Ten Years of Dual-Isotope Nitrate in New Zealand: Finding Opportunities to Enable Improved Agricultural Management to Reduce Eutrophication

Professor Troy Baisden[1], Professor Tim Clough[2], Dr Clinton Rissmann[3,4], Dr Tim Ellis[5], Dr Naomi Wells[6], Sephrah Rayner[2], Andy Phillips[7]
[1]University Of Waikato, Hamilton, New Zealand, [2]Lincoln University, Lincoln, New Zealand, [3]Waterways Centre Canterbury/Lincoln Universities, Christchurch, New Zealand, [4]e3 Environmental, Invercargill, New Zealand, [5]Environment Southland, Invercargill, New Zealand, [6]Southern Cross University, Lismore, Australia, [7]GNS Science, Lower Hutt, New Zealand

In 2008, ongoing intensification of New Zealand's pastoral agriculture provided justification for the developing and understanding the δ15N and δ18O of nitrate in New Zealand pastoral agriculture. Today, the capability developed at GNS is the only routine commercial provider of dual-isotope nitrate analyses in Australasia. The technique appears to be the most promising tool capable of identifying opportunities to reduce inflows of nitrate to aquatic ecosystems with minimal reductions in agricultural productivity. Dual-isotope nitrate offers the opportunity to find and confirm hot spots and hot moments of nitrate leaching that occur as a result of insufficient plant and microbial demand to retain soil nitrogen. Understanding these hot spots and hot moments will open a window of improved control points for nitrogen management with the potential to keep nitrogen on farms and enhance productivity, while mitigating nitrate leaching. An indicator framework has now been developed that allows high concentration breakthroughs of nitrate linked to urine, urea, other fertilizers, or effluent to be identified and targeted for improved management. The indicator framework utilises nitrogen and oxygen isotopes in nitrate, as well as nitrate concentrations, to define a "signature" for sources associated with unwanted "breakthrough" sources. The breakthrough source signatures can be distinguished relative to a frequently observed pattern of "normal nitrogen retention".

The framework can be applied to both surface water and groundwater, and can potentially avert the need to understand groundwater flow and processes. Progress with this tool also suggests that 2–5 ‰ shifts in nitrogen isotopes, algal particulate matter, periphyton, macrophytes or wider food webs can directly link aquatic impacts to manageable sources of excess nitrogen. The next steps in identifying management opportunities to reduce nitrate loads now requires application of these techniques in small streams, estuaries, or lakes, where inflows from groundwater and other sources require identification.

Seasonal variations in consumer nitrogen recycling in an oligotrophic lake: A stable isotope study

Mr Simon Stewart[1], Prof. Troy Baisden[1], Prof David Hamilton[2], Dr Piet Verburg[3], Dr Ian Duggan[1]
[1]University Of Waikato, Hamilton, New Zealand, [2]Australian Rivers Institute, Griffith University, Brisbane, Australia, [3]NIWA, Hamilton, New Zealand

Consumer nutrient recycling (CNR) is an important component of lake nutrient cycles but remains poorly understood. The importance of CNR for sustaining primary production is expected to vary in space and time. For warm monomictic lakes such as Lake Taupō, CNR likely becomes an important source of nutrients for pelagic phytoplankton during summer stratification when nutrients are depleted to severely limiting levels in the surface mixed layer. Quantifying CNR by traditional methods such as nutrient pool assessments has limitations as CNR demonstrates "high flux–small pool" dynamics with extended periods of stratification. Measuring the $\delta^{15}N$ stable isotope values of nitrogen pools within a lake is a promising method to investigate the significance of CNR. Recent stable isotope analytical advances now allow $\delta^{15}N$ determination from low-concentration ammonium and nitrate pools. In this study we performed a comprehensive stable isotope survey of nitrogen constituents in Lake Taupō over a complete annual cycle to investigate the significance of CNR as a nutrient source to phytoplankton. We tested if CNR is a ^{15}N-deplete nitrogen source by examining consumer excretion in incubations. Correlations of ammonium $\delta^{15}N$ values with zooplankton excretion $\delta^{15}N$ values suggested a significant contribution of zooplankton excretion to ammonium pools. A seasonal, whole-lake survey demonstrated that CNR contributed most to nutrient pools and phytoplankton nutrient uptake during the summer stratified period. These are discussed in the context of possible responses of Lake Taupō to changes in climate and the lake food web.

POSTER

An automated system for N2 headspace analysis

Mr Rad Bak[1], Prof Michele Burford, Prof Brian Fry
[1]Stable Isotopes Laboratory, Australian Rivers Institute, Griffith University, Nathan, Australia

The $^{15}N/^{14}N$ ratio of nitrogen gas is typically measured for a range of biogeochemical processes. This includes ^{15}N enriched nitrogen gas generated during denitrification rate measurements. There are a few existing methods available to do this, the principal one being the use of helium to flush headspace nitrogen into the mass spectrometer. We have developed and built a new alternative automated method with a twin-needle injection system that uses water to expel the nitrogen gas into a sample loop at atmospheric pressure. An aliquot of water is injected into a vial to displace the nitrogen headspace gas through a sample loop and then into the mass spectrometer. An advantage of the water displacement principle is that repetitive injections give equal concentrations with identical isotope values. This method is a cost effective alternative to the helium displacement method. We recommend this simple but effective method for analysis of nitrogen headspace samples.

Ross Sea Deglaciation – Environmental Reconstruction from the RICE Ice Core

Dr Nancy Bertler[1,2], Prof Howard Conway[3], Prof. Dorthe Dahl-Jensen[4]
[1]GNS Science-Institute of Geological and Nuclear Sciences Ltd, National Isotope Centre, Gracefield, New Zealand, [2]Victoria University of Wellington, Antarctic Research Centre, Wellington, New Zealand, [3]University of Washington, Seattle, USA, [4]Niels Bohr Institute, University of Copenhagen, Copenhagen, Denmark

The Roosevelt Island Climate Evolution (RICE) project recovered a 763.4 m deep ice core to bedrock during 2011-2013 from Roosevelt Island (RI), at the northern edge of the Ross Ice Shelf. The ice at RI is grounded 210 m below sea level and accumulates in situ, with the Ross Ice Shelf flowing around the rise. High resolution radar surveys show well-developed Raymond Arches of isochrones suggesting a stable ice divide.

Here, we show isotope and geochemical data spanning the past 30 ka and discuss reconstructions of sea surface and air temperature, sea ice extent, atmospheric circulation patterns, and ice shelf grounding line retreat. An ensemble of sensitivity modelling experiments is used to determine thresholds for the removal of RI ice and correlated grounding line and ice volume changes of the Ross Ice Shelf and the West Antarctic Ice Sheet.

Our data suggest that the onset of the Ross Ice Shelf grounding line retreat during the deglaciation was driven at least in part by the early deglaciation in West Antarctica as recorded in the WAIS Divide ice core, perhaps through a freshwater feedback. The Ross Ice Shelf grounding line started to retreat rapidly with the initiation of an ice shelf cavity. Atmospheric circulation changes precede the onset of the Antarctic Cold Reversal (ACR) by about 200 years. Maximum ACR sea ice extent is reached at the termination of the ACR and is maintained into the early Holocene, a time period of rapid atmospheric warming and circulation changes.

Revolutionising EA-IRMS: Getting more for less by ultra-high sensitivity

Dr Christopher Brodie[1], Dr Oliver Kracht[1], Dr Andreas Hilkert[1]
[1]*Thermo Fisher Scientific, Bremen, Germany*

The Thermo Scientific™ EA IsoLink™ IRMS System has revolutionised EA-IRMS by introducing *temperature ramped gas chromatography* with a single GC column and a helium management system that reduces cost per analysis. These innovative features open doors to push research boundaries at new levels, especially for the analysis of nitrogen, carbon and sulphur concentrations less than 5 µg (Table 1) and on very high C/N and C/S ratio samples (Figure 1), whilst delivering automated routine analysis. In figure 1, complete baseline separation is shown with sound background correction and sharp peak shapes for very large (7000 µg C) and very small (11 µg N and 0.8 µg S) analyte amounts. For 5 replicate measurements on wood, $\delta^{13}C$ = -24.10±0.06‰; $\delta^{15}N$ = 3.20±0.23‰ and $\delta^{34}S$ = 5.92±0.26‰.

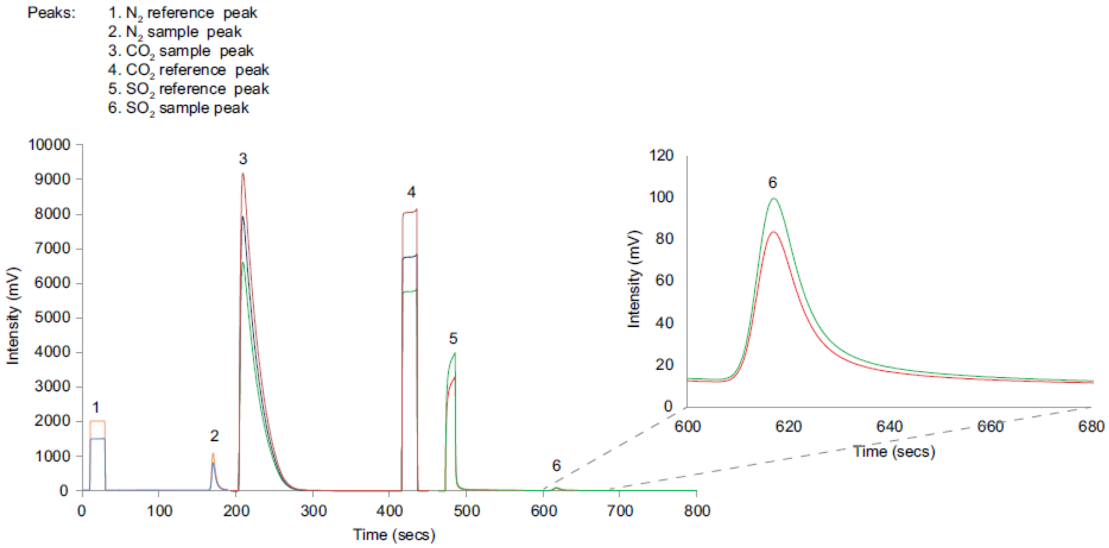

Figure 1. Simultaneous NCS analysis of wood (C/S ratios >7900:1) from a single sample drop using the EA IsoLink IRMS System. Analysis time <10 minutes using <1.4 liters of helium.

This presentation will focus on the analysis of small concentrations of carbon, nitrogen and sulphur and illustrate with data, how the EA-IRMS utilises chromatographic principles to routinely increase the sensitivity on NCS measurements and reduce cost per analysis. An example of the gains in sulphur sensitivity is shown in Table 1 from measurements on 1 mg of bone collagen, where data precision is significantly better than 0.3‰.

Table 1. Sulphur sensitivity on bone collagen determined by changing chromatographic parameters using the software.

Sample	**Weight (mg)**	**%S**	**µg S**	**Area (Vs)**	**Sensitivity (Vs/µg S)**
Bone Collagen	0.996	0.280	2.789	0.581	0.280
Bone Collagen	0.998	0.280	2.794	11.730	4.198

POSTER

Methods development and applications of N2 and N2O measurements in water and gas samples on a Gasbench II

Ms Julie Brown[1], Dr Andrew Kingston[1], Dr Craig Tobias[2], Dr Andrew McMillan[3], Dr Femke Rambags[4], Dr Sarah Bury[1]

[1]National Institute of Water and Atmospheric Research, 301 Evans Bay Parade, , Hataitai, New Zealand, [2]Department of Marine Sciences, University of Connecticut, 1080 Shennecossett Road, Groton, USA, [3]Landcare Research, Private Bag 11052, New Zealand, [4]National Institute of Water and Atmospheric Research, Gate 10, Silverdale Road, Hillcrest, New Zealand

Over the last two years we have been developing methods to analyse N_2 and N_2O in water and gas samples to support research investigating nitrogen cycle pathways. A GasBench II linked to a Delta V Plus isotope ratio mass spectrometer (IRMS) (Thermo Fisher Scientific, Germany) enables us to measure isotope ratios of $^{15}N/^{14}N$ of N_2, plus $^{15}N/^{14}N$ and $^{18}O/^{16}O$ of N_2O in natural abundance or enriched water or gas samples. We have modified methods in the literature to produce optimal conditions for accurate and precise N_2 and N_2O measurements, and here present details of our analytical set-up and quality control reporting parameters. We also present some case study applications and discuss future research opportunities.

Latitudinal isotopic variability in Southern Ocean suspended particulate organic matter validates Southern Ocean isoscapes and informs humpback whale trophic ecology

Dr Sarah Bury[1], Dr Matt Pinkerton[1], Dr Brittany Graham[1], Dr Jill Schwarz[2], Dr Clive Trueman[3], Ms Katie StJohn Glew[3], Ms Kylie Owen[4], Ms Julie Brown[1], Ms Anna Kilimnik[1], Dr Mike Double[5], Dr Nick Gales[5]
[1]National Institute Of Water And Atmospheric Research, Greta Point, 301 Evans Bay Parade, Hataitai, New Zealand, [2]School of Marine Science and Engineering, Plymouth Univeristy, Plymouth, United Kingdon, [3]3Ocean and Earth Sciences, National Oceanography Centre Southampton, University of Southampton Waterfront Campus, European Way, Southampton SO14 3ZH, United Kingdom., [4]Cetacean Ecology and Acoustics Laboratory, School of Veterinary Science, The University of Queensland, Gatton, Australia, [5]Australian Marine Mammal Centre, Australian Antarctic Division, 203 Channel Highway, Kingston, Australia.

A joint collaborative venture between National Institute of Water and Atmospheric Research (NIWA) and Australian Antarctic Division (AAD) resulted in two voyages to the Antarctic Ross Sea, the first in February/March 2010 and the second in February/March 2015. On both voyages, underway sampling of suspended particulate organic material (SPOM) was carried on latitudinal transects from New Zealand to the Ross Sea shelf and along the shelf edge. The SPOM samples were analysed to generate $\delta^{15}N$ and $\delta^{13}C$ phytoplankton baseline isotopic values in the areas traversed. Measurements of underway temperature, salinity, chlorophyll *a*, HPLC, and fluorometry have enabled key oceanographic features to be identified and variations in SPOM isotopic values to be interpreted. These data have been used to ground-truth a modelled Southern Ocean carbon and nitrogen isoscape, which has then been used to interpret the trophic status and diet of humpback whales studied around, and to the east of, the Balleny Islands.

POSTER

Expanding New Zealand's capability of stable isotope analysis in water, gas and organic samples

Dr Sarah Bury[1], Ms Julie Brown[1], Dr Andrew Kingston[1]
[1]*National Institute of Water and Atmospheric Research, 301 Evans Bay Parade, Hataitai,, New Zealand*

NIWA's recent multi-million dollar stable isotope facility upgrade has widened our spectrum of isotopic analyses to include a diverse array of water, gas and solid-matrix sample analyses delivering highly accurate and precise results. The investment included the acquisition of a GasBench II and Thermo Chemical Elemental Analyser (TCEA) linked to Delta V Plus isotope ratio mass spectrometers (IRMS) (Thermo Fisher Scientific, Germany). The GasBench II is an on-line preparation system to the IRMS, capable of high throughput analysis of carbon, nitrogen, oxygen and hydrogen isotopes in water and gas samples; whilst the TCEA enables us to measure O and H isotopes in organic, inorganic and water samples. Recent in-house methods developments on both these instruments now enables us to offer new applications to the isotope research community. The Gasbench II has been optimised to measure: $^{2}H/H$ in water through equilibration with H_2/Pt and $^{18}O/^{16}O$ in water through equilibration with CO_2, with applications relevant to climatic, hydrological, oceanic water mass, ecological and animal movement studies; $^{18}O/^{16}O$ and $^{13}C/^{12}C$ in carbonates for palaeoceanographic and climate studies; $^{13}C/^{12}C$ of dissolved inorganic carbon (DIC) for carbon flux and palaeoclimate research; and $^{15}N/^{14}N$ of N_2, plus $^{15}N/^{14}N$ and $^{18}O/^{16}O$ of N_2O for terrestrial, aquatic and atmospheric nitrogen cycle studies. We have also optimized the TCEA for analysis of $^{2}H/H$ and $^{18}O/^{16}O$ in solid organics, such as plants, soils, bird material (feathers, claws), tree-ring cellulose and chironomid head capsules (chitin) samples to support research in terrestrial water dynamics, palaeoclimate, climatology, animal migration and ecological studies. We will present some examples of these developments and applications.

Macrosopic controls on mean transit times in catchments

Professor Ian Cartwright[1], Dr Uwe Morgenstern[2]
[1]Monash University, Melbourne, Australia, [2]GNS Science, Lower Hutt, New Zealand

Elucidating the controls on the time required for water to be transmitted through catchments from where it recharges to where it discharges into a stream (the transit time) is critical in understanding catchment behaviour. The mean transit times in several catchments in southeast Australia estimated using ^3H vary from a few to several hundred years. There is no simple correlation between catchment attributes such as slope, area, or drainage density and the mean transit times within or between the catchments. Taken as a whole, however, the typical mean transit times are much longer than those estimated for comparable catchments in Europe or New Zealand. These large-scale differences are probably the result of low recharge resulting from a combination of factors. Firstly, native Australian eucalyptus vegetation has high evapotranspiration rates. Secondly, southeast Australia has relatively low rainfall and high evaporation rates. Lastly, the low organic carbon content of the soils and high clay content of the regolith result in low permeabilities.

The long mean transit times result in these catchments only responding slowly to land clearing and changes to rainfall totals and amounts. The transport of contaminants such as nitrates to the stream through the groundwater system is likely to be relatively slow, which may also promote attenuation of the contaminants (e.g., via denitrification). Understanding the controls on mean transit times within catchments is difficult as evapotranspiration rates and the hydraulic properties of the soils and regolith are difficult to measure and may be spatially heterogeneous. Nevertheless, the integration of mean transit time studies with those that examine the flow through catchments in detail would allow a better understanding of the controls on mean transit times.

POSTER

Respiration of new and old carbon in the surface ocean: implications for estimates of global oceanic gross primary productivity

Dr Matheus Carvalho[1], Dr Kai Schulz[1], Prof Bradley Eyre[1]
[1]*Centre for Coastal Biogeochemistry Research, Southern Cross University, Lismore, Australia*

New respiration (R_{new}, of freshly fixated carbon) and old respiration (R_{old}, of storage carbon) were estimated for different regions of the global surface ocean using published data (Carvalho et al., 2017). These consisted in simultaneous measurements of: 1) primary productivity using ^{14}C (^{14}PP); 2) gross primary productivity (GPP) based on ^{18}O or O_2; and 3) net community productivity (NCP) using O_2. The ratio R_{new} / GPP in 24 h incubations was typically between 0.1 and 0.3 regardless of depth and geographical area (Fig. 1A), demonstrating that values were almost constant regardless of large variations in temperature (0 to 27 °C), irradiance (surface to ~100m deep), nutrients (nutrient rich and poor waters), and community composition (diatoms, flagellates, etc). As such, between 10 and 30% of primary production in the surface ocean is respired in less than 24 h, and most respiration (between 55 and 75%) was of older carbon (Fig. 1B). R_{new} was most likely associated with autotrophs, with minor contribution from heterotrophic bacteria. Patterns were less clear for R_{old}. Short ^{14}C incubations are less affected by respiratory losses. Global oceanic GPP is estimated to be between 70 and 145 Gt C y^{-1}.

