METALS IN THE HUMAN ENVIRONMENT (MITHE) RESEARCH NETWORK
2006 ANNUAL SYMPOSIUM

AQUATIC ECOSYSTEM PROJECT ABSTRACTS

Project Title:
(A1) Generation & Field-Validation of Chronic Biotic Ligand Models for Fish

Principal Investigator and Co-investigators:
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Reehan S. Mirza[1,2] and Warren W. Green[1,2]

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Summary:
In Year 1 we attempted two sets studies. We conducted a reciprocal cross-transplant experiment where we transplanted yellow perch (YP) from a clean to a contaminated lake (and vice versa). Half the YP received food from their native lake and the other half from the transplanted lake to examine waterborne and dietary Cu uptake and binding dynamics in gill, gut and olfactory epithelia. Due to excessive water temperatures during the summer we experienced 100% mortality in our cages before the study could be completed. In our second study, we conducted two experiments to examine the influence of metals on olfactory function in wild YP. YP were sampled from 3 lakes along a metal contamination gradient between Sudbury and North Bay, Ontario, and we tested their integrated extracellular field potential response to stimulation of olfactory epithelium using electro-olfactogram (EOG) analysis. Olfactory epithelia were exposed to YP skin extract (alarm cue; YPSE), rainbow trout skin extract (RBT, injured fish odour control), L-alanine (amino acid standard) and a blank (DW, dechlorinated North Bay tap water). YP from contaminated lakes responded with significantly greater intensity EOG responses to YPSE and RBT than YP from the clean lake. We also exposed half the YP from each lake to YPSE from all 3 lakes. YP responded with the same intensity to YPSE, irrespective of source. This suggests that YP respond equivocally to YPSE regardless of donor population. In experiment 2, we exposed YP from each lake to either: YPSE, RTSE or DW and observed their antipredator behaviour. YP from the clean lake exhibited decreased activity (fright response) to YPSE, but there was no significant change in activity for YP from the contaminated lakes. These results suggest a metal-induced decoupling between signal reception and perception, and that signal propagation is impaired along the olfactory pathway. Year 2 of our project will focus on the influence of Cu, Cd and Zn on olfactory function in fishes. We will determine where along the olfactory pathway signal disruption is occurring. We will also determine the binding affinity and capacity of Cu and Cd in olfactory epithelium in development of a chronic chemosensory-based Biotic Ligand Model.

METALS IN THE HUMAN ENVIRONMENT (MITHE) RESEARCH NETWORK
2006 ANNUAL SYMPOSIUM

AQUATIC ECOSYSTEM PROJECT ABSTRACTS

Project Title:
(A2) Multiple Metal Interactions with Fish Gills and with Natural Organic Matter

Principal Investigator and Co-investigators:
Wilkie, M.

METALS IN THE HUMAN ENVIRONMENT (MITHE) RESEARCH NETWORK
2006 ANNUAL SYMPOSIUM

AQUATIC ECOSYSTEM PROJECT ABSTRACTS

Project Title:
(A3) Integration of Geochemical Speciation, Chronic Toxicity Tests and *In-Situ* Field Bioassays for Predicting the Ecotoxicity of Mine Effluents using BLM Approaches

Principal Investigator and Co-investigators:
C.L. Chakrabarti[1] , J. McGeer[2]
[1]Carleton University, [2]NRCan

Summary:
The objective of this project is to validate and develop the use of the BLM approach to predict: metal chronic toxicity, the toxicity of the metal mixtures, and metal toxicity in mine effluents; and to use it as a tool for the interpretation of Environmental Effects Monitoring (EEM) data in the context of the Metal Mining Effluent Regulations (MMER).
Project 1.Concentrations of free Ni and Cu ions and their other labile species decreased on dilution of Copper Cliff Mine Effluents with Vermillion River water (Reference Site). The pH of Copper Cliff Effluent samples changed from 7.6 to 7.0 when they were mixed with Sudbury Municipal Effluent and diluted with Vermillon River water. Concentration of free Ni and Cu ions changed on dilution as follows: absolute concentration of free Ni ion and other labile Ni species decreased from 1.1×10^{-6} M to 1.0×10^{-6} M; relative Ni free ions and its other labile species concentration increased from 67% to 90%; absolute concentration of free Cu ions decreased from 6.8×10^{-7} M to 5.8×10^{-7} M; relative free Cu ions concentration increased from 94% to 95%. This decrease in free metal ions and labile species concentrations was associated with an increase in the reproduction of *C.dubia* and growth of *L.minor* (i.e. reduction in toxicity).

