

Platform Presentation

Project Title:

(15) Development of *In vivo* Oral Bioavailability Data for Ni-contaminated Soils

Investigator(s):

Hale, B. and L. Vasiluk

Department of Land Resource Science, University of Guelph, Guelph, ON

Summary:

Sprague-Dawley male rats were gavaged with field-contaminated soils and placed in metabolic cages for 72 hours. Metabolic cages allowed collection of feces and urine separately. It was found that soil nickel is getting excreted almost entirely from the animals, likely due to it being present in the soils as insoluble forms. However, the initial studies had unexpectedly high variability, which was scrutinized to identify better methods which we then incorporated into a Standard Operating Procedure. In the initial studies, several replicate animals had an average excreted mass of Ni, at 24h, which was greater than the mass that was putatively ingested. The STD of fecal sub-samples (i.e. within animals) was also quite large, as well as were the coefficients of variation (CV), to make the case that one sub-sample was representative. So, we concluded that we needed to digest half of the fecal output of each animal, at each time point (with the remaining half archived). The second observation compared the mean excreted mass of Ni of the replicate animals, and their STD and CV, and the mean, STD and CV of the total Ni concentration in grab samples of the soils with which the animals were dosed. For several of the soils, the CV for the mean Ni concentration was much smaller than the CV for the excreted Ni mass, indicating that it would be better to make the gavaging dose for each animal individually, rather than one solution with contaminated soil divided among three replicates. Finally, a comparison between gavage carriers for the positive control (nickel sulphate) demonstrated that 0.5% methyl cellulose is the better carrier for soil particles, but it increases Ni bioavailability relative to 5% gum acacia. Using the finalized SOP, two *in vivo* studies have been conducted using field-contaminated soils which have been particle-size separated; fecal mass was analyzed for total Ni mass. Data analysis is still in progress, but preliminary results are that almost 100% of the Ni ingested with soil is excreted within 72h, with most of the excretion taking place within the first 24h. These *in vivo* results are supported by the *in vitro* assays on the same soils that estimate bioaccessible Ni in field-contaminated soils.

Platform Presentation

Project Title:

(16) Speciation of Arsenic, Vanadium, and Chromium

Investigator(s):

Le, X.C.

Poster – Student Competition

Project Title:

(I1) Exposures to Metals in Urban Canadian Shield Homes Assessed Using Wipe Sampling Methodologies

Investigator(s):

¹McDonald, L. (MSc Candidate), ²Chenier, M., ²Levesque, C., ^{1,2}Rasmussen, P. (PI)

¹Department of Earth Sciences, University of Ottawa, Ottawa ON

²Environmental Health Science and Research Bureau, Safe Environments Program, HECSB, Health Canada, Ottawa ON.

Summary:

Presently, there are no Canadian guidelines for metal concentrations in indoor residential dust. Dust is a matrix of particles varying in size consisting of a variety of organic and inorganic compounds, including metals. These metals are derived from both the indoor and outdoor environment. This study seeks to determine typical indoor dust loading values for seven metal(loid)s: arsenic, cadmium, chromium, copper, lead, nickel, and zinc for urban homes located on the Precambrian Shield. Yttrium is included in the analysis due to its recommended use as a soil tracer. Samples were collected from two Canadian Shield cities: Greater Sudbury and Thunder Bay, as well as from Barrie which provides a control as this city is located on Paleozoic bedrock. Due to different sources of metals, it is likely that the metal composition of house dust will vary between rooms in a home.

Following the ASTM 1728 protocol, 1372 samples were collected with Ghostwipes™ from uncarpeted floors in 222 homes. Rooms that were sampled include: entryway, kitchen, living room, family room, adult bedroom, child bedroom, and child's play room. For quality control and quality assurance, one field blank and one duplicate were taken per home. Samples were digested in acid, following a modified version of the ASTM 1644 protocol in which hydrofluoric acid was added to increase extraction efficiency. Sample digests were then analyzed using ICP-MS and ICP-OES.

Higher values of yttrium ($p=0.002$) were found in the entry way of Thunder Bay homes versus kitchens which may indicate tracking in outside dirt by residents and their pets. Arsenic ($p=0.001$), chromium ($p=0.0004$), and nickel ($p=0.00006$) were found to be significantly higher in entry ways versus kitchens ($n=68$) whereas cadmium ($p=0.117$), copper ($p=0.065$), and lead ($p=0.023$) were not. Future work will include identifying possible indoor and outdoor sources of exposure to metals. This dataset will help Health Canada develop guidance on metals in the home environment and provide information to Canadians on ways to reduce their exposures to metals.

