

METALS IN THE HUMAN ENVIRONMENT (MITHE) RESEARCH NETWORK 2007 ANNUAL SYMPOSIUM

Project Title:

(I4) Bioaccessible Metals from Ingested Foods and Soils

Principle Investigators and Co-investigators:

Steven Siciliano, Heather Jamieson, Derek Peak and Brian Laird

Summary:

It is widely accepted that the use total metal concentrations in soil over estimates metal risk from accidental human ingestion of contaminated soils. A variety of *in vitro* simulators have been used to estimate the fraction of arsenic present in soil that is bioaccessible in the human digestive track. These approaches assume that (1) the bioaccessible fraction remains constant across soil total metal concentrations and that (2) intestinal microflora do not contribute to arsenic release. Here, we evaluate both of these assumptions in two size fractions (bulk and < 38 μm) of mine tailings from Goldenville, Lower Seal Harbour, and Montague, Nova Scotia. These samples were evaluated using an *in vitro* gastrointestinal model, the Simulator of the Human Intestinal Ecosystem (SHIME). Arsenic bioaccessibility, which ranged between 2 and 20% in the small intestine and 4 and 70% in the colon, was inversely related to total arsenic concentration in the mine tailings. Additionally, arsenic bioaccessibility was significantly greater in the bulk fraction than in the < 38 μm fraction in both the small intestine and colon. Colon microbes significantly increased the bioaccessibility of arsenic in mine tailings while being involved in the production of a black precipitate, likely sulfide. These results suggest that using a constant percent arsenic bioaccessibility across all metal concentrations in a risk assessment framework needs to be revisited.

Based on these results, we are currently pursuing a three prong strategy to unravel why arsenic bioaccessibility is dependent on arsenic concentration.

- 1) Is arsenic and mercury release during digestion kinetically or thermodynamically limited?
- 2) Are there substantial modifications to arsenic and mercury speciation during digestion by gut microflora?
- 3) Do we observe similar contaminant release dynamics from other matrices like diverse northern foods.

The results from our proposed year 3 MITHE-RN research will allow us to develop a better understanding of the thermodynamics and geochemistry occurring during contaminant release from ingested particles.

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Project Title:

(I5) Bioaccessibility and Bioavailability: Development of Methods for the Measurement of Potentially Harmful Substances (PHSs) in Soil and Complex Foodstuffs.

Principle Investigators and Co-investigators:

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Summary:

Potentially harmful substances (PHSs), present in soil or other media, may pose a risk to human health, if present in a form that may be absorbed by ingestion processes. As a result various laboratory methods have been modified from the food and pharmaceutical industries and specifically developed to evaluate how much of a PHS is available for absorption through gastro-intestinal processes.

Bioaccessibility research is currently focussing on several key areas relating to the processes thought to govern the dissolution and absorption ingested PHSs, this includes investigation of the complex physical, chemical and biological reactions occurring in the human gut. Key gastric parameters to be discussed are solid:liquid ratio in the gut and the effect of the gastro-intestinal matrix of choice. Non-physiological parameters thought to influence bioaccessibility, and currently under investigation include the mineralogical form of the PHS in the contaminated substrate and its particle size distribution. In addition to the bioaccessibility of PHSs from soil another priority issue with respect to metals in the human environment is the dietary uptake of metals. As a result the dietary uptake of elements such as Cd, Cu and Ni from foodstuffs and soils is being studied using both bioaccessibility tests and Caco-2 cells; in the case of soils, bioaccessibility is being determined relative to particle size. Other areas under investigation include health food products and potentially contaminated seafood.

In addition to determining the bioaccessibility of priority contaminants, such as arsenic, in different substrates research continues in the area of speciation by XAS and conventional speciation techniques. This is a key area of research, as for arsenic, the different species of this element exert different degrees of toxicity or are even non-toxic as in the case of arsenobetaine. Speciation of arsenic in plants has begun to identify the forms of arsenic stored in plants and also the different parts of the plant that store the different species. This area of research has transferred assessing food chain exposure in small mammals in Nova Scotia.

The information provided by all of the different strands of research supports that provided by the bioaccessibility testing and provides a robust human health risk assessment, which provides conservative estimates of risk.

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Project Title:

(I6) Speciation of Arsenic, Vanadium, and Chromium

Principle Investigators and Co-investigators:

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Summary:

The first objective during the last year was to establish arsenic speciation in saliva as a biomarker. Prior to our work, there was no method for arsenic speciation in saliva, and it was not known what arsenic species might be present in saliva. We have developed a speciation technique that combine chromatography with two types of mass spectrometry. Using this speciation method, we are able to identify methylated arsenic metabolites as well as the inorganic arsenicals in human saliva. Our results suggest that arsenic speciation information in saliva could potentially be used as a marker of exposure. This method, along with our existing method for the speciation of arsenic in urine, makes it possible to determine the overall arsenic exposure by children after playing in playgrounds constructed with chromated copper arsenate (CCA) treated wood. We previously measured arsenic and chromium concentrations in children's hand-washing after playing in playgrounds. To determine the overall exposure to arsenic and chromium by children, we have collected urine and saliva samples from children following playing in 8 CCA and 8 non-CCA playgrounds. We are now in the process of determining arsenic and chromium speciation in these samples. We anticipate that there will be no significant difference in the speciation of arsenic and chromium between the two groups. The predominant source of arsenic and chromium intake is probably from the ingestion of food and water. The ingestion from the playground is likely a small contribution to the overall exposure.

The second objective was to determine arsenic speciation in food. To enable this study, we have developed a highly sensitive speciation technique using liquid chromatography separation and simultaneous detection by both inductively coupled plasma mass spectrometry (ICPMS) and electrospray mass spectrometry (ESMS). The detections by both ICPMS and ESMS are complementary because ICPMS offers high sensitivity for specific element detection while ESMS provides molecular information of the species. We have applied the speciation technique to the determination of arsenic species in urine, blood, fish, meat, and plants. Current effort is to determine arsenic species in moose and deer meat and cattail samples collected from the First Nations communities in northern Alberta. A previous assessment of arsenic in moose meat done by a commercial laboratory, using a method of poor detection limit, resulted in unwarranted public concern over arsenic in their food. Our present study provides critical data for a more meaningful exposure/risk assessment.

We have also carried out speciation of vanadium in oil sands and coke (a byproduct from oil

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sands processing). We have developed a technique that enables the speciation of V(III), V(IV), and V(V), and demonstrated its application to oil sands and coke analysis. Understanding the fate and speciation of vanadium during the different stages of oil sands processing will help develop improved techniques for minimizing the release of vanadium to the environment.