

New Zealand Trace Elements Group

tracenz

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## Conference 2020

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University of Waikato, Hamilton, New Zealand

10 - 12 February 2020



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## Sponsors

A large thank you to all those who have financially supported the NZTEG conference



## Conference organisers

### Convenor

Amanda French

### Conference committee

Megan Grainger

Gavin Robinson

Matthew Taylor

Adam Hartland

### Catering

Morning tea, lunch and afternoon tea supplied by Fresh Balance Catering

## Delegate Information

### Conference Venue

The conference will be held at Advantidrome, Cambridge  
15 Hanlin Road, Cambridge 3283  
This is ~20 minutes from Hamilton (depending on traffic)  
There is free parking on site.

### Presentations

Presentations have a 20 minutes slot. This is a ~15minute presentation followed by 5 minutes of questions.  
Presentations must be uploaded prior to the start of your session. Please aim to do this in the break prior to your session (if not earlier).

### Dress Code

The dress code is smart casual.

### Mix and Mingle

This is included in your registration fee.  
This will be held upstairs at **Onyx, 70 Alpha Street, Cambridge.**  
One free drink will be supplied (a drink voucher is in your conference pack)  
Platters of food will be provided

### Dinner Function

This is an additional cost to your registration fee.  
This will be held upstairs at **Onyx, 70 Alpha Street, Cambridge.**  
One free drink will be supplied (a drink voucher is in your conference pack)  
If you have not notified the committee of any dietary requirements, can you please e-mail Amanda French ([Amanda.french@waikato.ac.nz](mailto:Amanda.french@waikato.ac.nz)) ASAP.

### Waste Reduction

The committee is conscious about the environmental impact of hosting this event and, where possible, has chosen sustainable options.  
The abstract booklet has not been printed, but is available as PDF. If you wish to have a hard copy, please print your own before coming to the conference.  
Your registration pack includes a keep cup. We suggest that you bring it with you throughout the conference. We will also have ceramic coffee cups available.  
The catering company, Fresh Balance, are committed to reducing waste and work to a “Zero waste policy” where possible. Packaging that they use is completely compostable and is by customer request only.

### Student Competition

Student presentations are given the chance to win best student presentation and runner-up. The winner will receive a \$200 prize and the runner-up will receive \$100.

## Panel Discussion

This is your time to ask questions to our expert panel.

You can use the following link to submit questions or bring your questions on the day.



<http://q.xorro.com/axkm>

## Demonstrations

There are two workshops:

### **Perkin Elmer Demonstration** (Robinson Scientific)

Gavin Robinson will be in contact with more information for those who are registered.

### **Agilent Demonstration** (University of Waikato)

Amanda French will be in contact with more information for those who are registered.

## University of Waikato

Parking is \$2/day and the closest car park is Gate 10 on Silverdale road. From here walk up the stairs to Hillcrest road and along to gate 9. Walk into this building (C block), head to the 3<sup>rd</sup> floor. At the top of the stairs turn right and go to the end of the corridor. The ICP-MS suite is the last door on the left.

Details on parking can be found here: <https://www.waikato.ac.nz/contacts/parking-fees>

Campus map: <https://www.waikato.ac.nz/contacts/waikato-parking-zones-map.pdf>

## Programme Overview

Monday 10 February 2020	
From 8:15	Registration <i>Please sign in and take a name badge</i>
8:45	Welcome / Housekeeping
09:00 - 10:00	Keynote lecture
10:00 - 10:30	Morning Tea
10:30 - 11:50	Session 1
11:50 - 13:00	Lunch
13:00 - 14:20	Session 2
14:20 - 15:00	Session 3
15:00 - 15:30	Afternoon Tea
15:30 - 16:10	Session 4
17:00 - 18:30	Mix and Mingle/Networking
18:30 - 22:00	Evening Function/Dinner (*extra cost)

Tuesday 11 February 2020	
8:55	Welcome
9:00 - 10:00	Keynote lecture
10:00 - 10:30	Morning Tea
10:30 - 11:00	Keynote lecture
11:00 - 12:00	Session 5A
12:00 - 13:00	Lunch
13:00 - 14:00	Session 5B
14:15 - 14:30	Student Prizes / Closing
14:30 - 15:00	Afternoon Tea / End of Conference
15:00 - 17:00	Panel discussion ( <i>additional cost</i> )

Wednesday 12 February 2020 (Workshop – additional cost)	
9:30 - 12:30 *Approximate end time	Demonstrations off site: 1) Perkin Elmer (Cambridge) 2) Agilent (University of Waikato)
12:30 - 13:30	Lunch



## Programme Detail

Day 1 Monday 10 February 2020	
From 8:15	Registration
8:45	Welcome / Housekeeping
	<b>Keynote Lecture</b>
9:00	William Maher Advances in speciation analysis of metalloids by HPLC-ICPMS
10:00 – 10:30	Morning Tea
	<b>Session 1 Cadmium</b>
10:30	Niklas Lehto Environmental and edaphic factors affecting soil cadmium uptake by spinach, potatoes, onion and wheat in New Zealand
10:50	Dharshika Welikala Mobilization of cadmium in soils by organic matter rich amendments at different pHs
11:10	Mahdiyeh Salmanzadeh Isotopic differences in cadmium between soil types and land uses
11:30	Zicheng Yi Cadmium accumulation in New Zealand agricultural soils: probabilistic model predictions for the next 25 years
11:50-13:00	Lunch
	<b>Session 2 Toxicity</b>
13:00	Danny McDougall Trace metals in New Zealand green-lipped mussels and the effect of water treatment on trace metal bioavailability and mussel survival
13:20	Hayley Jensen The mobility of gallium and indium in the soil-plant system
13:40	Piet Verburg Low trace metal concentrations in Lake Taupo
14:00	Nicholas Ling Toxic elements in edible fish from a contaminated urban lake (Rotoroa)
	<b>Session 3 Paleoclimate</b>
14:20	Sebastian Höpker Towards quantifying palaeoclimatic cave drip rates from trace metals in stalagmites
14:40	Brittany Marie Ward Assessing deglacial Southern Hemisphere Westley Wind behaviour using speleothem trace element measurements
15:00 – 15:30	Afternoon Tea

