

Metal bioavailability incorporated in water quality assessments

CSIRO provides a specialist capability for sampling, analysis and bioavailability assessment of metals and metalloids in waters

In most waters, contaminants will be present dissolved, complexed, colloidal and particulate forms and the bioavailability of these forms differ considerably. Particulate and strongly complexed forms are not bioavailable, i.e. they are not taken up by an organism or directly available to cause biological effects. Information on the speciation (dissolved and particulate forms) and the chemical behaviour of the contaminant (diffusion, sorption, and partitioning) permits a more accurate assessment of risk.

In waters, the bioavailability of contaminants is closely linked to the freely dissolved concentration, which is most strongly influenced by the water characteristics that govern speciation (Figure 1). The filtration of water through the gills or cell membranes of aquatic organisms is a principal exposure route for most organisms, and influences the rate of contaminant uptake and internalisation (Figure 1). Direct absorption through other external tissues is generally a lesser exposure route for most metals and metalloids. For organisms where dietary exposure is significant, the uptake kinetics of contaminants associated with ingested solids is also an important consideration.

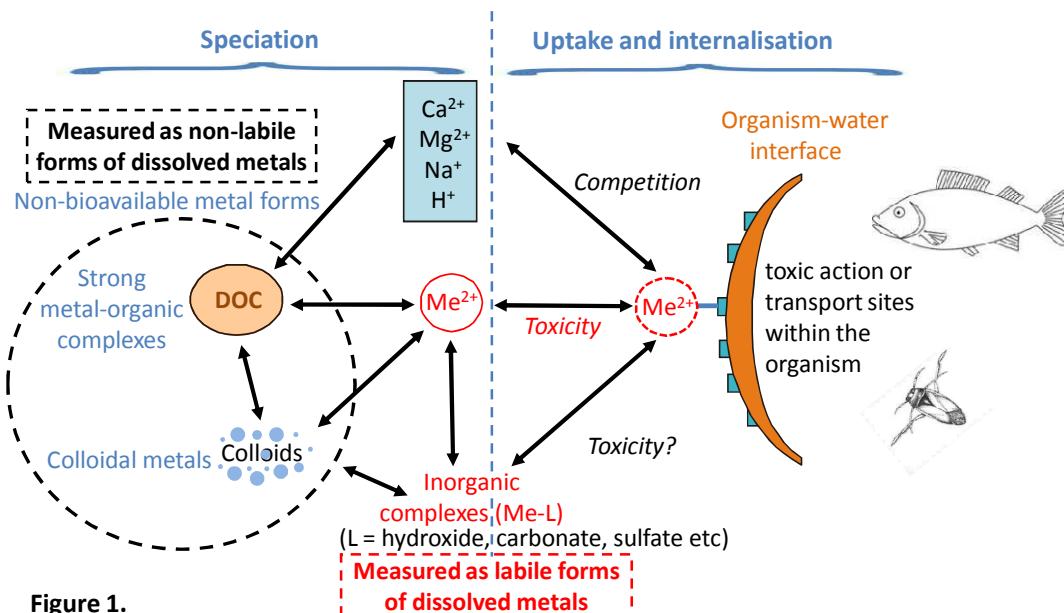


Figure 1.

Incorporating metal speciation when using water quality guidelines

The speciation of the metals in the dissolved phase will influence their bioavailability and the risk posed. This may be mediated by other cations (e.g. Ca^{2+} and Mg^{2+} or H^+) that compete for metal (Me) binding sites, by metal complexation by organic ligands, and by metals in colloidal forms associated with aluminium, iron and manganese surfaces of clays, aluminosilicates, oxyhydroxides and humic/fulvic acids (Figure 1).

Australia's water quality guidelines (WQGs) for the protection of aquatic ecosystem health were derived using species sensitivity distributions of chronic no observed effects concentrations (NOECs) or 10% chronic effect concentrations (EC10s) (ANZECC/ARMCANZ, 2000). These data were derived predominantly from laboratory-based bioassays on solutions of metals in highly labile and bioavailable forms, e.g. predominantly as free metal ions (e.g. Me^{2+}) or weak and labile inorganic metal complexes, with negligible strong metal–ligand complexes that are kinetically non-labile such as metal complexes with humic or fulvic acids.

In the application of the WQGs, when there is evidence that, in the test waters, a significant portion of the total dissolved concentration is present in forms that are not considered bioavailable (e.g. non-labile strong metal–ligand complexes that occur with humic and fulvic acids and or colloid-associated metals), it is appropriate to make the WQG comparison with just the labile fraction (determined by measurement or potentially by speciation modelling).

