A METAL ISOTOPE TOOLKIT FOR TRACING HEAVY METALS IN THE ENVIRONMENT

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ABSTRACT

Introduction

Declining water quality is of serious concern for most New Zealanders. Aotearoa New Zealand's freshwater streams, estuaries and harbours are pressured by increasing levels of metal contaminants from nearby transport, construction, agricultural and horticultural activity. At some sites, metal concentrations already exceed guidelines for ecological health. Mounting land-use pressures are only expected to intensify these adverse effects, through population, primary-industries, construction-sector and tourism growth.

Heavy metal contamination is traditionally monitored using metal concentrations and future predictions are based on our knowledge of existing sources. Although some sources of metals are well known (like zinc from vehicle tyres, copper from brake pads), there are major gaps in our knowledge of where anthropogenic heavy metals come from. For instance, we only know where about half of the copper in urban stormwater comes from (Kennedy & Sutherland 2008). The ubiquity of many metals limits our ability to identify specific pollution sources. Without knowing the sources of metals, our predictive models have high uncertainty, limiting the ability of New Zealand's regulatory authorities to anticipate contamination before it occurs.

To overcome this shortfall, our project will develop metal-isotope 'fingerprinting', to offer improved discriminatory power over concentrations alone for quantifying the sources, transport-pathways, and sinks of heavy-metal contaminants as they move through the environment.

Isotope analyses

Stable isotopes are used extensively internationally and within Aotearoa New Zealand to distinguish sources of water (^{1}H vs ^{2}H; ^{16}O vs ^{18}O), nutrients (^{14}N vs ^{15}N) and sediment (^{12}C vs ^{13}C). Recent advancements in analytical technology – with the development of multiple-collector-ICP-mass-spectrometry (MC-ICP-MS, see Rehkämper et al. 2001) – mean it is now possible to detect small isotopic variations (parts-per-10,000-level) in metals, including the metals that are of most concern for urban (and rural) pollution.

Cadmium, copper, lead, zinc and uranium each have multiple stable isotopes (Druce et al. 2020; Salmanzadeh et al. 2017; Samanta et al. 2017; Vance et al. 2008). The relative abundance of each isotope can be different, depending on the geological sources. Natural and anthropogenic processes also affect that abundance - a process termed isotope fractionation. For example, heating, such as in hydrothermal processes and ore purification and processing, will change the distribution and the isotopic signature (Stirling et al. 2007).

This may result in greater or lesser differences between sources. Furthermore, the signature will change within the aquatic environment, as metals re-distribute between the dissolved and particulate phases, or are taken up by biota. All of these processes need to be investigated in order to build the isotope toolkit.

Overall project plan

Our approach is based on identifying the metal isotope fingerprints of known pollution sources, alongside environmental samples of waters and sediments located along pollutant transport pathways.

We will use a case study in Auckland, New Zealand's most populated city, to obtain observations-based knowledge of heavy-metal sources, transport pathways and sinks in streams and estuaries. These independent observations will also provide new validation information for heavy metal distributions in Auckland Council's advanced contaminant-accounting model (Healthy Waters 2020). Our research has five aims:

Aim 1: Create a database of pollutant heavy metal isotope signatures

Aim 2: Identify heavy metal 'source-to-sink' transport pathways across Auckland's mixed-used rural and urban catchments

Aim 3: Measure isotope profiles of heavy metal pollutants trapped in sediment sinks to identify their accumulation trends over time

Aim 4: Quantify heavy metal contributions from varying polluting activities across Auckland's mixed-used rural and urban catchments

Aim 5: Calibrate the performance of heavy metal accounting in Auckland Council's freshwater management model

Metal isotope database

The initial step in this programme is to develop a database of metal isotope signatures for key contaminant sources. Differences between source signatures is essential for discriminating between sources in environmental (stream/sediment) samples. Table 1 lists the sources included for metal-isotope analyses, and the metal(s) targeted.

Table 1: List of sources included for metal isotope signature analyses.

Land Use	Category	Source	Cu	Pb	Zn	Cd	U
Natural	Soil, sediment, stream, atmospheric deposition	Natural geological sources	✓	✓	✓	✓	✓
Urban	Buildings	Paints		✓			
		Exposed metal cladding, roofing, flashings	✓		✓		

	Road transport	Tyres			✓		
		Brake pads/linings	✓				
		Road dust	✓	✓	✓		
Marine commercial, recreational	Harbour, marina transport	Antifouling paints	✓		✓		
Agriculture	Run-off, soil, sediment	Fungicides, herbicides, fertiliser	✓		✓	✓	✓

This task is in progress and results of these analyses will be discussed at the conference, including whether the analyses demonstrate useful differences in the isotope signatures between sources.

Case study field sampling

The field sampling part of this project focuses on a case study in Auckland's "Project Twin Streams" area. This area includes the Swanson, Opanuku and Oratia Streams which largely arise in forested headwaters, flow through to rural foothills and into residential and commercial/industrial land before entering the tidal Henderson Creek of Waitemata Harbour. The different land uses provide a suitable location for assessing the changes in metal concentrations and sources within the catchment.

