Remediation Australasia

CRCCARE

ISSUE 18/2017

Master of Environmental Risk Assessment and Remediation

Are you an environmental practitioner or consultant who is concerned about the risks (human and ecological) associated with environmental pollution and want to be involved in providing creative solutions to minimise those risks? The University of Newcastle's Master of Environmental Risk Assessment and Remediation can be the pathway to that position you've been dreaming of.

Overview

Providing you with specialised training in risk assessment and environmental remediation designed for the growing needs of the remediation industry both nationally and globally, this hands on practical and research-focused program will help prepare you for your dream job.

Using a balanced approach that includes both hands on and case studies, you'll examine the core concepts, principles and techniques underlying environmental risk assessment and remediation. You'll learn how to assess a contaminated site including following guidelines for contaminated site assessment (eg NEPM-ASC) and jurisdictional legislation regulating management of contaminated land; carry out desktop research for preliminary site investigation (PSI), develop conceptual site models, produce a sampling plan for a detailed site investigation using data quality objectives (DQOs) and evaluate contaminated site data to identify contaminant fate and pathways and assess the risk presented by the contaminant(s) detected on site and determine the need for further investigation or remediation.

On completion, you'll be able to provide full site assessment reports that exceed clients expectations, provide innovative solutions to remediation and/or risk assessment problems, and bring remediation projects to a successful conclusion.

Is it for you?

Environmental practitioners can have different backgrounds and their previous experience and knowledge often help shape the future direction of their careers. You may have a bachelor's degree in science or applied science (engineering) and now want to expand your skills and move into the growing field of environmental remediation. Or you may want to start a research career in the field of environmental chemistry, toxicology and technology.

Career opportunities

The University of Newcastle's Master of Environmental Risk Assessment and Remediation will prepare you for managing contaminated site(s) projects and developing remediation action plans for both private and public organisations. With a core focus on environmental risk assessment and remediation, you will have specialised and instrumental skills that will be highly valued by mining, property development and industrial sectors. Your capacity to work internationally will be supported by the University's own reputation in the field. Distance study may be possible; for more information contact ravi.naidu@newcastle.edu.au.

To register your interest in this program, visit gs.edu.au

Contents

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Cover photo

One of the by-products of burning organic material is the carcinogenic compound benzo[a]pyrene – one of several contaminants of emerging concern featured in this issue of *Remediation Australasia*.

Photo: Bert Knottenbeld

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Editor's note

It is my great pleasure to welcome you to issue 18 of *Remediation Australasia*. You may be aware that it has been a while since issue 17 was published. This is no accident. In 2015, CRC CARE relocated its headquarters from Adelaide to Newcastle, where we are now based at the University of Newcastle. Unsurprisingly, this heralded a disruption to business as usual, as dozens of staff, researchers and PhD students uprooted their lives to make a new home on the east coast. As a result, the past 2 years have allowed us to refocus our priorities and redouble our efforts to achieve a cleaner, safer environmental future – for not only Australia but also the wider world. The importance of this mission is underscored by a recent World Health Organization report revealing that, in 2012 alone, more than 12 million people died as a result of living or working in an unhealthy environment, with air, water and soil pollution, and chemical contaminant exposure the leading factors.

With *Remediation Australasia* on hold over this period, we have had the opportunity to freshen up the magazine's look and feel. We have also moved to a predominantly digital product, which will see 3 online issues per year with an annual print issue that compiles the best articles across the 12 months. By moving to a digital platform, the magazine will be easier to read online (be it on your desktop, laptop, tablet or phone) and much easier tosearch, with the ability to find articles based on a keyword search or according to a categorised list of topics. *Remediation Australasia* will still be downloadable as a PDF, either as individual articles or as the complete magazine.

We've also printed this first issue of the new-look *Remediation Australasia* so that it is available for delegates at the 7th International Contaminated Site Remediation Conference, or CleanUp 2017. This year, CleanUp incorporates the 1st International PFAS Conference, in recognition of the growing issue of per- and poly-fluorinated alkyl substances (PFAS). Indeed, this issue of the magazine takes a look at PFAS, particularly those that have received prominent recent news coverage because of their presence at sites contaminated through firefighting foam usage. We also examine other contaminants of emerging concern, including benzo[*a*]pyrene and methyl tert-butyl ether.

I very much hope that you enjoy the new *Remediation Australasia*. I would also like to extend my best wishes to those of you attending CleanUp 2017, where I hope to meet as many of you as I can.

Professor Ravi Naidu
Managing Director and CEO, CRC CARE
Editor-in-chief, *Remediation Australasia*

reMEDIAtion

A quirky snapshot of recent contamination and remediation issues in the media.

Protect Earth, but not from aliens

NASA recently advertised the job of 'planetary protection officer', setting off a glut of media stories about a position protecting Earth from aliens. The reality was a little more prosaic but no less important. The successful applicant will be responsible for preventing any unintentional contamination of planets or other celestial bodies by NASA spacecraft exploring the universe, and vice versa for craft that return to Earth. The job description explains that 'planetary protection is concerned with the avoidance of organic-constituent and biological contamination in human and robotic space exploration'. According to the Outer Space Treaty of 1967, which the United States has ratified, space missions must have less than 1-in-10 000 chance of contaminating any planetary bodies being explored. News outlets reporting the true nature of the job (and not the *Men in Black* version) included the *New Zealand Herald* (bit.ly/2vpBf5v).

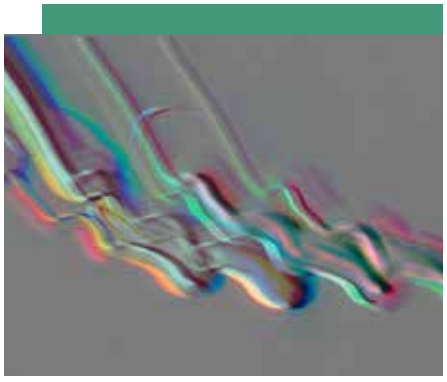


Photo: Sérgio Valle Duarte

Photo: NASA

Is the end nigh?

The Guardian (bit.ly/2hNHEoc) was one of many publications reporting on a new study suggesting that, between 1973 and 2011, the concentration of sperm in the ejaculate of men in western countries has halved. The international team that conducted the research, which was published in the journal *Human Reproduction Update*, claim that they have accounted for a range of factors that brought into question the credibility of previous studies indicating falls in male fertility. Although the study did not investigate causes, maternal or direct exposure to chemical contaminants, including endocrine disruptors found in common household products, has been suggested. There is much debate around the cause and veracity of the findings. Although there is no suggestion that a *Handmaid's Tale* dystopia is imminent, further research is needed urgently.

Photo: Lei Han

Climate change to increase air pollution deaths

Premature deaths due to air pollution – already estimated at more than 5 million per year globally – will increase as a result of climate change, according to recent research published in *Nature Climate Change*. Based on current trends, climate change will cause an additional 60 000 air pollution–related deaths per year by 2030, and more than 250 000 premature deaths by 2100. Reasons suggested for the increase in deaths include quicker reaction rates of pollutants in warmer temperatures, and higher pollutant concentrations in areas that become drier. The researchers, who predict an increase in air pollution–related deaths in all regions except Africa, call for stronger efforts to mitigate climate change. Outlets reporting the study included *CBS News* (cbsn.ws/2tY7cEw).

The good oil on mercury clean-up

Flinders University researchers have developed a way to clean up mercury pollution with a polymer created from mixing waste cooking oil and sulfur. The method is being trialled at mine sites with a view to commercial production. The Flinders team developed the approach in 2015 using orange oil, but the cost was prohibitive at commercial scales. In the recent study, published in *Chemistry – A European Journal*, the researchers were able to replace orange oil with cheap cooking oil (such as canola) or waste oil from the food industry, and, at the same time, improve the method by capturing a more diverse range of mercury species. Cooking oil and inexpensive sulfur are the only ingredients in the new polymer, which can be used to remediate contaminated soil, water or air. After irreversibly binding the mercury, the polymer granules can be stored safely. The work was reported in a number of publications, including *The Lead* (bit.ly/2vSk7I1).

From the fringe

Complementary medicines may not complement good health

Dr Shankar Bolan
GLOBAL CENTRE FOR ENVIRONMENTAL REMEDIATION, UNIVERSITY OF NEWCASTLE

Complementary medicines – also known as traditional, natural or alternative medicines – include vitamin and dietary health supplements, herbal medicines, and traditional Ayurvedic, Chinese and homeopathic medicines. Contaminants in complementary medicines can include pesticide residues, and toxic heavy metal(loid)s such as cadmium (Cd), arsenic (As), lead (Pb) and mercury (Hg).

This study examines the speciation and bioavailability of heavy metal(loid)s in 12 complementary medicines. We hypothesised that the bioavailability of heavy metal(loid)s in complementary medicines relates to the nature of their speciation.

Methods

The study analysed 6 herbal and 6 Ayurvedic medicine samples for (a) total heavy metal(loid) contents, including As, Cd, Pb and Hg; (b) speciation of heavy metal(loid)s using a sequential fraction technique; and (c) bioavailability of heavy metal(loid)s using a physiologically based in vitro extraction test (PBET). The daily intake of heavy metal(loid)s by consuming these medicines, as measured by total, soluble and bioavailable metal(loid) contents, was compared with the provisional tolerable weekly intake of these metalloids, which is set by the Joint FAO/WHO Expert Committee on Food Additives.

