AGMIN NEWSLETTER No. 416

Environmental Chemistry and Fate

1. Environmental Transport and Transformation

Copper compounds such as Kupramine® are intentionally applied to water to kill algae. Several processes influence the fate of copper in the aqueous environment. These include complex formation, sorption to hydrous metal oxides, clays and organic materials, and bioaccumulation. Information on the physicochemical forms of copper (speciation) is more informative than total copper concentrations. Much of the copper discharged to water is in particulate form and tends to settle out, precipitate out or be adsorbed by organic matter, hydrous iron, manganese oxides and clay in the sediment or water column. In the aquatic environment the concentration of copper and its bioavailability depend on factors such as water hardness and alkalinity, ionic strength, pH and redox potential, complexing ligands, suspended particulate matter and carbon, and the interaction between sediments and water.

Most copper deposited in soil is strongly adsorbed and remains in the upper few centimetres of soil. Copper adsorbs to organic matter, carbonate minerals, clay minerals, hydrous iron and manganese oxides. The greatest amount of leaching occurs from sandy acidic soils. In the terrestrial environment a number of important factors influence the fate of copper in soil. These include the nature of the soil itself, pH, presence of oxides, redox potential, charged surfaces, organic matter and cation exchange.

Bioaccumulation of copper form the environment occurs if the copper is biologically available. Accumulation factors vary greatly between different organisms, but tend to be higher at lower exposure concentrations. Accumulation may lead to exceptionally high body burdens in certain animals (such as bivalves) and terrestrial plants (such as those growing on contaminated soils). However, many organisms are capable of regulating their body copper concentration.

2. Environmental Levels of Copper

Copper levels in seawater of 0.15 µg/litre and in fresh water of 1-20 µg/litre are found in uncontaminated areas. Sediment is an important sink and reservoir for copper. Background levels of copper in natural freshwater sediments range from 16 to 5000 mg/kg (dry weight). Copper levels in marine sediments range from 2 to 740 mg/kg (dry weight). In anoxic sediments copper is bound strongly by sulphide and therefore not bioavailable. Median copper concentrations in uncontaminated soil were reported to be 30 mg/kg (range 2 – 250 mg/kg). Plants, invertebrates and fish accumulate copper. Higher concentrations of copper have been reported in organisms from copper-contaminated sites than in those from non-contaminated sites.

3. Effects of Copper on Humans

Copper is an essential element and adverse health effects are related to deficiency as well as excess. Copper deficiency is associated with anaemia, neutropenia and bone abnormalities but clinically evident deficiency is relatively infrequent in humans. Balance data may be used to anticipate clinical effects, whereas serum copper and ceruloplasmin levels are useful measures of moderate to severe deficiency but less sensitive measures of marginal deficiency.

For healthy, non-occupationally-exposed humans the major route of exposure to copper is oral. The mean daily dietary intake of copper in adults ranges between 0.9 and 2.2 mg. A majority of studies have found intakes to be at the lower end of that range. The variation reflects different dietary habits as well as different agricultural and food processing practices used worldwide. In general, total daily oral intakes of copper (food plus drinking water) are between 1 and 2 mg/day, although they may occasionally exceed 5 mg/day.

4. Effects of Copper on Biota

The adverse effects of copper must be balanced against it's essentially. Copper is an essential element for all biota, and care must be taken to ensure the copper nutritional needs of organisms are met. At least 12 major proteins require copper as an integral part of their structure. It is essential for the utilization of iron in the formation of haemoglobin, and most crustaceans and molluscs possess the copper-containing haemocyanin as their main oxygen-carrying blood protein. In plants copper is a component of several enzymes involved in carbohydrate, nitrogen and cell wall metabolism.

A critical factor in assessing the hazard of copper is its bioavailability. Adsorption of copper to particles and complexation by organic matter can greatly limit the degree to which copper will be accumulated and illicit effects. Other cations and pH can also significantly affect bioavailability.

In natural phytoplankton communities, chlorophyll *a* and nitrogen fixation were significantly reduced at copper concentrations of 20 µg/litre and carbon fixation was significantly reduced at 10 µg/litre. ED_{50}s (72 hrs) for algae, based on growth inhibition range from 47 to 120 µg Cu/litre.

For freshwater invertebrates, 48 hrs LC_{50}s range from 5 µg Cu/litre for a daphnid species to 5300 µg Cu/litre for an ostracod. For marine invertebrates 96 hrs LC_{50}s range from 29 µg Cu/litre for a bay scallop to 9400 µg Cu/litre for the fiddler crab. The acute toxicity of copper of freshwater and marine fish is highly variable. For freshwater fish 96 hrs LC_{50}s range from 3 µg Cu/litre (Arctic grayling) to 7340 µg Cu/litre (bluegill). For marine fish 96 hrs LC_{50}s range from 60 µg Cu/litre for Chinook salmon to 1400 µg Cu/litre for grey mullet.

Tolerance to copper has been demonstrated in the environment for phytoplankton, aquatic and terrestrial invertebrates, fish and terrestrial plants. Tolerance mechanisms which have been proposed in plants include binding of metal to cell wall material, presence of metal-tolerant enzymes, complex formation with organic acids with subsequent removal to the vacuole, and binding to specialized thiol-rich proteins or phytochelatins.

5. Environmental Effects

Protection of aquatic life in water with high bioavailability will require limiting total dissolved copper to some concentration less than 10 µg/litre; however, the appropriate concentration limit will depend on the biota and exposure conditions at sites of concern and should be set based on further evaluation of all relevant data.

At many sites, physicochemical factors limiting bioavailability will warrant higher copper limits. Regulatory criteria should take into account the speciation of copper if dischargers can demonstrate that the bioavailability of copper in the receiving water can be measured reliably.

Because copper is an essential element, procedures to prevent toxic levels of copper should not incorporate safety factors that result in recommended concentrations being below natural levels.

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