250 μm, 250–125 μm, 125–63 μm and <63 μm. Sediment with a grain size of <63 μm was utilised for metal digestion.

A HNO_3 digestion was used for the metal analysis (Jeffrey et al., 1985; Kramer et al., 1995; Groengroeft et al., 1998). Samples from each site were analysed in triplicate. Sediment (0.1 g) was placed in a digestion tube with 20 ml 65% HNO_3 and contacted for 48 h at room temperature. Samples were subsequently heated to 100 °C for 2 h. Another 10 ml 65% HNO_3 was added and the sample was heated to 150 °C for 1 h to reduce the volume to approximately 1 ml. Samples were cooled for 24 h at room temperature, filtered through Whatman No. 1 filter paper and made up to 25 ml with deionised water from an Analyst HP, Purite Select Deioniser (Purite Ltd., Leeds, UK). Metal concentrations were determined using an EG&G model 394 electrochemical trace analyser with a 303 A static mercury drop electrode (EG&G Instruments, Princeton Applied Research, CA, USA). Differential pulse polarogra-

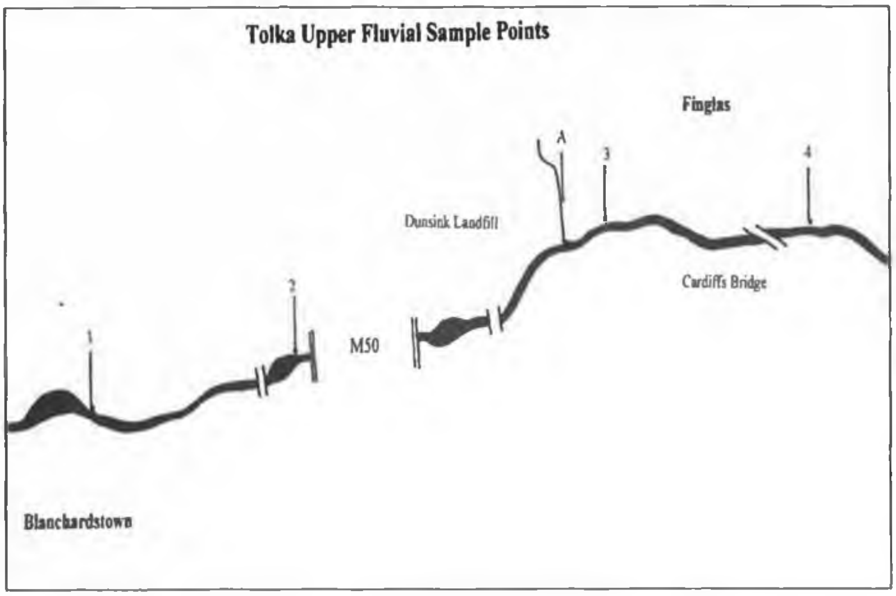

Fig. 2. Tolka River Upper Sampling Regime; Sites 1–4 and Site A.

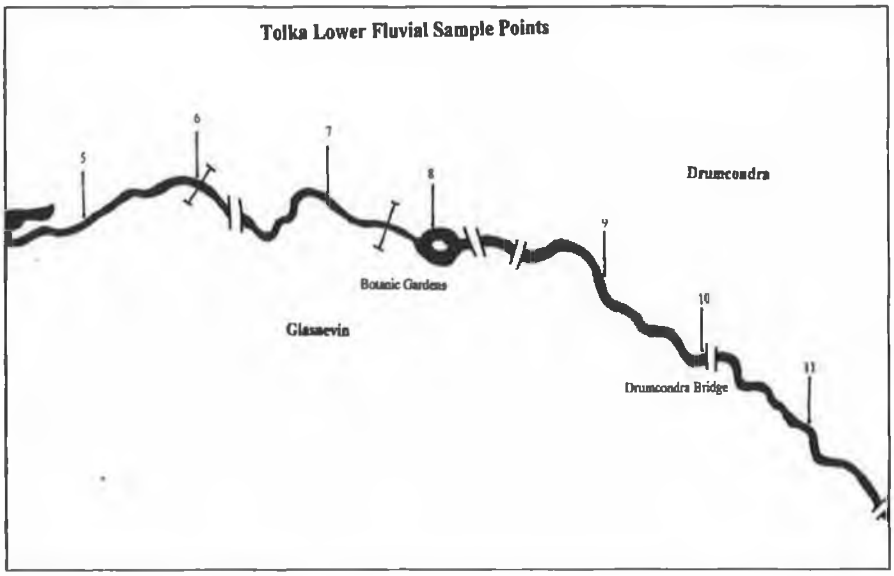

Fig. 3. Tolka River Lower Sampling Regime; Sites 5–11.

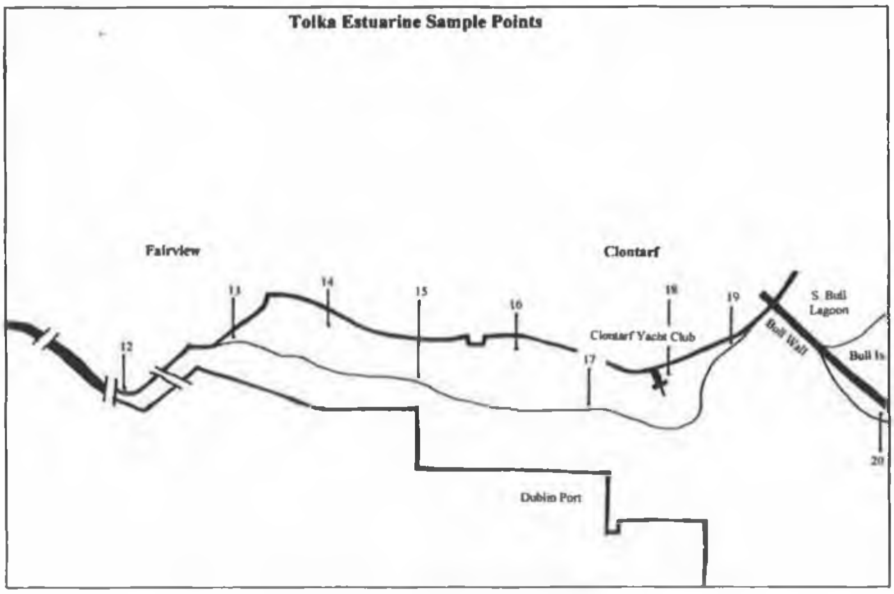

Fig. 4. Tolka Estuarine Sampling Regime; Sites 12–20.

phy (pulse amplitude 50 mV) and a hanging mercury electrode (HMDE) with appropriate supporting electrolyte solutions were employed for analysis (Princeton Applied Research, 2005). Samples were purged with N_2 for 240 s. The solutions were then scanned from 0.0 to −2.0 V with a scan rate of 4 mV/s and scan increment of 4 mV (Ghoneim et al., 2000). The metal electrolyte solutions, recommended peak wavelengths and actual peak wavelengths used are shown in Table 1. Acid digested samples required minor variations on electrolyte solution pH for clear peak definition and this is responsible for shifts in peak wavelength (Buggy and Tobin, 2003). All reagents were supplied by Sigma-Aldrich Ireland.

Table 1
Electrolyte solution guideline wavelengths (Princeton Applied Research, 2005) and operating wavelengths

Metal	Supporting electrolyte	pH	Recommended $E\frac{1}{2}V$	Actual $E\frac{1}{2}V$
As(III)	1 M HCl	1.8	−0.430	−0.392
Cd(II)	0.2 M NH_4 citrate	3.2	−0.620	−0.560
Co(II)	1 M NH_3–1 M NH_4Cl	2.5	−1.220	−1.410
Cr(III)	0.2 M KSCN	2.9	−0.850	−0.786
Cu(II)	0.2 M NH_4 citrate	3.2	−0.070	−0.008
Mn(II)	1 M NH_3–1 M NH_4Cl	2.5	−1.660	−1.086
Ni(II)	1 M NH_3–1 M NH_4Cl	2.5	−1.000	−1.212
Pb(II)	0.2 M NH_4 citrate	3.2	−0.450	−0.404
Zn(II)	0.2 M NH_4 citrate	3.2	−1.040	−1.020

The urban environment comprises approximately 50% of the river catchment area and urban runoff likely contributes appreciable metal concentrations across the complete river and estuarine system. However the riverine and estuarine sections of the Tolka exhibited differing metal spatial trends. Most noticeably, riverine surface sediment metal concentrations were elevated in proximity to a significant pollution source that distorts the spatial trend in the river's upper section. The Tolka River is located 200 m from the 32 ha Dunsink landfill. This landfill has a subterranean stream that enters the river upstream of Site 3. As the stream runs through the landfill, leachate contamination in the tributary sediment is expected and indeed appreciable metal concentrations were observed in this tributary prior to entering the Tolka River (Table 2). In consequence Sites 1 and 2 located farther upstream of the tributary had lower metal concentrations for several of the metals examined (As, Cd, Co, Pb and Zn) whereas Site 3, directly downstream of the tributary had the highest metal concentrations in the riverine section (Table 3). Clearly the landfill was the significant source of these metals in the river (Fig. 5(a)–(c), (h) and (i)). Downstream of Site 3 concentrations of Cd and Pb diminished to similar levels observed upstream of Site 3. Similarly, As, Co and Zn concentrations decreased downstream but were considerably higher than upstream Sites 1 and 2. While Cr, Cu, Mn, and Ni concentrations were elevated in the tributary and also were highest at Site 3 (Table 3), the distinct spatial distribution for the previous five metals was not evident (Fig. 5(d)–(g)). Metal concentrations were lower in the riverine section

Table 2
Surface sediment metal concentrations in Dunsink Tributary

Metal	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
Site A	110 ± 1.0	1.1 ± 0.1	77 ± 2.0	13 ± 0.2	115 ± 0.5	45 ± 0.5	21 ± 0.5	166 ± 5.0	97 ± 2.8

All data in mg/kg.

Table 3
Surface sediment sites of maximum metal concentration

Metal	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
Riverine site	(3) 89.2	(3) 0.27	(3) 56.0	(3) 8.29	(3) 19.3	(3) 41.0	(3) 11.1	(3) 76.5	(3) 65.6
Estuarine site	**(18)** 111.5	**(15)** 0.57	**(17)** 90.3	**(18)** 9.89	**(16)** 34.0	**(16)** 67.9	**(17)** 23.9	**(16)** 131.1	**(18)** 93.7

All data in mg/kg; sites in parentheses.

