Forensics in water quality investigations: Isotopic multi-tracer approaches

Proceedings of a CSIRO OCE Cutting Edge Science Symposium
5 – 8 March 2012, Canberra, Australia.

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June 2013
Water for a Healthy Country Flagship Report series ISSN: 1835-095X

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Acknowledgments

Funding for the Symposium was provided by CSIRO’s OCE Science Team and the Water for a Healthy Country Flagship. We would like to thank all the symposium participants for their excellent presentations and their contributions to the lively discussions. We would also like to thank Frederieke Kroon, Ian Prosser, Bill Young, Carol Couch, Keith Bristow, Peter Hairsine, and Hamish Cresswell for their support and advice, Jan Mahoney and Felicity Kelly for the website, Louise O’Brien and Cris Kennedy for organising the public lecture, Kristine Boyce for editing assistance, and Keith Sclater, Renate Metz, and Kristine Boyce for advice and help with symposium logistics.
Executive summary

CSIRO’s Cutting Edge Science Symposium Series aims to enhance the understanding of key challenges and developments at scientific frontiers, to share perspectives of world leaders, and to facilitate national and international collaboration. This Symposium on ‘Forensics in water quality investigations: Isotopic multi-tracer approaches’ brought together national and international scientists who work on tracer approaches to investigate catchment water quality. These methods can provide evidence of the sources and fate of nutrients and sediments in catchments and receiving water bodies, which can then be used to design effective remediation strategies.

The symposium presentations related to both nutrient and sediment tracers in a range of applications and environments, with the participants sharing a wide variety of findings as well as raising outstanding issues. These included demonstrations of the value of the various tracers, opportunities provided by multi-tracer approaches, technical aspects of data analysis and interpretation, and experiences relating to informing water quality management. The presentations were accompanied by lively discussions, including a final discussion focussing on lessons learned and future challenges and directions for both research and application.

This report provides a glimpse of these presentations and discussions, with references provided for further reading. Collectively the symposium proceedings clearly demonstrate the potential value that isotopic multi-tracer approaches can have in informing water quality management. For some management questions the applications of tracers are relatively straight forward, whereas for others the applications are still very much in the research domain. Selecting and judging the suite of tools required to build a robust case is typically a task that is performed by individual scientists, based on their own experiences. The symposium concluded that adoption (of methodology or the resulting evidence) by managers and policy makers may benefit from a better defined (whole of field) ‘science approach’.

Other points raised in the discussions included:

- ‘Piggybacking’ on water quality monitoring programs or other projects can potentially provide exciting opportunities. Archiving of (extra) samples should be adopted where possible for use with future research questions, new analysis techniques or additional funding.
- Data sharing should be encouraged more. Making data available through archives and data portals could be significantly improved.
- A collaborative tool box project that summarises the various tools and analyses and their strengths and suitability for different applications would be a valuable exercise to assist the whole of field ‘science approach’ and facilitate education and awareness of isotopic tracer techniques.
- Understanding of catchment hydrology and surface – groundwater interactions is usually critical for a successful interpretation of nutrient tracer data. It also affects the choice of suitable end-members and determines the pathway residence times. A range of tracing and age-dating techniques are available and could be used more widely in interdisciplinary studies.

Areas of future research needs identified include the use of isotopic techniques to improve the understanding of attenuation processes, characterisation of suitable end-members in a wider range of land use and land management systems, description of isotopic changes occurring in the vadose zone, statistical analysis of data, modelling of isotope fractionation in catchment and receiving water models as well as vadose zone models, and further development work on nitrogen isotopes of ammonia and dissolved organic nitrogen, use of oxygen isotopes of phosphate, compound specific analysis of organic matter, as well as carbon isotopes in dissolved inorganic and organic carbon.

The multi-disciplinary nature of the symposium was a highlight that many of the symposium participants commented on. Investigations tracing nutrients and sediments tend to be carried out by groups from separate disciplines. Seldom, both stable isotope and fall-out radionuclide techniques are applied, even if that provides the whole system context that catchment water quality management requires. The
symposium participants expressed the desire build on this symposium with further interdisciplinary collaborations and meetings. It is hoped that the reader of these proceedings will similarly be inspired to explore opportunities for collaboration, whether that is among scientists or between scientists and catchment managers.
Part I  Symposium proceedings
1 Introduction

Natural resource management organisations, state water departments and water corporations are increasingly faced with the need to investigate catchment water quality problems that can relate to both point and diffuse sources. To design effective remediation strategies, they need to target sources of excess nutrients and sediments in an efficient way. Tracers of nutrients and sediments and of water pathways can, when combined, form the evidence to support such strategies. Recent developments in the area of isotope analysis techniques – e.g. new dual $\delta^{15}$N–$\delta^{18}$O nitrate-specific isotope techniques (Sigman et al. 2001, Casciotti et al. 2002, McIlvin and Casciotti 2011), some new techniques to determine $\delta^{18}$O of phosphate (McLaughlin et al. 2006; Paytan and McLaughlin 2011; Tamburini et al. 2010), compound specific isotope methods (Gibbs et al. 2008), and use of fallout radionuclides (see special issue Hydrological Processes 27) – have enhanced opportunities to use isotopic tracing approaches as lines of evidence for sources, pathways and transformations of nutrients and sediments. The symposium brought together scientists who had applied multi-isotope tracer approaches to investigations of catchment water quality (e.g. tracing sources, pathways, biogeochemical processes) or were interested in learning more about these methods. By facilitating the sharing of experiences and new analysis techniques, the symposium aimed to provide insight into the state of art of the field and guidance on future scientific developments.

The symposium was held in Canberra as a stand-alone, workshop-like meeting. The program consisted of a mixture of longer and shorter talks, poster presentations and discussion sessions covering five themes:

1. Isotopic multi-tracer approaches to inform water quality management
2. Isotopic multi-tracer case studies
3. Isotopes and sediment tracing
4. Developments in isotopic tracer analysis techniques
5. Future directions (research and application)

These proceedings aim to provide a flavour of the presentations and lively discussions that were held at the symposium. In Part I we provide an overview of the themes and presentations, and a summary of the discussion findings. The program of the symposium is included in Part II and Part III contains the abstracts and biographies of all the participants, along with references to their work.
2 Overview of themes and presentations

In the Symposium Program the oral presentations were grouped by Theme with the intention to conclude each Theme with a discussion. In practice, there was an almost non-stop discussion throughout the sessions, including questions and comments during talks. The process of summarising findings was, therefore, incorporated into the final discussion session on Future directions. These findings are summarised in the next section. Here we give an overview of the themes and presentations. Further details can be found in the abstracts of the presentations and in some of the key references provided by the speakers.

Isotopic multi-tracer approaches to inform water quality management

The first Symposium Theme explored how isotope approaches can contribute to better informed water quality management. While some of the talks included examples of isotope tracer applications that had successfully informed water quality management, the focus was more on how the managers and policy can be engaged, how successful integration with monitoring programs can be achieved, and what challenges one faces when trying to answer questions at scales relevant to the managers.

An introductory presentation by Dr Kirsten Verburg set the scene for the Symposium. It also included a case study from a dairy catchment in Tasmania, where a number of geochemical and isotopic methods were used to trace the sources and pathways of nitrogen and phosphorus. Despite the study being only a methodological trial, it provided important insights for the local industry and natural resource managers. Presenting the results in the context of a spatial catchment diagnosis using multiple lines of evidence proved a transparent and effective way of communicating findings (Verburg et al. 2012).

The first keynote presentation by Dr Carol Kendall provided an overview of the various stable isotope approaches that can be combined to trace nutrient and organic matter sources and sinks in a range of environmental management settings. The power of combining multiple isotopes, including water isotopes, was evident in many of the examples presented. Some of the ‘lessons’ included in her presentation were to start with water isotopes to aid the understanding of the hydrology and groundwater-surface water interactions, to include and use as many tracers as possible to allow follow-up of hypotheses, to explore different ways of presenting the data (e.g. presentation as isotope contour maps (isoscapes), Kendall et al. 2010), and to not be disheartened by large spatial or temporal variations, as often data can be reduced and still be explained by simple mixing models. Dr Kendall also highlighted how piggybacking multi-isotope sampling onto large scale monitoring programs (Kendall et al. 2010) had been a successful approach, which allowed collection of large numbers of samples. By archiving these samples and analysing them gradually over time, the different and evolving questions of stakeholders could be addressed one at a time using different combinations of techniques.

In the second keynote presentation, Dr David Widory talked about his work in Europe. In his EU-LIFE ISONITRATE project (http://isonitrate.brgm.fr/) they demonstrated to water quality managers and policy makers that traditional nitrate concentration monitoring approaches could be enhanced significantly by using a multi-isotope approach that measured the nitrate isotopes ($\delta^{15}$N–$\delta^{18}$O nitrate) in conjunction with boron isotope $\delta^{11}$B. Four different scenarios were selected on the basis of land use and local knowledge. These were expected to be a case with natural (low concentration) nitrate source, a simple case with single nitrate source coming from mineral fertilisers, a complex case with several distinct nitrate sources, and a case demonstrating the effect of denitrification) (Widory et al. 2013). Each of these cases proved a little more complex than their original descriptions, but the multi-isotope approach successfully helped constrain the possible sources and processes involved. The presentation also included a cost-benefit analysis of the additional information from isotopic monitoring in the simple case, which identified a second source of pollution. Using Bayesian decision analysis it demonstrated that while the isotope analysis was more...
expensive, its additional information helped save money by having better designed remediation measures targeting both sources instead of only the anticipated one. The project also produced a guideline for policymakers and scientist on application of the multi-isotope approach (Bronders et al. 2012).

The final talk in this session was presented by Dr Travis Horton. It presented some of the challenges that were encountered in an (ongoing) attempt to elucidate the sources of nitrate at a regional scale, the agriculturally intensive Canterbury plains of New Zealand. Determining distinct end-member compositions are a challenge at this scale and require a good understanding of groundwater-surface water interactions and the role that nitrogen-fixing plants and land management histories can play. Simply adopting apparent global end-member compositions for different land-uses was not an option in this catchment. To ensure accurate estimates of the relevant amounts of nutrients from different sources requires some checking to see if the main sources have been adequately characterised and if these characterisations are relevant to the study at hand.

**Isotopic multi-tracer case studies**

The second Symposium Theme was closely related to the first. It presented a range of case studies of isotopic multi-tracer studies. As sediment tracing techniques were covered in Theme 3, the emphasis here was mostly on stable isotope techniques relating to nitrate and sulfate dynamics. While still relevant to management, the presentations in this session focussed more on illustrating opportunities and sharing experiences, including some data analysis and interpretation issues.

Ms Naomi Wells presented on the topical issue of assessing the impacts of the Christchurch earthquake of 22 February 2011. Raw sewage was leaked into the river and NO₃ and H₂O isotopic indicators were used to follow its fate and the functional recovery of the river. As well as looking at sources, this talk also introduced the topic of using nutrient isotopes to study attenuation during downstream transport. In-situ denitrification was identified through the parallel enrichment of δ¹⁵N and δ¹⁸O of nitrate (Wells et al. 2012).