Poster – Student Competition

Project Title:

(11) Geochemistry and Human Health: Spatial and Geochemical Techniques to Improve Assessment of Exposure to Manganese in Windsor, Ontario, Canada

Investigator(s):

Michelle Nugent (PhD candidate), University of Ottawa and Pat Rasmussen (PI), University of Ottawa and Health Canada

Summary:

This study was conducted to investigate the urban geochemistry of the Windsor area (Ontario) and to provide valuable information for human exposure studies, such as the Windsor Ontario Exposure Assessment Study. This study focuses on manganese and other trace element content of urban soils. Human exposure to high levels of manganese, via inhalation, can cause respiratory and/or neurological problems. The goal of this study was to assess and investigate the spatial variability, sources, and environmental pathways of manganese in urban Windsor soils. It was hypothesized that past and present industrial and vehicular emissions in Windsor, and its neighbouring city Detroit, are contributing to the manganese content of soils in the Windsor area. The sample collection scheme was designed to (1) determine the current and background soil concentrations of manganese in Windsor and (2) determine the spatial distribution of manganese in order to reveal sources of manganese, both anthropogenic and natural. The first phase of the study consisted of preliminary soil surveys to identify potential hot spots and to assess the range of soil manganese and other trace element concentrations. During this phase, a field portable X-ray fluorescence instrument was used in the field for comparison with more traditional trace element analysis such as ICP-MS. As a result of the first soil surveys, two areas of elevated manganese concentrations were revealed and were further investigated during the second phase of this study. This second phase allowed for a more comprehensive urban soil survey of Windsor. Soil samples were analyzed for total trace element content, pH, moisture, organic and inorganic carbon and mineralogy. Also during the second phase of this study, moss-bags were used as biomonitors of trace elements to determine total trace element concentrations and depositional rates of atmospheric particles that could potentially deposit onto the soil surface. Atmospheric particle speciation will be done by SEM. Data analysis is presently being done on the numerous and varied results.

Poster

Project Title:

(I1) Refined analysis and characterization methods for metals in urban residential air

Investigator(s):

^{1,2}Rasmussen, P., ²Wheeler, A., ²Niu, J., ²Chénier, M., ¹Nugent, M., and ¹Gardner, H.
¹University of Ottawa and ²Health Canada.

Summary:

Urban air pollutants, including metals in airborne PM, are routinely monitored across Canada under Environment Canada's National Air Pollutant Surveillance (NAPS) network, which includes monitoring stations located in Windsor, Ontario. Under the US-Canada Border Air Quality Strategy (BAQS), Health Canada conducted a series of exposure monitoring campaigns in Windsor from 2005 to 2006 to develop a more detailed understanding of the temporal and spatial variability of human exposures to a variety of urban air pollutants, including metals.

In the first four years of MITHE, techniques were developed to improve exposure assessments for metals in urban residential environments. In the present study these techniques are applied to field samples collected and archived under BAQS, with focus on lead (Pb) and manganese (Mn). These two metals are selected (as a starting point) in response to Health Canada's immediate requirement for information on Canadian exposures to Mn and Pb concentrations in airborne particulate matter (PM) and settled dust. The BAQS samples consist of 37 mm Teflon™ filters which were loaded with PM *in situ*, using small portable PM₁₀ and PM_{2.5} monitors located in various neighborhoods across Windsor, including private homes and the NAPS monitoring stations, and indoor settled dust samples which were collected from the living room areas of the participating homes.

Two physiologically-based extraction techniques (PBETs) are applied to the BAQS samples to determine the soluble (bioaccessible) fraction of particle-bound Mn and Pb under pH conditions relevant to the exposure pathway being considered. Results are expressed as a percentage of the total metal concentration measured in the same sample. The PBET for the ingestion pathway uses a weak hydrochloric acid extraction (0.07M; pH 1.5) to simulate gastric acid. Applied to settled dust samples (n=80), the gastric PBET yields bioaccessibilities (geomeans) of 58% for Pb and 48% for Mn. The PBET for the inhalation pathway uses an ammonium acetate buffer (0.01 M; pH 7) to simulate the neutral lung environment. Results of the pulmonary PBET, when applied to outdoor PM_{2.5} samples (n=36), indicates greater solubility for Mn (77%) compared to Pb (43%).

