Heavy Metals in Fish (Review)

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Abstract: Historically, heavy metals (i.e. zinc, copper, lead, cadmium, etc.) rank as major polluting chemicals in both developed and developing countries. Probably the most important heavy metal source was, and still is in some countries, the waste waters arising from mining activities, such as mine drainage water, effluent from tailings ponds (where waste crushed ore is settled out) and drainage water from spoil heaps. These sources can continue to discharge heavy metals into watercourses long after the original mining activities have ceased.
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Cadmium

Again, this metal has a high profile in human toxicology because of bases where it has been transferred at harmful concentrations to man through the food chain. In water, the main point source is effluents from electroplating works; also, there are numerous diffuse inputs from the widespread use of this metal as well as a few areas where cadmium is leached from geological deposits. Cadmium is strongly adsorbed onto organic and inorganic particles in the water but, although it can form soluble complexes with humic substances, the toxicity is not reduced as it is with coppers at least not in hard water. However, it is the binding on to solid particles that limits the importance of total cadmium levels in the water, but again most, if not all, of the bound metal will end up in sediment sinks. There is some evidence that this cadmium is available, to a limited extent, to invertebrates living in the sediment and can be passed on to fish which prey on them. However, the potential for significant accumulation by this route is uncertain and requires further research.

Toxic effects of cadmium

Calcium appears to reduce the toxicity of soluble toxic concentrations of cadmium in the water, but to a lesser extent than that for zinc and copper. There is, however, a major difference between cadmium's toxic action and that of the other heavy metals, in that there appear to be two separate and successive harmful effects. For rainbow trout, the toxicity curve over the first four days follows the normal shape for heavy metals and appears to approach a threshold value. However, continuation of the exposure causes mortalities at much lower concentrations and a further threshold is reached at a concentration considerably less than the 96 h LC50. The most logical explanation is that the efficiency of the detoxification mechanism for cadmium in the fish has a limited duration and therefore acts as only a short-term brake on the internal toxic action.

Zinc

Because of the relatively high solubility of zinc compounds, this metal occurs widely in freshwaters. Indeed, it is import ant that it should do so because it is an essential alement for acuatie life: for example. It occurs in the enzyme carbonic anhydrase which as described previously, catalyses the formation dicarbonic acid from carbon dioxide in the blood. Small amounts in the water or in the diet are therefore essential; it also follows that the organisms -will have an internal mechanism to transport zinc around the body in order to manufacture -such vital enzymes. When the zinc the water rises to a level where the, amount entering the organism through the gills exceeds the requirement for this metal the surplus has to be excreted and this will require a certain amount of energy. At higher levels this detoxification mechanism may be insufficient to cope with -the influx and the zinc will then exert a direct toxic action.

Toxic effects of zinc

It was originally thought that the direct toxic action of zinc-on fish was to precipitate the layer of mucus on the surface of the gills, causing suffocation. While this may still be true for those species which produce a copious supply of mucus, the white precipitate observed on the gills of say, rainbow trout is mainly composed of disintegrating epithelial cells which may be associated with the onset of mortality. However, zinc may also cause a certain amount of tissue damage by reacting with proteins and this could effect the respiratory efficiency as well as the osmoregulatory function of the gills

The major environmental factor which affects the toxicity of zinc to fish is the calcium concentration of the water. Calcium, like zinc, is a divalent ion and both compete for arising sites on protein molecules. Although some competition may occur on the gill surface, the main site of action may be inside the epithelial cell where the calcium concentration is in equilibrium with that in the surrounding water. Therefore, if fish are removed from a hard, calcium-rich water to a soft water, they will slowly lose their resistance to zinc toxicity as their body calcium is reduced to a lower equilibrium level. The relationship between the concentration of zinc acutely toxic to rainbow trout and the hardness of the water. Similar data exist for other species of fish, although in some cases an inadequate acclimation period to different water harnesses may affect the extent of the differences obtained.

As might be expected; Sub-lethal concentrations of zinc algicide and molluscicide. It is not surprising that copper is potentially more toxic to fish than zinc.

Toxic effects of copper

Good experimental data on copper toxicity are more difficult to obtain than for zinc. In hard water, copper precipitates out as a basic carbonate which is very slow to redissolve. It is difficult to prepare experimental solutions in such waters because the colloidal precipitate which can be formed is hot acutely toxic and the amount or copper present in the toxic ionized from may be variable. Also, soft waters can often contain dissolved organic material such as humic acids derived from peat, and these can form complexes with copper. These cupro-organic complexes have a much lower toxicity than the free ionized metal. Analyses of copper in water measure the concentration of total metal present and they do not normally distinguish between the toxic soluble form and the less toxic colloidal and organically complexed forms.

In some fish toxicity tests where the solutions were not renewed frequently, the organic matter produced by the fish might be able to complex some of the copper. The solution would then be rendered less toxic, thus producing higher LC_{50}s than would be otherwise obtained if all the copper was, present in an ionic form. Also, copper sulphate has been widely used in the past as an algaecide in fish-bearing-waters, at concentrations which would be toxic if the metal was present in the toxic ionized form. In practice, no fish mortalities have been reported as a result of these operations, presumably because the copper was rapidly precipitated or complexes into much less toxic forms. However most, if not all, of this inactive copper will ultimately enter sediment sinks where it may have a limited bioavailability for organisms living there. Again, this is an area where more research is required.

The acute toxic action of copper seems to be similar to that of zinc; also, there are similar reports of sub-lethal effects occurring at concentrations down to 10% of the threshold LC_{50}. For example, growth rates of fish are affected at these concentrations and for copper this may be due to a reduced rate of feeding or an increased rate of activity. However, there is little laboratory or field evidence for acclimation by fish to low levels of copper in the water. To some extent this is due to the problems in determining the actual amount of toxic copper present.

As with zinc, the main environmental factor affecting the toxicity of copper is the calcium concentration of the water, again because of the competition between these two ions for binding sites in the tissues of the gills and other organs. However, in contrast to zinc, salmonid species are not the most susceptible to copper toxicity; for example, perch may be three times as sensitive as rainbow trout to this metal. The reason for this difference in species sensitivity is not known and it is possible that the toxic actions of copper and zinc are in some way slightly different. The EEC Freshwater sets standards for copper that are common to both salmonid and cyprinid species, but takes into account the effect of water hardness and allows for the formation of less toxic organo-copper complexes.

Lead

Although lead has a high profile in human toxicology, it is A. much lesser importance for aquatic life. This is mainly due to a low solubility which limits its occurrence at significant concentrations in all but very soft waters. Sub-lethal effects include the darkening of the tails of salmonid fish and this can be diagnostic of low levels of lead in the water. Some evidence of this effect has been found in fish from rivers receiving discharges from old lead mines in mid-Wales.

Diffuse inputs of lead into surface-waters-arising from its widespread use in petrol and batteries may increase the concentrations in sediments but this does not appear to be significant for aquatic life.

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