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We investigated the individual effects of pH on the chronic toxicity of Pb²⁺ on *Daphnia magna* and *Ceriodaphnia dubia*. Until now the effects of pH on the acute and chronic toxicity of water flea species were not clear. This inhibited the development of a chronic BLM for this group of species. The effects of pH on the toxicity of lead were tested during 48 hours acute tests and a 21 and 7 days chronic reproduction test for *D. magna* and *C. dubia* respectively. The pH experiments were conducted with 4 pH levels (6.4, 7, 7.6 and 8.2). Results of the acute tests for both species showed that there was limited effect of pH when considering the dissolved lead fraction. When corrected for speciation however there was an increasing toxicity effect of the free metal ion (Pb²⁺) at higher pH. Preliminary results of the chronic test for *C. dubia* suggest that there were no effects of pH on the toxicity of lead. Initial results of the chronic test with *D. magna* showed an increasing toxic effect with decreasing pH. Finally based on the results we are developing a BLM for the *Daphnia* genus.

WE 017

Impact of incorporation of bioavailability on risk assessment of metals in Japanese surface waters

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It is generally accepted that the bioavailability and toxicity of trace metals in surface water to aquatic life depend on the speciation of metal, not on total or dissolved metal concentration.

Metal speciation is a function of water chemistry including temperature, pH, organic content, and the compositions and concentrations of ions and solid phases in solution. To develop efficient and effective methods of assessing and managing the risk posed by metals to aquatic life, it is important to determine the effects of water chemistry on the bioavailability of metals in surface water. For this reason, we have employed the technique called diffusive gradients in thin-films (DGT) in the study of several Japanese rivers, including meta-contaminated rivers adjacent to abandoned mines, to gain information on the bioavailability of metals in Japanese water systems. The measurements of labile metals as determined by the DGT technique suggest that the biologically available fractions of metals in urban rivers are relatively low compared with those in rivers adjacent to abandoned mines. The fractions of Zn and Cd appear to be higher than that of Cu. An inverse relationship was found between labile-Cu fraction and dissolved organic carbon (DOC). Our result suggested that large amount of Zn and Cd occurred as hydrated ions or small inorganic complexes in water of the rivers studied, whereas most of the Cu occurred as Cu-organic complexes. Moreover, we have examined the impact of incorporation of bioavailability on risk assessment of metals in various Japanese surface water types and to identify what types of Japanese surface waters and metals required to consider bioavailability when assessing risks on aquatic life.

WE 018

Delivering a practical methodology to account for metal (bio)availability in the water framework directive - case studies

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Significant scientific progress has been made for assessing the risk of metals in surface waters in recent years, both at a technical and regulatory level. The current state of the science has recently been incorporated into the new EU Technical Guidance for deriving Environmental Quality Standards (EQS) under the European Water Framework Directive (WFD). The guidance supports the use of a tiered compliance assessment regime for metals that incorporates bioavailability and recommends using Biotic Ligand Models (BLMs). This approach has been endorsed by the EU Scientific Committee on Health and Environmental Risks (SCHER). The bio-met project has developed an online resource (www.bio-met.net) that includes a user friendly BLM tool (the bio-met bioavailability tool) and associated guidance for simply determining the bioavailability of copper, nickel and zinc in European freshwaters and undertaking compliance assessment against a bioavailability based EQS. This poster describes a series of example case-studies conducted across EU Member States that compare the EQS compliance picture using the bio-met bioavailability tool compared to conventional (i.e. hardness-banded) EQS.

WE 019

Transformation/dissolution testing of metals and inorganic substances according to OECD guidance 29: technical challenges & experience