The results of this research enable us to: (1) evaluate how accurately the community-based NAPS monitoring stations represent indoor, personal and outdoor exposures experienced by residents of Windsor and surrounding areas; (2) place the Windsor Mn exposure measurements into the context of the proposed Health Canada reference concentration for inhaled Mn (0.05 µg/m³); and (3) provide unique information on Pb in house dust and Pb in indoor residential air that is required for Health Canada's current review of Canada's total daily Pb intake estimate (Health and Welfare Canada 1992).

Poster – Student Competition

Project Title:

(I2) Association of Scorodite-Bearing Hardpan Cement Formation with Historic Mine Waste Concentrate

Investigator(s):

DeSisto, S.L.¹, Jamieson, H.E.¹, Parsons, M.B.²

¹ Queen's University, Kingston, ON

² Geological Survey of Canada (Atlantic)

Summary:

Cemented layers, or hardpans, have been observed at Montague Gold Mines, Nova Scotia since 1871. Today, they occur across the site as broad, thin layers (1 – 3 cm thick), in thicker sections (~ 30 cm) and in some areas as dispersed pieces. The hardpan layers form *in situ* as a result of precipitation and subsequent cementation of secondary minerals in mine tailings. Arsenic is sequestered during hardpan precipitation, suggesting that this may be an ongoing method of natural metal(loid) attenuation. At Montague, tailings are partially cemented by scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$), a mineral known to effectively limit aqueous arsenic due to its relatively low solubility (<1 ppm, pH 5) and high arsenic content (~ 30 wt.%). The occurrence of this mineral may help to limit the release of arsenic from the tailings. However, arsenic concentrations would not be lowered to values below the Canadian drinking water guideline (0.010 ppm) and ingestion of arsenic-bearing particles may still be a risk.

Co-existing waters and solids were sampled in an effort to understand scorodite precipitation and dissolution reactions and the relationship between hardpan, tailings and water geochemistry. Examination of hardpan cements revealed amorphous and crystalline iron arsenates (including scorodite), as well as an iron oxyhydroxide component. The iron arsenate occurs as brown, colloform cement while the iron oxyhydroxide is present as an interstitial material in weathered sulfide cracks or as clustered gray rims. End-member pore water chemistry characteristics were identified based on pH and dissolved concentrations. These end-member values were extremes (e.g. pH 3.78, $\text{As}_{(\text{aq})}$ 35.8 ppm) compared to most other samples (e.g. avg. pH 6.41, $\text{As}_{(\text{aq})}$ 2.07 ppm).

The availability of oxidizing arsenopyrite is suggested as the limiting factor towards continued scorodite precipitation. Historical arsenopyrite-bearing concentrate is associated with nearly all hardpan and provides a source of acidity and dissolved As^{+5} and Fe^{+3} for scorodite precipitation. In the proposed model, localized grain-scale reactions show active scorodite precipitation is occurring but dependent on sulfide persistence. Permanent arsenic sequestration in hardpan is not expected, as continued oxidation will lead to complete sulfide consumption and consequent progression to more neutral conditions, thus destabilizing scorodite. Any future remediation efforts at Montague must carefully consider the wide range of arsenic-bearing phases in the tailings and the conditions required to maintain their stability in order to avoid increasing the flux of arsenic to downstream environments.

Poster

Project Title:

(I2) Arsenic mineralogy of near-surface tailings and soils determined by synchrotron micro-probe, sequential extraction and petrographic methods

Investigator(s):

Walker, S.R.¹; Parsons, M.B.²; Jamieson, H.E.¹

¹*Department of Geological Sciences, Queen's University, Kingston, Ontario K7L 3N6*

²*Geological Survey of Canada (Atlantic), Dartmouth, Nova Scotia B2Y 4A2*

Summary:

The mineral form and grain-size of As-bearing particles are important factors that influence the bioaccessibility of As in soils, sediments and mine wastes. Mining of arsenopyrite-rich gold ores in Nova Scotia in the late 1800s and early 1900s has left a legacy of weathered, generally small, but As-rich tailings deposits in more than 60 gold districts across the province. Two mill concentrate samples, 12 near-surface tailings samples and one soil from several former gold mines were sieved to <150 µm for bioaccessibility testing (Project I5). The mineralogy of these samples was characterized using conventional and synchrotron-based micro-analytical techniques. Selected samples were also analyzed by sequential extraction analysis (SEA).