Project 2. Sampling of Copper Cliff effluent served primarily to orientate research questions and to complete on going artificial stream experiment conducted on site in the summer of 2005 by M. Dubé and her colleague (University of Saskatchewan). Full dilution series and mixtures used in the mesocosm were tested for their sublethal impact. Within the test scheme, a natural source (Vermillion River) was used as dilution waters and results were compared with tests conducted for monitoring using standard lab water. For fathead minnow and algal tests there was no or little sublethal responses and no effects of the dilution water were observed. When effluent sources were mixed with standard lab water, strong inhibition of *C. dubia* reproduction and *L. minor* growth was observed. These responses were dramatically reduced when Vermillion River water was used as the dilution water, illustrating the potential of trace metal to contribute to the observe toxicity.

METALS IN THE HUMAN ENVIRONMENT (MITHE) RESEARCH NETWORK
2006 ANNUAL SYMPOSIUM

AQUATIC ECOSYSTEM PROJECT ABSTRACTS

Project Title:
(A4/A8) Environmental risk assessment of metals in water and sediment: Importance of dietary uptake and water-sediment interactions to *Hyalella azteca*.

Principal Investigator and Co-investigators:
D.G. Dixon[1], U. Borgmann[2], L. Golding[1], L. Alves[1].
[1]University of Waterloo, Waterloo, ON, [2]Environment Canada, Burlington, ON

Summary:
(A4) One of the most pressing questions currently facing aquatic environmental risk assessment is the degree to which metal accumulation from food contributes to, or is equivalent to, toxicity observed when the metal is accumulated from water. In other words, should dietary metal be considered in environmental risk assessment (ERA), assessment that is currently based almost exclusively on waterborne metal concentration. The work proposed here will define the degree to which dietary and waterborne metal (specifically Cd) contributes to metal tissue concentration and toxicity in aquatic invertebrates (specifically the amphipod *Hyalella azteca*). This will allow us judge the degree to which ERA based solely on waterborne metal concentrations is compromised, and whether dietary metal concentrations should be considered in such assessments.

(A8) The second area of research proposed here focuses on the ERA of uranium in aquatic sediments. Previous work has demonstrated that overlying water chemistry has a dramatic effect on toxicity to *Hyalella* of Cd, but not of Ni, in sediment. There is considerable interest in Canada in developing either sediment quality guidelines for U, or an experimental approach to determining the risk associated with U-contaminated sediments, particularly in the dilute waters of Canadian shield lakes. We propose, once again using *Hyalella*, to determine the role of overlying water chemistry, and the relative contributions of dissolved vs. solid phase U, to the bioaccumulation and toxicity of U from sediments. We will also determine if U toxicity is predictable from tissue concentration, as is the case for Cd, Ni and Tl, and if U bioaccumulation from field-collected sediments can be used to quantify the contribution of U to overall sediment toxicity in *Hyalella*. Finally we will determine if a biotic ligand modelling (BLM) approach is applicable for assessing the impacts of, and regulating the concentrations of, environmental U.

METALS IN THE HUMAN ENVIRONMENT (MITHE) RESEARCH NETWORK
2006 ANNUAL SYMPOSIUM

AQUATIC ECOSYSTEM PROJECT ABSTRACTS

Project Title:
(A6) Impact of selenium on the aquatic biota in the Prairie ecosystems

Principal Investigator and Co-investigators:
A. Hontela, L. Miller, J.B. Rasmussen, Dept. Biological Sciences, Univ. of Lethbridge; V. Palace, Fisheries and Oceans Canada, Winnipeg; F. F. Wang, X. Hu, Dept. Environment and Geography, and Dept. of Chemistry, Univ. of Manitoba.