The ANZECC/ARMCANZ (2000) decision framework for metal toxicants incorporating speciation–bioavailability assessment is summarised below using the example of aluminium and copper in a freshwater

(Figure 2). The measurement of metal concentrations in unfiltered samples is often quite meaningless as these forms have differing bioavailabilities, although this might be used where total concentrations are expected to fall below water quality guideline values (GVs). The first assessment step usually involves the comparison of the measured dissolved concentration (<0.45 µm filtered) with the GV. If the GV is exceeded, speciation methods are undertaken. These might involve a size-based separation of the larger colloidal species or passage through a column of chelating resin (Chelex-100) to remove the weakly bound, labile or potentially bioavailable forms for assessment against GVs.

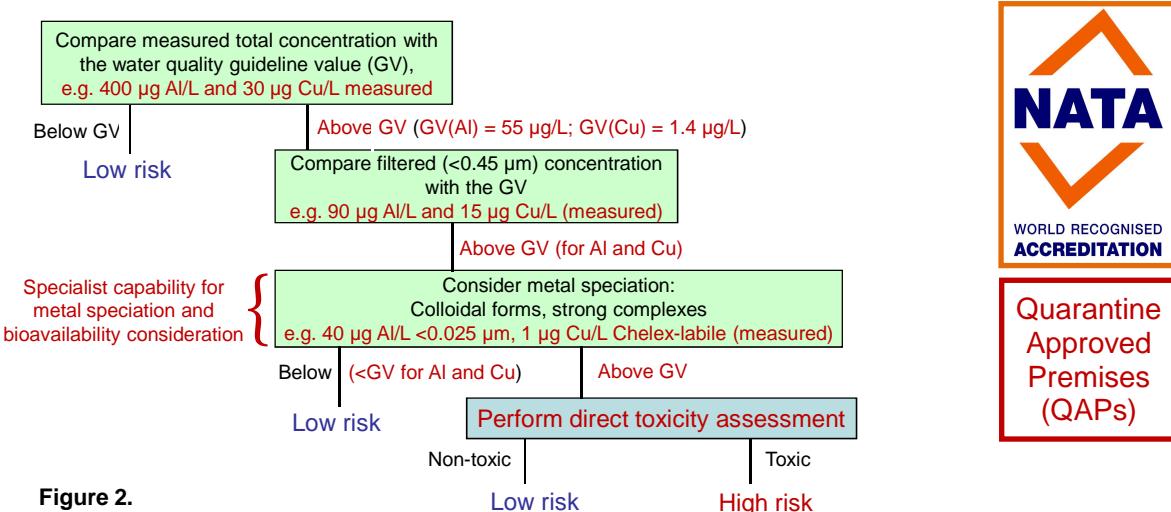


Figure 2.

Specialist applications

The CSIRO Centre for Environmental Contaminants Research (CECR) situated at Lucas Heights, in Sydney, has NATA-accreditation and quarantine-approved premises for its highly proficient specialist capabilities in metal speciation, bioavailability and toxicity assessment. This capability has been applied in a wide range of studies both within Australia and internationally within the Asia-Pacific region, particularly in relation to compliance and the optimisation of how industries manage discharges to waterways.

CSIRO provide assessments of total, dissolved and labile metals using a range of techniques to provide detailed information on the form and potential bioavailability of the filterable metals. Chelex-labile metal measurements are one the major tools developed by CSIRO for this purpose (Bowles et al., 2006). The combination of this technique with size fractionation / filtration techniques allows clear differentiation between truly dissolved labile and non-labile forms and colloidal forms (Cresswell et al., 2013; Simpson et al., 2013). These techniques work effectively for both marine and freshwaters.

CSIRO undertakes NATA-accredited metal analyses, speciation, bioavailability and toxicity testing as part of water quality and environmental impact assessments (EIA) for both industry and regulators, including:

- trace metal sampling and analyses (with sampling advice and provision of bottles if required);
- metal speciation (including methyl-mercury) and bioavailability assessments;
- process-related studies to understand chemical fate and transformations;
- ecotoxicological studies to link metal exposure with effects and derive site-specific guidelines or for hazard and risk assessment.

References

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- Simpson, S.L., Vardanega , C.R., Jarolimek, C., Jolley, D.F., Angel, B.A., Mosley, L.M. (2014). Metal speciation and potential bioavailability changes during discharge and neutralisation of acidic drainage water. *Chemosphere*, 103, 172–180.

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