Two mill concentrates (> 20% As) were dominated by a single (but different) As mineral. In one case the concentrate (originally arsenopyrite-rich) was almost completely altered to scorodite (FeAsO₄•2H₂O), while the other was largely unweathered (primary) arsenopyrite (FeAsS). For tailings samples (0.7 to 7% As), scorodite and amorphous hydrous ferric arsenate (HFA) were the most common As-bearing major components. However, some tailings samples had other As minerals in abundance including: kankite (FeAsO₄•3.5H₂O), As-bearing amorphous hydrous ferric oxyhydroxides (HFO), pharmacosiderite (KFe₄(AsO₄)₃(OH)₄•6-7H₂O), yukonite (Ca₇Fe₁₂(AsO₄)₁₀(OH)₂₀•15H₂O) and amorphous Ca-Fe arsenates. Primary arsenopyrite was only a major As constituent in two of the tailings samples (one water saturated and one carbonate rich). Arsenic-bearing ferric oxyhydroxides with up to 10% As (HFO, goethite, lepidocrocite and akaganeite) were common minor to trace constituents in most samples. Arsenic-bearing HFO (2.5% As) and goethite (0.08% As) were identified in the single B horizon soil sample investigated. Sequential extraction results on pure mineral standards demonstrate good selectivity for arsenopyrite and scorodite. For yukonite, As is largely released in the amorphous Fe oxide step. The SEA results for As are in general agreement with the mineralogical data, and help to quantify the percent of total As hosted by different primary and secondary minerals.

Major mineralogical differences (e.g. Ca Fe arsenate, yukonite-pharmacosiderite and ferric arsenate rich samples) may be predictable based on bulk chemistry, mineral processing factors (gravity concentration) and geochemical weathering history (i.e. carbonate-buffered pH neutral, post-neutral, and acidic conditions, respectively). Secondary mineral grains and grain coatings exhibit a range of crystallinity from fine, well crystallized material to nanocrystalline and poorly crystalline or X-ray amorphous phases. In mineralogically complex materials such as the Nova Scotia tailings, the bioaccessibility of As is expected to be influenced by the extent of weathering (amount of relic arsenopyrite), the local

geochemical conditions (acidic or pH neutral), and the textures, crystallinity, and grain size of secondary As phases.

Poster

Project Title:

(I2) Characterizing the Forms of Arsenic in Soils from the North Brookfield Gold Mine, Nova Scotia and the Giant Gold Mine, Northwest Territories

Investigator(s):

Wrye, L.A.¹; Jamieson, H.E.¹; Parsons, M.B.²; Walker, S.R.¹

¹*Department of Geological Sciences, Queen's University, Kingston, Ontario K7L 3N6*

²*Geological Survey of Canada (Atlantic), Dartmouth, Nova Scotia B2Y 4A2*

Summary:

Natural and anthropogenic sources of arsenic (As) have been identified in gold mining-impacted soils from the North Brookfield, NS (1886-1906) and the Giant Mine, NT (1948-1999). Both used ore-roasting to extract gold from the arsenopyrite, releasing arsenic trioxide ($\text{As}^{3+}_2\text{O}_3$). Arsenic trioxide is considered soluble and ingestion of soils containing oxidized forms of As, from either natural or anthropogenic sources, can pose a risk to human health as these are potentially more bioaccessible than naturally occurring arsenopyrite.

The purpose of this study is to compare the mineral form and oxidation state of As in soils surrounding these two mines. Shallow soil cores were taken upwind and downwind of the roasters and sub-samples were analyzed using sequential extraction analysis (SEA), synchrotron-based X-ray diffraction and absorption spectroscopy, and environmental scanning electron microscopy.

Soil profiles from the North Brookfield mine show low total As (2 ppm to 45 ppm), with the exception of surface soils close to the roaster (4300 ppm). Identified As-bearing phases include roaster-derived iron oxides (RFO) (containing As^{5+}), As-rich rims on oxides, and As associated with clays. Adjacent to the roaster, SEA determined that As was primarily in the amorphous iron-oxide phase which may be in part due to As-bearing weathering rims on arsenopyrite. No relic As_2O_3 grains were identified in North Brookfield soils. Giant soils show elevated As at the surface (140-3300 ppm) across the property. Mineralogical examination of surface soils identified arsenopyrite, As_2O_3 grains, and RFO (containing As^{3+} and As^{5+}). Previous work and SEA results show evidence that As_2O_3 is somewhat resistant to weaker leaches and is primarily leached in the crystalline iron-oxide and scorodite steps.

