

# CRITICAL REVIEW OF ZINC TRENDS IN AUCKLAND STREAMS, ESTUARIES AND HARBOURS

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## ABSTRACT

Zinc in stormwater has been identified by Auckland Council as a priority contaminant of concern for Auckland harbours, estuaries and streams. This is particularly evident in the source control measures specified in the Proposed Auckland Unitary Plan. Such concerns are primarily based on observations of temporal trends in contaminant concentrations for marine sediment, where it is claimed that some sites have seen increasing zinc levels. The present paper critically assesses that analysis and, as a result thereof, identifies serious concerns with the reliability of those conclusions. Furthermore, the present paper examines the temporal trends for zinc in freshwater streams using data obtained from Auckland Council. It is concluded that where statistically significant trends occur for zinc levels in streams, estuaries and harbours, they are mostly observed to be reducing. Freshwater streams in particular are consistently observed to have declining levels of zinc over the last two decades of monitoring. This finding is consistent with the comprehensive stormwater contaminant modelling by NIWA of the Upper Waitemata Harbour and Southeastern Manukau Harbour, which predicted a decreasing trend in zinc loads between 2001 and 2015-20 as existing galvanised roofs are replaced by zinc aluminium coated steel, followed by a slow increase as vehicles become the dominant source of zinc. This paper concludes that instituting zinc source control for roofing and cladding is not justified as it would have an insignificant impact on contaminant levels in stormwater.

## KEYWORDS

**Streams, estuaries, harbours, sediment, water, zinc, metals, contaminants, trends, Proposed Auckland Unitary Plan.**

## 1 INTRODUCTION

Auckland Council is in the process of developing a Unitary Plan for the Auckland region, described by the Council as “the rulebook that shapes the way Auckland grows. It will set out what can be built and where, in order to create a higher quality and more compact Auckland while still providing for rural activities and maintaining the marine environment”.

The notified September 2013 Proposed Auckland Unitary Plan (PAUP) restricts the installation of “high contaminant-yielding roofing, spouting, cladding material or architectural features” to not exceed: 1) 25m<sup>2</sup> in urban environments, or rural environments where run off is piped directly to a watercourse; and 2) 250m<sup>2</sup> in rural environments where run-off is directed to vegetated drain/swale, wetland or similar. For roofing and cladding areas larger than the 25m<sup>2</sup> or 250m<sup>2</sup>, this becomes a controlled activity and the stormwater must be discharged through devices that will limit the discharge of total zinc to <30µg/L. These rules have “immediate legal effect”, though the PAUP is still subject to an extensive submission, hearing and decision process that is in its early stages. The rules have the effect of requiring resource consents where they were not previously required (under the previous planning regime), and this is a significant deterrent for potential users. Further, there are potentially significant financial implications of compliance.

The term “high contaminant-yielding roofing, spouting, cladding material or architectural features” is not defined within the PAUP. However, there is a definition for “high contaminant-generating areas”. This definition includes “high contaminant yielding roofing, spouting, cladding or architectural features using

materials with an: ... exposed surface or surface coating of metallic zinc or any alloy containing more than 10 per cent zinc”.

The technical basis of these contaminant management requirements were presented in Auckland Council (2013). The design effluent quality requirement (DEQR) for zinc appears to have been arbitrarily set at 30µg/L, based on the typical effluent concentration achievable from a variety of stormwater treatment systems. Thus, the DEQR is a highly conservative “zero tolerance” criterion which assumes that effluent must have the lowest practical level of contamination. The DEQR was not based on quantitative assessment of tolerable zinc levels in stormwater effluent via modelling, and appears to give only cursory consideration to the economic implications of source control restrictions.

In view of these recent developments, it is important to consider whether or not zinc contamination in Auckland streams, estuaries and harbours is presenting a growing threat that requires such a serious response.

## 2 MARINE SEDIMENT MONITORING

### 2.1 MONITORING PROGRAMMES

Marine sediment contaminant monitoring has been conducted by Auckland Regional Council (ARC) and now Auckland Council since 1998 in three complementary programmes (Mills et al, 2012):

1. The State of the Environment (SoE) marine sediment monitoring programme, covering 27 sites monitored every two years since 1998 (13 years of data 1998-2011), with the aim of long-term status and trends assessment, conducted by National Institute of Water & Atmospheric Research Ltd (NIWA) for Auckland Council.
2. The Regional Discharges Project (RDP), covering 54 sites of which 19 sites have been monitored every two years since 2004 (8 years of data 2004-2012), with the aim of stormwater impacts assessment. Conducted by Diffuse Sources Pty Ltd for Auckland Council.
3. The Upper Waitemata Harbour (UWH) benthic ecology programme, which has monitored 14 sites annually since 2005 (6 years of data 2005-2011), primarily focused on ecological health monitoring. Sampling frequency was changed to biannual after 2009.

The contaminant chemistry components of the SoE, RDP, and UWH programmes have continued under the Auckland Council, integrated into a single programme – the “Regional Sediment Chemistry Monitoring Programme” (RSCMP). Sampling of all sites has been standardised at two year intervals, with SoE and UWH in odd years and RDP in even years.

Temporal trends in contaminant concentrations between 1998 and 2010 were recently reported by Mills et al (2012), focusing on copper, lead, zinc and polycyclic aromatic hydrocarbons (PAH). Mills et al concluded that trends in zinc were variable, with no obvious consistent pattern among sites. However, they emphasised that some sites have seen increasing trends in zinc.

The purpose of the present paper is to provide a critical assessment of the trend analysis. Raw data from the RSCMP was provided to New Zealand Steel by Auckland Council under Official Information Request No. 9000128580. This data has been analysed for the present paper, providing an updated view of temporal trends for zinc in marine sediments, including new data from 2011 and 2012 sampling years. Data from the 2013 sampling year was not supplied.

### 2.2 TOTAL METALS VS EXTRACTABLE METALS

Two different analytical methods are routinely used by Auckland Council for measuring metals in sediments (ARC 2002, ARC 2004):

1. **Total metals** analysis involves strong acid digestion of the freeze dried <500µm sediment fraction in aqua regia (HCl/HNO<sub>3</sub>) at 100-110°C. This is a standard method of US EPA (Martin et al, 1994), and represents the total amount of metal in sediments, regardless of the metal bioavailability.

2. **Extractable metals** analysis involves weak acid digestion of the <math><63\mu\text{m}</math> mud fraction in 2M HCl at room temperature. This method was developed by NIWA and is intended to reflect bioavailable metals from fine sediments that are digested inside organisms.

The total metals result is used for rating contamination of Settling Zones (SZ), while the higher value of either the total metals or extractable metals result is used for rating of Outer Zones (OZ). Settling Zones are the sheltered tidal creeks and embayments where catchment-derived sediments tend to settle and accumulate. Beyond the Settling Zones are the Outer Zones, which tend to have lower levels of sedimentation and less contamination. The classification of individual sites is assigned arbitrarily based on morphology, catchment size and intertidal excursion (ARC 2002a).

It is argued by Mills et al (2012), that extractable metals are the preferred indicators for temporal trend assessment because they more closely approximate bioavailable metal fraction, and have reduced variability associated with particle size variations which improves the comparability between sites and over time. This interpretation is debatable for the following reasons:

1. Sediment quality guidelines (SQG), such as MacDonald et al (1996) and ANZECC (2000), were derived from relationships between total metals and the observed environmental impacts. Therefore the use of these SQG necessitates adoption of the same standard method for measurement of metals in sediment, that is the total metals analysis method. It is incorrect to assume that the SQG will be applicable to the extractable metals analysis method.
2. The benthic health model developed for Auckland Council has shown that biotic assemblages have the strongest relationships with total metals data rather than with extractable metals data (Anderson et al, 2006). Separate benthic health models have been constructed using the total metals and mud fraction data in preference to the extractable metals data (Hewitt et al, 2012).
3. Extractable metals data from 2003, 2005 and 2007 in the SoE programme was considered by Mills et al (2012) to be "higher than usual" and replicates retested in 2009 gave lower results. This 2003-2007 data was consequently removed from the data analysis by Mills et al. However, any test method used for examining temporal trends must be capable of producing reliable and reproducible results, eliminating the need for selective deletion of data.
4. It has been assumed that weak acid digestion extracts only the bioavailable metals from sediment samples (ARC 2002, ARC 2004), and therefore it should observe lower concentrations than the strong acid digestion as the non-bioavailable component would logically remain undissolved. However, Figure 1 shows that there is a strong 1:1 linear correlation between extractable zinc and total zinc at Settling Zones suggesting that the extractable zinc measurement is not necessarily the bioavailable component. Furthermore, the extractable zinc measured at Outer Zones tends to be much higher than the total zinc, for reasons explained in the next point.
5. The high levels of extractable zinc in Outer Zone sediments are arguably a consequence of particle size distribution. Outer Zones tend to have low mud content and Figure 2 shows that those with less than 25% mud tend to have elevated ratios of extractable zinc to total zinc. This is a natural consequence of zinc and other contaminants being preferably retained within the mud of sediments (ARC 2002, ARC 2004). Therefore, the extractable zinc method tends to grossly exaggerate the perceived level of zinc contamination in Outer Zones, as it represents only the mud fraction and therefore a small proportion of the sediment particle size distribution. For example, the extractable zinc level at Awaruku and Browns Bay in 1999 was about six times higher than the total zinc, although the mud fraction utilised for this measurement was only 2-3% of the sample.