Session 4 Geochemistry	
15:30	Sharon Tenger Inorganic Background Soil Ranges - TP153 Special Case
15:50	Karyne Rogers Geochemical baseline soil surveys from New Zealand and Loyalty Islands
16:10	End of lectures for day 1
17:00 – 18:30	<b>Mix and Mingle event / networking</b> (*Included in registration price) Onyx – upstairs venue 70 Alpha Street, Cambridge
18:30 – 22:00	<b>Dinner</b> (*Requires ticket) Onyx – upstairs venue

<b>Day 2 Tuesday 11 February 2020</b>	
8:55	Welcome
	<b>Keynote Lecture</b>
9:00 – 10:00	Fui Yuen (Steven) Pang Reclaim Your Wasted Remeasurement Time with A Next Generation AI-Powered ICP-OES
10:00 – 10:30	Morning Tea
	<b>Keynote Lecture</b>
10:30 – 11:00	Gavin Robinson Advances and applications of nanoparticle analysis by ICP-MS
	<b>Session 5A Applications</b>
11:00	Sukhjeet Singh Novel Gas use for Spectral Interference Reduction of Sulfur in Inductively Coupled Plasma Mass Spectrometry (ICP-MS)
11:20	Alla Marchuk Decrease trace elements content in biosolids using Ca bentonite
11:40	Matthew Taylor Tyre weights; an unrecognised source of lead and antimony
12:00 – 13:00	Lunch
	<b>Session 5B Applications</b>
13:00	Gordon Miskelly Effect of seawater immersion on trace element content of paint
13:20	Brendan Hicks Life history analysis of chinook salmon from the West Coast, South Island, NZ, by otolith microchemistry
13:40	Sheila Skeaff Accurately determining fluoride intakes of New Zealand children
14:15 - 14:30	<b>Student prizes and closing function</b>
14:30 – 15:00	Afternoon Tea End of Conference
	<b>Panel Discussions <i>*Extra registration required</i></b>
15:00 – 17:00	Panel discussions with our keynote speakers

## Day 3 Wednesday 12 February 2020

### Instrument Demonstrations (\*Extra registration cost)

9:30 - 12:30 *Approximate end time	Demonstrations off site: 1) Perkin Elmer (Cambridge) Held at: Robinson Scientific  2) Agilent Held at: University of Waikato C.3.11 Come through gate 9, Hillcrest road into C block and head to third floor. Turn right and go along to the end of the corridor  Closest parking is Gate 10
12:30 - 13:30	Lunch

## Abstracts

### Keynote (Monday 9 – 10 am)

**William Maher**

Advances in speciation analysis of metalloids by HPLC-ICPMS

**Authors:** William Maher

**Organisation(s):** <sup>1</sup>Ecochemistry Laboratory, Institute for Applied Ecology  
University of Canberra, Bruce, Australia, 2601

#### **Abstract**

The use of high-pressure liquid chromatography coupled to an inductively coupled plasma mass spectrometer and a mass spectrometer for the measurement of As, Se, Hg and Sb species in food and vitamin supplements is described. Five modes of using coupled ICPMS systems; HPLC-ICPMS, HPLC-HG-ICPMS, Cryogenic trapping ICPMS, in-situ Cryogenic trapping ICPMS and GC-ICPMS are described and their application. Two classes of metalloid species are described; “Easy” and “Hard” to extract and measure by HPLC-ICPMS. Measurements described include, Arsenic species: arsenobetaine, arsenoribosides, As bound to phytochelatins, As-lipids and 10 minor As species including thio-As species. Selenium species: include those produced by animals; selenocysteine and selenomethionine and plants such as Se-methyl selenomethionine, Se-methyl selenocysteine, ,  $\gamma$ -glutamyl-Se-methyl selenocysteine, methylselenide and dimethyldiselenide. Mercury species: inorganic Hg and methyl Hg. Antimony species: antimonite and antimonate. Problems with extracting species from sample matrices and preserving the integrity of species are discussed as well as the use of standardless measurement of species

## Cadmium Session 1 (Monday 10:30 – 11:50)

**Niklas Lehto**

Environmental and edaphic factors affecting soil cadmium uptake by spinach, potatoes, onion and wheat in New Zealand

**Authors:** Zicheng Yi<sup>a</sup>, Niklas J. Lehto<sup>a\*</sup>, Brett H. Robinson<sup>b</sup>, Jo-Anne E Cavanagh<sup>c</sup>

**Organisation(s):** <sup>a</sup> Faculty of Agricultural and Life Sciences, Lincoln University; <sup>b</sup> School of Physical and Chemical Sciences, University of Canterbury; <sup>c</sup> Manaaki Whenua – Landcare Research, Lincoln 7640.