Factors influencing the presence and persistence of As_2O_3 at Giant in comparison to North Brookfield include: different roasting techniques and processing technology, ore mineralogy (especially the presence of Sb minerals at Giant), duration and ore tonnages processed, climate and soil type. The results of this study have shown that understanding the form and distribution of As phases is critical because this directly influences the potential risk to human and ecosystem health associated with ingestion of soil particles, as well as the total dissolved As in local surface and groundwaters.

Poster

Project Title:

(I3) Pulmonary absorption and toxicity of metals: *in vitro* speciation studies.

Investigators:

Jumarie, C. (PI)¹, Mantha, M.¹, El Idrissi, L.¹, Bernier, J.², Fortin, C.²

¹Département des Sciences Biologiques, Université du Québec à Montréal, CP 8888, succ. Centre ville, Montréal (Qué.) H3C 3P8.

²Institut national de la recherche scientifique, Centre Eau, Terre et Environnement, 490 rue de la Couronne, Québec (Qué.) G1K 9A9

Summary:

The pulmonary absorption and toxicity of metal compounds are influenced by their solubility in biological fluids as well as metal speciation. In addition, metal availability from metal mixtures is subjected to metal interactions. Our main goals are: i) to better characterize metal toxicity in alveolar vs. bronchiolar cells; ii) to study the influence of metal interactions on metal transport and toxicity in relation to metal speciation; iii) to correlate the levels of exposure and of cellular accumulation to toxicity. Our long term goal is to estimate to what extent lung cells may adapt to chronic metal exposure.

Our study focuses on Cd, Pb and Hg and uses two different *in vitro* models: the human cell lines A549 (ATII cells) and H441 (Clara cells). Our previous results have shown that, under **inorganic exposure conditions**, Cd uptake in both cell lines involves pH-sensitive specific transport mechanisms. Higher uptake levels were recorded in a nitrate medium compared to chloride (used to increase the level of dissolved Cd²⁺). Two-fold higher K_m and V_{max} values have been estimated in the A549 cells. Viability studies performed with MTT assay and FACS Scan analysis following a 24-h exposure to metals in **serum-free culture media** revealed lower LC₅₀ values for Cd compared to Hg. No significant cell mortality could be observed with Pb up to 500 µM. A549 cells were more sensitive to Cd compared to H441 cells. This was not related to higher cellular accumulation suggesting different constitutive resistances between cell lines. Parallel MTT and uptake measurements showed that additive effect between Cd and Hg toxicity in A549 cells could be the result of higher accumulation levels, possibly as a result of cell volume disruption. On the other hand, the protective effect of Pb against Cd toxicity in both cell lines would be the result of inhibition of Cd uptake. In collaboration with Claude Fortin (project A5) we have calculated/measured **metal speciation** in the serum-free culture media to enable us to analyze our uptake and cytotoxicity data in relation to metal speciation. We have identified the most relevant organic ligands for Cd, Pb and Hg (L-cysteine being a major one) and have performed MINEQL⁺ calculations. Cd is strongly complexed (Cd²⁺ represents less than 1 % of total dissolved Cd) but addition of Pb or Hg increases up to 200 and 80 times, respectively, the proportion of free Cd in both media. These calculations provided a starting point for the actual measurements of free Cd using an equilibration ion-exchange technique (IET). Studies performed on A549 and H441 **cell monolayers grown on filters** reveal different permeability coefficient for Cd. Co-exposures with either Pb or Hg significantly inhibited cellular accumulation but increase the transepithelial transport of Cd in the apical-to-basolateral direction.

The authors gratefully acknowledge the support of the NSERC MITHE Strategic Network

Poster – Student Competition

Project Title:

(15) The Effect of a Glycine Buffer in Estimating the Bioaccessibility of Arsenic from Soils

Investigator(s):

Meunier, L., M. Lord-Hoyle, I. Koch and K.J. Reimer

Environmental Sciences Group, Royal Military College of Canada, Kingston, Ontario.