Results

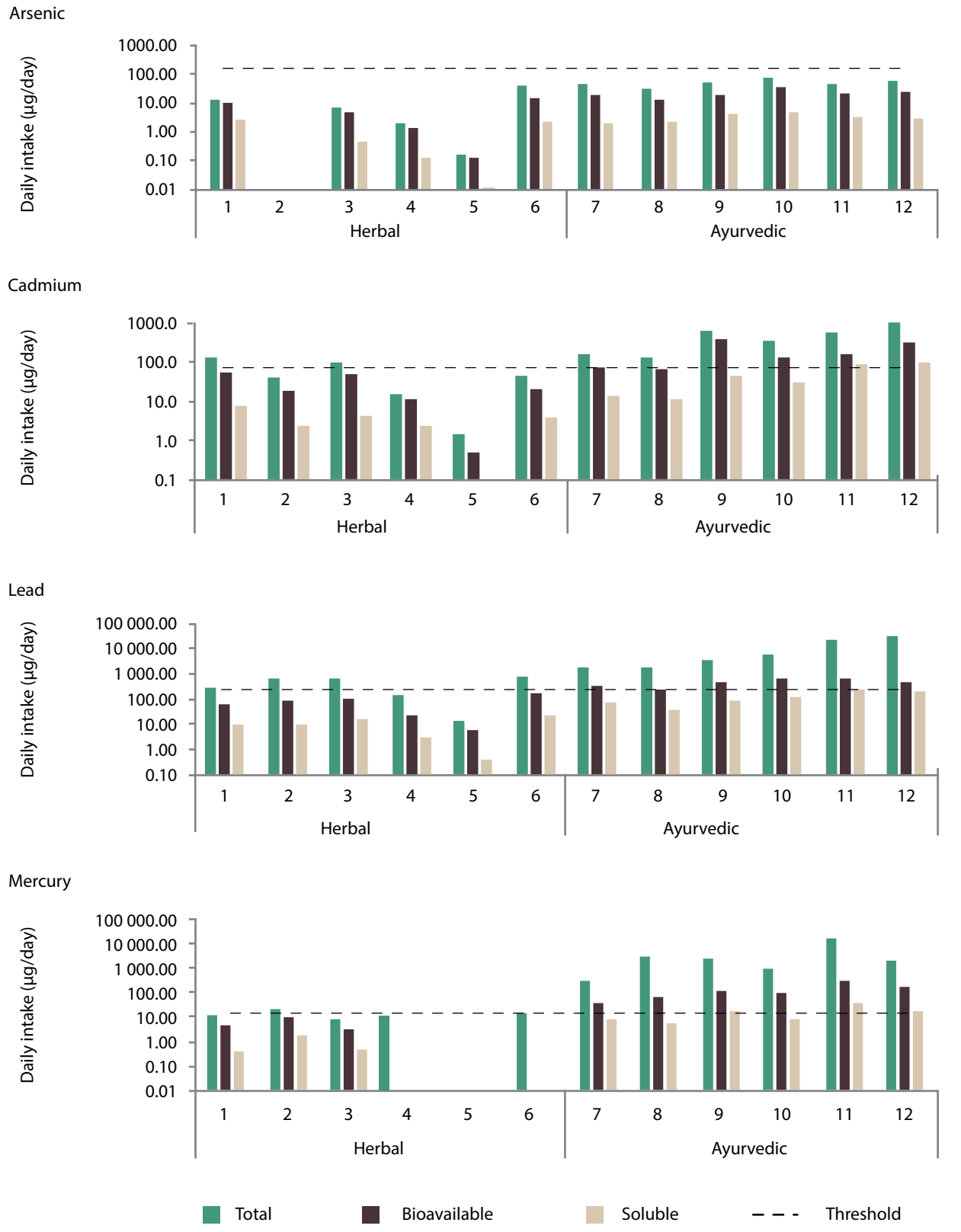
The results indicated that Ayurvedic medicines generally contained higher levels of As, Cd, Hg and Pb than herbal medicines. Of the 4 metal(loid)s, the amount of Pb was by far the highest. The sequential fractionation study indicated that organic-bound metal(loid) species dominated the herbal medicines, and inorganic-bound metal(loid) species dominated the Ayurvedic medicines. This indicates that, for herbal medicines, most heavy metal(loid)s are derived from plant uptake, whereas for Ayurvedic medicines, these heavy metal(loid)s are derived from inorganic mineral input.

The PBET data showed that bioavailability was higher in Ayurvedic medicines than in herbal medicines. This means that heavy metal(loid) s added as a mineral therapeutic input are more bioavailable than those derived from plant uptake. There was a positive relationship between soluble metal(loid) fraction and bioavailability, indicating that solubility is an important factor for controlling bioavailability of heavy metal(loid)s in complementary medicines.

The daily As intake values, as estimated by total, soluble and bioavailable metal(loid) contents, are unlikely to exceed the safe threshold level for both herbal and Ayurvedic medicines (Figure 1). However, the daily intake values for Cd, Hg and Pb, as estimated by total and bioavailable metal(loid) contents, are likely to exceed the safe threshold level in certain Ayurvedic medicines.

Conclusion

This work demonstrates that the bioavailability of heavy metal(loid)s in complementary medicines correlates with the soluble fraction of the respective metal(loid)s. Thus, soluble fractions could be used to predict bioavailability. Heavy metal(loid) toxicity is likely to result from the regular intake of these medicines, which requires further investigation.



µg = microgram

Figure 1 Estimated daily intake of heavy metal(loid)s through complementary medicines based on total, bioavailable and soluble metal(loid) contents, and their corresponding safety guidelines (threshold)

CARE catch-up

Minimising uncertainty in risk assessment

Professor Jack Ng
UNIVERSITY OF QUEENSLAND

As CRC CARE moves into the 6th year of its 2nd funding cycle, its 'Minimising uncertainty in risk assessment' program saw completion of 8 projects, including 3 carryover projects from its first funding cycle. Currently, 4 projects are ongoing, with most likely to be completed in the next 1–2 years.

Table 1 outlines the projects and some of their highlights. CRC CARE recognises that collaboration and interaction are key to its quality outputs. Most of the projects in the risk assessment program involved multiple CRC CARE research providers and partners.

Flagship project on mixed contamination risk assessment

The flagship project on mixed contamination risk assessment involved researchers from the University of South Australia (UniSA; now at the University of Newcastle) and the University of Queensland (UQ). CRC CARE partners, including the environmental protection agencies, consulting companies and external industry professionals, are helping with suitable site identification to provide samples to the project.

This project has also established a new collaborator in China, the Shandong Academy of Occupational Health and Occupational Medicine (SAOHOM), where additional in vivo research is being conducted. The

Table 1 CRC CARE I and II project achievements

Status	Projects
Completed projects	• Development of an in situ, in vitro cell system for real-time measurement of toxicological effects of organic mixtures in the air and groundwater • Development of a unicellular tool for toxicity assessment of individual, and a mixture of, metals and metalloids • Adsorbed chemical species on inhalable iron-rich particles. In vitro toxicology of respirable iron-rich particles relevant to mining industry: a high throughput framework for interpreting environmental particulate matter toxicity (PhD thesis) • Assessing the risk to human health and the environment from mixed contamination • Environmental risk assessment of nanomaterials for soil and groundwater remediation • Data collection to support Port Hedland health risk assessment guidelines • Development of Australian Petroleum Vapour Intrusion (PVI) Guidance • Arsenic bioavailability, biomagnification, detoxification in aquatic systems and ecotoxicological validation
Ongoing projects	• Risk compliance modelling • Mineralogical constraints associated with contaminant bioaccessibility in mine and smelter impacted soils • Create database of speciation, toxicity and bioavailability for prioritised contaminant • Mobility and bioavailability of arsenic and cadmium in biochar-amended paddy soils

Dr Cheng Peng at the Shandong Academy of Occupational Health and Occupational Medicine conducting an in vivo experiment to study DNA damage in mice exposed to mixed contamination of polyaromatic hydrocarbons and metals

in vivo component is not funded by CRC CARE, but the work will complement the in vitro research that is being done by CARE researchers in Australia. So far, 3 PhD students in the project have graduated, and another has nearly completed their studies. One of the mixture toxicology papers published by the UQ team in *Toxicology Research* in 2016 was selected as one of the top 30 most downloaded articles published in the journal that year.

Dr Cheng Peng has been appointed as an Adjunct Professor at SAOHOM. In 2016, Dr Peng was also awarded a 3-year Senior Research Fellowship from Tsung Cho Chang Education Foundation, and is currently working with Prof Jack Ng. Dr Sasikumar Muthusamy (former PhD student) was awarded the best student paper by the Australasian College of Toxicology and Risk Assessment in 2013. He was successfully recertified as a Diplomate of the American Board of Toxicology in 2016. (Prof Jack Ng was recertified in 2015.) Mr Vincent Lal (current PhD student) won a Greg Urwin Award under the Pacific Leadership Program in 2017.

Port Hedland dust project

Scientists from Chemistry Centre Western Australia worked closely with collaborators from the Western Australia (WA) Department of Environment Regulation on the Port Hedland dust project. Other interested parties included the WA Department of Health (DoH), the local community and industry. The research findings provided the basis of a source apportionment model for inputting data into the Port Hedland health risk assessment. A health risk assessment report commissioned by WA DoH was completed in 2016. Toxicity data obtained from another project were also used to support the Port Hedland Interim Air Quality guideline in a recent review report prepared by Prof Jack Ng for the town of Port Hedland in March 2017.

