Human and ecological risk assessment of contaminated sites – Key knowledge gaps

Ravi Naidu[A,B], Nanthi Bolan[A,B], Mallavarapu Megharaj[A,B], Albert Juhasz[A,B], Enzo Lombi[A,B] and Euan Smith[A,B]

[A]Centre for Environmental Risk Assessment and Remediation (CERAR), University of South Australia, Mawson Lakes, Adelaide, South Australia, Australia – 5095.
[B]Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE), University of South Australia, Mawson Lakes, Adelaide, South Australia, Australia – 5095. Email: ravi.naidu@crccare.com

Abstract
Since the inception of the Industrial Revolution, human activities have substantially accelerated the cycling of contaminants in the environment. This has resulted in a large number of contaminated sites worldwide. Environmental legislation dealing with risk assessment and remediation has been traditionally based on total contaminant concentrations. The main cause for this pragmatic approach has been related to knowledge gaps in human and ecological risk assessment. Here we discuss a number of important gaps, namely contaminant bioavailability, mixed contaminant ecotoxicology and emerging contaminants. The concept of bioavailability has gained significant acceptance but its implementation into the terrestrial regulatory framework is still hindered by the limited availability of validated methodologies. While in the case of lead and arsenic human risk assessment the state-of-the-art is such that bioavailability-based risk assessment will be incorporated in the near future into legislation, the situation for other inorganic and organic contaminants is still far from being resolved. The second key knowledge gap is related to mixture of contaminants. While contaminant mixtures represent the norm in real case scenarios, environmental legislations are generally based on individual contaminants. These knowledge gaps also apply to the area of emerging contaminants that in itself is challenging in terms of human and ecological risk assessment.

Key words
Bioavailability, emerging contaminants, human and ecological risk assessment, mixed contaminants, remediation

Introduction
Over the past 150 years, urban development, industrial, agricultural, military, mining and medical activities have generated large quantities of hazardous wastes that have resulted in environmental contamination issues. Thousands of organic and inorganic contaminants enter the soil environment as a result of these activities, with physical, chemical and biological processes including sorption to soil surfaces, diffusion into nanopores and mineral particles, partitioning into organic material, volatilization, degradation (biotic and abiotic), transformation etc. influencing their fate and potential hazard. While it is difficult to quantify, it has been estimated that the number of contaminated sites in Australia is approximately 100,000 with an estimated remediation / management cost of $5-8 billion. These values are small compared to the number of contaminated sites and estimated remediation costs in Europe and the US. Due to the toxic, mutagenic, teratogenic and carcinogenic properties of many environmental pollutants, there is great concern regarding the presence of these substances in the environment. While the cost to society of exposure to environmental contaminants is difficult to calculate, in the US alone, it has been estimated that the cost of cancer resulting from environmental pollutant exposure in 2008 was in excess $13.7 billion (ACS 2009).

As a result of the potential risk to human and environmental health from the exposure to these contaminants, remediation of contaminated land has become an increasing priority. The major objective of any remediation process is to reduce the actual or potential environmental threat and reduce unacceptable risks to man, animals and the environment to acceptable levels. Strategies to either manage and/or remediate contaminated sites have developed largely from application of stringent regulatory measures set up to safeguard ecosystem function as well as to minimize the potential adverse effects of contaminants on environmental and human health. While our understanding of contaminant fate and transport is ever increasing, knowledge gaps still exist which may impact remediation requirements and the associated resources and expense. Key knowledge gaps for environmental risk assessment include:

1. Contaminant bioavailability
2. Mixed contaminants
3. Emerging contaminants

Contaminant bioavailability

This area of research has attracted considerable investment in the last few decades. Bioavailability assessment in the context of environmental risk is a considerable task as contaminant bioavailability is not only controlled by the chemical-physical processes occurring in the soil but also by the variability in biological response between different animal, plant and microbial species. In the context of human health risk assessment and remediation decisions, contaminant bioavailability is fundamental in determining acceptable endpoints and potential clean up options. Bioavailability controls the amount of the contaminant, obtained via ingestion, inhalation or dermal pathways, that reaches systemic circulation. As a result, to enhance risk assessment and remediation decisions, fundamental knowledge is required on how to assess contaminant bioavailability, the impact of physicochemical parameters on bioavailability and how this information can be used to better quantify exposure for human health risk assessment. While it is assumed that contaminant bioavailability may vary depending on a variety of environmental parameters, its determination in the context of human health risk assessment is lacking for the majority of contaminants.