Summary:

The bioaccessibility of arsenic from soil is becoming more commonly used in risk assessment; however, concerns remain on the reliability of these gastro-intestinal *in-vitro* tests. Bioaccessibility is defined as the fraction of a contaminant that may become soluble in the gastro-intestinal tract and is available for systemic absorption (*i.e.* bioavailable). The bioaccessibility of arsenic from solid samples may be susceptible to varying liquid-to-solid ratios, and depends on sample composition, particle size as well as the chosen buffer system used in these tests. For a series of reference materials, soils and tailings, two methods were compared: a modified version of the Solubility/Bioavailability Research Consortium (SBRC) method which uses glycine as a buffer, and a physiologically based extraction test (PBET), which includes organic acids as a buffer. Results suggest that the bioaccessibility of arsenic estimated by the PBET method is not significantly affected by varying liquid-to-solid ratios, whereas large differences were observed at different ratios for the SBRC method. In addition, the results from the SBRC method were affected by the concentration of glycine used. The differences between measurements in the gastric and intestinal phases of the tests were also greater in the case of the SBRC method than in the PBET method for solid matrices containing high ratios of iron to arsenic. Both methods returned similar results for each particle size tested. In the glycine buffered system, iron may more readily remain in solution by forming a complex with glycine and thus influencing the concentration of arsenic in solution. Using glycine as a buffer in *in-vitro* estimations of the bioaccessibility of arsenic may unduly influence the results. The choice of a PBET method may be more appropriate to achieve consistently representative values toward estimating risks of arsenic bioaccessibility to human health.

Correspondance

Louise Meunier, louise.meunier@rmc.ca; Megan Lord-Hoyle, megan.lord-hoyle@rmc.ca;

Iris Koch, koch-i@rmc.ca; Ken Reimer, reimer-k@rmc.ca

Environmental Sciences Group, Royal Military College of Canada

P.O. Box 17000, Station Forces, Kingston, ON, K7K 7B4

Poster

Project Title:

(15) Bioaccessibility and speciation of arsenic and chromium in environmental matrices

Investigator(s):

Ken Reimer, Iris Koch, Louise Meunier, Megan Lord-Hoyle, Jared Saunders, Maeve Moriarty, Breanne Gibson; Royal Military College of Canada
Chris Ollson; Jacques Whitford, Burlington

Summary:

At RMC we have continued our work on studying bioaccessibility methods for arsenic in soil and expanded it to chromium in tannery contaminated soils. A comparison of three bioaccessibility methods modeling the human oral ingestion route, using three different contaminated soils was carried out and results show that a physiologically based extraction test (PBET) (modified from Ruby) method is both repeatable and reproducible; the Solubility/Bioavailability Research Consortium (SBRC) method (which contains glycine) method does not seem to correlate with any of the other methods. Further testing with the in vitro gastric (IVG, after Rodriguez and Basta 1999) method in October 2008 to determine the variables affecting differences in the results between our laboratory and the Basta laboratory showed that pH control (and low buffering capacity of the IVG method) appear to have the largest effect. Arsenic and iron bioaccessibility from solid matrices at varying liquid to solid ratios using the SBRC and PBET methods showed different tolerances for the two methods and results are summarized in an accompanying poster. In our studies of speciation, especially as it relates to bioaccessibility, our earlier work that attempted to link arsenic mineralogy with bioaccessibility, was augmented with X-ray absorption spectroscopy (XAS) work to determine the effects of redox conditions and organic carbon on arsenic speciation in soils and tailings from Yellowknife, which will be related to bioaccessibility results. Chromium bioaccessibility in samples (measured in Jan and Aug-Sept 2008) from a Kingston brownfield site was measured to give low percent bioaccessibility of Cr (generally <10%) from heavily contaminated (former tannery site) soils and sediments, associated with Cr(III) species (matched to Cr(III) sulfate, the form used in the tanning process). The identification of the Cr(III) species and the absence of Cr(VI) (the more toxic form) was confirmed by XAS. To study the relationship of bioaccessibility with animal body burdens, food chain studies in Nova Scotia were continued; an accompanying poster describes a small mammal food chain. Bioaccessibility and speciation of bioaccessibility extracts were determined in an insect food chain link (accompanying poster). Deer mice and plants from the tannery property (brownfield site) mentioned previously are being analyzed to determine if uptake into local biota is taking place.

