

# FATE OF STORMWATER-DERIVED METALS IN TIDAL CREEKS

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## ABSTRACT

Complex interactions occur in tidal creeks with changes in salinity and mixing causing flocculation of sediments and deposition of metals, as well as dissolution of some metals from bottom sediments into the overlying water column. A study in Henderson Creek (Central Waitemata Harbour, Auckland) is investigating processes that occur in tidal creeks to further our understanding of the fate of stormwater-derived contaminants in wider estuarine receiving waters. Hourly water samples were collected over a complete tidal cycle and analysed for dissolved and total metals, sediment and pore water samples were also collected with the ultimate aim of constructing a metal budget for Henderson Creek that accounts for metal fluxes and sources and sinks of particulate and dissolved metals. A further aim is to assess potential effects of metals on estuarine biota. Preliminary results will be presented and discussed in relation to model predictions of stormwater-derived metal accumulation in the Waitemata Harbour.

## KEYWORDS

**Metals, fate, bioavailability, flux, tidal creek, Henderson Creek, Auckland**

## PRESENTER PROFILE

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## 1 INTRODUCTION

Stormwater contaminants discharged into marine environments accumulate in estuarine sediments and can reach concentrations that are harmful to benthic organisms. Stormwater treatment devices aim to remove contaminants before they reach receiving environments, but in most cases, the removal rates are low for dissolved contaminants, including metals. Therefore, we need to better understand the processes occurring in receiving environments, to enable accurate predictions of accumulation and adverse effects. This paper discusses projects currently being undertaken to investigate processes in tidal creeks, which are an important link between freshwater streams and the wider estuary.

These projects are part of a larger study into the dynamics of tidal creeks. Research has focused on Henderson Creek, it discharges stormwater from one of the largest sub-catchments of the Central Waitemata Harbour and has been identified as a major source of contaminants (Green 2007).

## 2 TIDAL CREEK PROCESSES

Tidal creeks are the zones where freshwater streams discharge into estuaries. Complex biogeochemical processes occur in these locations due to their physical and chemical features. The physical shape of tidal creeks limits the fetch and therefore wind-generated circulation, mixing and wave resuspension of bottom sediments (Hume et al. 2007). Upper arms of creeks are characterized by weak stratification and salt wedges (Hume et al. 2007). Net circulation is driven by the difference in density between freshwater and high-salinity sea water. Low-density river water lies over the higher density seawater. Mixing occurs when sea water from the tidal wedge is entrained to the surface as the flows change direction (Pinet 2009). In tidal creeks, the tidal prism makes up a large proportion of the tidal volume, whereas river inputs make up a smaller volume (Hume et al. 2007).

Another characteristic of tidal creeks is their high turbidity (Hume et al, 2007; Ralston & Stacey 2007). This is due to both hydrodynamic and chemical processes. Chemical processes alter the fine suspended particles transported down the river. Clay mineral and particulate iron particles are negatively charged which keeps them suspended in solution; on mixing with saline water, with its high concentrations of positively charged sodium, potassium and calcium ions, these particles are bound together and then flocculate into larger particles (Postma 1980). Organic matter rapidly increases the rate of flocculation, leading to iron oxide-organic complexes (Benjamin & Honeyman 1992).

Hydrodynamic processes keep particles in suspension and result in a maximum turbidity zone (MTZ) in low saline regions (Kempe 1988). The flow of the incoming tide against the flow of the river results in a zone with a longer residence time (Kempe 1988). In addition, freshwater from the river, containing suspended sediments, flows out on top of the incoming salt water (Kempe 1988). Any sediments settling from the freshwater are entrained in the salt water below and then transported back inland, with this cycle trapping sediment in the MTZ of the tidal creek (Kempe 1988).

Freshwater and seawater differ not only in their salinity and suspended-particle concentrations, but also in the chemistry of the dissolved constituents. Seawater composition is dominated by sodium, chloride, calcium, magnesium, potassium and sulphate (Murray 1992). Freshwater is more abundant in iron, manganese, silica, aluminium, carbonate and bicarbonate and dissolved organic matter (Benjamin & Honeyman 1992) from the weathering and erosion of rocks, soils and vegetable matter. When the high concentrations of some constituents, such as silica, mix with the low concentrations in seawater, dilution occurs. This mixing is conservative (Figure 1).