Dr Jianyao Chen presented two studies from the North China Plain and the Pearl River Delta. The first related to identification of nitrate contamination of groundwater under a wastewater irrigated field. Mixing (dilution of waste water) and denitrification were resolved through the use of water isotopes, chloride data and δ¹⁵N (Chen et al. 2006). The second study included analyses of chloride, water isotopes, δ¹⁵N, and δ¹⁸O of nitrate data to distinguish mixing and denitrification in groundwater wells affected by a landfill. In both studies stable isotopes were helpful in determining pollutant sources, but it was shown that interpreting the results in the context of hydrological processes and geochemical analyses was critical to reduce uncertainty.

Dr Brian Fry concluded Day 1 with a presentation that highlighted the importance of the nitrogen cycle causing perturbations in many ecosystems and provided examples of how isotopes can help understand these. This included a case study (from Korth et al. 2013) from the Baltic Sea, which is well-known for its critical eutrophication status along its coastlines. Nitrogen turnover in the receiving lagoon waters of two rivers were studied using δ¹⁵N–δ¹⁸O nitrate isotopes. Slope relationships were used to suggest that in one of the lagoons denitrification was fuelled not only by incoming nitrate fluxes, but also remineralisation of particulate matter and coupled nitrification/denitrification processes. Conceptual models of the interacting processes proved powerful for interpretation of the data and Dr Fry suggested that a next step would be to incorporate the isotope information into a whole system model (e.g. like in Pätch et al. 2013).

The next morning Dr Bernhard Mayer in his key note presentation presented a range of case studies to illustrate the types of questions that can be answered using nitrate and sulfate isotopes in concert with hydrological and chemical information. This included nitrogen from agricultural and waste sources (Rock and Mayer 2006, Chao et al. 2013), and mobilisation of sulphur by agricultural drainage activities (Rock and Mayer 2009) and hydrological events (Mayer et al. 2010). Dr Mayer presented a schematic diagram of the typical ranges of δ¹⁸O – δ³⁴S values of sulfate from various sources and processes (e.g. Mayer 2005), but reiterated the need to carry out local source characterisations. He also brought up the issue of transit times and delays in the unsaturated zone in the context of a lysimeter study (Sebillo et al. 2013) and in reference to a New Zealand study in the Mangatararere Catchment.
Dr Bill Showers introduced the Symposium participants to what he called ‘river mapping’: the use of high frequency nitrate sensors to obtain high resolution temporal or spatial data in or along rivers. The RiverNet Program (http://rivernet.csu.edu/) collects water quality data (incl. nitrate concentration) continuously (at 15-min intervals) at stations in the Neuse and Cape Fear River Basins. Some of the stations have run continuously since 2000. Since 2004 optical sensors have been used. The data provide an opportunity to explore how climatic oscillations affect discharge and nutrient fluxes. In addition to these stations that provide continuous, high temporal data, the sensors have also been used in conjunction with boats and canoes to get spatial mapping of water quality along rivers and streams and in reservoirs. This allows identification of inputs of contaminated ground- or surface water. Stable isotope analyses (of δ¹⁵N and δ¹⁸O of nitrate) have been carried out in conjunction with the program to identify origin of nitrate sources.

For the last presentation in this Theme, Dr Glenn Harrington introduced some different techniques. His presentation illustrated the use of multiple isotope tracers to gain insights into groundwater – surface water interactions in large tropical rivers in northern Australia (Gardner et al. 2011; Harrington et al. 2011, 2013; Smerdon et al. 2012). The tracers used included ²²²Rn for quantifying total groundwater discharge to the river, ⁴He for quantifying the component of groundwater discharge sourced from deep regional aquifers, ⁸⁷Sr/⁸⁶Sr and chloride for providing additional constraints on the source aquifers.

Isotopes and sediment tracing

The third Symposium Theme shifted the focus onto sediment source tracing. Dr Gary Hancock’s key note presentation set the scene with an overview of tracers used in this field: geochemical tracers relating to regional geology, carbon isotope signatures to trace organic matter and fallout radionuclides labelling surface soil. Dr Hancock explained that characterising the sources is not a trivial task due to concentrations being variable (affected by variable rainfall and particle size differences between sources and sinks) and the difficulty of obtaining representative samples. The tracers do behave conservatively during transport and are hence (usually in combination) able to discriminate soil sources and determine relative proportions (but not loads). The presentation also included diagrams and case study examples of the combined use of ¹³⁷Cs, ⁴¹⁰Pb and ⁷Be as erosion process tracers (distinguishing sheet erosion, scalds and rills, gully floors, fully walls and channel banks; Hancock and Caitcheon 2010; Hancock et al. 2013) and mentioned the use of compound specific isotopes as a future direction – a topic revisited in the next Symposium Theme.

Dr Grant Douglas presented the results and findings from a series of studies characterising the sediment sources and depositional characteristics in the Fitzroy River and estuary in Queensland, Australia (Douglas et al. 2006a, 2006b, 2008, 2010; Smith et al. 2008). This catchment is a major source of sediment and associated nutrients and contaminants to the Great Barrier Reef. The interpretation of contemporary and historical sediment sources in these studies was underpinned by major and trace element geochemistry, U-Th and Sr-Nd isotope geochemistry, and the use of a purpose-built Bayesian model (BestSedS; Palmer and Douglas 2007) to estimate catchment sediment proportions. One highlighted finding related to the different composition of sediment deposited in the estuary versus that transported by the river, particularly during flood events which dominate sediment delivery. Another was the finding that the basaltic source that dominated sediment composition during flood events originated from less than 10% of the catchment area.

Next Dr Peter Wallbrink looked back at a study (Wallbrink et al. 2001, 2003) that determined the relative contributions of sediment and sediment bound phosphorus from different land uses and erosion sources in a tropical catchment in northern Australia and in a temperature catchment in NSW, Australia. Fallout radionuclide tracers (¹³⁷Cs, ⁴¹⁰Pb) were used to identify erosion processes (surface vs. subsoil), X-ray fluorescence to determine %P, and the weight ration of neodymium, a rare earth element, to phosphorus (Nd/P) (Martin and McCulloch, 1999) to determine the %of phosphorus from fertiliser origin. Subsoil was found to dominate sediment (~70%) and P delivery (~60%) at the catchment scale in the temperate catchment, whereas in the tropical catchment erosion of surface soil dominated the supply of sediment bound phosphorus in the tropics (~70%). The scale (catchment vs. land use/farm) of evaluation was found to be an important factor. In the temperate catchment surface erosion of phosphorus was significant at the land use/farm scale (e.g. ~60% from pasture lands), but at the catchment scale the contribution of surface
eroded, bound P from pasture lands was small compared with the contributions from cultivated land and from gullies and channels within and between the different land use areas. Fertiliser phosphorus transported with the surface eroded sediments contributed significantly to catchment phosphorus in the tropical catchment, whereas in the temperate catchment it was less important (~10%) but highly variable.

To conclude the sediment tracing Theme, Dr Scott Wilkinson presented three case studies on sediment tracing and sediment budget modelling. The first study focussed on the sources and fate of sediments within a catchment post-wildfire (Wilkinson et al. 2009b). Fallout radionuclides $^{137}$Cs and $^{210}$Pb were used to identify a switch in sediment sources from 80% subsoil derived from gully and river bank erosion to 86% topsoil derived from hillslope surface erosion. The second case study illustrated the value of modelling spatially distributed sediment budgets (SedNet model) to relate erosion processes to suspended sediment yields (Wilkinson et al. 2009a). Exploring the model inputs and outputs, especially in conjunction with tracer data, provided valuable lessons on the relative importance of processes and adjustments to understanding and assumed rates. The final case study used sediment tracing to assess processes and spatial patterns of erosion in a grazed rangeland catchment in northern Queensland (Wilkinson et al. 2012). It applied a combination of fallout radionuclides ($^{137}$Cs and $^{210}$Pb) to trace the contribution of surface sheet-wash erosion to river sediment and geochemical tracers to identify the contribution of geological source areas. A Monte Carlo mixing model was used and parameter selection procedure discussed.

Developments in isotopic tracer analysis techniques

The aim of this fourth Theme of the Symposium was to inspire the group to look beyond current analyses towards new techniques and applications. The key note presentation was delivered by Dr Adina Paytan. She presented the latest on tracing phosphate through the measurement of $\delta^{18}$O of phosphate (see e.g. Paytan and McLaughlin 2011). This relatively new technique can be used in a wide range of applications, looking at both cycling and sources. For the latter, it is important that isotopic signatures of end-members are sufficiently unique and that phosphate cycling within the system is limited compared to input fluxes. Hence, sources of phosphate are more easily determined in systems that are eutrophic than ones that are nutrient limited.

The next two presentations related to compound specific stable isotope (CSSI) analysis. Dr Max Gibbs presented recent work on quantifying sediment erosion by land-use in the Waitetuna River catchment in New Zealand. Compound specific isotope analysis was used in conjunction with mineralogical and radionuclide techniques ($^{210}$Pb). It provided proportional soil contribution estimates to the river from each tributary. In terms of providing information for catchment management, the CSSI results proved powerful: they indicated that more than half the sediment came from about a third of the catchment.

Dr Andrew Revill presented recent work with Dr Gary Hancock (Hancock and Revill, 2013) assessing the ability of $\delta^{13}$C signatures of fatty acid compounds to discriminate erosion sources (channel bank, forest, pasture, cultivated, subsoils) in a rural, subtropical Australian catchment. Surface soil from forest, pasture and cultivated land-uses were well-discriminated, as were sub-surface soil sources associated with channel bank erosion, gullies and hillslope scalds. The IsoSource mixing model (Phillips and Gregg, 2003) was used with a subset of the data to determine erosion sources contributing sediment in the catchment and the results were consistent with fallout radionuclide and element geochemistry tracing.

Dr Kevin Petrone delivered the last presentation of the Symposium. After explaining the importance of dissolved organic carbon and nitrogen in the Swan-Canning River system (Petrone 2010), he presented work on characterising the bioavailability and composition of dissolved organic carbon and nitrogen using incubation and resin isolation techniques (Petrone et al. 2009). Dr Petrone also showed how fluorescence spectroscopy successfully fingerprinted distinct dissolved organic matter sources (Petrone et al. 2011) and how $^{14}$C carbon dating had determined the age of different sources of dissolved organic carbon.
Future directions (research and application)

The fifth and final Symposium Theme was explored in the final group discussion on the final afternoon. It looked back at findings and extended these into future directions for both research and applications. This discussion is summarised in the next section.
3 Summary of discussion findings

The final discussion on the last day of the symposium provided an opportunity for participants to highlight lessons learned, express their views on the state of the art of the field, and suggest areas requiring further research. Below a summary of the points that were raised during a lively, 2-hour discussion.

