556 X-ray fluorescence based examination of zinc distribution and speciation in rainbow trout gills: interactions with copper or cadmium

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The current framework of the biotic ligand model (BLM) is based on the metal binding to the fish gills. Although the BLM approach has been successfully used to predict the toxicity of single metals in aquatic organisms, its potential to evaluate the metal mixture toxicity is presently under investigation. Understanding metal interactions in the fish gills would be a key step in the process of developing a sound metal mixture BLM. To this end, we employed X-ray fluorescence imaging (XFI) and micro X-ray absorption near-edge spectroscopy (XANES), which are both synchrotron based techniques, to examine: (i) the spatial distribution and chemical speciation of Zn and its co-localization pattern with other essential elements (Ca, S and Fe), and (ii) the effect of competing metals (Cd and Cu) on the Zn distribution and speciation in fish gills. Ranbow trout (150-200g) were exposed to acute (96-h LC-50) levels of waterborne Zn, singly and in combination with Cu or Cd, for 24-h. Following exposure, gills were dissected out, and 5 micron thick sections were prepared to anylyze Zn distribution and speciation profiles in the rainbow trout gills using the multi-element hard X-ray microprobe at the VESPER beamline, Canadian Light Source, Saskatoon, Canada. Zinc was found to accumulate mainly in the primary lamellae of the gill, which corresponded to the high density of chloride cell localization, supporting the putative roles of these cells in branchial metal uptake. In addition, Zn was found to predominantly co-localize with Ca and S, but not with Fe, indicating that the Ca- and S- containing moieties are involved in intracellular Zn handling. The spatial distribution of Zn in the gills was markedly reduced during co-exposure to Cd, but not to Cu, suggesting a competitive interaction between Zn and Cd for branchial uptrake. Moreover, the predominant chemical species of Zn in the trout gills were Zn-phosphate, Zn-oxide and Zn-cysteine. Co-exposure to Zn and Cu did not alter the chemical speciation of Zn, however a notable increase in the fraction of Zn-cysteine was recorded during co-exposure to Zn and Cd, possibly due to the metallothionein induction (increased detoxification capacity) in fish. To the best of our knowledge, this is the first study to examine how metal mixture interactions influence the spatial distribution and chamical speciation of metals in the fish gills, and our findings have important implications for understanding metal mixture toxicity in fish.

557 Interaction and toxicity of cadmium, copper, and nickel on the olfactory system of rainbow trout Oncorhynchus mykiss Walbaum, 1792

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Water quality criteria are mainly based on the effects of individual contaminants, even though numerous studies have demonstrated that interactions among contaminants may affect the overall toxicity. In the present study the toxic effects and interactions of nickel (Ni), cadmium (Cd), and copper (Cu) on the olfactory response of rainbow trout were determined. To study the toxic effect of single metals on the olfactory system, rainbow trout were exposed to a geometric dilution series of each metal for 24 h. Olfactory acuity was tested using electro-olfactography (EOG). Based on the inhibitory concentration (IC) curves the 20% inhibitory concentration (IC20) of each metal was calculated. Fish were exposed to binary and ternary mixtures of the three metals at the determined IC20 for each metal for 24 h and the acuity of the olfactory system was measured using EOG. In order to find out whether or not rainbow trout can detect the metals using olfaction, fish were tested for their EOG response to 10^{-6} M and water quality criterion concentrations of each metal. The IC20 of Cd and Cu on olfactory function of rainbow trout was calculated at 24.4 and 4.6 µg/L (2.2×10^{-7} and 7.2×10^{-8} M), respectively. Nickel did not impair rainbow trout olfactory function at environmentally relevant concentrations, therefore, in the mixture experiment the acute water quality criterion for Ni 770 µg/L (13.6×10^{-6} M) was used. Binary mixtures of Ni + Cd and Ni + Cu showed synergic olfactory impairment, while Cd + Cu showed an antagonistic olfactory impairment. Rainbow trout were able to detect all three metals at both 10^{-6} M and water quality criteria concentrations. The results of the current study suggest that some of the criteria used for the protection of aquatic life, such as the Cu acute criterion, might not be protective against adverse effects of even single contaminants on the olfactory system of fish. Additionally, interactions between some specific contaminant mixtures, such as Ni with Cd or Cu, might increase the toxicity of each individual contaminant. Current water quality criteria do not take these mixture interactions into account. On the other hand, rainbow trout may be able to detect and probably avoid contaminant metals at criteria concentrations.