Summary:
Selenium (Se) is an essential element, toxic at excess concentrations. Irrigation, with the increased drainage of surface soils and fluctuations in ground water levels, is a potential source of Se for the aquatic environment, as is mining and combustion of coal. An increase in Se bioavailability is among the emerging issues linked to climate change and recent droughts in Western Canada, and the increasing demands for irrigation waters for agriculture. The objectives of this study are to: 1) assess Se levels and speciation in water, sediment, benthos and fish in surface waters situated in irrigation areas and at various distances from coal mines in Alberta and Manitoba, 2) provide data on the transfer of Se in the aquatic food chains and distribution in fish tissues, 3) elucidate the mechanisms of Se toxicity in fish, and the cellular constituents underlying species differences in vulnerability to Se. Laboratory exposures and field studies were used to investigate the impacts of Se on the aquatic biota.

Juvenile rainbow trout were exposed to waterborne $SeNa_2O_3$ for 96 hrs and 30 days in the laboratory and the effects of Se were evaluated by endpoints of the physiological stress response (plasma cortisol and glucose), gill Na/K-ATPase activity and growth indices. Acute exposures activated the neuroendocrine stress response while chronic exposures had no effect on cortisol secretion or plasma glucose but decreased the NaK-ATPase activity. Oxidative stress indices (GSH/GSSG, SOD, GPX, LPO) will be measured in liver of Se-exposed fish. Vitamin A and E analyses are in progress.
Field studies were done in Alberta and Manitoba. Suckers and fathead minnow were sampled in irrigation canals in Southern Alberta in summer and fall. Analyses are in progress. Benthos samples were also collected and food chain characteristics are being determined from stomach contents of the fish. Seasonal sampling of surface water, sediment, sediment porewater, and plant samples were also collected from Delta Marsh and Stephenfield Reservoir in Manitoba.

In collaboration with Alberta Environment, rainbow trout and brook trout were sampled at four sites near the coal mine in Hinton (Alta.), Luscar creek, Gregg river, Deerlick, Cold and Wampus creeks. Physiological and biochemical analyses are in progress.
(Financial support from the MITHE-RN, CRC and NSERC is gratefully acknowledged.)

AQUATIC ECOSYSTEM PROJECT ABSTRACTS

Project Title:
(A7) Contaminant burdens in scaup staging on the lower Great Lakes

Principal Investigator and Co-investigators:
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Ken G. Drouillard, Great Lakes Institute for Environmental Research, University of Windsor, Windsor, Ontario, N9B 3P4, Canada kgd@windsor.ca

Summary:
The lower Great Lakes (LGL) receive substantial amounts of industrial, urban, and agricultural contaminants and the region is an important staging and wintering area for scaup. We collected 122 lesser (*Aythya affinis*) and 69 greater scaup (*Aythya marila)* on the LGL during fall 1999 and spring 2000 and tested specimens for organic contaminants, metals, and trace elements. Sum PCB and organochlorine concentrations were below thresholds known to cause reproductive and health-related problems in waterfowl. Of 18 metals and trace elements tested, only selenium (Se) was detected at high enough levels to potentially adversely affect scaup reproductive output or survival. Although no lake effect was detected (lakes Ontario, Erie, St. Clair), there were interspecific, season, and age-related differences in Se burdens. During fall, 34% of adult and 12% of juvenile greater scaup and 11% of adult and 3% of juvenile lesser scaup had elevated levels of Se ($\geq 10\ \mu g \cdot g^{-1}$ liver dry mass). In contrast, 93% of greater scaup and 75% of lesser scaup collected in spring had elevated Se burdens. Seasonal differences in scaup Se burdens are likely attributed to seasonal Se variation in zebra mussels and the fact that both scaup species tend to eat more zebra mussels in spring. Although scaup are acquiring potentially unhealthy burdens of Se while staging on the LGL, additional research is required to determine if exposures are high enough to cause chronic health-related problems or cross-seasonal affects on reproduction. Greater scaup warrant concern since they had particularly high Se burdens in spring and a large portion of the continental population of this species winters on the LGL.