However, other processes may occur in tidal creeks that result in non-conservative mixing (Figure 1), such as sorption to particles and flocculation, resulting in removal from solution (loss), or desorption from particles, resulting in addition to solution (Benjamin & Honeyman 1992). These processes are important for maintaining the composition of the oceans by trapping terrestrial-derived constituents in estuaries, and they also affect the composition of estuarine sediments (Kempe 1988).

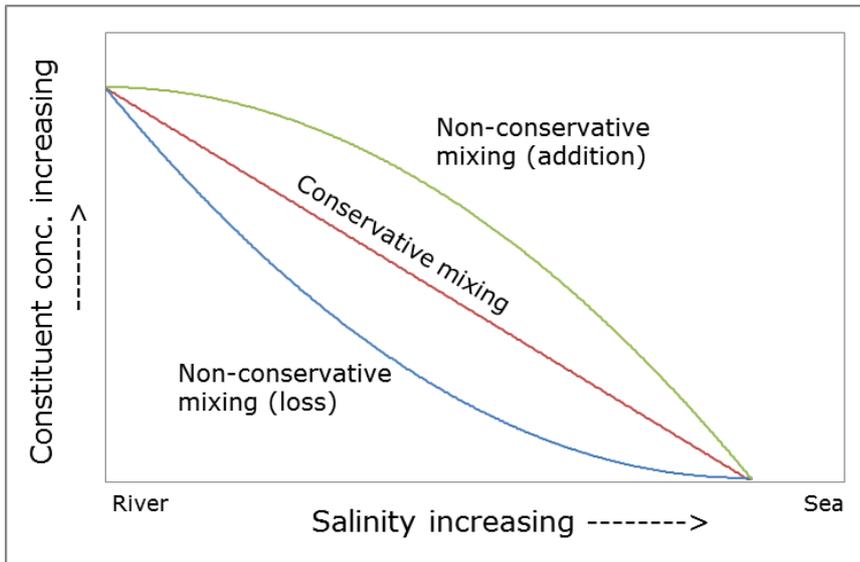


Figure 1: Schematic of conservative and non-conservative mixing of constituents when river water meets sea water.

Mixing of iron is non-conservative, being removed from solution rapidly in estuaries due to flocculation and coagulation in the water column, and reduction and precipitation in sediments (Benjamin & Honeyman 1992). Many trace metals, including some of those derived from stormwater, also behave non-conservatively. This largely depends on their affinity to iron and particulate organic matter, as the drivers of flocculation (Benjamin & Honeyman 1992). Understanding these interactions for trace metals is essential for understanding their fate, specifically whether they are transported out of the creek into the wider estuary or accumulate in bottom sediments.

### 3 PREVIOUS STUDIES AND KNOWLEDGE GAPS

Over the last ten years, there has been considerable effort applied to predict the accumulation of stormwater-derived contaminants in harbour sediments in the Auckland Region. This has included large modelling studies incorporating contaminant load models, stormwater treatment models, and sedimentation and accumulation models (the USC-3 model), with the aim of predicting the dispersal and accumulation of contaminants (sediments and metals) in harbours under a range of potential catchment development scenarios. There are improvements that could be made to the models if some knowledge gaps can be filled.

A key parameter in the calibration of the USC-3 model is the metal retention factor (MRF), which is the proportion of the metal load that is discharged from the catchment in stormwater but that is retained in tidal creeks (as opposed to being exported from the tidal creeks into the larger harbour). This accounts for metals that enter the harbour in particulate form but become dissolved or attached to very fine particles that never settle in harbour beds. The MRF is determined during a calibration procedure that seeks to match model hindcasts with observations over a 50-year historical period. For the Central Waitemata Harbour, a value of 0.4 was found (that is, 40% of the catchment metal runoff was retained in tidal creeks) and for the Southeast Manukau Harbour, a value of 0.3 was found. However, as pointed out by Green (2008), the MRF may be acting as a surrogate for other processes that are not explicitly modelled. Hence, the MRF values determined by calibration need to be verified by experimental or field studies.