For the above five reasons, the present paper is focused on the temporal trends in total zinc and does not consider the extractable metals data. The extractable metals method is considered by the present author to be highly questionable. It is recommended that Auckland Council re-evaluate their ongoing use of this test method for sediment analysis.

Figure 1: Extractable zinc versus total zinc in Settling Zones (left) and Outer Zones (right) for all monitoring sites during 1998-2012.

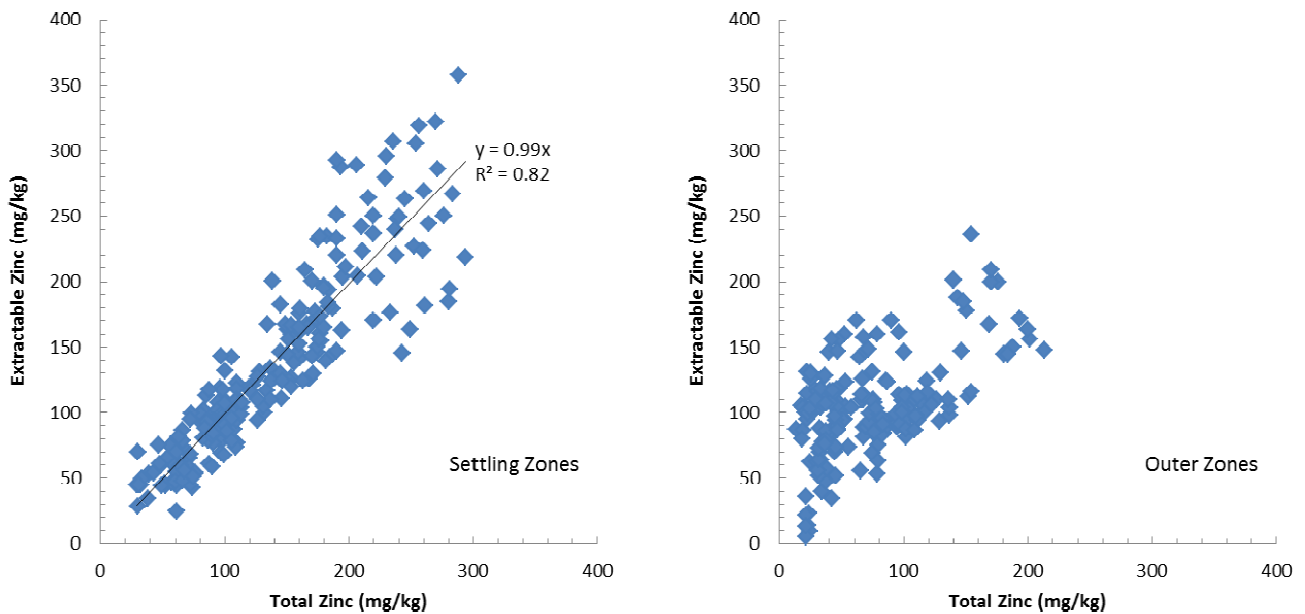
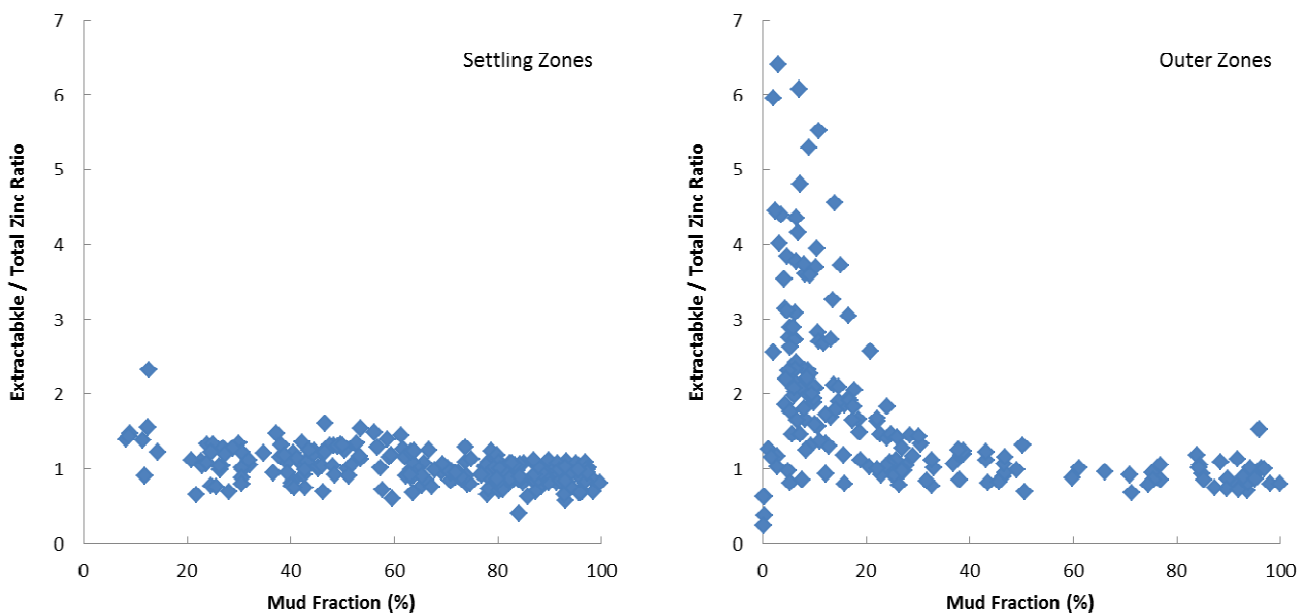


Figure 2: Ratio of extractable zinc to total zinc as a function of mud content in Settling Zones (left) and Outer Zones (right) for all monitoring sites during 1998-2012.



## 2.3 ZINC IN MARINE SEDIMENTS

The three sediment contaminant programmes have adopted different approaches to sampling and testing. Sites from the RDP and UWH programmes have been tested in triplicate for each sampling period (biannual for RDP, annual for UWH), while those from the SoE programme had only one test result up to 2007 then triplicate tests from 2009 onwards. Previous trend analysis by Mills et al (2012) incorrectly combined these single and triplicate data points, which had the effect of biasing the importance of the 2009 results in their trend analysis. This practice has been avoided in the present study by averaging the triplicate results for each sampling period, and using this average data point to represent each sampling period.

Statistical analysis of trends in total zinc was conducted with the Mann Kendall test using the “Time Trends” software package (NIWA and Jowett, 2012). The criterion adopted for inclusion in the analysis was that the sites were sampled at least four times for a period of at least six years. This meant that one UWH site and 34 RDP sites were excluded from the analysis as they had insufficient monitoring data. The sample size for all sites was less than 11, and small sample size probabilities were used in the Mann Kendall test. The absolute magnitude of long-term trends was obtained from the median annual slope (Sen slope estimate, SSE), expressed in units of mg/kg/y. The relative magnitude of the trend (relative Sen slope estimate, RSSE), was obtained from the median annual slope divided by the median value, expressed as a percentage. A trend was considered statistically significant if the test p value was less than 0.05 and the annual trend was more than  $\pm 1\%$  of the median value (RSSE).

Table 1 summarises the results of Mann Kendall trend tests of total zinc in sediments. Significant trends were found for only 7 of the 59 sites. This indicates that the vast majority of sites tested (almost 90%) are not showing any change for the zinc present in sediments. Of the 7 sites with significant trends, all except Whau Entrance were from the SoE programme, demonstrating the necessity for long term monitoring in order to reliably detect temporal trends for zinc in sediments. The increasing trend for Whau Entrance was from a low base of 33mg/kg median zinc, and a low number of observations. It is suggested that monitoring at the RDP and UWH sites will require at least another 2 years and 4 years respectively, before reliable trends are likely to be obtained from them.

The absolute trends in total zinc at the SoE sites are shown in Figure 3, while the relative trends are shown in Figure 4. Three sites had significantly decreasing trends of -1.2% to -2.1% per year (Anns, Mangere Cemetary, Meola Inner), while three other sites had significantly increasing trends of 1.3% to 3.2% per year (Middlemore, Pakuranga Lower, Pakuranga Upper). The three increasing trends were in the upper reach of the Tamaki estuary, while the decreasing trends were in the Mangere Inlet and Central Waitemata Harbour. Closer inspection of the Sen slope trends for the Tamaki sites in Figure 5 suggests that there has been little variation after 2001. It is noteworthy that the analysis method for the SoE sites was changed from Atomic Absorption Spectroscopy in 1998-2001, to Inductively Coupled Plasma Mass Spectrometry in 2003-2011. Therefore, it seems possible that the significant trends noted in Table 1 may be influenced by changes in the analytical method.

