

INTEGRATING EMERGING METAL RISK ASSESSMENT TECHNOLOGIES INTO LIFE CYCLE IMPACT ASSESSMENTS

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The state-of-the-science for performing ecological and human health risk assessment has been rapidly advancing over the past decade. New models have emerged that allow for calculating bioavailability of metals in environmental compartments (water, sediment, soil, and air) as well as uptake and transfer of metals by organisms. The biotic ligand model is an example of one such aquatic ecological model that allows for a calculation of the amount of metal that must reach the site of action (fish gill) for toxicity to occur. The model accounts for total metal, site conditions and organism of interest. A key facing scientists is how to merge quantitative advancements in the science of risk assessment into LCA impact assessments. Frequently the metrics are not compatible between ecological and human health risk assessment and LCA impact assessments, Further, LCA impact assessments are not structured to consider benefits from essential elements. Differences between risk assessment and impact assessment will be explored as well as possible alternatives that may utilize common metrics.

ISSUES IN THE RISK ASSESSMENT OF METALS AND METALLOIDS

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Risk assessment (RA) is a process that evaluates the potential for adverse ecological effects that may occur as a result of exposure to contaminants or other stressors. The basic RA paradigm for contaminants involves determining the predicted environmental concentration (PEC) then dividing this by the predicted no effect concentration (PNEC). At its simplest level this calculation yields a hazard quotient; more certainty requires probabilistic assessment. Determining the PEC for metals and metalloids requires: determining natural background; considering essentiality; evaluating speciation and the effects of modifying factors; and, assessing bioavailability. The PNEC is developed through appropriate testing, statistical extrapolations, and/or mechanistic approaches such as the Biotic Ligand Model (BLM). RA issues specific to metals and metalloids include: natural occurrence; transformation; bioavailability; both positive and negative effects for essential elements. Recent research findings from the Metals in the Environment Research Network (MITE-RN) will be reviewed including both terrestrial (metals cycling in northern forests) and aquatic components (dietary exposure routes, metal-sulfur complexes, critical body concentrations, food chains, and revisions to the BLM). The significance of these and other recent metals findings to RA of metals and metalloids will be discussed.

Key Considerations in Assessing Environmental Impacts of Essential Metals

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The EU risk assessment zinc, currently being carried under EU Regulation 93/793, has identified a number of critical issues in environmental impact assessment for natural and essential metals such as zinc. Much of this experience and data generation is of significant value in life cycle impact considerations.

The paper will explore the key critical issues, including:

- influence of natural background concentrations on biological sensitivity
- importance of data quality
- relevance of eco-regions
- integration of bioavailability

The results of recent and extensive research work conducted to support the EU risk assessment for zinc will be used to highlight issues and considerations of importance for all the essential metals.

PARTITIONING AND SPECIATION OF METAL AND METALLOIDS IN SURFACE SOIL: INFLUENCE ON ECOTOXICITY ASSESSMENT

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Multi-media fate models developed to assess the impact of metals usually do not take into account the fact that under specific environmental conditions, the properties exhibited by metals could be quite different. In fact, the physicochemical properties of surface soil (pH, CEC, organic matter content, etc.) can strongly influence metal speciation and, consequently, its mobility, bioavailability and toxicity. Moreover, the type of soil (clayed, loamy, silty or sandy soil) also plays a major role. To assess the environmental impact of metals in soils, knowledge of the total concentration of a specific metal without considering its speciation is not sufficient.

This paper reports on the influence of surface soil composition on partitioning and speciation of metals with an emphasis on arsenic, copper and chromium. The effect of the metal forms on the toxic response of contaminated soil was also assessed. Sequential extraction and modified solvent extraction were used to assess Cu and Cr partitioning and As speciation (As III or As V) in nine soils of different composition. Soil toxicity was assessed using two bioassays, earthworm mortality and barley growth. Results indicated that organic matter content influences the mobility and the bioavailability of the metals. In fact, average metal retention in mineral soils was low for Cu and Cr but increased dramatically in highly organic soils. Results also revealed that in all types of soils studied, As was principally in the pentavalent (As V) state. However, As III was found in significant proportions in highly organic soils. Bioassays indicated that the presence of organic matter reduced the toxic response of some receptors (e.g.: earthworms).

These results suggest that the final species of metals need to be considered before they are used in a multi-media fate model. Moreover, since geologic conditions vary with

geographic location, a weighting system considering the types of soils encountered is necessary. A model based on the DRASTIC aquifer vulnerability assessment model is therefore proposed.