A study by Ellwood et al. (2008) provides some direct verification of the calibrated MRF values. Through water sampling in the Whau Creek, Ellwood et al. (2008) calculated that 70% of zinc in the particulate phase entering the creek becomes dissolved and is

therefore discharged from the creek. This is equivalent to an MRF of 0.3. Zinc mixed non-conservatively, with a maximum concentration at mid-salinity along the creek, representing desorption from sediments. Cadmium showed the same pattern, while by contrast, copper mixed conservatively and lead was lost to sediments.

Ellwood et al. (2008) also demonstrated a substantial flux of zinc from sediments into the overlying water column. From this they estimated that over 300 kg of zinc could be lost across the sediment–water interface annually. These processes reduce the concentration of zinc in the sediment and consequently model predictions may over-estimate the actual concentrations.

Transfer of metals from particulate form to dissolved form has implications not only for transportation and accumulation of metals, but also affects the bioavailability of metals to sediment infauna. It is recognized that the dissolved form is most bioavailable to organisms and of greater toxicological risk. As the ratio between dissolved and particulate metal changes with salinity, locations with highest concentrations in sediment may not necessarily present the greatest risk to biota. To understand organism exposure and risk, it is important to identify the locations along a tidal creek where there are fluxes from particulate to dissolved form of metals such as zinc.

## **4 RESEARCH OBJECTIVES AND STUDIES UNDERWAY**

### **4.1 OBJECTIVES**

The overall aim is to validate the MRF values found by model calibration, which is to be achieved by constructing a metal budget for Henderson Creek that accounts for metal fluxes and sources and sinks of particulate and dissolved metals. A further aim is to assess potential effects of metals on estuarine biota. We report here on initial work.

### **4.2 WATER SAMPLING AND ANALYSIS**

Water samples were collected over a tidal cycle on 2 June 2010 after a rain event. Samples were collected across two transects in the tidal creek – near the confluence of the two upstream arms (Henderson and Huruhuru Creeks) and at the mouth of the tidal creek. Samples were collected at three locations across each transect and at two depths: 0.5 m below the surface and 0.5 m from the bottom.

Water samples were collected using Teflon tubing and a peristaltic pump and either transferred directly into acid-preserved bottles or filtered on site with a 0.2 µm filter capsule (polyethersulphone membrane) into acid-preserved bottles. Water samples were digested according to the total recoverable method (US EPA 200.2) using 4mL 50% HNO<sub>3</sub> and 10 mL 20% HCl. Metals (copper and zinc) were measured by ICP-MS by Hill Laboratories.

### **4.3 SEDIMENT SAMPLING AND ANALYSIS**

Cores were collected in the intertidal sediments at four locations within the tidal creek: at the mouth of the creek (site name = mouth), at a point midway along the creek (mid-estuary), near the confluence of Henderson & Huruhuru arms (confluence), and further upstream in the Henderson Creek arm (Henderson). Cores were collected to a depth of 40 cm using 13 mm diameter cores. These were capped and transported on ice to the laboratory. In the laboratory, cores were sectioned at 1 cm intervals from 0 cm to 15 cm, then at 3 cm intervals from 15 cm to the final depth which ranged from 33 to 39 cm.

Sediments were digested according to the total recoverable method (US EPA 200.2) using 4mL 50% HNO<sub>3</sub> and 10 mL 20% HCl. Metals were measured by ICP-MS.