Other projects

The compliance model project is led by Professor Ravi Naidu. The project team receives advisory input from senior university researchers at the University of Queensland and from the United Kingdom, and from regulatory agencies. This ensures rapid adoption of the project outcome in the future.

The nanoparticle project has seen extensive collaborative effort between UniSA and the University of Technology Sydney (UTS), and key players in Europe. Project leader Dr Erica Donner was awarded an Australian Research Council Future Fellowship.

Another productive project in terms of new knowledge gained is the arsenic project, led by UTS in collaboration with UniSA. In particular, the paper on arsenic in Australian rice has drawn media attention and public awareness.

For more about the CRC CARE's risk assessment program, contact Program Leader Professor Jack Ng, University of Queensland.

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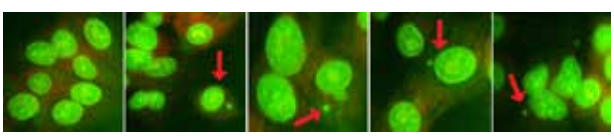

Micronucleus assay to assess chemical-induced DNA damage: normal cells are shown at top, red arrows indicate cells with a micronucleus

Regulator roundup

Per-and poly-fluoroalkyl substances (PFAS) are stable chemical compounds with multiple industrial uses, including as components in firefighting foams, nonstick cookware, food packaging, insecticides, and waterproof and fire-resistant fabrics. However, the stability that makes PFAS so useful also prevents them from breaking down readily. Thus, they can accumulate in the environment, and in the bodies of people and animals exposed to them.

PFAS National Environmental Management Plan released for consultation

Environment protection authorities (EPAs) are developing a PFAS National Environmental Management Plan that aims to provide governments with a consistent, practical, risk-based framework for the environmental regulation of PFAS-contaminated materials and sites.

A draft version of the plan has been released for public consultation by EPA Victoria, which is leading development of the plan. Also involved is the National Chemicals Working Group of the Heads of EPAs Australia and New Zealand (HEPA) in consultation with relevant Australian Government, state and territory agencies.

The plan:

- seeks to build a nationally collaborative approach and national consistency, allowing actions to be implemented in a way that becomes 'business as usual'
- will be designed to respond and adapt to emerging research and knowledge
- will allow implementation through individual jurisdictional mechanisms
- aims to be a reference on the state of knowledge of the environmental regulation of PFAS

As a how-to guide for the investigation and management of PFAS contamination and waste management, the plan seeks to inform actions by EPAs.

The recently released consultation draft provides some background on the state of knowledge of environmental regulation of PFAS and seeks feedback on experiences and views. For more information and to download the draft, visit bit.ly/2vm5uua. The deadline for submissions is 25 September 2017.

PFOS and PFOA to be banned in South Australia

Earlier this year, the South Australian Government announced its intention to ban the future use in South Australia of potentially hazardous firefighting foams containing the PFAS perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), or any other chemicals that degrade to PFOS or PFOA.

The move would see South Australia join Queensland – which in July 2016 introduced a policy to ban the use of the same class of firefighting foams – as one of the first 2 states to implement such a ban.

Although the use of firefighting foams containing PFOS and PFOA has been largely phased out in South Australia, some stockpiles of these foams still exist. The Metropolitan Fire Service has stopped using firefighting foams containing PFOS and PFOA, and has replaced them with alternatives that are not considered to be as potentially harmful to waterways and groundwater.

The South Australian Government will require any existing stocks of foams containing PFOS or PFOA, or chemicals that degrade to PFOS or PFOA, be withdrawn from use.

Earlier this year, South Australia EPA invited public comment on a consultation document outlining the proposed ban. The EPA has since been leading public and industry consultation to determine the best approach to implementation. Topics covered at consultation sessions have included cost and effectiveness of alternative foams, implementation costs for industry, safety issues, and the lack of viable disposal pathways.

The EPA will release a report on the submissions and responses in the coming months.

New guidance on contaminants of emerging concern for contaminated sites

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CRC CARE, NEWCASTLE, AND FUTURE INDUSTRIES INSTITUTE, UNIVERSITY OF SOUTH AUSTRALIA

Dr Bruce Kennedy
CRC CARE, NEWCASTLE

In 2012, CRC CARE identified and prioritised contaminants of emerging concern (CECs) for contaminated site assessment, management and remediation. The priority contaminants are the perfluorinated chemicals perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), methyl tertiary-butyl ether (MTBE), benzo[*a*]pyrene (B[*a*]P), weathered hydrocarbons, and polybrominated diphenyl ethers.

CRC CARE completed literature reviews for these CECs in 2013–14 (see CRC CARE Technical Reports 24, 29 and 32, which can be downloaded at www.crccare.com/publications/technical-reports). Based on the findings, CRC CARE started developing guidance for PFOS/PFOA, MTBE and B[a]P in consultation with industry, regulators and experts in 2015.

CRC CARE has developed risk-based guidance for the assessment, management and remediation of site contamination that is contaminant specific. Human health screening levels (HSLs) and ecological screening levels (ESLs) have been generated for the contaminants.

The guidance is consistent with the National Environment Protection (Assessment of Site Contamination) Measure (ASC NEPM), which focuses on the assessment of contamination. The guidance is also intended to be implemented in a manner consistent with the National Water Quality Management Strategy (eg ANZECC & ARMCANZ,[1] NHMRC,[2] NHMRC & NRMMC[3]).

The guidance is also intended to complement the National Remediation Framework (NRF), which harmonises guidance and best practice for remediation and management of contaminated sites across Australia. More information on the NRF is available at www.crccare.com/knowledge-sharing/national-remediation-framework.

Contaminants of emerging concern

Methyl tertiary-butyl ether

MTBE is not used as an additive for petrol in Australia, although it may be present at levels up to 1% in imported fuels. There are sites at which MTBE contamination occurred before the introduction of the *Fuel Quality Standards Act 2000* and the Fuel Quality Standards Regulations 2001, and so contamination of groundwater at legacy sites is an important consideration.

When it enters the environment through soils, MTBE preferentially enters groundwater or surface waters because of its high water solubility and low affinity to soils. Consequently, limited international guidance is available for MTBE in soil and soil vapour. If MTBE is present in surface waters, it will readily volatilise. For aquatic species, MTBE has relatively low acute and chronic toxicity, with marine species generally showing a greater sensitivity.

MTBE has a low odour threshold, which makes drinking water unpalatable at MTBE concentrations well below those that would affect human health. A screening level based on aesthetics can therefore be used to assess groundwater that is, or may be used for, potable and nonpotable purposes.

The CRC CARE guidance provides a risk-based approach for assessing potentially contaminated sites, and for managing and/or remediating groundwater contamination. Published in CRC CARE Technical Report 36, *Guidance on the assessment, remediation and management of methyl tertiary-butyl ether*, it comprises:

- an odour-based screening level in water
- ecological screening levels that have been derived using a methodology based on ANZECC & ARMCANZ[1] and ASC NEPM

- contaminant-specific considerations for site investigations, including developing the conceptual site model (CSM).

Benzo[*a*]pyrene

B[a]P is a ubiquitous environmental contaminant, particularly in urban areas. It tends to be of greater concern in soil and sediment matrices than in groundwater or surface water because of its very low solubility. B[a]P is persistent in the environment and does not readily degrade, making B[a]P-contaminated soils and sediments difficult and costly to remediate.

The NEPM provides health investigation levels (HILs) and ESL values for B[a]P. There is some concern that these values may be overly conservative. This is because the bioavailability of B[a]P (and hence toxicity to human and ecological receptors) can be reduced, given the tendency of B[a]P to sorb to organic sorb fractions, the age of contamination, soil properties and other factors. Using bioavailability or bioaccessibility measures to derive site-specific criteria for organic contaminants is not well established, and this guidance provides information on the current status to assist decision making.

Further, the NEPM provides ESLs for B[a]P based on the (now outdated) Canadian soil quality guidelines. The CRC CARE guidance reviews several newly available studies and applies Australian methodology (ie ANZECC & ARMCANZ[1]) to generate ESLs that are more reliable.

To understand the implications of HIL and ESL exceedances for some contaminated sites, and the risks posed by B[a]P contamination to human and ecological receptors, it is important to develop a site-specific CSM. The CRC CARE guidance – see Technical Report 38, *Guidance on the risk-based remediation and management of benzo[a]pyrene* – details the potential sources, potential receptors and exposure pathways by which receptors may contact B[a]P.

For situations where B[a]P-contaminated media needs remediation, guidance on developing a remediation strategy is provided. Typical response actions will include no action, re-use, in situ or ex situ treatment, containment or institutional controls, or excavation (soil) / extraction (groundwater) and offsite disposal. Because of the recalcitrance of B[a]P in soil material, treatment options can be limited, making it difficult to reach the low concentrations indicated by the HILs and ESLs. In these circumstances, consideration of the bioavailability of B[a]P becomes important, because this may mean that higher soil concentrations are acceptable.

Perfluorooctanesulfonate and perfluorooctanoic acid

PFOS and PFOA belong to a large group of compounds called per-and poly-fluoroalkyl substances (PFAS). All PFAS are highly persistent, bioaccumulative, and potentially toxic to humans and the environment. They have been found at concentrations of potential concern at a number of sites, particularly where firefighting foams have been used. PFOS is listed as a persistent organic pollutant under the Stockholm Convention.