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Within the framework of the European REACH- and CLP regulations, data are needed to characterise the ecotoxic potential of metals and metal substances. The ecotoxicity of soluble inorganic metal compounds depends on released metal species and the composition of the medium. Furthermore, ecotoxicity scores may be read-across based on dissolved metal concentrations and molecular weight conversions. To facilitate read-across of ecotoxic effects to sparingly soluble metal substances, it may become necessary to investigate the rate and extent to which these compounds can produce soluble ionic and other metal bearing species in aqueous media according to OECD Series No. 29 (2001). A test system that meets the specifications of this OECD protocol has been successfully implemented to examine the transformation/dissolution behaviour of a range of metal substances, including redox-sensitive metals. The aqueous test media are based on reconstituted water prepared according to ISO 6341 with pH values in the range of 5.5 - 8.5. The OECD protocol requires exact and comprehensible procedures (e.g. accurate loadings, temperature monitoring, performance of mass balance at test end, and tests were performed in accordance with GLP requirements. In addition to a strict execution of the experimental test procedure, methods for the quantification of dissolved metal ions and species were developed and applied. Element-specific determinations by ICP-OES or ICP-MS were used and validated by appropriate QA/QC measures, including the analysis of certified reference materials, fortified samples, reagent and method blanks and recalibration samples. If different redox-species were formed during a test, dedicated coupling methods, i.e. liquid chromatography coupled to ICP-MS, were developed and successfully applied to separate metal species in different oxidation states. Due to redox equilibrium processes, the stabilization of the formed redox-species immediately after sampling was critical. Differences in transformation/dissolution were observed in response to varying loadings, solution pHs, exposure times and particle surface areas. Our results furthermore emphasize the need to perform the test with sufficient replication as well as the benefits of testing samples with narrow particle size distributions. The relevance of these findings for read-across and the respective classification and labelling will be discussed as well as strengths and weaknesses of the current OECD protocol.

WE 020

The critical surface area-toxic units approach to the hazard classification of metals and alloys

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In the search for standard, reproducible and reliable methods for the aquatic hazard classification of alloys under the GHS (Globally Harmonized System of Classification), the Critical Surface Area-Toxic Units (CSA-TU) approach offers a dependable way to derive acute aquatic hazard classification proposals based on laboratory T/D (Transformation/Dissolution) data. The CSA is the surface area loading of a substance, usually a metal, alloy or sparingly soluble inorganic metal compound, to an aquatic medium that delivers a selected acute or chronic ERV (ecotoxicity reference value) to the medium at a specified time. To derive a GHS hazard classification, T/D data, consisting of dissolved metal concentrations in an aqueous test medium, are compared to acute and chronic ERVs. In this presentation, we use worked examples to show how the CSA TU approach can be applied to derive acute GHS hazard classification proposals for nickel-silver, ferronickel, Monel, brass and Inconel alloys, and Ni and Co metals. To derive an acute hazard classification proposal for nickel-silver alloy from the pH 6 T/D data, we compared the 168-hr concentrations with a relevant ERV among 29, 120 and 70 µg/L for Cu, Ni and Zn, respectively, but because of the disparities in the reactivities of the alloy components and in the ERVs, it was difficult to select one 168-hr metal concentration over another for comparison with an ERV. However, calculating the 168-hr TUs for each component and plotting these as a function of total surface area loading enables the derivation of a CSA for nickel-silver from which can be calculated a minimum specific surface area of 5.88x10⁵ m²/g above which, and a maximum critical diameter of 11.5 mm below which, nickel-silver would classify as acute GHS. We show how the alloys can be compared on the basis of the CSA required to reach TU = 1, revealing that the order of reactivity was nickel-silver > ferronickel > Monel > brass > Co metals > Ni metals > Inconel. For Ni and Co metals, we show how extrapolating 168-hr concentrations for 10 and 100 mg/L loadings to 672 hr can be combined with existing 1 mg/L 672-hr T/D data to yield their respective chronic CSAs. The CSA-TU approach is valuable in aquatic hazard classification because a CSA-TU dataset need be generated only once for a given alloy from a particular production method and may be used repeatedly to classify various specific surface areas and particle sizes of the alloy as they are produced.

WE 021

Transformation/dissolution of lead substances for environmental classification

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For environmental classification under the UN GHS and its equivalent European CLP system, a metal or poorly soluble metal substance is tested according to a transformation/dissolution protocol (TDp) developed under the framework of the OECD to determine metal availability in a standard solution, and then the outcome of the TDp testing is compared with ecotoxicity reference values (ERV) of the metal for the hazard identification in the aquatic environment. The TDp was tested on lead in the form of metal powder (diameter: 75 µm), metal compounds (lead distearate & trilead dioxide phosphonate), and high-purity metal massive (99.99%) as available on the market. In general, the assays were performed in mass or equivalent surface loadings of 1, 10, and 100 mg/L at pH 6, 7, and 8, as appropriate, for screening (24 h) and/or full tests for acute (7 d) and chronic (28 d) classifications. Lead metal powder showed the solubility (> 3000 µg/l) that was above the ERV for lead. The two lead compounds