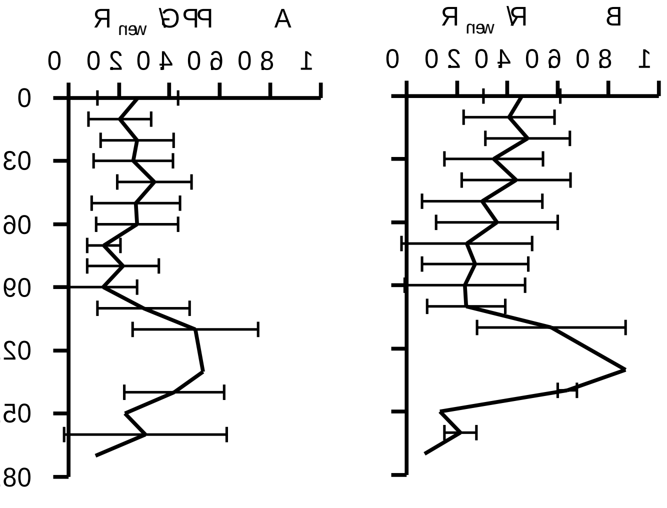

Figure 1: Depth profiles for averages of R_{new} / GPP (new respiration divided by gross primary productivity) and R_{old} / R_{total} (old respiration / total respiration) covering several different areas of the global surface ocean. Error bars show the standard deviation for different means at the same depth. Data were pooled for depths in groups of 10 meters. Source: Carvalho et al., 2017.

REFERENCES

Carvalho M.C. Schulz K.G. Eyre B.D. 2017. Respiration of new and old carbon in the surface ocean: implications for estimates of global oceanic gross primary productivity. Global Biogeochemical Cycles 31: 975–984.

Low-cost and easy analytical solutions enabled by AutoIt

Dr Matheus Carvalho[1], Mr Mitchell Call[2], Dr Kai Schulz[1], Dr Damien Maher[2], Prof Bradley Eyre[1]

[1]Centre for Coastal Biogeochemistry research, Southern Cross University, Lismore, Australia, [2]Southern Cross Geoscience, Southern Cross University, Lismore, Australia

Combining analytical instruments has been traditionally recognized as a difficult task, especially if the instruments are made by different manufacturers. This limitation can hamper research progress due to technical or economic factors.

With AutoIt, a scripting language for the Windows operating system, combining instruments becomes a trivial task (Carvalho, 2016). Some examples are: 1) using low-cost, general purpose robotic arms as autosamplers for water analyses (Fig. 1, Carvalho and Eyre, 2013); 2) using the autosampler of an instrument with a different one (Carvalho, 2013); 3) performing unattended experiments without any complex change in the analytical setup (Fig. 2, Call et al., 2017); 4) converting autosamplers into liquid handlers without expensive or complex procedures; 5) integrating devices through the internet (Carvalho, 2016).

AutoIt, together with open-source hardware and crowdfunding, enables true democratization of science by radically reducing the costs necessary to undertake it.

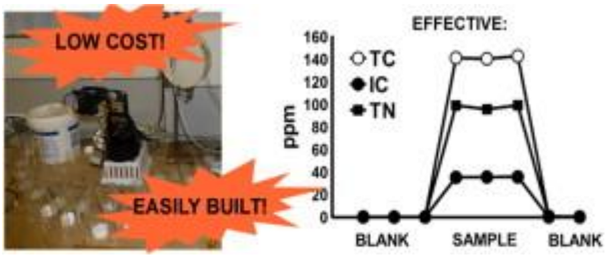

Figure 1: Robotic arm used as an autosampler (Carvalho and Eyre, 2013).

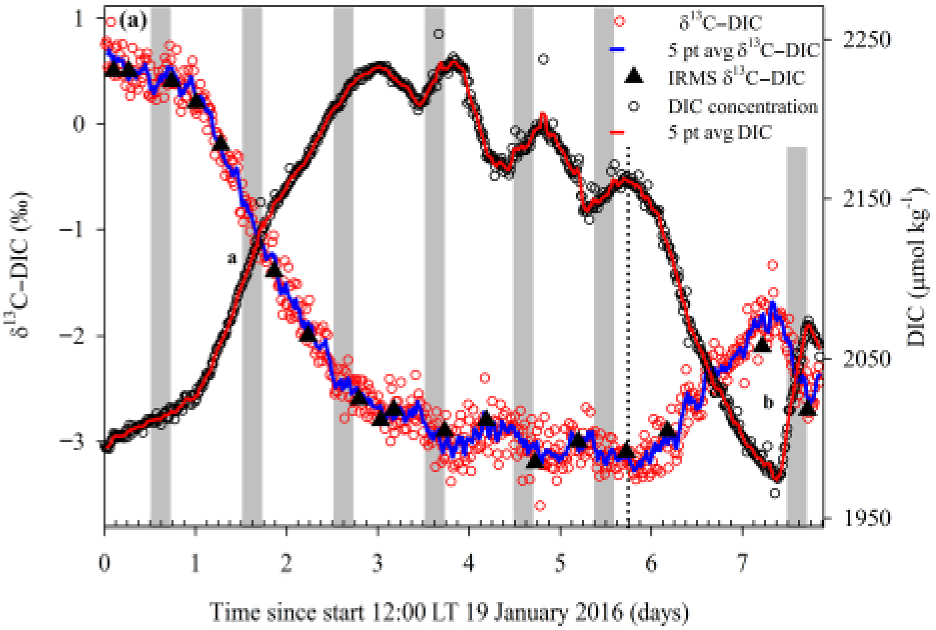

Figure 2: High-frequency, unattended measurements of dissolved inorganic carbon concentrations and stable isotopes measured using a high-precision sampling system coupled to cavity-ring mass spectroscopy compared to traditional low-frequency mass spectrometry measurements (Call et al., 2017).

REFERENCES

Carvalho M.C. 2013. Integration of analytical instruments with computer scripting. Journal of Laboratory Automation 18: 328-333.

Carvalho M.C. 2016. Practical laboratory automation made easy with AutoIt, 226p, Wiley-VCH.

Carvalho M.C. & Eyre B.D. 2013. A low cost, easy to build, portable and universal autosampler for liquids. Methods in Oceanography 8: 23-32.

Call M. Schulz K.G. Carvalho M.C. Santos I.R. Maher D.T. 2017. Coupling infrared gas analysis and cavity ring down spectroscopy for autonomous, high temporal resolution measurements of DIC and δ13C-DIC Biogeosciences 14: 1305-1313.

Application of stable isotope pore water equilibration method in upland swamps underlain by underground mines

Mrs Katarina David[1,2], Dr Wendy Timms[1,2], Dr Catherine Hughes[3], Prof Andy Baker[2]

[1]UNSW, School of Mining Engineering, Sydney, Australia, [2]CWI UNSW, Sydney, Australia, [3]ANSTO, Sydney, Australia

The upland swamps in the Sydney Basin have Endangered Ecological Community status under the Commonwealth Government and are important for biodiversity, supporting threatened flora and fauna. These swamps are important hydrologically because they maintain stream flow and water quality (Young, 2017). However, the hydrological function of the swamps is threatened by erosion, changing climate, landuse, wildfires and in some areas, underground mining and associated subsidence, upsidence and valley closure.

We use novel stable isotope pore water equilibration method along with stable isotopes of rainfall, surface water, pore water within peat and groundwater to understand the hydrogeological processes within the swamps. Our study is supported by moisture content data, organic matter content and lithology profiles. We collected samples from three swamps in the vicinity of longwall panels prior to their extraction with sampling undertaken on three occasions.

We found an overall similarity in swamp response to recharge and flow even though the morphology of each swamp is different. Stable isotope values of swamp moisture, measured by pore water-vapour equilibrium techniques, become more negative with depth and reached values similar to groundwater at a depth of around 60-80cm. Within the upper 40-60 cm in the vadose zone, there is overall enrichment in δ^{18}Oand δ^{2}H as a result of evaporation. We conclude that although rainfall infiltration reaches the saturated zone within the swamp quickly, the upper shallow organic rich zone has high water retention capacity even during dry weather periods. The stable isotope signature at the base of the swamp indicates lateral baseflow contribution is also an important source of water for the swamp.

The findings of this study and the application of this novel pore water equilibration method provide good understanding of the swamp groundwater movement to assist with future management.

REFERENCES

Young, A. 2017. Upland swamps in the Sydney region. Thirroul. ISBN 978-0-9943814-1-5.

Geochemical, Sulfur Isotopic Characteristics and Source Contributions of Size-Aggregated Aerosols Collected at Baring Head, New Zealand

Dr Perry Davy[1], Dr Mike Harvey[2], Mr Jianghanyang Li[3], Dr Greg Michalski[3,4], Dr Tanya Katzman[4], Dr Benjamin Wilkins[4]

[1]Institute Of Geological And Nuclear Sciences, Lower Hutt, New Zealand, [2]National Institute of Water and Atmospheric Research, Wellington, New Zealand, [3]Department of Earth, Atmospheric, and Planetary Sciences, Purdue University, West Lafayette, USA, [4]Department of Chemistry, Purdue University, West Lafayette, USA

Marine sulfate aerosols in the Southern Ocean are critical to global radiation balance, yet the sources of sulfate and their seasonal variations are unclear. We evaluated the sources of sulfate in coarse (0.95-10 µm) and fine (0.05-0.95 µm) aerosols over a one-year sampling campaign collecting both marine and ambient aerosols at Baring Head, New Zealand. In both collectors, sea-salt sulfate ($SO_4^{2-}{}_{SS}$) mainly existed in coarse aerosols and non-sea-salt sulfate ($SO_4^{2-}{}_{NSS}$) dominated the sulfate in fine aerosols, although some $SO_4^{2-}{}_{NSS}$ appeared in coarse particles in summer due to rapid growth. $SO_4^{2-}{}_{NSS}$ in the marine aerosols was mainly (88-100%) from marine biogenic dimethyl sulfide (DMS) emission, while the $SO_4^{2-}{}_{NSS}$ in the ambient aerosols was a combination of both DMS emission (73-79%) and SO_2 emissions from shipping activities (~21-27%). The seasonal variations of $SO_4^{2-}{}_{NSS}$ concentrations in both collectors were mainly controlled by the DMS flux. We compare these spatio-temporal observations with other complimentary New Zealand sulfur speciation datasets from both urban and coastal settings.

POSTER

Discrimination of geographical origin of Chinese tea from stable isotopes and muti-elements using a machine learning method

Associate Professor Xunfei Deng[1,2], Professor Xiaonan Lv[1,2], Assistant Professor Zhi Liu[2,3], Professor Yuwei Yuan[2,3]

[1]Institute of Digital Agriculture, Zhejiang Academy Of Agricultural Sciences, Hangzhou, China, [2]Key Laboratory of Information Traceability for Agricultural Products, Ministry of Agriculture of China, Hangzhou, China, [3]Institute of Quality and Standard of Agro-products, Zhejiang Academy of Agricultural Sciences, Hangzhou, China

The geographic origin of tea is a critical feature determining its quality and fame, so the reliable origin authentication is critical for geographical origin protection. A total of 129 tea samples from Shandong and Zhejiang province were collected in 2013, and the content of stable isotopes and multi-elements derived from tea plant and soil were measured by isotope ratio mass spectrometry (IRMS) and inductively coupled with plasma mass spectrometry (ICP-MS), respectively. A random forest model, as a machine learning algorithm with superior predictive performance over parametric statistical models (Breiman, 2001), combining 32 input predictors (e.g., $\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$, ^{95}Mo, and ^{208}Pb) was developed to discriminate different geographical origins of Chinese tea. Our results indicated that the random forest model well discriminated the tea from Zhejiang and Shandong province with the accuracy of 99.2%. The tea origins from Zhejiang and Shandong province were also well classified with the estimated accuracy of 97.3% and 76.5% respectively. ^{95}Mo, ^{39}K, $\delta^{2}H$ are the most important factors on determining the province origins of tea with their expandability of 11.6%, 9.8%, and 7.9%, respectively. The $\delta^{13}C$, ^{65}Cu and ^{39}K are the most important ones for discriminating the tea origins of Hangzhou West Lake (a famous tea geographic origin) and other regions in Zhejiang province. The results showed that the random forest method is superior or equivalent to those methods using principle component analysis and linear discriminate analysis (PCA-LDA), multilayer perceptron (MLP), and Bayes (Laursen et al., 2011; Yuan et al., 2016). It provides an alternative choice for discriminating the geographical origins for tea and other agro-products.

REFERENCES

Breiman, L., 2001. Random Forests. Machine Learning 45: 5-32.

Laursen, K. H., Schjoerring, J. K., Olesen, J. E., Askegaard, M., Halekoh, U., Husted, S., 2011. Multi-elemental fingerprinting as a tool for authentication of organic wheat, barley, faba bean, and potato. Journal of Agricultural and Food Chemistry 59: 4385 − 4396.

Yuan, Y., Hu, G., Chen, T., Zhao, M., Zhang, Y., Li, Y., Xu, X., Shao, S., Zhu, J., Wang, Q., Rogers, K.M., 2016. Improved Discrimination for Brassica Vegetables Treated with Agricultural Fertilizers Using a Combined Chemometric Approach. Journal of Agricultural and Food Chemistry 64: 5633-5643.

First Measurement of Field Samples at the Southern Hemisphere's First Noble Gas Facility

Dr Alec Deslandes[1], Dr Axel Suckow[1], Stan Smith[2], Christoph Gerber[1]
[1]CSIRO, Urrbrae, Australia, [2]Utah Geological Survey, Salt Lake City, USA

The noble gas facility at CSIRO's Waite site is the only laboratory in Australia and on the southern hemisphere dedicated to measure the concentrations of all noble gases (He, Ne, Ar, Kr, Xe) and the activities of the radioactive noble gas isotopes ^{222}Rn, ^{85}Kr, ^{39}Ar and ^{81}Kr in water samples.

Application of the radioactive noble gas isotopes as tracers, and other tracers like CFCs and SF_6 can be supported by the information derived from measurements of stable noble gases. For example, quantification of excess air (from Ne concentrations) is needed to interpret SF_6 results, and recharge temperatures best derived from the heavy noble gases Ar, Kr, Xe are useful for interpreting CFCs and H1301. The quantification of helium in groundwater and pore water, being either radiogenic or mantle-derived, allows estimates of residence times, groundwater influx from deeper formations and aquifer connectivity. This information can decrease uncertainty of models that are based upon tracer results.

A fully-automated measurement system that is supported by an offline extraction system has been under development from 2014-2016 for the measurement of He, Ne, Ar, Kr, and Xe. Since January 2017 we have advanced to measuring samples from groundwater and surface water field projects, together with series of gas standards and water standards. This talk will feature results that highlight performance characteristics of the measurement system during this commissioning phase.

Ongoing optimisation of the measurement process includes investigation of the adsorption and desorption kinetics during the cryogenic gas separation, which is of particular importance for our types of samples given the large ranges of gas amounts that are analysed.

Hydrogeological insights from stable isotopes - a window into the functioning of arid environments

Dr Shawan Dogramaci[1]
[1]*Rio Tinto Iron Ore, Perth, Australia*

Arid and semi-arid regions around the world are characterised by severe rainfall deficit, resulting in scarce surface water as well as ground water resources that may not be replenished by modern recharge. The competing demands of the environment with various end users of these limited resources requires deep understanding of the interactions among all components of the system, including climate patterns, landscape structure, hydrological processes and groundwater recharge dynamics. The role and relative importance of potentially complex interactions can be revealed using both stable and radioactive isotopes of chemical elements that make up the environment. We present here a case study focussed on the Hamersley Basin of the Pilbara region of northwest Australia to demonstrate how a multi-isotope tracer (δ^{2}H, δ^{18}O, TU, δ^{13}C, ^{14}C, ^{39}Ar, ^{85}Kr) approach can significantly enhance understanding of the chemical and physical processes that control water quality, the mode of occurrence of surface water features, unsaturated flow, recharge and groundwater dynamics, and their interactions. Analysis of δ^{2}H and δ^{18}O showed that intense rainfall events of >20 mm with limited evaporation prior to infiltration currently contribute the most to recharge. In contrast, the δ^{2}H, δ^{18}O values and chemical composition of the relatively saline groundwater in the discharge zone of the Basin suggest that groundwater evolved through mixing of highly evaporated old groundwater and recent recharge from flood water. The groundwater dating tracers (TU, δ^{13}C, ^{14}C, ^{39}Ar, ^{85}Kr) provided estimates of recharge that ranged from < 1 mm/a to 10mm/a. The δ^{87}Sr, and $\delta^{34}S_{SO4}$ suggests that groundwater evolution in the Basin is dominated by de-dolomitisation that added SO_4 and Mg into surface and groundwater. The Cl and isotope mass balance and dating tracers also show the groundwater is a mixture of old ~ 1000 years and new <50 years. The evolution of groundwater chemistry from recharge down gradient to the main discharge zone has been taking place over the last 40,000 to 160,000 years. This detailed case study demonstrates that accurate identification of recharge-discharge characteristics, as well as clear understanding of key physical and chemical processes occurring over a long period of time can only be accomplished through combination of conventional hydrologic methods with isotopic measurements.

Effect of Different Soil Structure on 15N Uptake Rate of Maize in Black Soil

Dong Wu[1], Professor Sen Dou[1], Rui Ma[1], Shuai Xie[1]
[1]*Soil Science Department, Jilin Agricultural University, Changchun, China*

*Corresponding author, dousen1959@126.com

Soil has a three-dimensional structure composed of solid-phase particles or aggregates and soil pores. Better soil structure facilitates nutrient uptake of plants and reduces nutrient loss. In order to verify the effects of different soil structure on the utilization rate of nitrogenous fertilizer of maize, ^{15}N tracing technique was used in this study with PVC pipe (diameter 40cm, height 40cm) embedded in black soil. 6 treatments were conducted including CK(PVC pipe directly embedded in the soil column), A (<0.5mm), B (0.5-1mm), C (1-7mm), E (<7mm) and D (0-20 cm soil layer mixed with peat). Except CK and D treatment, all the other treatments of soil were stratified out and sieved according to the original soil layer sequence. The results showed that with the enhance of aggregate size, the rate of nitrogen utilization increased 13.1~18.0%.The treatment E (unsieve-fractionated) was in intermediate state, which indicated that the treatment with large particle size could promote the ^{15}N absorption. Compared with CK, treatment D increased ^{15}N utilization from 15.7% to 22.7%, which illustrated that the application of peat ameliorated soil structure and improved nitrogen utilization. Therefore, the application of peat and large-size particle treatment could promote soil structure, increase the absorption and utilization of nitrogen in maize. However, the small-size particle plays an important role in enhancing the soil residue and reducing the nitrogen loss.

Acknowledgements: This work was financially supported by the National Key Research and Development Program of China (grant No. 2016YFD0200304).

Optical measurements of radiocarbon (14C) using cavity ring-down spectroscopy

Dr Adam Fleisher

Optical spectrometers capable of high precision in situ sensing of stable carbon isotopes (e.g. ^{13}C, ^{12}C) have enabled numerous field campaigns to expand our knowledge of atmospheric carbon sources and sinks. Similar laser-based spectrometers for the detection of radiocarbon (^{14}C) would unambiguously differentiate between carbon of biogenic or petrogenic origins, and thus, be of great value to elucidating carbon cycles on various temporal and physical scales. The main challenge in designing an optical sensor for ^{14}C is its extremely low natural abundance, with a modern value of 1.176 pmol/mol (parts-per-trillion). Therefore, traceable and robust optical techniques of the highest possible sensitivity are required.

Here we present our first-generation spectrometer for the detection of ^{14}C below a fraction modern of one ($F^{14}C = 1$ is defined as $^{14}C/^{12}C = 1.176$ pmol/mol) (Trumbore et al., 2016). The mid-infrared laser spectrometer is based on the principles of cavity ring-down spectroscopy in the familiar linear absorption regime (Fleisher et al., 2017). By probing the rotationally resolved vibrational spectrum of $^{14}C^{16}O_2$ near 2209 cm^{-1} at low temperature (220 K) and low pressure (0.9 kPa), samples of high-purity CO_2 were analysed to determine their absolute ^{14}C content. In our initial demonstration, the spectrometer unambiguously identified commercially prepared biogenic and petrogenic CO_2 samples, and reported a value of $F^{14}C = 0.75 \pm 0.11$ for the biogenic sample that was in good agreement with the value of $F^{14}C = 0.86$ independently measured by accelerator mass spectrometry. Recent progress towards a second-generation spectrometer with increased sensitivity will also be discussed.