Industry and public awareness of PFAS both in Australia and internationally is growing rapidly. PFOS contamination is reported frequently in the media, with concerns being raised regarding the possible health risks to humans who may have been exposed.

Information surrounding the occurrence, fate and toxicity of PFAS in the Australian context is limited and incomplete, apart from some hotspots. Because of the persistence and difficulty of treating PFAS contamination, there is also considerable uncertainty about how such contamination can be managed and remediated.

In 2014, when this project started, there were no recognised criteria in Australia for protecting human health and ecological systems, making it difficult to determine the risk posed by contamination. CRC CARE was advised by its Project Advisory Group to invite relevant stakeholders to act as consultants to the project. A large consultation forum was developed comprising regulators, industry and experts, which helped to develop the draft guidelines for PFOS and PFOA in 2015.

The purpose of the CRC CARE guidance is to provide a consistent, risk-based approach to the assessment, management and remediation of PFAS contamination in Australia, specifically:

- HSLs and ESLs for PFOS and PFOA contamination in soil, groundwater, surface water and sediment
- a framework and discussion about applying these screening values
- a risk-based approach to managing and remediating PFOS and PFOA contamination.

In June 2016, enHealth, the peak environmental health body in Australia, selected the European Food Safety Authority health reference values for PFOS (and perfluorohexane sulfonate [PFHxS] combined) and PFOA as interim measures (available at bit.ly/2izR72N. A review of the enHealth position concluded that this was appropriate, given that Food Standards Australia New Zealand (FSANZ) was to conduct a further review.

In April 2017, FSANZ released recommended total daily intakes for PFOS and PFOA, which now take precedence. FSANZ published additional trigger points that should be used when comparing measurements in homegrown produce and food consumption (eg fruits, vegetables, fish, crustaceans, meat, honey, milk, poultry, eggs). In March 2017, before the FSANZ publication, CRC CARE published its interim guidance, with caveats to indicate that the guidance would be revised following the pending FSANZ work (see www.crccare.com/knowledge-sharing/pfos-and-pfoa-guidelines).

The CRC CARE guidance has been updated and will be published following a review by the Project Advisory Group, which includes representatives from regulatory agencies and industry.

What is in the PFAS guidance?

The revised guidance focuses on PFOS and PFOA, which are the most well understood PFAS, and are those most commonly encountered in the environment and in wildlife. Limited information is available for other PFAS compounds. Work on PFOS by both enHealth and FSANZ also considers PFHxS; and therefore, the CRC CARE guidance on HSLs states that PFOS and PFHxS exposures should be combined.

In developing ESLs, the guidance uses Australian methodologies as per ASC NEPM 2013 and the National Water Quality Management Strategy.[1] After the project commenced, the Australian Government Department of the Environment and Energy (DoEE) joined the CRC CARE consultation forum as observers. DoEE started to develop freshwater guideline values for PFOS and PFOA in 2015. CRC CARE continued to develop soil and marine water guideline values, and to provide further guidance on the application of all ESLs. DoEE issued some interim guidance, drawing on the draft CRC CARE guidance document, which can be accessed at bit.ly/2wirOpj.

The CRC CARE document is a comprehensive risk-based guidance for the assessment, management and remediation of PFOS- and PFOA-contaminated sites. The guidance comprises 5 parts.

Part 1: Background

- background to the guidance document
- an overview of PFAS, in particular PFOS and PFOA
- physicochemical properties
- overview of human health and ecological toxicity
- prevalence and behaviour of PFOS and PFOA in the environment
- overview of international guidance and criteria available (at the time of publication)
- current situation in Australia.

Part 2: Human health screening levels

- PFOS and PFOA toxicity in humans
- toxicokinetics of PFOS and PFOA in humans
- human health guideline values
- derivation of human health guideline values
- application of the human health guideline values.

Part 3: Ecological screening levels

- ecological receptors and ecotoxicity of PFOS and PFOA
- factors influencing toxicity, such as bioaccumulation and bioaccessibility
- guideline values for terrestrial and marine aquatic ecosystems
- derivation of ecological guideline values
- considerations in the application of guideline values.

Part 4: Application of human health and ecological screening values

- standalone summary of the human health and ecological guideline values and application information
- essential information to apply the human health and ecological guideline values (users can then refer to parts 2 and 3 for the technical detail and derivation process, if required).

Part 5: Risk-based management and remediation

- framework for the risk-based management and remediation of PFOS- and PFOA-contaminated soil, sediment and water, linking back to the human health and ecological guideline values
- development of a site-specific CSM for PFOS- and PFOA-contaminated sites
- aspects that should be considered in the management and remediation of PFOS- and PFOA-contaminated media.
- available technologies to treat PFOS- and PFOA-contaminated soil, sediment and groundwater, and applications of technologies.

Status of guidance development

The guidance for MTBE, B[a]P and flux has been published, and the guidance documentation for PFOS/PFOA is near completion and expected to be endorsed later in 2017. Following endorsement, all guidance can be downloaded at www.crccare.com/publications/technical-reports.

Opportunities and challenges

The development of guidance for CECs presented several opportunities and challenges. The development of guidance provides invaluable opportunities to integrate science and policy, taking into account the interests of stakeholders in government, industry and academia (and beyond). It is also a positive step towards national harmonisation of approaches, particularly for PFAS, about which there has been much contention in the media in the past 24 months.

The key challenge was the need to balance scientific and practical perspectives, given that knowledge about adverse effects on human health and the environment is still evolving (see Naidu et al[4,5]). The guidance documents provide a collective view of the available science and application of Australian approaches on the development of human health and ecologically based criteria. The guidance emphasises that exceedance of HSLs and ESLs does not necessarily imply that the contamination poses an unacceptable risk, and that the HSLs and ESLs should not be used as remediation targets, since this could result in unnecessary remediation.

Given that the guidance is in the final stage of development, it is important that it is adopted by Australian jurisdictions. It is expected that the engagement of jurisdictions in the development of the guidance will pave the way for consistency in contaminated site practices at the national level.

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National framework for remediating and managing contaminated sites in Australia

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CRC CARE is developing a National Remediation Framework (NRF) for remediating and managing contaminated sites. The NRF is designed to harmonise guidance and best practice in the remediation and management of contaminated sites in Australia, and builds on existing best practice and regulation.

This work is mandated by CRC CARE's agreement with the Australian Government, and is being developed in consultation with governments, industry and experts. The NRF will complement the National Environment Protection (Assessment of Site Contamination) Measure, which deals only with the assessment of contaminated sites. The NRF will not be a legal instrument and therefore will not impinge on the policy and decision making of states and territories.

A harmonised national approach to remediation

A harmonised national approach for remediating and managing contaminated sites will support:

- a nationally consistent approach to managing contaminated sites
- ready transfer of best practice among jurisdictions
- use of national expertise across jurisdictions, thereby improving overall standards over time
- cost-efficiencies for remediation
- a common remediation language across jurisdictions
- training efficiencies, including the ability to ensure that all practitioners meet a recognised professional standard, improved workforce mobility and mutual recognition of skills, and improved recognition of the contaminated sites profession
- improved confidence and certainty.

In addition, the guidance will provide practical procedural guidance to people managing sites, and will educate and inform government, industry and the community about remediation issues.

The aims of the NRF are to:

- protect human health and the environment
- facilitate more effective and efficient remediation

- provide net community benefit (including through consideration of the broader economic context).

National Remediation Framework Steering Group

The NRF Steering Group provides strategic direction for the development of the framework. Its members have significant expertise in the remediation and management of contaminated sites, and include senior representatives from industry (the owners of contaminated sites and the consulting industry), auditors, state and territory environment protection agencies, and the wider community. Other sectors, such as Australian Government agencies, and the airport, planning and health sectors, are also represented.

Status of the framework

The NRF comprises 2 principal areas: philosophy and practice.

The philosophy component includes the agreed principles for the NRF, which are similar to those in the Inter-Governmental Agreement on the Environment, and to those specified in state and territory environment protection legislation. The principles are explained in more detail in Technical Reports 22, 27 and 28, which are part of a series of background reports that can be accessed at www.crccare.com/publications/technical-reports.

The practice component harmonises existing guidance, and documents current Australian practice. A modular approach (comprising topic-specific guidelines) has been adopted to allow the NRF to be updated as circumstances require. Twenty-six draft guidelines can be grouped under three headings:

- development of remediation action plans
- implementation of remediation action plans
- post-remediation considerations.

As draft guidelines are developed and approved for consultation, they are circulated to governments and industry for comment, and posted on the CRC CARE website to enable a broader audience to access them. It is expected that stakeholder feedback will improve the utility of the documentation. Stakeholders include industry (eg site owners, consultants and auditors, financial and planning sectors), regulators and the public.

Draft guidelines released for public consultation can be accessed at www.crccare.com/knowledge-sharing/national-remediation-framework.

Adopting the framework

Wide acceptance of the NRF depends on:

- employing credible expertise in its development
- involving stakeholders through the NRF Steering Group and through consultation on draft documents
- meeting the needs of practitioners and site owners
- ensuring alignment with the objectives and requirements of regulatory agencies.

With the above perspectives in mind, chief executive officers of the government regulatory agencies that oversee environmental protection will be approached to endorse the NRF.