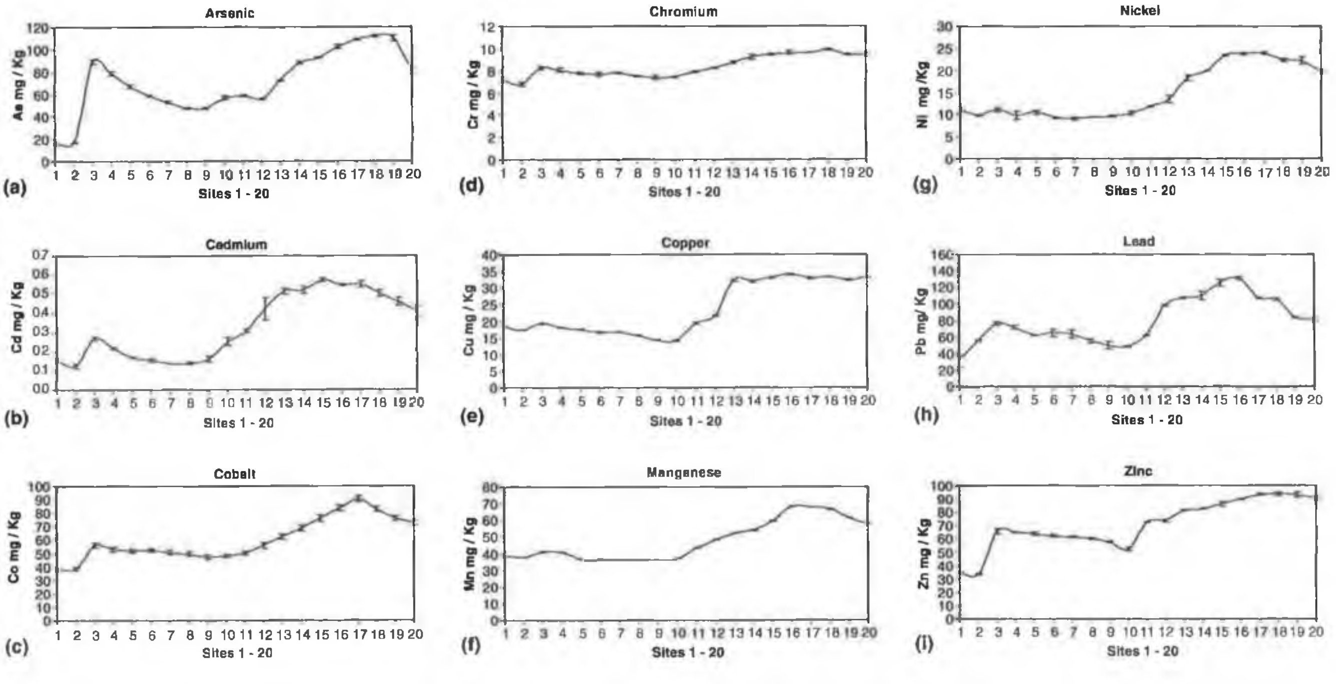

Fig. 5. (a)–(i) As, Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn concentrations, Sites 1–20. Error bars indicate the standard deviation of triplicate sampling preparation.

Table 4
Norwegian classification of environmental quality and degree of pollution

Metal	Good	Fair	Poor	Bad	Very bad
Arsenic	<20	20–80	80–400	400–1000	>1000
Cadmium	<0.25	0.25–1	1–5	5–10	>10
Chromium	<70	70–300	300–1500	1500–5000	>5000
Copper	<35	35–150	150–700	700–1500	>1500
Lead	<30	30–120	120–600	600–1500	>1500
Nickel	<30	30–130	130–600	600–1500	>1500
Zinc	<150	150–650	650–3000	3000–10,000	>10,000

All data in mg/kg (IADC/CEDA, 1997).

Table 5
Irish Estuarine Research Programme Guideline Metal Concentrations

	Metal								
	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
Baseline	5	0.5	5	5	5	150	5	10	20
Threshold	100	1.5	10	50	50	500	20	100	100

All data in mg/kg (Jeffrey et al., 1985).

than the estuary due to its constant flushing of contaminants downstream. Riverine surface sediment metal concentrations were well within Irish and Norwegian acceptable guideline levels (Tables 4 and 5).

The estuary exhibits a distinct spatial trend. Generally the lowest concentrations were found in inner and outer estuarine sections with the maximum contamination observed in the middle estuary. The metal load of the Tolka River is the primary metal source to the inner estuary. Here, metal concentrations were lower and increased through the middle section of the estuary, and reached a plateau before dropping in the outer section of the estuary. Local boating activity in the middle and outer estuary likely contributes significant quantities of metals from yacht antifouling paints to these estuarine zones. As, Cd, Cr, Cu, Pb and Zn have been used in antifouling paints in recent years as an alternative to tributyltin (Bryan and Langston, 1992; Yebra et al., 2004). In particular As and Zn concentrations were elevated at Site 18 and adjacent sites and are likely associated with antifouling paint residues arising from boat maintenance and cleaning in the sites vicinity. Generally the influence of boating activity on metal concentrations at sites of the middle estuary may be seen in the elevated metal concentrations between Sites 15–18 (Table 3). Also the yachting channel runs directly from this point to the Liffey Channel and pollutant backwash in this channel may have contributed metals to this zone. Influx of marine water through the ports retaining walls forces the Liffey riverine water up the yachting channel to mix with the Tolka riverine water in the middle estuary. Deposition of the Liffeys suspended load occurs in this section and contributes to elevated metal concentrations in the middle estuary.

The convergence zone between marine waters and freshwaters is often called the mid-estuarine maximum and makes the middle estuary sites the most contaminated in the sample network. In the Tolka this area was situated approximately between Sites 14 and 18. This mid-estuarine maximum has been observed in other estuaries (Caccia et al., 2003; Gerringa et al., 2001; Yang and Sanudo-Wilhelmy, 1998). This spatial trend is more distinct for As, Cd, Mn and Pb (Fig. 5(a), (b), (f) and (h)).

Some metal concentrations observed in this work may be considered deleterious to the estuarine ecosystem as indicated by IERP guideline threshold levels (Table 5). In particular As, Co, Ni and Pb sediment concentrations were above the threshold level at certain sites of the middle estuary. In contrast Norwegian guidelines classify the Tolka estuary as in a fair condition, Cr, Ni and Zn concentrations were good, Cd and Cu were fair and only As and Pb concentrations were classified as poor (Table 4).

Construction of the new 21 ha of Dublin Port will require 409,000 m^3 to be dredged from the Tolka estuary and Liffey Channel over an eight-month period. Fill material (1.2 million m^3) will be deposited in this area during reclamation. This will primarily consist of recycled construction materials from the Dublin Port Tunnel project (Dublin Port Authority, 2002). Intermittent introduction of metals to the estuarine aquatic system from sub surface sediments during dredging and reclamation would increase metal concentrations in surface sediment in the tidal zone and would have an adverse effect on biota in the estuary. The project will also constrict the throat of the Tolka estuary. This would result in an increase of tidal flow strength entering and leaving the estuary. Because of the disparity in volume either side of the reclamation/North Bull Wall throat, currents are likely to increase in the outer Tolka estuary (Dublin Port Authority, 2002). This constriction of the mouth of the estuary will also impede flushing of the estuary and increase siltation within the estuary, which may be expected to further increase metal concentrations in surface sediment. The clockwise rotational gyre which carries water from the Liffey River into the Tolka estuary is also expected to increase in strength after the reclamation process (Dublin Port Authority, 2002). A subsequent increase in metal contamination from the Liffey River depositing in the Tolka estuary might be expected.

In conclusion, metal concentrations in sediment of the Tolka River are not of a significant level except in close proximity to the landfill leachate stream. However, metal concentrations in the estuary can be categorised as potentially harmful to the benthic community of this system. Also, the possibility exists for the Tolka estuary to change from a fair to a poor or bad condition. This will depend largely on the management and future impact of the Dublin Port reclamation project.

Acknowledgements

The authors wish to acknowledge the support of the Environmental Protection Agency of Irelands ERTDI programme, Dublin City University and Wexford County Council for supporting this study.

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Seasonal and spatial distributions of tributyltin in surface sediment of the Tolka Estuary, Dublin, Ireland

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TBT concentrations varied with seasons and correlated well with organic matter.

Abstract

Aquatic pollution by tributyltin (TBT) is of concern because of its high toxicity to marine life. TBT loadings of estuarine sediments may remain elevated because of long flushing times in estuaries due to their enclosed physicality. The Tolka Estuary, Co. Dublin, Ireland, is a typical Irish urban estuary. It has a significant pollution loading. The results of 12 months' analysis of TBT spatial and temporal distributions in this estuary are presented in this paper. Data from a total of 10 sample points are presented. The concentrations of TBT in the sediment were analysed using differential pulse polarography. Significant seasonal and spatial trends in TBT distribution were observed over the 12-month period. TBT concentrations ranged from 0.1 ppb in winter to 8.6 ppb in summer with a 1.5 ppb average. Organic matter (OM) concentrations of sediment exhibited similar seasonal trends and a positive correlation between OM and TBT distributions was observed.

Keywords: Seasonal; Sediment; Tributyltin; Polarography; Estuary; Ireland

1. Introduction

Sediments are increasingly being used to assess anthropogenic impacts on the estuarine environment (Bryan and Langston, 1992; Breslin and Sanudo-Wilhelmy, 1999). Sediments provide a temporally integrated indication of estuarine conditions, and act as a reservoir for various anthropogenic contaminants and so contain concentrations greater than the overlying water column (Caccia et al., 2003). Temporal variation at a site includes natural variance associated with physical, chemical and biological processes. Small-scale spatial variations hinder accurate interpretation of temporal contamination. If these are excessive, larger local and regional trends may be obscured. When temporal trends are large, a single synoptic survey may be insufficient to determine contaminant loading, degradation and circulation over time. Multiple repeated sampling over an extended period at each site is required to address seasonal variation (Birch et al., 2001). Seasonal variation in metal contamination has been observed in aquatic environments (Birch et al., 2001; Caccia et al., 2003). Butyltins are persistent anthropogenic contaminants in aquatic systems (Alzieu, 1998; Meador, 2000; Konstantinou and Albanis, 2004) and seasonal variability of butyltin compounds has been observed previously in mussel tissues (Rivaro et al., 1997) and the estuarine water column (Bancon-Montigny et al., 2004). To date, however, no comprehensive investigation has examined whether butyltin contamination of estuarine sediments may also exhibit temporal variation.