A major constraint in the assessment of contaminant bioavailability is the associated costs. Although *in vivo* studies utilizing appropriate animal models are an appropriate method for determination of contaminant bioavailability for inclusion in human health exposure assessment, the time required for *in vivo* studies, the expense of animal trials and ethical issues preclude their use as routine bioavailability assessment tools. As a result, rapid, inexpensive *in vitro* methods simulating gastrointestinal conditions in the human stomach have been developed as surrogate bioavailability assays. These assays determine contaminant concentrations that are solubilised following gastrointestinal extraction and are therefore available for absorption into systemic circulation (bioaccessible fraction). *In vitro* assays have the potential to overcome the time and expense limitations of in vivo studies thereby providing a surrogate measurement of bioavailability that is quick and inexpensive compared to animal models (Ruby *et al.* 1996; Basta *et al.* 2001). However, before these assays can act as a surrogate measurement for contaminant bioavailability, the correlation between *in vivo* bioavailability and in vitro bioaccessibility is a mandatory prerequisite for both regulatory and scientific acceptance. While *in vivo-in vitro* correlations have been determined for inorganic contaminants (Figure 1) such as arsenic (Rodriguez *et al.* 1999; Basta *et al.* 2001; Juhasz *et al.* 2007; Juhasz *et al.* 2009a) and lead (Schroder *et al.* 2001; Drexler and Bratton, 2007; Juhasz *et al.* 2009b), a dearth of information is available on the assessment of organic contaminant bioavailability for refining exposure for human health risk assessment. The development of validated tools for quantifying contaminant bioavailability is an ongoing research priority as outcomes will reduce the uncertainty associated with exposure assessment which will refine risk calculations.

It should also be noted that human health risk assessment for contaminated soil based on bioavailability poses some challenges in terms of future liability. In fact, bioaccessibility measurements are based on an assessment at a specific time and environmental conditions. Changes in these conditions over time may enhance or reduce bioaccessibility in ways that are difficult to predict. A consequence of this is that, if bioaccessibility is used as a driver and as an assessment of remediation, the longevity of a remediation treatment must also be considered in terms of bioaccessibility in the medium to long term. In other words, because of the dynamic nature of bioaccessibility, remedial actions driven by a bioaccessibility may require long-term monitoring.

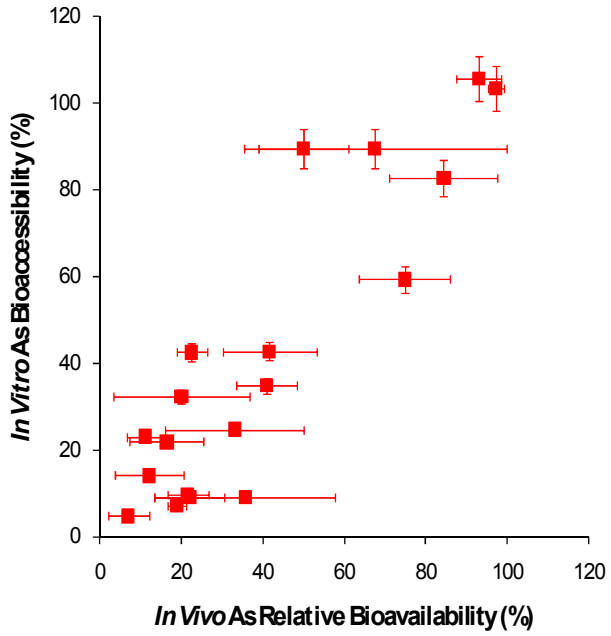

Figure 1. Relationship between arsenic relative bioavailability, determined using an *in vivo* swine assay and *in vitro* arsenic bioaccessibility using the gastric phase of the SBRC assay (SBRC-G). Arsenic relative bioavailability (%) = 0.99 x SRBC-G + 1.66, r2 = 0.75; Pearson correlation = 0.87 (Juhasz *et al.* 2009a).

Mixed contaminants

At the majority of contaminated sites, pollutants are present as mixtures. This is due to both geogenic and anthropogenic processes. In the case of heavy metals and metalloids, specific mineralogical associations can be found in nature and are due to chemical and physical similarities of various elements. For instance, zinc ores also contain significant amounts of lead and cadmium while arsenic is often associated with gold or copper ores. Consequently, mining and smelting operations almost always result in multi-element contamination. Other common sources of contamination, such as the use of pesticides, the disposal of sewage sludge, animal manures and slurry, and waste-derived products (e.g. composts) on land, also results in the release into the environment of a complex mixture of organic and inorganic contaminants. Consequently, both human and ecological receptors are exposed to contaminant mixtures. However, toxicological research is dominated by studies of single contaminant exposure rather than assessing mixture toxicity. This approach neglects mixture effects that could reduce or enhance contaminant toxicity due to antagonistic or synergistic processes. In the environment it is often the case that many contaminants may be present at concentrations close or below their individual no observed effect concentrations (NOEC), yet in a mixture they may contribute to substantial effects (Altenburger *et al.* 2003). Also, the presence of toxicant mixtures in the field has been identified as one of the key factors causing differences between laboratory and field based toxicity data (Weltje 1998).

At the legislative level, the need to incorporate mixture interaction in the regulatory framework has been recognised by regulating authorities but the process of incorporation of mixture toxicity in regulations has been hindered by the paucity of studies available, especially for the terrestrial environment. This translates into regulations that focus on the effects of individual chemicals where mixture effects are considered only indirectly via safety/assessment factors, which are often contentious. The development of scientifically-based regulations can only be achieved when the relevant information is available. However, work focusing on mixture toxicity in the terrestrial environment has been fragmented and the information available is scarce and inconsistent especially in the case of plant and microbial toxicity. Possibly the main reason is related to the fact that information regarding mixture toxicity requires a very large number of observations. However, various approaches for testing this type of interactions have been proposed that allow extraction of the relevant information while substantially decreasing the amount of data required.