\*Corresponding author: Niklas J. Lehto

### **Abstract**

Efforts to predict and mitigate the potential risks resulting from plant uptake of cadmium (Cd) into edible plant parts are often confounded by the various factors that influence metal accumulation in those tissues. Our aim was to identify important drivers that determine Cd concentrations in spinach leaves, potato tubers, onion bulbs and wheat grain grown in commercial horticultural operations across New Zealand (NZ). We collected paired soil and plant samples (n = 147) from farms across different NZ growing regions. We measured Cd concentrations in the plant tissues and compared the ability of four different soil Cd tests to represent those concentrations: pseudo-total and porewater concentrations, 0.05 M Ca(NO<sub>3</sub>)<sub>2</sub>-extraction and diffusive gradients in thin-films (DGT). We also collected information on a range of soil and climatic variables. We show that soil Cd concentrations determined by the different tests were positively related to plant concentrations and that there were clear regional differences between these relationships. The Ca(NO<sub>3</sub>)<sub>2</sub> extraction predicted over 76% of the variability in Cd concentrations in onion bulbs and spinach leaves, once regional differences were considered. Likewise, we had to consider regional differences to allow for potato tuber and wheat grain Cd concentrations to be represented, here DGT and porewater Cd provided the best estimates, respectively, once the influence of certain other environmental and soil variables was included. Our results suggest that Cd accumulation by these plants varies widely between Regions and confirm the importance of some key factors in controlling the extent to which this happens.

## Dharshika Welikala

Mobilization of cadmium in soils by organic matter rich amendments at different pHs

**Authors:** Dharshika Welikala<sup>1</sup>, Niklas Lehto<sup>1</sup>, Adam Hartland<sup>2</sup>, Brett Robinson<sup>3</sup>

**Organisation(s):** <sup>1</sup> Department of Soil and Physical Sciences, Faculty of Agriculture and Life Sciences, Lincoln University, New Zealand. <sup>2</sup> Environmental Research Institute, School of Science, Faculty of Science and Engineering, University of Waikato, New Zealand. <sup>3</sup> Department of Physical and Chemical Sciences, College of Science, University of Canterbury, New Zealand.

\*Corresponding author: Dharshika Welikala

### Abstract

Organic matter (OM) amendments such as compost and lignite have been successful in reducing the plant uptake of Cd from contaminated soils. However, dissolved organic matter (DOM) released from these amendments has been shown to increase trace metal mobility in soil. The mobilization of Cd by Cd-DOM complexes may depend on the extent to which Cd partitions to Cd-DOM complexes. The resistance of OM amendment derived-DOM to biodegradation, and hence its quality is also likely to be important. We sought to investigate Cd mobilization by OM amendments and the importance of DOM qualitative characteristics. We amended three soils with two different OM amendments (compost and peat: 2.5% TOC wt/wt) and limed them to achieve two different pHs (5.4 and 6.3). Potentially mobile Cd and DOM were collected from a column leaching experiment. Colloidal and “truly” dissolved (<5kDa) Cd fractions were separated from the leachates by ultrafiltration, which revealed that >50% of Cd leached from OM amended soils was associated with larger colloids. This fraction was greater in leachates from compost-amended soils than in the peat-amended soils and increased with pH in all treatments. Peat OM appeared to be more susceptible to solubilization due to pH increment than the OM in compost. Spectroscopic analysis of leachates revealed that the DOM released from peat-amended soils consisted of molecules with a higher degree of aromatic condensation than DOM from compost-amended soils at both pHs. We conclude that the colloidal-Cd may be an important vector for mobilizing Cd from OM amended soils at elevated pHs.

## Mahdiyeh Salmanzadeh

### Isotopic differences in cadmium between soil types and land uses

**Authors:** Mahdiyeh Salmanzadeh<sup>1</sup>, Adam Hartland<sup>1</sup>, Matthew Taylor<sup>2</sup>, Claudine Stirling<sup>3</sup>, Ejin George<sup>3</sup>

**Organisation(s):** <sup>1</sup> University of Waikato, <sup>2</sup> Waikato Regional Council, <sup>3</sup> University of Otago

\*Corresponding author: Mahdiyeh Salmanzadeh

#### Abstract

Cadmium (Cd) isotope analysis is a potentially powerful tool for distinguishing Cd sources in contaminated systems, and considerable interest exists in New Zealand in differentiating Cd derived from fertilisers and Cd originating from other natural sources. This approach has recently been demonstrated at a long-term field trial where Cd isotope ratios ( $\delta^{114/110}\text{Cd}$ ) of fertiliser and native sub-soil were distinct (separated by up to 0.5 ‰). But a key test of the application of isotope tracing to the problem of distinguishing sources more generally (e.g. in waterways, biota, etc) is that background Cd (e.g. in non-fertilised soils) should be isotopically distinct from phosphate fertilisers. Therefore we set out to determine the isotope ratio of Cd ( $\delta^{114/110}\text{Cd}$ ) in topsoil from unfertilised (n=8), pastoral (n=6) and cropping (n=4) land-uses. The results showed that on average soils showed a hierarchy of increasingly positive  $\delta^{114/110}\text{Cd}$  values between unfertilised ( $0.10 \pm 0.07$  ‰), cropping ( $0.14 \pm 0.07$  ‰) and pasture ( $0.20 \pm 0.07$  ‰) soils, consistent with mixing between native (less positive  $\delta^{114/110}\text{Cd}$ ) and pre-2000 phosphate fertiliser (more positive  $\delta^{114/110}\text{Cd}$ ) sources. However, the potential for aeolian transport of Cd from the surrounding fertilised lands cannot be excluded as an additional factor perturbing the unfertilised  $\delta^{114/110}\text{Cd}$  results. Therefore, further experiments are needed to define a pre-human  $\delta^{114/110}\text{Cd}$  for New Zealand settings before Cd isotope tracing can be applied more generally to the New Zealand environment.



Zicheng Yi

Cadmium accumulation in New Zealand agricultural soils: probabilistic model predictions for the next 25 years.