For many years tributyltin (TBT) compounds were the most widely used biocidal additives in antifouling ship-paint formulations (Wade et al., 2004). TBT contamination of the coastal environment has been researched since the 1980s after investigations revealed that TBT released from antifouling paints caused sexual malformations and growth reductions in the

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oyster *Crassostrea gigas* (Alzieu et al., 1986; Bryan et al., 1989; Champ and Wade, 1996). TBT has since been shown to be highly toxic to a wide range of living organisms, particularly gastropods (Fent, 1996). TBT is responsible for imposex, the development of male sexual organs in females of species of neogastropods and megagastropods (Bauer et al., 1995; Gibbs and Bryan, 1996). A few nanograms of TBT can cause sterility in several species of gastropod (Stroben et al., 1992; Santos et al., 2004). TBT has the highest toxicity of the butyltin group (Maguire, 1987). Legislation in many countries including Ireland has banned the application of TBT-based antifouling paints to vessels <25 m (Oireachtas Eireann, 1987). TBT is listed on the European list of most hazardous pollutants to the marine environment in its directive 2455/2001/EC (E.C.O.J., 2001). The International Maritime Organisation (IMO) and the Marine Environmental Protection Committee (MEPC) have recently announced a proposed ban on the use of TBT as antifouling agent on all ships (Konstantinou and Albanis, 2004).

TBT contamination in estuarine sediments can result from direct and indirect sources (Santos et al., 2004). TBT can be transported to an estuary through the fluvial network like other contaminants (Elbaz-Poulichet et al., 2001; Hatje et al., 2001). Besides the direct input of TBT from ships, discharges of dredged sediment can contribute to the TBT load of the water column and recirculate TBT through the estuary (Fent, 1996). TBT half-life in surface aerobic sediments is reported to be in the range of 113–775 days (Waldock et al., 1990; Dowson et al., 1993) while in anaerobic sediments TBT half-life is in the order of tens of years (Dowson et al., 1993). Subsurface sediments therefore act as a reservoir of TBT that can be remobilised and circulated by the water column around the estuary (Unger et al., 1988). TBT can also enter estuarine systems via landfill leachate seepage into rivers and groundwater (Hoch, 2001; Hoch et al., 2003; Asakura et al., 2004; Sudaryanto et al., 2005).

This study is aimed at investigating the spatial and temporal distributions of TBT in an urban estuary. TBT concentrations in sediment were observed at 10 sample points in the estuary and 1 sample point in an upstream tributary every month over a 12-month period.

2. Sample area – Tolka Estuary, Co. Dublin

The Tolka Estuary is approximately 2 km^2 and has man-made margins. It is located entirely in the urban landscape of Dublin City (Fig. 1). It is bounded by the suburbs of Fairview and Clontarf to the west and north, Dublin Port and East Point business park to the south and the Bull Wall and Bull Island to the east. Its main freshwater source is the Tolka River. The Tolka River originates in Co. Meath, its route is primarily over post-glacial tills and gravels, and its subsurface geology is carboniferous limestone and Silurian sandstone. For a large portion of its course the river is exposed to this bedrock. The river is marginally acidic (pH 5–6.5; Buggy and Tobin, 2003). The river course is urban for 12 km. It flows through the suburbs of Tyrrellstown, Blanchardstown, Finglas, Glasnevin, Drumcondra and Fairview before entering the estuary. The Tolka River has been noted for fish kills caused by pollution incidents (Department of Environment and Local Government, 1998; Dublin Bay Project, 2001).

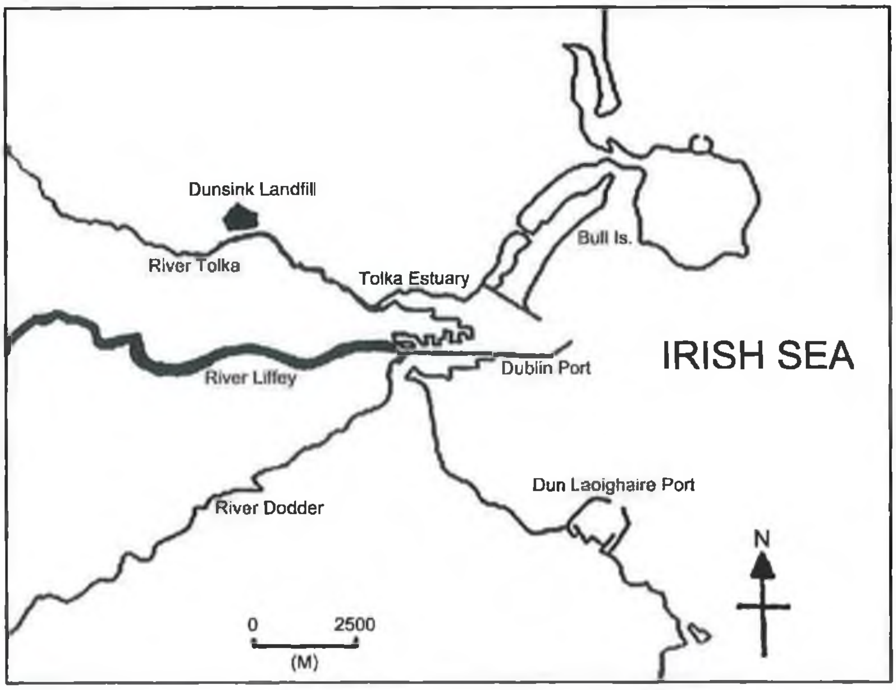

Fig. 1. Map of Dublin Bay and the Tolka River Estuary.

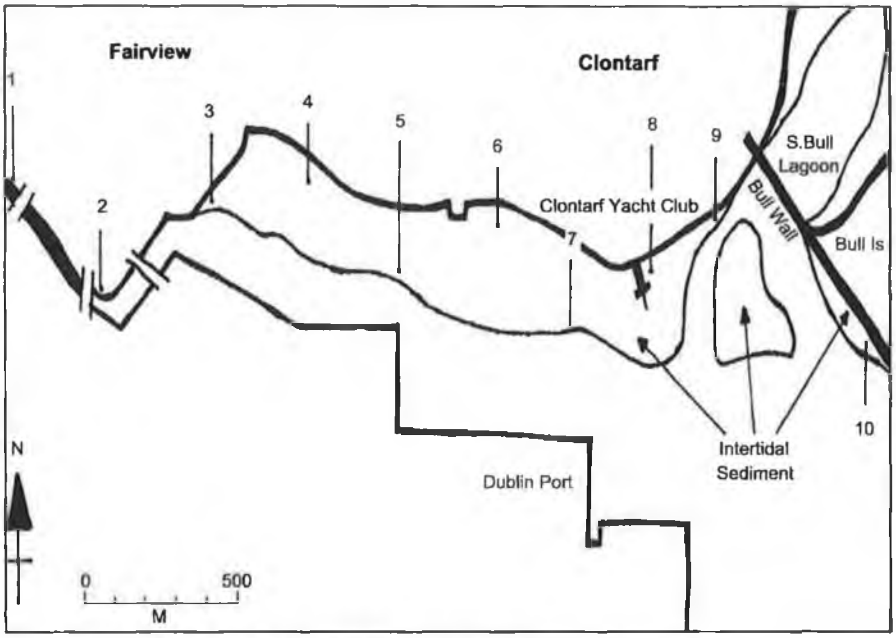

Fig. 2. Map of Tolka estuarine sampling points 1–10.

The Tolka Estuary is subjected to sedimentation from the Tolka River (Jeffrey et al., 1985) but internal circulation between Dublin Ports retaining sea walls also deposits sediment from Dublin's primary river – the Liffey, into the estuary. The enclosed nature of the estuary minimises marine flushing, increases sediment deposition and retention, and allows clearer determination of seasonal contaminant trends in surface sediment. The 10 sample points were located in the intertidal sediment area of the estuary (Fig. 2). The supplementary sample point in the Dunsink Tributary was located 20 m upstream from its confluence with the Tolka River.

3. Materials and methods

3.1. Sediment sampling and treatment

Sediment was sampled at 30-day intervals at each site over a 12-month period. Sampling took place over a 6-h period. Standard sampling methods as defined by the Irish Estuarine Research Group (IERP) were utilised (Jeffrey et al., 1985). Sediment from the surface oxygenated layer was sampled. Visual identification of the oxic layer was sufficient for this sampling mode. The time of year determines the depth of oxygenation. Winter layer was approximately 100 mm deep while summer usually varied between 20 and 50 mm. The pH of sediment porewater was measured in situ using a Hanna (HI 98127 PHEP 4 WP) pH tester. A 1-m^2 quadrat was used to mark the boundary of sampling at the site. All surface sediments were sampled within this area using a Teflon coated plastic spatula. Approximately 1 kg wet weight of sediment from each sample point was placed in acid washed polythene vacuum-sealed bags and transported to the laboratory at 4 °C. The sediment was dried at 105 °C for 48 h to remove water content. After drying, the sediment was disaggregated, sieved (Loring and Rantala, 1992) and stored at 40 °C in acid washed polythene vacuum-sealed bags. Sediment size was graded by sieving into the following sieve ranges; >500 μm, 500–250 μm, 250–125 μm, 125–63 μm and <63 μm. Sediments with a grain size of <63 μm sieve were utilised for TBT extraction. Sample variance is substantially reduced by analysing this fine-grained fraction of sediment to minimise the confounding effects of variable grain size (Birch and Taylor, 1999).

3.2. Tributyltin extraction

A recently developed organotin extraction was utilised for tributyltin (Bancon-Montigny et al., 2004; Munoz et al., 2004; de Mora et al., 2003). Ten grams of dried sediment was contacted with 10 ml of glacial acetic acid, 30 ml of methanol and 60 ml of sodium acetate buffer 0.2 M, adjusted to pH 5.3. Samples were agitated for 24 h followed by 180 min in an ultra-sonic bath and centrifuged at 3000 rpm for 30 min. Control samples including procedural blanks, matrix spikes (10 samples of contaminant free estuarine sediment spiked with 10 ppb TBT) and certified reference materials supplied by the Marine Institute of Ireland, were analysed to establish that the methods used were providing valid results. All samples were run in triplicates and the results given in the study are mean values. The mean recovery rate for TBT was 91% with an SD of ±3.2% ($n = 10$).