AQUATIC ECOSYSTEM PROJECT ABSTRACTS

Project Title:
Evolution of the intracellular distribution of Cd, Ni and Tl in chemostat cultured phytoplankton

Bernier, J.; Fortin, C. and Campbell P.G.C., *INRS-ETE*

Within the framework of MITHE-RN research project A5: *Metal transfer along aquatic food chains*, the objective of this subproject is to study the evolution of Cd, Ni and Tl intracellular distribution in phytoplankton cells. To do so, the phytoplankton cells will be exposed to the metals for long periods (up to ~ 1 month) in a chemostat, which provides a constant renewal of the exposure medium and thus minimizes metal depletion and changes in chemical conditions within the exposure medium. Moreover, the metal-laden phytoplankton cells produced by the uptake experiments will serve as food in trophic transfer experiments with herbivores.

Chlamydomonas reinhardtii will serve as the initial test phytoplankton species because of its wide utilization in toxicity and uptake experiments and the relative ease with which the algal cells can be lysed (for the subsequent determination of the intracellular distribution of the metals). Also, a freshwater diatom may be used for comparing the evolution of metal intracellular distribution among different phytoplankton species. We will use a modified HSM medium (low ionic strength) [1] for the culture and metal exposure of *C. reinhardtii*. Using the chemical speciation modeling software MINEQL+ (ver. 4.5) with revised hydrolysis constants for Tl (I) and Tl (III) [2], we determined, for the modified HSM medium (which contains the metal complexing buffer EDTA), that added total dissolved concentrations of 10^{-7} M Cd, 10^{-7} M Ni, 10^{-9} M Tl(I) and 10^{-6} M Tl(III) provide environmentally realistic free ion concentrations of 10^{-8} M, 10^{-9} M, 10^{-9} M and 10^{-11} M respectively. These sublethal free metal ion concentrations should ensure normal cell growth while providing measurable metal cell burdens (ICP-MS). The redox state of Tl (Tl^{+} vs. Tl^{3+}) will be followed in the chemostat using an ion-exchange separation technique [3] that we have modified for the use of small samples (5 mL) (in testing) while free Cd^{2+} and Ni^{2+} will be monitored using an ion-exchange equilibration technique [4]. Finally, the metal intracellular distribution will be examined by cell lysis (sonication) and subsequent differential centrifugation [5].

Reference list

[1] Fortin, C., Campbell, P.G.C. (2000) Environ Toxicol Chem. **19**: 2769-2778.
[2] Lin, T.-S., Nriagu, J. (1998) J. Air & Waste Manage. Assoc. **48**: 151-156
[3] Lin, T.-S., Nriagu, J. (1999) Anal. Chim. Acta. **395**: 301-307
[4] Fortin, C., Campbell, P.G.C. (1998) Intern. J. Environ. Anal. Chem. **72**: 173-194
[5] Vijver, M.G., VanGestel, C.A.M., Lanno, R.P., VanStraalen, N.M., Peijnenburg, W.J.G.M. (2004) Environ. Sci. Technol. **38**: 4705-4712

AQUATIC ECOSYSTEM PROJECT ABSTRACTS

Project Title:
Quest for The Holy Grail: mechanistic linkages between metal speciation and ecotoxicity in multi-metal mixtures of Sudbury (Ontario) mining and municipal effluents.

P. Chakraborty, C.L. Chakrabarti,
Ottawa-Carleton Chemistry Institute, Department of Chemistry, Carleton University, 1125 Colonel By Drive, Ottawa, Ontario K1S 5B6, Canada.