REFERENCES

Trumbore S.E. Sierra C.A. Hicks Pries C.E. 2016. Radiocarbon nomenclature, theory, models, and interpretation: measuring age, determining cycling rates, and tracing source pool. In *Radiocarbon and Climate Change*, Schuur E.A.G. Druffel E.R.M. Trumbore S.E. eds. (Springer) Ch. 3, pp. 45–82.

Fleisher A.J. Long D.A. Liu Q. Gameson L. Hodges J.T. 2017. Optical measurement of radiocarbon below unity fraction modern by linear absorption spectroscopy. Journal of Physical Chemistry Letters 8: 4550–4556.

Combining the use of sulfur isotopes with carbon and nitrogen to improve our understanding of aquatic food webs and animal connectivity and movement

Ms Vanessa Fry[1], Professor Michele Burford[1], Professor Stuart Bunn[1]

[1]Australian Rivers Institute, Griffith University, Nathan, Australia

Natural abundance carbon and nitrogen isotopes have traditionally been used to develop our understanding of the sources of production, and transfer and fate of energy and nutrients in aquatic ecosystems. More recently, sulfur isotope analysis has emerged as a complementary method to resolve the challenges faced with identifying sources and sinks, and tracing movement patterns of aquatic animals. However, the analytical methods surrounding sulfur analysis are challenging and time consuming, and hence analyses are more expensive than carbon and nitrogen alone. We have improved on the existing analytical methods to provide a reliable, routine and cost-effective process for analysing sulfur isotopes. For example, we have applied this method to trace the movement patterns of highly mobile fish and crocodiles within a tropical floodplain river system in northern Australia. In this case, carbon and sulfur isotopes were used together as a conservative tracer to identify the degree of utilisation of food sources across different habitats. The study found that large bodied fish, as a barramundi, were well subsidised by floodplain food sources and moved widely through the waterways to access food supplies, indicating a high degree of hydrological connectivity in the system (Jardine et al., 2012). Furthermore, results indicated that whilst seasonal migrations among large-bodied fish were common, they still largely retained the carbon and sulfur isotopic compositions of the restricted waterholes they reside in during much of the year. We believe that our newly developed capability in analysing sulfur isotopes will substantially improve our ability to interpret stable isotope results, and ultimately result in an improved understanding of aquatic food webs.

REFERENCES

Jardine T.D. Pusey B.J. Hamilton S.K. Pettit N.E. Davies P.M. Douglas M.M. Sinnamon V. Halliday I.A. Bunn S.E. 2012. Fish mediate high food web connectivity in the lower reaches of a tropical floodplain river. Oecologia 168: 829-838.

POSTER

37Ar as tracer for groundwater residence times of a few months: A case study in the Emmental, Switzerland

Dr Christoph Gerber[1,2], Dr Roland Purtschert[2], Dr Oliver S Schilling[3,4], Dr Daniel J Partington[5], Dr Matthias S. Brennwald[6], Prof Dr Rolf Kipfer[6], Prof Dr Daniel Hunkeler[3], Prof Dr Philip Brunner[3]

[1]CSIRO Land & Water, Glen Osmond, Australia, [2]Climate and Environmental Physics and Oeschger Center for Climate Change Research, University of Bern, Bern, Switzerland, [3]Centre for Hydrogeology and Geothermics (CHYN), University of Neuchâtel, Neuchâtel, Switzerland, [4]Department of Geology and Geological Engineering, Université Laval, Québec, Canada, [5]National Centre for Groundwater Research and Training, School of the Environment, Flinders University, Adelaide, Australia, [6]Department of Water Resources and Drinking Water, Swiss Federal Institute of Aquatic Science and Technology (eawag), Dübendorf, Switzerland

Significant exchange fluxes are often observed between streams and connected alluvial aquifers. Estimating these fluxes and the associated residence time scales can be challenging, because there is a lack of tracers for groundwater residence times of weeks to months. In this age range ^{222}Rn is not sensitive anymore and other tracers such as CFCs, SF_6, ^{3}H, or ^{85}Kr are not yet sensitive enough. We investigate the possibility of filling this gap in groundwater dating with radioactive ^{37}Ar (half-life of 35 days).

Measurements of ^{37}Ar are done by decay counting on large-volume gas samples extracted from groundwater in the field. Production of ^{37}Ar is mainly via capture of cosmogenic neutrons and muons in the shallow subsurface resulting in a depth-dependent secular equilibrium concentration of ^{37}Ar.

We established such a secular equilibrium concentration profile in the Emmental, a shallow alluvial system in Switzerland, as a basis for interpreting the first ^{37}Ar measurements undertaken as part of a study of the exchange processes in this alluvial system (Schilling et al., 2017). Additional tracer measurements and a coupled groundwater-surface water numerical model of the system provide a good basis to evaluate the novel ^{37}Ar tracer.

REFERENCES

Schilling, O. S., Gerber, C., Partington, D. J., Purtschert, R., Brennwald, M. S., Kipfer, R., Hunkeler, D. Brunner, P. (2017). Advancing Physically-Based Flow Simulations of Alluvial Systems Through Atmospheric Noble Gases and the Novel ^{37}Ar Tracer Method. Water Resources Research, 53. https://doi.org/10.1002/2017WR020754

Application of 39Ar as a tracer for recent anthropogenic change of a groundwater system: The Red River Delta in Vietnam

Dr Christoph Gerber[1,2], Dr Roland Purtschert[2], Dr Flemming Larsen[3], Dr Hoan van Hoang[4], Dr Long V. Tran[4], Dr Luu T. Tran[4], Dr Nhan Q Pham[4], Dr Jürgen Sültenfuss[5]

[1]CSIRO Land & Water, Glen Osmond, Australia, [2]Climate and Environmental Physics, Physics Institute and Oeschger Centre for Climate Change Research, University of Bern, Bern, Switzerland, [3]GEUS, Copenhagen, Denmark, [4]Hanoi University of Mining and Geology, Hanoi, Vietnam, [5]University of Bremen, Bremen, Germany

Groundwater with residence times of a few hundred years is difficult to date because of a lack of suitable tracers in that time window. ^{39}Ar is a radioactive noble gas which covers exactly that time window (half-life 269 years) and is projected to become a more accessible tracer over the coming years due to improvements in the new Atom Trap Trace Analysis (ATTA) measurement technique. Here, the potential of and possible issues with ^{39}Ar dating are discussed based on a case study from northern Vietnam.

In the south of Nam Dinh Province, Red River Delta, Vietnam, fresh Pleistocene groundwater has been identified to exist next to brackish pore waters in the Red River area (Wagner et al. 2011). Extensive exploitation of the fresh water results in decreasing groundwater heads and sea-water intrusion (Wagner et al., 2012). In order to understand the dynamics and origin of the fresh and saltwater and to predict the future evolution of the resource an extensive investigation using environmental tracers has been carried out (^{39}Ar, ^{85}Kr, ^{3}H, stable noble gas measurements, ^{18}O, ^{2}H, and major chemical elements).

Depleted stable noble gas concentrations correlate with high concentrations of dissolved methane suggesting degassing due to the high methane partial pressure. Measurements of ^{39}Ar are insensitive to this degassing because the isotopic ratio is measured rather than absolute concentrations. ^{39}Ar results show that groundwater generally flows northwards as well as towards the coast on timescales of hundreds of years from an elevated and hilly recharge area in the west of the delta. A comparison of measured total dissolved solids as a function of ^{39}Ar ages reveals that both old paleoseawater as well as recently intruded seawater are present.

REFERENCES

Wagner, F., Trung, Đ. T., Phúc, H. Đ., Lindenmaier, F., 2011, Assessment of Groundwater Resources in Nam Dinh Province, Final Technical Report, Part A, Improvement of Groundwater Protection in Vietnam.

Wagner, F., Ludwig, R. R., Noell, U., Hoang, H. V., Pham, N. Q., Larsen, F., Lindenmaier, F., 2012, Genesis of economic relevant fresh groundwater resources in Pleistocene/Neogene aquifers in Nam Dinh (Red River Delta, Vietnam). EGU 12. European Geosciences Union, Vienna.

Application of 81Kr to assess old groundwater systems: the Baltic Artesian Basin (BAB)

Dr Christoph Gerber[1,2], Prof Dr Rein Vaikmäe[3], Prof Dr Werner Aeschbach[4], Dr Alise Babre[5], Dr Wei Jiang[6,8], Prof Dr Markus Leuenberger[2], Prof Dr Zheng-Tian Lu[6,8], Prof Dr Robert Mokrik[7], Dr Peter Müller[8], Dr Valle Raidla[3], Dr Tomas Saks[5], Dr Niklaus Waber[9], Therese Weissbach[4], Dr Jake C. Zappala[8], Dr Roland Purtschert[2]

[1]CSIRO Land & Water, Glen Osmond, Australia, [2]Climate and Environmental Physics, Physics Institute and Oeschger Centre for Climate Change Research, University of Bern, Bern, Switzerland, [3]Tallinn University of Technology, Institute of Geology, Tallinn, Estonia, [4]Institute of Environmental Physics, University of Heidelberg, Heidelberg, Germany, [5]Department of Geography and Earth Sciences, University of Latvia, Riga, Latvia, [6]The University of Science and Technology of China, Hefei, China, [7]Department of Hydrogeology and Engineering Geology of Vilnius University, Vilnius, Lithuania, [8]Physics Division, Argonne National Laboratory, Argonne, USA, [9]Institute of Geological Sciences, University of Bern, , Switzerland

Recent improvements in analytical techniques and the ongoing effort to build a measurement system for ^{81}Kr in Adelaide raise the prospect of ^{81}Kr as a viable and powerful alternative to tracers such as ^{36}Cl and ^{4}He for estimating groundwater ages and flow patterns on time scales of hundred thousands of years.

Here we present a case study from the multi-layered sedimentary Baltic Artesian Basin (BAB, Gerber et al., 2017) to showcase what ^{81}Kr can achieve and discuss possible caveats when interpreting ^{81}Kr data. We focus on the Cambrian Aquifer System (CAS), which is the lowermost aquifer of the BAB, and considered for storage of CO_2 or radioactive waste, as well as being an important source of drinking water for northern Estonia.

Samples from seven deep wells (up to 1800 m) were analysed for a suite of dating tracers (^{85}Kr, ^{39}Ar, ^{81}Kr, $^{4}He_{rad}$, and $^{40}Ar_{rad}$), noble gas concentrations, ^{18}O, ^{2}H, and chemistry. The results are consistent with mixing of three water types: (i) fresh meteoric water, (ii) glacial meltwater, and (iii) a brine end member. These end members are expected to also have different residence times, which need to be deconvoluted. The noble gas concentrations of the different end members turned out to be very important for the deconvolution.

For the brine component, ^{81}Kr ages exceed the dating range of the ATTA 3 instrument of 1.3 Ma. Ages of >1 Ma for the brine component are also supported by $^{4}He_{rad}$ and $^{40}Ar_{rad}$. In turn, ^{81}Kr ages of the fresh meteoric and glacial meltwater components range from 300 ka to 1.3 Ma. The spatial pattern of these ages implies that past flow patterns must have differed from today's flow patterns. A conceptual model shows that it is plausible that the flow direction reversed during the advances of the Scandinavian Ice Sheet.

REFERENCES

Gerber, C., Vaikmäe, R., Aeschbach, W., Babre, A., Jiang, W., Leuenberger, M., Lu, Z.-T., Mokrik, R., Müller, P., Raidla, V., Saks, T., Waber, N., Weissbach, T., Zappala, J., Purtschert, R. (2017). Using ^{81}Kr and noble gases to characterize and date groundwater and brines in the Baltic Artesian Basin on the one-million-year timescale. Geochimica et Cosmochimica Acta, Volume 205, https://doi.org/10.1016/j.gca.2017.01.033.

Discriminating natural from anthropogenic climate change effects in upland agro-ecosystems

Dr Andrew Swales[1], Dr Max Gibbs[1], Mr Greg Olsen[1], Mr Ron Ovenden[1]

[1]Niwa, Hamilton, New Zealand

Land-use change is a likely outcome of climate warming over the next few decades. In upland agroecosystems, warming climate will allow some plant communities to naturally extend their growth range to higher altitudes where conditions previously limited them to a lower elevation zone. This warming will also make it possible for farmers to extend pastoral agriculture and cropping to higher elevations, where previously this was not possible.

A consequence of higher/increased intensity of rainfall associated with climate warming, will be an increase in upland soil erosion. The resulting increases in sediment transport rates will impact downstream ecosystems and damage water supplies with higher suspended sediment loads that can smother stream beds and infill reservoirs. To mitigate the impact of these effects we need to be able to distinguish between erosion that is a direct consequence of climate change and may not be amenable to management, and erosion from agricultural practices made possible by climate change and where management may be possible.

In this paper, we present a concept, using the compound specific stable isotopic (CSSI) signatures of intrinsic biomarkers in the soil, for achieving this discrimination. The preliminary results of measurements along a 30-year pine–to–pasture chronosequence are used to support this concept.

Unlocking the history of ENSO stored within south-east Queensland's fossil leaves

Ms Jacinta S. Greer[1,2], Dr Francesca A. McInerney[1,2], Dr John Tibby[2,3], Dr Cameron Barr[2,3], Dr Quan Hua[4]
[1]Department of Earth Sciences, University Of Adelaide, Adelaide, Australia, [2]Sprigg Geobiology Centre, University of Adelaide, Adelaide, Australia, [3]Department of Geography, Environment and Population, University of Adelaide, Adelaide, Australia, [4]Australian Nuclear Science and Technology Organisation, Lucas Heights, Australia

The El Niño–Southern Oscillation (ENSO) effects 2/3 of the planet's population, and understanding its evolution is critical to anticipating future changes. However, Pacific records of the behaviour of ENSO over the past millennium disagree about the timing and intensity of El Niño- and La Niña- dominated phases, presenting a challenge to testing hypotheses of ENSO response to changing background conditions. There is a need for further records from ENSO affected regions, especially Australasia, which is under-represented in the literature. Here we present a ~1500 year quantitative precipitation record from sub-tropical Australia, based on the carbon and oxygen isotope ratios (δ^{13}C and δ^{18}O) of sub-fossil *Melaleuca quinquenervia* leaf fragments preserved in the sediments of Swallow Lagoon, North Stradbroke Island, south-east Queensland. Previous work has shown that the carbon isotope discrimination (Δ) calculated from the bulk leaf δ^{13}C of modern *M. quinquenervia* responds to local precipitation (Tibby et al. 2016). Here the Δ values of sub-fossil *M. quinquenervia* are compared to instrumental rainfall data from the past century to test this established relationship through time. We also examine the δ^{18}O of leaf cellulose allowing for both for the carbon and oxygen isotope signals to be related to rainfall. The Δ and δ^{18}O records from sub-fossil leaves are then used to quantitatively reconstruct rainfall over the last 1500 years. We tested hypotheses which suggest that the Medieval Climate Anomaly (MCA) was more La Niña-like than the Little Ice Age (LIA) (Mann et al. 2009). The results of our work suggest La Niña-dominated conditions in sub-tropical Australia during both the LIA and MCA, possibly indicating that ENSO was not controlled by external climate forcing over these intervals.

REFERENCES

Tibby J., Barr C., McInerney F.A., Henderson A.C., Leng M.J., Greenway M., Marshall J.C., McGregor G.B., Tyler J.J., McNiel V. 2016. Carbon isotope discrimination in leaves of the broad-leaved paperbark tree, Melaleuca quinquenervia, as a tool for quantifying past tropical and subtropical rainfall. Global Change Biology.

Mann M.E., Zhang Z., Rutherford S., Bradley R.S., Hughes M.K., Shindell D., Ammann C., Faluvegi G., Ni F. 2009. Global Signatures and Dynamical Origins of the Little Ice Age and Medieval Climate Anomaly. Science. 326: 1256-1260

Presence of adjacent grasses enhances while 14NH4+–addition to receiver-pines reduces 15N-movement between paired-pine saplings in a Californian pine forest

Professor Xinhua He[1]

[1]Southwest Univ, China/Univ Western Australia, Chongqing, China

Nutrient movement in common mycorrhizal networks (CMNs) has often been demonstrated, but the mechanism and significance of such nutrient movement in the field remains uncertain. Previously, we have demonstrated ^{15}N-movement between ectomycorrhizal (EM) pine (*Pinus sabiniana*) trees. In that study, arbuscular mycorrhyzal (AM) plants surrounding EM trees received an equivalent amount of ^{15}N from the donor-tree, suggesting root exudation is an important transfer mechanism. In a follow-up experiment, we removed the grass vegetation between donor- and receiver-trees to test the hypothesis that more ^{15}N would move between trees in the absence of grasses. We performed the following treatments: (1 and 2) ^{15}N application to donor-pine needles in the presence or absence of grasses and (3 and 4) with or without ^{14}N application to receiver-pine needles. We found that needle δ^{15}N values of receiver-pines (462‰) growing in the presence of grasses were significantly greater compared to receiver-pines (320‰) growing in the absence of grasses. Receiver-pine roots in the presence of grasses also became significantly more enriched (42‰) than pine-receiver roots (29‰) in the absence of grasses. The ^{14}N application to the receiver-tree reduced ^{15}N movement from tree to tree regardless of the presence or absence of grasses. Grasses appeared to facilitate the transfer of N between trees in all four treatments. The movement of ^{15}N to grass roots when present, expressed as concentrations, was similar to the receiver-pine roots. The movement of N from a pine rhizosphere and common EM network to a common AM network suggests that root and/or hyphal leakage is an important process that circulates N in the rhizosphere. Our results indicate that root exudation may be an important indirect transfer and reallocation mechanism of N and other nutrients among plants and diverse CMNS. Our results have important implications for nutrient movement between diverse plants in terrestrial ecosystems.

Keywords: ^{14}N/^{15}N, common mycorrhizal networks, grass, N transfer, paired pines

He XH, Bledsoe CS, Zasoski RJ, Southworth D, Horwath WR. **2006**. Rapid nitrogen transfer from ectomycorrhizal pines to adjacent ectomycorrhizal and arbuscular mycorrhizal plants in a California oak woodland. *New Phytologist* **170**: 143-51.

He XH, Xu MG, Qiu GY, Zhou JB. **2009**. Use of ^{15}N stable isotope to quantify nitrogen transfer between mycorrhizal plants. *Journal of Plant Ecology* **2**: 107-18.

Presence of adjacent grasses enhances while $^{14}NH_4^+$–addition to receiver-pines reduces ^{15}N-movement between paired-pine saplings in a Californian pine forest

Xinhua HE[1, 2, 3]

[1]Centre of Excellence for Soil Biology, College of Resources and Environment, Southwest University, Chongqing 400715, China; [2]Department of Land, Air and Water Resources, University of California, Davis, CA 95616, USA and [3]School of Biological Sciences, University of Western Australia, Crawley 6009, Australia

86-18723289058, xinhua.he@uwa.edu.au

Nutrient movement in common mycorrhizal networks (CMNs) has often been demonstrated, but the mechanism and significance of such nutrient movement in the field remains uncertain. Previously, we have demonstrated ^{15}N-movement between ectomycorrhizal (EM) pine (*Pinus sabiniana*) trees. In that study, arbuscular mycorrhyzal (AM) plants surrounding EM trees received an equivalent amount of ^{15}N from the donor-tree, suggesting root exudation is an important transfer mechanism. In a follow-up experiment, we removed the grass vegetation between donor- and receiver-trees to test the hypothesis that more ^{15}N would move between trees in the absence of grasses. We performed the following treatments: (1 and 2) ^{15}N application to donor-pine needles in the presence or absence of grasses and (3 and 4) with or without ^{14}N application to receiver-pine needles. We found that needle ⍰^{15}N values of receiver-pines (462‰) growing in the presence of grasses were significantly greater compared to receiver-pines (320‰) growing in the absence of grasses. Receiver-pine roots in the presence of grasses also became significantly more enriched (42‰) than pine-receiver roots (29‰) in the absence of grasses. The ^{14}N application to the receiver-tree reduced ^{15}N movement from tree to tree regardless of the presence or absence of grasses. Grasses appeared to facilitate the transfer of N between trees in all four treatments. The movement of ^{15}N to grass roots when present, expressed as concentrations, was similar to the receiver-pine roots. The movement of N from a pine rhizosphere and common EM network to a common AM network suggests that root and/or hyphal leakage is an important process that circulates N in the rhizosphere. Our results indicate that root exudation may be an important indirect transfer and reallocation mechanism of N and other nutrients among plants and diverse CMNS. Our results have important implications for nutrient movement between diverse plants in terrestrial ecosystems.