TBT concentrations were determined using an EG&G model 394 electrochemical trace analyser with a 303A static mercury drop electrode (EG&G Instruments, Princeton Applied Research, California, USA). Differential pulse polarography (pulse amplitude 50 mV) and a hanging mercury electrode (HMDE) were employed for analysis. A 0.16-M ammonium chloride in 40% ethanol at pH 2.5 electrolyte solution was utilised for TBT determination (White, 2002). Samples were purged with N_2 for 240 s. Solutions were scanned from −0.2 to −1.0 V with a scan rate of 6 mV/s and scan increment of 6 mV. Optimisation of the polarograph resulted in a TBT peak at a half-wave potential of −0.788 mV (Fig. 3). Polarographic analysis precision was determined using standard reference procedural sediments supplied by the Marine Institute of Ireland. The Marine Institute utilises Quality Assurance of Information of Marine Environmental Monitoring (QUASIMEME) materials for laboratory proficiency testing. The mean precision was 93.5% with an SD of ±2.9%.

3.3. Organic matter titration

A Walkey–Black titration was utilised for readily oxidizable organic carbon (Gaudette et al., 1974; Loring and Rantala, 1992). This method differentiates humic matter from anthropogenic sources of organic carbon such as coal and graphite.

All reagents were supplied by Sigma–Aldrich Ireland Ltd.

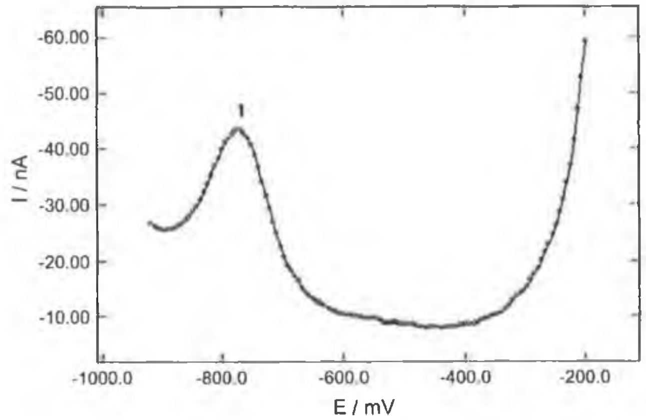

Fig. 3. Differential pulse polarogram of TBT in 0.16 M ammonium chloride in 40% ethanol at pH 2.5.

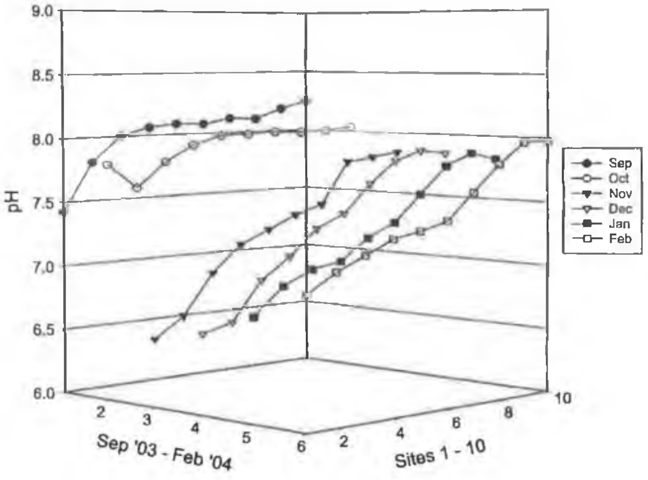

Fig. 4. pH of porewater, Sites 1–10, September 2003 to February 2004.

4. Results

4.1. Sediment composition

The estuarine intertidal sediment may be classified as having two layers. The surface sediment layer depth ranged from 20–50 mm in summer to 100 mm in winter. Mid-estuarine Sites 5–8 had the highest levels of fine-grained sediments (125–63 μm and <63 μm): 40, 50, 47 and 41%, respectively (Table 1). Samples of the subsurface layer were analysed in the laboratory and were found to be principally composed of coarse limestone and sandstone gravel >2.5 mm, and coarse sand >1 mm.

4.2. pH

Spatial and temporal measurements of porewater pH were made at Sites 1–10 over a 12-month period: September 2003 to August 2004 (Figs. 4 and 5). Spatially, the pH increased from the inner to the outer estuary where a maximum pH of 8.35 at Site 10 was recorded in July 2004. The lowest pH level – 6.52 was recorded at Site 1 in the inner estuary in November 2003. Over the 12-month period, pH ranged between 6.5 and 8.4 across the estuary. Winter pH levels were slightly lower than summer levels, e.g. pH ranged from 6.52 to 7.84 for Sites 1–10 in November and 6 months later ranged from 7.68 to 8.21 in May.

Table 1
Mean sediment composition, Sites 1–10

Sediment fraction composition					
Site	500 μm	250 μm	125 μm	63 μm	<63 μm
1	22	30	30	12	6
2	16	26	40	16	2
3	6	28	42	18	6
4	4	22	48	17	9
5	8	18	34	30	10
6	6	16	28	36	14
7	2	15	36	36	11
8	3	16	40	31	10
9	12	22	48	16	2
10	16	24	46	10	4

4.3. Tributyltin distribution

Spatial and temporal distributions of TBT were observed at Sites 1–10 over a 12-month period; September 2003 to August 2004 (Figs. 6 and 7). TBT distribution for the same period was also observed in the Dunsink Tributary. Site 1 in the river channel exhibited no TBT during the 12 months. Sites 2–4 are located in the inner estuary, Sites 5–8 are in the mid-estuary and Sites 9 and 10 are located in the outer estuary. Spatially, TBT distribution exhibited maximum concentrations in the mid-estuary with lower concentrations in the inner and outer estuaries. The highest TBT concentrations were observed

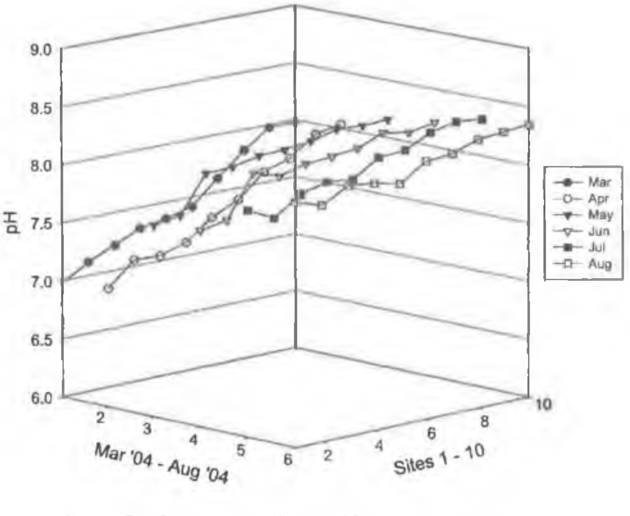

Fig. 5. pH of porewater, Sites 1–10, March to August 2004.

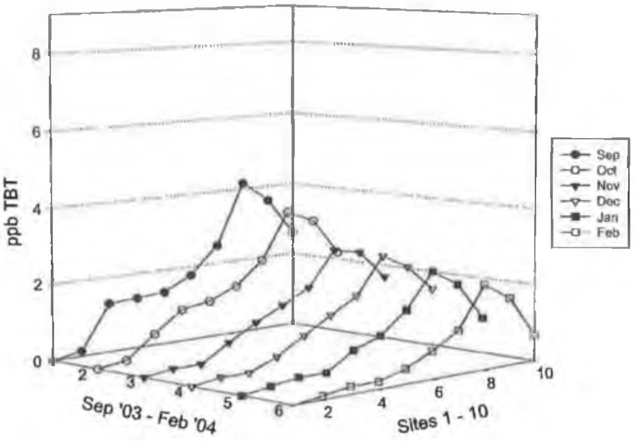

Fig. 6. TBT concentrations, Sites 1–10, September 2003 to February 2004.

between Sites 6 and 10, specifically at Site 8. At this site TBT concentrations decreased from 4.2 ppb in September 2003 to 2.0 ppb in April 2004 and subsequently concentrations fluctuated between 8.6, 6.9, 7.5 and 3.0 ppb TBT for May, June, July and August, respectively.

TBT concentrations exhibited a distinct temporal distribution. TBT concentrations were elevated in late summer. Concentrations decreased during autumn and winter months to lowest concentrations in March and April 2004 and increased again in summer 2004. This temporal trend was observed at all sites except Site 1 in the sample area. Site 7 in the mid-estuary provided a good example of this trend. TBT concentrations decreased from 2.5 ppb in September 2003 to 1.0 ppb in March 2004. Concentrations increased from 1.4 to 4.2 ppb between April and July 2004. Subsequently, TBT concentrations decreased to 2.3 ppb in August 2004.

A key source of TBT contamination is the Dunsink landfill tributary. This is located 8 km upstream of the estuary. This tributary has an annual average of 4.5 ppb TBT in its surface sediment. It did not have a fluctuating temporal distribution reflected by a relatively constant TBT concentration.

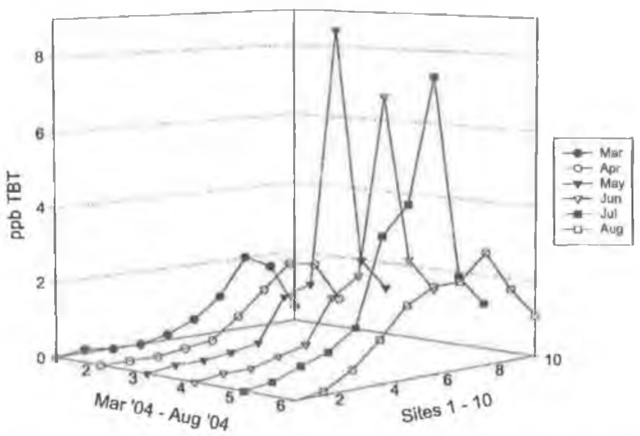

Fig. 7. TBT concentrations, Sites 1–10, March to August 2004.

