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 4º C cool box.

2.2 Sediment Treatment and Digestion

Sediment was dried at 60º 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 170º C for 2 h and

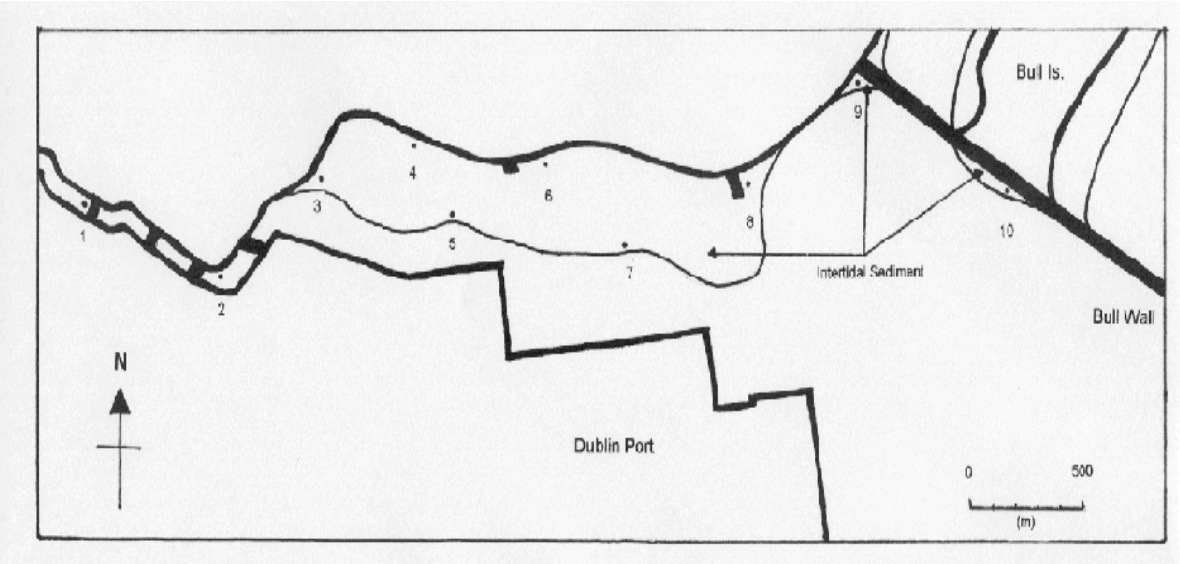

Figure 1. Tolka Estuary Sample Point Map.

then at 200º 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.

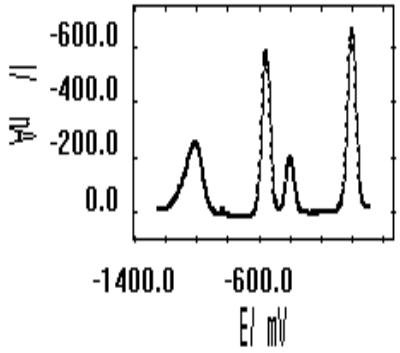

Figure 2. Polarogram of Zn, Cd, Pb and Cu

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.

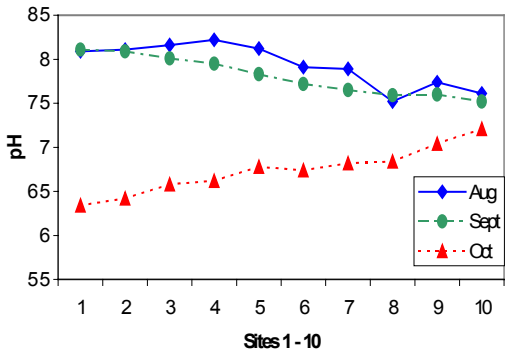

Figure 3, pH Levels at Sites 1 - 10.

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.

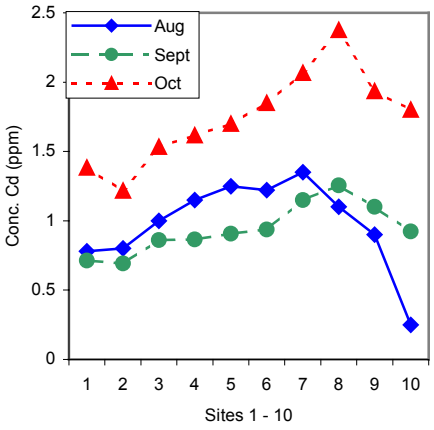

Figure 4. Cd levels at Sites 1 - 10.

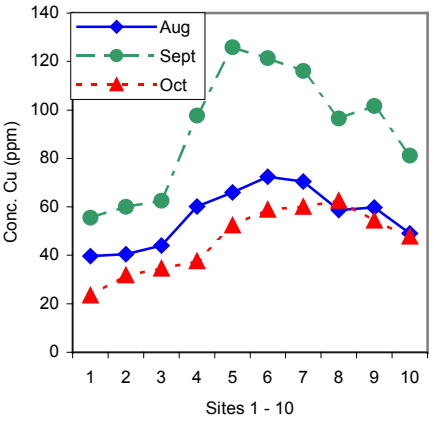

Figure 5. Cu levels at Sites 1 – 10

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

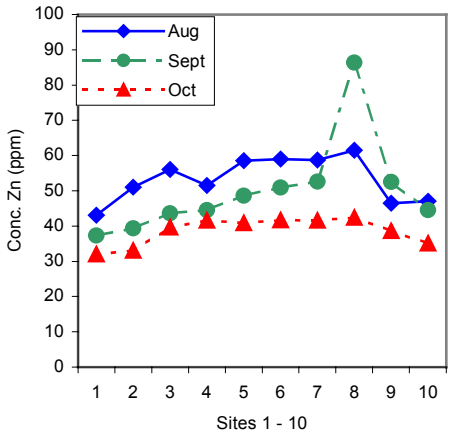

Figure 6. Pb levels at Sites 1 - 10

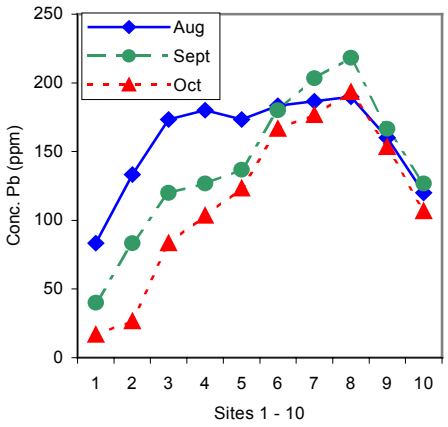

Figure 7. Zn levels at Sites 1 - 10

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.

ACKNOWLEDGEMENTS

This project is part funded by the Environmental Protection Agency and Wexford County Council.

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