**Authors:** Zicheng Yi<sup>a</sup>, Niklas J. Lehto<sup>a</sup>, Brett H. Robinson<sup>b</sup>, Jo-Anne E Cavanagh<sup>c</sup>

**Organisation(s):**

<sup>a</sup> Faculty of Agricultural and Life Sciences, Lincoln University

<sup>b</sup> School of Physical and Chemical Sciences, University of Canterbury.

<sup>c</sup> Manaaki Whenua – Landcare Research, Lincoln.

\*Corresponding author: Niklas.Lehto@lincoln.ac.nz

### Abstract

Cadmium (Cd) accumulation in agricultural soils caused by long-term phosphorus (P) fertiliser application may impact negatively on global food security. Our aim was to carry out a probabilistic risk-based assessment of future soil Cd accumulation in New Zealand (NZ) agricultural systems. We validated a previously published numerical model that simulates Cd fluxes in soils against historic soil Cd data (1952-2003) from the Winchmore Research Station. We then applied the probabilistic Monte-Carlo method to the modelling framework to estimate rates of Cd accumulation arising from varied agricultural practices on a range of soil types in different NZ Regions over the next 25 years. Our model results confirm that fertiliser Cd concentration plays an important role in soil Cd enrichment and suggest that Organic soils have the largest potential to accumulate Cd, while the Sedimentary soils have the lowest. Moreover, we found that Cd leaching induced by irrigation may reduce soil Cd accumulation rates and, accordingly, that up to 22% of unirrigated NZ dairy farms may see soil Cd concentrations exceeding  $1.0 \text{ mg kg}^{-1}$  in the next quarter of a century, when modelled at the conservative 95<sup>th</sup> percentile rate of accumulation. Under typical maintenance P fertiliser recommendations and the current long-term average fertiliser Cd concentrations, our model estimates that farms in the Waikato are likely see a slight increase in the soil Cd concentrations, while concentrations in Canterbury should remain relatively stable.

## Toxicity Session 2 (Monday 13:00 – 14:20)

Danny McDougall

Trace metals in New Zealand green-lipped mussels and the effect of water treatment on trace metal bioavailability and mussel survival.

**Authors:** D. R. McDougall, D. J. McGillivray, G. M. Miskelly, A. G. Jeffs

**Organisation(s):** The University of Auckland

\*Corresponding author: Daniel McDougall – Email: dmcd582@aucklanduni.ac.nz

### Abstract

The green-lipped mussel (*Perna canaliculus*) is New Zealand's most valuable aquaculture export and is of significant value to New Zealand's economy. Trace metals such as Cr, Cu, Zn, As, Cd, Hg, and Pb present in the seawater can be toxic to New Zealand green-lipped mussels as well as most other aquaculture shellfish grown worldwide. Common practice to alleviate the toxicity of trace metals is to add the metal chelating agent, EDTA, to the seawater used for incubation of the shellfish in their rearing tanks. This works extremely well, improving survival of shellfish as they develop from a fertilised egg to a 2 day old larvae from as low as 0% to up to 100%. It is assumed that this improvement results from the high binding affinity EDTA has for trace metals and therefore it reduces their bioavailability, however, this mechanism of action has not been evidenced. This PhD research analysed the concentrations and distributions of trace metals in *P. canaliculus* larvae using ICPMS at the University of Auckland and XFM at the Australian Synchrotron. An experiment incubated *P. canaliculus* larvae for 2 days with EDTA or a more readily biodegradable alternative (EDDS) at a mussel hatchery near Nelson, and the effect of these treatments on concentrations and distributions of trace metals were compared with 2 day old larvae reared without chelating agent added. Survival was significantly improved with the addition of EDTA or EDDS, and significant differences in the concentrations of several trace metals were observed.

Hayley Jensen

The mobility of gallium and indium in the soil-plant system

Organisation(s): University of Canterbury

**Abstract**

Gallium (Ga) and indium (In) are increasingly susceptible to soil contamination via disposal of electronic equipment. I sought to determine the extent and nature of Ga and In mobility in the soil - plant system to understand their potential to enter the food chain. Batch sorption experiments showed that both elements are potentially strongly retained to the soil matrix, with distribution coefficient (KD) values of up to 2697 and 1803 L kg<sup>-1</sup> for Ga and In respectively. Variation in values and trends were observed with the four soil types used. Generally KD increased with Ga or In concentration, attributed to precipitation of excess ions as insoluble hydroxides, and pH trends were often non-linear, due to peak precipitation and transitioning between cations and anions within the soil pH range. Movement into the aboveground portions of perennial ryegrass (*Lolium perenne* L.) from a high fertility silt loam (pH 5.95, CEC 22 meq 100 g<sup>-1</sup>) was low, with bioaccumulation factors of 0.0037 for Ga and 0.0002 for In; foliar concentrations peaked at 11.6 mg kg<sup>-1</sup> and 0.015 mg kg<sup>-1</sup> respectively. The mobility of Ga and In in the soil - plant system in its entirety is low compared to other common trace element contaminants such as cadmium, copper, and zinc. Therefore, Ga and In are likely to accumulate in soils. Soil ingestion, either directly, via inhaled dust, or dust attached to food, will be the largest pathway into the food chain.

## Piet Verburg

### Low trace metal concentrations in Lake Taupo

**Authors:** Piet Verburg<sup>1\*</sup> and Sylvia Sander<sup>2</sup>

**Organisation(s):** <sup>1)</sup> National Institute of Water and Atmospheric Research <sup>2)</sup> International Atomic Energy Agency (IAEA), IAEA Environment Laboratories, Monaco

\*Corresponding author: Piet Verburg

#### **Abstract**

Lake Taupo is a large deep oligotrophic lake. Soils in the catchment are low in trace metals that algae need for growth and trace metals needed by diazotroph cyanobacteria to enable them to fix atmospheric nitrogen. This poses the question whether trace metal concentrations in Lake Taupo are low enough to potentially limit algal growth and nitrogen fixation. We sampled dissolved trace metal concentrations at 7 depths ranging from the surface layer to the near bottom water. We found low concentrations of a number of trace metals essential for algal growth. This talk will compare trace metal concentrations in Lake Taupo with those in other lakes from literature and discuss potential implications for limitation of algal growth.