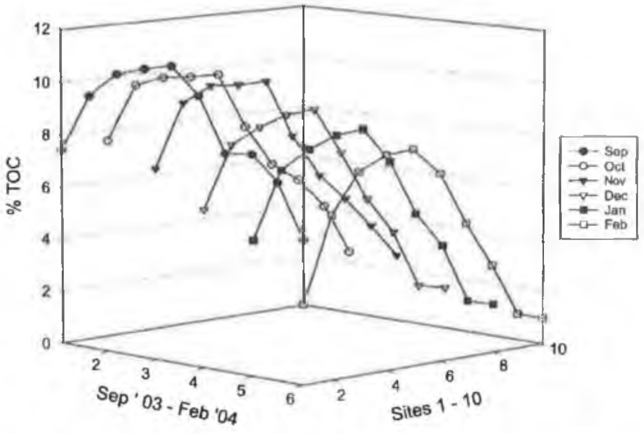

Fig. 8. OM concentrations, Sites 1–10, September 2003 to February 2004.

4.4. Organic matter distribution

OM concentrations in the estuary displayed similar spatial and temporal distributions (Figs. 8 and 9). Spatially OM concentrations were highest in the inner and mid-estuarine sections with lower concentrations in the riverine section and outer estuary. Results of sampling in September 2003 showed OM concentrations ranging from 7.5% at Site 1 to 10.2% at Sites 3–5. Concentrations decreased from 8.9 to 2.6% between Site 6 in the mid-estuary and Site 10 at the estuarine margin. This initial spatial distribution was observed every month for the 12-month period. OM concentrations also exhibited a temporal distribution similar to TBT. Concentrations were elevated in autumn 2003, subsequently decreasing during winter months to lowest concentrations in February and March 2004. Concentrations increased from April to August 2004. Site 6 provides a good example of this temporal distribution. Between September 2003 and March 2004, concentrations decreased from 8.9 to 6.6% whereas

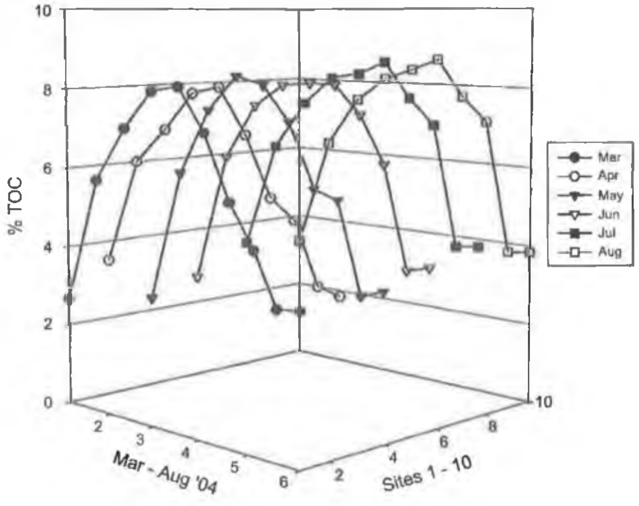

Fig. 9. OM concentrations, Sites 1–10, March to August 2004.

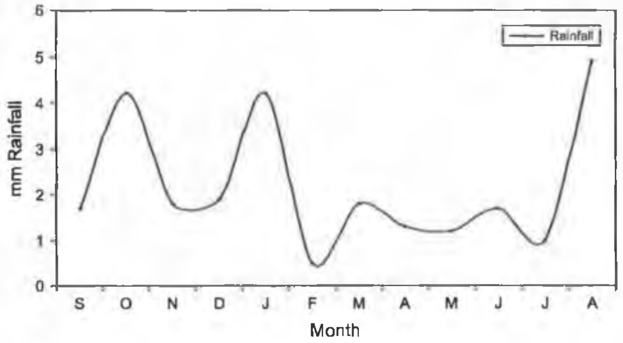

Fig. 10. Average daily rainfall (Met Eireann, 2004).

concentrations increased from 6.7 to 8.8% between April and August 2004.

4.5. Average monthly weather conditions

Daily rainfall data as supplied by Met Eireann (The Irish Meteorological Service) were noted. Average monthly rainfall showed a seasonal distribution (Fig. 10). The weather station is located 10 km north of the Tolka Estuary.

5. Discussion

Porewater pH levels had marginal spatial and temporal distributions. Over the 12-month period pH increased spatially from the inner to the outer estuary indicating that marine influx was the dominant factor in controlling pH levels. During winter months pH was reduced slightly due to elevated freshwater input from the Tolka River while in summer months when the river was in low flow, marine water influx from Dublin Bay controlled the pH of the estuary.

Spatially, TBT and OM concentrations in the estuarine surface sediment exhibit distinct and similar trends. Generally, the inner estuary TBT and OM concentrations were lower and increased through the middle section of the estuary, and reached a plateau before dropping in the outer section of the estuary. The middle estuary is a convergence zone between marine and freshwaters. This phenomenon known as the mid-estuarine maximum has been observed in other estuaries in relation to metal concentrations (Caccia et al., 2003; Gerringa et al., 2001; Thompson et al., 1984; Yang and Sanudo-Wilhelmy, 1998). Sediment homogeneity is a key factor in the occurrence of this estuarine feature. Surface sediment in the Tolka Estuary does not have significant size variability. Fine-grained sediment across an estuary's extent provides a stable environment for contaminant retention. Contaminant loss from fine-grained sediment is dependent on in situ physical factors such as marine influx with tides, turbulence associated with adverse weather conditions and freshwater influx from riverine systems. Contaminant loss occurs at estuarine margins because of these factors whereas contaminant concentrations at the middle of the estuary are relatively unaffected (Miles and Tome, 1997). Also, remobilization of particle-bound trace elements down estuary, together with the influx of clean marine sediments through the estuarine mouth are known to account for the gradual seaward decline in contaminant concentrations of estuarine sediments (Kennish, 1995).

A large proportion of organotin contaminants such as TBT are found to be associated with the clay fraction of particulate matter (Hoch, 2001; Hoch et al., 2002). Adsorption and concentration onto this fraction are important controlling mechanisms concerning distribution and fate of TBT in the estuarine environment (Hall et al., 1987; Hoch, 2001; Hoch et al., 2003; Hoch and Schwesig, 2004). Sample sites with elevated levels of this fine fraction would also have a higher association with TBT concentrations (Langston and Pope, 1995; Hoch and Schwesig, 2004). Here, Sites 5–8 in the mid-estuary had the highest levels of fine-grained sediment and the corresponding TBT concentrations were the highest in the estuary.

The outer estuary can also function as a source of TBT to the mid-estuary. TBT in the outer estuary can be removed and relocated to the middle and inner estuary regions and redistributed over the course of a tidal cycle that increases mid-estuary concentrations. In the aquatic environment, TBT has low aqueous solubility and low mobility, and is easily adsorbed onto suspended particulate matter (SPM). This is an important process in the fate of TBT in the aquatic system (Hoch, 2001; Hoch et al., 2003). In the Tolka, the outer estuary exhibits lower TBT concentrations. The influx of seawater from Dublin Bay and freshwater from the Liffey River carries TBT further into the Tolka Estuary. Dublin Port located at the mouth of the Liffey River has significant TBT contamination and levels of 78 ppb were measured in surface sediment from Alexandria Dock in 2004 (Davoren et al., 2005). TBT trapped in the matrices of colloidal particles and in solute form in the water column is likely to be transported on the tide up the estuary from the outer margins and deposited as the tide recedes (Luoma, 1990). OM is transported to the mid-estuary by the same tidal force. This appears to account for a reduction in TBT and OM concentrations at Sites 9 and 10.

Site 8 had a monthly average of 3.9 ppb TBT. It is likely that local boating activity and mooring facilities close by contribute quantities of TBT from antifouling paints to this site and subsequently to the mid-estuary. From Figs. 6 and 7 it can clearly be seen that these factors impact on spatial and temporal TBT distributions in the estuary. The increased levels of TBT at Sites 8–10 in May are consistent with increased boating activity that lasts over the summer months till September. Approximately 8 km upstream of the estuary, TBT contamination in the river originates from a municipal landfill. The Dunsink landfill, Finglas, Co. Dublin has a tributary of the Tolka River flowing around its perimeter. This tributary is contaminated by landfill leachate. TBT from this source is transported bound to SPM and in solution by the river and is deposited in the inner and mid-estuary. These sources strongly influence TBT distribution in the estuary.

A distinct temporal distribution was observed over the 12-month period. A reduction of TBT and OM in the surface sediment occurred from autumn to winter, and lowest concentrations were observed in February/March. Both TBT and OM increased gradually in spring and reached a maximum in July/August. Understanding the causes of temporal variability in contaminant concentrations in estuaries can be complicated by interrelationships among potential controlling factors and anthropogenic inputs (Hatje et al., 2003). Seasonally variable environmental factors can include rainfall and temperature. Stability of surface sediment is affected by tides and by turbulence in the estuary. Rainfall influences OM and contaminant transportation and retention time significantly in aquatic systems. In Dublin, rainfall was highest in winter months. Due to increased freshwater—seawater mixing induced by higher rainfall, rougher seas, higher tides and increased wind effects, turbulence in the estuary itself is higher in winter than summer months. Resuspension of surface sediment by this increased turbulence leads to SPM bound TBT entering the water column (Wheatcroft and Butman, 1997). As a result the estuarine system is flushed during winter.

Distribution, transport and fate of contaminants in estuarine systems are significantly influenced by OM (Singer, 1977; Rubio et al., 2000; Hoch, 2001). Metals and organometals are associated with OM in the fine-grained sediment fraction, such as detritus and organic material coating mineral particles and colloids (Bryan et al., 1989). Fine-grained sediments can have relatively high metal and organometal contents due, in part, to the high specific surface area of OM content. This enrichment is mainly due to surface adsorption and ionic attraction binding to OM (Wangersky, 1986; Horowitz and Elrick, 1987). OM concentrations greater than 0.2% of surface sediment appear to be a major controlling factor for sediment—water partitioning of TBT (Di Toro et al., 1991; Langston and Pope, 1995; Meador, 2000). Lowest OM concentrations in the Tolka Estuary were 1.0%. The proportion of OM in surface sediment is considered to be the most important parameter controlling TBT distribution (Poerschmann et al., 1997; Arnold et al., 1997; Hoch and Schwesig, 2004). TBT is more strongly adsorbed to fine-grained sediments containing OM than to sediments without OM. TBT adsorption to OM is dependent both on pH and on the mineral constituents of the sediment. Optimal adsorption to fine-grained clay rich sediments similar to surface sediment in the Tolka occurs between pH 6 and 7, while optimal adsorption to OM occurs between pH 6 and 8 (Hoch and Schwesig, 2004). The average annual pH range of the Tolka estuarine porewater is 7.3—8.0. This facilitates optimal conditions for TBT adsorption to the estuarine sediment over the 12-month period. While pH levels only had minimal seasonal variation, it is considered that pH played a tertiary role in TBT temporal distribution after the primary role of organic matter distribution and secondary role of anthropogenic seasonal input.