Poster – Student Competition

Project Title:

(15) Biomarkers of Arsenic Exposure in Meadow Voles at Montague, Nova Scotia

Investigator(s):

Jared Saunders¹, Loren Knopper², Iris Koch¹ and Ken Reimer¹

1 – Environmental Sciences Group, Royal Military College of Canada, Kingston, ON

2 – Jacques Whitford, Ottawa, ON

Summary:

Elevated concentrations of arsenic are generally found at abandoned or current gold mining areas throughout Canada. When arsenic is consumed by mammals – even at low concentrations – it can lead to adverse health effects, including carcinogenesis in humans. A previous study at Seal Harbour, Nova Scotia concluded that arsenic species are transformed through a small terrestrial food chain and sub-cellular effects on voles were present due to the presence of arsenic. Depressed glutathione (GSH) and increased frequency of micronuclei in red blood cells in meadow voles were observed as a result of the elevated arsenic concentrations. The current field study at Montague, NS, was initiated to determine if previous results from Seal Harbour were valid at other contaminated sites. In addition, Montague has significant human relevance due to its proximity to residences as well as some of the highest tailings arsenic concentrations (up to 42,000 ppm) in the province.

Twenty meadow voles (*Microtus pennsylvanicus*) were captured in Sherman live traps at Montague and at a nearby reference site without anthropogenic arsenic influences. On the mine impacted site, elevated concentrations of arsenic translate throughout each level of the food chain and less metabolized forms of arsenic are present in the voles. Further research was conducted to determine if the elevated concentration of arsenic were having an effect on the mammals living on the site. A significant increase in the number of micronuclei in red blood cells was observed at the mine impacted site at Montague. A reduction in GSH was found to be related to the total arsenic concentration in vole livers. This work at Montague confirms work conducted in Seal Harbour, NS in that even when the ecosystem looks healthy, the elevated concentrations of arsenic are having sub-cellular effects on the mammals living there. Ultimately, these results will be incorporated into an ecological risk assessment for the Montague mine site and will provide insight into the behaviour of arsenic in mammals which is critical in fully understanding how arsenic affects humans.

Poster – Student Competition

Project Title:

(16) Hyphenated Chromatography and Mass Spectrometry Techniques for Arsenic Speciation in Human Urine

Investigator(s) :

Chen, Lydia W. L.¹; Lu, Xiufen²; Le, X. Chris^{1,2}

¹Department of Chemistry, ²Division of Analytical and Environmental Toxicology, Department of Laboratory Medicine and Pathology, University of Alberta, Edmonton, Alberta, Canada, T6G 2G3

Summary:

Arsenic contaminated drinking water and food are serious health issues because chronic exposure to arsenic may lead to the formation of skin lesions, hyperkeratosis, and the development of skin, bladder, and lung cancers. There has been limited arsenic speciation analysis conducted on Canadian population who experience low to medium exposure of arsenic. This double-blind epidemiological research will determine the concentrations of arsenic species in 110 human urine samples collected from Quebec. Two groups of the general populations are targeted based on their arsenic exposure level in drinking water: less than 5 µg/L and 10 to 50 µg/L. The Canadian drinking water guideline for arsenic is 10 µg/L.

Inductively coupled plasma mass spectrometry (ICP-MS) is used to detect arsenic species after separation by high performance liquid chromatography (HPLC). The separation techniques are Anion Exchange chromatography, Cation Exchange chromatography, and Ion Pair Chromatography where each technique has its distinct strength in separating different arsenic species of arsenite (As^{III}), arsenate (As^V), monomethylarsonic acid (MMA^V), dimethylarsinic acid (DMA^V), and arsenobetaine (AsB) in the urine samples. Hydride generation is coupled between HPLC and ICPMS to further improve sensitivity and to differentiate AsB from As^{III}.

Based on Cation Exchange Chromatography, the average AsB concentration is 6.29±0.21 µg/L. Based on Ion Pair Chromatography, the average concentration of DMA^V, MMA^V, and As^V is 6.53±0.40 µg/L, 1.82±1.84 µg/L, and 0.80±0.14 µg/L. Based on Anion Exchange Chromatography, the average As^{III} concentration is 1.81±0.10 µg/L.

AsB constitutes 23±21% of the total arsenic in the urine samples, suggesting exposure to arsenic from food. Excluding AsB, the distribution of the other four arsenic species is 14±14% As^{III}, 60±13% DMA^V, 16±5% MMA^V, and 10±6% As^V. This metabolite profile is consistent with those observed from other populations exposed to higher levels of arsenic from drinking water.