**Nicholas Ling**

Toxic elements in edible fish from a contaminated urban lake (Rotoroa)

**Organisation(s):** School of Science, The University of Waikato

**Abstract**

Lake Rotoroa (Hamilton City) is a shallow urban lake (56 ha, maximum depth 6.5 m) receiving suburban stormwater inflows, but also contains a toxic legacy from arsenical aquatic macrophyte treatment in 1959. With a residence time of 2.4 years and an estimated 0.004% of sediment bound arsenic released to the water, Lake Rotoroa sediments retain significantly elevated arsenic concentrations sixty years after macrophyte treatment.

Several large bodied fishes occur in the lake and are fished recreationally for food and sport. Several studies have examined arsenic and other selected elements in Lake Rotoroa fish, but the last comprehensive study occurred in 1995 and temporal changes in arsenic bioavailability have not been examined. This study measured total arsenic and other selected elements (copper, zinc and lead) in muscle flesh and liver tissue in all large bodied fish species in the lake.

Concentrations of all elements were below recommended safe food limits indicating consumption of Lake Rotoroa fish does not pose health concerns. Concentrations differed between species with brown bullhead catfish having generally highest concentrations and the lowest concentrations were in perch, however, bioaccumulation in species did not seem to be related to trophic guild or association with sediment. Although arsenobetaine is generally dominant in the tissues of marine and freshwater fish, organic arsenicals vary between fish species and differences in relative lipid content of species may be a factor in bioaccumulation but has not been comprehensively investigated. Further investigation of organoarsenical compounds across species in this lake may provide greater understanding of arsenic metabolism in freshwater fishes.

## Paleoclimate Session 3 (Monday 14:20 – 15:00)

### Sebastian Höpker

Towards quantifying palaeoclimatic cave drip rates from trace metals in stalagmites

**Authors:** Sebastian Höpker<sup>1\*</sup>, Megan Grainger<sup>2</sup>, Bedartha Goswami<sup>3</sup>, Adam Hartland<sup>1</sup>

**Organisation(s):** <sup>1</sup>Environmental Research Institute, School of Science, University of Waikato, New Zealand, <sup>2</sup>Chemistry, School of Science, University of Waikato, New Zealand, <sup>3</sup>Potsdam Institute for Climate Impact Research (PIK), Germany

\*Corresponding author: Sebastian Höpker

### Abstract

The study of environmental conditions through geological time is critical for improving our understanding of Earth's climate system, and its sensitivity to natural and anthropogenic forcings. In this regard, cave carbonate deposits (speleothems) have proven particularly valuable for the extraction of information on past environments over a range of temporal and spatial scales, given their essentially continuous growth and exceptional suitability for radiometric dating.

To complement existing techniques for speleothem-based palaeoenvironmental reconstructions, we investigate the reliability of a new class of proxies using first-row transition metals (e.g., Cu, Ni, Co) that are incorporated during calcite precipitation. The transport of the trace metals from the surface to the speleothem is largely governed by the binding of the metals to natural organic matter (NOM) present in cave dripwaters. The rate of dissociation of such metal-NOM complexes at the water-calcite interface has been recently proposed to determine the accumulation of transition metals in speleothems. This link presents an opportunity to quantitatively relate respective metal concentrations in speleothems to the time available for complexes to dissociate, which in turn is a direct function of the drip rate.

Through experimental, field, and modelling studies we aim to further explore the chemistry of a suite of transition metals in cave systems, and ultimately establish novel quantitative records of Holocene hydroclimate variability in New Zealand and the South Pacific.

## Brittany Marie Ward

Assessing deglacial Southern Hemisphere Westley Wind behaviour using speleothem trace element measurements

**Authors:** <sup>1</sup>Brittany Marie Ward, <sup>1</sup>Andrew Pearson, <sup>1</sup>Adam Hartland, <sup>1</sup>Amanda French, <sup>2</sup>Sebastian Breitenbach, <sup>3</sup>John Hellstrom

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### Abstract

Aotearoa is located in an advantageous region to study modern and past Southern Hemisphere climate dynamics, including behavior of the Southern Hemisphere Westerly Winds (SWW). However, few SWW-centered paleoclimate studies exist in Aotearoa. Further, there are few speleothem-based studies within the broader paleoclimate literature of Aotearoa. Existing speleothem-based studies are dominated by the use of stable isotope proxy records, which are often ambiguous and difficult to interpret in Aotearoa's climatic setting. We aim to fill these knowledge gaps by constructing speleothem-based trace element records from three cave sites (Waipuna Cave, Waipuna Scenic Reserve, Waitomo; Hodge's Creek, Kahurangi National Park; Dave's Cave, Fiordland National Park) spanning 10° of latitude, in order to assess past latitudinal behavior of the SWW in this region. Speleothem trace element (i.e., Mg, Sr, Ba) to calcium ratios (X/Ca) have proven to be viable proxies of past wet versus dry conditions in the local cave environment, and thus are useful in assessing past local precipitation behavior.

In this presentation we demonstrate i) the conceptual framework of speleothem X/Ca values as a proxy of wet versus dry conditions, ii) numerical exercises to test the viability of the X/Ca values as a proxy at specific sites, and iii) introduce results from our paleo-SWW study.