3.1 Potential opportunities from ‘piggybacking’

The idea of piggybacking on water quality monitoring programs presented by Dr Carol Kendall in her key note presentation was explored further with the suggestion that this could lead to exciting opportunities if we were to piggyback on each other’s projects and apply a range of techniques (stable isotopes of nutrients and bulk organics, compound specific isotopes of organics in sediments, fallout radionuclides) on the same sample set. Sometimes this could be as simple as collecting a few extra samples for a colleague. Other times, application for top-up funding to value-add to existing projects would be required. There was clear agreement that it was worthwhile to take extra samples and archive these wherever possible – either for retrospective analysis if funding became available later or for use with new future analysis techniques.

3.2 Thoughts on sampling design and protocols

It was pointed out though that experience with piggybacking on water quality monitoring programs has not always been positive, mainly due to incorrect sampling or sample storage. Forming close partnerships, personally providing hands-on training, provision of bottles, courier labels and coolers, and clear protocols were found to be the most effective in resolving these problems. Attention to sampling design, both in time and space, was considered a critical factor too. For example, making those running the water quality monitoring program aware of the potential fluctuations in nutrient dynamics (e.g. tidal influences), which can affect sampling results dramatically if timing of sampling is not considered carefully. The increased use of hydrograph (event) based sampling was also considered encouraging; with the added suggestion that use of an in-situ laser spectrophotometer would provide a detailed record of temporal variations in water isotopes (see e.g. Berman et al 2009).

Longitudinal sampling using high resolution nutrient monitoring equipment dragged behind a boat, as presented by Dr William Showers, was suggested as a means to inform spatial monitoring design. High resolution in-situ chemical sensors provide an assessment of temporal variability in rivers. The discussion on this topic concluded with the suggestion that oversampling, or sampling ‘anything you are looking at a bit longer’, might be the way to go. To address the issue of limited budgets, the actual analyses of these collected samples could be staged – more of the cheaper analyses over a broader set of samples and applying the more complex or costly analyses strategically afterwards, with the remaining samples archived. In this context, it was also suggested that once a monitoring program has been established it should not be reduced. Long term, strategic monitoring may answer the questions of tomorrow!

3.3 Publishing data

The archiving of samples then led onto the topic of publishing data to make them available more widely. Usually journal publications do not include the complete data set, limiting its use by others. It was suggested that publishing the data as a supplement to the journal article might be a useful approach. Copyright issues might, however, need to be explored. Some funding bodies, including NSF, now require projects to have a plan for data distribution and archiving. Indeed some organisations and research fields have data archives available (e.g. data.csiro.au; Rolling Deck to Repository http://www.rvdata.us/).
suggestion was made that maybe we needed to aspire to make an effort in this space and create data archives as good as GIS data bases.

3.4 Interdisciplinary approaches

Many of the studies presented at the symposium involved multiple tracers. It was, however, acknowledged that often these were still within the same discipline: stable isotopes were seldom mixed with fall-out radionuclides. While these disciplinary studies are often successful, they could be taken further if a system’s approach was adopted. Having been exposed to techniques from other disciplines during the symposium, there was general agreement during the final discussion that we need to work more as a community and use truly interdisciplinary approaches to gain a complete view of systems. After all, as someone commented, the river system knows no boundaries, so we should cross disciplinary boundaries and frame funding proposals in terms of what analyses are required to understand the complete system, rather than how best to use our own tools.

The disciplinary boundaries partly exist because the different disciplines have their own meetings and conferences. There is also the issue that a small research group can only manage analyses of a limited number of materials and isotopes with normal equipment and funding budgets. As the aphorism states, if all you have is a hammer, you only see nails. Multidisciplinary meetings are critical to raise awareness of possibilities for collaboration and cross-fertilisation of ideas. The hope was expressed that the symposium group would build on connections made during the week. A next step would be to exchange information on instrumentation, sample preparation, and to identify who can provide different analyses. More on the topic of future, multidisciplinary meetings is included in Section 3.14 below.

3.5 Potential role for a tool box

Interdisciplinary collaborations can also help determine what analyses could best provide the required system insights as every catchment will be different and need a different mix of methods. This led to a discussion of the idea to develop a toolbox: summarising the various tools and analyses available and their strengths and suitability for different applications. This was not seen as something prescriptive – the creativity of a skilful scientist is often the key to the success of research applications. Benefits considered during the discussion, therefore, focussed more on awareness and education – of students as well as water quality (catchment) managers and policy makers. There are some websites already available, including some from university classes that include nice examples, although most are more in the traditional forensic application space, in food provenance, or in ecology. The idea of creating a new field of forensic hydrology was floated and it was pointed out that there would be many suitable case-studies around that could provide inspiration to all. The various tracers should, however, be tested in more and different environments, including case studies in developing countries. This would test and better define the strengths and suitability of different techniques in different environments and for different applications.

3.6 Communication with managers and policy makers

As Dr David Widory presented in his key note presentation, demonstrations and examples can prove very effective. His experience in Europe was that one successful story caused other water agencies to come knocking on the door. The legal requirements from the European Framework Directive have helped drive this. People are desperately looking for solutions.

Another aspect of the communication with managers and policy makers that was discussed was the need for more consistency across the spectrum of expertise and recommendations. Finding a way to bring together techniques and form protocols for certain applications. In other words, creating a (whole of field) ‘science approach’ rather than individual approaches. The Forensic Isotope Ratio Mass Spectrometry (FIRMS) network provides accreditation for forensic practitioners with court-approved methods. The toolbox idea could be useful here too.
3.7 Defining suitable end-members

At this point the discussion switched to identifying a range of areas where further research was deemed necessary. One of these areas related to defining suitable end-members. The difficulty of determining end-members had already been raised in some of the presentations, especially in relation to different environments, complex surface-groundwater connections, and current and past landuse practices. Another point, raised in the key note presentation of Dr Bernhard Mayer and re-emphasised in the discussion, was the characterisation of fertiliser end-members when these undergo changes within the vadose zone. To what extent denitrification hinders source assessment was considered another outstanding question, as were the effects on isotopic signatures of the different processes used in waste water treatment plants and for handling manure. More international collaboration on isotopic signatures was also suggested.

3.8 Untangling surface-groundwater interactions and residence time

As mentioned above, surface-groundwater interactions can be complex and affect the choice of suitable tracer end-members. A range of methods to untangle these interactions were identified, including water isotopes, CFCs, \(^{3}He\), \(^{87}Sr/^{86}Sr\), \(^{222}Rn\), \(^{1}H\) and geochemical tracers. The discussion emphasised that it is not only a case of resolving the interactions, but also understanding residence times. Depending on pathways and travel times legacy nitrate sources may impact on stream concentration levels decades later (Stewart et al. 2011; Tesoriero et al. 2013). Age dating pollution and understanding the time frames of remediation are important, especially when current land owners are concerned about being blamed for the pollution. As was suggested by one of the symposium participants, isotopic techniques can be used to discover the innocent! Understanding the time frames for remediation is also important for making sensible cost-benefit decisions, and ensuring that stakeholders are patient about seeing environmental improvements. The methodology to untangle surface-groundwater interactions and residence times using tracers is a topic of active research (see e.g. Stewart et al. 2010, 2012), with the various methods having complementary strengths (see also summary of Dr Harrington’s presentation above).

3.9 Other chemical tracers

Another opportunity highlighted during the discussion was looking out for alternative chemical tracers or markers – those beyond traditional disciplines within the water quality research area – e.g. anthropogenic chemicals used for MRI, heart disease drugs, hormone replacements, and oral contraceptives. Some of these tracers may only work on a local scale, but they certainly expand our opportunities to gain insights into processes and sources affecting water quality (see e.g. review by Fenech et al. 2012).

3.10 Sediments vs. nutrients and their relative importance

There was a brief discussion about how much we know about links between sediment and nutrient transport. To what extent do these co-vary, and what determines their relative importance in different catchments. In some systems, the biggest polluter is clearly sediment, with nutrients playing a minor role. In others, both are important. It was suggested that a greater awareness about algal dominated rivers might open some eyes and cause managers (and researchers) to less quickly settle on a single main cause.
for water quality problems. It comes back to interdisciplinary work and thinking! Work on compound specific organic matter, DOM isotopes, as well as $^{13}$C in DIC and DOC may be well worth here.

### 3.11 Statistical analysis

The topic of statistical mixing models had already been debated earlier during the symposium with views being mixed as to how successful and supported these models were. During this final discussion it was suggested that this is probably an area that has held us back, with statistical analysis of the data often being left to the end of a study. It was suggested that we could be more planned and strategic about it and that it would be useful for the community (across disciplines) to exchange information on methods used. A paper by Dr Brian Fry on this topic has since been published (Fry 2013).

### 3.12 Modelling opportunities

A different type of modelling was also suggested: the incorporation of isotope fractionation into catchment and receiving water models. Some attempts in this area have been made (e.g. Turner et al. 2006; Pätch et al. 2013) and it appears to be a promising avenue to explore processes affecting nutrient turnover (e.g. denitrification) or to do some desktop pre-experimentation.

### 3.13 Other areas requiring further research

A couple of other areas of potential further research were floated but not discussed in depth. These include more work on the nitrogen isotopes of NH$_3$ and DON, more research on isotopomers, more use of oxygen isotopes of phosphate, and compound specific analysis of organic matter.

### 3.14 Opportunities to continue the dialogue

The discussion finished with a brain storm on possible opportunities that could allow us to build on the symposium and continue the dialogue. Catchment (watershed) forensics was suggested as a good descriptor of the interdisciplinary nature that the follow-up meetings should have. Meeting before or after one of the bigger conferences was considered an option, with AGU providing small grants for workshops at the start or end of its meetings. The Research Coordination meetings (RCMs) of NSF were identified as another potential source of funding. The International Association of Hydrological Sciences (IAHS) International Commission on Water Quality (ICWQ) is inviting suggestions for workshops or symposia within IAHS Assemblies. The Association for the Sciences of Limnology and Oceanography (ASLO) is also known for its interdisciplinary meetings and special symposia on emerging topics as is the International Atomic Energy Agency (IAEA). It may also be possible to piggyback big-river oriented multi-national studies on the IAEA’s GNIR (Global Network of Isotopes in Rivers) program. No immediate action plan was prepared, but there are obviously many opportunities to follow up and inspire others with the enthusiasm that was so abundant at this CSIRO OCE Cutting Edge Science Symposium.
References


Hancock GJ, Wilkinson SN, Hawdon AA, Keen RJ (2013) Use of fallout tracers $^7$Be, $^{210}$Pb and $^{137}$Cs to distinguish the form of sub-surface soil erosion delivering sediment to rivers in large catchments. Hydrological Processes (submitted).


Rock L, Mayer B (2009) Identifying the influence of geology, land use, and anthropogenic activities on riverine sulfate on a watershed scale by combining hydrometric, chemical and isotopic approaches. – Chemical Geology, 262: 121-130.