Table 2
OM/TBT correlation coefficients, Sites 1—10, September 2003 to August 2004

Site specific organic matter/TBT 12-month correlation	
Site	r^2
1	N/A
2	0.376
3	0.634
4	0.724
5	0.643
6	0.829
7	0.811
8	0.508
9	0.763
10	0.406

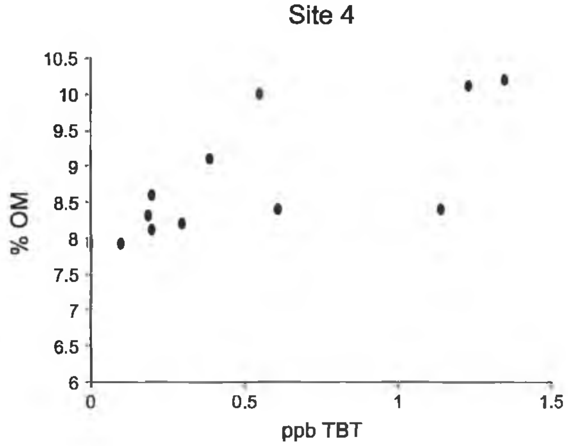

Fig. 11. OM/TBT correlation, September 2003 to August 2004, Site 4.

Positive correlations between OM and TBT distributions at each site for 12 months are indicated in Table 2 with higher r^2 values noted in the mid-estuary. Figs. 11—16 indicate the correlations for the 12-month period between OM and TBT concentrations for Sites 4—9. Noticeably, Site 8 has a less significant correlation, which is likely due to local boating activity elevating TBT concentrations at this site.

Positive correlation between OM and TBT underscores the relationship between the two parameters. TBT in the water

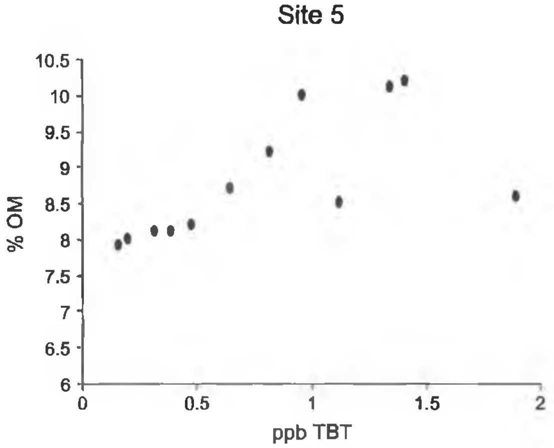

Fig. 12. OM/TBT correlation, September 2003 to August 2004, Site 5.

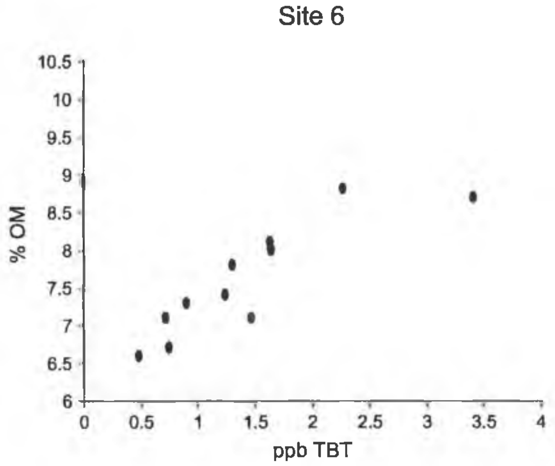

Fig. 13. OM/TBT correlation, September 2003 to August 2004, Site 6.

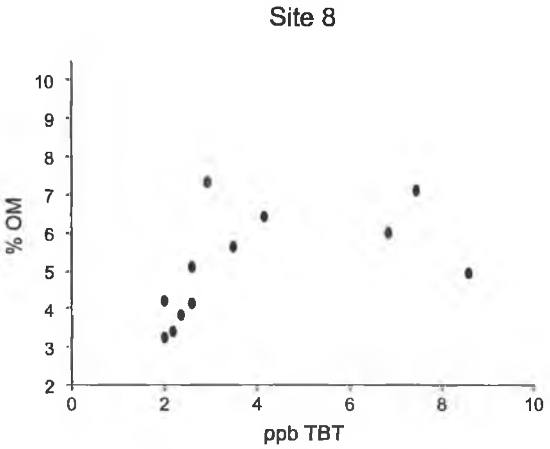

Fig. 15. OM/TBT correlation, September 2003 to August 2004, Site 8.

column, in solute form and bound to SPM is deposited to surface sediment and retained by OM during calm summer conditions in the estuary. As OM content increased during this period, TBT accumulation in surface sediment increased. During winter months as OM was lost due to increased turbulence in the estuary, TBT was released into the water column and transported out of the estuary.

6. Conclusion

This study has shown that TBT has a variable temporal distribution over a 12-month period. TBT concentrations in surface sediment are influenced by environmental factors including OM content of sediment and by fluctuating anthropogenic inputs. At a basic level, the seasonal distribution can be described as a flushing and retention mechanism induced by fluctuating environmental conditions. Continued TBT contamination of the Tolka indicates that anthropogenic input is an ongoing issue that has not been completely resolved despite regulation of TBT use in the 1980s (Alzieu, 1998). The Tolka sediment TBT levels range from 0 to 8.6 ppb with a 1.5-ppb annual average. According to recent Australian guidelines, acceptable TBT levels in estuarine sediment range from 0.5 to 7 ppb (DoE, Australia, 2002). In general, the Tolka falls within this range. Continued research on elucidating the transportation, circulation, retention and persistence of TBT in estuarine environments is required as the continued release of these toxic pollutants is a matter of concern.

Acknowledgements

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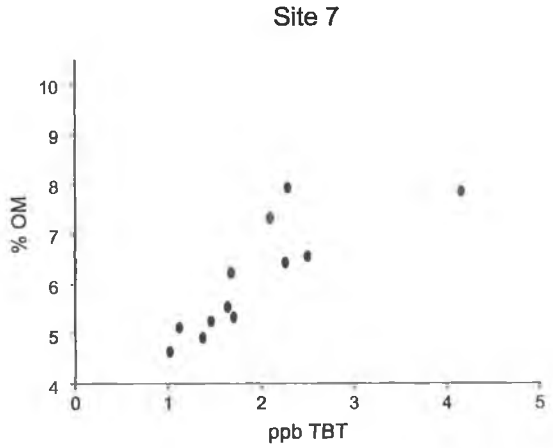

Fig. 14. OM/TBT correlation, September 2003 to August 2004, Site 7.

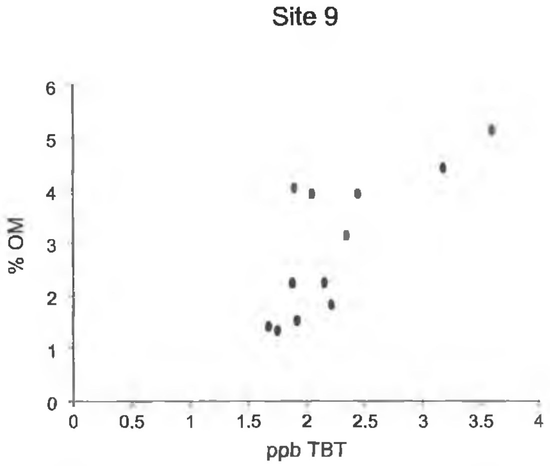

Fig. 16. OM/TBT correlation, September 2003 to August 2004, Site 9.

Dublin City University and Wexford County Council for supporting this study.

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POLAROGRAPHIC ANALYSIS OF ESTUARINE SEDIMENT IN AN IRISH ESTUARY

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ABSTRACT

Estuaries are large sediment traps at the freshwater-saltwater interface. Moreover, metal loading of estuarine sediments may be elevated because of long flushing times in estuaries due to their enclosed physicality. The Tolka River Estuary, Co. Dublin, Ireland, is an urban estuary that is canalised for most of its route but has a large flat mouth with high sedimentation and is a typical Irish urban estuary. It is known to have a significant pollution loading. This paper represents the results of the first three months of a two-year project on temporal trends in metal distribution in an urban estuary. Data from a total of ten sample points in the estuary are presented. The concentrations of four priority metals in the sediment are being analysed using polarographic and AAS methods. Temporal trends in relation to sediment composition and distribution and to pH are observed.

RÉSUMÉ

Les estuaires sont de grands pièges à sédiment à l'interface d'eau douce-eau de mer. D'ailleurs, des charges de pollution en métaux des sédiments d'estuaire peuvent être élevées en raison de longues périodes de rinçage dans les estuaires dus à leur physicalité close. L'estuaire de fleuve de Tolka, Cie. Dublin, Irlande, est un estuaire urbain qui est canalisé pour la majeure partie de son itinéraire mais a une grande embouchure évasée avec une sédimentation élevée et est un estuaire urbain irlandais typique. On le connaît pour avoir un chargement significatif de pollution. Cet article représente les résultats des trois premiers mois d'un projet de deux ans sur des tendances temporelles dans la distribution en métal dans l'estuaire urbain. Des données d'un total de dix points d'échantillonnage dans l'estuaire sont présentées. Les concentrations de quatre métaux prioritaires dans le sédiment sont analysées en utilisant des méthodes polarographiques et des d'AAS. On observe des tendances temporelles par rapport à la composition et à la distribution du sédiment et du pH.

1. INTRODUCTION

An estuary is a partly enclosed tidal inlet of the sea in which seawater and riverwater mix to some degree (Little, 2000). Estuaries may vary in size from a few square kilometres to hundreds of square kilometres yet most have many similar features and patterns. Factors affecting estuaries include freshwater saltwater mixing, tides, wave action, sediment transport, erosion and deposition, biota, and temporal cycles (Zhang *et al*, 2001). Generally estuaries can be divided into three sectors; (1) a marine or lower estuary in free connection with the open sea; (2) a middle estuary subject to strong salt and freshwater mixing and (3) an upper or fluvial estuary characterised by freshwater but subject to daily tidal action (Kramer *et al*, 1995).