Keywords: ^{14}N/^{15}N, common mycorrhizal networks, grass, N transfer, paired pines

He XH, Bledsoe CS, Zasoski RJ, Southworth D, Horwath WR. **2006**. Rapid nitrogen transfer from ectomycorrhizal pines to adjacent ectomycorrhizal and arbuscular mycorrhizal plants in a California oak woodland. *New Phytologist* **170**: 143-51.

He XH, Xu MG, Qiu GY, Zhou JB. **2009**. Use of ^{15}N stable isotope to quantify nitrogen transfer between mycorrhizal plants. *Journal of Plant Ecology* **2**: 107-18.

Nano-scale secondary ion mass spectrometry (nano-SIMS) images can differentiate organo-mineral complexes and associated carbon preservation in a Chinese red soil

Professor Xinhua He[1], Professor Guanghui Yu[2]

[1]Centre of Excellence for Soil Biology, College of Resources and Environment, Southwest Univ, China/Univ Western Australia, Chongqing/Perth, China/Australia, [2]National Engineering Research Center for Organic-based Fertilizers, Nanjing Agricultural University, Nanjing, China

The submicron information about *in situ* mechanisms of fertilization practices affecting organo-mineral complexes and associated carbon (C) preservation is limited. Recently, a novel imaging facility, nano-scale secondary ion mass spectrometry (Nano-SIMS), is capable of the concurrently quantitatively high spatial resolution imaging of five stable isotopes (e.g., $^{1}H/^{2}H$, $^{12}C/^{13}C$, $^{14}N/^{15}N$, $^{16}O/^{18}O$, $^{31}S/^{34}S$, etc.) with high sensitivity at ≥50 nm metric and ppm atom scales. Nano-SIMS analyses are particularly powerful when combining with ^{13}C- and ^{15}N-labelled amino acids, which can bound to their amino, carboxyl or both groups depending on their size. The quantitative of molecular and isotopic patterns of inorganic and/or organic C and N source could be hence imaged and detected. We applied Nano-SIMS, X-ray photoelectron and X-ray absorption fine structure spectroscopies to examine submicron effects of 24-year long-term inorganic (NPK: nitrogen, phosphorus & potassium) vs. organic (M: manure; and NPKM) fertilization on associations of organic and mineral components in a red soil in south China. Results showed that organic amendments had significantly increased the mineral availability, particularly in the short-range-ordered (SRO) phases. Nano-SIMS images provided direct evidence that citric acid, a major component of root exudates, promoted the formation of SRO minerals, which acted as "nuclei" for C retention, and that the submicron elemental distribution and spatial heterogeneity in the soil colloids and the ratios of $^{12}C^{-}/^{27}Al^{16}O^{-}$ and $^{12}C^{-}/^{56}Fe^{16}O^{-}$ were greater under NPKM or M than under NPK. The C-binding loadings of Al and Fe minerals in colloids at submicron scales, and the concentrations of highly reactive Al and Fe minerals, were greatly enhanced under NPKM or M than under NPK. Our submicron-scale findings suggest that both the reactive mineral species and their associations with C are differentially affected by 24-year inorganic and organic fertilization.

Xiao JA, Wen YL, Li H, Hao JL, Shen QR, Ran W, Mei XL, He XH, Yu GH. 2015. *In situ* visualisation and characterisation of the capacity of highly reactive minerals to preserve soil organic matter (SOM) in colloids at submicron scale. Chemosphere 138: 225-232.

Xiao JA, He XH, Zhou Y, Zheng LR, Hao JL, Ran W, Shen QR, Yu GH. 2016. New strategies for submicron characterization the carbon binding of reactive minerals in long-term contrasting fertilized soils: Implications for soil carbon storage. Biogeosciences 13: 3607-18.

POSTER

Alien species provenance and validation using stable isotopes

Miss Katherine Hill[1], Mrs Kristine Nielson[1], Ms Jennifer Pistevos[2], Associate Professor Phillip Cassey[1], Dr Jonathan Tyler[1], Dr Francesca McInerney[1]

[1]The University of Adelaide, Adelaide, Australia, [2]Centre de Recherche Insulaire et Observatoire de l'Environnement (CRIOBE) , French Polynesia

The illegal wildlife trade facilitates the global movement of exotic animals as pets, creating pathways for non-native species to establish wild populations as individuals escape from captivity or are intentionally released (SCBD, 2010; García-Díaz et al., 2016). Novel surveillance tools are required to detect, prevent and respond to the evolving threat of exotic pet incursions. This study aims to develop a set of best-practice methods using stable isotope ratios of key alien vertebrate species to determine the environmental history and provenance of seized or at-large specimens.

We focus on the red-eared slider turtle (*Trachemys scripta elegans*), a North American species with established wild populations worldwide due to unregulated pet trade until the 1970s (García-Díaz et al. 2015). Five specimens with different incursion and seizure histories were selected and stable carbon, nitrogen, and oxygen isotope ratios in scute keratin were measured. Additionally, elemental analysis of bone (vertebra, femur, and toe) and scute keratin was performed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Variation was minimal across each turtle carapace and bone. However, differences in oxygen isotope ratios, and concentrations of uranium (U_{238}) and barium (Ba_{137}) were correlated to environmental history. Thus, chemical differentiation of captive and wild animals appears promising.

REFERENCES

García-Díaz P. Ross J.V. Ayres C. Cassey P. 2015. Understanding the biological invasion risk posed by the global wildlife trade: propagule pressure drives the introduction and establishment of Nearctic turtles. Global Change Biology 21: 1078-1091.

García-Díaz P. Ross J.V. Woolnough, A.P. 2016. The illegal wildlife trade is a likely source of alien species. Conservation Letters 10: 690-698.

Secretariat of the Convention on Biological Diversity 2010. Pets, Aquarium, and Terrarium Species: Best Practices for Addressing Risks to Biodiversity. Technical Series 48: 1-46.

Biosecurity intelligence: biogeochemical clues to high-risk pest natal origins

Peter Holder
Lincoln University

Based on the same principles used to investigate cosmic processes and provenance of items of forensic and commercial value, stable isotope and trace element biogeochemical signatures show promise as markers of an insects' natal origin.

In the context of national biosecurity, point of origin discrimination of pests detected in MPI surveillance and border security programs can be of significant economic and social value; as provenance information can identify risk pathways; as well as distinguish whether samples from surveillance traps are non-established new arrivals – or if they represent an established population. Therefore, this information can direct appropriate operational responses in exotic pest eradication campaigns, as well as support maintaining "area pest free" status and thereby preserving export trade access for NZ produce.

Here we will briefly review the comparatively new field of tracking insect movement using natural abundance biogeochemical markers. Recent advances, including a much improved understanding of fundamental principles, will be discussed, focusing on research which has used high-impact internationally distributed pests and real-world pest incursion case-studies. These works have shown strong potential for entomological provenance resolution through the multivariate examination of both climatically and geologically linked spatial markers, namely $\delta^{2}H$, $\delta^{18}O$, $^{87}Sr/^{86}Sr$, $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ isotope ratios. The provenance value of trace element concentration signatures will also be discussed.

From this body of work, the potential and constraints of this technology are revealed, and future technological developments identified.

The drivers of rainfall isotope variability in Australia and why groundwater is often different

Dr Cath Hughes[1], Dr Jagoda Crawford[1], Dr Dioni Cendón[1], Dr Karina Meredith[1], Dr Suzanne Hollins[1]
[1]Australian Nuclear Science And Technology Organisation, Lucas Heights, Australia

Rainfall stable isotope composition varies dramatically across Australia. Using monthly ^{2}H and ^{18}O data from 15 Global Network of Isotopes in Precipitation (GNIP), sites the underlying causes for the spatial and temporal variability have been investigated. Because of the island nature of Australia, moisture originates from the Indian Ocean to the west and the Pacific Ocean to the east, and is dominated by the monsoon and tropical cyclones to the north and frontal and low pressure systems to the south. Simple rainfall amount or temperature relationships don't explain the observations because of the huge spatial variability in moisture source and synoptic processes. However, latitude, elevation and continentality were found to have some influence on the isotopic average at the 15 sites. Using relationships developed with data from the 15 GNIP sites and additional data from higher elevation sites, an isoscape has been developed. This is used to investigate what drives groundwater recharge at a variety of locations across Australia. In many regions groundwater recharge can be linked isotopically to extreme high rainfall events such as tropical cyclones, east coast lows or major troughs which may occur on sub-annual or decadal time scales. For many inland sites, recharge from such events results from widespread flooding over hundreds or thousands of kilometers, introducing an evaporated signature to groundwater, or one that reflects a different composition to local rainfall. In contrast, reliable seasonal rainfall from the monsoon in the north, or winter rainfall in the south west leads to groundwater signatures in alluvial, karst and fractured rock aquifers that reflect wet season averages. A better understanding of how these processes vary across the continent improves our ability to apply stable isotopes to trace groundwater recharge and ultimately provides valuable information for water resource managers in sustainably managing groundwater and connected surface water systems.

Dynamic rainfall isoscapes for biosecurity and hydrology

Dr Elizabeth Keller[1], Prof Troy Baisden[2], Dr Peter Holder[3], Ms Silvia Canessa[1], Ms Vanessa Trompetter[1], Ms Abigail Lovett[1]
[1]GNS Science, Lower Hutt, New Zealand, [2]University of Waikato, Hamilton, New Zealand, [3]Lincoln University, Christchurch, New Zealand

We describe the development of an irrigation and tap water isoscape model for biosecurity and hydrology research in New Zealand. New Zealand's location in the Southern Ocean exposes it to unique weather patterns and alternations of sub-tropical northerly and sub-Antarctic southerly storm tracks that result in high spatial and temporal variability in precipitation. We have previously demonstrated (Baisden et al., 2016) that dynamic precipitation isoscapes (maps of δ^2H and δ^{18}O in rainfall) can be calculated and compiled at monthly resolution using daily gridded weather data weighted by precipitation amount. The isoscapes enable applications in hydrology, paleoclimate, agricultural authentication, and biosecurity. Here, we focus primarily on biosecurity, where a number of sap-sucking insects with severe invasive potential are frequently intercepted at the border and occasionally found deep within New Zealand. For this class of insects, H and O isotope ratios can help determine whether an insect is part of an established breeding population in New Zealand or a single exotic, non-breeding individual.

We have redeveloped our existing precipitation isoscape model to take advantage of an additional two years of daily event-based precipitation collection at major ports (run by the Better Border Biosecurity (B3) Programme), augmenting the ~3 years of monthly data from 50 stations used to develop our previous model. The new model is tested against previously acquired data from groundwater and monthly samples in 77 major river sites, enabling the calculation of an empirical relationship between precipitation and groundwater / surface water. This forms the basis of an irrigation and tap water isoscape that can be compared against isotope ratios in insect samples.

REFERENCES

Baisden W.T. Keller E.D. Van Hale R. Frew R.D. Wassenaar L.I. 2016. Precipitation isoscapes for New Zealand: enhanced temporal detail using precipitation-weighted daily climatology. Isotopes in environmental and health studies 52: 343-352.

Mountains to the sea: quantifying the transfer of terrestrial organic matter to the deep ocean in submarine canyons

Dr Daniel Leduc[1], Max Gibbs[2], Andrew Kingston[1], Andrew Swales[2], Brittany Graham[1], Scott Nodder[1], Ashley Rowden[1]

[1]NIWA, Wellington, New Zealand, [2]NIWA, Hamilton, New Zealand

Deep-sea canyons that incise the continental shelf can facilitate the transfer of terrestrially and coastally-derived organic matter to the deep ocean, thus potentially providing important food resources to deep-sea benthic communities. Accordingly, some canyons are recognised as hot-spots of benthic biomass and activity; none more so than the Kaikōura Canyon, which hosts among the highest biomass yet recorded at the deep seabed globally (Figure 1). In this study, we compare the contribution of land and coastal-derived plant material to the sediment of the high productivity Kaikōura Canyon and the low productivity Hokitika Canyon using the compound-specific stable isotope (CSSI) technique and multivariate mixing models (Gibbs 2008). This method, which is used for the study of connectivity between nearshore and deep ocean ecosystems for the first time, provides new insights into the mechanisms responsible for the exceptionally high productivity of Kaikōura Canyon seabed communities, which may be driven by food inputs from outside the canyon. The application of this and other tracer methods will help clarify the fate of the vast quantities of fine, land-derived organic matter entering the oceans.

REFERENCES

Gibbs, M. M. 2008. Identifying source soils in contemporary estuarine sediments: a new compound-specific isotope method. Estuaries and Coasts 31: 344–359.

Nitrogen attenuation, dilution and recycling at the groundwater - surface water interface of a subtropical estuary

Dr Sébastien Lamontagne[1], Frederic Cosme[2], Andrew Minard[2], Andrew Holloway[3]
[1]Csiro Land And Water, Urrbrae, Australia, [2]Golder Associates, Melbourne, Australia, [3]Golder Associates, Sydney, Australia

Groundwater – surface water interactions in estuaries can promote the attenuation and dilution of groundwater-borne contaminants. For an Australian subtropical estuary, up to 80% of the N load in contaminated groundwater (>300 mg N L^{-1}) was removed during passage through the riverbed. The remaining N was also diluted by a factor of two or more by mixing before being discharged to the estuary. Most of the mixing occurred in a 'hyporheic zone' in the upper 50 cm of the riverbed. However, groundwater entering this zone was already partially mixed (12 – 60%) with surface water via a tidal circulation cell. Below the hyporheic zone (50 – 125 cm below the riverbed), NO_3^- concentrations declined slightly faster than NH_4^+ concentrations and and gradually increased, suggesting a co-occurrence of anammox and denitrification. During transport through the hyporheic zone, continued to become enriched (consistent with either denitrification or anammox) but became more depleted (indicating some nitrification). The discrepancy between (23 – 35‰) and (1.2 – 8.2‰) in all porewater samples indicated that the original synthetic nitrate pool (⍰^{15}N ~ 0‰; ⍰^{18}O ~ 18 – 20 ‰) had turned-over during transport in the aquifer before reaching the riverbed. Whilst porewater NO_3^- was more ⍰^{18}O depleted than its synthetic source, porewater (–3.2 to –1.8‰) was enriched by 1–4‰ relative to rainfall-derived groundwater mixed with seawater. Isotopic fractionation from H_2O uptake during the N cycle and H_2O production during synthetic NO_3^- reduction are the probable causes for this enrichment.

POSTER

Quantifying groundwater discharge using radon-222 to understand groundwater-surface water dynamics

Miss Heather Martindale[1], Mr Rob van der Raaij[1], Dr Matthew Knowling[1], Dr Uwe Morgenstern[1]
[1]*Gns Science, Lower Hutt, New Zealand*

The aim of this study was to investigate whether quantifying groundwater (GW) discharge using the soluble, unstable isotope, radon (Rn) could provide further insight into GW-surface water (SW) interaction processes in the New Zealand riverine environment. In particular, hyporheic and parafluvial flows are investigated.

Radon samples were collected from two study sites, the Shag and Te Arai Rivers, at a spatial resolution of 500m, under low flow conditions. A mass-balance approach for quantifying GW flux using Rn was then applied to the gaining reaches (Cartwright and Hofmann 2016; Equation (1)).

Equation 1

Where I is the GW inflow along a reach ($\mathrm{m^3\ m^{-1}\ day^{-1}}$), Q is river discharge ($\mathrm{m^3\ day^{-1}}$), x is the distance of the reach measured (m), w is stream width (m), E is the evaporation rate ($\mathrm{m\ day^{-1}}$), F_h is the flux of Rn from the hyporheic zone ($\mathrm{Bq\ m^{-1}\ day^{-1}}$), F_p is the flux of Rn from the parafluvial zone ($\mathrm{Bq\ m^{-1}\ day^{-1}}$) k is the gas transfer coefficient ($\mathrm{day^{-1}}$), d is river depth (m), λ is the Rn decay constant (0.181 $\mathrm{day^{-1}}$), c_{gw} is the concentration of Rn in GW ($\mathrm{Bq\ m^{-3}}$) and c_r is the Rn concentration in the river water ($\mathrm{Bq\ L^{-3}}$).

To express the uncertainty associated with the input variables in Equation (1), a Monte Carlo sampling approach was applied. This allows for the uncertainty in calculated discharge rates based on Equation (1) to be estimated. Discharge flux is calculated here in the absence of a distinct input of Rn from parafluvial flow (Fp). When the calculated discharge from Equation (1) significantly exceeds the discharge indicated by concurrent gauging, it is assumed that the discrepancy is an indication of the contribution of discharge from parafluvial flow.

REFERENCES

Cartwright, I., & Hofmann, H. (2016). Using radon to understand parafluvial flows and the changing locations of groundwater inflows in the Avon River, southeast Australia. *Hydrology and Earth System Sciences*, 20(9), 3581-3600.

Seeing the forest through the leaves: Isotopic and morphological proxies for canopy closure in ancient forests

Dr Francesca McInerney[1], Dr. Lucas Cernusak[2], Dr. Alex Cheesman[2], Ms. Heather Duff[1]

[1]*University of Adelaide, Adelaide, Australia,* [2]*James Cook University, Cairns, Australia*

Forests canopy structure controls the penetration of light, relative humidity, and the isotopic composition of CO_2 in the understory. These factors influence the carbon isotope signatures of plants at different levels of the forest as well as their leaf morphology (e.g. undulation index, leaf mass per area). Leaves from closed canopy forests have more ^{13}C-depleted and more variable carbon isotope ratios than open forests (Graham et al., 2014), while undulation index in phytoliths has been linked to Leaf Area Index (LAI) (Dunn et al., 2015). However, our application of these proxies together in the fossil record has proven challenging (Bush et al., 2017). To explore the controls on carbon isotope ratios and leaf morphology in a modern closed canopy forest, we quantify the variability in these traits in relation to light in the Daintree Rainforest in Queensland, AU.

Leaves from five species of rainforest trees were sampled from the upper canopy, interior canopy and understory of intact rainforest, as well as from a forest gap. The goal was to characterise variation in leaf traits and isotopic composition within species across a canopy-induced light gradient, as well as to examine the effects light wells. The light environment for each foliar sample was quantified in terms of leaf LAI, which ranged from 0 to 7.

Carbon isotope ratio increased with light exposure, with similar scale of response in all species. In contrast, the responses in undulation index, cell area, and leaf mass per area differed among species, indicating that reconstructions based on leaf traits will require careful selection of taxa. No differences were detected between gap understory and control understory sites. This is encouraging for applying these methods to the fossil record because most fossil floras are biased towards forest gaps where water bodies accumulate and preserve fossil leaves.

REFERENCES

Graham H.V. Patzkowsky M.E. Wing S.L. Parker, G.G. Fogel, M.L. and Freeman, K.H. 2014. Isotopic characteristics of canopies in simulated leaf assemblages. Geochimica et Cosmochimica Acta 144: 82-95.

Bush, R.T. Wallace J. Currano E.D. Jacobs, B.F. McInerney F.A. Dunn R.E. and Tabor N.J. 2017. Cell anatomy and leaf $\delta^{13}C$ as proxies for shading and canopy structure in a Miocene forest from Ethiopia. Palaeogeography, Palaeoclimatology, Palaeoecology 485: 593-604.

Dunn R.E. Strömberg C.A.E. Madden R.H. Kohn M.J. and Carlini A.A. 2015. Linked canopy, climate and faunal evolution in the Cenozoic of Patagonia. Science 347: 258-261.