Part II  Program
# Program

## Day 1 – Monday 5 March 2012

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<thead>
<tr>
<th>Time</th>
<th>Activity</th>
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<tbody>
<tr>
<td>4:00pm – 6:00pm</td>
<td>Arrival and check in</td>
</tr>
<tr>
<td>6:30pm</td>
<td>Barbecue dinner</td>
</tr>
<tr>
<td>7:30pm – 8:30pm</td>
<td>Introduction to the conference</td>
</tr>
<tr>
<td>7:30pm</td>
<td>Welcome by Dr Carol Couch, Theme leader in CSIRO Water for a Healthy Country Flagship</td>
</tr>
<tr>
<td>7:40pm</td>
<td>Introductions</td>
</tr>
<tr>
<td>8:00pm</td>
<td>Kirsten Verburg “Isotopes, forensics and water quality investigations: Setting the scene”</td>
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</tbody>
</table>

## Day 2 – Tuesday 6 March 2012

<table>
<thead>
<tr>
<th>Time</th>
<th>Activity</th>
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<tbody>
<tr>
<td>8:55am</td>
<td>Introductory comments by Kirsten Verburg</td>
</tr>
<tr>
<td>9:00am – 12:30pm</td>
<td>Theme 1: Isotopic multi-tracer approaches to inform water quality management</td>
</tr>
<tr>
<td>9:00am</td>
<td>Key note Carol Kendall “Lessons learned from 25+ years of piggybacking multi-isotope studies onto water quality, ecological, and atmospheric deposition monitoring programs”</td>
</tr>
<tr>
<td>10:00am</td>
<td>Morning tea</td>
</tr>
<tr>
<td>10:30am</td>
<td>Key note David Widory “The multi-isotope approach: towards new methods to manage nitrate pollution within the European Water Frame Directive”</td>
</tr>
<tr>
<td>11:30am</td>
<td>Travis Horton “Stable isotopic compositions of the Canterbury, New Zealand, hydrosphere: moving from the global to the regional scale”</td>
</tr>
<tr>
<td>12:00pm</td>
<td>Poster thumbnails</td>
</tr>
<tr>
<td>12:30pm – 2:30pm</td>
<td>Lunch and poster session 1</td>
</tr>
<tr>
<td>12:30pm</td>
<td>Lunch and poster viewing</td>
</tr>
<tr>
<td>2:30pm – 5:30pm</td>
<td>Theme 1 &amp; Theme 2: Isotopic multi-tracer case studies</td>
</tr>
<tr>
<td>2:30 pm</td>
<td>Naomi Wells “Tracing the impact of the Feb. 22 Christchurch earthquake on urban waterways using multiple stable isotopes”</td>
</tr>
<tr>
<td>2:55pm</td>
<td>Jianyao Chen “Nitrogen aspects of hydrological processes with case studies in China”</td>
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<tr>
<td>3:20pm</td>
<td>Afternoon tea</td>
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<tr>
<td>3:40pm</td>
<td>Brian Fry “Dual isotope studies of nitrate show coupled nitrification/denitrification dynamics in Baltic Sea bottom waters”</td>
</tr>
<tr>
<td>4:20pm</td>
<td>Discussion: Reflecting on Day 2</td>
</tr>
<tr>
<td>5:30pm – 6:30pm</td>
<td>Free time</td>
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<tr>
<td>6:30pm</td>
<td>Dinner</td>
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<tr>
<td>8:55am</td>
<td>Introductory comments by Kirsten Verburg</td>
</tr>
<tr>
<td>9:00am – 12:30pm</td>
<td>Theme 1 &amp; Theme 2 continued</td>
</tr>
<tr>
<td>9:00am</td>
<td>Key note Bernhard Mayer “Tracing nitrate and sulfate in the hydrosphere using hydrological, chemical and isotopic techniques.”</td>
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<tr>
<td>10:00am</td>
<td>Morning tea</td>
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<tr>
<td>10:30am</td>
<td>Bill Showers “Nitrogen flux in watersheds: Nutrient mapping in rivers and drinking water reservoirs”</td>
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<tr>
<td>10:55am</td>
<td>Glenn Harrington “Using helium, radon and strontium isotopes to constrain locations and sources of groundwater discharge to tropical rivers in northern Australia”</td>
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<tr>
<td>11:20am</td>
<td>Discussion: Reflecting on Isotopic multi-tracer case studies</td>
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<tr>
<td>12:10pm</td>
<td>Poster thumbnails</td>
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<tr>
<td>12:30pm – 2:00pm</td>
<td>Lunch and poster session 2</td>
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<tr>
<td>12:30pm</td>
<td>Lunch and poster viewing</td>
</tr>
<tr>
<td>2:00pm – 4:45pm</td>
<td>Theme 3 Isotopes and sediment tracing</td>
</tr>
<tr>
<td>2:00pm</td>
<td>Key note Gary Hancock “Determining erosion sources contributing sediment to waterways and coastal regions using tracers”</td>
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<tr>
<td>2:50pm</td>
<td>Grant Douglas “Sediment sources and depositional characteristics in the Fitzroy river and estuary, Queensland, Australia”</td>
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<tr>
<td>3:20pm</td>
<td>Afternoon tea</td>
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<tr>
<td>3:35pm</td>
<td>Peter Wallbrink “Time warp – Looking back on a method for quantifying sources and delivery of suspended sediment and phosphorus to two Australian rivers”</td>
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<tr>
<td>4:00pm</td>
<td>Scott Wilkinson “Sediment source tracing and sediment budget modelling”</td>
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<tr>
<td>4:25pm</td>
<td>Discussion: Reflecting on Isotopes and sediment tracing</td>
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<tr>
<td>4:45 – 7:00pm</td>
<td>Free time</td>
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<tr>
<td>5:00 – 6.30pm</td>
<td>Public lecture Discovery Theatre (by Dr Kendall and Dr Douglas)</td>
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<tr>
<td>7:15</td>
<td>Dinner</td>
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<tr>
<td>8:55am</td>
<td>Introductory comments by Kirsten Verburg</td>
</tr>
<tr>
<td>9:00am – 12:30pm</td>
<td>Theme 4: Developments in isotopic analysis techniques</td>
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<tr>
<td>9:00am</td>
<td>Key note Adina Paytan “The use of oxygen isotopes of phosphate for determining phosphate sources and cycling: Method development, application and challenges”</td>
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<tr>
<td>10:00am</td>
<td>Morning tea</td>
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<tr>
<td>10:20am</td>
<td>Max Gibbs “Quantifying sediment erosion by land-use in a small multi-land-use watershed from a single storm event using compound-specific stable isotope and other techniques”</td>
</tr>
<tr>
<td>10:50am</td>
<td>Andy Revill “Erosion source discrimination of soil and carbon sources contributing sediment in a rural Australian catchment using Compound Specific Isotope Analysis (CSIA)”</td>
</tr>
<tr>
<td>11:15am</td>
<td>Kevin Petrone “Origin, age and function of dissolved organic matter in agro-urban coastal streams”</td>
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<tr>
<td>11:40am</td>
<td>Discussion: Reflecting on new developments</td>
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<tr>
<td>12:30pm – 1:30pm</td>
<td>Picnic lunch (weather permitting)</td>
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<tr>
<td>1:30pm – 4:00pm</td>
<td>Theme 5: Future directions (research and application)</td>
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<tr>
<td>1:30pm</td>
<td>Final discussion: Identification of key issues and core partnerships; plan for communication of symposium outcomes</td>
</tr>
<tr>
<td>3:30pm</td>
<td>Afternoon tea</td>
</tr>
<tr>
<td>4:00pm</td>
<td>Departure</td>
</tr>
</tbody>
</table>
Part III  Abstracts and participant biographies
Participant details

Name: Keith L. Bristow
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Key references


Biography

Dr Keith L. Bristow is a Senior Principal Research Scientist with CSIRO Land and Water and Honorary Professor at the University of Pretoria in South Africa. He is a soil physicist/hydrologist by training with 25 years experience in scientific research and leadership. Dr Bristow’s primary research areas include soil physics, hydrology, irrigated systems and integrated water resources management. He has extensive national and international research experience and is an expert in tropical water systems.
Nitrogen aspects of hydrological processes with case studies in China

Jianyao Chen¹, Yinglin Luo¹, Changyuan Tang²
¹ School of Geography and Planning, Sun Yat-sen University, China
² Faculty of Horticulture, Chiba University, Japan

Nitrogen transformation is closely associated with hydrological cycle and processes, which requires a coupling approach to understand and analyze water quality in either saturated or unsaturated zones. Major impact factors of macro scale on NAHP in terms of natural processes and human activities were presented, while factors of micro scale related to nitrification, denitrification and etc were enumerated. Two case studies of North China Plain and Pearl River Delta were used to explain the main relevant ideas. Stable isotopes were helpful in identifying pollutant sources and relevant mechanisms, and yet many more aspects to be explored. Multiple tracers, including major ions need to be combined with ground truths to reduce uncertainty in forensics analyses of water quality in the field.

Key references

Biography

Professor at Sun Yat-sen University in Guangzhou) and has PhDs in hydrology and Hydrogeology. He has a strong background in physical, chemical and microbiological aspects of hydrological processes as well as the
study of groundwater and surface interactions using geochemical and model approaches. He has more than 20 years of research experience, having worked in China, Japan and Australia. He is co-chair of the commission on groundwater and climate change of the IAH and member of Editorial Board for Isotopes in Environmental and Health Studies.
Carol Couch

Participant details

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Biography

Dr Carol Couch leads the Ecosystems and Contaminants theme of the Water for a Healthy Country Flagship. She leads a team of scientists who are tackling both national and international water availability and water quality challenges by applying a systems framework in the conduct of field studies, ecological modelling, risk assessment, integration and synthesis across diverse fields of knowledge.

Dr Couch joined CSIRO in 2011 from Georgia in the United States of America.