Metals tend to be trapped in estuaries and are of particular concern in this environment. Metal concentrations in the particulate form are 3 - 5 orders of magnitude higher than in the dissolved form (Comber *et al*, 1995) and so the bulk of the trapped metals tend to accumulate within the estuarine sediment (Jones & Turki, 1997).

The Tolka Estuary, Dublin, Ireland is the study area of this project. The Tolka estuary is approximately 2 km^2 and has man-made margins. It is bounded by the suburb of Clontarf to the north, Dublin Port to the south and the Bull Wall and Bull Island to the east. See Figure 1. It is primarily subjected to sediment deposition from the Tolka River entering its western margin. It has suffered from metal pollution from various sources in the past (Jeffrey *et al*, 1985). A ten point sampling regime was established. Samples were obtained on the 25th of August, September and October 2002. Sediment was analysed for Cd, Cu, Pb and Zn to establish the metal contamination of the estuary.

2. MATERIALS AND METHODS

2.1 Sediment Sampling

Standard sampling methods defined by the Irish Estuarine Research Group (IERP) were utilised (Jeffrey *et al*, 1985). Sediment samples were obtained at low tide for each month. Sediment from the top 50 mm of the surface layer was sampled. Samples were collected by hand using a Teflon coated plastic scoop. Approximately 1 kg of wet sediment from each sampling point was placed in polythene vacuum sealed bags and transported to the laboratory in a 4° C cool box.

2.2 Sediment Treatment and Digestion

Sediment was dried at 60° C for 48 h to remove all water content. After drying the sediment was disaggregated and sieved through 2 mm, 1 mm and 63 µm sieves to determine sediment size range. Sediment in the 63 µm sieve was utilised for the acid digestion. The HNO_3 digestion is a 3 h digest preceded by a 48 h soak in HNO_3. (Jeffrey *et al*, 1985; Kramer *et al*, 1995; Groengroeft *et al*, 1998). 0.5 g of sediment was placed in a digestion tube with 10 ml 65% HNO_3 and contacted for 48 h at room temperature. Samples were subsequently heated to 170° C for 2 h and

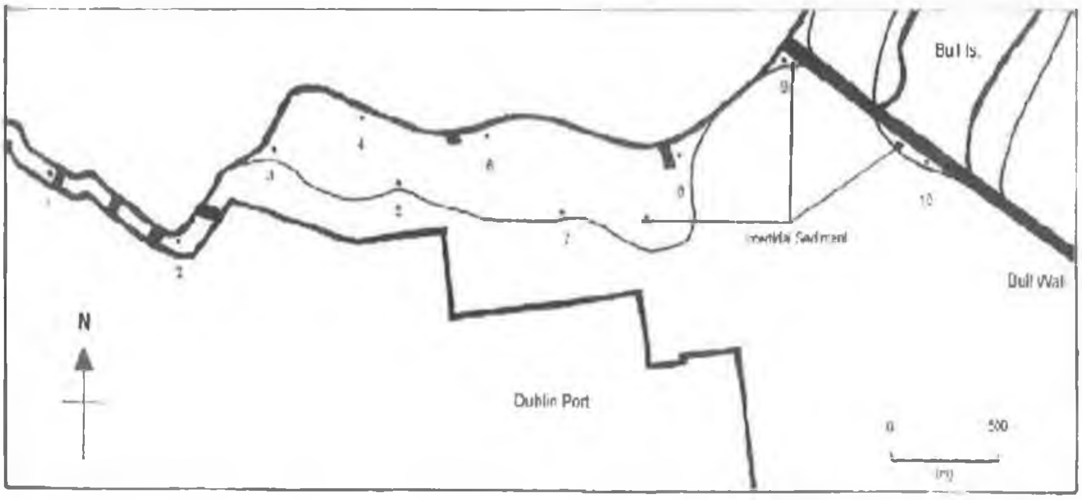

Figure 1. Tolka Estuary Sample Point Map.

then at 200° C for 1 h to reduce the volume to approximately 1 ml. Samples were cooled for 24 h at room temperature, filtered through Whatman No. 1 filter paper and made up to 25 ml with deionised water from an Analyst HP, Purite Select Deioniser (Purite Ltd., Leeds, UK).

2.3 Differential Pulse Polarography

Metal concentrations were determined using an EG&G model 394 electrochemical trace analyser with a 303A static mercury drop electrode (EG&G Instruments, Princeton Applied Research, CA). Differential Pulse Polarography (pulse amplitude 50 mV) and a hanging mercury working electrode (HMDE) were employed for analysis. A 0.2 M ammonium citrate at pH 3.2 electrolyte solution was utilised for Cd, Cu, Pb and Zn. Samples were purged with N_2 for 240 s. The solutions were then scanned from 0.1 to -1.2 V with a scan rate of 4 mV /s and scan increment of 4 mV (Ghoneim *et al*, 2000). Optimisation of the polarograph resulted in peaks for the four metals obtained at the following half-wave potentials (V): Cu; -0.008, Pb; -0.404, Cd; -0.560 and Zn; -1.020. A polarogram of the four metal peaks is illustrated in Figure 2. Peaks are usually obtained at pH 3.0 at the following half-wave potentials (V): Cu; -0.07, Cd; -0.62, Pb; -0.45 and Zn; -1.040, (Princeton Applied Research, CA, USA). However using acid digested samples required a minor variation on the pH for clear peak definition and this is responsible for the minor shift in metal peaks. To ensure that the polarograph analysis was accurate, samples were analysed by AAS for comparison.

2.4 AAS Analysis

Cd, Cu, Pb and Zn were analysed using a Perkin Elmer 3100 Atomic Absorption Spectrophotometer (Perkin Elmer, Nerwalk, Ct., USA), fitted with a single slot burner head, with an air-acetylene flame. Concentrations were determined, after dilution to a suitable concentration, by reference to appropriate standard solutions.

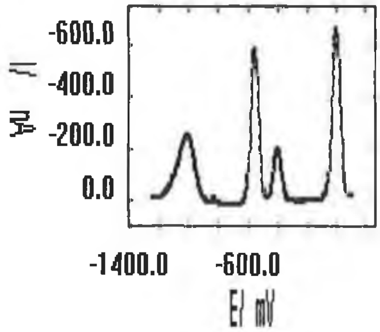

Figure 2. Polarogram of Zn, Cd, Pb and Cu

3. RESULTS

3.1 Sediment Composition

The upper sediment bed of the estuary is composed of two layers. The surface layer ranges between 100 - 150 mm in depth and is composed of approximately 86.2% silt, 7.0% sand and 6.8% gravel, as indicated in Table 1. The depth of this layer reduced toward the mouth of the estuary. The variability of results between the three sampling times was marginal as shown. Samples of the subsurface layer were analysed in the laboratory. The subsurface layer is composed of coarse limestone gravel, sandstone gravel

Table 1. Mean Sediment Composition (%) of Sites 1 - 10.

Site	Silt (%)	Sand (%)	Gravel (%)
1	84	8	8
2	90	4	6
3	84	6	10
4	89	5	6
5	85	5	10
6	90	4	6
7	91	9	0
8	95	5	0
9	75	15	10
10	79	9	12

and sand. This layer is approximately 70% sandstone, 20% limestone, and 10% granitic stone.

3.2 pH Levels

The pH levels for August and September were similar as seen in Figure 3. Alkalinity levels decreased marginally towards the estuary mouth, ranging from a pH of 8.1 at Site 1 to 7.6 at Site 10 for August and a pH of 8.1 to a pH of 7.5 in September. In contrast in October alkalinity increased marginally towards the estuary mouth. The pH ranged from 6.3 at Site 1 to 7.2 at Site 10.

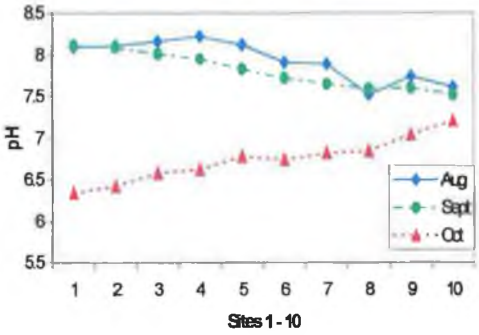

Figure 3, pH Levels at Sites 1 - 10.

3.3 Cadmium Levels

Cd levels for August and September were similar in trend. Low concentrations in the inner estuary increased through the middle estuary and then dropped at the outer margins. The trends are shown in Figure 4. 0.8 ppm Cd and 0.7 ppm Cd were recorded at Site 1 in the August and September samples. The September concentrations were lower as far as Site 7 but exceeded August Cd concentrations beyond that point. Cd levels for October were higher than August and September, but similar in distribution. The lowest level each month was at Site 2. In September 0.7 ppm Cd was recorded. The highest levels taken on the estuary occurred at Site 8 - 2.4 ppm Cd in October.

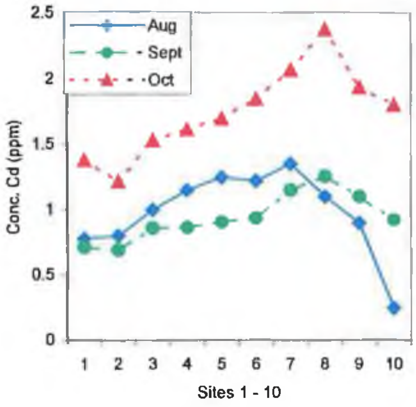

Figure 4. Cd levels at Sites 1 - 10.

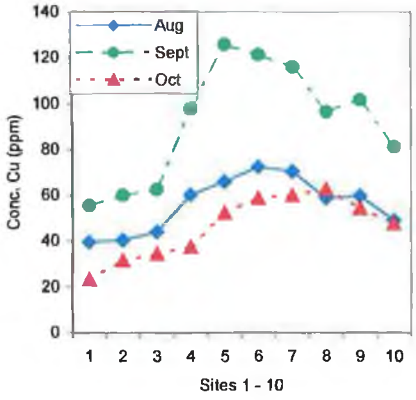

Figure 5. Cu levels at Sites 1 – 10

3.4 Copper Levels

Cu had similar distribution levels along the length of the estuary for the three months. Lower Cu concentrations in the inner estuary increased through the middle section and then decreased in the outer section of the estuary. However the monthly levels varied as seen in Figure 5. The August and October samples had similar concentrations although the values were marginally lower. The September sample had higher Cu levels. In some sites Cu levels were double that recorded in August. Site 1 had the lowest Cu levels for each month, 40 ppm, 55 ppm and 23 ppm Cu recorded consecutively. Site 5 had the highest Cu level recorded, 126 ppm Cu in September.