An intensive field sampling campaign was undertaken in May 2022, collecting samples from nearly 100 sites across 2-3 days, during baseflow conditions. Water samples were collected for total and dissolved metals (field-filtered to 0.22μm) and analysed in University of Otago's trace metal clean laboratory for a suite of over 40 elements, including the five of primary interest zinc, copper, cadmium, lead and uranium.

This data set has demonstrated (with higher resolution than previous monitoring) the change in stream metal concentrations as the catchment changes from rural to urban (see zinc data in Figure 1). Importantly for this study, we will use this information to select sites for further investigation – focusing on the metal isotope signatures.

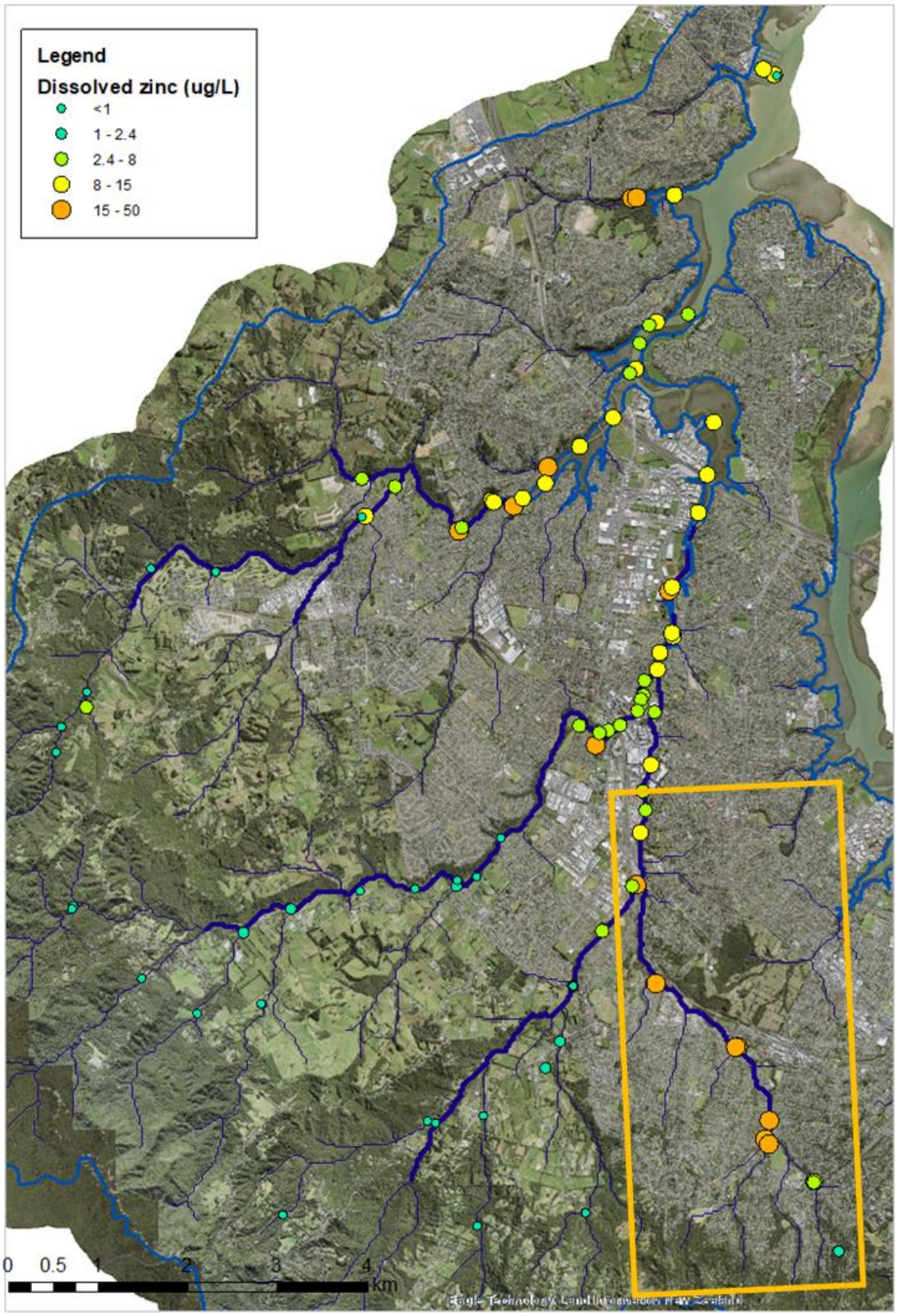

Figure 1: Indicative dissolved zinc concentrations in the "Twin Streams" area of Swanson, Opanuku and Oratia Streams.

Next steps

During 2023, we will:

- Build the isotope database for the sources described above.
- Assess differences in metal isotope signatures at selected sites in our case study catchment
- At selected sites, assess how metal isotope signatures change during processes such as sediment partitioning and deposition and biological uptake.

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KEYWORDS

Stormwater, contaminants, metals, industrial, sources, isotopes