Future work

A 12-month project for compiling and editing the NRF started in December 2016 to prepare the complete NRF for final consultation. This project includes addressing feedback from consultations, ensuring consistency across guidelines (eg terminology), cross-linking to the NEPM and within the NRF, and inserting user-friendly flow charts. This project will assist the Steering Group to finalise the structure of the complete framework package, to prepare it for final consultation in early 2018.

Photo: Arthur Tress

Title blight: is our public policy for contaminated sites creating barriers to remediation?

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Since the 1970s, legislation and regulations have been progressively developed and more stringently implemented in Australia to protect human health and the environment from the adverse effects of land and water contamination. Little research on the consequences of these actions and the extent of the impact on remediation efforts exists in Australia.

An adage among property developers is 'don't buy trouble'. Since the introduction of public policy measures through legislation and regulation to manage site contamination in Australia, developers seem to view parcels of land that require remediation as trouble. That is, they present a number of hurdles, or barriers, to redevelopment, and are perceived as being afflicted with 'title blight' and the attendant reduced value. Many of these barriers have their genesis in the requirements for compliance with, and obligations under, legislation and regulation for managing contaminated sites.

Projected population growth over the next 20 years and the subsequent need for residential housing in Australian capital cities are creating pressure for redevelopment of previously industrial (contaminated) urban sites. Remediation and redevelopment of these sites is considered essential to the sustainable management and allocation of land resources for competing residential, commercial and industrial uses. Currently, there appears to be widespread reluctance by developers to remediate and redevelop contaminated sites that are not, prima facie, profitable.

Do we need government intervention or other measures?

CRC CARE has provided a PhD scholarship to research whether the effects of current Australian environmental public policy for managing contaminated sites has contributed to title blight, and to what extent these effects have created barriers to remediation and redevelopment of sites. This research also aims to determine whether options for mitigation of public policy effects of title blight, including government intervention, are required and justified. Unremediated sites are noted internationally, with some jurisdictions introducing incentives schemes, tax concessions and funding schemes to promote remediation and redevelopment of idle sites.

The literature on barriers to contaminated site redevelopment focuses on:

- fears over future liability, and the legal and litigation costs associated with any disputes with other legally liable parties
- lender reluctance and the difficulty of obtaining finance
- economic uncertainty – the ratio of investment to clean-up and compliance costs
- public perceptions.

There is also a paucity of research, particularly in Australia, that explores the development of incentives schemes as a means to address the effects of specific aspects of public policy designed to protect human health and the environment from site contamination.

Surveys have been developed to gain insight from environmental consultants and auditors, owners of contaminated sites and developers, and real estate agents.

Your help in completing and submitting the survey between now and October 2017 is needed for this important research. Survey links have been delivered to peak industry bodies such as ACLCA and ALGA.

New guidance on flux-based assessment and groundwater management

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In the past, the assessment and management of groundwater contamination has been driven by contaminant concentrations. However, concentration data alone are sometimes not sufficient to fully understand the behaviour or effect of a plume over time. Mass flux and mass discharge estimates are important tools to help practitioners and regulators characterise and remediate groundwater contamination. Their inclusion within remedial design and optimisation, when relevant, may ultimately result in time- and cost-efficient groundwater remediation programs.

In 2014, CRC CARE completed an initial review of available technical information on flux-based criteria for management of groundwater.[1] This review served as the background for developing guidance on flux-based assessment and management of groundwater contamination.

The CRC CARE guidance illustrates how flux concepts, tools and measurements can be used to assess and manage groundwater contamination.[2] Further to the guidance, numerical site-specific metrics for mass flux and mass discharge may need to be developed on a site-specific basis. Mass flux and mass discharge estimates are typically used to complement concentration-based assessments, rather than to replace them.

Using mass flux-based techniques to support regulations

Australian regulations generally emphasise a pragmatic, risk-based approach to the management of groundwater contamination. Mass flux-based techniques are a valuable tool in supporting this approach, in some circumstances. Acceptance of mass flux-based tools and techniques in the management of site contamination will depend on their technical basis and how they are relevant to achieving the overall objectives for a site. For example, by demonstrably reducing risk to an acceptable level.

Mass flux and mass discharge concepts can help fill the gap in understanding, and have been applied successfully both in Australia and internationally to:

- enhance the conceptual site model
- complement concentration criteria
- assist with remedy selection
- optimise remedial design
- assess remedial performance
- demonstrate risk reduction
- evaluate compliance/long-term monitoring.

Environmental effects on mass flux

At a location along a groundwater contaminant plume, the mass flux represents the integrated effects of transport, storage and degradation along the flow path. By definition, mass flux estimates are impacted by factors that affect groundwater flow, such as the hydraulic conductivity and the hydraulic gradient. Therefore, estimates of mass flux are affected by such things as:

- changes in groundwater extraction rates
- groundwater elevation changes
- seasonal variations in velocity or flow directions.

Mass flux estimates are also affected by variations in contaminant concentrations. Factors that may cause contaminant concentrations to vary include redox changes as a result of the infiltration of rainwater, and variations in dissolved phase concentrations due to sorption and the precipitation/dissolution of contaminants.

Heterogeneity in the lithology can significantly affect mass flux. Thus, heterogeneity should be understood before implementing a program to measure and use mass flux at a site. Rather than being homogeneous across the full extent of an aquifer, groundwater flow tends to be concentrated in zones of high hydraulic conductivity that often occupy a relatively small proportion of the aquifer cross-section. This heterogeneity results in a range of mass fluxes across the aquifer.

Estimating mass flux and mass discharge for dissolved phase contaminants in water

In many circumstances, mass flux and mass discharge can provide useful information in addition to concentration data, to help define the contamination plume structure and its evolution over time. Typical monitoring focuses on delineating plume boundaries and concentration trends. However, both concentrations and groundwater flux can vary greatly across a plume, and by focusing only on the plume boundaries, areas of significant contaminant mass flux may be missed.

The CRC CARE guidance identifies 5 key methods to derive mass flux and mass discharge estimates for dissolved phase contaminants in groundwater:

- transect methods
- passive flux meters
- well capture or pump test methods
- transects based on iso-contours
- solute transport models.

As with other site investigation approaches, it is necessary to determine the acceptable level of uncertainty for the intended application of the mass flux and/or discharge information, and how that level of uncertainty can be achieved, managed and assessed.

About the guidance

The guideline provides practical steps on communicating results, along with information on mass flux within the Australian regulatory context for the assessment and remediation of contaminated land.

The guidance on flux has been endorsed for release by stakeholders engaged in the project; see Technical Report 37 on the CRC CARE website at www.crccare.com/publications/technical-reports.

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Photo: Dennis Cowals

Photo: Dennis Cowals

PFAS proficiency testing: better measurement, better management

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PFAS (per- and polyfluoroalkyl substances) are toxic synthetic chemicals known to have potential health and environmental impacts. PFAS are highly resistant to degradation and are very mobile. They are also ubiquitous because of their use in common industrial products such as firefighting foams and nonstick coatings.

In Australia, PFAS have been the subject of recent considerable interest to communities near sites known or believed to be affected by PFAS contamination. These complex contaminants are challenging to measure in the environment and significant discrepancies in laboratory results have been reported. An assumption of measurement reliability and comparability is inherent in the environmental management framework. Guidance, regulation and site assessment can only be effective if the associated data are reliable and comparable. Confidence in the reliability and comparability of the data is vital to deciding the best approach to managing each case.

Proficiency testing (PT) refers to the 'evaluation of participant performance against pre-established criteria by means of interlaboratory comparisons'[1] and provides an independent assessment of performance for participating laboratories. It is a widely accepted approach for improving comparability between laboratories, and it can offer insights into the reasons for variability in analytical results from a variety of methods or laboratories. This knowledge is also of value to anyone who uses and relies on laboratory analysis data, in particular consultants, regulators, auditors, site managers, toxicologists and researchers.

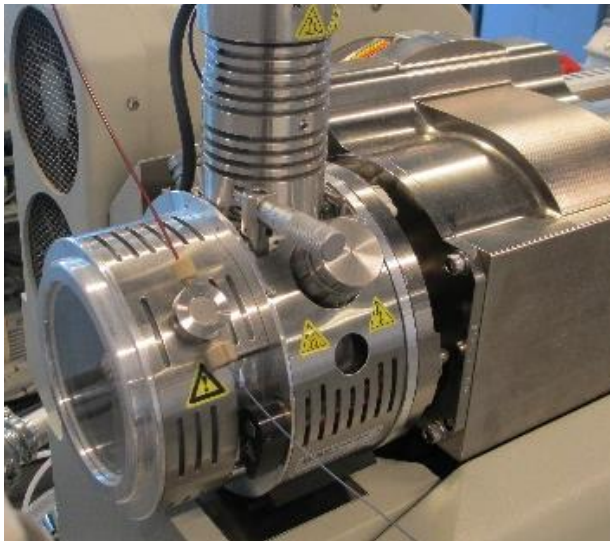
PFAS proficiency testing in Australia

In 2013, the National Measurement Institute (NMI) identified PFAS PT as a significant gap in Australian analytical methodology for environmental measurement.[2] At that time, PT for PFAS was only available through a small number of schemes run occasionally by commercial overseas providers, where local needs might not always align with those of Australia. NMI, with the support of CRC CARE and EPA Victoria, responded to this gap by developing and implementing Australia's first PFAS PT program.

Significant technical challenges had to be overcome in establishing this new national capability, such as the development of innovative sample preparation methods to ensure homogeneity and stability in challenging matrices, and the investigation of factors affecting analysis results. End-user education through national workshops forms an integral part of the NMI PFAS PT program. The program has generated much interest and support from the Australian environment sector.