Figure 3: Median annual Sen slope of total zinc in marine sediments for SoE sites. Red data points indicate significant trends ( $p < 0.05$  and  $RSSE > \pm 1\%$ ), while blue data points are not significant ( $p \geq 0.05$ ). The error bars correspond to 95% confidence intervals.

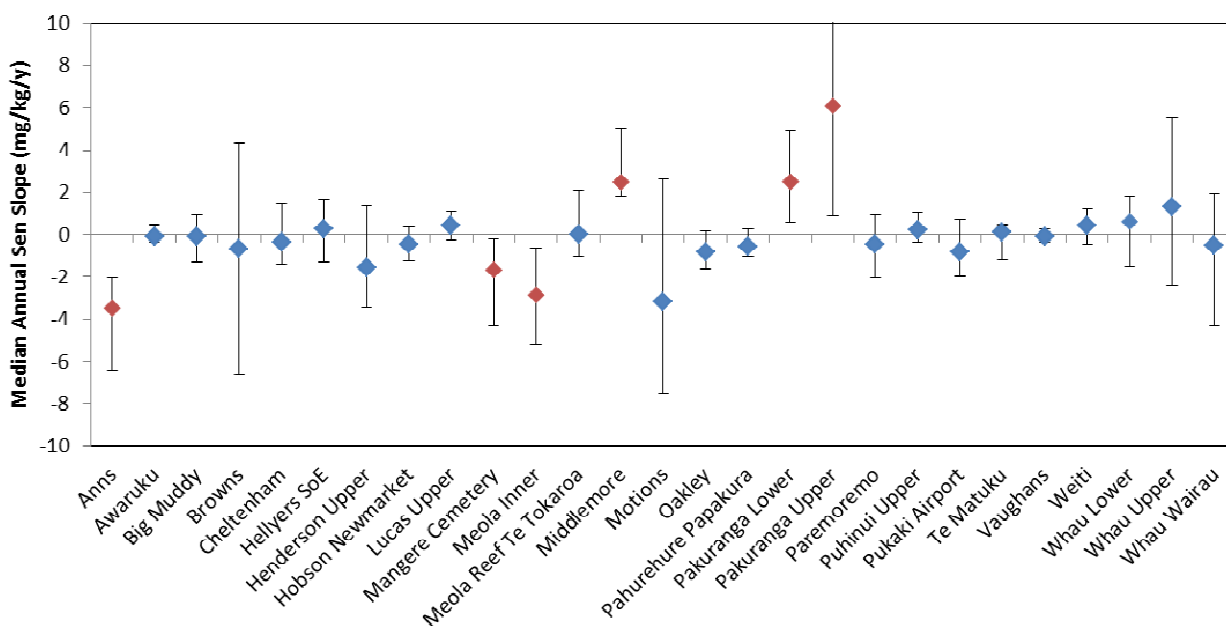


Table 1: Summary of Mann Kendall trend tests for total zinc in marine sediments. Bold text indicates trends that are statistically significant ( $p < 0.05$  and  $RSSE > \pm 1\%$ ).

Site	Programme	Years	Obs.	Median Total Zn (mg/kg)	Trend test p	SSE (mg/kg/y)	RSSE	Sig.
<b>Anns</b>	<b>SoE</b>	<b>13.6</b>	<b>8</b>	<b>165</b>	<b>0.01</b>	<b>-3.5</b>	<b>-2.1%</b>	<b>Y</b>
Awaruku	SoE	13.4	8	24	0.27	-0.1	-0.4%	
Benghazi	RDP	8.2	5	75	0.24	1.7	2.2%	
Big Muddy	SoE	13.6	7	57	0.28	-0.1	-0.2%	
Bowden	RDP	8.2	5	200	0.41	3.0	1.5%	
Brighams UWH	UWH	6.1	6	101	0.24	1.9	1.8%	
Browns	SoE	9.2	5	34	0.33	-0.7	-1.9%	
Central Main Channel	UWH	6.1	6	102	0.50	0.9	0.9%	
Central Waitemata East	UWH	6.1	6	116	0.50	0.4	0.4%	
Chelsea	RDP	8.2	5	46	<b>0.04</b>	0.3	0.6%	
Cheltenham	SoE	13.4	7	42	0.39	-0.4	-0.8%	
Coxs	RDP	8.2	5	68	0.24	1.1	1.6%	
Hellyers SoE	SoE	13.5	8	98	0.24	0.3	0.3%	
Hellyers Upper UWH	UWH	6.1	6	130	0.14	2.0	1.5%	
Hellyers UWH	UWH	6.1	6	83	0.36	-0.8	-1.0%	
Henderson Entrance	RDP	8.3	5	69	0.24	-0.5	-0.7%	
Henderson Lower	RDP	8.2	5	146	0.41	1.9	1.3%	
Henderson Upper	SoE	13.6	8	179	0.27	-1.5	-0.9%	
Herald Island North	UWH	6.1	6	50	0.50	-0.4	-0.7%	
Herald Island Waiarohia	UWH	6.1	6	19	0.36	-0.4	-2.2%	
Hillsborough	RDP	6.1	4	69	0.63	-0.4	-0.7%	
Hobson Awatea	RDP	7.2	4	106	0.38	0.3	0.3%	
Hobson Newmarket	SoE	13.6	8	42	0.27	-0.5	-1.1%	
Hobson Whakataka	RDP	6.2	4	90	0.17	-1.8	-2.1%	
Hobsonville	UWH	7.2	8	26	0.50	0.0	0.0%	
Kendall	RDP	8.2	5	32	0.41	0.0	-0.1%	
Lucas Te Wharau UWH	UWH	6.1	6	83	0.50	0.2	0.3%	
Lucas Upper	SoE	13.5	7	99	0.19	0.4	0.4%	
Lucas UWH	UWH	6.1	6	98	0.50	-1.0	-1.0%	
<b>Mangere Cemetery</b>	<b>SoE</b>	<b>13.6</b>	<b>8</b>	<b>136</b>	<b>0.02</b>	<b>-1.7</b>	<b>-1.2%</b>	<b>Y</b>
<b>Meola Inner</b>	<b>SoE</b>	<b>13.7</b>	<b>8</b>	<b>244</b>	<b>0.03</b>	<b>-2.8</b>	<b>-1.2%</b>	<b>Y</b>
Meola Outer	RDP	8.2	5	34	0.12	0.6	1.9%	
Meola Reef Te Tokaroa	SoE	13.7	8	96	0.55	0.0	0.0%	
<b>Middlemore</b>	<b>SoE</b>	<b>13.5</b>	<b>8</b>	<b>186</b>	<b>0.00</b>	<b>2.5</b>	<b>1.3%</b>	<b>Y</b>
Motions	SoE	13.7	8	255	0.17	-3.2	-1.2%	
Oakley	SoE	13.7	8	160	0.11	-0.8	-0.5%	
Otahuu	RDP	8.2	5	177	0.24	1.5	0.9%	
Outer Main Channel	UWH	6.1	6	62	0.14	4.8	7.7%	
Pahurehure Papakura	SoE	13.6	8	66	0.27	-0.6	-0.9%	
<b>Pakuranga Lower</b>	<b>SoE</b>	<b>13.5</b>	<b>7</b>	<b>153</b>	<b>0.04</b>	<b>2.5</b>	<b>1.6%</b>	<b>Y</b>
<b>Pakuranga Upper</b>	<b>SoE</b>	<b>13.5</b>	<b>8</b>	<b>190</b>	<b>0.02</b>	<b>6.1</b>	<b>3.2%</b>	<b>Y</b>
Panmure	RDP	8.2	5	175	0.24	2.5	1.4%	
Paremoremo	SoE	13.5	7	91	0.39	-0.5	-0.5%	
Point England	RDP	6.1	4	88	0.17	2.3	2.7%	
Princes	RDP	8.2	5	148	0.12	2.7	1.8%	
Puhinui Upper	SoE	13.6	8	107	0.17	0.2	0.2%	
Pukaki Airport	SoE	13.6	7	66	0.19	-0.8	-1.2%	
Purewa	RDP	8.2	5	156	0.12	2.3	1.5%	
Rangitopuni UWH	UWH	6.1	6	103	0.10	1.2	1.2%	
Shoal Hillcrest	RDP	8.2	5	113	0.24	1.9	1.7%	
Shoal Lower	RDP	6.2	4	41	0.17	1.7	4.2%	
Te Matuku	SoE	12.3	6	32	0.50	0.1	0.3%	
Upper Main Channel	UWH	6.1	6	99	0.24	1.3	1.3%	
Vaughans	SoE	13.4	8	22	0.17	-0.1	-0.4%	
Weiti	SoE	13.5	8	49	0.27	0.4	0.9%	
<b>Whau Entrance</b>	<b>RDP</b>	<b>8.2</b>	<b>5</b>	<b>33</b>	<b>0.04</b>	<b>2.2</b>	<b>6.7%</b>	<b>Y</b>
Whau Lower	SoE	13.5	8	168	0.45	0.6	0.4%	
Whau Upper	SoE	13.7	8	255	0.20	1.3	0.5%	
Whau Wairau	SoE	13.7	8	218	0.45	-0.5	-0.2%	

Figure 4: Relative Sen slope of total zinc in marine sediments for SoE sites. Red data points show significant trends ( $p < 0.05$  and  $RSSE > \pm 1\%$ ), while blue data points are not significant ( $p \geq 0.05$ ).