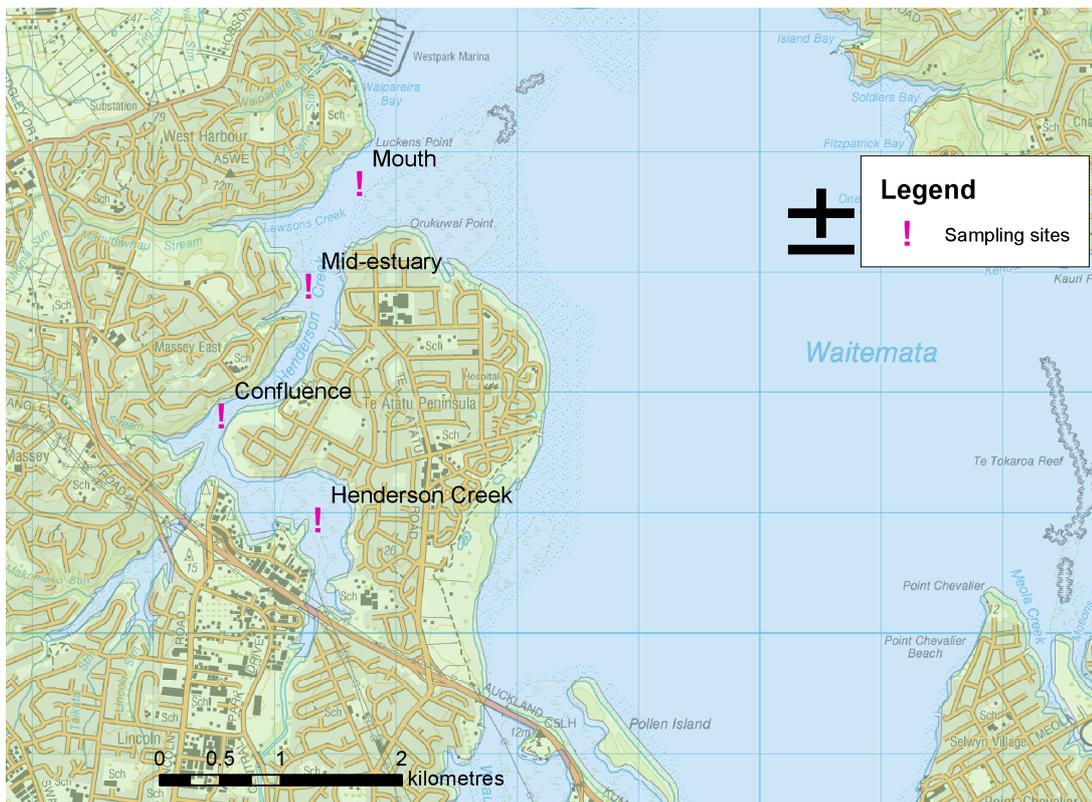


Figure 2: Location of sampling sites within Henderson Creek.

#### 4.4 DGT AND DET PROBES

DGT (diffusive gradients in thin films) is a technique to passively accumulate over time dissolved substances, such as trace metals. Dissolved metals in natural waters, including pore waters, diffuse through a porous gel layer and bind in a Chelex gel. The concentration of the dissolved metals in situ can be calculated from known diffusion rates of the metal and the exposure time. DET (diffusive equilibration between thin films) is a similar technique, where dissolved constituents diffuse into the gel until concentrations in the gel and water are equal (i.e., equilibration is reached). This method is used for iron and manganese.

DGT and DET probes were deoxygenated then deployed in the field at the same sites as sediment sampling by inserting in the sediment until ~2 cm of the probe was above the sediment–water interface. After 48 hours, the probes were retrieved. DGT probes were washed with deionised water then placed in a plastic bag on dry ice to freeze immediately. DET probes were placed into a bottle containing 0.02 M NaOH to fix the iron and manganese and prevent loss of spatial resolution (Davison et al. 1994). DGT and DET probes were sliced at 3 mm and 5 mm intervals, digested in acid and then analysed for trace metals, iron and manganese.

#### 4.5 TOXICITY TESTING

Diffusion plates were used to collect pore waters for toxicity testing. These consisted of 96-well plates (Nunclon) with a 10 µm mesh glued to the top. Plates were filled with Milli-Q water under vacuum and then deployed in the field by pushing into the sediments at each site. Pore water contaminants diffused into the MQ water and equilibrated over the 48 hour deployment period.

Wells were pooled to produce a single sample which was then filtered through 0.45 µm filters. Toxicity testing was based on a 48 hour chronic algal growth test using the marine algae *Minutocellus polymorphus*. Four dilutions and a control (offshore seawater from the

Southern Ocean) were prepared for each sample in sterile 96-well plates, with 10,000 cells mL<sup>-1</sup> added. After 48 hours of exposure at 25°C the number of cells was counted to establish the endpoint of growth inhibition.