The first Australian PFAS PT study[3] was conducted in 2015. This study compared data for PFOS (perfluorooctane sulfonate) and PFOA (perfluorooctanoic acid), the 2 best known PFAS, in soil and water samples. NMI conducted a follow-up study in 2016,[4] expanding the matrices tested to include biota. A 2017 study will focus on expanding the number of compounds under consideration.

A key decision in the design of every PT program is the level of contamination to target for the samples provided to program participants. The levels chosen need to address contaminant levels commonly encountered in practice, as well as threshold levels recommended in local guidance. Practical considerations such as the number of participating laboratories able to achieve meaningful results at those levels also need to be considered. For example, the 2015 study concentrated on the 2 matrix types of greatest interest, while using a range of samples that would reflect both typical



Equipment used for PFAS analysis
Photo: National Measurement Institute

environmental background levels as well as the higher concentration levels that might be found in contaminated sites.

A strong emphasis on education and dissemination of study findings to end users beyond the laboratory is a key feature of the Australian PFAS PT program. A workshop has been held after each study to communicate the significance of the results, so that end users across the country can share their views in live discussion on the future gaps that should be addressed by NMI's ongoing PT program.

Findings to date

There has been strong uptake of this initiative by laboratories in Australia and overseas, with 11 laboratories participating in the first study and 24 in the second. The 2016 study included 15 participants from Asia, Europe and North America. Two key indicators of performance, z-scores and En-scores, are related to the difference between an individual laboratory result and the sample value assigned by the study administrator. Some improvement in laboratory performance is apparent between 2015 and 2016, with the percentage of satisfactory z-scores increasing from 79% to 92%. There was little change in the percentage of satisfactory En-scores. The limited data available from 3 international studies suggest that laboratory performance in the Australian studies is at least comparable.

The NMI study AQA 17-08 is currently under way
Photo: National Measurement Institute

Workshop discussions indicate that key technical concerns for end users include:

- the degree and causes of variability between results from different extraction or analysis methods
- whether the type of calibration standards used by laboratories can affect the result and, if so, by what amount
- availability of high-quality standards and any consequent effects on laboratory results
- identifying and addressing the compounds and matrices most likely to be of significance in the future.

These questions have been partly addressed by data from the 2015 and 2016 studies; outstanding issues will continue to be considered in upcoming studies.

Impact of PFAS proficiency testing

The development of an Australian capability for PFAS PT will have a positive impact on the full range of organisations involved in dealing with PFAS contamination. High-quality, transparent proficiency studies provide government policy makers and regulators with the confidence that compliance against environmental guidelines can be assessed and demonstrated. Laboratories have a means for independent comparison of their results against those of their peers; they can use the study results to improve their analysis performance and accuracy. The wider environment sector benefits through an improved understanding of how to use measurement data for their purposes. Auditors and consultants have greater confidence in the recommendations they make based on laboratory data, and site managers are better able to decide the optimal approach for dealing with contamination. Finally, and perhaps most importantly, all of these will ultimately build community trust and confidence in government and industry decisions.

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Is your site contaminated by firefighting foam?

Known as aqueous film-forming foams (AFFFs), some firefighting foam used for many years at airports and fire training facilities contained the potentially toxic chemicals PFOS and PFOA. In many cases, these chemicals have spread to groundwater, drinking water, plants and animals.

This is affecting local communities and is the focus of investigations by regulatory bodies.

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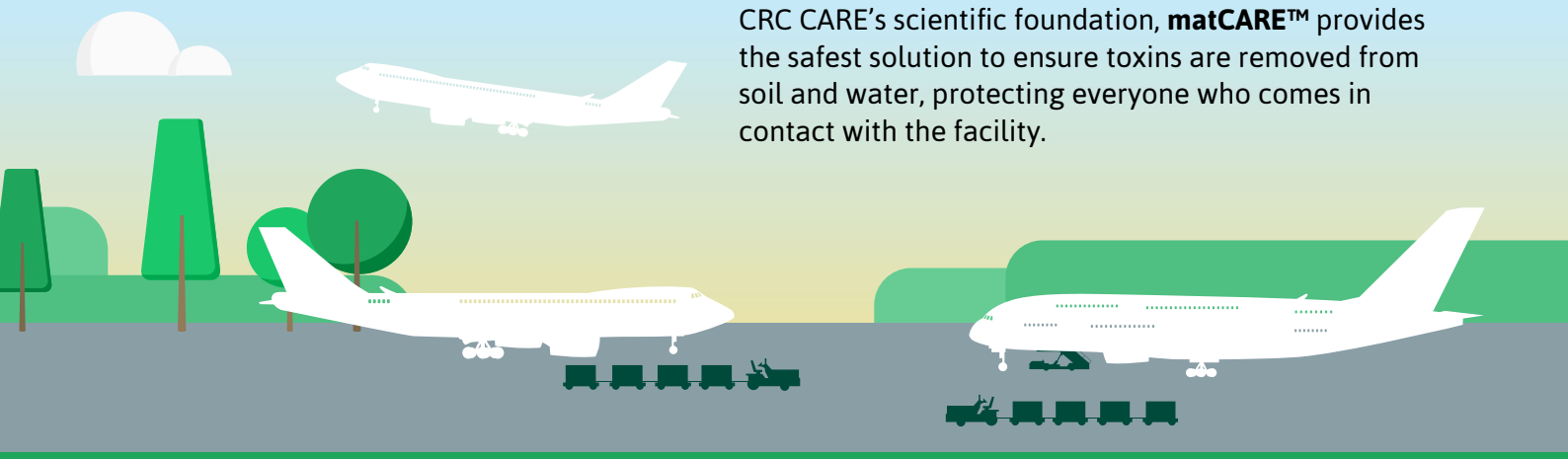

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Developing new adsorbent technologies for removing nitrate from water

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Elevated nitrate concentration is a multifaceted problem. In surface water and groundwater, it can cause eutrophication. When present in drinking water, nitrate can threaten human health – for example, it can cause methemoglobinemia in infants. Thus, finding a way to remove nitrates from water is important for human and environmental health.

Adsorption technology is an attractive method to remove nitrate compared with other technologies in terms of simplicity, cost, design, operation and maintenance, and effectiveness. However, adsorbents with high capacity to selectively adsorb nitrate in the presence of coexisting anions are required to effectively remove nitrate from water. Common adsorbents used for nitrate removal do not have sufficient adsorption capacity. Although some of the commercial adsorbents have high adsorption capacity, they are expensive to use. Cost is especially an issue in developing countries, where nitrate pollution of water is a serious problem due to excessive fertiliser and manure use, and sewage leakages.

Chemical modification of surface charges

In 2013, CRC CARE funded a project that looked to develop novel adsorbents that had high nitrate adsorption capacities, and were effective in remediating nitrate-contaminated waters. An anion-exchange resin, Dowex 21K XLT, was modified by incorporating iron (Fe) on its surface (Dowex-Fe). This increased the surface positive charges. The resin was then tested for its ability to remove nitrate.[1]

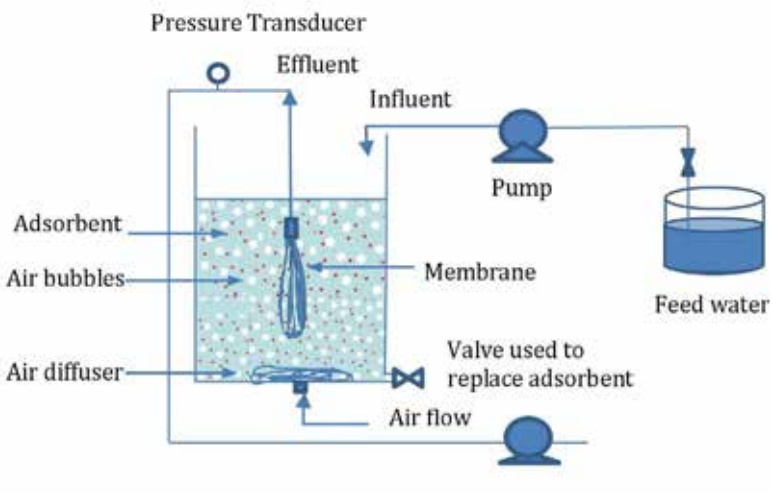
Batch adsorption data showed that the Langmuir adsorption maximum capacity for Dowex-Fe was nearly 3 times (75 milligrams of nitrogen per gram [mg N/g]) that of the unmodified Dowex (28 mg N/g), and higher than many of the values reported in studies involving other adsorbents. The fluidised-bed adsorption capacity was also higher for Dowex-Fe. The resin was successfully regenerated by leaching the resin beds with 1 M potassium chloride (KCl) (more than 95% of nitrate was desorbed). The adsorption capacity of the resin decreased only very little after successive regenerations. The high adsorption capacity and easy regeneration of Dowex-Fe for its repeated use makes it an attractive adsorbent for removing nitrate from water.