ESTIMATING THE FATE, BIOAVAILABILITY AND POTENTIAL RISK OF METALS IN THE ENVIRONMENT

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Estimating metal fate and potential toxicological risk demands consideration of metal speciation and distribution among phases, which are functions of the particular metal and site-specific environmental conditions. This need arises because of the differential mobility of different species and the dependence of bioavailability, and hence toxicity, on species composition.

To address this need, we have adapted fugacity-based models (a) to treat non-volatile chemicals (since the fugacity formulation pertains to chemicals with a measurable vapour pressure), and (b) to estimate the fate and concentrations of multiple interconverting species. For aquatic systems, we can estimate aqueous speciation and solid phase complexation by means of an equilibrium speciation model that defines metal chemistry under specified conditions, where these estimates of species composition and phase distribution are used as inputs for the fate model. The coupled TRANsport and SPECiation model, TRANSPEC, considers metal inputs from atmospheric deposition, river inflow and sediment feed-back (as occurs with contaminated systems), assumes instantaneous interconversion among species within compartments, and calculates species concentrations and interconversion rates in the water column and underlying sediments. Steady-state and time-dependent versions of TRANSPEC have been used to describe Zn dynamics in a complex system for which the sediments act as an in-place loading source. TRANSPEC is also being developed to consider mercury which necessitates consideration of the volatile elemental Hg species. For terrestrial and aquatic environments, we have adapted our multimedia model to consider the fate of total metal and are working towards a version that considers multiple interconverting metal species. This model tracks the fate of a metal through air, water, surface sediments, soil, vegetation and the organic film that develops on impervious surfaces (e.g., in cities). The output of this model, species concentrations in each compartment, is used to calculate exposure and potential toxicological risk posed to terrestrial and aquatic receptors using four screening level calculations in this risk assessment formulation.

DEVELOPMENT OF DAMAGE FUNCTIONS CONSIDERING TOXIC IMPACTS OF ECOSYSTEM IN JAPAN

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METI funded to support constructing LCA database for Japanese LCA practitioner. To promote this project effectively, 3 committees have been organized. One of the committee, impact assessment committee aims at the development of Japanese LCIA methodology. This methodology can be divided in 3 parts; Characterization, Damage assessment, Weighting. The potential damages of safeguard subjects will be addressed in the damage assessment. The damage for biodiversity has been considered as a representative impact of ecosystem. We adopted the number of extinct species as an indicator expressing the loss of biodiversity.

Damage function is composed of 2 parts; fate exposure analysis and effect assessment. In the former part, a multimedia fate model considering Japanese background was developed. This model covers more than 200 chemicals and heavy metals released in Japan. Effect assessment in this study relates exposure of pollutants with increased number of extinct species. This methodology employs an extinction probability model that estimate the increased risk of extinction of species caused by the decrease of intrinsic rate of natural increase. The relationship between the variation of intrinsic rate of natural increase and the increased exposure level of toxic substance are assumed from the experimental studies.

The calculated result from this methodology enables us to compare with that caused by the other environmental problems such as land use and to aggregate them into the potential risk of biodiversity.

AMI: ASSESSMENT OF THE MEDIAN IMPACT OF METALS ON AQUATIC ECOSYSTEMS FOR LCA

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The current methods of the Life Cycle Impact Assessment on ecosystems are derived from risk assessment and are conservative rather than comparative. During a first time period of work at GECOS, the AMI method has been developed for the assessment of impacts on ecosystems in Life Cycle Assessment [Assessment of the Median Impact]. It is based on a comparative approach that considers the diversity of chemicals, the diversity of organisms and the diversity of ecosystems. This method is currently the only one that is able to associate an uncertainty with the calculated characterisation factors.

A non-parametric approach enables the calculation of characterisation factors without the need for assuming a distribution. A characterisation factor based on the median response of species, with the associated uncertainty based on bootstrap avoid the assumption of a simple parametric distributions like log-normal, log-logistic, and log-triangular which are statistically rejected for several compounds. An extrapolation from acute EC50 to Chronic EC50 is more reliable because the variability due to the experimental design is avoided if we considered the EC50 instead of the NOEC. The acute-chronic relation is better if it is based on the median response of at least five EC50 per chemical.

The method is applied to characterize the impact on aquatic ecosystems of 10 different metals and compare them with organic substances. The importance of formulation/associated substances and metal speciation will be discussed

ENDPOINT MODELLING OF METALS LIFE CYCLE IMPACTS ON HUMAN HEALTH

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To characterize human health impacts of metals and organic substances, a new approach has been developed to calculate Disability Adjusted Life Years (DALY's) for carcinogens and non-carcinogens, based on epidemiological data when available or on ED10h (best estimate of the effect dose inducing a 10% added risk for humans). The ED10h is calculated directly from bioassays available in IRIS and extrapolation to low dose exposure is discussed in details. ED10h are also correlated to the more widely available tumour dose TD50 (carcinogens) and NOAEL (non-carcinogens) to quantify the slope factor of more than 900 chemicals.