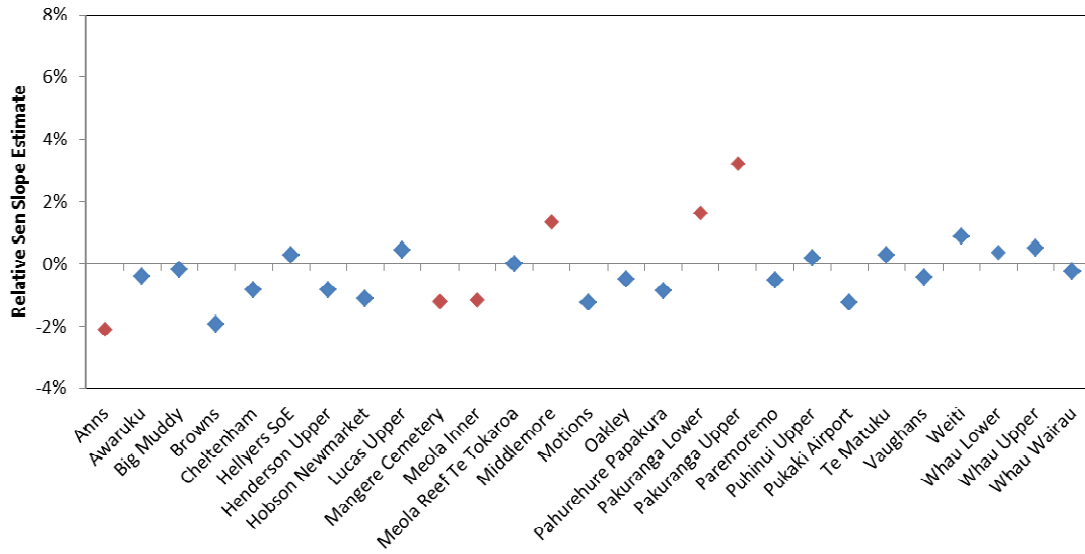
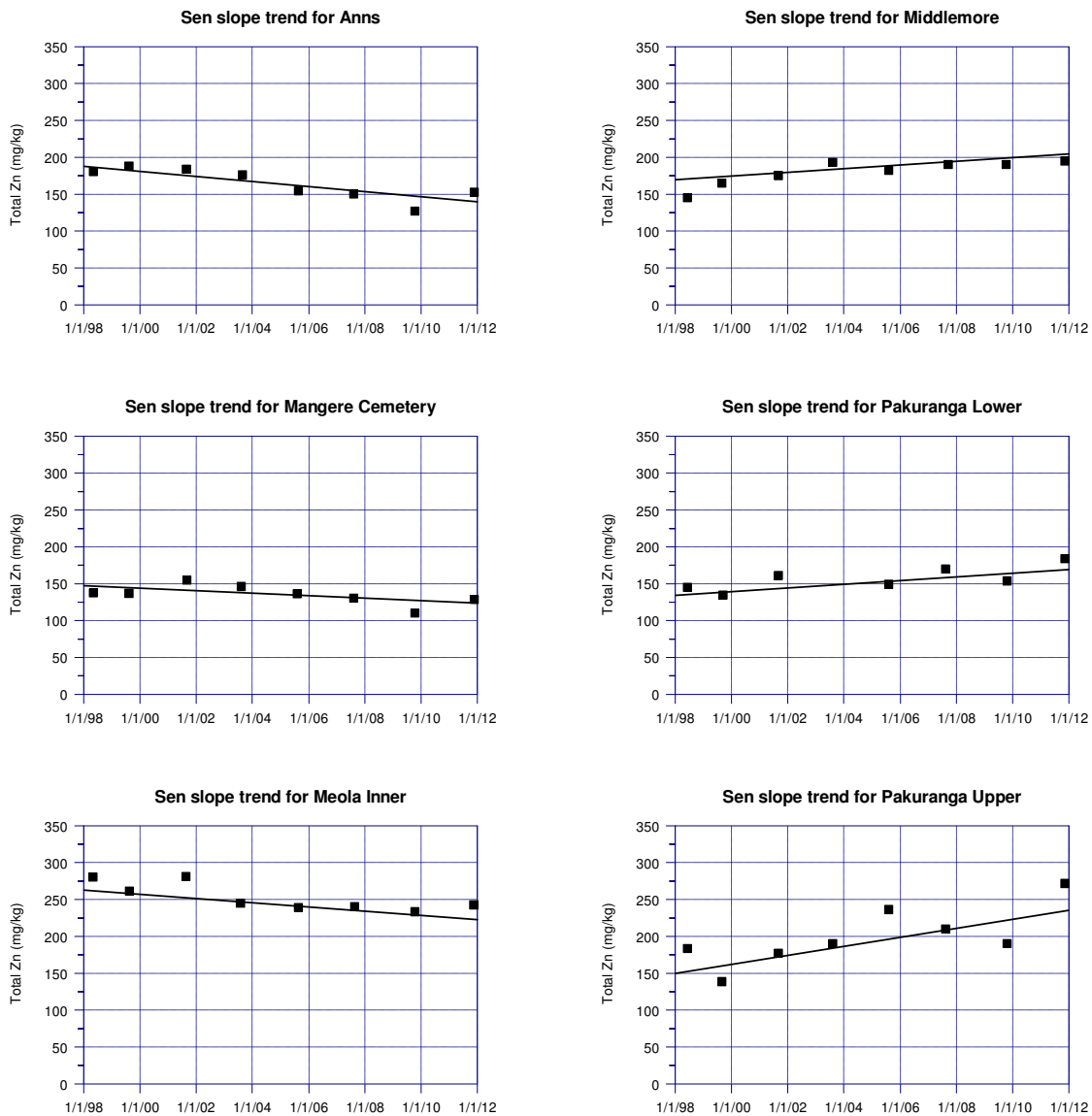


Figure 5: Sen slope trends for total zinc at the six SoE sites where significant trends were observed.



Auckland Council adopted Environmental Response Criteria (ERC) that are based on very conservative interpretations of international sediment quality guidelines (SQGs), as summarised in Table 4.1 of Mills et al (2012). It is notable that none of the 59 sites listed in Table 1 have median total zinc exceeding the 271mg/kg “Probable Effect Level” (PEL) of MacDonald et al (1996), let alone the 410mg/kg “ISQG-High” of ANZECC (2000). Only five sites (Bowden, Meola Inner, Motions, Whau Upper and Whau Wairau) have median total zinc exceeding the 200mg/kg “ISQG-Low” of ANZECC (2000).

When compared against international SQGs (MacDonald et al 1996, ANZECC 2000), it appears that the vast majority of sediments tested in the Auckland region have only low levels of zinc contamination, thereby offering a high level of protection for sediment-dwelling species. Furthermore, the above trend analysis indicates that the level of zinc in sediments is static in the vast majority of cases.

## **2.4 OTHER CONTAMINANTS OF CONCERN**

When considering the linkage between sediment contaminants and environmental risks, it is important to appreciate that zinc is only one of many contaminants that can be present. Lead and copper have been evaluated in parallel to zinc for all of the above sediment monitoring programmes. Both have strong linear correlations with the zinc content in the sediment, as shown in Figure 6. Cadmium, mercury and antimony were measured in 2005 at the 27 SoE sites by McHugh and Reed (2006). Figure 6 shows that all of these metals are linearly correlated with zinc. High molecular weight polycyclic aromatic hydrocarbon (HWPAAH) was also measured in 2005 by McHugh and Reed (2006), and Figure 6 shows that HWPAAH is linearly correlated with zinc. A wide variety of organochlorine pesticides were measured in 2007 at 9 SoE sites and reported by Mills (2014). Generally these contaminants were present at very low levels but they were still correlated with the zinc in the sediment – the example of dieldrin is shown in Figure 6.

These strong correlations between zinc and other contaminants have been previously highlighted by Timperley (2008). Based on these correlations, Timperley concluded that measures designed specifically to target reductions in single contaminants such as zinc will not necessarily reverse observed biological changes. Timperley urged a more encompassing approach to stormwater contaminant management rather than targeting single contaminant sources.