## Geochemistry Session 4 (Monday 15:30 – 16:10)

Sharon Tenger

Inorganic Background Soil Ranges - TP153 Special Case Pupuke, Auckland  
Basalts Tuff, Auckland Volcanic

**Authors:** Sharon Tenger, Garry Cepe, Jordan Vaughn, Zeljko Viljevac

**Organisation(s):** Soil & Rock Consultants

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### Abstract

**Background/Objectives** Preliminary and Detailed Site Investigations of sites located in the Auckland Basalts Tuff of the Auckland Volcanic Field in the vicinity of Lake Pupuke identified Chromium (Cr) and Nickel (Ni) concentrations elevated above the Auckland Region background volcanic soils concentrations (ARC Technical Publication TP153). Consents are therefore required for earthworks under the NES and AUP contaminated land regulations and any soils removed from the site must be disposed of to an authorised landfill. However, scientific evidence and site historical information indicate that these soils are not contaminated.

**Approach/Activities** A study was undertaken to ascertain whether elevated Cr and Ni soil concentrations are natural or anthropogenic in origin. The study assessed potential anthropogenic contamination sources, undertook physical and geochemical soil characterisation, a literature review of parent rock geochemistry and a statistical analysis of the Cr and Ni concentrations in the site soils. Background ranges were determined and the NES and AUP regulatory requirements and soil management and disposal options re-assessed. Groundwater sampling and leaching tests were undertaken to assess for any potential effect on the environment.

**Results/Lessons** Learnt Evidence indicates that these volcanic soils with 'elevated' Cr and Ni are natural background levels of the Auckland Basalts tuff derived from the local parent rock. TP153 acknowledges data set gaps exist in local volcanic lithologies with soil concentrations reflecting the parent rock geochemistry and identifies these as 'special cases' that need to be considered individually. Background ranges were calculated using the methodology and analysis established in TP153.

Assessing the Pupuke, Auckland Basalts tuff concentrations as natural background levels, the NES does not apply and discharges are a Permitted Activity under the AUP within the Tuff locality. However, outside of the Tuff locality, the NES and AUP apply and these soils cannot be disposed of as Cleanfill. MfE cleanfill waste disposal criteria do not allow for 'special case' natural background soils above the TP153 published dataset. Groundwater analysis show Cr and Ni are not significantly leaching and there is no effect on the environment.

**Recommendations** Local background concentrations are better used to define background. The Pupuke Auckland Basalts Tuff, and other 'special case' localities, should be added to both the Auckland Region Background levels (TP153) and MfE Landfill Waste Acceptance Criteria; disposal of such soils cleanfill should be permitted.



## Karyne Rogers

### Geochemical baseline soil surveys from New Zealand and Loyalty Islands

**Authors:** Karyne Rogers, Rose Turnbull, Adam Martin, Mark Rattenbury, Delphine Rakowski, Julie Jeanpert

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Soil is the interactive nexus between natural surface geology and anthropogenic human contributions and contains a range of inputs from both. Unravelling anthropogenic contributions from chemically and geologically diverse landscapes is an interesting challenge being met by scientists at GNS Science over the last few years with comprehensive rural and urban soil surveys taking place in Southland-Otago, Dunedin City and Buller-Nelson-Marlborough regions. Another smaller survey has been undertaken in the Loyalty Islands (near New Caledonia), which are remote karstic islands near New Caledonia. Unsurprisingly, in all regions, geochemical anomalies occur; and these can cause problems ranging from missing critical trace elements, excessive quantities of nutrients to high levels of potentially toxic and illness-inducing heavy metals.

These studies inform land owners, regional and local authorities, public health, mineral exploration, land developers, farmers and recreation participants about aspects of soil quality, soil contaminants and its long-term sustainability. Recent studies have shown strong correlation between land-use (undeveloped islands, regional, rural or urban) and elemental concentrations, and these can be attributed differing levels of human inputs on natural geogenic variation.

We present an overview of the soil surveys undertaken in the last 5 years, and present multi-variate chemometric data integrating elements on a local and regional scale to highlight the importance of identifying geochemical anomalies recorded in soils.

## Day 2

### Keynote (Tuesday 9:00 – 10:00)

#### PANG, Fui Yuen (*Steven Pang*)

**Steven Pang** is presently Agilent's Spectroscopy Business Manager for Singapore and Indonesia. He joined Agilent Technologies in 2010 as an ICP-MS Applications Chemist. Steven has extensive work experience in the field of Instrumental Analysis, and has previously worked for a multinational testing laboratory, and prominent analytical instrumentation companies. Steven has published in peer-reviewed journals, and presented papers in both international and in Agilent's seminars relating to the field of Applied Spectroscopy.

Steven holds a B.S. (*cum laude*) in Biology and Chemistry from Campbell University, USA, M.Phil. (University of Malaya), and M.B.A. (University of South Australia).



#### Presenter: Fui Yuen (Steven) Pang

Title: Reclaim Your Wasted Remeasurement Time with A Next Generation AI-Powered ICP-OES

Author: Steven Pang

Organisation(s): Agilent Technologies Singapore

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#### Abstract

Since the introduction of the ICP-OES in the 1960's, there has been a consistent development and adoption of *best-in-class* technology to improve upon the analysis dynamics of this technique. The introduction of solid state device detectors, e.g. the Varian (now Agilent) VistaChip Charge-coupled Device Detector have facilitated the popularity of the ICP-OES for simultaneous multi elemental analysis in a variety of sample matrices.

In this presentation, explore and discover how the new Agilent 5800/5900 incorporates Artificial Intelligence (AI) to make recommendations and solve ICP-OES analysis problems before they occur. This smart functionality will reduce the number of remeasurements, allowing you to achieve confidence in your results and concurrently, achieve both costs and productivity gains. Examples of actual application into established ICP-OES standard methods will be discussed.