#### 4.6 PORE WATERS

Pore waters were analysed for ammonia and sulphide to help explain toxicity results. To extract porewaters, additional sediment samples were collected using cores to a depth of 10 cm and transported to the laboratory on ice. Sediments were transferred to centrifuge tubes within a glove box filled with nitrogen and operating under positive pressure. After centrifuging at 2000 rpm for 20 mins at 10°C, tubes were returned to the glove box and the supernatant was removed for analysis.

The pH was measured using a WTW 3400i multi-parameter meter. Samples for ammonia were analysed by phenol/hypochlorite colorimetry, flow injection analyser (modification of APHA 4500-NH<sub>3</sub> H) by NIWA's water quality laboratory in Hamilton. Samples for sulphide analysis were preserved with zinc acetate and analysed using gas diffusion and methylene blue colourimetry (APHA 4500-S<sub>2</sub> E) by Hill Laboratories.

### 5 PRELIMINARY RESULTS

#### 5.1 METAL CONCENTRATIONS IN THE TIDAL CREEK WATERS

Copper and zinc (both dissolved and particulate) concentrations were higher at the confluence site, within the tidal creek, than at the mouth of the creek. Metal concentrations at both transects were highest at low tide, when flow was directed downstream into the harbour and lowest during high tide, when flow was directed upstream.

The ratios of dissolved to particulate concentration for both metals were different at each site, showing the influence of mechanisms other than simple conservative mixing between the lower concentration seawater and higher concentration freshwater. At the confluence site, just under half of the copper was in dissolved form, whereas at the mouth site, about 2/3 of the copper was in dissolved form. A possible explanation for this is the deposition of particulate copper within the tidal creek, with only minor loss of dissolved copper. In comparison, 1/2 to 2/3 of zinc at the confluence was in dissolved form, whereas at the mouth, about 1/4 to 1/3 was in dissolved form. The higher ratio of dissolved zinc at the confluence site could indicate this site is located close to the mid-salinity maximum for the Henderson Creek.

Table 1: Metal and TSS concentrations in tidal creek waters.

	Dissolved copper (mg m <sup>-3</sup> )	Total copper (mg m <sup>-3</sup> )	% copper dissolved	Dissolved zinc (mg m <sup>-3</sup> )	Total zinc (mg m <sup>-3</sup> )	% zinc dissolved	TSS (g m <sup>-3</sup> )
Confluence							
Surface	2.6	5.3	44	11	23	64	29
Bottom	2.0	4.4	50	12	19	51	31
Mouth							
Surface	1.8	3.1	70	5	12	26	20
Bottom	1.3	2.0	66	3	9	34	16

## 5.2 METAL CONCENTRATIONS IN SEDIMENTS AND PORE WATERS

This work is still in progress but will be available for presentation at the time of the conference.

## 5.3 TOXICITY TESTING

The toxicity testing indicated that pore waters are toxic to marine algae and there is a possibility that this may also be toxic to invertebrates. The ammonia concentrations exceed ANZECC water quality guidelines (ANZECC & ARMCANZ 2000), and are within the range that can cause toxicity or reduce growth in algae, suggesting that ammonia may be a possible cause of the toxicity observed in the test. Once metal concentrations in the sediments and pore waters have been measured, these will be evaluated to assess the likelihood that they caused the observed toxicity.

Table 2: Results of toxicity testing of pore water samples.

	EC50 (%)	EC10 (%)	NOEC (%)	No toxicity dilution
Henderson Creek	34.0	16.5	12.5	5.6 x
Confluence	37.3	16.8	12.5	5.6 x
Mid-estuary	47.1	15.3	12.5	5.6 x
Mouth	>69.2	33.0	25	2.7 x

Table 3: Results of water quality measurements of pore water samples.

	Total sulphide (g m <sup>-3</sup> )	Ammonium (NH <sub>4</sub> -N) (g m <sup>-3</sup> )
Henderson Creek	0.05	1.42
Confluence	<0.02	1.39
Mid-estuary	<0.02	0.49
Mouth	<0.02	0.49

## 6 CONCLUSIONS

This study is still in progress and no definitive conclusions can yet be made about the dynamics of metals in the water or sediment column, or the effects of the metals on biota. More results and conclusions will be presented at the conference. It is anticipated that the study will yield useful data to assist in verifying predictive models and assessing effects of metal-contaminated sediments on biota.

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