# **3 WATER QUALITY MONITORING**

## **3.1 MONITORING PROGRAMME**

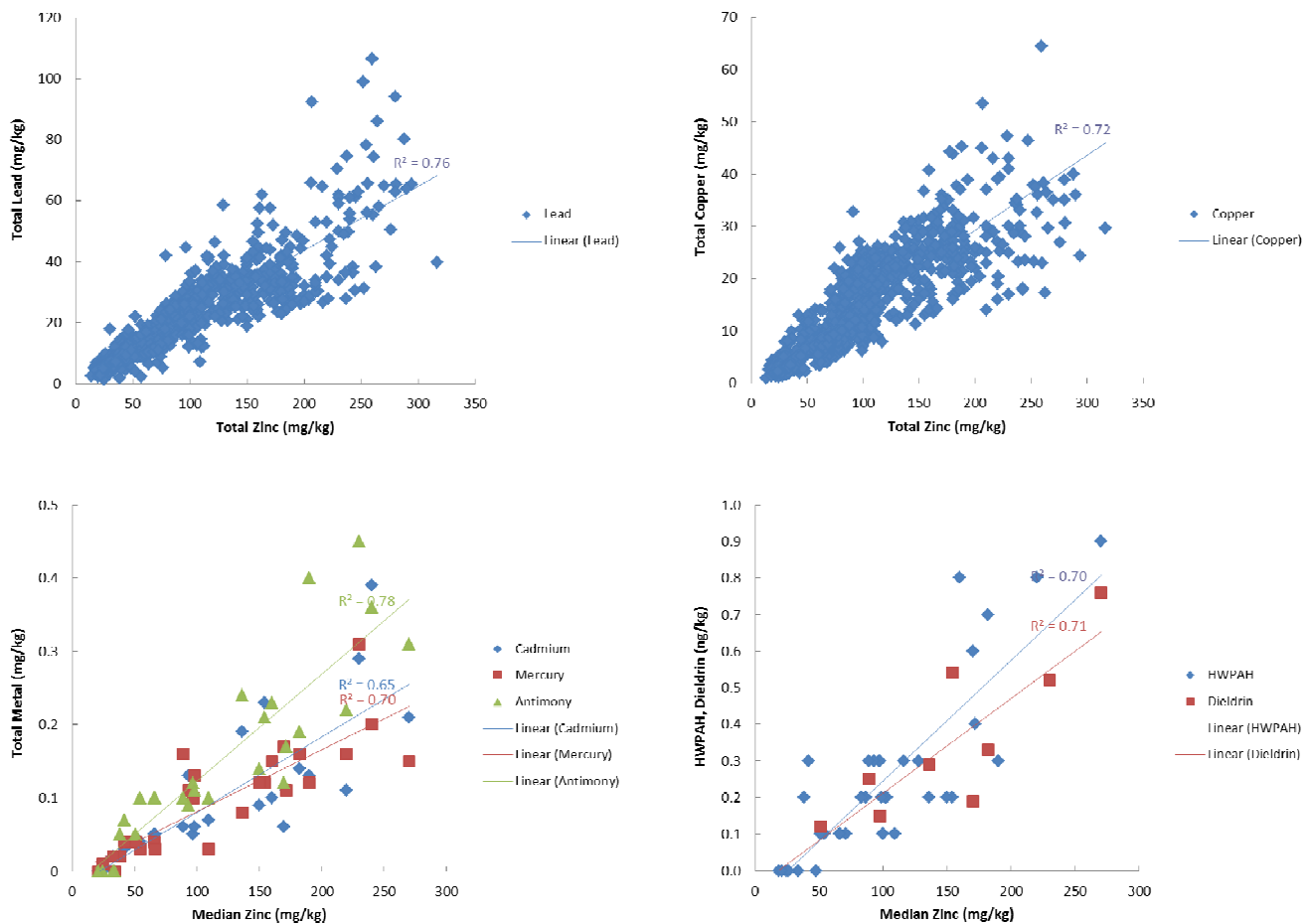
The Water Quality Programme for freshwater rivers has been conducted continuously on a monthly basis since 1986 by Auckland Regional Council and now Auckland Council (Lockie and Neale, 2013). The programme monitors the physical, chemical and microbiological properties of rivers at 34 sites. This monitoring provides information on the temperature, amounts of nutrients, oxygen, sediment and other pollutants in the sampled rivers. The programme has evolved throughout its duration, with sites added or moved according to requirements.

The Water Quality Programme has included measurement of metals concentration in freshwater every month since 1995. Temporal trends in water quality parameters have been reported by Scarsbrook (2007), focusing on dissolved oxygen, temperature, conductivity, pH, suspended solids, turbidity, ammoniacal nitrogen, nitrate/nitrite nitrogen, total Kjeldahl nitrogen, total nitrogen, dissolved reactive phosphorus, total phosphorus, chloride, and faecal coliforms. It appears that no statistical analysis has been reported for trends in metals contamination, including zinc. Trend plots for the 1995-2003 period at four sites have been published (Wilcock and Martin 2003, Macaskill and Martin, 2004), but no statistical analysis was presented. The number of sites where zinc is tested has been steadily increased from 4 in 1995-2003 to 24 in 2012 (Lockie and Neale, 2013). This is aligned with the Council’s apparent focus on zinc in stormwater. Thus it is surprising that a statistical trend analysis of the metals data does not appear to have been completed to date.

Raw data for zinc in freshwater was provided to New Zealand Steel by Auckland Council under Official Information Request No. 9000128580. This data has been analysed for the present paper, providing a statistical interpretation of temporal trends for zinc in freshwater streams between 1995 and 2013.



Figure 6: Correlations between zinc and other contaminants in marine sediments.



### 3.2 ZINC IN FRESHWATER STREAMS

Temporal trends for zinc in freshwater streams were analysed using the “Time Trends” software package (NIWA and Jowett, 2012). The criterion adopted for inclusion in the analysis was that the sites were sampled for a period of at least three years, reducing the number of sites from 34 to 21. The samples were collected at a monthly frequency, and the zinc concentrations were observed to show both seasonal and long term trends; for example refer to Figure 7. The non-parametric seasonal Kendall trend test is the recommended method for analysing this type of data (Helsel and Hirsch, 2002). Since the data was measured monthly, the seasons were defined as the twelve months of the year. The absolute magnitude of long-term trends was obtained from the median annual slope of seasonal pairs (Sen slope estimate, SSE), expressed in units of  $\mu\text{g/L/y}$ . The relative magnitude of the trend (relative Sen slope estimate, RSSE), was obtained from the median annual slope divided by the median value, expressed as a percentage. A trend was considered statistically significant if the test p value was less than 0.05 and the annual trend was more than  $\pm 1\%$  of the median value (RSSE).

Table 2 summarises the results of non-parametric seasonal Kendall trend tests of total zinc in freshwater streams. The absolute trends in total zinc are shown in Figure 8, while the relative trends are shown in Figure 9. Significant trends were found for 9 of the 21 stations, and in all cases the total zinc was observed to have a decreasing trend ( $\text{SSE} < 0$ ). No sites had an increasing trend for total zinc. Monitoring periods of at least 8 years appear to be necessary to reliably detect trends in the data. Large confidence intervals tend to occur for sites with 6 years or less data, which reflects the inherent variability in contaminant levels.

- Four urban sites have been monitored since 1995 (18 years): Lucas Creek, Oakley Creek, Oteha Stream, Puhinui Stream. The Sen slope trends are shown in Figure 10. All four sites have significant decreasing trends in zinc level, ranging from -1% to -8% per year.

- One urban site at Pakuranga Ck Greenmount has been monitored since 2001 but was not tested between 2003 and 2007. It has a significant decreasing trend in zinc level of -5% per year.
- One rural and two urban sites have been monitored since 2005 (8.5 years): Vaughan Stream, Okura Creek, Otara Creek Kennel Hill. All three sites show decreasing trends in zinc of -5% to -10% per year, although the trend is not significant at the rural Vaughan Stream.
- The remaining 13 sites have been monitored for 3 to 6 years and the only significant trends are at rural sites Matakana River and Waiwera Stream with zinc decreasing at -42% and -27% per year.

Figure 7: Total zinc concentration for freshwater at Oteha Stream, demonstrating seasonal and long-term variations.

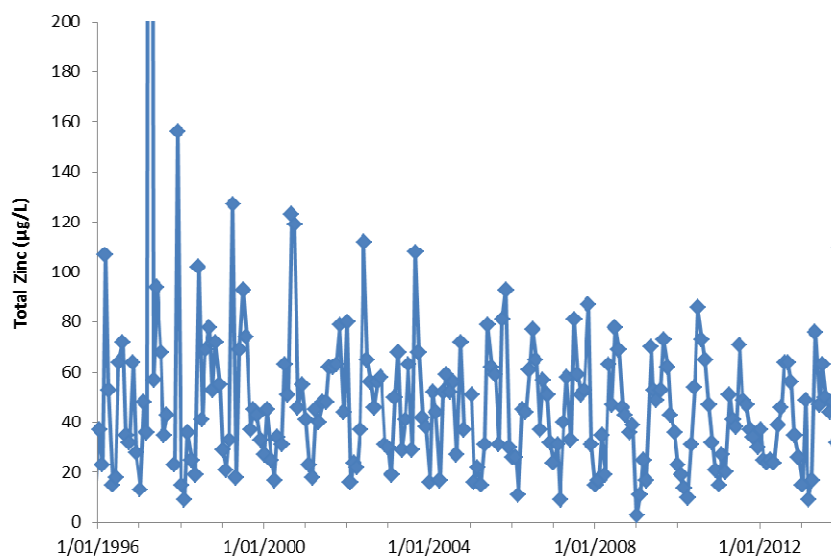


Table 2: Summary of non-parametric seasonal Kendall trend tests for total zinc in freshwater streams. Bold text indicates trends that are statistically significant ( $p < 0.05$  and  $RSSE > \pm 1\%$ ).