## Keynote (Tuesday 10:30 – 11:00)

**Presenter:** Gavin Robinson

Title: Advances and applications of nanoparticle analysis by ICP-MS

**Authors:** Gavin Robinson (Robinson Scientific), Dr Chady Stephan (PerkinElmer)

**Organisation(s):** Robinson Scientific Ltd, PerkinElmer

**\*Corresponding author:** Gavin Robinson (gavin@icpms.co.nz)

### Abstract

The use of modern Inductively Coupled Plasma Mass Spectrometer (ICP-MS) instrumentation for analysis of nanoparticles using Single Particle (SP) ICP-MS is described. Single Particle ICP-MS theory, instrument hardware, software and data interpretation including the use of both ionic and particle calibrations are covered, together with important practical considerations, including the requirement for extremely rapid data acquisition in order to accurately determine particle concentrations and sizes, and the necessary ability to obtain and manipulate large data volumes. A number of real-world application examples are described, including nanoparticle measurements in surface water, drinking water, waste water, food, biological, cosmetic and clinical analyses. Single Cell ICP-MS is also discussed along with several practical applications including improving drug therapies utilising Single Cell ICP-MS and environmental uptake considerations. The relationship between dissolved fractions and nanoparticle components, size, shape and concentration, along with agglomeration and dissolution will be discussed, in addition to the importance of understanding the fate of nanoparticles in the food chain and environment.

## Applications Session 5A (Tuesday 11:00 – 12:00)

Sukhjeet Singh

Novel Gas use for Spectral Interference Reduction of Sulfur in Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

**Authors:** Sukhjeet Singh<sup>1\*</sup>, Megan Grainger<sup>2</sup>, Michael Mucalo<sup>2</sup>, Steven Haylett-Petty<sup>1</sup>

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### Abstract

Sulfur is a particularly challenging element to measure by inductively coupled plasma – mass spectrometry (ICP-MS). Not only does it have a high first ionization potential (10.4 eV), but all isotopes are subject to severe background interferences common across most matrices measured. This results in a lower signal to background ratio and poor detection limits.

To date, very few reaction gases have been investigated that aid with the measurement of sulfur by ICP-MS, with oxygen being the most common. Having limited options for reaction gases can reduce flexibility with instrument configuration. This research explored the use of methane as another potential reaction gas for the measurement of sulfur in plant, soil and environmental water acid digestion samples.

Quadrupole inductively coupled plasma – mass spectrometry (Q-ICP-MS) and tandem inductively coupled plasma – mass spectrometry (ICP-MS/MS) were used to measure the CH<sub>2</sub>-SH<sup>+</sup> cluster at  $m/z$  47 and  $m/z$  49 to quantify sulfur. Performance was assessed by considering interferences, detection limits, the measurement of proficiency samples and comparison to inductively coupled plasma – optical emission spectroscopy (ICP-OES).

Using methane to measure the CH<sub>2</sub>SH<sup>+</sup> cluster by Q-ICP-MS was unsuitable due to interferences from Ti<sup>+</sup> and CCl<sup>+</sup>. However, CH<sub>2</sub>SH<sup>+</sup> cluster results generated by ICP-MS/MS (using a mass shift from  $m/z$  34 to  $m/z$  49) were free from interferences and in agreement with ICP-OES. The additional mass filter on ICP-MS/MS along with methane shows potential as an alternative for sulphur determination in difficult matrices.

**Alla Marchuk**

Decrease trace elements content in biosolids using Ca bentonite

**Authors:** Alla Marchuk Serhiy Marchuk

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**Abstract**

Disposal biodegradable waste from industry considered as non-sustainable from the environmental and resource recovery viewpoints. Agricultural recycling can be beneficial because biosolids contain plant nutrients and organic matter. But biosolids is not a balanced fertiliser, apart from valuable nutrients it contains trace elements which could adversely affect biochemical functions in plants and soil. The toxicity of trace elements depends on their concentrations and bioavailability, *i.e.* on their chemical forms in both organic and inorganic matrices. The objective of this study was to transform biosolids from wastewater treatment facilities into higher grade of biofertilizer through the addition of Ca bentonite aiming to decrease the concentration and mobility of trace elements to the environment. Dried biosolids (BS) and Ca bentonite clay (C) were thoroughly mixed in the following proportions: BS100%+C0%, BS70% +C30%, BS50%+ C50%, wetted with deionised water to saturate biosolid-clay mix, dried at 60° for 24 hours and then grinded to yield 300g of final formulation. The mixtures were analysed in five replicates for soluble fractions of Ni, Cu, Zn, and As, as most significant pools regarding biosolid's trace elements toxicity. The total concentrations were also determined. Compared to the BS100%, the addition of bentonite decreased concentrations of soluble Ni, Cu, Zn, As in BS70%+C30% mix by 41%, 23%, 29% and 14% respectively, while mix BS50%+C50% by 58%, 44%, 51% and 49% respectively. The addition of 30% of clay allowed effectively improve total Zn and Cu concentrations in biosolids from Grade C to Grade B according to Queensland legislation requirement.