Atmospheric deposition from smelting operations and discharge of mines and municipal effluents in Canada has resulted in metal contamination of freshwater resources. Mechanistic biogeochemical models, especially, Biotic Ligand Model (BLM) shows promise of providing direct, quantitative estimates of metal bioavailability across a wide range of water quality parameters, e.g. pH, hardness, Dissolved Organic Carbon (DOC). Most current approaches for chemical speciation only provide results that are operationally-defined, and hence, their results are not environmentally significant. The objective of this project is to test the hypothesis that there exist mechanistic linkages between free metal ion plus other labile metal species and their bioavailabilty and ecotoxicity to freshwater biota. Two completely independent metal speciation techniques have been used to investigate mining and municipal Effluents from Sudbury, Ontario, including Junction Creek Effluents. Kinetic speciation results from Competing Ligand Exchange Method (CLEM)/ Adsorptive Cathodic Stripping Voltammetry (AdCSV) and Competing Ligand Exchange Method (CLEM) / Graphite Furnace Atomic Absorption Spectrometry (GFAAS) are in excellent agreement, thereby validating the results of both techniques. The results of toxicity tests and chemical speciation studies show that Junction Creek Effluents to be a highly confounded system. Contributory factors include metal speciation such as (i) different [M]/ [DOC] ratios, (ii) competition of trace metals with the target metals, (iii) effect of major cations, and (iv) different sources of DOC. The quest still has not yielded some of the missing mechanistic links between metal speciation and ecotoxicity to biota.

AQUATIC ECOSYSTEM PROJECT ABSTRACTS

Project Title:
Trophic transfer of Cd and Se along a benthic invertebrates food chain.

Dubois M., Hare L., INRS-ETE, Université Du Québec, Québec, QC, Canada.

Food is an important exposure route to consider when assessing risks associated with trace elements presence in aquatic ecosystems. Therefore, better understanding of the pathways of contaminants within food chains will help to predict potential adverse effects on populations. The transfer of Cd and Se has been assessed in a freshwater benthic laboratory food chain in regard with the subcellular partitioning in prey. By mean of radioisotopes technique and differential centrifugation, we observed the uptake of ^{109}Cd and ^{75}Se in the Diptera *Chironomus riparius* and in the Oligochaeta *Tubifex tubifex* living in contaminated sediments. The latter were then fed to the predatory insect and proposed biomonitor, *Sialis*. Using concentrations beyond the toxicity treshold, our results enlighted the fact that detoxification strategies used by prey for an element may modulate their bioaccessibility to *Sialis*. We will further relate the assimilation efficiency of Cd and Se in the predator to the different intracellular fractions associated with elements found in prey.

AQUATIC ECOSYSTEM PROJECT ABSTRACTS

Project Title:
Thallium And Nickel Transfer From Prey To The Aquatic Insect *Sialis*

Dumas, J., Hare, L., INRS-ETE, Université du Québec, Québec, QC, Canada.

Larvae of the alderfly *Sialis* take up many trace elements (As, Cd, Co, Cu, Pb, Zn) almost exclusively from their aquatic prey. Metals present in prey are likely to be more or less available to this predator depending on how they are bound within prey cells.

To test this idea, we exposed two types of prey (an oligochaete and an insect) to sediments spiked with nickel (Ni) and thallium (Tl) at concentrations found in metal-contaminated lakes. When prey reached a steady-state in their metal concentrations, they were offered to *Sialis* as food (1 prey daily for up to 4 days).

Preliminary results suggest that assimilation efficiencies of the two metals are high, and are similar for the two prey types. Our next step is to measure the subcellular distribution of Tl and Ni in prey to determine if they also are similar between prey types.

AQUATIC ECOSYSTEM PROJECT ABSTRACTS

Project Title:
Metal speciation within algal cells: efficiency of different cell homogenisation methods and measurements of thiols in three phytoplanktonic species

M. Lavoie, C. Fortin and P.G.C. Campbell.

Institut National de la Recherche Scientifique, centre Eau, Terre et Environnement (INRS-ETE)