Station Name	Start	End	Years	Obs	Median Total Zn (µg/L)	Trend test p	SSE (µg/L/y)	RSSE	Sig.
Kumeu River	30/08/2010	3/12/2013	3.4	40	4	0.49	-0.4	-10%	
<b>Lucas Creek</b>	<b>5/12/1995</b>	<b>5/12/2013</b>	<b>18.1</b>	<b>215</b>	<b>14</b>	<b>0.00</b>	<b>-1.1</b>	<b>-8%</b>	<b>Y</b>
Mahurangi River FHQ	30/08/2010	3/12/2013	3.4	40	1	0.35	-0.1	-11%	
Mahurangi River WS	7/05/2009	3/12/2013	4.7	42	3	0.38	-0.2	-6%	
Makarau @ Railway	30/08/2010	3/12/2013	3.4	40	1	0.13	-0.1	-12%	
<b>Matakana River</b>	<b>30/08/2010</b>	<b>3/12/2013</b>	<b>3.4</b>	<b>40</b>	<b>1</b>	<b>0.04</b>	<b>-0.5</b>	<b>-42%</b>	<b>Y</b>
<b>Oakley Creek</b>	<b>6/12/1995</b>	<b>4/12/2013</b>	<b>18.1</b>	<b>214</b>	<b>27</b>	<b>0.00</b>	<b>-0.8</b>	<b>-3%</b>	<b>Y</b>
<b>Okura Creek</b>	<b>1/06/2005</b>	<b>5/12/2013</b>	<b>8.6</b>	<b>103</b>	<b>5</b>	<b>0.01</b>	<b>-0.3</b>	<b>-6%</b>	<b>Y</b>
Omaru @ Maybury	27/01/2009	16/12/2013	5.0	60	110	0.43	-4.6	-4%	
Otaki Creek	11/09/2007	16/12/2013	6.3	76	45	0.73	-0.5	-1%	
Otara Ck East Tamaki	11/09/2007	16/12/2013	6.3	76	29	0.40	-0.7	-2%	
<b>Otara Ck Kennel Hill</b>	<b>7/07/2005</b>	<b>16/12/2013</b>	<b>8.5</b>	<b>102</b>	<b>16</b>	<b>0.00</b>	<b>-1.6</b>	<b>-10%</b>	<b>Y</b>
<b>Oteha Stream</b>	<b>5/12/1995</b>	<b>5/12/2013</b>	<b>18.1</b>	<b>215</b>	<b>43</b>	<b>0.05</b>	<b>-0.4</b>	<b>-1%</b>	<b>Y</b>
Pakuranga Ck Botany	11/09/2007	16/12/2013	6.3	76	26	0.58	-0.5	-2%	
<b>Pakuranga Ck Greenmt.</b>	<b>22/01/2001</b>	<b>16/12/2013</b>	<b>13.0</b>	<b>99</b>	<b>24</b>	<b>0.03</b>	<b>-1.3</b>	<b>-5%</b>	<b>Y</b>
Papakura Stream Porchr.	2/09/2010	4/12/2013	3.3	40	6	0.71	-0.6	-10%	
<b>Puhinui Stream</b>	<b>6/12/1995</b>	<b>4/12/2013</b>	<b>18.1</b>	<b>212</b>	<b>44</b>	<b>0.00</b>	<b>-2.2</b>	<b>-5%</b>	<b>Y</b>
Riverhead Stream	30/08/2010	3/12/2013	3.4	40	7	0.25	-0.7	-10%	
Vaughan Stream	1/06/2005	5/12/2013	8.6	102	4	0.26	-0.2	-5%	
Wairoa River	2/09/2010	4/12/2013	3.3	40	1	0.13	-0.3	-18%	
<b>Waiwera Stream</b>	<b>30/08/2010</b>	<b>3/12/2013</b>	<b>3.4</b>	<b>40</b>	<b>1</b>	<b>0.04</b>	<b>-0.3</b>	<b>-27%</b>	<b>Y</b>

Figure 8: Median annual Sen slope of the total zinc concentration for freshwater streams. Red data points indicate significant trends ( $p < 0.05$  and  $RSSE > \pm 1\%$ ), while blue data points are not significant ( $p \geq 0.05$ ). The error bars correspond to 95% confidence intervals.

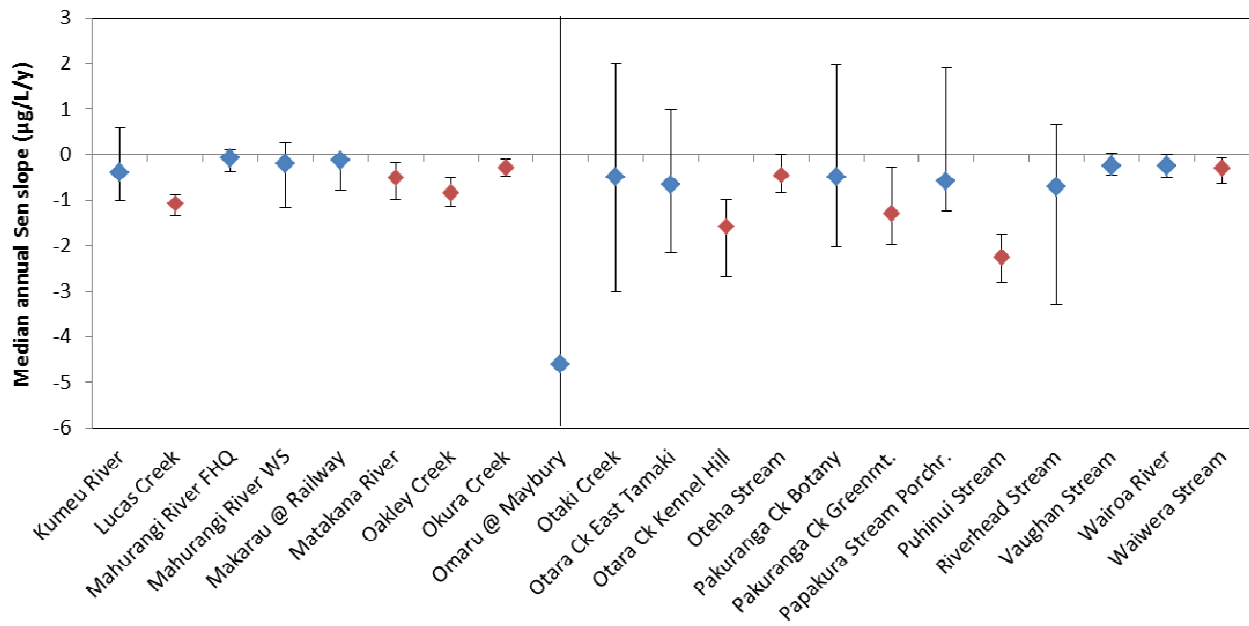


Figure 9: Relative Sen slope of the total zinc concentration for freshwater streams. Red data points show significant trends ( $p < 0.05$  and  $RSSE > \pm 1\%$ ), while blue data points are not significant ( $p \geq 0.05$ ).

