

European Workshop on Metals in the Environment

Incorporation of Metal Bioavailability into Regulatory Framework

Report by the workshop organizers

Venue, Participants and Aim

The workshop on incorporation of metal bioavailability into the different existing regulatory frameworks was held from 1 to 2 April 2009 in Hamburg, Germany. It was organized by the TuTech Innovation GmbH, hosted by the Hamburg University of Technology, and the German Federal Environmental Agency supported the meeting.

Fourty-one experts from regulation, science and industry attended the workshop. From following countries: Belgium, France, Germany, the Netherlands, Sweden, United Kingdom, and the USA. Ms. S. Heise from the Hamburg University of Applied Sciences, and Mr. W. Ahlf from the Hamburg University of Technology chaired the meeting.

The general aim of the workshop was to discuss the incorporation of bioavailability into the Environmental Risk Assessment of metals. Considerable scientific progress has been made with regard to a better understanding of chemical and biological mechanisms responsible for metal uptake and toxicity. The purpose of the workshop was to discuss and review the scientific progress and the possibilities of implementation metal bioavailability into legislation.

Bioavailability Modelling: State of the Art and Open Questions

The Biotic Ligand Model (BLM) and the concept of sulphide bound metals described by the ratio of Simultaneously Extracted Metals and Acid Volatile Sulphides (SEM-AVS) have been developed to consider the (bio)availability of metals. It is assumed that the free ionic form of metals is the most relevant for uptake and hence the most relevant contribution to toxicity of metals. Aiming at a more realistic risk assessment of metals, (bio)availability is taken into account in a tiered approach which is described in the Metals Environmental Risk Assessment Guidance (MERAG). This approach has been implemented in the guidance document R7.13-2 assisting REACH registrants to perform risk assessments of metals.

The workshop discussed the BLM approach in detail. The participants agreed that so far the BLMs are only applicable for well buffered freshwater containing fairly high dissolved organic carbon (DOC). For marine or estuarine systems they may only be used after thorough evaluation. In marine systems, where pH and salinity are relatively constant, dissolved organic carbon (DOC) is presumably the main variable with respect to metal bioavailability and toxicity. The geochemical dynamics of estuaries are complex and several steps need to be evaluated before these systems can be covered by the BLM. There is some evidence demonstrating that estuarine organisms are less sensitive to metals (e.g. copper) than freshwater or marine organisms due to osmo-regulatory responses.

It was concluded that BLMs should not be used under geochemical conditions such as extreme pH, extreme water hardness or low ionic activity which are not covered by BLMs.

Overall, there is still need of BLM-research to evaluate quantitatively the manner in which site-specific water chemistry affects the speciation and bioavailability of metals.

Terrestrial bioavailability models (empirical regression models) have been developed for zinc, nickel, and copper. Problems arise concerning the spiking of the soil. So far terrestrial bioavailability models have been developed on the basis of data from spiked soils without leaching which is not a realistic scenario. For sediments bioavailability corrections for metal-organic carbon and metal-sulphide binding (SEM-AVS) have been developed and validated in the field and/or laboratory, but no BLM for sediments has been developed for practical application until the present time.

One possible boundary discussed, is the equilibrium status which is in principle never given in nature but which is assumed by the BLM. This issue was discussed for scenarios such as the influx of particulate bound metals into the river Elbe or influx from manure or freshly sedimented particles. Presumably absence of equilibrium may not be important however it has not been investigated. In principle a true steady state will not be achieved but a steady state within a 20%-range of parameters would be sufficient, and would avoid the enormous complexity of dealing with kinetics and history.

Mixtures of metals and mixture toxicity was discussed but considered to be an issue for future research.

The relative importance of the uptake of dissolved metals ions versus the dietary uptake was especially discussed by one working group. The mechanistic baseline of the physiology behind the Biotic Ligand Model (BLM) has been well established for several metals under acute exposures where the site of metal toxicity is at a site of immediate accessibility, e.g., the gill. In contrast dietborne metals must go through many processes (e.g., dissociation from food, uptake across the gut, first pass elimination by liver/hepatopancreas, absorption by plasma proteins or by metallothionein, sequestration in granules and elimination) prior to the point where interaction of metals with the site of action can take place. This pathway gains more importance if considering chronic toxicity. The workshop considered a systematic evaluation of relevant studies on dietary exposure of aquatic organisms as important, because information on dietary accumulation of metals is at least an added value that may increase the understanding of the accumulation-toxicity relationship. The use of the term bioavailable in the BLM tool was discussed as being misunderstanding, as each metal ion regardless of its speciation is bioavailable but only some of the metal trigger toxic effects. Therefore, important for consideration are not the possible uptake routes but the toxic routes.