Graham H.V. Patzkowsky M.E. Wing S.L. Parker G.G. Fogel M.L. and Freeman K.H. 2014. Isotopic characteristics of canopies in simulated leaf assemblages. Geochimica et Cosmochimica Acta 144: 82-95.

A decade of isotopic investigations of drought and flood cycles of the Darling River

Dr Karina Meredith

Australian Nuclear Science and Technology Organisation, Australia.

The Barwon-Darling River system is the longest river in Australia (2,735 km). It faces environmental pressures from both climate change and anthropogenic activities, impacting the availability of water resources in the semi-arid environment. The motivation for this study was to provide water resource managers with a firm understanding of recharge characteristics, the evolution of saline groundwater and the impact of drought on water quality. As part of this ten year study, various hydrochemical and isotopic tracers were used to understand these fundamental hydrological and hydrogeological processes.

Water-limited environments are particularly difficult to monitor due to the large time lags between floods, the remoteness and expense of studying hydrologically complex systems in detail. High resolution surface water sampling using hydrochemical and stable isotope (δ^{18}O and δ^{2}H) data allowed us to quantify the contribution of evaporation, bank storage release and saline groundwater influx to the Darling River (Meredith et al., 2009). Non-traditional isotopes such as the trace element isotopes (δ^{7}Li, δ^{11}B and ^{87}Sr/^{86}Sr) were essential in differentiating saline groundwaters of different origin (Meredith at al., 2013).

Recharge frequency and the sources of water were identified using δ^{18}O, δ^{2}H and ^{3}H in groundwater, soil water, rainfall and river waters, before extended drought and then again after recharge. It was found that large overbank flood events were responsible for groundwater recharge over decadal time periods (Meredith et al., 2015). Understanding groundwater residence times using ^{14}C in this water-limited environment was challenging because of the mixing of different water and carbon sources. High evaporation rates also impacted the carbon dynamics in the groundwater system. It was found that various water-sediment processes occur to promote greater calcite dissolution in saline groundwater leading to the input of a higher than predicted 'dead' carbon source (Meredith et al., 2016).

The outcomes of this ten year study highlight the importance of using a multi-tracer approach, which includes trace element isotopes, stable isotopes, radioactive and hydrogeological methods in resolving complex geochemical processes that lead to the evolution of surface and groundwater in water-limited environments.

References:

Meredith, K.T., Hollins, S. E., Hughes, C. E., Cendón, D. I., Hankin, S.. Stone, D. J. M. (2009) Temporal variation in stable isotopes (18O and 2H) and major ion concentrations within the Darling River between Bourke and Wilcannia due to variable flows, saline groundwater influx and evaporation. Journal of Hydrology 378, 313-324.

Meredith, K., Moriguti, T., Tomascak, P., Hollins, S. and Nakamura, E. (2013) The lithium, boron and strontium isotopic systematics of groundwaters from an arid aquifer system: Implications for recharge and weathering processes. Geochimica et Cosmochimica Acta 112, 20-31.

Meredith, K.T., Hollins, S.E., Hughes, C.E., Cendón, D.I., Chisari, R., Griffiths, A. and Crawford, J. (2015) Evaporation and concentration gradients created by episodic river recharge in a semi-arid zone aquifer: Insights from Cl−, δ18O, δ2H, and 3H. Journal of Hydrology 529, Part 3, 1070-1078.

Meredith, K.T., Han, L.F., Hollins, S.E., Cendón, D.I., Jacobsen, G.E. and Baker, A. (2016) Evolution of chemical and isotopic composition of inorganic carbon in a complex semi-arid zone environment: Consequences for groundwater dating using radiocarbon. Geochimica et Cosmochimica Acta 188, 352-367.

Isotopic fractionation and geochemical evolution of subaqueous deposited sulfide-rich mine tailings: Implications for mine closure

Dr Mike Moncur[1,2], Dr Carol Ptacek[2], Dr David Blowes[2], Dr Matt Lindsay[3], Dr Jean Birks[1,2], John J. Gibson[1]
[1]InnoTech Alberta, Calgary, Canada, [2]University of Waterloo, Waterloo, Canada, [3]University of Saskatchewan, Saskatoon, Canada

The oxidation of sulfide minerals in subaerial tailings deposits generates acid and releases sulfate and metals to pore water. Subaqueous disposal of tailings is a common method for limiting sulfide-mineral oxidation. Short-term studies have demonstrated that shallow water covers are effective at limiting oxygen diffusion to submerged tailings; however, long-term studies are lacking. The former Sherritt-Gordon Zn-Cu mine, located in Sherridon, Manitoba, Canada, deposited sulfide-rich tailings into Fox Lake during 1951. The tailings formed a number of small exposed islands with the majority of material submerged underwater. Mineralogical examination of the land-deposited tailings showed a well-defined, ochreous oxidation zone that extended from surface to about 40 cm depth. The interval from 40 to 60 cm was a transitional zone of much weaker oxidation, and at depths >60 cm sulfide minerals in the tailings were not altered. In contrast to the thickness of the oxidation zone in the land-based tailings, the equivalent zone in the submerged tailings extended <6 cm below the water-solids interface. Porewater collected from the land-based tailings was characterized by low pH, depleted alkalinity and elevated concentrations of dissolved sulfate and metals. Conversely, development of strong reducing conditions in the subaqueous tailings had resulted in circumneutral pH conditions, low concentrations of dissolved sulfate and metals, H_2S production and strong $\delta^{34}S-SO_4$ and $\delta^{13}C$ fractionation indicating microbially-mediated sulfate reduction. Within the submerged tailings, secondary marcasite was observed in the relic ochreous zone occurring as coatings on primary minerals. This observation indicates that, following a period of oxidation, metals were subsequently sequestered from solution in this zone. This finding further emphasizes the influence of reducing conditions and microbial activity on metal mobility within mine tailings. Results from this study provide insight for the submergence of sulfide-rich tailings under a shallow water cover as a viable method for long-term storage.

Heretaunga Plains: groundwater dynamics and source from age tracers, isotopes, and hydrochemistry

Dr Uwe Morgenstern[1], John Begg[1], FRob W van der Raaij[1], Magali Moreau[1], Matt Knowling[1], Heather Martindale[1], Chris Daughney[1], Rachel Franzblau[1], Michael Stewart[2], Mike Toews[1], Vanessa Trompetter[1], Johannes Kaiser[1], Dougall Gordon[3], Pawel Rakowski[3], Jeff Smith[3], Thomas Wilding[3]

[1]Gns Science, Lower Hutt, New Zealand, [2]Aquifer Dynamics and GNS Science, Lower Hutt, New Zealand, [3]Hawke's Bay Regional Council, Private Bag 6006, Napier 4142, New Zealand

Aims

This collaborative study between Hawke's Bay Regional Council, Hastings District Council, Napier City Council, and GNS Science aims to improve our understanding of the Heretaunga Plains aquifers in regards to groundwater recharge sources and rates, flow dynamics, and interaction between groundwater and surface water. This information is key to sustainable management of this hydrologic system including preserving the drinking water security, and the integrity of the aquifers and surface waters that receive inflows from groundwater.

Method

This study utilises tritium, CFCs, SF_6, ^2H, ^{18}O, Ar, N_2, CH_4, radon and major/minor ion hydrochemistry data with respect to understanding the dynamics of the groundwater from recharge to discharge and interaction with surface water, and understanding the processes that control the hydrochemical properties (quality) of the groundwater including denitrification.

Age tracer and isotope data are available from c. 160 ground- and surface water sites. Groundwater wells are located across the Heretaunga Plains. In the west, near the Ngaruroro River, the wells are typically shallow, with depth ranging from 7 to 40 m. In the east, towards the coast, wells are typically becoming deeper as the depth to the confined aquifer increases. Around Hastings, a number of wells are significantly deeper, between 100–200 m.

Historic and recent tritium and SF_6 data show that the groundwater abstracted from wells in the Heretaunga Plains has often a complex age distribution. A refined 3D geologic model developed by GNS' Urban Geology programme captures the complex structure of the aquifer system, where well screens intersect multiple layers of a heterogeneous aquifer. Highly conductive Holocene river gravel fans are inter-fingered with the main aquifer. This refined geological model underpinned development of a new groundwater mixing model.

We used binary mixing models (BMM) consisting of two parallel exponential piston flow models to represent complex age distribution. The BMMs produce excellent matches to the measured multi-age-tracer time-series data collected for most (>90%) of the drinking water wells. Due to the complex hydrogeologic setting, very young water from shallow flow pathways can be 'hidden' in overall old water from the deep main aquifer. Matching the BMM to the multi-age-tracer time-series data enabled identification of such young water.

Results

Hierarchical Cluster Analysis (HCA) results provide context for the main drivers of hydrochemistry and recharge source, including oxic rivers and river-recharged groundwaters with little or no elevation of nutrient concentrations, association with limestone or carbonate geology, oxic rainfall-recharged groundwaters with moderate land-use impact and anoxic groundwater with chemistry typical of natural conditions.

The age tracers indicate that groundwater in most of the wells within the Holocene unconfined gravel fans of the Ngaruroro River and the Tukituki River are relatively young with mean residence time (MRT) 0 – 10 years, and from the area of the main water loss from the Ngaruroro River towards the coast, the groundwater within the confined aquifer becomes progressively older. The drinking water wells southwest of Napier contain water with MRT between 20–40 years. Further toward the coast, the groundwater becomes significantly older with MRT 40–80 years, and close to the coast the water is even older, indicating sluggish flow at this part of the aquifer. More vigorous groundwater flow in the confined aquifer toward the coast is indicated further south in the centre of the Plains. A tongue of very young groundwater with MRT < 5 years extends nearly half way towards the coast, and the groundwater near the coast is still relatively young with MRT 27–34 years. At the southern margin of the confined aquifer, older water of MRT >70 years prevails, again indicating more sluggish flow on the margin of the aquifer. Only around the Holocene gravel fan of the Tukituki River very young groundwaters of MRT <10 years occur.

The recharge source indicators (Ar, N_2, ^{2}H, ^{18}O, nitrate, excess-nitrogen, and CFCs) show a strong pattern of recharge source within the Heretaunga Plains aquifer. Two areas show a strong indication of aquifer recharge from the Ngaruroro River: around and southwest of Napier, and a band of river-recharged groundwater located at the centre of the Plains. It is likely that this band represents a buried paleo river channel that is still hydraulically connected to the Ngaruroro River and thus enables fast seaward flow of water lost from the river. This band of river-recharged groundwater coincides with the band of young groundwaters. The Tutaekuri River appears not to be connected to this aquifer. The unconfined area of the Ngaruroro River shows a clear indication of local rain recharge, similar to the southern half of the Heretaunga Plains aquifer.

Radon data, despite being sparse, show a clear discharge pattern, which is consistent with observed gain-loss patterns in rivers and streams. Low radon concentrations, indicative of no or little interactions with groundwater, are found in the lower reaches of the Tutaekuri River. High radon concentrations south of the Tutaekuri River indicate high groundwater discharge into the streams, water lost from the upstream reaches of the Tutaekuri River as indicated by water mass-balance. High radon concentrations in the gaining reaches of the Ngaruroro River and its tributaries confirm groundwater discharge into the River and streams. High radon concentrations in the drainage area south of the Ngaruroro River indicate discharge from the groundwater system, potentially resurfacing water lost from the Ngaruroro River further upstream. High radon concentration in the lower reaches of Karamu Stream and one of its tributaries also indicate discharge from the groundwater system.

Conclusions

Despite the still-remaining limitations of the Heretaunga Plains age, gas, and isotope tracer data set, it already has revealed details on large-scale groundwater processes that are not obtainable by other hydrologic methods, with implications to the management of these water resources.

AMS measurement of 32Si in Antarctic snow and ice

Dr Uwe Morgenstern[1], Prof Keith L Fiefield[2], Mr. Robert G Ditchburn[1], Robert Delmas[3], Prof. Jean R Petit[3]
[1]Gns Science, Lower Hutt, New Zealand, [2]The Australian National University, Canberra, Australia, [3]Univ. Grenoble Alpes, Grenoble, France

^{32}Si allows dating of ice cores and sediments over the last several hundred years, an important period for assessing anthropogenic impacts on earth. An issue with the ^{32}Si technique is, however, the relatively high uncertainty of its half-life. We aim to address this by measuring the ^{32}Si decay rate in well dated ice cores covering the last 1000 years. Cold Antarctic ice offers the advantage of good preservation of silicon and age markers (e.g. tritium and sulphur from large volcanic events). Our results show that the half life of ^{32}Si is significantly lower than thought.

Acknowledgement: This work was supported by Marsden Grant 01-GNS-009 ESA of the Royal Society of New Zealand.

Isotopic insights into plant carbon metabolism with climate warming

Professor Elise Pendall[1], Morgan Furze[2], John Drake[1], Craig Barton[1], Yolima Carrillo[1], Andreas Richter[3], Mark Tjoelker[1]
[1]Western Sydney University, Penrith, Australia, [2]Harvard University, Boston, USA, [3]University of Vienna, Vienna, Austria

Isotopic insights into plant carbon metabolism with climate warming
Climate warming has the potential to alter the balance between photosynthetic carbon assimilation and respiratory losses in forest ecosystems, leading to uncertainty in predicting their future physiological functioning, with implications for ecosystem carbon fluxes. The effects of warming on plant respiration have been well studied, but effects on carbon allocation and residence time have received less attention. We conducted an isotopic tracer study to evaluate effects of warming on assimilation, sugar metabolism, transport, storage, respiration and root exudation. *Eucalyptus parramattensis* trees were grown in the field in whole-tree chambers operated at ambient and ambient +3 °C temperature treatments (n=3 per treatment). The unique chambers were 9-m tall, with a volume of 57 m^{3}, and were equipped with independent canopy and below-ground compartments. We applied a $^{13}CO_2$ pulse and followed the label in plant sugars, bulk tissues and soil microbes, and in CO_2 respired from leaves, canopy, roots and soil over a 3-week period in conjunction with measurements of tree growth. Periodic monitoring of ^{13}C-CO_2 values in the canopy and soil compartments allowed us to quantify the total amount of $^{13}CO_2$ assimilated and respired by each tree. Compound-specific ^{13}C measurements of leaf sucrose, glucose and raffinose indicated that warming did not affect ^{13}C enrichment of these primary and secondary metabolites. However, warming appeared to reduce the residence time of carbon respired from the canopy, and especially from roots and soil. The proportion of the assimilated $^{13}CO_2$ retained by the trees was reduced by ~10% with warming, indicating that autotrophic respiration has the potential to feedback to climate change. This isotopic pulse-chase experiment provides insights into how rising temperatures may affect the fate of assimilated carbon from the leaf to the ecosystem scale.

Dual-isotope nitrate measurements to support nitrogen management in New Zealand

Andy Phillips[1], Professor Troy Baisden[1], A Immers[1], J Cooper[1]
[1]*GNS Science*

New Zealand is far away from other industrialised countries and has a population of only 5 million people, so that our rivers, lakes and streams have minimal impacts from atmospheric pollution. This creates a unique and ideal natural laboratory to study isotope effects associated with nitrogen cycling process, including denitrification, in our natural and managed ecosystems. New Zealand contains vast areas unaffected by human activities, but also has major rivers with large contributions from pastoral agriculture, cropping and horticultural systems, forestry, waste water treatment, meat processing, and other nitrogen sources.

Our continuing studies have shown that we can distinguish between some of these contributing sources to the nitrate levels and have assisted councils monitor and regulate water quality.

Choosing a method for dual-isotope nitrate measurements was a particular challenge within New Zealand. The genotypes of the denitrifying bacteria used most commonly around the world to produce nitrous oxide are difficult to import and use under restrictive biosecurity regulations. At GNS Science we have adapted the McIlvin and Altabet cadmium-azide chemical reduction method. We use customised automated pre-concentration device connected to an IsoPrime IRMS, which analyses nitrous oxide delivered by sparging, pre-concentration, and isothermal gas chromatic separation.

We have successfully analysed fresh to saline waters across a wide range of concentrations, following a convenient sample preservation technique matched to our laboratory methods, for measurement of N and O isotope ratios in nitrate and nitrite, and N isotopes in ammonium.

I highlight key methodogical advances, findings and challenges, and welcome discussion with other groups doing or considering this analysis.

Combining stable isotopes and mass-balance modelling to understand the Ross Sea ecosystem

Dr Matt Pinkerton[1], Dr Sarah Bury[1], Ms Julie Brown[1], Mr Jeff Forman[1]
[1]*Niwa, Wellington, New Zealand*

The world's largest Marine Protected Area (MPA) was established in the Ross Sea region of the Southern Ocean in December 2017. The MPA was designed to help understand the effects of climate change and fishing, and to mitigate threats to the integrity of the ecosystem. Setting up monitoring, tracking ecosystem change and understanding the conservation value of the MPA requires knowledge of how organisms are inter-related, especially through feeding (trophic) links.

A trophic mass-balance model of the Ross Sea ecosystem (Pinkerton et al., 2010) was developed. Initial values for all parameters were determined from survey and literature data, and then the model was balanced by adjusting all parameters simultaneously according to estimates of their relative uncertainties. This balanced model has been used to identify groups with high trophic importance to prioritise monitoring (Pinkerton & Bradford-Grieve, 2014), design spatial management to mitigate threats from fishing (Sharp et al., 2010), and to investigate the potential for changes due to fishing to cascade through the ecosystem (Pinkerton et al., 2016).

However, the balanced Ross Sea trophic model is highly under-constrained; there is a large family of possible solutions all of which are feasible according to the conceptual framework and available empirical data. Stable isotopes can help to explore the "feasible parameter space" of food web models such as this and provide estimates of uncertainty on ecosystem properties derived from them. More than 1300 measurements of bulk-tissue $\delta^{15}N$ and $\delta^{13}C$ have been made on organisms across the Ross Sea ecosystem from particulate organic matter (POM), copepods, pteropods, salps, krill, silverfish, myctophids, cephalopods, and 18 species of demersal fish (Pinkerton et al., 2013). We show how Bayesian Markov chain Monte Carlo modelling can be used to determine the distribution of model parameters and emergent ecosystem properties consistent with the isotope data.

REFERENCES

Pinkerton M.H. Bradford-Grieve J.M. 2014. Characterizing foodweb structure to identify potential ecosystem effects of fishing in the Ross Sea, Antarctica. ICES Journal of Marine Science 71: 1542-1553.

Pinkerton M.H. Forman J. Bury S.J. Brown J. Horn P. O'Driscoll R.L. 2013. Diet and trophic niche of Antarctic silverfish (*Pleuragramma antarcticum*) in the Ross Sea, Antarctica. Journal of Fish Biology 82: 141–164.

Pinkerton M.H. Lyver P.O'B. Stevens D.W. Forman J. Eisert R. Mormede S. 2016. Increases in Adélie penguins in the Ross Sea: could the fishery for Antarctic toothfish be responsible? Ecological Modelling, 337: 262–271.

Pinkerton M.H. Bradford-Grieve J.M. Hanchet S.M. 2010. A balanced model of the food web of the Ross Sea, Antarctica. CCAMLR Science 17: 1–31.

Sharp B.R. Parker S.J. Pinkerton M.H. 2010. Bioregionalisation and Spatial Ecosystem Processes in the Ross Sea Region. CCAMLR document WG-EMM-10/30, Hobart, Australia.

Nitrogen sources, transfer pathways, processing and fate in the complex Peel Harvey Estuarine System, Western Australia.