Within project A5 we are exploring the influence of algal cellular partitioning on metal transfer to herbivores. Determination of metals, phytochelatins and low molecular weight thiols within phytoplankton species requires cellular disruption and quantification of the number of broken cells. Different homogenisation methods have been tested (bead beater, freeze-thaw, sonication) with three green algal species (*Pseudokirchneriella subcapitata*, *Chlamydomonas reinhardtii*, *Chlorella pyrenoidosa*). Sonication is the most efficient method to break cells, and, moreover, proved to be the simplest and quickest approach. The estimation of the number of broken cells has been done with a particle counter. The size distribution of different algal suspensions before and after homogenisation have been use to quantify the proportion of broken cells. *C. pyrenoidosa* and *P. subcapitata* cells were more difficult to break than *C. reinhardtii* cells. In fact, virtually all the *C. reinhardtii* cells were broken after 6 minutes of sonication (power = 22 Watts, pulse = 0.2 sec/sec). However, only about a third of *P. subcapitata* and *C. pyrenoidosa* cells respectively were broken after 10 minutes of sonication (power = 22 Watts, pulse = 0,2 sec/sec). In parallel, preliminary measurements of basal cysteine and glutathione content were done in control algal cultures by HPLC with monobromobimane (mBBr) pre-column derivatisation [1]. Cysteine and glutathione concentrations were much higher in *C. pyrenoidosa* (700 amol cysteine/cell and 4590 amol glutathion/cell) than in *C. reinhardtii* (51 amol cysteine/cell and 236 amol glutathion/cell) suggesting potentially contrasting initial metal binding capacities in these two species. In a *P. subcapitata* control culture, a concentration of 81 amol glutathione/cell was measured whereas cysteine was below detection limit.

[1] Morelli E. and Scarano G. (2004). Plant Sci 167: 289-296.

AQUATIC ECOSYSTEM PROJECT ABSTRACTS

Project Title:
(A6) The effects of selenium on the physiological stress response in rainbow trout and brook trout from a coal mining area

Miller, L.L., J.B. Rasmussen, V. Palace, and A. Hontela.

Selenium (Se), an essential element that can also be toxic when available in excess, is found at high concentrations in runoff from some coal mines. Exposures (estimated by Se muscle concentrations) that cause teratogenesis in rainbow trout (*Oncorhynchus mykiss)* do not have similar effects in brook trout (*Salvelinus fontinalis)*. The physiological stress response enables fish to maintain homeostasis during exposure to stressors and, if compromised, survival, quality of gametes, and reproductive recruitment may be adversely affected. The objective of the present study is the compare the physiological stress response in the two salmonids sampled from streams situated in a coal mining area and from reference areas. Parameters measured include: muscle Se, plasma cortisol, plasma glucose, gill Na^+/K^+ ATPase, and the ability of the head kidney to secrete cortisol. Se, at levels sufficient to induce teratogenesis, did not activate the physiological stress response of rainbow trout (no significant difference in measured parameters); although, Se may have compromised the rainbow trout's ability to secrete cortisol. Brook trout analyses are in progress. The effects of Se on brook trout's physiological stress response will also be discussed.
(Financial support from the MITHE-RN and NSERC is gratefully acknowledged.)

AQUATIC ECOSYSTEM PROJECT ABSTRACTS

Project Title:
(A5) Modeling the effect of water quality and natural organic matter (NOM) on trace metal speciation in natural freshwaters

Mueller, K.K.[1], Campbell, P.G.C.[1], Fortin, C.[1]

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The bioaccumulation of environmentally significant metals, such as Ni, Cd, and Tl, is of major concern with respect to elevated concentrations in aquatic food chains and the consequent effects. Of great value would be the ability to accurately and precisely predict the bioavailability of metals to aquatic organisms at various food chain levels. Water quality variables such as pH, alkalinity, ionic strength and major ion, metal and ligand concentrations affect the speciation and, therefore, the bioaccumulation of metals in aquatic systems. With specific reference to ligands, the complexation of trace metals by natural organic matter (NOM) ligands is of particular interest. However, the heterogeneity and complexity of aquatic NOM lead to difficulties in predicting the extent of these complexation reactions with metals in the aquatic environment.