3.5 Lead Levels

Pb levels were low in the inner estuary, Pb increased and plateaued out in the middle estuary and subsequently declined in the outer estuary. There was a steady decrease in levels from August to October. This is seen in Figure 6. In the outer estuary Pb was similar in concentration for each month. Site 1 had the lowest Pb levels for each

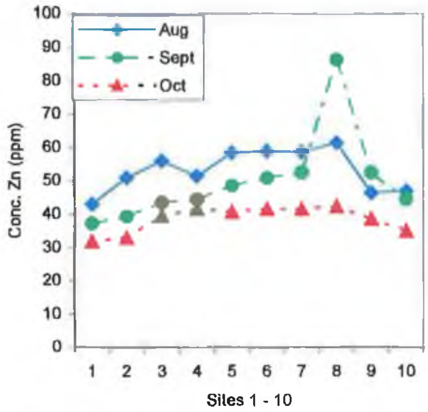

Figure 6. Pb levels at Sites 1 - 10

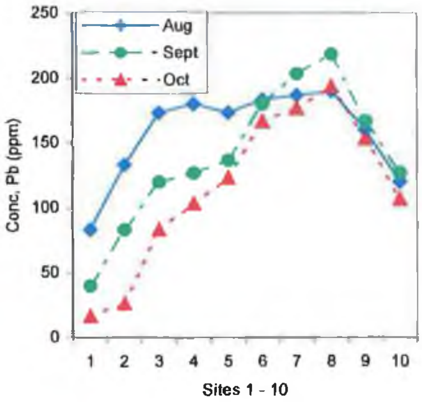

Figure 7. Zn levels at Sites 1 - 10

month; 83 ppm, 40 ppm and 17 ppm Pb recorded in order. Site 8 recorded the highest Pb levels for each month, 190 ppm, 218 ppm, and 193 ppm Pb consecutively.

3.6 Zinc Levels

The trends in Zn levels were relatively constant. There was a marginal increase in Zn concentrations between the inner and middle estuarine sections followed by a marginal decline in concentrations in the outer estuary. Zn concentrations decreased each month except in September at Site 8 and 9. The highest Zn concentrations occurred at Site 8 in September, 86 ppm Zn. The lowest Zn concentrations were at Site 1 each month: 43 ppm, 28 ppm and 32 ppm Zn recorded in August, September and October consecutively.

4. DISCUSSION

The Tolka estuary is located in an urban area. It has man-made boundaries. It is in close proximity to high usage shipping lanes and Dublin Port. These are contributory factors to the accumulation of metal concentrations in the estuary. The four metals chosen for analysis in the Tolka estuary are recommended by the Irish Estuarine Research Programme (Jeffrey *et al*, 1985). Their guideline concentrations are shown in Table 2. Baseline level indicates natural background levels of the metal, the Threshold level indicates metal concentration in sediment above which deleterious effects are likely to occur in the estuary.

Table 2. IERP Guideline Levels of Estuarine Metals, metal concentrations in PPM, (Jeffrey *et al*, 1985).

Pollutant	Cd	Cu	Pb	Zn
Threshold	1.5	50	100	100
Baseline	0.5	5	10	20

4.1 Metal Concentrations in Comparison to Sediment Composition

Sediments faithfully record and time integrate the contaminant status of an estuarine environment (Birch & Taylor, 1999). The concentration of metals in sediments can be related to physical characteristics e.g. particle size and or the chemical conditions of the sedimentary environment (Birch & Taylor, 1999). The Tolka estuary is very homogenous in its sediment composition. Variation between sites was marginal. Samples were taken from the surface layer that consisted overall of 86.2% silt, 7% sand and 6.8% gravel. Clearly there was little variability between sample sites along the estuary both physically and temporally.

Metal concentrations did reflect the minor variations in sediment composition. At sites with lower sand and gravel percentages metal concentrations increased. Site 8 clearly illustrates this. Site 8 is composed of 95% silt and 5% sand and had the highest levels of Cd, Pb and Zn in the three months sampled. Conversely sites containing higher quantities of sand and gravel had lower concentrations of metals. Site 1 is a good example of this lower metal accumulation. Site 1 had 16% sand and gravel in its composition, and recorded the lowest levels in Cu, Pb and Zn. Sediment composition did not vary from month to month, and so temporal variation in metal levels compared to sediment is negligible. Fine grained sediments often show higher concentrations of metals due to their greater surface to volume ratio and enrichment of organic matter and Fe-Mn oxides (Zhang *et al*, 2001).

4.2 Metal Concentrations in Comparison to pH Levels

The pH results for each month approach neutrality. The pH of seawater at the centre of Dublin Bay is 8-8.3 (Costello *et al*, 1999); the levels in the estuary are marginally lower. The outer section of the estuary is close to pH 8 but still somewhat below that of Dublin Bay. The inner and middle sections of the estuary vary from month to month but still remain close to neutrality. Anthropogenic sources can alter the pH of an estuary (Achterberg *et al,* 2003). The pollutant load of the Tolka River entering the estuary will further alter the pH of the estuary, and due to the enclosed nature of the Tolka estuary the sea would not have a major impact on the pH. Just as parent material of the estuary floor contributes to the metal levels in the estuary, it can also affect pH levels (Liu *et al,* 2002). As the upper sediment layer of the Tolka is composed mainly of limestone, $CaCO_3$ will be released into the overlying mixed salinity water and affect the estuarine pH.

The pH results offer an insight into how weather conditions can influence an estuary. Five days before sampling in October flooding occurred in the estuary following high rainfall and a high tide. The estuary became more acidic after this flooding. This may be due to a combination of run off from roads, and from elevated leachate levels from a 32 ha landfill site upstream of the Tolka River, (Dept. of Environment and Local Government, 1998). It is likely that this may account for the high Cd concentrations in October. Cd pollution can arise from landfills which leach into groundwater and riverine systems (Clarke, 1997). Sources include Ni-Cd batteries. Moreover sewage sludge contains up to 30 ppm of $CdOH^+$ (Gray, 1999), and dried sludge has been placed in the landfill close to the early stages of the Tolka river since 1992 (DOELG, 1998). Abiotic conditions in the estuary may induce the precipitation of sulphides of Cd and Zn. Cd and Zn are released into the water column giving rise to a so-called mid-estuarine maximum of their dissolved concentrations (Gerringa *et al,* 2001). Experimentation and field assessments have shown that Cd bound to suspended matter is desorbed when river water mixes with seawater. Speciation calculations suggest that the desorption process is due to formation of Cd-chloroplexes during estuarine mixing. Organic complexation in the dissolved phase occurs, but to a lesser extent for Zn and Cu (Zwolsman *et al,* 1997).

4.3 Metal Distribution in the Estuary

The distribution of the metals in the estuary exhibits similar trends. The inner estuary metal concentrations are lower and increase through the middle section of the estuary, and then plateau out before dropping in the outer section of the estuary. This mid-estuarine maximum has been observed in other estuaries (Gerringa *et al,* 2001; Yang *et al,* 1998). The sediment in the estuary does not have significant variability, which would account for this trend. However sediment transportation within the estuary may be a factor. Desorption and diagenetic remobilization of particle-bound trace elements down estuary, together with the influx of clean marine sediments through the estuarine mouth are known to account for the gradual seaward decline in the metal content of estuarine sediments (Kennish, 1995).

The outer estuary can function as a source of metals to the upper estuary. Metal contaminants in the outer estuary can be removed and relocated to the middle and inner estuary regions and redistributed over the course of a tidal cycle that increases the middle and inner estuary metal concentrations. In the Hudson estuary, fine grained bottom sediments were resuspended by currents and along with associated contaminants were mixed in the water column and transported over a 10-20km distance along the axis of the estuary during a semi-diurnal tidal cycle (Feng *et al,* 2001).

The overall relative abundance of metals in sediments in the Tolka Estuary was in the order Cu>Zn>Pb>Cd based on molar quantities. This pattern is consistent through the estuary and it is influenced by local catchment, geology and anthropogenic inputs. The metal load of the Tolka River contributes to the metal concentrations in the inner estuary. They are relatively low in comparison to the rest of the estuary. The river itself has a low flow rate and flooding is not a common occurrence on this river (Dublin Bay Project, 2001).

The Tolka river is located 200 m from a 32 ha landfill. This landfill has a leachate stream exiting its base that enters the Tolka River in this early stage. In the upper river section elevated metal concentrations have been observed, similar to the levels observed in the middle estuary. It is likely that this landfill is a source of metals in the river and so one of the sources for metal pollution in the estuary. The landfill is a likely source of the elevated Cu, Cd and Pb concentrations that exceed the IERP guideline levels.

Contamination from Dublin Port is another potential source of metal concentrations entering the middle estuary. Metals trapped in the matrices of colloidal particles will be transported on the tide up the estuary from the outer margins and will be deposited as the tide recedes (Luoma, 1990). The man-made margins of the estuary contribute to the spatial distribution of the metals in the estuarine sediment. The estuary is widest at the middle section; its mouth is narrow due to confining walls of Dublin Port. The distribution of metals was generally higher in the middle estuary which is similar to previously reported estuarine trends (Attrill and Thomas, 1995; Zwolsman *et al,* 1997). This pattern may reflect the effects of local anthropogenic sources such as Dublin Port and the mixing of contaminated sediments with relatively clean marine sediments, and/or the release of metals to the water as freshwater and seawater mix (Zwolsman *et al,* 1997). The distribution suggests that local elevations in metal concentrations are the result of direct anthropogenic inputs rather than the fluxes between sediment and water, or sediment mixing. This has previously been observed on the Orwell Estuary, England, a similar shaped estuary with port facilities like the Tolka Estuary (Wright and Mason, 1999).

5. CONCLUSION

The Tolka Estuary is a trap for metal contaminants from various anthropogenic sources. Temporal variation in metal levels is recorded in the estuarine sediment. The sediment composition does not greatly affect the distribution of metals within the estuary. Metal concentrations are highest in the middle estuary with lower concentrations in the inner and outer margins. pH varied little over the three months and so far does not appear to affect metal concentrations.

Metal contamination has resulted in the abioticism of the Tolka Estuary, (Dublin Bay Project, 2001). Continued assessment of the sediment in the Tolka Estuary may allow for temporal trends in metal contamination and its affecting factors to become apparent.

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