Mustefa Yasin Reshid[1], Dr Naomi Susane Wells[1], Prof Bradley Eyre[1]

[1]*Southern Cross University, EAST LISMORE, Australia*

Isotopes are useful tool for tracking the sources and fate of nitrogen that is over-enriching coastal waters and driving eutrophication. However, untangling the sources and fate of nitrogen using isotope signatures requires careful delineation of flow paths and instream processing. The complex hydrology, which includes wetlands, three rivers, two estuaries and extensive artificial-drainage network, of the Peel-Harvey Estuarine system (PHES) in Western Australia presents a unique challenge to using isotope tracers to track nitrogen. This is further complicated by extreme wet and dry seasons and the multiple nitrogen sources. We measured δ^{15}N-NO_3^-, δ^{18}O-NO_3^-, and δ^{15}N-NH_4 to track nitrogen sources and fate from the farm through the drains and rivers to the estuary along with δ^2H-H_2O, δ^{18}O-H_2O, and ^{222}Rn which help determine major transfer pathways. Samples were collected from drains (*n* = 53), rivers (*n* = 125), estuaries (*n* = 62), groundwater (*n* = 21), and precipitation (*n* = 20) in the dry season (February 2017) and wet season (July 2017). NO_3^- isotopes in summer showed a distinct spatial pattern. In the estuary, δ^{15}N-NO_3^- and δ^{18}O-NO_3^- values ranged from 0.3‰ and 40.1‰ at the ocean entrance, to 5.0‰ and 3.5‰ at the river mouth, respectively. The two major rivers had distinct δ^{15}N-NO_3^- (mean of 6.2‰ and 10.3‰) and δ^{18}O-NO_3^- values (mean of 12.5‰ and 8.2‰). The high δ^{15}N-NO_3 (mean = 18.8‰) and δ^{18}O-NO_3 (mean = 28.7‰) values in many drains most likely reflect denitrification in the artificial-drainage network. Wastewater effluent was identified as a potential point source, but the NO_3^- isotope signature was not distinct within hundreds of meters of outflow drain due most likely to NO_3^- assimilation and formation of fresh NO_3^- from the nitrification of NH_4^+. These first results from NO_3^- isotopes alone show the practicality of our approach for tracing nitrogen in the complex hydrology of the PHES.

Differentiating drivers of pelagic food webs in the central and eastern Great Australian Bight using compound specific amino acid nitrogen isotopes

Dr Andrew Revill[1], Dr Rudy Kloser[1], Caroline Sutton[1]

[1]*Csiro Oceans And Atmosphere, Hobart, Australia*

A key objective of this study was to, investigate the trophic linkages and pathways between the central and eastern regions of the Great Australian Bight with the hypothesis that the central region is driven more by “microbial” processes while the east experiences more upwelling and is therefore a more “traditional” food web.

Recently, compound specific nitrogen isotopes (CSIA) in individual amino acids have been used to investigate a wide variety of trophic interactions (Chikaraishi et al. 2009, Lorrain et al. 2009, Dale et al. 2011). Of particular interest for this study is the fact that certain “source” amino acids are incorporated with very little isotopic fractionation and are thus indicative of isotopic composition of the foodweb base.

Using these techniques we were clearly able to elucidate differences between the food webs operating in the eastern and central upper slope GAB with the east apparently being much more reliant on upwelled nutrients and the central GAB under an increased influence by picoplankton and nitrogen fixation.

The Great Australian Bight Research Program is a collaboration between BP, CSIRO, the South Australian Research and Development Institute (SARDI), the University of Adelaide, and Flinders University. The Program aims to provide a whole-of-system understanding of the environmental, economic and social values of the region; providing an information source for all to use

REFERENCES

Chikaraishi Y, Ogawa NO, Kashiyama Y, Takano Y, Suga H, Tomitani A, Miyashita H, Kitazato H, Ohkouchi N (2009) Determination of aquatic food-web structure based on compound-specific nitrogen isotopic composition of amino acids. Limnology and Oceanography-Methods 7:740-750

Dale JJ, Wallsgrove NJ, Popp BN, Holland KN (2011) Nursery habitat use and foraging ecology of the brown stingray Dasyatis lata determined from stomach contents, bulk and amino acid stable isotopes. Marine Ecology Progress Series 433:221-236

Lorrain A, Graham B, Menard F, Popp B, Bouillon S, van Breugel P, Cherel Y (2009) Nitrogen and carbon isotope values of individual amino acids: a tool to study foraging ecology of penguins in the Southern Ocean. Marine Ecology-Progress Series 391:293-306

EVALUATING ANTHROPOGENIC INFLUENCES ON NEW ZEALAND REGIONAL AND URBAN SOILS USING MULTI- ISOTOPES AND ELEMENTS

Dr Karyne Rogers[1], Dr Rose Turnbull[2], Dr Adam Martin[2], Ms Grace Frontin-Rollet[3], Dr Mark Rattenbury[1]
[1]GNS SCIENCE, LOWER HUTT, NEW ZEALAND, [2]GNS SCIENCE, DUNEDIN, NEW ZEALAND, [3]NIWA, WELLINGTON, NEW ZEALAND

Human influences on global landscapes are more frequently being assessed by regional and urban soil surveys. Recently, a geochemical baseline survey of regional Southland and southern Otago soils, along with Dunedin City has been undertaken (Martin et al. 2016, Turnbull et al. 2017).

Stable isotopes and trace elements are increasingly being used in environmental studies as tracers of anthropogenic influences. Soil chemistry is found to be controlled by source rock type (geogenic), soil formation processes (detrital), topography and climate. However, the New Zealand landscape has been significantly altered by humans, especially over the last two centuries. We present results from a multi-isotope and elemental study of pristine, rural and urban landscapes which investigates anthropogenic changes attributed to industrial, agricultural, farming, mining, forestry and urbanisation activities.

Elemental and isotopic (C, N, S) data have been acquired for soils sampled across a variety of land uses (e.g. pristine national park versus urban or intensively farmed pastures), climates (e.g. Fiordland >6000 mm annual rainfall, Middlemarch <500 mm annual rainfall), topography (sea level to >2300 m asl), and soil parent materials (e.g. sandstone, schist, basalt) (Rogers et al. 2017). We demonstrate the effectiveness of chemometrics using statistical integration of the geochemical data (PCA and LDA) to identify human impacts on New Zealand's landscape, and to discriminate between different land uses and the heritage effects of early settlement around Dunedin City compared to newer residential areas and other landuse activities.

References

Martin, A.P.; Turnbull, R.E.; Rattenbury, M.S.; Cohen, D.R.; Hoogewerff, J.; Rogers, K.M.; Baisden, W.T.; Christie, A.B. 2016. The regional geochemical baseline soil survey of southern New Zealand: design and initial interpretation. *Journal of geochemical exploration, 167:* 70-82; doi: 10.1016/j.gexplo.2016.05.009

Rogers, K.M.; Turnbull, R.E.; Martin, A.P.; Baisden, W.T.; Rattenbury, M.S. 2017. Stable isotopes reveal human influences on southern New Zealand soils. *Applied Geochemistry, 82:* 15-24; doi: 10.1016/j.apgeochem.2017.05.006

Turnbull, R.E.; Martin, A.P.; Rattenbury, M.S.; Rogers, K.M.; Strong, D.T.; Morgenstern, R. 2017. Urban Geochemical Atlas of Dunedin City, New Zealand. Lower Hutt (NZ): GNS Science. 187 p. GNS Science report 2017/31. Doi:10.21420/G22P8N

GEOGRAPHICAL TRACEABILITY USING STABLE ISOTOPES AND MULTI-ELEMENT FINGERPRINTS

Dr Karyne Rogers[1]
[1]*GNS SCIENCE, LOWER HUTT, NEW ZEALAND,* [2]*INSTITUTE OF QUALITY AND STANDARDS FOR AGRICULTURAL PRODUCTS, ZHEJIANG ACADEMY OF AGRICULTURAL SCIENCES, HANGZHOU, CHINA*

Food safety is a growing concern particularly in countries where mislabelling and fraud are frequently found in high-value or frequently consumed food products. Stable isotopes are now widely recognised as a scientific tool which is leading the way to combat and detect food fraud, with food forensics becoming well-established globally (Carter & Chesson, 2017). While stable isotopes have been frequently used in the past to determine authentication and origin, more recently a combination of isotopes and elemental abundances are now being used in more sophisticated ways such as multi-variate chemometric analyses which statistically clusters similar origin or authentic products together using much large groups of parameters (10-50 parameters). Chemometrics uses Primary Component Analyses (PCA) and Linear Discriminant Analyses (LDA), and this technique is also capable of machine learning to identify unknown products.

The application of these discrimination techniques are far-reaching beyond food and can be used for environmental, industrial, geological or inorganic products. We will present three case studies to demonstrate the utility and robustness of these techniques when identifying growing methods of organic vegetables (Yuan et al 2016) and organic rice (Yuan et al. 2018) from conventional products, and confirm the geographical origin of high-value green tea (Yuan et al. 2018a).

References

Food Forensics. Stable isotopes as a guide to authenticity and origin. 2017. Editors James Carter and Lesley Chesson. Taylor & Francis Group, ISBN 9781498741729 (hardback).

Yuan, Y.; Hu, G.; Chen, T.; Zhao, M.; Zhang, Y.; Li, Y.; Xu, X.; Shao, S.; Zhu, J.; Wang, Q.; Rogers, K.M. 2016. Improved discrimination of Brassica vegetables treated with agricultural fertilizers using a combined chemometric approach. Journal of Agricultural and Food Chemistry, 64(28): 5633-5643; doi: 10.1021/acs.jafc.6b00453.

Yuan, Y.; Zhang, Y.; Liu, Z.; Yuanzhi, S.; Hu, G.; Zhu, J.; Rogers, K.M. 2017. Determination of the geographical origin of Chinese green tea by chemometrics using stable isotopes and trace elements. Journal of Agriculture and Food Chemistry (Submitted).

Yuwei, Y.; Weixing, Z.; Yongzhi, Z.; Zhi L.; Shengzhi, S.; Li, Z.; Rogers, K.M. 2017. Differentiating Organically Farmed Rice from Conventional and Green Rice in China using Stable Isotopes and Multi-Element Chemometrics. Food Chemistry (Submitted).

Stable isotopes analysis: a neglected tool for placing parasites in food webs

Dr Amandine Sabadel[1], Dr Anthony Stumbo[2], Dr Colin MacLeod[3]
[1]University Of Otago, Dunedin, New Zealand, [2]Otago Museum, Dunedin, New Zealand, [3]University of British Columbia, Vancouver, Canada

Parasites are often overlooked in the construction of food webs, despite their ubiquitous presence in almost every type of ecosystem. Researchers who do recognise their importance often struggle to include parasites using classical food web theory, mainly due to their multiple hosts and life stages. A novel approach using **compound-specific stable isotope analysis** promises to provide considerable insight into the energetic exchanges of parasite and host which may solve some of the issues inherent in incorporating parasites using a classical approach. Understanding the role of parasites within food webs, and tracing the associated biomass transfers, are crucial to constructing new models that will expand our knowledge of food webs.

This talk will focuses on stable isotope studies published in the last decade, and will introduce compound-specific stable isotope analysis as a powerful, but underutilised, newly developed tool that may answer many unresolved questions regarding the role of parasites in food webs.

REFERENCES

Sabadel A.J.M. Stumbo A.D. MacLeod C.D. 2018. Stable isotopes analysis: a neglected tool for placing parasites in food webs. Journal of Helminthology (accepted manuscript).

Characterisation of particulate organic matter cycling during a summer North Atlantic phytoplankton bloom using compound-specific stable isotopes of amino acids

Dr Amandine Sabadel[1], Dr Nicolas Van Oostende[2], Prof Bess Ward[2], Mr E. Malcolm S. Woodward[3], Dr Robert Van Hale[1], Prof Russell Frew[1]
[1]University Of Otago, Dunedin, New Zealand, [2]Princeton University, Princeton, USA, [3]Plymouth Marine Laboratory, Plymouth, UK

Determining the fate of fixed carbon and nitrogen in marine food webs requires a deeper mechanistic understanding of the processes through which organic matter pools originate and the pathways through which they are transformed. We used compound-specific stable isotope analysis of individual amino acids (CSIA-AA) to characterize particulate organic matter (POM) sources and transformations in surface waters of the temperate and subarctic Atlantic Ocean. The robustness of several recently developed AA *in situ* biomarkers and proxies was assessed by comparison with pigment and flow cytometric community analyses. Trophic level (TL ~ 1.5) indicated the presence of higher trophic matter in POM, such as heterotrophic microeukaryotes and multicellular zooplankton. The carbon pattern indicated a switch in biomass nutritional mode, from autotrophic biomass dominating the euphotic zone to POM of mostly heterotrophic origin below the mixed layer. The nitrogen pattern in the euphotic zone could discern between PON of mostly autotrophic eukaryotic origin at one station and a higher fraction of detrital matter at the second station in a more advanced state of bloom decline. The ΣV parameter, proxy for heterotrophic bacterial AA resynthesis, indicated no major resynthesis in the mixed layer with POM mainly composed of live biomass (ΣV ~ 1.3). At 100 m POM exhibited a strong heterotrophic bacterial alteration signature (ΣV = 2.5) indicating active AAs are recycling. The robustness of all these tested proxies will be discussed during the presentation.

REFERENCES

A.J.M. Sabadel, N. Van Oostende, B.B. Ward, E.M. S.Woodward, R. Van Hale and R.D. Frew. *Geochimica et Cosmochimica Acta* (In prep)

Soil and plant water isotope composition across land-use types in the tropics

Dr Luitgard Schwendenmann[1]
[1]*School Of Environment, University Of Auckland, Auckland, New Zealand*

Land-use and plant community composition influence ecosystem water fluxes. In this study, water stable isotopes were used to (1) monitor the variation in the isotopic composition of soil and plant water across land-use types and seasons, (2) to test if different pools of soil water can be identified and (3) to determine plant water sources.

Plant xylem and soil samples (0-10, 10-30, 30-50, 50-70 cm) were collected in Panama (native tree plantation, pasture, subsistence agriculture, secondary forests) and Indonesia (cacao agroforest, native forest). Soil water was obtained by cryogenic vacuum extraction (bulk water) and suction lysimeters/piezometers (mobile water). All samples (n = 1700) were analyzed for δ^2H and δ^{18}O using TC/EA-IRMS.

The δ^2H and δ^{18}O values ranged from -100 to 15 ‰ and from -15 to 2 ‰, respectively. Independent of land-use, the seasonal pattern was most pronounced in bulk and mobile soil water collected from the top 30 cm. More positive plant and soil water δ^2H and δ^{18}O values during drier periods were related to the input of more enriched precipitation and/or evaporation. The isotopic separation between bulk and mobile soil water and xylem water was relatively small and only observed during drier periods at sites characterised by a distinct dry season.

Xylem δ^2H and δ^{18}O values of grass and herbaceous species showed a strong overlap with the isotopic signature of shallow soil water (0-30 cm depth). In contrast, trees obtained most of their water from layers below 30 cm depth and some tree species showed seasonal shifts in water uptake.

In summary, this study revealed that most plant, mobile and bulk soil δ^2H and δ^{18}O values plotted largely on or between the local and global meteoric water line. Thus, this study provides only limited evidence to support the ‘two water world’ hypothesis.

Soil moisture drying-wetting cycle driven by cyclonic events in the arid subtropics

Dr Grzegorz Skrzypek[1], Dr Shwan Dogramaci[2], Dr Pauline Grierson[1]
[1]Ecosystems Research Group and West Australian Biogeochemistry Centre, School of Biological Sciences, The University of Western Australia, Crawley,, Australia, [2]Rio Tinto Iron Ore, Perth, Western Australia, Perth,, Australia

SkrzypekG_etal_AICE2018.docm (could not be inserted) Large but infrequent precipitation events are of critical importance for many types of ecosystems in arid and semi-arid zones of Australia. These ecosystems rely on soil moisture contents overwhelmingly driven by spatial and temporal distributions of large-volume cyclonic precipitation events. In this study, we analyzed the precipitation stable hydrogen and oxygen isotope compositions of soil and multiple rainfall events over the 2010-2017 period, including large cyclones. Large events (>100 mm/day) had very negative but also highly variable spatial and temporal $\delta^{18}O$ values strongly reflecting continental and rainout effects. For example, at a site ~300 km from the coast, rainfall $\delta^{18}O$ decreased from -13.7‰ to -19.3‰ over 5 hrs of a rain event, resulting in floodwater $\delta^{18}O$ of -13.4 to -16.5‰. These signatures are distinct from those of regional groundwater in alluvial aquifers ($\delta^{18}O$ -8.0±0.8‰) and clearly visible in wetting fronts moving downward during infiltration of floodwater through soil horizons. For example, pre-cyclone dry soils at 4 m had $\delta^{18}O$ values of -4.1‰ but four weeks after flooding -16.1‰. Analyzes of $\delta^{18}O$ of soil in multiple cores along transects reviled that soil moisture has been completely replaced by infiltrating floodwater down to 3.5 m as a response to 213 mm of precipitation from a cyclone over 5 days. The soil moisture $\delta^{18}O$ returned to its pre-cyclone value after 21 months reaching -5.00‰ in upper 2 m. Our study reveals considerable spatial and temporal complexity in determining the fate of rainwater in arid environments, and thus its significance for different soil levels and types.

POSTER

Where is the missing CO2? A novel multi-species approach to trace the fate of atmospheric CO2.

Peter Sperlich[1], Sara Mikaloff Fletcher[1], Gordon Brailsford[1], Rowena Moss[1], Jocelyn Turnbull[2], Liz Keller[2], Steve Montzka[3], Mao-Chang Liang[4]

[1]Niwa, Wellington, New Zealand, [2]GNS, Lower Hutt, New Zealand, [3]NOAA, Boulder, USA, [4]Academica Sinica, Taipei, Taiwan

A robust understanding of CO_2 fluxes is vital for accurate estimates of future atmospheric carbon dioxide (CO_2) levels. However, current estimating techniques show large disagreement on terrestrial CO_2 fluxes. In particular, the net CO_2 sink in Fiordland, one of New Zealand's largest indigenous forests, has recently been suggested to be larger than previously thought. We have been awarded a Marsden Fast-Start grant to test the hypothesis that Fiordland's forest is more productive than previously thought.

We plan to make atmospheric measurements before and after the air has passed over Fiordland's forests. The measured differences will enable the quantification of biogeochemical trace-gas exchange (Figure 1). We will use an innovative ensemble of multi-tracer carbon cycle observations. While measurements of CO_2 mole fractions indicate CO_2 level changes directly, measurements of $\delta^{13}C\text{-}CO_2$ distinguish terrestrial net CO_2 uptake, due to the characteristic isotope fractionation during photosynthesis. On the other hand, $\delta^{18}O\text{-}CO_2$, which is controlled by the exchange of oxygen with leaf water, will provide information on photosynthetic CO_2 uptake. We will measure $\Delta^{14}C\text{-}CO_2$ as a tracer for fossil CO_2 as well as ecosystem respiration. Additional measurements of COS will provide an independent tracer for photosynthetic CO_2 uptake. Furthermore, we will test $\Delta^{17}O\text{-}CO_2$ and clumped isotopes in CO_2 as novel tracers to further constrain regional CO_2 fluxes. Our measurement results will be interpreted using state-of-the-art bottom-up and top-down models.

This study will help to better understand regional CO_2 fluxes on process levels, with the overall goal to reduce the uncertainty in New Zealand's greenhouse gas emissions that are reported to the United Nations Framework Convention on Climate Change.

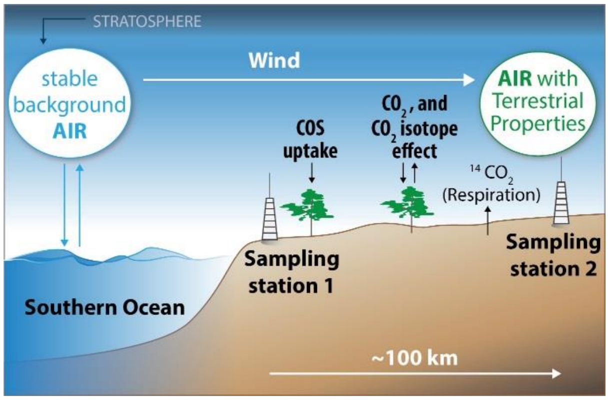

Figure 1. Schematic of observation strategy and selected tracers.