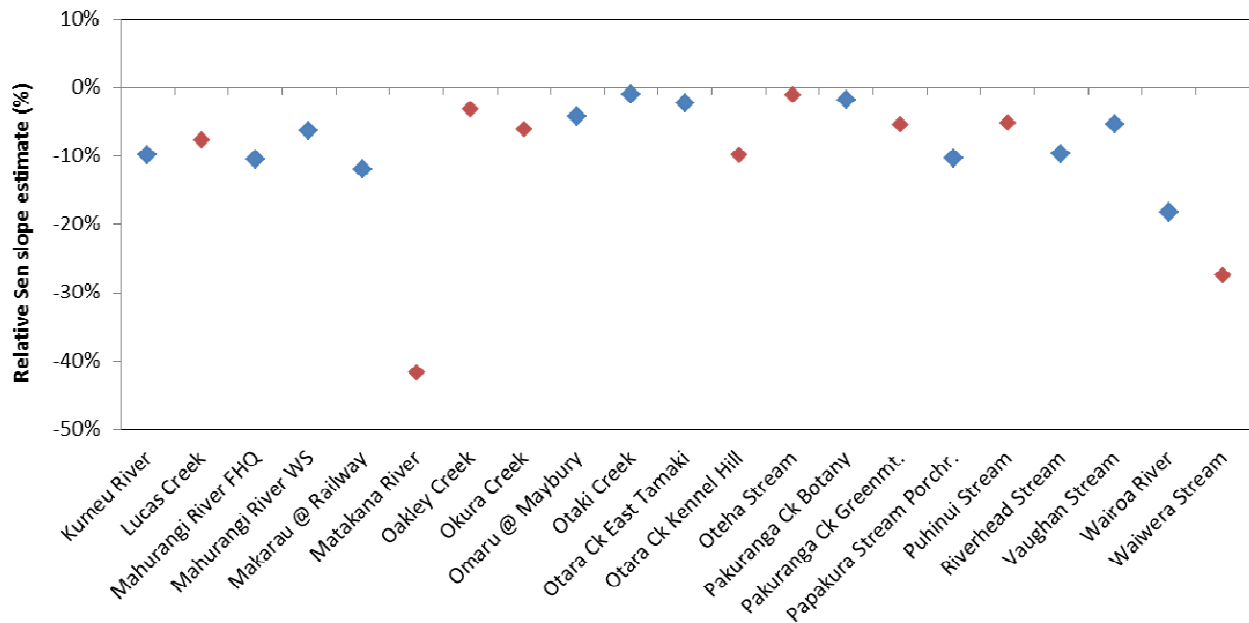
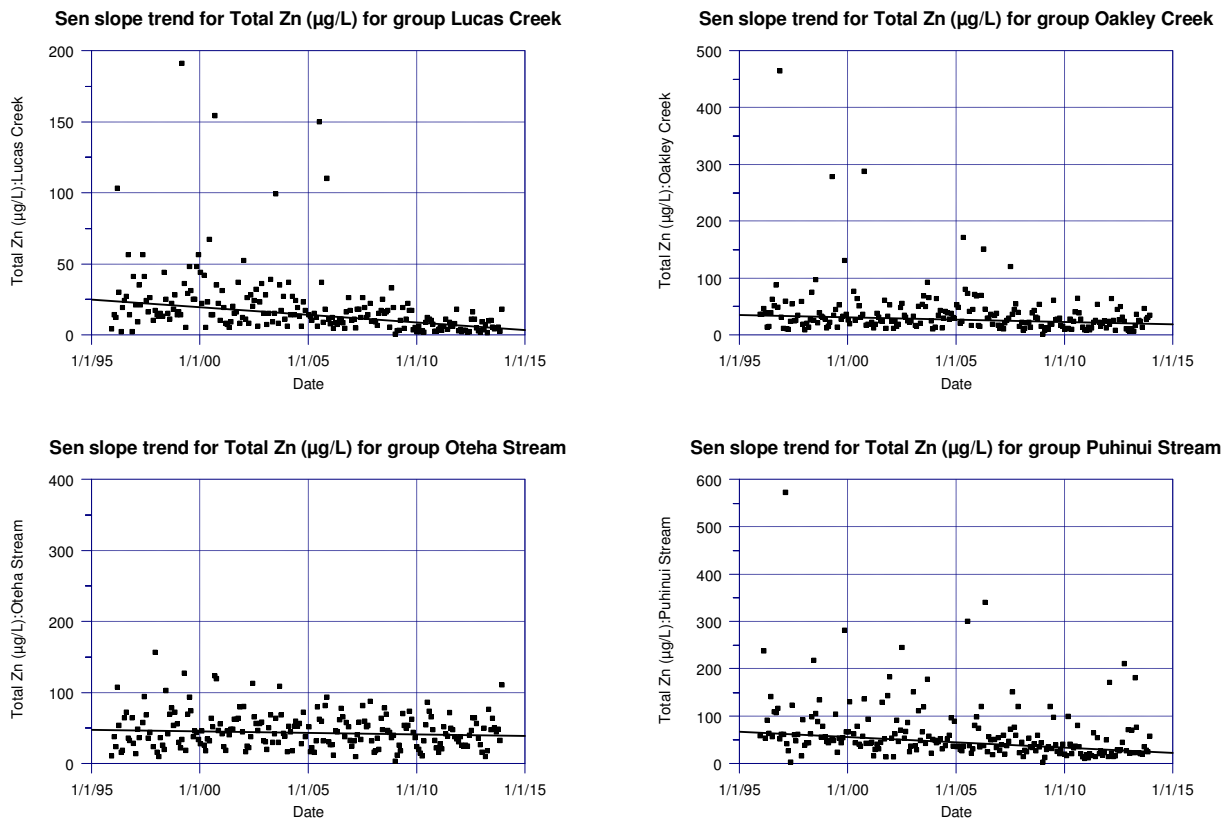


Figure 10: Sen slope trends for total zinc concentration in freshwater streams.



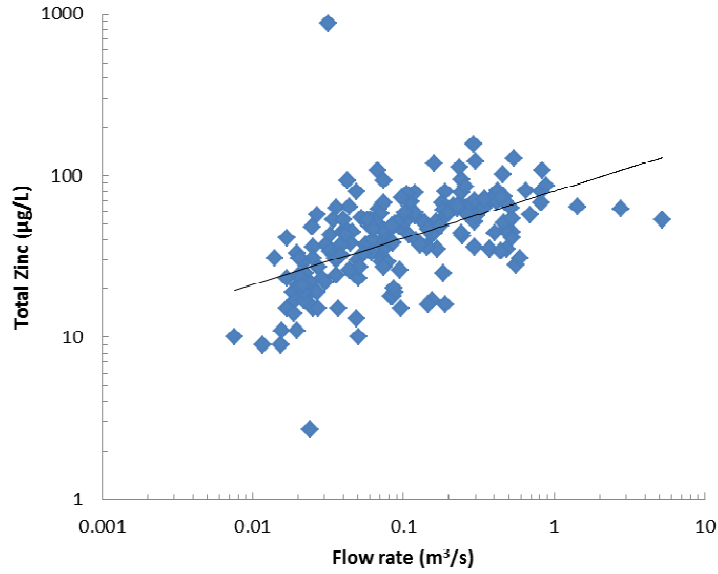
### 3.3 EFFECT OF STREAM FLOW RATE

The concentration of contaminants in streams is usually influenced by their flow rate (Helsel and Hirsch, 2002). This is a consequence of two different physical effects. Firstly, a contaminant that is discharged at a reasonably constant rate tends to be diluted as the flow rate of the stream increases. Hence, the concentration of dissolved contaminants can decrease as flow increases. Secondly, high flow rates can encourage sediment from overland flows to enter streams via a wash-off effect. In this case, the concentration of contaminant in the stream tends to increase with flow rate. A combination of both effects is also possible, resulting in complex relationships between concentration and flow rate.

An example of the correlation between total zinc concentration and flow rate is shown in Figure 11 for the Oteha Stream monitoring station. The flow rate data in this plot was extracted from Auckland Council GIS Viewer (2011), and is the mean daily flow rate corresponding to each date of water sampling. Ideally, the instantaneous flow rate should be used for this analysis, since it varies dramatically throughout any given day in response to rain events. However, it is still apparent from Figure 11 that there is a general trend for increasing zinc concentrations as flow rate increases, which is consistent with a sediment wash-off effect. Note that the data point shown at  $0.032\text{m}^3/\text{s}$  and  $872\mu\text{g/L}$  (2 Apr 1997) is likely to be corrupt since the soluble zinc level in the same sample was  $<2\mu\text{g/L}$ .

If flow rate data is available, it is recommended to treat it as an exogenous co-variable in non-parametric seasonal Kendall trend tests of contaminant trends (Helsel and Hirsch, 2002). Removing the variation in contaminant concentration caused by flow rate has the advantage of reducing the background variability, and thereby increases the ability to detect trends in the data.

Figure 11: Total zinc concentration for freshwater at Oteha Stream as a function of mean daily flow rate for 1995-2011 sampling period.

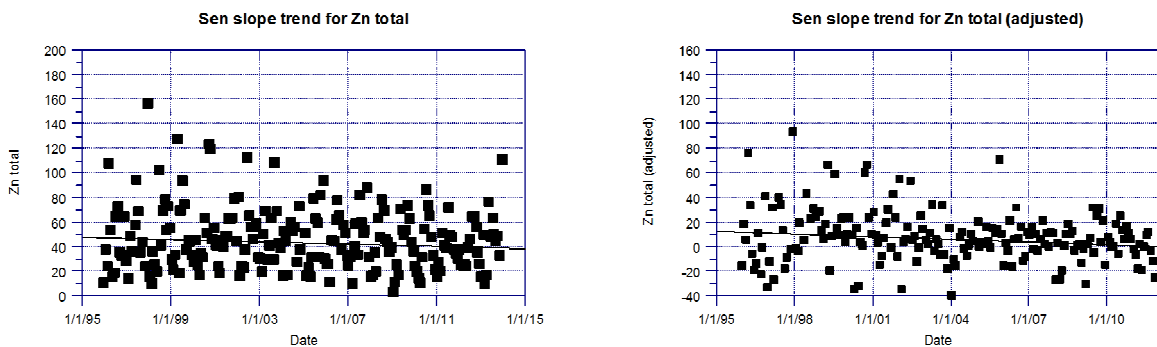


In order to demonstrate the effect of flow rate on total zinc trends, the data for Oteha Stream (Figure 7) was reanalysed using the Lowess covariate adjustment method and the trend analysis is summarised in Table 3. With no adjustment for seasons or flow, there was no significant trend in zinc level ( $p=0.28$ ). Adjusting for seasonal variation revealed a significant temporal trend ( $p=0.05$ ). Furthermore, an additional adjustment for mean daily flow rate accounted for another 2.7% of the variation, improving the p-value to 0.02 and increasing the Sen slope estimate. Figure 12 shows that including adjustment for flow has the effect of reducing scatter and revealing stronger Sen slope trends.