## Matthew Taylor

Tyre weights; an unrecognised source of lead and antimony

**Authors:** Matthew Taylor<sup>a\*</sup>, Niklas Kruger<sup>ab</sup>

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<sup>b</sup>Technischen Universität Braunschweig, Germany

\*Corresponding author

### Abstract

Lead (Pb) remains elevated in road runoff and roadside dust, which has been attributed to legacy Pb from leaded petrol. However, “lead” tyre weights, an alloy of 95% Pb and 5% Sb, may be a relatively unrecognised diffuse source of Pb and Sb as they are still used in many countries with an unknown number of these weights dropping off tyre rims onto the road. Motor vehicles driving over deposited weights abrade the weights; the weights eventually disperse as dust or wash into water ways as road runoff, potentially causing adverse environmental effects. The type, number and weight of tyre weights lost from motor vehicles were characterised for a range of roading infrastructures and motor vehicle intensities in a 38 month long study of a 6.9 km length of road in Hamilton City, New Zealand. Overall, 1070 tyre weights with a combined mass of 18.6 kg were collected. About 96.4% of the collected weights were made of “lead” indicating tyre weights can be a major source of Pb and Sb in urban areas. The tyre weight distribution on roads used in this study depended mainly on traffic density and the prevalence of “start stop” patterns in traffic flow.

## Applications Session 5B (Tuesday 13:00 – 14:00)

Gordon Miskelly

Effect of seawater immersion on trace element content of paint

**Authors:** Matthew Harvey<sup>1</sup>, Sally Coulson<sup>2</sup>, Stuart Morrow<sup>3</sup>, Gordon Miskelly<sup>1\*</sup>

**Organisations:**<sup>1</sup> Forensic Science Programme, School of Chemical Sciences, University of Auckland, Private Bag 92019, Auckland 1142; <sup>2</sup> ESR Ltd., Private Bag 92021, Auckland 1142; <sup>3</sup> School of Chemical Sciences, University of Auckland, Private Bag 92019, Auckland 1142

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### Abstract

A recent prosecution in New Zealand included comparison of the elemental composition of paint on fish that had been dumped at sea to paint on a fishing boat that was the suspected source. The suspect pleaded guilty before trial, so the science of matching such paint samples was not examined in a court of law. We investigated whether and by how much the elemental composition of paint changed upon immersion in seawater, and the timescale of any changes.

Glass plates were coated with acrylic latex paint or alkyd resin paint and then immersed in synthetic and natural seawater for differing time periods. The changes in elemental concentrations were then examined using both laser ablation inductively-coupled plasma – mass spectrometry (LA-ICP-MS) and laser-induced breakdown spectroscopy (LIBS). Repeated ablations at the same location were used to provide an estimate of elemental depth profiles. The elemental composition of the paint changed upon immersion in seawater, with distinct patterns of incorporation of different elements that differed for the two types of paint. The alkyd resin paint showed diffusive incorporation of elements such as magnesium and strontium, increasing over time. The concentrations of higher abundance elements such as aluminium and titanium were unchanged. Depth profiling showed incorporation occurred from the seawater side of the paint film.

The acrylic latex paint did not show such clear diffusion profiles, and this may be due to the more heterogeneous nature of this paint and the greater ability of seawater to penetrate within the paint.

## Brendan Hicks

Life history analysis of chinook salmon from the West Coast, South Island, NZ,  
by otolith microchemistry

**Authors:** Brendan Hicks, Ray Tana and John Charteris

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### Abstract

Trace elements in otoliths (calcium carbonate ear bones) were used to examine salmon life histories and the success of hatchery releases in augmenting natural salmon runs. Salmon from the Pacific Northwest of North America, such as the chinook salmon (*Oncorhynchus tshawytscha*), are anadromous, generally spawning in freshwater but migrating as juveniles to the sea to grow to adulthood. Chinook have been successfully naturalised in New Zealand, mostly in east-coast rivers of the South Island. In addition, rivers of the central West Coast of the South Island have a small, iconic salmon fishery comprising about 1000 chinook adults in total, and these have highly variable life histories. While most chinook migrate to the sea to grow to adulthood, age at migration is unpredictable and some remain in fresh water their entire lives. Primary spawning sites for West Coast chinook are MacDonalds Creek, a tributary of Lake Mapourika, and Windbag Stream, a tributary of Lake Paringa; a proportion of the chinook population enter these lakes as juveniles and remain there until spawning.

To increase the number of adults returning to the fishery, artificially-bred chinook from two hatcheries have been released into Lake Mapourika between 2011 and 2014. Juveniles from these hatcheries have distinctive elemental signatures, with significantly different concentrations of boron, magnesium, manganese, strontium, and barium in their otoliths. Analysis of the otoliths of 54 returning adults suggests that hatchery juveniles comprised 20% of the returning chinook adults, which is a significant contribution to the salmon fishery.



## Sheila Skeaff

### Accurately determining fluoride intakes of New Zealand children

**Authors:** S Skeaff and J Munro

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#### Abstract

Dental caries is the most prevalent disease in New Zealand children. The cause of dental caries is multi-factorial, however, use of fluoride in different vehicles is one of the most important and cost-effective ways of reducing the risk of dental caries. The aim of this study was to measure fluoride intakes from food, beverages and toothpaste, in children aged 9-11 years living in fluoridated and non-fluoridated areas of the South Island.

Between 2017-2018, 102 children participated in the study, with 74 children from fluoridated and 28 children from non-fluoridated areas. Children, with their parents, recorded all food and drink consumed over a day. Diet records were entered in FoodWorks, a nutrient analysis software package with an extended version of the New Zealand Food Composition Database. For a sub-sample of children, a duplicate portion of all food and drink consumed was also obtained on that day, and the fluoride content measured, after acid digestion, using a fluoride-selective electrode. Fluoride ingested during toothbrushing was also calculated for each child.

The mean age of the children was 9.6 years: 52% were boys. Analysis of the diet records indicated that diet (foods and water) contributed ~36% and 11% of the recommended intake of fluoride, respectively, in fluoridated and non-fluoridated areas, whereas ~50% of the recommended fluoride intake was obtained from ingested fluoride. The fluoride content of the duplicate diet samples is being analysed, and a comparison of fluoride values determined from the diet records and diet samples will be presented at the conference