POSTER

Developing a measurement technique for nitrous oxide isotopomers in air

Peter Sperlich[1], Mike Harvey[1], Ross Martin[1], John McGregor[1], Zoe Buxton[1]
[1]Niwa, Wellington, New Zealand

Nitrous oxide (N_2O) is a long-lived greenhouse gas that has been accumulating in the atmosphere due to increased usage of N fertilisers in agricultural production. The main removal mechanism is chemical destruction in the stratosphere. The global budget is relatively well known but processes that control individual source contributions and the relative importance of several microbial pathways that lead to N_2O emission from soils and the oceans are poorly understood.

N_2O isotopomers provide a method to improve knowledge of N_2O formation processes. The 4 most abundant isotopic variants are $^{14}N^{14}N^{16}O$, $^{14}N^{14}N^{18}O$, $^{14}N^{15}N^{16}O(\alpha)$ and $^{15}N^{14}N^{16}O(\beta)$. The site preference variable ($SP = \delta^{15}N\alpha - \delta^{15}N\beta$) is thought to be independent of the substrate isotopic composition and depends only on the reaction(s) forming and destroying N_2O. Therefore, SP provides a possible tool to differentiate between nitrification and denitrification production pathways.

A new generation of quantum cascade laser spectrometers has potential to make rapid measurement of isotopomer variants. We show our preliminary experiments using a Los Gatos Research analyser, coupled to a custom-made instrument for N_2O pre-concentration. Pre-concentration of N_2O increases the signal-to-noise ratio, which is needed to resolve variations of N_2O-isotopomers in air. It is intended to use the new technique in soil chamber and emission experiments to provide new insights into N_2O formation processes.

Uncertainties of tritium streamflow ages

Dr Michael Stewart[1], Mr Mike Toews[2], Mr Rob van der Raaij[2], Dr Uwe Morgenstern[2], Dr Maksym Gusyev[3]
[1]Aquifer Dynamics & GNS Science, Lower Hutt, New Zealand, [2]GNS Science, Lower Hutt, New Zealand, [3]ICHARM, Tsukuba, Japan

Tritium-based age uncertainties due to measurement errors and model parameter choices were investigated using Monte Carlo sampling in a generalised likelihood uncertainty estimation (GLUE) framework (Gallart et al., 2016) for a variety of lumped parameter models. The models were the exponential piston flow (EPM), dispersion (DM) and gamma (GM) models. These single models are appropriate for homogeneous catchments. We also looked at double versions of these models, which allow for extreme heterogeneity (i.e. two distinctive parts) in a catchment, to check for spatial aggregation effects on tritium ages (Stewart et al., 2017)

The ranges of the parameters examined were limited to those that can occur in nature. This required eliminating L-shaped transit time distributions (i.e. those with dispersion parameters greater than 0.8 for the DM, and alpha less than 1.0 for the GM; Bardsley, 2017). These ranges enable consistent MTTs to be obtained with the different models.

The method was applied to data from the Waikoropupu Main Spring using a program written in R. Age uncertainties expressed as standard deviations about the mean or 5/95 % spreads were derived. Differences in mean ages obtained from the single and double models indicated aggregation effects because two types of water feed the spring.

REFERENCES

Bardsley E. 2017. Transit time distributions are not L-shaped. Hydrology and Earth System Sciences Discussions, https://doi.org/10.5194/hess-2017-497.

Gallart F. Roig-Planasdemunt M. Stewart M.K. Llorens P. Morgenstern U. Stichler W. Pfister P. Latron J. 2016. A GLUE-based uncertainty assessment framework for tritium-inferred transit time estimations under baseflow conditions. Hydrological Processes 30: 4741-4760.

Stewart M.K. Morgenstern U. Gusyev M.A. Maloszewski, P. 2017. Aggregation effects on tritium-based mean transit times and young water fractions in spatially heterogeneous catchments and groundwater systems. Hydrology and Earth System Sciences 21, 4615-4627.

A Multi-Tracer Study in a Complex Aquifer System: Surat Basin, Queensland

Dr Axel Suckow[1], Dr Matthias Raiber[2], Dr Alec Deslandes[1], Andrew Taylor[1], Dr Karina Meredith[3]
[1]CSIRO, Urrbrae, Australia, [2]CSIRO, Dutton Park, Australia, [3]ANSTO, Lucas Heights, Australia

Within the framework of GISERA (Gas Industry Social and Environmental Research Alliance) we performed several field campaigns to study a complex multi-aquifer system in the Surat Basin, Queensland. We used multiple environmental tracers (water chemistry, ^{18}O, ^{2}H, ^{3}H, ^{13}C, ^{14}C, ^{36}Cl, $^{87}Sr/^{86}Sr$, stable noble gases and ^{85}Kr, ^{39}Ar, ^{81}Kr) to assess recharge rates and flow velocities in the Hutton and Precipice Sandstone aquifers.

Face value groundwater ages for ^{14}C were contradicted by those for ^{36}Cl by a factor of ten in the Hutton Sandstone. It was possible to resolve this discrepancy by describing the aquifer as a large-scale “dual porosity” system with only <30% of its thickness conducting effective groundwater flow and the remainder being stagnant. This model allowed for the first time to quantify the effective deep recharge rate for this aquifer.

The groundwater flow of the Precipice sandstone aquifer has not previously been assessed by tracer measurements and exhibits high hydraulic conductivities, our tracers demonstrate high groundwater velocities and is regarded as the future fresh water source for the cattle industry in the region.

Our stable noble gas measurements show vertical upward groundwater movement along faults. This is demonstrated by local occurrences of water exhibiting high helium concentrations that can be described as small admixtures of old and deep groundwater ascending along the fault.

Introducing ArDB: The Cutting-Edge Analytical Results Database and Data Visualisation Software from Elementar

Dr Kyle W. R. Taylor[1], Mr Michael Sudnik[1], Mr Michael Seed[1]
[1]*Elementar UK Ltd, Stockport, United Kingdom*

ArDB stands for Analytical Results Database and is a completely new software product for the stable isotope community and beyond. ArDB has been created to extend the envelope of data analysis beyond simply data processing. Perhaps more so than any other analytical technique, stable isotope ratio mass spectrometry is about comparison. Comparisons of one stable isotope to another; comparisons of a sample to a standard, and comparison of unknown samples to known samples within a database. Until now, IRMS manufacturers have concentrated solely on software to generate results. With ArDB, we provide powerful new results management and analytical tools.

For any environmental sample, there will be many associated parameters which place the analytical results into context. For example: latitude/longitude, depth, proximity to potential source of pollution, season, storage conditions, etc. These parameters are what are commonly known as "metadata", and ArDB allows your analytical results to be evaluated in the context of these metadata. ArDB makes it possible to recognize patterns in data, evaluate similarities between unknown and known samples, and visualize data on maps and charts (i.e. ArDB may be used as a Geographical Information System, GIS). With this metadata-handling functionality, ArDB can be used to plan, coordinate and manage your sampling strategies and maintain quality through to the final data analysis. ArDB also incorporates the capability to apply common statistical methods to datasets, such as Principle Component Analysis (PCA) and Linear Discriminant Analysis (LDA), as well as supporting integration with the statistical software package R.

As a database is constructed, it becomes possible to compare unknown samples with known samples within the database and evaluate statistical similarities or difference, which in turn can be used to inform likely sources of an analytical signal and potential trace that signal to likely sources, in environmental and forensic contexts.

POSTER

Geolocation of Cotton Using Stable Isotope Profiling

Miss Melenaite Tohi[1], Professor Russell Frew[1], Dr Robert Van Hale[1], Dr Kiri McComb[1]
[1]*University Of Otago: Chemistry Department, North Dunedin, Dunedin 9016, New Zealand*

The unique characteristics of raw cotton cannot be replicated by other fibers. Its ability to extent into a tubular fibre which can then be spun into a yarn highlights its importance in manufacturing industries of yarns and textiles (Khadi et al., 2010). Every production year the demand for high quality cotton rises and so does the profit for manufacturing companies. However, success for businesses in countries like Egypt, China and the USA depends upon the quality of the cotton accompanied by the correct label of its origin. To avoid losses due to documentations for cotton commodity being falsified (Schenk., 2012), establishing a means for independent determination of cotton origin becomes crucial. The use of isotope ratio mass spectrometry (IRMS) as a tool for raw cotton fibre stable isotope analysis to investigate the provenance of un-dyed spun cotton fibre have only been reported as a proof-of-concept study (Daéid et al., 2011). This work strives to contribute to the field by using a larger number of unprocessed cotton samples of known origin to examine the extent of the following hypothesis: Do the isotope ratios H and O from cotton provide a fingerprint for determining the geographic origins of the cotton.

Measurements of H and O isotope composition were obtained of 145 raw cotton samples from known countries of origin and investigated for discriminatory information that could be used to determine origin. This yielded isotope ratio values specific to the origin of the raw cotton, its purity, the manufacturing processes involved with its production and more (Bowen., 2010 & Lennard., 2012). The isotopic ratio values deduced for the raw cotton samples were found to be consistent with their known country of origin.

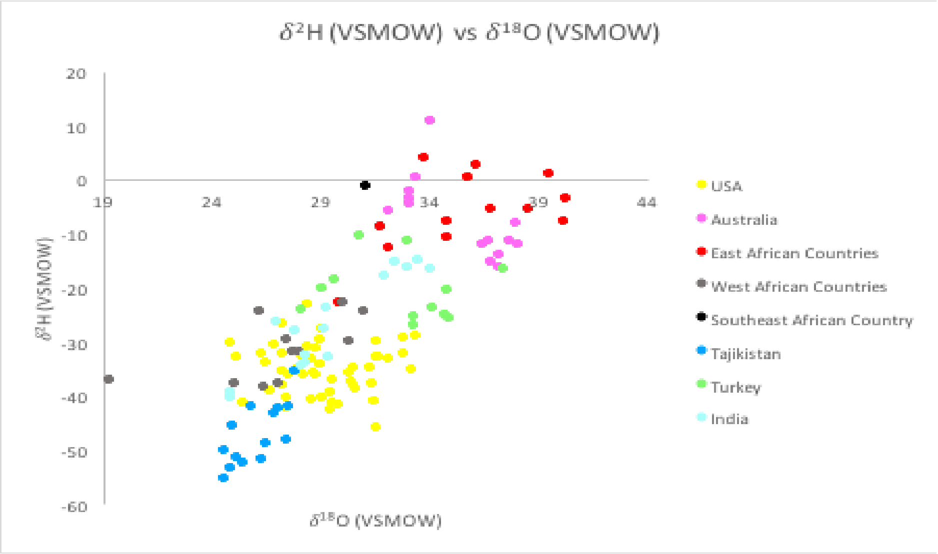

Figure 1. The overall results from the adjustment process of all the raw cotton sample data used for this project.

REFERENCES

Bowen G.J. 2010. Spatial Pattern in Isotopic Biochemistry. Annual Review. Earth Planet Science 38: 161-187.

Daéid N.N. Meier-Augenstein W. Kemp H.F. 2011. Investigating the provenance of un-dyed spun cotton fibre using multi-isotope profiles and chemometric analysis. Rapid Communications in Mass Spectrom 25: 1812-1816.

Khadi B.M. Santhy V. Yadav M.S. 2010. Cotton: an introduction. In cotton. Biotechnology in Agriculture and Forestry book series 65: 1-14.

Lennard C. 2012. Review of Stable forensics: an introduction to the forensics application of stable isotope analysis. Australian Journal of Forensic Sciences 316-317.

Schenk E.R. 2012. Geographical Provenancing of Unprocessed Cotton Using Elemental Analysis and Stable Isotope Ratios. Florida International University Electronic Thesis and Dissertation Paper 803: 1-288.

Spatial and temporal variation of residence time of spring and groundwater in multiple watersheds, Japan and New Zealand

Dr Maki Tsujimura[1], Mr Koichi Sakakibara[1], Mr Yuki Imaizumi[1], Dr Maksym Gusyev[2], Dr Uwe Morgenstern[3], Dr Michael Stewart[3]

[1]University of Tsukuba, Tsukuba, Japan, [2]ICHARM, Tsukuba, Japan, [3]GNS Science, Lower Hutt, New Zealand

We performed an investigation on spatial distribution of spring water age using SF_6, CFCs, and microbe in the spring water, and an evaluation of groundwater storage volume based on water budget analysis in multiple watersheds underlain by different lithology in Japan and New Zealand. Also, we investigated a temporal variation of spring water age in a small forested headwater catchment underlain by granite, Fukushima, Japan.

The spring water age ranges from less than one year to more than 20 years, and the storage volume of the groundwater ranges from 10^3 m^3 to 10^6 m^3 in volume in the headwaters in Japan. The age of the spring water varies from less than one year to more than 10 years, and it tends to show high values specifically during the rainstorm events. We are also going to present a preliminary result on comparison of the spring water age between Japan and New Zealand.

Application of hydrochemical and isotopic methods to assess water source and contaminant pathways in the Waiokura catchment, Taranaki, New Zealand

Mr Rob van der Raaij[1], Ms Heather Martindale[1], Mr Regan Phipps[2]

[1]*GNS Science, Lower Hutt, New Zealand,* [2]*Taranaki Regional Council, Stratford, New Zealand*

This study aimed to contribute towards an understanding of nutrient loads from groundwater reaching the spring-fed Waiokura Stream, and to help resolve flow paths and origin of water and contaminants, using a suite of hydrochemical and isotopic tracers (stable isotopes ($\delta^{18}O$ and $\delta^{2}H$ of water, $\delta^{15}N$ and $\delta^{18}O$ of NO_3), hydrochemistry (Cl, Br, Na, Ca, Mg, K, Alkalinity, DOC, SO_4, N, P, and SiO_2), radon and age tracer data (tritium, CFCs, SF_6)).

Differences in stable isotopes of water between groundwater and stream water reflect the influence of local versus higher altitude inputs and/or seasonal effects. One well with different isotopic and chemical composition than other groundwater samples appears to have a separate recharge source. $\delta^{15}N$ and $\delta^{18}O$ measurements in dissolved nitrate sit above the denitrification line typical of New Zealand samples from pasture and forest sites suggesting breakthrough of urea/urine or fertiliser N.

The mean residence time (MRT) of groundwater, from wells 5 to 14 m deep, ranged between 1 and 49 years, with most having MRTs of 1 to 2 years. One well had a mix of very young groundwater with much older water, suggesting a highly stratified aquifer system. Waiokura Stream samples had MRT between 6 and 14 years, implying inflows of older groundwater than observed at most wells.

Chemistry data for the Waiokura Stream and nearby groundwater showed relationships indicating the influence of groundwater age and water-rock interaction as well as land-surface inputs. Time series chemistry data for the Waiokura Stream display seasonal variations related to either seasonal changes in uptake of nutrients by instream biota or changes in composition of inflowing groundwater due to changes in groundwater MRT. Nitrate concentrations in one well vary considerably. The groundwater at this well appears to alternate over time between younger, oxic water with high nitrate, and older anoxic water with low nitrate.

Stable Isotope Analysis in Aquatic Ecosystems

Mrs Jennifer van Holst[1], Dr. Debashish Mazumder[1], Mrs. Barbora Gallagher[1]
[1]*ANSTO, Lucas Heights, Australia*

Aquatic ecosystems, both marine and freshwater, are essential to the economy and health of the population. These ecosystems serve a number of important ecosystem services including natural filtration, pollution reduction, flood mitigation as well as groundwater recharge and carbon sequestration. Aquatic habitats act as nurseries for many species of commercially valuable fish.

Stable isotope analysis (SIA) has proved instrumental in assessing the health of these ecosystems and the subsequent food webs within. Carbon and nitrogen SIA is used to determine energy and nutrient flow across all trophic levels. Nutrient flow changes can help researchers determine limiting factors within a specific ecosystem, thus being able to suggest improvements that will increase biome health.

ANSTO is collaborating with universities, management agencies and industries to ensure that there is the most efficient use of facilities to understand ecosystem functionality. Here we report how SIA helps aquatic ecosystems management decisions. These studies include; freshwater wetlands at Murray-Darling basin, looking at changes in trophic connectivity between species of fish during variable water conditions (Mazumder et al., 2011; Mazumder et al., 2012 Mazumder et al., 2017), the effects of man-made barriers on aquatic food webs (Mazumder et al., 2016), nutrient assimilation of bivalves to streamline oyster aquaculture production (Liu et al., 2016) and tracking the movement of nitrogen pollutants in an aquatic food chain through a major urban river.

REFERENCES

Liu A. Mazumder D. Dove M. Sheng Lai T. Crawford J. Sammut J. 2016 Stable Isotope Analysis of the Contribution of Microalgal Diets to the Growth and Survival of Pacific Oyster Crassostrea gigas (Thunberg, 1979) Larvae. Journal of Shellfish Research, 35: 63-69.

Mazumder D. Saintilan N. Wen L. Kobayashi T. Rodgers K. 2017 Productivity influences trophic structure in a temporally forced aquatic ecosystem. Freshwater Biology, 62: 1528-1538.

Mazumder D. Williams R. Wen L. Saintilan N. Walsh C. 2016 Impoundment constraint of fish niche diversityin a temperate Australian river 2016 Hydrobiologia 771: 195–206.

Mazumder D. Johansen M. Saintilan N. Iles I. Kobayashi T. Knowles L. Wen L. 2012 Trophic Shifts Involving Native and Exotic Fish During Hydrologic Recession in Floodplain Wetlands. Wetlands 32: 267–275

Mazumder D. Saintilan N. Williams R. Szymczak R. 2011 Trophic importance of a temperate intertidal wetland to resident and itinerant taxa: evidence from multiple stable isotope analyses. Marine and Freshwater Research 62: 11–19

Problems of authenticating processed food and beverages - an investigation into changes occuring during coffee roasting.

Professor Stewart Walker[1], Mr Peter Tran[1]

[1] *Flinders University, Adelaide, Australia, Adelaide, Australia*

There is a growing interest in authenticating food and beverage for a number of reasons including:- security of food supplies, preservation of agricultural industry, economic protection from cheap/inferior imports, prevention of spread of disease (quarantine and exclusion zones), ensuring consumers get what they pay for and preventing criminals from benefitting from food or beverage forgery. To this end many researchers have investigated the ability of authenticating origin of a material by comparison of the stable isotopes and trace metals of questioned material to examples of material known to come from a particular source. However, if a product is processed this can change the composition of the product and, therefore, make it impossible to compare processed with raw material. As part of ongoing research, this project has considered the effect of roasting of raw coffee beans.

Using a temperature programmed 'roaster' for reproducibility a range of raw/green coffee beans from different growing regions were roasted to 'light', 'medium' and 'dark' roast. Analysis of trace metals by ICPMS of microwave acid digested beans and ^{13}C:^{12}C and ^{15}N:^{14}N ratios by IRMS indicated that there were some elements that were 'conserved' and these could be used as indicators of changes during the processing, some increased (relative to total weight of the bean) and some decreased indicating that they were being lost during the process.

Development of online microdialysis-mass spectrometry to determine turnover of organic compounds in soil

Dr Charles Warren[1]

[1]*University Of Sydney, Camperdown, Australia*

The metabolism of low molecular weight organic compounds by soil microbes is the rate-limiting step in many terrestrial biogeochemical cycles. Existing methods for determining the turnover of low molecular weight organic compounds (e.g. amino acids) suffer drawbacks. The most common method is to add ^{13}C or ^{14}C-labelled substrate to soil and quantify evolved $^{13}CO_2$ or $^{14}CO_2$ (i.e. mineralisation). However, mineralisation is a misleading indicator of turnover of organic compounds because CO_2 evolution reflects metabolic cycling after uptake. A better indicator might be how rapidly added compounds are removed from soil solution, yet we currently don't have methods capable of measuring soil solution concentrations at high temporal resolution.