Prior to joining CSIRO she had an 18-year public service career in the US which combined ecological research with scientific and executive leadership at state, regional and national levels.
Sediment sources and depositional characteristics in the Fitzroy River and estuary, Queensland, Australia

Grant Douglas¹, Phillip Ford², Mark Palmer³, Lynda Radke⁴, and Jodie Smith⁴
1 CSIRO Land and Water, Floreat, WA, 6019, Australia.
2 CSIRO Land and Water, ACT, 2601, Australia
3 CSIRO Mathematical and Information Sciences, Floreat, WA, 6019, Australia
4 Geoscience Australia, ACT, 2601, Australia

The Fitzroy River Estuary is located on central Queensland coast, eastern Australia. The adjoining Fitzroy River Basin (FRB) at 144,000 km² is Australia’s second largest seaward-draining catchment. Annual sediment yields from the FRB to the Fitzroy Estuary typically vary from 4-9 Mt per year. As a major sediment source to the adjacent Great Barrier Reef (GBR), understanding the sources, cycling and deposition of sediment and associated nutrients and contaminants is pivotal to the long-term management of the GBR ecosystem. Increased sediment exports since European settlement threaten to degrade inner shelf reef and benthic ecosystems. Contemporary sediment sources to the Fitzroy River coastal zone have been quantified using an integrated geochemical, Nd-Sr isotopic and modelling approach comparing the compositions of major catchment soils and estuary sediments. The FRB geology is complex, comprising five major catchment units and over 100 rock types. Geochemical and Nd-Sr isotopic data indicate a sediment composition consistent with derivation from mixed catchment sources. Coastal sediments, however, display little geochemical variation as a result of hydrodynamic mixing and homogenisation. Sediment deposited within the Fitzroy Estuary and adjacent coastal zone has a substantially different composition to that transported in rivers, particularly during flood events which dominate the hydrology of the FRB. Longitudinal variations in sediment composition deposited in the Fitzroy Estuary are also apparent. Variations in rainfall occurrence and intensity due to intermittent cyclonic activity, as well as catchment clearing following European settlement, have a substantial effect on the relative contributions of the catchment sources delivered to, and deposited in, the estuary. Basaltic soils, although representing <10 percent of the catchment, are more readily mobilised than other catchment soils. These soils are also transported further within freshwater flood plumes that penetrate from the Fitzroy Estuary and deep into the adjacent coastal zone. It is likely that in large flood events this basaltic material may reach the coral-dominated GBR outer shelf. This study demonstrates that a multi-faceted approach can be used to identify sources of sediment transported to, and deposited within, a large estuarine system and to inform land management practices to reduce sediments and nutrients to the coastal zone.
Key references


Biography

Grant Douglas is a geochemist and Senior Principal Research Scientist at CSIRO Land and Water in Perth. Since completing his PhD in the early 1990’s on the geochemical and isotopic characteristics of suspended particulate matter in the Murray-Darling River system, he has pursued an integrated geochemical, isotopic and modelling approach to identify sediment sources to a variety of aquatic systems including the Moreton Bay, Maroochy and Fitzroy estuaries, a number of impoundments in southeast Queensland including the Lakes Wivenhoe and Samsonvale, Burragorang Dam in NSW and in rivers and billabongs elsewhere in Australia. The Bayesian modelling program, BESTSEDS, developed in conjunction with CMIS has proven particularly effective to determine sediment sources. More recent research has also employed geochemical and U-Th series isotopic techniques to characterise uranium mine tailings and wastewaters, and in the development of stabilisation and remediation techniques. A recently developed hydrotalcite-based remediation technique is covered by two patents and is currently being commercialised with Virtual Curtain Limited. This follows the successful development, patenting and commercialisation of Phoslock™, a selective P-absorbent clay that is the basis of an ASX-listed company and is used in 25 countries internationally.
Coastal zones which receive high nitrogen loads from rivers often suffer substantially from eutrophication. This is true for the Baltic Sea, which is well-known for its critical eutrophication status especially along the coastlines. Although the nutrient concentrations decrease rapidly offshore, the uptake and turnover processes near-shore are not well understood. The Rivers Oder and Nemunas, the second and third largest nitrogen contributors, drain into the Szczecin and Curonian lagoon, respectively, before they enter the coastal area of the Baltic Sea. During peak outflow, in March 2009 nutrient concentrations, nitrate uptake rates and dual isotopes (δ¹⁵N-NO₃− and δ¹⁸O-NO₃−) in nitrate were measured in the outflows of the lagoons to characterize nitrate turnover processes and its fate in the coastal zone. In the Curonian lagoon outflow the isotopic signature was dominated by mixing, whereas in the Szczecin lagoon outflow the isotope values were influenced by the ongoing spring phytoplankton bloom. Nitrate assimilation was indicated in the surface waters of the Szczecin lagoon outflow by a parallel enrichment of ¹⁵N and ¹⁸O. In the near bottom waters denitrification was the main process controlling isotopic signals in nitrate, but a 1.3:1 slope relationship occurred in plots of δ¹⁸O-NO₃− versus δ¹⁵N-NO₃− rather than the usual 1:1 relationship. The 1.3:1 slope suggests that denitrification was not only fueled by nitrate fluxes from the water column into the sediments, but also from nitrate derived from remineralization of particulate matter and coupled nitrification/denitrification. Moreover, the fractionation factors of ¹⁵ε of 9.9‰ and ¹⁸ε of 10.1‰ in near bottom waters infer that the isotopic enrichment from sedimentary denitrification may be higher in sandy sediment than in muddy sediments.

Key references

Biography

Brian Fry is a Senior Research Fellow in the Australian Rivers Institute, Griffith University. His area of interest is the interface between aquatic ecology and sustainable development. He works with stable isotope tracers to evaluate ecosystem dynamics, from primary production to fish migrations, especially studying the great experiments of our time imposed on the planet by our growing human population. These grand yet unintentional experiments involve human alteration of our planetary biosphere at many levels, from acid rain effects on inland lakes, to eutrophication effects on coastal fisheries, to global warming effects on all aquatic systems. Brian arrived at ARI in September 2011 from the USA. He has started work on fisheries in Moreton Bay, targeting eastern king prawns in time for traditional Christmas lunches. He is also participating in river floodplain research in northern Australia, with plans to set up further collaborations in Tasmania and in China.
Max Gibbs

Presentation abstract

Quantifying sediment erosion by land-use in a small multi-land-use watershed from a single storm event using compound-specific stable isotope and other techniques

Max Gibbs¹, Sandy Elliott¹, Les Basher² and Brenda Rosser³

¹National Institute of Water and Atmospheric Research (NIWA), PO Box 11-115, Hamilton 3251, New Zealand.
³GNS Science, PO Box 30-368, Lower Hutt 5011, New Zealand.

A range of techniques including mineralogy, radionuclides, modelling and stable isotopes of biomarkers, were used to assess the provenance of sediment eroded from the Waitetuna River watershed (167 km²) during a short but intensive summer storm event. Conventional geological techniques using mineralogy of the <10 micron sediment fraction failed to resolve tributary contributions using samples upstream and downstream of the confluence, but identified that most of the sediment was alluvial top soil rather than being derived directly from the five geological members underlying this watershed. Radionuclide techniques, using lead-210 excess, indicated that the fine soil had been rapidly transported through the Waitetuna River system and deposited in the estuary. The selective winnowing of fine sediment from the river channel sampling sites may explain the lack of resolution by the geological techniques. In contrast, a compound-specific stable isotope (CSSI) technique (Gibbs 2008) provided proportional soil contribution estimates to the river from each tributary. These were consistent with mean annual proportional contributions determined from a GIS-based regional regression model, SPARROW (Elliott et al., 2008). The CSSI technique identified proportional contributions from the three main land-uses – pasture, native forest, and production pine forest - and also provided estimates of sediment contributions from the three main pasture land-uses – sheep, beef, and dairy farming. The CSSI technique results indicated that more than half the sediment leaving the Waitetuna River watershed during the storm event came from about one third of the watershed.

Key references

Biography

Dr Max Gibbs is a limnologist and environmental chemist who has worked for the National Institute of Water and Atmospheric Research (NIWA) and its predecessors for 47 years. He has extensive experience in analytical chemistry, instrumentation and the development of new techniques. Max specialises in nutrient dynamics at the sediment–water interface and the study and restoration of lakes throughout New Zealand. For this work, Max was awarded an Honorary Doctorate from the University of Waikato in May 2010.

His work mitigating the effects of pollution also focuses on sediment impacts on lakes, wetlands and estuaries, and he developed a forensic technique using compound-specific stable isotope (CSSI) analysis of fatty acid biomarkers in the soil to determine the provenance of soil contributing to contemporary sediments. Max has used the CSSI technique in several studies to identify and apportion areas sensitive to land degradation / erosion by linking biomarkers of land use to the sediment in deposition zones. The CSSI technique has also been tested in 15 countries around the world through an IAEA-funded Co-ordinated Research Project to conserve soil for sustainable food production.
Gary Hancock

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Presentation abstract

Determining erosion sources contributing sediment to waterways and coastal regions using tracers

Tracing the origins of sediment and associated pollutants allows for the efficient application of remedial actions designed for erosion mitigation. Ideally, sediment tracers uniquely characterise soil grains from which the sediment is derived and are transported conservatively with the sediment. The erosion source information provided by tracers aids in the calibration and validation of catchment erosion model predictions.

The range of tracers commonly used include the major and tracer element composition as derived from the regional geology (soil geochemistry), organic matter (carbon isotope signature) and surface soil labelling (fallout radionuclides). In combination these tracers provide information on the spatial distribution, associated land-use and dominant erosion processes responsible for the delivery of sediment to the river network. The use of these tracers on a catchment-wide scale introduces some difficulties concerning characterisation of soil sources, including the need for representative sampling, and correcting for variable tracer concentrations associated with varying rainfall and soil/sediment particle size distributions.

This presentation will discuss the strengths and limitations of using sediment tracers in large catchments, and provide an example of how the combined use of these tracers can identify erosion sources. The presentation will introduce the use of $^7$Be as a fallout tracer to augment $^{137}$Cs and $^{210}$Pb, allowing the differentiation of sub-surface soil sources such as channel banks and hillslope scalds and/or gullied drainage lines, a distinction that is often difficult to obtain.

Key references


**Biography**

Gary Hancock is a Senior Research Scientist at CSIRO Land and Water specialising in the application of natural and anthropogenic radionuclides to tracing and dating of sediment aimed at determining the origins and history of the delivery of eroded soils.
Using helium, radon and strontium isotopes to constrain locations and sources of groundwater discharge to tropical rivers in northern Australia

It is widely recognised that groundwater discharge is responsible for maintaining dry-season flows in perennial rivers, and careful management of the extraction of groundwater near streams is critical for ensuring the long-term sustainability of in-stream aquatic ecosystems. Despite the common application of single tracers (e.g., radon-222) to identify locations and quantify rates of groundwater discharge to gaining streams, relatively few studies have used multiple isotope tracers of different types to gain insights into the source aquifer(s) for the groundwater discharge. Unless the source of groundwater discharge is known, simple models and management of shallow groundwater in alluvial aquifers may not achieve the desired outcomes.

This presentation will demonstrate the benefits of using multiple environmental tracers, including $^4$He, $^{87}$Sr/$^{86}$Sr, $^{222}$Rn and chloride, to study three large tropical rivers in northern Australia. In at least two of these rivers – the Daly River (NT) and Fitzroy River (WA) – the tracer data reveal spatial variations in the rate of groundwater discharge, as well as the relative contributions of shallow ‘local’ groundwater and deep ‘regional’ groundwater. When this tracer data is combined with existing geological knowledge and recently acquired geophysical data, it enables the construction of detailed conceptual models of groundwater – surface water interaction, which are proving invaluable for water resource managers.