The study included chemically modifying inexpensive agricultural wastes to increase their nitrate-adsorption capacities.[2] Low-cost agricultural wastes, corn cobs and coconut copra were surface modified, but by incorporating amine groups to increase the surface positive charges. The Langmuir nitrate adsorption capacities (mg N/g) were 50 and 59 for the amine-grafted (AG) corn cob and AG coconut copra, respectively, at pH 6.5. Fixed-bed adsorption capacities were also high for these adsorbents. The adsorption capacities are higher than many of the other AG agricultural wastes and commercially available ion-exchange resins. In both batch and column experiments, nitrate adsorption decreased in the presence of sulfate, phosphate and chloride, with sulfate being the most competitive anion. More than 95% of adsorbed nitrate was desorbed by 1 M KCl in 4 adsorption/desorption cycles, and the adsorbents were successfully regenerated in each cycle with little reduction in adsorption capacity. Overall, the study showed that the modified agricultural wastes are attractive low-cost biosorbents that can be used in many countries, especially in rural areas where these wastes are produced in large amounts.

Submerged membrane (microfiltration) adsorption hybrid system

A submerged membrane (microfiltration) adsorption hybrid system (SMAHS) was also used for the continuous removal of nitrate with minimal amount of adsorbent. This system can be applied in a real-life process, similar to the column mode of removal described previously. The study showed that the volume of water treated to maintain the nitrate concentration below the World Health Organization limit of 11.3 mg N/L and the amount of nitrate adsorbed per gram of adsorbent for all 4 fluxes tested were in the order Dowex-Fe > Dowex > AG coconut copra > AG corn cob.[3] Increasing the flux increased the volume of water treated and the nitrate adsorbed. The benefits of the SMAHS is that the adsorbent particle size can be small, so that high-adsorption capacities are achieved.

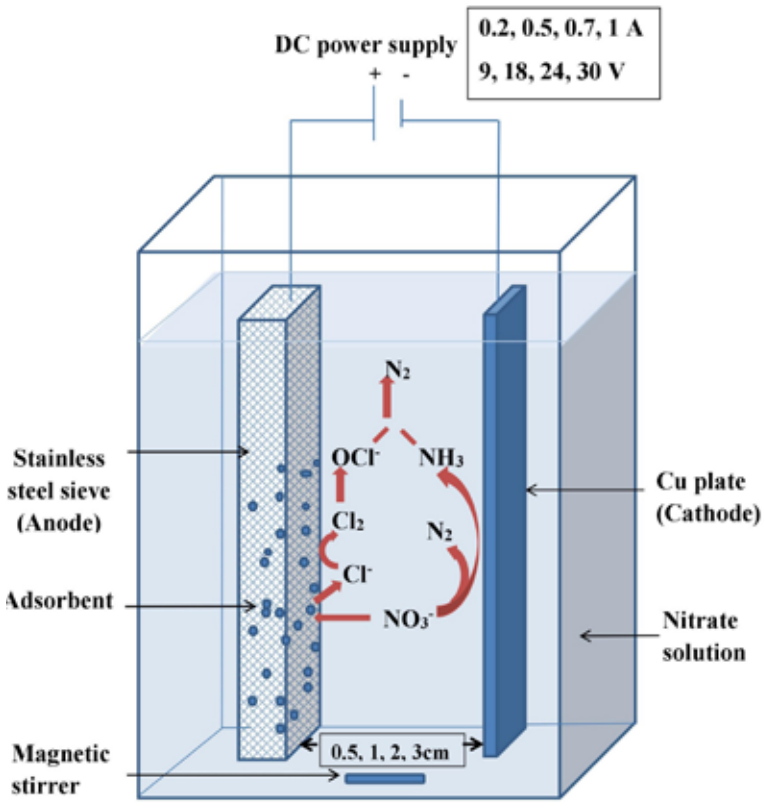
The exhausted agricultural waste adsorbents in the column and SMAHS processes can be directly applied to land as nitrate fertilisers. The desorbed nitrate solution containing potassium can be used in fertigation to supply nitrogen and potassium to plants.



Cross-section diagram of a submerged membrane (microfiltration) adsorption hybrid system

Electrochemical method

The electrochemical method of removing pollutants in water is widely used for treating water and waste water. It is an environmentally friendly treatment technology for removing nitrate and a wide range of pollutants, with less sludge production and less use of chemicals than other treatments. In this treatment method, nitrate ions are converted to nitrogen gas (the main byproduct) and released to the environment. An electrochemical-adsorption system with a Dowex adsorbent was used to determine if it removed nitrate simultaneously



Cross-section diagram of the electrochemical method of removing pollutants in water

using both the adsorption and electrochemical methods. The nitrate removal was found to be high and occurred quickly. This study is novel in that the electrochemical system is integrated with the adsorption process, so that the adsorbent is kept intact with the anode. This is the first time this approach has been tested. In this system, Dowex was added inside an anode stainless steel box, and a copper plate was used as the cathode. The optimum nitrate removal for the integrated system was pH 7, 1 ampere and 31 volts, with the electrodes 1 centimetre apart. Nitrate removal in the integrated system is approximately the sum of the removals from the individual processes.

The results seen in the single-cell system are encouraging. We propose to extend the single-cell system to a series of cells connected to each other for continuous nitrate removal.

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Using smartphones to detect PFAS in aqueous film-forming foam

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A monitoring tool that can prescreen aqueous film-forming foam (AFFF) for the contaminants perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) would be incredibly useful to industry. Ideally, the tool could be used onsite or in nonspecialised laboratories, and have high sensitivity, specificity and selectivity. CRC CARE has recently developed a smartphone app to selectively detect PFOA/PFOS down to 0.5 parts per billion (ppb), which could be this prescreening tool.

Poly- and perfluoroalkyl substances (PFAS) are a human-made family of compounds, to which PFOA and PFOS belong. PFAS generally contain multiple F–C bonds, which lead to their unique properties, such as simultaneous hydrophobicity and oleophobicity, that is not seen in other compounds.[1] Consequently, PFAS have become widely used in items such as clothing, upholstery, carpeting, painted surfaces, food containers, cookware and firefighting foams.[2] Unfortunately, the F–C bond is among the most stable covalent bonds known in chemistry, and is highly resistant to degradation. For example, PFOA has been reported to have a half-life of about 40 years and PFOS of about 91 years in water (USEPA 505-F-14-001). Because of their widespread use and high persistence, they are detected all over the world – from in humans to the deep sea. PFOA/PFOS have been reported to have adverse effects on humans, and have been listed as emerging contaminants and persistent organic pollutants. Thus, their monitoring is urgently needed.

Problems with current monitoring methods

Currently, high-performance liquid chromatography-mass spectrometry (HPLC-MS) is used to analyse substances for the presence of PFOA/PFOS.[3] However, HPLC-MS is time-consuming, expensive (>$100/sample) and must be carried out in professional laboratories. Therefore, a mechanism that allows them to be detected by a nonspecialised laboratory or even onsite using prescreening tools before quantitative measurement is highly desirable. Recently, CRC CARE has explored several testing kits or sensors, such as astkCARE™, an improved version of methylene blue active substrates, molecular-polymer-based ion-selective electrode (ISE) and surface-enhanced Raman scattering. However, the selectivity and sensitivity have been challenged in these solutions, or cumbersome set-up or instrumentation is needed.

A colour-based assay may be the simplest way to test for PFOA/PFOS, such as that used in astkCARE, an assay previously developed by CRC CARE. Here, anionic surfactants, including PFOA/PFOS, react with the cationic dye in the test to form an ion pair. This ion pair is hydrophobic, because the hydrophilic terminate has been blocked by the dye. Consequently, this ion pair is immiscible in the aqueous phase, so that it can be extracted into a non-aqueous phase for colour justification. However, this visual detection is highly dependent on the colour justification with the colour chart provided as reference, which means it is a semi-quantitative test with a large variation. Furthermore, the visual fatigue and the interference from illumination in the background may also be problematic.[4]

Taking advantage of mobile technology

Mobile phones are now incredibly widespread. As of 2016, more than 1 billion iPhones alone had been sold. Modern high-tech smartphones are equipped with features such as a high-resolution camera, high-speed processor, touchscreen display, high memory capacity and long-life battery. Therefore, smartphones offer a platform to increase sensor availability and accessibility, particularly for portable sensors and kits. In addition, with the development of user-friendly smartphone apps,

combined with other gadgets – such as GPS to mark the test position, network connectivity to share the information, online help and demos – smartphones could drive a new direction in sensor development for onsite testing.

App-based sensors

An app-based sensor might lose some sensitivity when compared with a more sophisticated instrument. For example, the concentration of PFOA/PFOS is usually at the ppb level, which is much lower than that of inorganic ions, such as chloride at the parts per million (ppm) level or higher. Fortunately, the possible interference from inorganic ions can be removed by solid phase extraction (SPE). Furthermore, by using SPE, PFOA/PFOS can be concentrated (by 100–1000 times in volume) to a higher concentration level (such as ppm) before the assay, to improve the testing sensitivity.

Another issue is the selectivity of the sensor. In principle, any anionic surfactant – such as sodium dodecyl benzene sulfonate (SDBS), a commonly used detergent – will demonstrate interference when it forms an immiscible ion pair and is extracted using SPE to enter the non-aqueous layer. Fortunately, F-SPE is now well established and offers a good opportunity to extract F–C skeletons because of the unique F–F interaction. In this case, only PFOA/PFOS that contain F–C chains will be extracted, whereas other anionic surfactants, including SDBS, which do not share an F–C skeleton, will not be extracted. Consequently, PFOA/PFOS will be tested without interference originating from the nonfluorinated compounds, such as SDBS.