Microdialysis could be one means of probing soil solution concentrations at high temporal resolution. Microdialysis is intrinsically suited to continuous sampling, yet most commonly dialysates are collected over a period of 20-30 minutes and the discrete samples are subsequently analysed offline. Microdialysis with offline analysis may be too slow to track the fate of small organic compounds added to soil, and even a small experiment may generate too many samples for subsequent offline analysis to be practicable. Hence, the aim of this study was to develop an online microdialysis-mass spectrometry system that would permit the continuous measurements of soil solution concentrations of isotope labelled compounds.

The online microdialysis-mass spectrometry system involved dialysate from a microdialysis probe merging with a stream of desolvation/internal standard solution (75% methanol, 0.2% formic acid, U-$^{13}C^{15}N$-Gly) before entering the ESI source of the mass spectrometer wherein compounds were identified and quantified by MS^2. Detection limits for amino acids were 0.1-1 µM, and detection was linear over three orders of magnitude. Measurements on soil showed that the system can reliably measure the rapid appearance and disappearance of labelled amino acids added to soil (Fig 1).

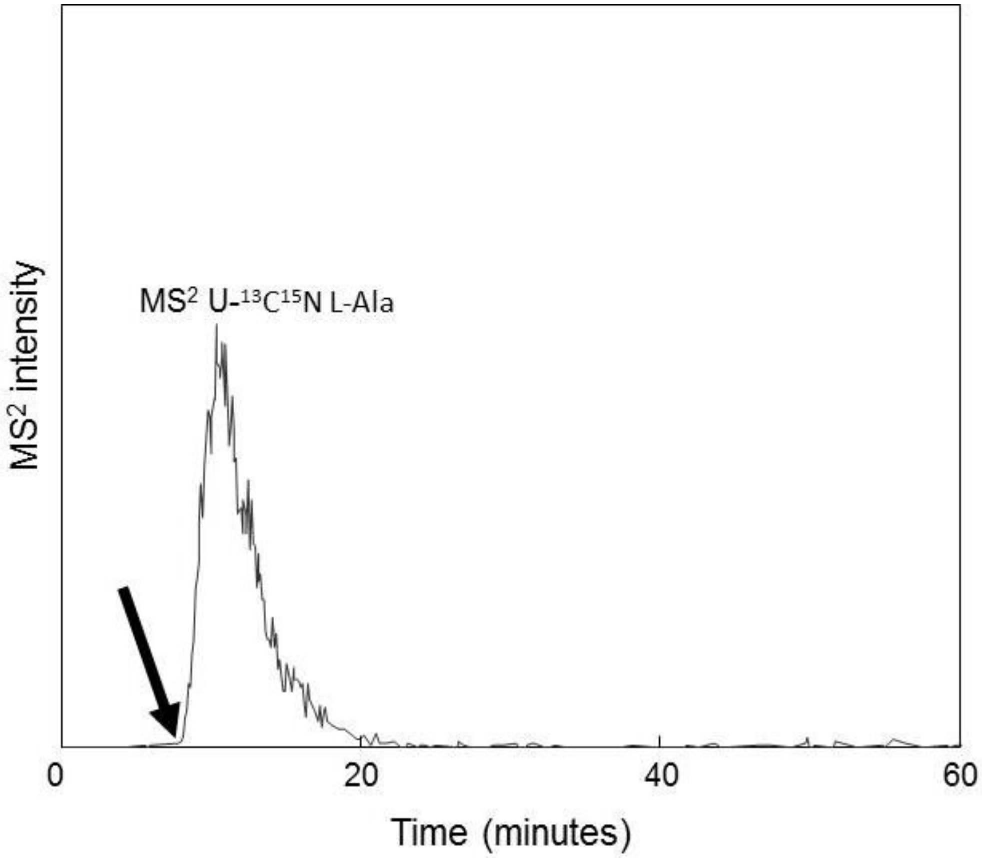

Fig 1. Extremely rapid loss of L-alanine added to soil, as measured by online microdialysis-mass spectrometry. 4.0 mL of 100 µmol L^{-1} U-^{13}C,^{15}N-L-Ala was added at the time indicated by the arrow.

A multi-(nitrogen) species approach to measuring aquatic ecosystem function

Dr Naomi Wells[1], Prof. Bradley Eyre[1]

[1] *Southern Cross University, Lismore, Australia*

Nitrate stable isotopes ($\delta^{15}N$-NO_3^-, $\delta^{18}O$-NO_3^-) have emerged as a powerful tool for evaluating the sources and fate of reactive N in aquatic environments. However, this approach is inherently limited in sub-tropical and tropical waterways, where organic forms dominate the N pool and NO_3^- concentrations are often negligible. To overcome this limitation we developed a multi-species $\delta^{15}N$ mass balance approach that allowed us to assess the degree of whole-system N 'recycling' (assimilation, mineralisation) and removal (denitrification, anaerobic ammonium oxidation) (Fig. 1). We used this model to evaluate N turnover in 'pristine', moderately impacted, and degraded sub-tropical Australian estuaries under wet and dry season conditions. The measured shift in the difference between the $\delta^{15}N$ of the inorganic (nitrate + ammonium + nitrous oxide) v. organic (particulate + dissolved organic N) pools from +20 ± 8 ‰ (degraded) to 0 ± 2 ‰ (pristine) indicates that net assimilatory N cycling decreases with ecosystem degradation. At the same time the degraded estuary also had negligible dissimilatory N removal, as determined from the magnitude of offset between measured and 'expected' (marine-freshwater mixing) inorganic pool $\delta^{15}N$ values. Dissimilatory N removal instead peaked in the moderately impacted estuary (offsets of 50‰ - 100‰ integrated over estuary length). The isotopic model developed here to evaluate changes in N sources and processes provided revealed how increasing degradation can switch estuaries from 'reactors' assimilating terrestrial N to 'pipes' transporting reactive N directly to the coast. This finding reveals the importance of considering both organic and inorganic N forms in isotope-based, as well as conventional, N monitoring efforts.

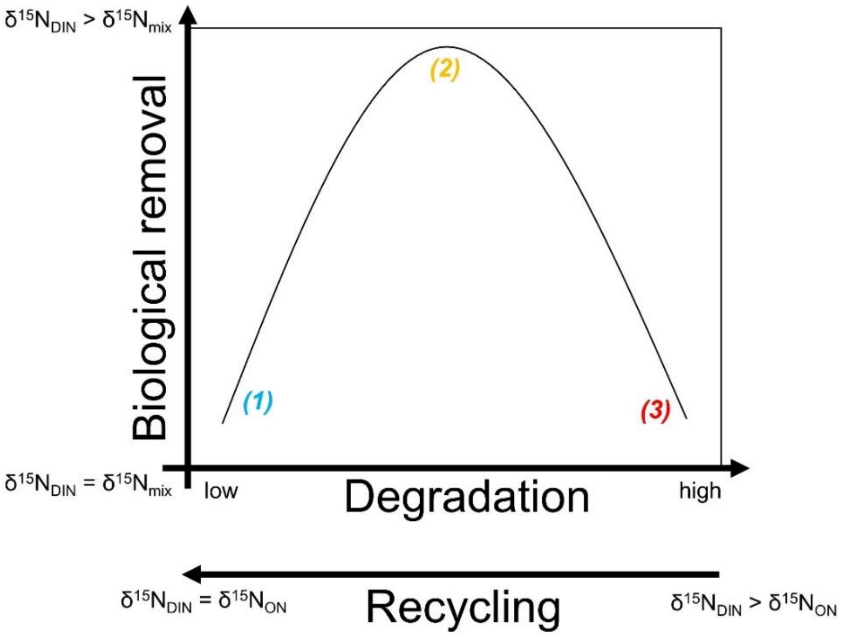

Figure 1. A conceptual model demonstrating the relationship between ecosystem degradation, N recycling (difference between δ^{15}N-DIN and δ^{15}N-ON), and net biological N removal (difference between δ^{15}N-DIN and the δ^{15}N composition predicted based purely on source mixing, δ^{15}Nmix). Increased degradation shifted estuaries from systems, (1) dominated by an ON pool tightly coupled to a small DIN pool, to, (2), dominated by dissimilatory inorganic N cycling that drives net estuary N removal, to, (3) dominated by downstream transport and with minimal biological recycling or removal.

POSTER

Quality control materials for H(deuterium) isotopic measurements

Mr Kavindra Wijenayake[1], Prof Russell Frew[1]

[1]*University Of Otago, New Zealand, Otago, New Zealand*

Measuring hydrogen isotope ratios of natural products have been important in fields such as forensics, food authentication and ecology. Quantifying hydrogen isotope ratios on organic materials has been controversial. Difficulties arises from the presence of acidic hydrogen within organic matter that can exchange with hydrogen from ambient water (Augenstein et al., 2011). Furthermore, complete exclusion of adhering water is much more difficult with a finely ground organic powder than for a polymer (eg: IAEA-CH7). To obtain consistent data a strict, tedious sample treatment protocol involving equilibration of samples with waters of known isotopic composition must be adhered to. However, when making a measurement on samples with the same matrix the Principle of Identical Treatment (PIT) can be applied as long as suitable QC materials are available (Carter and Fry, 2013). Provided the QC materials and samples having same matrices and have been subjected to same recent history (e.g. 10-day equilibration on the bench, 5 days drying in vacuum oven) a normalization based on expected values of the QC samples may be applied.

Here we report on efforts to determine non-exchangeable hydrogen isotope ratios of several widely available materials that could be used for normalization of hydrogen isotope data. Several IAEA standards were equilibrated with three types of waters (ICE = -260.3, SEA = -1.66, Enriched = +535 ‰) for 10 days then vacuum dried for 5 days. The fraction of hydrogen that exchanged and isotopic ratio of the non-exchangeable hydrogen were calculated for each material. Milk powder (IAEA 153) had the highest portion of exchangeable hydrogen (0.067) while Italian Rice Std had the poorest reproducibility in isotopic measurement (S.D. = ± 4.35 ‰). IAEA 372 (Grass) had much lower exchangeable hydrogen (0.012) and a better reproducibility in hydrogen isotope measurement was represented by Cotton wool In-house Std (± 1.38 ‰). Further experiments are proposed to distinguish exchangeable hydrogen from residual water not removed by the drying process.

Keywords- Hydrogen; Isotopes; Fractionation; Mass spectrometry; Exchangeable

References

Carter, J.F. and Fry, B., 2013. Ensuring the reliability of stable isotope ratio data—beyond the principle of identical treatment. *Analytical and bioanalytical chemistry*, *405*(9), pp.2799-2814.

Meier-Augenstein, W., Chartrand, M.M., Kemp, H.F. and St-Jean, G., 2011. An inter-laboratory comparative study into sample preparation for both reproducible and repeatable forensic 2H isotope analysis of human hair by continuous flow isotope ratio mass spectrometry. *Rapid Communications in Mass Spectrometry*, *25*(21), pp.3331-3338.

Qi, H. and Coplen, T.B., 2011. Investigation of preparation techniques for δ2H analysis of keratin materials and a proposed analytical protocol. *Rapid Communications in Mass Spectrometry*, *25*(15), pp.2209-2222.

Schimmelmann, A., 1991. Determination of the concentration and stable isotopic composition of nonexchangeable hydrogen in organic matter. *Analytical Chemistry*, *63*(21), pp.2456-2459.

Soto, D.X., Koehler, G., Wassenaar, L.I. and Hobson, K.A., 2017. Re-evaluation of the hydrogen stable isotopic composition of keratin calibration standards for wildlife and forensic science applications. *Rapid Communications in Mass Spectrometry*.

Authentication of organically farmed food using stable isotopic and multi-element features with chemometrics – Keeping food safe

Professor Yuwei Yuan[1,2], Dr. Zhi Liu[1,2], Mrs Karyne Rogers[3]

[1]Institute of Quality and Standard for Agro-products,Zhejiang Academy of Agricultural Sciences, Hangzhou, China, [2]Key laboratory of Information Traceability for Agricultural Products, Ministry of Agriculture, Hangzhou, China, [3]GNS Science, National Isotope Centre, Lower Hutt, New Zealand

Organically farmed agro-products are well-recognized health food and often deliberately faked by non-organic products with less safety for higher price, which seriously disrupts commercial trust and destroys consumption confidence. Many researches have reported that stable isotope features (e.g. $\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$ and $\delta^{18}O$) can be as important indexes for the authentication of organic and non-organic agro-products (Yuan, et al., 2014; Yuan, et al., 2012). Besides, trace element concentrations can be also used for the classification (Yuan, et al., 2016). However, traditional comparison methods based on just a single or two variable(s) often cannot clearly discriminate, in which overlaps frequently occur. In this context, chemometric data-processing strategies based on multi-variable analysis, such as principal component analysis (PCA), linear discriminant analysis (LDA) and partial least square-discriminant analysis (PLS-DA), are applied for comprehensively extracting feature information of all variables (stable isotopes and trace elements), building models for significantly improving the discriminant accuracy of organic ago-products. This novel strategy that combines stable isotopic and multi-element features with chemometric approaches can be promising as an available tool to authenticate organic ago-products, enhance government regulation and protect the rights and interests of enterprises and consumers.

References

Yuan, Y., Hu, G., Chen, T., Zhao, M., Zhang, Y., Li, Y., Xu, X., Shao, S., Zhu, J., & Wang, Q. (2016). Improved Discrimination for Brassica Vegetables Treated with Agricultural Fertilizers Using a Combined Chemometric Approach. Journal of Agricultural & Food Chemistry, 64(28), 5633-5643.

Yuan, Y., Hu, G., Zhao, M., Chen, T., Zhang, Y., Zhu, J., & Wang, Q. (2014). Variations in the natural ^{15}N abundance of Brassica chinensis grown in uncultivated soil affected by different nitrogen fertilizers. Journal of Agricultural & Food Chemistry, 62(47), 11386-11392.

Yuan, Y., Zhao, M., Zhang, Z., Chen, T., Yang, G., & Wang, Q. (2012). Effect of different fertilizers on nitrogen isotope composition and nitrate content of Brassica campestris. Journal of Agricultural & Food Chemistry, 60(6), 1456-1460.

Development of a surface water isotope information for New Zealand

Dr Bruce Dudley[1], **Dr Christian Zammit[1]**
[1]NIWA, Riccarton, New Zealand

The stable isotope values of oxygen and hydrogen in river and stream water store information on catchment water sources and evaporative fluxes. Hence, a national map of surface water isotope values is a potentially powerful tool in the development of a national hydrological model. We present methods and available data for a GIS-based model of long-term annual average surface water isotope ratios in New Zealand. We will use gridded precipitation isotope maps developed by GNS, as well as NIWA Virtual Climate Station Network precipitation and evapotranspiration data as model inputs. This method will allow us to incorporate monthly variation in precipitation evapotranspiration (P-E) differences into calculations of isotope values of catchment surface water flows.

Start new paragraphs indented like thisFor validation, we will use river water samples from the NIWA National Water Quality Monitoring Network as well as regional water isotope sampling carried out under the National Hydrological Programme in collaboration with Regional Council partners.

Stable isotopes indicate potential ecosystem bottom-up effects on the population decline of a rare albatross

Dr Jingjing Zhang[1], Dr. Jim Roberts[1], Dr. Brittany Graham[1], Dr. Sarah Bury[1], Ms. Julie Brown[1], Dr. David Thompson[1], Dr. Kath Walker[2], Dr. Graeme Elliott[2], Dr Ian Tuck[1]

[1]National Institute of Water and Atmospheric Research, Wellington, New Zealand, [2]Department of Conservation, Wellington, New Zealand

Increasingly it is being recognised that dynamic bottom-up processes affect populations of marine apex predators. Long-term population studies have identified a ongoing decline in the main breeding population of Antipodean albatross (*Diomedea antipodensis*) on the Antipodes Islands in the New Zealand Sub-Antarctic, since the mid-2000s (Elliott & Walker, 2017). Demographic assessment shown that this was partly driven by an adverse shift in the age at first breeding, breeding rate and breeding success—consistent with a protracted period of nutritional stress, although there has been no assessment of their diet and/or trophic environment across this time (Edwards et al., 2017).

In this study, we use stable isotope analysis of blood carbon ($^{13}C/^{12}C$, or $\delta^{13}C$) and nitrogen ($^{15}N/^{14}N$, or $\delta^{15}N$) to investigate the possible changes in diet of this species following population decline. The blood samples analysed were collected from adult birds on Antipodean Island before (1998) and at the onset (2005) of the population started declining.

Analysis showed that $\delta^{13}C$ values of blood were lower in Antipodean albatrosses in 2005, compared to 1998. Lower carbon isotope values can indicate changes in plankton communities at the base of the foodweb, which could contribute to a population decline. However, reduced $\delta^{13}C$ could also indicate foraging in more southern latitudes, so this difference could also be explained by changes in foraging distribution. There was no evidence for any associated shift in trophic level, given the similarity of $\delta^{15}N$ signatures comparing 1998 and 2005 samples. Females have higher $\delta^{13}C$ and $\delta^{15}N$ values than males, which is consistent with sex-differences in foraging distribution and demographic rates during the study period. This study demonstrates the power of isotopic analyses to examine temporal trends in the trophic environment and further highlights the potential role of bottom-up processes in mediating populations of Antipodean albatross and other marine apex predators.

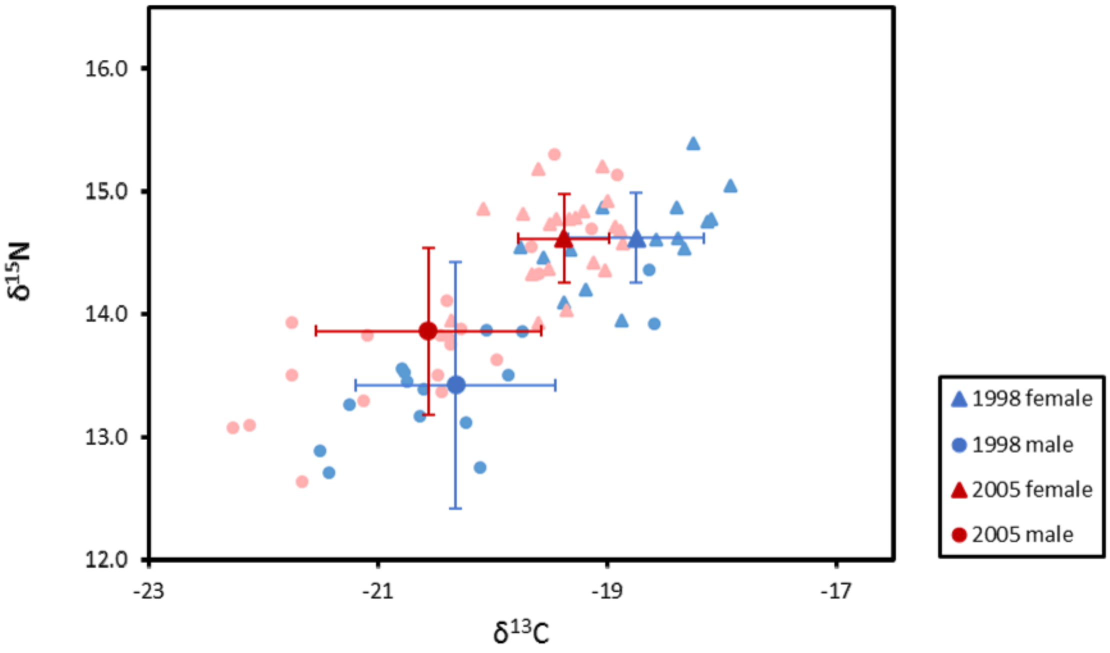

Figure 1. Biplots depicting the overall annual δ13C and δ15N isotope ratios of Antipodean albatross in years 1998 (blue) and 2005 (red). The mean sample results of males and females are represented by circles and triangles with standard deviations as error bar. The light shaded circles and triangles are results of individual birds.

REFERENCES

Edwards, C. T. T., Roberts, J. O., Walker, K., & Elliott, G. (2017). Quantitative modelling of Antipodean wandering albatross. *New Zealand Aquatic Environment and Biodiversity Report No. 180*.

Elliott, G., & Walker, K. (2017). Antipodean wandering albatross census and population study 2017.