Humic Acid Effect on the Bio-Availability of Mercury in Fish

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Abstract: The complexity of mercury chemistry is linked to the many possible species that may occur in the environment with different bio-chemical and physico-chemical properties. The formation of mercury complexes depends upon the kind and concentration of the ligands involved in the system. Both speciation and complexation control mercury mobility and bio-availability.
In this regard, the presence of dissolved organic acids in soils and river waters may oxidize elemental mercury, increasing its solubility via a dissolution-complexation mechanism. However, the literature indicates discrepancies about the correlation between the levels of organic acids in river waters and the concentration of mercury in fish.
This study was designed to investigate the interaction of elemental mercury with humic acid and the impact of this interaction in water and in biota emphasizing the bio-availability of mercury in fish.
Studies were conducted in fish aquariums with varying concentrations of humic acid in the presence of fixed amount of elemental mercury. The concentrations of mercury species in water and the concentrations of total and methylmercury in fish were measured after 30 days and after 60 days.
Results indicate that the concentrations of total Hg in the water compartment increases with the increase of humic acid treatment. Although the concentration of total Hg in fish slightly increases with humic acid dose, the concentration of Methyl Hg in fish remains constant.

Key words: bio-availability, speciation, fish aquarium, bio-accumulation, solubility

INTRODUCTION
The complexity of mercury chemistry in the environment is linked to the many possible species that may occur with different bio-chemical and physico-chemical properties. Adicionaly, the formation of mercury complexes depends upon the kind and concentration of the ligands involved in the system. Thus, both speciation and complexation control mercury mobility and bio-availability.

The extensive use of elemental mercury (Hg⁰) for gold recovery has been contributing for the dispersion of Hg to the atmospheric aquatic and terrestrial environments. Although the mobility and solubility of Hg⁰ are low (HEM, 1970), the transformations of Hg⁰ to other species may modify both the solubility and the mobility as well of Hg bio-availability. Once dischared to the ecosystems, Hg⁰ may undergo a series of transformations to methyl mercury (CH₃Hg), which is highly soluble in lipids, with the potential to be incorporated by the aquatic biota, accumulating in the food chain, and consequently causing irreversible damage to the central nervous system of man (CLEARY ET AL., 1994; WOOD ET AL., 1978).

According to Eh versus pH stability diagrams (HEM, 1970), it is estimated that, a maximum concentration of 25 ppb of Hg would be generally found in river waters. However, the presence of dissolved organic acids may oxidize Hg⁰, increasing its solubility above the
values predicted for inorganic systems (Veiga, 1994; Melamed et al., 1997), through a dissolution-complexation mechanism (Liu Ching-I and Tang Hongxiao, 1985), and also to remobilize Hg adsorbed by sediments (Melamed et al., 1997). This is of special concern in dark river waters with high levels of dissolved organic acids.

Studies conducted by Silva-Forsberg et al. (1999) showed positive correlation between the concentration of Hg in hair of riverin peasants with the level of dissolved organic carbon (DOC). However, the literature show inconsistencies in the correlation between Hg in fish and DOC: Haines et al. (1994) reported positive correlation, Grieb et al. (1990) found a negative correlation and Driscoll et al. (1995) reported no correlation. Wattras et al. (1998) suggest that these discrepancies are related to a significant degree of interaction among variable involved and/or multiple effects of isolated variables, which may be illustrated by the bio-accumulation model described by Sunda and Huntsman (1998):

\[ C_{\text{biota}} = \frac{V_{\text{net}}}{\mu} \]  

where: \( C_{\text{biota}} \) is the concentration of the metal in the biota; \( V_{\text{net}} \) is the net rate of metal absorption and \( \mu \) is the rate of growth of the organism.

The model above infers that a complex net of interdependencies defines \( C_{\text{biota}} \), because many regulating factors operate through the various processes related to \( V_{\text{net}} \) and \( \mu \). This study had the goal to investigate the interaction of \( \text{Hg}^0 \) with humic acid and the impact of this interaction in water and in biota with emphasis in the bio-availability of Hg in fish.

**Methodology**

The bio-availability of Hg in fish were conducted in aerated aquariums containing 1g of \( \text{Hg}^0 \) and increasing levels of humic acid. Four levels of humic acid were used, corresponding to concentrations of: 0, 6.25, 12.5 and 25 mg/L. One aquarium was established as the control where there was no \( \text{Hg}^0 \) neither humic acid. The fish species used were gold fish (cyprinus carpio) with similar weights and sizes, 20 g and 10 cm, respectively. The experiments were repeated twice, so that each result reflects the average of 2 samplings. Also, each aquarium contained two fishes so that samples were taken in two periods, 30 days and 60 days.

In the water compartment, the concentration of inorganic mercury (HgA), composed of the level of ionic mercury (Hg(II)) plus elemental mercury (Hg\(^0\)) was analyzed through direct reduction of the sample to Hg vapor with staneous chloride. The concentrations of other complexes dissolved in water were calculated as the difference of total mercury (HgT), which was obtained via a previous digestion of the sample with BrCl (Robertson et al., 1987; Wilken and Hintelmann, 1991), minus other species (HgA), determined by reduction with staneous chloride. The analyses were carried out by cold vapor atomic absorption spectrophotometer.

For the determination of Total Hg in fish we utilized the methodology of Akagi and Nishimura (1991). For the determination of Methyl Hg in fish we also followed Akagi and Nishimura (1991) with analyses conducted in a Gas Chromatograph-Ni detector (Yanaco G6800).
RESULTS AND DISCUSSION

Figure 1 shows the concentrations of Hg species in the water of the aquariums and in the fish after 60 days of exposure to Hg\(^0\) and humic acid treatments.

![Figure 1](image.png)

**Figure 1.** Hg concentrations in dissolved in the water compartment (HgA and HgX) and in fish (Hg\(^\text{total}\) and Methyl-Hg) after 60 days of exposition to Hg\(^0\) and to humic acid. Level 0 = control; level 1 = only Hg\(^0\); levels 2, 3 and 4 = Hg\(^0\) + increasing doses of Humic Acid.

The concentrations of HgA and HgX increased with increasing levels of humic acid, reflecting in the enhanced level of total Hg dissolved in the water of the aquariums. The concentration of total Hg in fish increases only when samples of the aquarium with the higher dose of humic acid is compared to the control (level 0), which was attributed to increased concentration of HgA. However, the levels of Methyl-Hg in fish does not increase by increasing the doses of humic acid, on the contrary they even show a decreasing trend. SJOBLOM ET AL. (1999) concluded that Hg complexed by humic substances, after demonstrating that the absorption of \(^{203}\)Hg by the larvae *Chaoborus sp.* decreases with increasing levels of humic substances.

We observed, at the aquariums where only Hg0 was added (level 1), in the absence of humic acid, a peak in the concentration of Hg total and Methyl-Hg in fish. The mechanisms of Hg absorption by fish in experiments with additions of HgCl\(_2\), were discussed by IKINGURA AND AKAGI (1999). The mechanisms of Methyl-Hg production in fish in the presence of Hg\(^0\) solely is intriguing and deserves further investigation.
REFERENCES