Future investigation will involve statistical analysis to determine any correlation between the concentrations of urinary arsenic species and other biomarkers of potential health effects (data obtained by our collaborators).

Poster

Project Title:

(16) Arsenic Concentration and Speciation in Cattail Plants

Investigator(s):

Lu, X.¹, N. Nguyen¹, S. Gabos² and X.C. Le¹

¹ Division of Analytical and Environmental Toxicology, Department of Laboratory Medicine and Pathology, University of Alberta, Edmonton, AB, Canada T6G 2G3.

²Health Surveillance Branch, Alberta Health and Wellness, Edmonton, AB, Canada

Summary:

Cattail plants grow in and around ponds and wetlands, and they are commonly used (e.g., by the First Nations in northern Alberta) as traditional food and medicinal ingredients. Previous analyses of cattail plants collected in northern Alberta have shown high (yet not consistent) levels of arsenic. There have been concerns in the local communities over the levels of arsenic in cattail plants. The objectives of this research were to identify and quantify arsenic species in cattail plants and to determine the distribution of arsenic species in the various components of the plant.

Cattail plant samples were collected from the northern Alberta where previous reports showed high levels of arsenic. The plants were dissected into fine root, skin, and starch of root. Total concentrations in the acid digested samples and arsenic species in the methanol-water extracts were determined either by using inductively coupled plasma mass spectrometry (ICPMS) or by using high performance liquid chromatography separation and ICPMS detection.

Inorganic arsenite, arsenate, dimethylarsinic acid, monomethylarsonic acid, and arsenobetaine were found present in various components of the cattail plants. The two inorganic arsenic species accounted for >80% of the total arsenic. Total arsenic concentrations in the various compartments of the plants were 200 µg/kg (range 37-600 µg/kg) in the whole tuber, 6 µg/kg (5-12 µg/kg) in the stem, 1120 µg/kg (range 68-2600 µg/kg) in the fine (hairy) root, 575 µg/kg (16- 1400 µg/kg) in the skin of the tuber, and 26 µg/kg (2- 82 µg/kg) in the core of the tuber. Further analyses of arsenic and iron concentrations showed a strong correlation between arsenic concentrations and iron concentrations in the fine root and root skin samples. These results confirm the previous finding that arsenic and iron are co-localized (co-deposited) in the skin of the cattail plants. This research show arsenic speciation and provide quantitative measures of arsenic concentration in the various compartments of the plants. This information is useful in order to reliably assess human exposure to arsenic from the use of plants as food and medicine.

Poster – Student Competition

Project Title:

(16) Arsenic and Invertebrates

Investigator(s):

Moriarty, M., I. Koch and K.J. Reimer

Environmental Sciences Group, Royal Military College of Canada, Kingston, ON

Summary:

Arsenic concentrations and arsenic speciation in invertebrates has not been well characterized. As part of an investigation of how arsenic is distributed in the terrestrial ecosystem, researchers from the Environmental Science Group (ESG) collected representative insects from three arsenic-contaminated mine sites in Nova Scotia, Canada in August 2007. Organisms were sorted and identified prior to being analyzed using two complementary methods. The first method was traditional speciation analysis (high performance liquid chromatography inductively coupled plasma mass spectrometry, HPLC ICP-MS), which requires initial extraction of arsenic from the tissues. The second was solid state speciation analysis (X-ray Absorption Spectroscopy, XAS), which requires minimal sample pre-treatment. Both methods indicate the majority of arsenic in invertebrates is inorganic arsenic, and XAS revealed that much of this is present *in vivo* in reduced forms containing As-S bonds. A number of invertebrates, especially spiders, were found to contain various amounts of organoarsenicals including the non-toxic arsenobetaine; one can only speculate whether they are producing this compound or are preferentially accumulating it. Physiologically based extraction tests (PBET) were performed on bulk insects and soils from the three mine sites and one background site. Liquid:solid ratios of 40:1 were used for insects and 400:1 for soils to model the gastrointestinal fluids of both fed and fasted small mammals. The percent bioaccessibilities of the insects from all four sites was $42 \pm 7\%$ as compared to $25 \pm 11\%$ for soils from the contaminated sites. Despite arsenic being stored in an inorganic form, arsenic within insects is more bioaccessible than the mineral arsenic they are ingesting.