Key references

Biography

Dr Glenn Harrington is the Stream Leader for Groundwater Characterisation and Management within CSIRO Water for a Healthy Country Flagship. He is also Deputy Program Leader for Groundwater Hydrology within CSIRO Land and Water. Dr Harrington has almost 20 years postgraduate experience in a variety of government, academic and private consulting roles. His primary research interests are surface water – groundwater interaction, arid-zone and tropical hydrology, and groundwater flow and solute transport in low-permeability media.
Stable isotopic compositions of the Canterbury, New Zealand, hydrosphere: moving from the global to the regional scale

Stable isotopic tracers are potentially powerful tools for determining the relative contributions of different material sources in a hydrological system. However, most hydrospheric tracers rely on well-constrained datasets collected over long periods of time and appropriate spatial resolution. Where such datasets are available, and distinct end-member compositions have been defined with confidence, simple mass-balance mixing models can be applied in an effort to determine the relative contributions to a specific hydrological domain. Where such datasets are not available, as is the case in most regional scale scientific initiatives, applied research questions often garner ambiguous answers. As such, there is an urgent need to monitor the isotopic and chemical composition of the hydrosphere at spatial and temporal scales relevant to regional practitioners and decision-makers.

In the agriculturally intensive Canterbury plains of New Zealand, nitrate concentrations are on the rise and many stake-holders want to know how to stop it and who to blame. Solving this growing problem is important to sustaining the quality of water resources across the region, and the stable isotopic compositions of both water and nitrate may help identify viable solutions. However, long-term stable isotopic monitoring programmes are not in place across Canterbury and the confidence with which we can apply stable isotopic tracers to the ‘nitrate problem’ remains somewhat limited. Nevertheless, we are collecting data and starting to explore complementary tracers of nitrate sources across the plains. Our preliminary results suggest that: 1) stable isotopic mixing models of groundwater-surface water interaction are viable and robust; 2) nitrogen-fixing plants, such as gorse and clover, represent potentially significant sources of excess nitrogen; 3) there is no clear correlation between land-use and the isotopic composition of nitrate in both surface and groundwater systems.

In an effort to apply isotopic tracers to regional scale problems, my students and I have collected more than 100 individual precipitation events and groundwater bore samples, in addition to multiple longitudinal surface water transects from the central Canterbury plains over the past three years. These datasets provide a reasonable foundation upon which further multi-proxy hydrospheric research projects can build, helping move the science from the global to the regional scale.

Key references


Biography

Travis Horton is a Senior Lecturer of Environmental Geochemistry in the Department of Geological Sciences at the University of Canterbury, Christchurch, New Zealand. Travis holds a Ph.D. from Stanford University in Geological and Environmental Science, and M.Sc. and A.B. degrees from Dartmouth College in Environmental Earth Science. Since moving to New Zealand in 2007, Travis and his students have initiated a number of stable isotope-based research projects on crustal fluid-flow, earthquake hydrology, paleotopography, animal migration, tracing geothermal and hydrological resources, Quaternary climate change, dendrochemistry, plant physiology, aquatic ecosystems, and New Zealand paleoenvironments.
Presentation abstract

Lessons learned from 25+ years of piggybacking multi-isotope studies onto water quality, ecological, and atmospheric deposition monitoring programs

This presentation presents an overview of how a multi-isotope approach can be useful for tracing nutrient and organic matter sources and sinks, and biogeochemical processes, in large river basins, wetlands, and airsheds – especially when piggybacked onto large-scale monitoring programs with abundant chemical and hydrologic data. A variety of examples from recent studies will be discussed and used to suggest guidelines for successful pilot studies and future monitoring programs in biologically active and human-impacted aquatic ecosystems.

Key references


Biography

Dr Carol Kendall is the head of the USGS Isotope Tracers research project. The purpose of this National Research Program project is to develop new isotope methods and applications to solve problems of national importance. Her main research focus is tracing sources of nutrients, organics, and water in human-impacted aquatic ecosystems, especially ones suffering from hypoxia and foodweb problems. She was elected an AGU Fellow in 2010 for “outstanding contributions to isotope hydrology and biogeochemistry, and specifically for her pioneering work on the dual isotopes of nitrate”.

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Presentation abstract

Key references


Biography

Dr Frederieke Kroon is a Principal Research Scientist at CSIRO Sustainable Ecosystems, where she is conducting research to improve water quality, aquatic biodiversity and fisheries production in tropical and sub-tropical coastal zones. Her research informs rehabilitation of coastal zones using a collaborative and integrated approach to both catchment management and aquatic health, to improve water quality, aquatic biodiversity and fisheries production. Dr Frederieke Kroon currently leads the Catchment and Aquatic Health Stream within CSIRO’s Water for a Healthy Country Flagship Program.
Tracing sulphate and nitrate in the hydrosphere using hydrological, chemical and isotopic techniques.

The isotopic compositions of sulphate and nitrate can provide unique information about the sources and the biogeochemical processes these dissolved constituents have undergone in watersheds. To obtain the full information from these tracers it is important a) that the isotopic data are interpreted in concert with hydrological and chemical information, and b) that the isotopic compositions of all major sulphur and nitrogen sources are known. This presentation will describe a number of case studies in which the combination of hydrological, chemical and isotopic approaches allowed quantitative assessments of contributions from a variety of isotopically distinct sulphur and nitrogen sources to sulphate and nitrate fluxes in aquatic systems. In addition, the transit time of sulphate and nitrate in the water-unsaturated zone will be discussed using selected isotope data.

Key references

9. CHAO, J., MAYER, B. & RYAN, M. C.: ISOTOPIC APPORTIONMENT OF NITRATE SOURCES IN THE BOW RIVER ALBERTA, CANADA. – APPLIED GEOCHEMISTRY, IN REVISION.
Biography

Dr. Bernhard Mayer is a Professor of Isotope Geochemistry in the Department of Geoscience at the University of Calgary (Alberta, Canada). His Applied Geochemistry research group (AGg) employs chemical and isotopic techniques to trace water, carbon, nitrogen, and sulfur compounds in surface and subsurface environments.

Dr. Mayer has (co-)authored more than 95 papers in international refereed journals and 10 book chapters. His innovative research has contributed to various provincial, national, and international research programs, including the Alberta Ingenuity Center for Water Research (AICWR), the Alberta Ingenuity Center for In-Situ Energy (AICISE), the Carbon Management Canada (CMC) and the Canadian Water Networks (CWN) of Centers of Excellence (NCE), and the United Nations SCOPE Nitrogen group.

Dr. Bernhard Mayer received his PhD in Isotope Geochemistry in 1993 from the University of Munich (Germany). After an 18 months stint as postdoctoral fellow at the University of Calgary, he returned to Germany as an Assistant in the Department of Sedimentary and Isotope Geology at the Ruhr-University Bochum (1994-1997). In September 1997, Dr. Mayer accepted a professorial appointment at the University of Calgary.
Tony Nicholas

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Key references


Biography

PhD thesis submitted Dec 2012, University of Wollongong: Aminostratigraphy of semi-enclosed basins. Principal Supervisor, Prof. Allan Chivas, UoW

Currently employed at Geoscience Australia as Marine Sedimentologist working on coastal and marine topics, predominantly involving investigations into sediment transport, sources and sinks.

Previously employed at School of Earth & Environmental Sciences, University of Wollongong, in a number of teaching (Geology) and technical roles, the latter principally as Laboratory Technician in the Geochemistry Laboratories (principally ICP-MS and HPLC, also basic water quality instrumentation, and sample prep for a wide range of techniques including the above methods and XRD, XRF, and isotopes).
"The use of oxygen isotopes of phosphate for determining phosphate sources and cycling - Method development, application and challenges"

Phosphorous (P) is an essential nutrient for all living organisms and when available in surplus could cause eutrophication in aquatic systems. While P has only one stable isotope, P in most organic and inorganic P forms is strongly bonded to oxygen (O), which has three stable isotopes, providing a system to track phosphorus cycling and transformations using the stable isotopes of O in phosphate (PO$_4$), $\delta^{18}$Op.

This isotope system has only recently been utilized in aquatic environments or in soils. Available data obtained from different settings indicate that $\delta^{18}$Op of dissolved phosphate in aquatic systems and in some soils can be applied successfully for identifying sources and cycling of phosphate in a broad range of environments. Specifically, work to date indicates that $\delta^{18}$Op is useful for deciphering sources of phosphate to aquatic systems if these sources have unique isotopic signatures and if phosphate cycling within the system is limited compared to input fluxes. In addition, because various processes are associated with distinct fractionation effects, the $\delta^{18}$Op tracer can be utilized to determine the degree of phosphorous cycling within the biomass and shed light on the processes imprinting the isotopic signatures. As a better understanding of the systematics of and various controls on $\delta^{18}$Op is gained, it is expected that $\delta^{18}$Op would be extensively applied in research geared to understand phosphorous dynamics in many environments.

Key references

2. de Sieyes NR.; Yamahara KM.; Paytan A; Boehm AD (2011) Submarine Groundwater Discharge to a High-Energy Surf Zone at Stinson Beach, California, Estimated Using Radium Isotopes ESTUARIES AND COASTS Volume: 34 Issue: 2 Pages: 256-268 DOI: 10.1007/s12237-010-9305-2
Biography

The major focus of my research is understanding past and present marine biogeochemical cycles. I was born and raised in Israel, and after two years of mandatory military service I traveled to India and Nepal and hiked the Himalayas for another two years. I obtained my B.Sc. double major in Biology and Geology from the Hebrew University in Jerusalem. Realizing how important science education is to the well-being of our planet, I pursued a M.S. degree in science education at the Weizmann Institute of Science in Rehovot. I developed a curriculum in field geology for high school students, which was implemented successfully, and then pursued another masters degree, this time in oceanography, at the Hebrew University in Jerusalem. My thesis was on oxygen isotope exchange between water and phosphate via biological cycling. In 1989 my husband Ron and I, moved to San Diego to take part in the Ph.D. program at the Scripps Institute of Oceanography. My thesis was on marine barite as a recorder of oceanic chemistry, productivity, and circulation. After 6 years, I graduated with a degree and a daughter (Tali) and stayed in San Diego (UCSD) for a post doc, this time producing a high resolution sea water S isotope curve for the past 120 Ma. In the summer of 1999, I moved to Stanford, where I worked for 8 years as a professor in the department of Geological and Environmental Sciences. Currently I am a Research Scientist at the Institute of Marine Sciences at the University of California Santa Cruz and I am affiliated with the Departments of Earth and Planetary Sciences and Ocean Sciences and teach and mentor students from these departments.