Emerging contaminants

The widespread occurrence of newly identified contaminants such as polybrominated diphenyl ethers (PBDEs), perfluorinated chemicals (PFOS, PFOA etc.), illicit drugs, personal care products, antiviral agents, nanoparticles etc. in the environment is of growing concern. While information regarding their fate,

transport and human/ecological effects is starting to emerge, limited data is available which could be used for regulatory guidance. For example, PBDEs and perfluorinated chemicals are a class of industrial chemicals widely used in various industrial applications including as fire retardants, are highly resistant to degradation, bioaccumulative and have behavioral properties similar to persistent organic pollutants (e.g. PCBs, DDT). Human exposure to PBDEs is reflected by the considerable increase in the concentration of PBDEs in breast milk. Birnbaum and Staskal (2004) reported that PBDEs in breast milk of North American women increased from <1 μg/l to 200 μg/l over a 25 year period while Meironyté *et al.* (1999) reported a 60-fold increase in the concentration of PBDEs in Swedish woman breast milk between 1972 and 1997. While international efforts have documented the accumulation of PBDEs in humans, regulatory guidance on these compounds is lacking. In Australia, recent research revealed the presence of PBDEs in carpet dusts and soil from several peri-urban localities. Greater than 65% of soil and sediment samples (n = 60) collected from industrial, recreational and waste dumps in Adelaide (South Australian) contained PBDEs including BDE- 7, 17, 28, 47, 77, 100, 119, 99, 85, 154, 153, 138, 183, 196, 197, 207, 206 and 209. The concentrations of ∑PBDEs in samples ranged from 320 to 1050 ng/g while at point sources, ∑PBDEs ranged from 230 to 3470 ng/g. This study illustrated that the use of PBDEs at point sources (e.g. plastic industries) may lead to contamination of nearby environments, however, their potential impact on environmental health is largely unknown. A major challenge associated with emerging contaminants, such as PBDEs, include the evaluation of their health risks given limited knowledge on the toxicity and environmental behaviour of these chemicals.

References

ACS (2009) Cancer facts and figures. American Cancer Society, Atlanta, Georgia.

Altenburger R, Nendza M, Schüürman G (2003) Mixture toxicity and its modeling by quantitative structure-activity relationships. *Environmental Toxicology and Chemistry* **22**, 1900-1915.

Basta NT, Rodriguez RR, Casteel SW (2001) Bioavailability and risk of arsenic exposure by the soil ingestion pathway. In 'Environmental Chemistry of Arsenic'. (Ed WT Frankenberger Jr) (Marcel Dekker, New York).

Birnbaum LS, Staskal DF (2004). Brominated flame retardants: cause for concern? *Environmental Health Perspectives* **112**, 9-17.

Drexler JW, Brattin WJ (2007). An in vitro procedure for the estimation of lead relative bioavailability: with validation. *Human and Ecological Risk Assessment* **13**, 383-401.

Juhasz AL, Smith E, Weber J, Rees M, Rofe A, Kuchel T, Sansom L, Naidu R (2007) Comparison of in vivo and in vitro methodologies for the assessment of arsenic bioavailability in contaminated soils. *Chemosphere* **69**, 961-966.

Juhasz AL, Weber J, Smith E, Naidu R, Rees M, Rofe A, Kuchel T, Sansom L (2009a) Assessment of four commonly employed in vitro arsenic bioaccessibility assays for predicting in vivo relative arsenic bioavailability in contaminated soils. *Environmental Science and Technology* **43**, 9487-9494.

Juhasz AL, Weber J, Smith E, Naidu R, Marschner B, Rees M, Rofe A, Kuchel T, Sansom L (2009b) Evaluation of SBRC-gastric and SBRC-intestinal methods for the prediction of in vivo relative lead bioavailability in contaminated soil. *Environmental Science and Technology* **43**, 4503-4509.

Meironyté D, Noren K, Bergman A (1999) Analysis of polybrominated diphenyl ethers in Swedish human milk. A time-related trend study, 1972-1997. *Journal of Toxicology and Environmental Health* **58**, 329-341.

Rodriguez RR, Basta NT, Casteel SW, Pace L (1999) An in-vitro gastro-intestinal method to assess bioavailable arsenic in contaminated soils and solid media. *Environmental Science and Technology* **33**, 642-649.

Ruby MV, Davis A, Schoof R, Eberle S, Sellstone CM (1996) Estimation of lead and arsenic bioavailability using a physiologically based extraction test. *Environmental Science and Technology* **30**, 422-430.

Schroder JL, Basta NT, Casteel SW, Evans TJ, Payton ME, Si J (2004) Validation of the in vitro gastrointestinal (IVG) method to estimate relative bioavailable lead in contaminated soils. *Journal of Environmental Qual*ity **33**, 513-521.

Weltje L. (1998) Mixture toxicity and tissue interactions of Cd, Cu, Pb and Zn in earthworms in laboratory and field soils: A critical evaluation of data. *Chemosphere* **36**, 2643-2660.