A range of geochemical phases, including sulphides, organic carbon, clays, and iron and manganese oxyhydroxides can bind metals. All binding forms influence biological uptake and toxicity. The SEM-AVS concept has been shown to be predictive for the lack of toxicity for metals having a high affinity for sulphides. It was discussed whether the evidence showing relationships between the occurrence of these phases and the toxicity of metals to benthic organisms is always clear-cut as apart from geochemical conditions, which control free metal concentration, bioavailability is additionally a result of contaminant/particle interaction and of organisms' activity such as

bioturbation. In this regard, the SEM-AVS concept, which considers only sedimentary metals in anoxic sediments, was considered more effective in predicting metal concentrations in pore waters than sediment toxicity in general. Thus it appears that the SEM-AVS approach is not sufficient for a predictive tool of sediment toxicity in general.

Regulatory Aspects

Practical and organisational challenges associated with the use of BLMs were discussed. Concerning regulatory aspects the issue was raised that scientific sophistication is one among several conflicting objectives e.g. transparency of the decision process or required time for results, which need to be balanced. Considering the Water Frame Directive one important step is the status determination of the water bodies which must be based on clear and litigable decisions. An example was shown for the environmental quality standard (EQS) for Cadmium in the EU directive 2008/105/EG, which depends on hardness. There could exist circumstances of concentration and hardness during a year, where compliance is dependent on the kind of averaging over the year. It could be averaged: a) Cd-concentrations and hardness values, b) yes/no compliance decisions for every sample or c) risk ratios for each sample. It was also discussed to which extent a change in monitoring practice would increase the required time, effort and staff training due to additional parameters which need to be monitored, if BLMs are taken into account to determine the status of water bodies.

It was agreed that it is important to know the uncertainties to define the boundaries of BLMs and that an overall understanding of BLMs is necessary. Geochemical limits such as extreme pH, water hardness or low ionic activity not covered by BLMs have to be communicated clearly and transparently. One possibility could be to decide about the level of protection or vice versa about the share of "not protected parameter combinations".

The level of protection of water bodies was discussed concerning EQS related either to a bioavailable i.e free ionic fraction, dissolved fraction or related to total concentration. It was questioned whether the precautionary principle is being taken into account sufficiently if assuming that the free ionic form is the most relevant form for uptake and toxicity as important uptake pathways such as the uptake via food are not reflected in the approach. However, precaution may be implemented into EQS based on the bioavailable fraction.

It was discussed whether the system to derive EQS does necessarily need to be changed. One alternative approach to the conventional risk assessment approach with the comparison of a derived PNEC with a derived PEC as it is set in the guideline for the risk assessment of metals (R 7.13-2 Guideline) are EQSs related to the natural background-concentration. This approach follows the concept, that the biosphere is adapted to background concentrations of metals as natural substances.

It was concluded that bioavailability cannot be included into all regulations in the same way. For example emission control and emission limit (e.g. in the Integrated pollution prevention control (IPPC) directive) could not include bioavailability. On the other hand methodology of environmental standards should be the same / at least comparable in different regulations. In this respect REACH was mentioned. The

assessemnt is based on the ECHA guideline R 7.13-2, which suggests a tiered approach. Up to which tier is taken into account depends on whether a risk has been identified or not, availability of physico-chemical data and availability of a speciation model or Biotic Ligand Model for the metal regarded. Here the assessment is due to the manufacturers and importers.

For river basin management according to the WFD additional difficulties rise compared to the „Total“ metal approach. E.g. substance fluxes in river systems may be calculated with total concentrations only. Flux calculations are necessary for emission controls in case of non-compliance of EQS in downstream water bodies. That means, monitoring of total concentrations is necessary and river basin management based only on monitoring of dissolved or even bioavailable shares is impossible.

A tiered approach was proposed with EQS for the total concentration and additional assessment of the bioavailable part in case of non-compliance to assess the needs of restoration.

It was discussed, if simplifications for the administration would be possible. One could be to average risk ratios of „BLM-normalized“ concentrations instead of the concentrations itself (see Cd-example above). These would not be applicable for extreme conditions. To use default values for hardness, pH and DOC to reduce monitoring was considered not practicable.

Concerning political implementation the workshop could not conclude about the question, if there is really a need to change the EQS-system. The approach based on total concentrations fits better to emission control needs in water management and is conform to precautionary requirements.

Conclusion

If bioavailability is taken into account using SEM-AVS, a speciation model or BLMs, remaining uncertainties as dicussed in this workshop need to be taken into account: geochemical conditions not covered by the approaches and the relative importance of other uptake pathways apart from the free ionic form of metals. It is important to know these uncertainties and boundaries and communicate these clearly and transparently.

Bioavailability cannot be included into all regulations in the same way. Substance fluxes in river systems for river basin management can only be calculated with total concentrations. As far as BLMs are available for the metal regarded BLMs can be used for the determination of EQS but precaution should be implemented taking the uncertainties into account as mentioned above. It is however not necessary to change the overall procedure of the EQS derivation. In the case the derivation of EQS is based on the background concentration or a PNEC (based on dissolved metal) the level of protection of a waterbody is not decreased as the consideration of bioavailbility is not more precautionous than the above mentioned method.

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