My principal research interests lie in the fields of biogeochemistry, chemical oceanography and paleoceanography. The goal of my research is to use the chemical and isotopic records enclosed in wide range of earth materials to study present and past biogeochemical processes. This research spans a wide range of temporal (seasons to millions of years) and spatial (molecular to global) scales. An over-arching goal of this research is to understand the processes and feedbacks operating in the earth System and how they relate to global changes in climate and tectonics. In addition, I am interested in natural and anthropogenically induced perturbations that affect biogeochemical processes and their impact on humans and the environment.
Kevin Petrone

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Presentation abstract

Origin, age and function of dissolved organic matter in agro-urban coastal streams

Dissolved organic matter (DOM) is ubiquitous in the Perth metropolitan area with elevated concentrations of dissolved organic carbon and nitrogen found in groundwater, streams and estuarine waters. Various geochemical, fluorescence, and isotopic (stable and radiocarbon) techniques have recently been used to identify the source and age of dissolved organic matter that when combined with bioassays provides a quantitative link between organic matter composition and function in aquatic ecosystems. In streams we found that bioavailable DOM was negatively related to humic-like fluorescence, but positively related to protein-like fluorescence. In estuaries, fluorescence spectroscopy fingerprinted distinct estuarine DOM sources from vascular plant material, fresh autochthonous sources, and degraded marine sources. Lastly, radiocarbon techniques have identified both old and new DOM in agro-urban streams. Highly aged carbon (70-80 percent modern) in streams draining urban catchments suggests that DOC is either from the mobilization or decomposition of aged peat or it contains a significant proportion of hydrocarbon material from anthropogenic activities. Conversely, relatively modern DOC (>95 percent modern) in agricultural catchments suggests that DOC loads are related to native vegetation and/or agricultural sources. Our findings demonstrate that simple fluorescence and bioassay techniques can be used better understand the flow of carbon and nutrients in aquatic food webs. Further, radiocarbon isotope techniques can be used to determine how anthropogenic activities influence the mobilization of organic matter in urban environments.

Key references

http://www.springerlink.com/content/j24u76423p433r4/
Biography

Dr Kevin Petrone received his PhD from the University of Alaska and completed a Carl Tryggers Postdoctoral Fellowship at the Swedish University of Agricultural Sciences before joining CSIRO as a postdoctoral fellow in 2006. He is now a Senior Research Scientist with CSIRO Land and Water and an Adjunct Assistant Professor with the School of Plant Biology at UWA. His research focuses on hydrologic and biogeochemical cycles at the catchment scale, particularly how ecosystems retain and transport water, carbon and nutrients, including linkages between soils, groundwater and streams.
Lynda Radke

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Presentation abstract

see abstract by Grant Douglas

Key references


Biography

Lynda Radke works in the Marine and Coastal Environment Group at Geoscience where she manages the OzCoasts website, and provides geochemical characterisations of seafloor environments for the purposes of biodiversity conservation.
Erosion source discrimination of soil and carbon sources contributing sediment in a rural Australian catchment using Compound Specific Isotope Analysis (CSIA).

Compound Specific Isotope Analysis (CSIA) has been used to assess the ability of $\delta^{13}C$ signature of fatty acid compounds to discriminate erosion sources in a rural Australian catchment. The study focussed on a high flow event (ten year recurrence interval) which occurred in the Logan-Albert catchment in January 2008 and has built on a previous sediment tracing study undertaken in 2008 using fallout radionuclides and major/minor element geochemistry.

It is found that surface soil from forest, pasture and cultivated land-uses are well discriminated using CSIA. Furthermore, sub-surface soil sources associated with channel bank erosion and exposed subsoils (gullies and hillslope scalds) occurring specifically in the mid-western Logan catchment could also be discriminated.

Selected fatty acid and bulk carbon $\delta^{13}C$ data were used in the IsoSource mixing model to determine erosion sources contributing sediment to the flood event. The results were compared with results obtained using other sediment tracers. For the lower Logan River, the CSIA tracing results are consistent with fallout and element geochemistry tracing, with channel bank erosion being confirmed as the major sediment source. Moreover CSIA has quantified the significant contribution of exposed subsoils originating on hillslopes and drainage lines from the mid-western region of the Logan catchment. In the Albert River catchment about 50% of sediment comes from forest land-use, although more than half of apparently comes from sub-surface sources.

These results have demonstrated that the CSIA technique has the potential to significantly enhance the ability of sediment tracing studies to determine the extent that different land-uses and erosion processes are contributing eroded soil to rivers, thus testing and validating model predictions and calibration of model parameters.

Key references


**Biography**

Andy Revill leads a team of researchers involved in estuarine biogeochemistry, focusing on the use of stable isotopes and lipid biomarkers to help understand carbon and nitrogen cycles. He has 15 years of experience in Organic biogeochemistry and has been involved with major research projects investigating the Huon river estuary (TAS), Fitzroy river estuary (Qld) and the Lower Ord river (WA). He is actively supervising biogeochemistry PhD students and has collaborative projects with researchers at several universities and other research institutions. Current projects include using compound specific nitrogen isotopes of amino acids to investigate diet shifts in marine ecosystems due to climate change and to model nitrogen turnover in marine predators. We are also using compound specific isotopes of various biomarkers to distinguish carbon sources in estuaries and to determine the importance of these in estuarine and coastal food webs.
Sherry Schiff

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Presentation abstract

Linking cycles of O₂ and N in a large impacted river in S. Canada: Isotopic insights for biogeochemistry and ecology

Population growth in Canada is increasing the pressure on freshwater systems for two essential but diametrically opposed services: the provision of drinking water and the assimilation of wastes. In many cities, wastewater treatment plants (WWTPs) discharge effluent directly into rivers. The Grand River watershed is home to 950,000 people. Projected population increase is over 40% within 20 years. Currently, more than 500,000 people rely on the Grand River for drinking water while there are 26 WWTPs along the river. Non point source nutrient loads are also extremely high, as agriculture (including large livestock operations) is the dominant land use. To accommodate this new growth, billion dollar decisions for wastewater and drinking water treatment and agricultural land management have been taken. Aquatic diel cycles of N, P and O₂ are linked through biological demands and redox chemistry. Here we examine the concomitant use of isotopes, δ¹⁸O in O₂, δ¹⁸O and δ¹⁵N in NO₃⁻ and N₂O, δ¹⁵N in NH₄⁺, δ¹³C and δ¹⁵N in DOM, POM, macrophytes and benthic invertebrates, δ³⁴S and δ¹⁸O in SO₄, with stoichiometric ratios to tease apart the sources and cycling of O₂, N, and P in various reaches of this 7th order river from the headwaters to the mouth at Lake Erie. Five approaches with differing spatial and temporal resolution are used: longitudinal surveys conducted at several times on the same day from headwaters to mouth (300 km), diel sampling (sampling every 2 hours over 28 hours), WWTP plume chasing surveys, year-round biweekly sampling at selected sites, and manipulation experiments with chambers installed on the river bed. In the central part of the watershed, NH₄⁺ released from main WWTPs has 3 fates that can be followed with isotopes: nitrification, volatilization and plant uptake. We are currently developing an isotopic model to compare to field data collected in WWTP plume chasing surveys. The relative importance of these three processes is critical to predicting the ecosystem impact of converting the WWTP operations to a nitrifying process.

Key references


**Biography**

Sherry Schiff is a University Research Chair in Watershed Biogeochemistry and Professor in the Department of Earth & Environmental Sciences at the University of Waterloo, Canada. Research interests include the use of isotopic tracers for biogeochemical and hydrological processes in watersheds, groundwaters, lakes, and rivers. Recent work has focussed on nitrogen cycling in rivers and agricultural catchments, the use of \( \delta^{18}O \) in dissolved O\(_2\) for ecosystem metabolism, \( \delta^{13}C \) for CO\(_2\) loss from boreal streams, and the systematics of \( \delta^{18}O \) and \( \delta^{15}N \) of N\(_2\)O.
Nitrogen flux in watersheds: Nutrient mapping in rivers and drinking water reservoirs

Quantifying the flux of nitrate from different landscape sources in watersheds is important to understand the increased flux of nitrogen to coastal ecosystems. The RiverNet program has measured the nitrate flux in the Neuse River Basin, NC on a 15 minute interval over the past ten years. Discharge and N flux in the basin also has significant inter-annual variations associated with El Nino oscillations modified by the North Atlantic oscillation. To understand how climate oscillations affect discharge and nutrient fluxes, we have continuously mapped nitrate concentrations, with Chlorophyll a and CDOM to understand how nitrogen is transported across landscapes to the coastal ecosystems. Hydric soil spatial distributions are an excellent predictor of nutrient transport in watersheds, and are related to the distribution of biogeochemical “hotspots”. Detailed spatial analysis indicates that nitrate, Chlorophyll a, and CDOM are not spatially coherent and one concentration cannot be used to predict the distribution of the other parameters as suggested by some regulatory agencies. These results also indicate that the contribution of wastewater treatment plants from urban watersheds has been greatly under-estimated in current models while the transport of agricultural nitrogen is controlled by hydric soil distributions and riparian buffer size. Prediction of future changes in discharge and nutrient flux by the modelling of climate oscillations has important implications for water resources policy and drought management for public policy and utility managers.

Key references

5. William J. Showers , Bernie Genna, Timothy McDade, Rick Bolich, and John C. Fountain Nitrate Contamination in Ground Water on an Urbanized Dairy farm. ES&T Vol 42(13) 4683.


Biography

William Showers grew up in southern California and got a BS in Geology from UC Santa Barbara in 1973. He entered graduate school at UC Davis and made two trips to Antarctica. He wintered over at Palmer Station in 1975, and participated on the Ross Ice Shelf Drilling Project in 1978. He completed an MS in Geology in 1978 and moved to the University of Hawaii where he joined the Tahiti Shuttle Experiment. He worked on the equatorial Pacific upwelling zone from 1978 to 1982. In 1982 he completed his PhD in Oceanography and Marine Geochemistry at UH, and then joined the faculty at North Carolina State University in Raleigh, NC. He worked on the Amazon Fan from 1983 to 1996, and participated on Leg 155 of the Ocean Drilling Program in 1994. He worked with Dale Russell and Reese Barrick on the oxygen isotopic composition of dinosaurs in the 1990’s working on specimens from Utah, mid-west USA, and Argentina. In 1999 he started the RiverNet program (http://rivernet.ncsu.edu/) to accurately measure nitrogen flux in North Carolina Watersheds to the coastal ocean. This program continues today with ties to stakeholders, agribusiness corporations, state policy makers and regulators. By combining research efforts with educational outreach programs, RiverNet seeks to train the scientists, regulators and policy makers of the future. In the end we will improve the public’s understanding of water resource issues and the essential social, economic, and environmental value of local water resources for all persons and sectors of society.
Isotopes, forensics and water quality investigations: Setting the scene

Targeting actions to address water quality issues within catchments requires an understanding of how the catchment ‘works’. It is important to know which nutrients, and in what form, contribute to the problem, the origin of the nutrients, and the location of critical source areas within the catchment. Knowledge of the nutrient pathways and where they reach the stream is also critical – not only for the choice of management action, but also for the design of monitoring to evaluate its effectiveness. In other words, for management actions to be efficient and useful they need to be underpinned by a spatial ‘diagnosis’ of catchment water quality. Geochemical and isotope tracing methods can provide important insights for catchment diagnoses, in particular in terms of identifying sources of water and solutes. Catchment managers are, however, less familiar with these methods, their strengths and their requirements. A case study carried out as part of Landscape Logic demonstrated the potential strength of tracing methods to local catchment managers and stakeholders. Some questions remained, however, about extent of data required to disentangle different processes and the impacts of agricultural systems and practices that were different from those presented in the literature. The CSIRO Cutting Edge Symposium on ‘Forensics in water quality investigations: Isotopic multi-tracer approaches’ was organised to bring together scientists who have applied or are interested in multi-isotope tracer approaches to investigations of catchment water quality. By facilitating the sharing of experiences and new analysis techniques, the symposium will define the state of art of the field and guide future scientific developments. This will help determine the pathway to wider adoption of these techniques for spatial catchment diagnoses.