My primary research question is as follows: Is it possible to model the chemical speciation of environmentally significant metals in natural systems as a function of measurable water quality variables, such as pH, alkalinity and ionic strength, and the composition/heterogeneity of the NOM present? In order to address this research question, I propose the extension and/or combination of existing chemical equilibrium models, such as the Windermere Humic Aqueous Model (WHAM) and the Non-Ideal Competitive Adsorption-Donnan (NICA-Donnan) model, to include not only water quality variables, but also the spatial and temporal characterization of NOM. First, lakes within Quebec with a broad range of characteristics will be sampled using clean techniques for water quality, trace metals (using *in situ* diffusion sampling) and NOM. Sample analyses will consist of 1) analysis of pH, alkalinity, ionic strength and major ion concentrations, 2) free trace metal ion analysis (Ni, Cd, Tl) using an ion-exchange technique and 3) quantitative analysis of NOM using TOC analysis and qualitative NOM analysis using optical characterisation methods such as fluorescence and absorbance spectrometry. Determined water quality, metal and NOM values will be used to test the metal speciation prediction capabilities of existing chemical equilibrium models and to refine the existing models to accurately predict trace metal speciation in natural aquatic systems while taking into account the spatial and temporal trends in NOM character.

The measurements and predictions resulting from the proposed project will also be tested in conjunction with a mechanistic bioaccumulation model to be created within the same research group for the prediction of metal transfer between food chain trophic levels.

AQUATIC ECOSYSTEM PROJECT ABSTRACTS

Project Title:
An Investigation of Copper Speciation in Mining Effluents Water Samples by Differential Pulse Anodic Stripping Voltammetry using Copper Titration

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Metal bioavailability and toxicity are known to be linked to metal speciation. The high sensitivity of Differential Pulse Anodic Stripping Voltammetry (DPASV) allows for the determination of metal speciation in natural waters without the necessity of external pre-concentration that can disturb the chemical equilibrium of the sample. The objectives of this research were: 1) to investigate the chemical speciation of copper in mining effluent water samples from Sudbury, Ontario, where the mining operation had been going on for decades, and 2) to compare the speciation of copper in the same samples using Windermere Humic Aqueous Model (WHAM) VI. The experimental investigation was done by copper titration using DPASV. The concentrations of free copper ion were found to be significantly higher in the Copper Cliff mining effluent sample than in the two mixture water samples, one of them containing 45% the same effluent plus 55% Vermillion River water, and another sample containing 30% of the same effluent plus 30% Vermillion River water plus 40% Sudbury municipal effluent. The increase in ecotoxicity to the freshwater biota correlated with the increase in the free copper ion concentrations in the samples. The experimentally measured concentration of the representative organic complexant and the stability constant of the copper complex by one-ligand model in Vermillion River water sample suggested presence of different compositions of Dissolved Organic Carbon in the Copper Cliff mining effluent sample and in the Sudbury municipal effluent sample. The results of different samples showed that the concentrations of free copper ion were loosely dependent on the mole ratio of total copper to Dissolved Organic Carbon. The differences between the experimental results and the WHAM predictions will be presented and critically evaluated.

AQUATIC ECOSYSTEM PROJECT ABSTRACTS

Title:
Water and dietary exposure of fathead minnows (*Pimephales promelas*) to nickel, thallium and cadmium: a foretaste.

Dominique Lapointe and Patrice Couture

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Recent studies have suggested that dietary sources may contribute significantly to metal uptake and toxicity in aquatic organisms. Metal uptake and subsequent subcellular partitioning may also differ between trophic levels, species or route of exposure even though all organisms in the trophic chain live in the same contaminated environment. Moreover, subcellular partitioning of metals at a given trophic level may influence their transfer efficiency to higher consumers. Unfortunately, guidelines for the protection of freshwater aquatic life are often established on the basis of acute and/or chronic exposure of organisms to dissolved metals, ignoring the influence of dietary uptake on metal bioaccumulation. In this project, we will study transfer, accumulation and effects of dietary and waterborne nickel, thallium and cadmium in fathead minnows (*Pimephales promelas*). Our main objective is to determine the importance of metal partitioning in preys on metal accumulation and toxicity in our predator. Specific objectives are to (1) measure accumulation and transfer of dietary and waterborne Ni, Tl and Cd in fathead minnows at different life stages, (2) relate metal accumulation to standard toxicity endpoints (survival, growth, metabolic capacities) and (3) determine the importance of dietary exposure on metal accumulation. To this end, our first steps will be to expose larvae, juveniles and adult fathead minnows to environmentally-relevant concentrations of dissolved metals, and feed juveniles and adults with invertebrate preys that vary in their subcellular metal partitioning.