CRC CARE has improved astkCARE by developing a smartphone app to read the PFOA/PFOS concentration with a digital output. By using a reading kit to stabilise the background illumination, the assay establishes a link between the colour and the concentration. The output concentration variation is successfully restricted to <10% in a range of 10–1000 ppb. Furthermore, CRC CARE recommends using SPE to preconcentrate the PFOA/PFOS to improve the assay's sensitivity, followed by F-SPE to remove the interference from nonfluorinated anionic surfactants. Thus, CRC CARE's app can detect PFOA/PPFOS with a limit of detection of 0.5 ppb, suggesting the app could be used as a prescreening tool in the common laboratory and for onsite testing.

PFAS analysis and remediation technologies

In addition to astkCARE**, CRC CARE has developed several technologies for analysing or cleaning up PFAS contamination.**

matCARE™

matCARE is a modified clay sorbent that irreversibly immobilises PFAS, including PFOS and PFOA, in soil and water. This technology remediates PFOS and PFOA in AFFF-contaminated wastewater to <0.002 µg/L, which is well below the US EPA's 2016 drinking water health advisory levels of 0.07 parts per billion.

pfasCARE™

pfasCARE is a new technology developed by the CRC CARE. It uses electricity to generate extremely strong oxidising agents (including free radicals) that strip the PFAS molecules of electrons, thus breaking them down into smaller – and safer – components. Previously, this approach has been prohibitively costly, requiring expensive materials, such as diamonds, to be effective. pfasCARE uses lead peroxide (a common, inexpensive industrial material) to dramatically cut the cost of production.

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A real-time, in situ technology for measuring ions in water

Professor Ravi Naidu, Dr Liang Wang, Associate Professor Zuliang Chen and Professor Megharaj Mallavarapu

CRC CARE AND GLOBAL CENTRE FOR ENVIRONMENTAL REMEDIATION, UNIVERSITY OF NEWCASTLE

Controlling the quality of irrigation water is important for crop and plant growth. Water quality can be monitored in situ using an ion-selective electrode (ISE) array with suitable data processing algorithms. CRC CARE has developed a novel technique – the probeCARE™ system – for measuring ions in solution, using ISE arrays[1-2] and software that allows real-time measurement.

The probeCARE system can measure common ions – such as sodium (Na), potassium (K) and calcium (Ca) – in complex solute matrices, even in coloured solutions. This is of value to agricultural irrigators, and for monitoring water quality in lakes and streams.

The probeCARE unit in use onsite

Advantages of probeCARE

Existing techniques for measuring water quality use laboratory equipment that is too large and heavy to use in the field. In addition, the processing times and equipment costs are prohibitive. The probeCARE system is small and portable. It uses probes with wireless data loggers, and the mobile phone network sends data from the field to a computer.

Currently, for online in situ monitoring of irrigation water qualities, only information such as pH, electrical conductivity (EC) and total dissolved salt content can be measured. Individual components of the nutrient solution cannot be simultaneously monitored. By using the probeCARE system, all the essential macroelements in irrigation water such as Ca, chloride (Cl), nitrate (NO_3), K and Na can be simultaneously measured, within acceptable error ranges.

These qualities make probeCARE a cost-effective, fast and accurate technology.

Real-world application: using probeCARE to create an intelligent fertigation system

Fertigation is the application of liquid fertiliser into irrigation systems. Liquid fertilisers are injected directly into the irrigation water and carried to the plant root zone. Inorganic fertilisers are usually used with fertigation systems, because inorganic fertilisers have the advantage of being quick-release formulations that allow nutrients to become rapidly available to plants.[1]

However, the disadvantage of inorganic fertilisers is that nutrients are also easily leached from the soil by rain or excess irrigation.[3] When fertilisers are applied to fields, the

plants do not use it all. Excess fertiliser infiltrates the soil and accumulates in aquifers. Therefore, to avoid excess use of inorganic fertilisers, recycling the water and fertiliser are important components of the fertigation system.

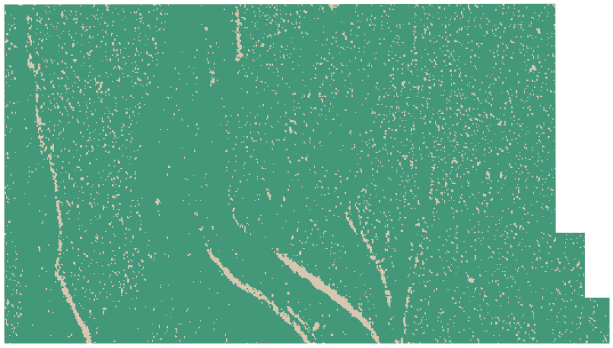
To optimise crop production, it is necessary to know the type and quantity of fertilisers to be added to the fertigation system at each stage of plant growth. To control several fertilisers that need to be added to the system, the water quality of the irrigation water sources must be understood in real time. Furthermore, after fertilisers are injected into the system, the final water quality carried to the plant root zone has to be determined. Therefore, real-time, in situ water quality monitoring is essential.

The probeCARE system can measure the responses from the ISE array in any unknown solution and predict the concentration directly using the novel pattern recognition procedure. To determine irrigation water quality, two important indexes are used:

- salinity, which is the total soluble salts in the water
- sodicity, measured as the sodium adsorption ratio (Na + K : Ca + Mg).

Inorganic fertilisers contain the primary macronutrients NO_3 and K.

Therefore, 6 important elements should be monitored by the fertigation system: Ca, Cl, Mg, NO3, K and Na. These microelements, which are commonly found in high concentrations in irrigation waters, are essential for determining water quality and influencing crop yield, soil productivity and environmental contamination. Unfortunately, when using traditional techniques for analysis, the interaction and interference that occur among these elements in environmental samples may severely limit the application of ISEs.[4,5] However, determining these elements simultaneously and directly using the probeCARE system may offer a way to develop an intelligent fertigation system.



Other potential applications

The probeCARE system gives fast and accurate results that can be used:

- in agronomy and horticulture
- to support management strategies for cropping, fertigation and effective use of recycled water
- to monitor for possible pollutants to ensure environmental protection agency standards are achieved
- as a real-time nutrient monitoring system for many vegetable crops
- to analyse irrigation water quality
- in natural environment management, such as for waste water management
- as a nutrient monitoring system for freshwater waterways and reservoirs.

In addition, probeCARE is being developed with internet connectivity to support remote sensing and continuous monitoring of critical resources. The technology is in the early stages of commercialisation, but its commercial potential is likely to improve in the medium to long term.

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Training and events calendar

2017

10–14 September
CleanUp 2017 – the 7th International Contaminated Site Remediation Conference incorporating the 1st International PFAS Conference
CRC CARE/Melbourne
www.cleanupconference.com

13 September
Environmental Law and Policy Update Seminar
Australian Sustainable Business Group/Sydney
http://bit.ly/2fok68r

26–28 September
Conference and Exhibition on Emissions Monitoring
ILM Exhibitions/New Delhi, India
www.ilmexhibitions.com/cemindia

11–12 October
Waste Expo Australia
Reed Exhibitions Australia/Melbourne
www.wasteexpoaustralia.com.au

29 October – 1 November
Environment Institute of Australia and New Zealand Annual Conference
EIANZ/Wellington, New Zealand
www.eianz.org/conference-information/conference

29–30 November
Petroleum, Petrochemical and Chemical Conference (PEFTEC) 2017 International Conference
ILM Exhibitions/Antwerp, Belgium
www.peftec.com

2018

20–22 February
Australian Waste to Energy Forum
Australian Industrial Ecology Network/Ballarat
http://aien.com.au/wteforum

5–7 March
20th World Congress on Biotechnology and Biotech Industries Meet
ConferenceSeries/London, UK
http://biotechnology.conferenceseries.com

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Publications update

This section contains publications from research institutions, regulators or industry groups, which have been published since the last issue of *Remediation Australasia*. Email us at RAmag@crccare.com if you have any publications to be considered for inclusion (no promotional material).

CRC CARE has published several new Technical Reports, all of which are available for free download, along with all of those previously published, at www.crccare.com/publications/technical-reports:

- Technical Report 25 – *A framework for selecting, designing and implementing a permeable reactive barrier system* (national guideline document)
- Technical Report 30 – *Landfill futures*
- Technical Report 33 – *Advanced Lidar Port Hedland dust study: broadscale, real-time dust tracking and measurement*
- Technical Report 35 – *Value-based land remediation: Improved decision-making for contaminated land*
- Technical Report 36 – *Guidance for the assessment, remediation and management of MTBE*
- Technical Report 37 – *Flux-based groundwater assessment and management*
- Technical Report 38 – *Assessment, management and remediation for PFOS and PFOA* (parts 1 to 5)[a]
- Technical Report 39 – *Risk-based remediation and management guidance for benzo[a]pyrene*.

CL:AIRE. *Petroleum hydrocarbons in groundwater: guidance on assessing petroleum hydrocarbons using existing hydrogeological risk assessment methodologies,* CL:AIRE, London, 2017, www.claire.co.uk/phg.

Nuruzzaman M, Rahman MM, Liu Y, Naidu R. Nanoencapsulation, nano-guard for pesticides: a new window for safe application. *Journal of Agricultural and Food Chemistry* 2016;64(7):1447–1483. This publication was ranked in the journal's 5 most read papers in 2016 for the Biological Chemistry and Applied Chemistry categories.

a At the time of publication, this report was considered draft and interim, particularly in relation to health-based screening values. In response to recently revised health reference values, the health-derived values in CRC CARE's guidance are being updated, and the guidance will be reissued.

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