Table 3: Summary of non-parametric trend tests for total zinc in freshwater at Oteha Stream.

Test	Start	End	Years	Obs	Median Total Zn (µg/L)	Trend test p	SSE (µg/L/yr)	RSSE
Mann-Kendall (no adjustment)	5/12/1995	5/12/2013	18.1	215	43	0.28	-0.3	-0.8%
Seasonal Kendall (12 seasons/year)	5/12/1995	5/12/2013	18.1	215	43	0.05	-0.4	-1.0%
Seasonal Kendall with flow adjustment	5/12/1995	2/11/2011	16.0	186	50	0.02	-0.7	-1.4%

Figure 12: Sen slope trends for total zinc in freshwater at Oteha Stream without adjustment for flow (a) and with Lowess adjustment for flow (b). Less scatter and stronger trend are apparent in (b).



(a)

(b)

The above example demonstrates the value of accounting for flow rate in analysis of freshwater contaminant trends. Unfortunately, the River Water Quality and River Water Quantity programmes are maintained via independent databases even though many of the monitoring sites are the same. Therefore, it is a complicated and laborious task to retrospectively extract the instantaneous flow rate data for each water quality sampling point. It is highly recommended that Auckland Council record the instantaneous flow rate in the water quality database for all future sampling points.

## 4 DISCUSSION

### 4.1 ZINC TRENDS SUMMARY

In the assessment of trends of metals in marine sediments for the period 1998-2010, Mills et al (2012) concluded:

*“where changes in Zn concentrations have occurred, these have mainly been increases, which supports a generally held view that Zn concentrations are likely to increase over time at most urban sites.”*

This statement is not consistent with the new analysis in the present paper, which includes new data from 2011 and 2012 sampling years, and is focused exclusively on total metals data. Zinc levels in the vast majority of marine sediment sites have remained static during the monitoring period. For the small number of sites showing significant trends, there is an even mix of increasing and decreasing trends and the rate of change is small (RSSE  $<\pm 2\%$ ). This might be expected in complex systems such as estuarine environments, but the key issue is that there is no evidence of the overall increasing trend, which has been the putative basis for Council policies focusing on reduction of zinc runoff.

The present analysis of temporal trends for zinc in freshwater streams has revealed that no sites are experiencing increasing levels of zinc. In contrast, almost half the monitoring stations have observed significant decreasing trends between 1995 and 2013. The rate of change for zinc in freshwater is also relatively high (median RSSE is -6%) compared with marine sediments.

The inconsistency of temporal trends for marine sediment and freshwater is somewhat puzzling. How could it be possible that streams are showing reducing trends in zinc concentration, while the downstream sediments generally show no change in zinc levels? Streams are experiencing significantly decreasing concentrations of zinc, and therefore it would naturally be expected that the sediments should also show decreasing trends. It appears that marine sediments are relatively insensitive to changes in stream contaminants. Perhaps this might be due to dilution effects, although it is beyond the scope of this paper to investigate further. However, this observation does invite the question: if zinc concentrations in streams are already decreasing with little impact on zinc levels in the receiving sediments, why would further restrictions on stormwater contamination change the situation for marine sediments?

### 4.2 SOURCE CONTROL OF ROOFING PRODUCTS

The PAUP has introduced the effective requirement for “source control” of roofing products by controlling the use of “exposed surface or surface coating of metallic zinc or any alloy containing greater than 10% zinc” (Auckland Council 2013). This requirement potentially restricts the use of zinc aluminium coated steel because the metal coating contains approximately 43wt.% zinc. Roofing and cladding made from zinc aluminium coated steel would therefore require painting or stormwater treatment by filtration devices before discharging. Whilst the PAUP does not prohibit the use of these materials, the requirement to obtain a resource consent for their use, and/or to treat stormwater, is a potential deterrent for users, both from a financial (cost) perspective and because it introduces another regulatory requirement.

Despite the metal coating being 43wt.%, zinc runoff from zinc aluminium coated steel at Pukekohe, New Zealand has been found to be between 81% and 92% lower than galvanised steel, with the relative difference increasing as the products weather (Shedden et al, 2007). The Contaminant Load Model developed by ARC (2010) and utilised in the PAUP (Auckland Council, 2013), assumes a zinc yield of 0.2g/m<sup>2</sup>/y for unpainted zinc aluminium coated steel, which is 91% lower than the 2.24g/m<sup>2</sup>/y yield for unpainted galvanised steel. The zinc yield from unpainted zinc aluminium coated steel is similar to that of painted galvanised steel when new, and it

is improved further by the effects of weathering. There is no debate that zinc aluminium coated steel provides a remarkable reduction in zinc runoff compared with traditional steel roofing materials.

The New Zealand roofing and cladding market has been almost completely converted from heavy usage of galvanised steel following the introduction of zinc aluminium coated steel to New Zealand in 1994. As such, Shedden et al (2007) predicted that the net zinc load from steel roofing in the urban Auckland region would be reduced by 95% for modern steel roofing (zinc aluminium coated steel in unpainted and prepainted forms) compared with past usage of galvanised steel. Source control rules that restrict the usage of unpainted zinc aluminium coated steel would therefore deliver negligible reductions in total zinc load. Therefore, source control of new developments appears unjustified, and lobbying instead for the replacement of old galvanised steel roofing in existing developments with modern steel roofing would deliver substantial improvements in stormwater quality.

### **4.3 CONTAMINANT MODELLING**

The changed market for roofing products was recognised by NIWA in contaminant modelling of the Central Waitemata Harbour (ARC, 2008a) and Southeastern Manukau Harbour (ARC, 2008b) for the period 2001 to 2100. These two lengthy series of reports were published in December 2009 and October 2010 respectively, after a long period of preparation and international peer review. These studies aimed to test the efficacy of stormwater treatment and industrial roof contaminant source control. A central conclusion in both series of reports was:

*“Zinc source control targeting industrial building roofs produced limited reduction of zinc accumulation rates in the harbour because industrial areas cover only a small proportion of the catchment area and most unpainted galvanised steel roofs are expected to be replaced with other materials within the next 25 to 50 years.”*

Zinc source control was defined as the painting of existing unpainted and poorly painted galvanised steel industrial building roofs. The change in roofing materials was highlighted by Timperley and Reed (2008), based on data and information provided by New Zealand Steel. Unpainted zinc aluminium coated steel and painted zinc aluminium coated steel were not regarded as high-contaminant generating roofing material, and their continued use was found to contribute to a decrease in zinc load between 2001 and 2015-20 as existing galvanised roofs are replaced by zinc aluminium coated steel. It is notable that this modelling is validated by the present observations of declining zinc levels in freshwater streams.

Beyond 2020, a slow increase in zinc was forecast as vehicles become the dominant source of zinc (ARC 2008a, ARC 2008b). Therefore, source control of industrial galvanised steel roofs was claimed to be irrelevant since the market has already converted to low-contaminant generating roofing material, including unpainted zinc aluminium coated steel. The Central Waitemata Harbour (ARC, 2008a) and Southeastern Manukau Harbour (ARC, 2008b) studies reversed the previous recommendation for source control by Timperley and Green (2005). Timperley and Green did not account for the market conversion from galvanised steel to zinc aluminium coated steel for roofing and cladding. Having now accounted for these changes in roofing and cladding practices in ARC (2008a) and ARC (2008b), it is clearly demonstrated that source control is ineffectual and therefore it should be removed from the PAUP.

## **5 CONCLUSIONS**

Where statistically significant trends occur for zinc levels in streams, estuaries and harbours, they are mostly observed to be reducing. Freshwater streams in particular are consistently observed to have declining levels of zinc over the last two decades of monitoring. This finding is consistent with the comprehensive stormwater contaminant modelling by NIWA of the Upper Waitemata Harbour and Southeastern Manukau Harbour, which predicted a decreasing trend for zinc loads in stormwater between 2001 and 2015-20, as existing galvanised roofs are replaced by zinc aluminium coated steel, followed by a slow increase as vehicles become the dominant source of zinc. Consequently, instituting zinc source control for roofing is not justified as it would have insignificant impact on contaminant levels in stormwater.

## 6 RECOMMENDATIONS

In the interests of optimising data reliability and significantly reducing analysis costs, it is recommended that Auckland Council cease the practice of contaminant analysis of <63µm sediment fraction using the extractable metals method. Future analysis of sediments should focus on the <500µm total contaminant and corresponding particle size analysis for three replicate samples.

It is highly recommended that Auckland Council include the instantaneous flow rate in the water quality database for all future sampling points. This would permit the accounting for flow rate in analysis of freshwater contaminant trends.

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