A weighting is proposed to account for effect severity. For carcinogenic endpoints, the DALYp per affected person amounts on average to 11 years of life lost per affected person and is dominated by mortality. For non-carcinogenic effects, a simplified categorization of the adverse effects into three categories is chosen: 11, 1.1 and 0.11 YLL/person are respectively assigned to high, medium (default) and low severities.

To illustrate its potential, the method is combined with calculated exposure efficiencies and applied to different metals, yielding effect and characterization factors for 10 different metals. Their relative importance is shown through a case study and the need for modelling metal speciation is discussed

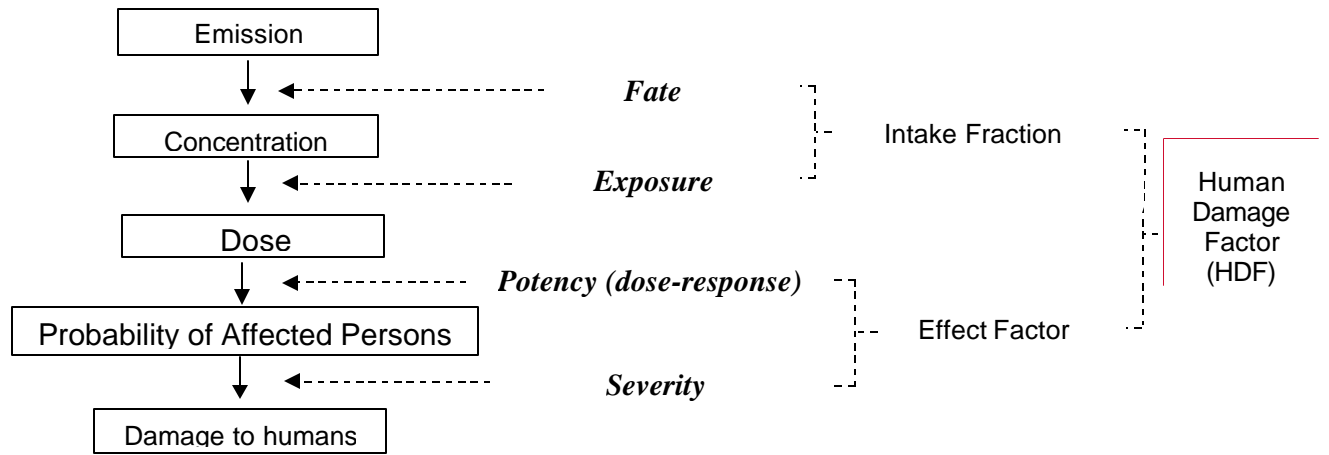


Figure 1 Outline of stages for the characterisation of human health effects.

ENVIRONMENTAL TOXICITY AND IMPACT ASSESSMENT MODELS FOR METALS

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Modelling the environmental fate and ecotoxicological impact of anthropogenic releases of metals is complicated by natural occurrence, essentiality, acclimation and adaptation. In general, LCA and risk assessment approaches need to incorporate these complexities into current methodologies. For example, bioaccumulation (B), along with persistence (P) and toxicity (T), is often used in models for evaluating potential impacts. However, the measures used for bioaccumulation, the bioaccumulation factor (BCF) and bioconcentration factor (BAF), have been shown as inappropriate for assessing the bioaccumulative potential of metals and inorganic metal compounds. As well, the criterion persistence, while a useful for organic substances has no discriminatory power for substances that occur on the periodic table. Moreover, recent research has dramatically advanced the understanding of the toxicology of metals. The development of site-specific mechanistically based toxicity models, or biotic ligand models, for metals provides a new approach for advancing improvements to water quality criteria and guidelines. The presentation will review the application of the PBT approach for metals and inorganic metal compounds with a view to possible directions to improve the methodologies for assessing environmental impact in LCA.