Key references


Biography

Dr Kirsten Verburg leads research exploring ways to build catchment water quality diagnoses to identify sources of nutrients and sediments and their pathways to the waterways using multiple lines of evidence. This includes the use of ‘snapshot’ sampling, geochemical and isotopic analysis, and high frequency nutrient monitoring.
Her other research interests include: quantitative analysis of soil water and nutrient flows in agricultural systems using simulation modelling and their use to explore management strategies, analysis of the impact of climatic variability using stochastic climate data, and identification of objective measures and design of smart monitoring that provides 'system feedback' to guide specification of land use and management options.
Time warp – Looking back on a method for quantifying sources and delivery of suspended sediment and phosphorus to two Australian rivers

Changes in sedimentation patterns after European arrival has resulted in severe degradation of Australian river systems. Eutrophication is a major associated issue, and the persistent occurrence of algal blooms has been linked with excess available P. The total amount of P in these systems has been shown to be dominated by the sediment bound load derived from erosion of diffuse sources, although fertiliser P has also been implicated. The major diffuse sources of sediment include surface erosion from cultivated, pasture and steep forested land as well as subsoil erosion from the significant number of channels and gullies present within these systems.

In this project we determined the relative contributions of sediment and sediment bound P from different landuses and erosion sources in two contrasting catchments. The Bundella Creek catchment (8,700 ha) is in the Liverpool Plains of NSW; and the Berner Creek catchment (1069 ha) is in tropical north QLD. Overall there are important similarities and differences in the delivery of sediment and P from these temperate and tropical systems. Subsoil was found to dominate sediment (~70%) and P delivery (~60%) at the catchment scale in Bundella creek. However, P concentrations in surface soils are about a factor of 2 higher than in underlaying subsoils, and so surface erosion of P could be significant (~60% from pasturelands) at the smaller landuse/farm scale. Conversely erosion of surface soil dominated the supply of sediment bound P in the tropics (~70%) at the catchment scale. This was heavily influenced by the considerable surface erosion that occurred from cultivated lands containing high concentrations of P. For both geographic regions, the relative yield of sediment and sediment bound P was many times higher from cultivated lands compared to areas that had not been cultivated. There was little overall contribution of sediment or sediment bound P from surface erosion of pastureland areas in either region.

A variety of geochemical methods showed that Fertiliser P is transported with surface eroded sediments in both regions and can contribute to downstream P concentrations. For example ~ 42% of the sediment P from cultivated areas in Berner Creek was from fertilisers, this contributed significantly at the catchment scale (~42%). In contrast fertiliser P only contributed ~ 3% to sediment P in erosion from cultivated lands in Bundella Creek. The difference between the two was attributed to the method by which the fertiliser was applied. In the tropics it is applied to the surface, from where it is easily removed by surface erosion, in Bundella Creek it is applied below the surface at about 10 cm depth. The contribution of fertiliser P at the catchment scale in the latter catchment was less important (~10%) but highly variable.
Key references


Biography

Dr Peter Wallbrink is currently the Executive Manager, eWater CRC for the Rivers and Catchments projects. These projects are delivering the next generation of Planning and Operations river and land use models, in combination known as the Source integrated modelling Suite (IMS) suite. This integrated modelling package encompasses most aspects of prediction and quantification for water quantity and quality, volume, trade, storage and operations, ownership, storages as well allowing forecasts of climate change and land use impacts, on water. Previous roles include: the Director for Research & Education at the eWater CRC.; Deputy director and the Program Leader of the Co-operative Research Centre for Catchment Hydrology CRCCH: He has also been a project leader for various collaborative projects investigating catastrophic events on delivery of sediments and nutrients to water supply catchments as well as fate and origin of sediment and nutrients in catchments and river systems generally. From 1995-2005 he was the Australian representative to various International Atomic Energy Agency (IAEA) Coordinated Research Programs.
Naomi Wells

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Presentation abstract

Tracing the impact of the Feb. 22 Christchurch earthquake on urban waterways using multiple stable isotopes

Following the Feb. 22, 2011 Christchurch earthquake urban streams were inundated with silt/sand from liquefaction as well as raw sewage from broken infrastructure. In order to, 1) assess the functional recovery of the river, and, 2) quantify the fate of sewage-derived nitrogen, we measured nitrate and water isotopes, combined with microbial and chemical indicators, along an impact gradient on the Heathcote River over a period of 6-months. Although liquefaction and hydrological changes associated with the quake itself did not have a detectable long-term impact on stream function (indicated measurements of NO\textsubscript{3} and H\textsubscript{2}O isotopes immediately following a M6.3 aftershock on June 13), the impact of the sewage influx was dramatic. Downstream of severely damaged areas dissolved oxygen dropped to < 1 mg l\textsuperscript{-1} and the concentration of dissolved organic carbon increased x10. However, within 40-days of the initial quake water chemistry had returned to normal levels. Over these 40-days the dominant source of available nitrogen in the stream shifted from sewage (\textsuperscript{15}N = 6±2‰) to a more typical 'soil N' value (\textsuperscript{15}N = 1.5±2 ‰). During the period of high sewage input, N cycling was dominated by in-situ denitrification, as indicated by \textsuperscript{15}N:\textsuperscript{18}O of NO\textsubscript{3} over transport distance. Microbial biofilm populations began shifting back towards pre-quake assemblages after 60-days, corroborating the isotopic indicators of functional recovery of the Heathcote River.

Key references

1. Naomi S Wells1, Timothy J Clough1, Gavin Lear1, Travis W Horton3, Troy T Baisden. (2012) Stable isotopes as a tool for quantifying sources and sinks of New Zealand’s growing nitrate problemhttp://fallmeeting.agu.org/2012/eposters/eposter/b51f-0617/

Biography

Naomi is currently working towards her PhD in soil science at Lincoln University (New Zealand) on the topic of ‘nitrate isotopes as indicators of the fate and transport of excess nitrogen’, with anticipation to finish by the end of 2012. While working on her PhD she was also able to spend 10-months as a visiting scholar at
the International Rice Research Institute thanks to a Fulbright scholarship. She received her MSc in soil science from the University of Aberdeen (United Kingdom) in 2008 and her Bachelor’s degree in environmental science and geosciences from Wellesley College (USA) in 2006.
Presentation abstract

The multi-isotope approach: towards new methods to manage nitrate pollution within the European Water Frame Directive

D. Widory, E. Petelet-Giraud, A. Brenot (BRGM), P. Boeckx (U. Gent) J. Bronders and K. Tirez (VITO)

Today, the environmental management of surface/groundwater quality with respect to nitrate contamination is almost exclusively based on monitoring nitrate (NO₃⁻) concentration levels in a selection of sites and samples through time. However, there is now ample evidence that this concentration approach does not allow to establish unambiguously the different sources and their respective contributions to nitrate pollution. It is also observed that increasing the density of data points by increasing the number of environmental monitoring stations and/or the number of samples (reducing periodicity between sampling) does not help much and generates extremely high additional costs. A direct consequence of this is that it is often difficult to design and verify the effect of environmental management measures and plans implemented to control nitrate contamination in a given area.

The results of recent research work showed that the limitations of the concentration monitoring approach can be overcome by using an isotopic approach. This approach is based on measuring natural isotopes of the nitrate molecule (δ¹⁵N and δ¹⁸O) and associated dissolved species (δ¹¹B) present in both pollution sources and water. Although the application of the isotopic tracing approach to nitrate pollution issues is recent, it has proven to be very effective at precisely discriminating the different vectors of nitrate in water (i.e. urban and agricultural sources), identifying these sources of pollution and quantifying their respective contributions to a contaminated water body.

The objective of the ISONITRATE project was to demonstrate to policy-makers and -implementers that a water quality monitoring network, operated over several years and integrating isotopic data (that inherently have a far greater information content than chemical data alone) is feasible technologically and economically cost-gaining, and leads to more effective planning of environmental management measures specifically targeted against nitrate pollution in water bodies.

The demonstration project was carried out by characterizing the isotopic composition of all identified potential nitrate sources, and by collecting and analyzing (chemically and isotopically) water samples from boreholes and rivers over a period of 15 months, on four distinct locations representing the different hydrogeological contexts encountered by most authorities in charge of providing potable water:
a) Natural nitrification of the soil: sampling sites representing the local background NO₃ levels in water (i.e. samples with higher NO₃ are considered polluted). The measured low NO₃ concentrations need not to result from attenuation by natural denitrification, but clearly from natural nitrification.

b) Natural denitrification: sampling sites along a gradient of natural denitrification, all groundwater.

c) Simple case: sampling sites located in a zone where only one pollution source controls the NO₃ budget in water.

d) Complex case: sampling sites where NO₃ in water results from the combination of distinct sources with various contributions along the hydrological cycle.

Key references

1. Widory, D., Petelet_Giraud, E., Bregnot, A., Bronders, J., Tirez, K., Boeckx, P. (2013). Improving the management of nitrate pollution in water by the use of isotope monitoring: the \(\delta^{15}\text{N}, \delta^{18}\text{O} \& \delta^{11}\text{B}\) triptych, Isotopes in Environmental and Health Studies, 49, 29-47.


Biography

Holder of a PhD in Physical Sciences (Fundamental and Applied Geochemistry section), D. WIDORY started his career in 1999 as a research assistant at the Université Paris 7 – Denis Diderot. After a one-year post-doctorate at the University of Toyama (Japan) where he studies the use of Zelkova Serata leaves as isotopic tracers of atmospheric pollution, he joins the BRGM in 2001 as a post-doctorate in the Water Division. Within the frame of research programs, he studies the isotopic fingerprinting of nitrates sources in groundwater (\(\delta^{15}\text{N} \& \delta^{11}\text{B}\)), and develops the isotopic fingerprinting of atmospheric particles in urban environments (\(\delta^{13}\text{C}, \delta^{15}\text{N}, \frac{87}{86}\text{Sr} / \frac{86}{86}\text{Sr} \& \text{Pb isotope ratios}\)). Shifted to permanent position in September 2002.

Stable Isotope Laboratory Manager at BRGM from 2004-2012 (Metrology Measures and Analysis Division). Professor at University of Quebec, Montreal since 2012.
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Presentation abstract

Sediment source tracing and sediment budget modelling

Sediment source tracing provides valuable data to evaluate spatial models of sediment budgets, and for investigating the effect of land management on sediment sources. This presentation will describe recent studies in grazing land and following forest wildfire. Monte-Carlo mixing models are used to assess quantitative source contributions with associated confidence intervals to evaluate tracing results.

Key references


Biography

Scott Wilkinson researches sediment mobilisation and transport from paddock to river basin scales using field measurement, river monitoring, source tracing and spatial modelling. His main focus has been developing the use of sediment budget modelling as a framework to assemble disparate information on material fluxes and their management at river basin scale.
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