558 Metal-mixture toxicity (Copper + Nickel + Zinc) to aquatic insect communities in mesocosms

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Surface waters are nearly always comprised of mixtures of metals while aquatic life criterions are applied one metal at a time. There is virtually no data on metal mixture effects on aquatic insect communities, thus it is generally unknown if metal-mixtures are more or less toxic than expected from the sum of effects of metals individually (response addition). We have conducted four, 30-day mesocosm evaluations of metal-mixtures with the goal of developing a predictive model of the effects of metal-mixtures on aquatic ecosystems. Having executed experiments using Copper (Cu), Cadmium (Cd), and Zinc (Zn) singularly and in mixture, here we present early results of a Cu, Nickel (Ni), and Zn experiment. Nominal aqueous dissolved concentrations ranged from 1 – 100 µg/L for Cu, 0.3 – 800 µg/L for Ni, and 1 – 1600 µg/L for Zn. Average water quality characteristics were 15 mg/L alkalinity as $CaCO_3$, 16.6 mg/L hardness as $CaCO_3$, and 3.2 mg/L dissolved organic carbon. Toxicity to mayfly abundance was greater for Cu (LC50 = 16.6 µg/L nominal) then for Ni (53.62 µg/L nominal) or Zn (198.5 µg/L nominal). LC50 values are expected to fall once measured concentrations are available because observed concentrations in mesocosms are regularly 30-60% lower than nominals. In all cases, given the assumptions of response addition, Ni + Zn mixtures were less toxic than expected, as was true for Cu + Ni + Zn. Prior mesocosm tests also support this finding; generally metal-mixtures are less toxic than expected but not grossly different from additivity. Thus, the assumption of additivity commonly used in risk assessments of the effects of metal-mixtures on aquatic insect communities continues to be a reasonable assumption.

559 Modeling the Chronic Effects of Metal Mixtures to Aquatic Organisms: A Meta-analysis

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Although metals in the aquatic environment mostly occur as mixtures, ecological risk assessment procedures are currently based on a metal-by-metal approach. Recently, different methods to evaluate risks of metal mixture exposures have been proposed. These methods combine the bioavailability-based SSD-approaches of the individual metals with two generally used mixture reference models, concentration addition (CA) and independent action (IA). However, the assumptions underlying each of these methods have not yet been tested. In several experiments conducted over the past years, we investigated chronic toxicity of Ni, Zn, Pb, Cu and Cd mixtures in different combinations to the crustacean Ceriodaphnia dubia (7d reproduction), Daphnia magna (21d reproduction) and the algae

Pseudokirchneriella subcapitata (72h growth). In the present study, we combined all our mixture toxicity data in a meta-analysis to evaluate two risk assessment related questions at the single species-level: I) Which of the two commonly applied mixture reference models (CA or IA) describe metal mixture toxicity most accurately; II) Which of those two models is most conservative for chronic mixture toxicity? For C. dubia, the IA model described metal mixture toxicity clearly more accurately than the CA model. However, for D. magna and P. subcapitata the CA model performed slightly better than the IA model. In general, the CA model was the most conservative model. In addition, we observed that the CA model was generally protective at the effect sizes relevant for environmental risk assessment frameworks, but also overestimated metal mixture toxicity at the EC10 level on average by 1.4 fold. Finally, we compared the prediction performance of two metal mixture bioavailability models (MMBM), an IA based MMBM and a CA based MMBM (WHAM-F_{Tox}) for predicting chronic Ni-Zn-Pb mixture toxicity to C. dubia. The IA MMBM predicted metal mixture toxicity more accurately than the WHAM-F_{Tox} model. In addition, the MMBM had a higher predictive potential than an IA model simply relying on free metal activity or on the dissolved metal concentration. Overall, our study confirms that the CA reference model can be used as a conservative first tier in a tiered metal mixture risk evaluation scheme, but more accurate models are needed in higher tiers. Calibrated metal mixture bioavailability models can predict mixture toxicity more accurately than models merely based on dissolved concentrations or free ion activities.