Consideration of Metal Availability and Fate in Life Cycle Assessments

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An important step in a Life Cycle Assessment (LCA) for a product is the Impact Assessment (IA). The purpose of the IA is to examine potential and actual environmental and human health effects that result from releases of materials, be they organic chemicals, metals or metal compounds, to the environment. While the magnitude of the mass loading rate of a substance to the environment is likely to be an important factor in the IA, it should be viewed in combination with other factors that affect its potential for causing effects. This is because there are likely to be complex interactions of the substance with numerous environmental factors, and these interactions may alter its availability to biota and its ultimate environmental fate as well. The significance of such factors will vary by substance, and hence it is important that they not be disregarded in the LCA, especially if cross-product comparisons are to be made. Fortunately, methods are available for use by the LCA analyst that will facilitate the incorporation of such considerations into an LCA. The biological availability of a metal that is released to a terrestrial or aquatic system is particularly likely to be influenced by the physical-chemical characteristics of a particular medium. Hence it is important to consider the factors that affect metal availability, to the degree possible. The biotic ligand model (BLM) is an example of a computational tool that is being developed for use in performing an assessment of metal availability and toxicity in the water column of aquatic systems, and its potential for use in benthic sediments and terrestrial settings is under consideration as well. Further, while metals are often viewed as being conservative, in that the ultimate degradation to an end product such as CO₂ does not occur, failure to consider that the exposure levels of the available metal forms will likely decrease over time will detract from the validity of an LCA. A unit world model framework for metals is proposed as a way to quantitatively consider these factors in the context of an LCA. Use of this type of approach should facilitate the completion of meaningful assessments of exposure levels and the potential for effects. While the results of such an evaluation should ultimately be of use in making cross-product LCA comparisons, methods for integrating the results across impact categories, and for making such comparisons generally, require further development.

ON THE AQUATIC HAZARD CLASSIFICATION OF METALS AND ALLOYS

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The use of chemicals is fundamental to the economic development of all countries and, at the same time, may pose a risk to human health and the environment if not managed responsibly (OECD, 2001). Environmental protection may be achieved by identifying and communicating potential hazards to users of chemicals so that they can take measures to avoid and manage such risks as may occur. For metals in their bioavailable form, it is considered that the aquatic environment is at the most risk, compared to air, sediments and soils.

Accordingly, within the OECD Harmonised Integrated Classification System (HCS) For Human Health and Environmental Hazards of Chemical Substances and Mixtures (OECD, 2001), a scheme to classify chemical substances has been developed, a section of which has been adapted to enable the classification of metals and metal compounds, and has the potential for extension to alloys.

The scheme is driven by data from a draft Transformation/Dissolution (T/D) Protocol which is a simple experimental procedure, under a set of standard laboratory conditions representative of those generally occurring in the environment, applied to various weighed amounts of powders or granules of the solid substances, loaded to 1 L of an aqueous medium such as OECD 203 or OECD 201. This system recognizes the unique nature of metals and inorganic metal compounds and their distinct properties compared to synthetic organic substances.

To establish the hazard classification of a metal-bearing substance, data from the draft T/D Protocol are compared to existing ecotoxicity data as determined under similar conditions. Additionally, toxicity testing may be used to validate the linkage between transformation chemistry and literature values for toxicity.

In this presentation, we review the HCS and draft T/D Protocol, and present some of our recent results on the T/D characteristics of such metals and nickel and zinc, and such alloys as cartridge brass, stainless steel and Monel, as well as discuss the implications for the hazard classifications of these substances.

METALS IN THE OCEAN: AN ADAPTED FATE MODEL

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The use of multimedia models for fate modelling in LCA has largely improved LCA characterization factors for toxicity. As a side effect, however, characterization factors of metals tend to become comparatively much higher than we should reasonably expect. This phenomenon is eventually caused by the fact that metals are non-degradable. This causes them to end up largely in the ocean, from where they can only be removed by sedimentation: a very slow process. Since concentrations are mathematically integrated over time (and space) in the LCA calculation process, long residence times result in high characterization factors. Calculations are accordingly very sensitive to errors in the modelling of oceanic processes. Therefore, these processes should be handled with more care than they currently are. We tried to make a first step in this direction. First, we considered the relationship between concentration and exposure. In most multimedia models, oceans are handled as homogeneous compartments. Human exposure, however, is related only to the upper layer. Effective residence times in this layer are generally orders of magnitudes smaller than overall oceanic residence times. Therefore, we distinguished two separate layers in the ocean: a mixed surface layer with a depth of 100 m, and a deep ocean layer. For human exposure, we considered concentrations in the surface mixed layer only. As a first approach, we did the same for ecotoxicity. We used empirical data on individual metal residence times for this layer, thereby abandoning the modelling concept on sedimentation rates. To account for decreased availability by speciation and by non-ideal effects in saline waters, we used the 'free ion activity' concept. For mercury, we used a individual approach, taking into account the ratio in which elemental, inorganic and organic species occur in the different media. Modelling results will be available very soon. We expect that the current disproportionality of LCA characterization factors between metals and organics will largely disappear.