Developments and Barriers in the Adoption of Amendments for Soil and Sediment Remediation

560 Tools to overcome barriers for in-situ sediment treatment in the U.S

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Extensive experimental studies and field trials have shown that, when applied correctly, in-situ treatment via contaminant sequestration and immobilization using a sorbent material such as activated carbon has now progressed from an innovative sediment remediation approach to a proven, reliable technology. However, there are still significant institutional barriers that limit its application. This presentation will summarize key tools that have proven effective in advancing this technology and getting in-situ treatment incorporated into the remedy at a site. First, an important initial step is to develop a robust conceptual site model that presents a clear understanding of sediment dynamics and stability, and ongoing sources and background levels of contamination. This step is essential for gaining regulatory and stakeholder acceptance of sites for which in-situ treatment can be effective. Second, comparative evaluations of remedial alternatives, building on laboratory and field studies and using modeling as appropriate, are needed to accurately contrast the short- and long-term impacts and effectiveness of in-situ treatment versus more traditional remediation methods such as dredging and capping or natural recovery processes. This allows for proper site-specific balancing of the potential benefits, risks, ecological effects, and costs of in-situ treatment relative to other sediment cleanup technologies. In particular, the type and size of amendments can have effects on persistence, kinetics driving bioavailability, and ecological effects, often defining clear tradeoffs that have differing importance with key stakeholders and resource and regulatory agencies. Third, while there are few remaining technical issues associated with in-situ treatment that have not already been thoroughly addressed in previous field trials and full-scale applications, performing pilot studies focused on specific agency or stakeholder concerns can be pivotal to achieving acceptance. Such trials are important because contaminated sediment sites often have unique physical, chemical, and hydrodynamic factors affecting remedial design. Finally, early identification and focus on cost-effective designs and application methods that appropriately address site-specific conditions can streamline the overall evaluation. Lessons learned from completed and ongoing in-situ treatment projects will be reviewed.

561 Modeling Activated Carbon Amendments in Shallow Ecosystems

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In the past decade significant advancements have been made to understand the effectiveness and ecological benefits of amending activated carbon (AC) to sediments contaminated with hydrophobic organic compounds (HOCs). Laboratory as well as pilot-scale field studies have shown that application of up to 4% AC results in effective removal of sediment porewater HOC and consecutively reduced bioaccumulation in benthic invertebrates and fish [1,2]. Therefore, amendment strategies involving AC are rapidly gaining popularity and viewed as a sediment management option. However, integrative models of the fate and transfer of HOCs in AC amended ecological systems in situ are scarce. Current biouptake models may not adequately explain responses to different AC treatments in natural ecosystems with varying food availability and thus predict long-term bioaccumulation of HOCs in aquatic organisms. In this study, we developed an integrated mass balancing approach to model fate and transfer of polychlorinated biphenyls (PCBs) in ditch ecosystems amended with powdered (PAC), granular AC (GAC) and with subsequent removal of AC granules, i.e. sediment stripping to interpret the bioaccumulation results in our test systems. The PCB concentrations in the aqueous phase was modeled using multiple terms for exchange between (a) porewater, (b) overlying water, (c) air (d) fish, (e) macrophytes, (f) zooplankton, (g) invertebrates, (h) slow sediment sorption domains, (i) PAC or GAC and (j) degradation. This presentation will focus on the development and application of the ecosystem model and discuss the application of the model for AC amended systems. Specifically, the agreement of the model with observed PCB body burdens for fish, macrophytes and zooplankton with and without sorbent amendment will be discussed. The model integrates across the various phases and fauna and provides a more realistic assessment of the ecological response to AC in field settings.

562 Activated carbon amendments in PCB contaminated sediment: full life cycle test with Chironomus riparius

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Carbon amendments have been shown to be an effective in-situ remediation method for contaminated sediments. Especially activated carbon (AC) amendments have a strong sorption capacity towards many hydrophobic organic compounds, and they have been shown to reduce aqueous and bioaccumulated concentrations both in laboratory and field studies. Along with the remedial benefits, direct adverse effects of these amendments have been reported, but the mechanism behind the adverse effects is still unknown. In addition, the effects of amendments on transport of contaminants directly from aquatic to terrestrial ecosystems by metamorphic species has not been considered before. The objectives of this study were to examine the remediation potential and possible secondary effects of AC on Chironomus riparius in a full life cycle test. AC (ø 63−200 µm) mixed into the sediment efficiently reduced PCB bioavailability determined by C. riparius bioaccumulation tests and passive samplers. Additionally, the PCB concentrations in midges emerging from AC treated sediments were reduced. Slightly improved reproduction, survival, larvae growth and gut wall microvilli length was observed with low AC (0.5% sediment dw) dose in the sediment with low organic carbon content. However, higher AC doses (2.5% sediment dw) caused adverse effects on emergence and larval development in both study sediments. In addition, morphological changes in the gut wall microvilli layer were observed. Metamorphic species, such as C. riparius, may act