The Behaviour of Mercury in the System Water-Fish

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Analytical data have shown that many pollutants (e.g. heavy metals), which are present in aqueous ecosystems in very low concentrations are accumulated by certain organisms up to critical, toxical amounts (KECKES and MIETTINNEN 1970, WOOD 1974, FISHBEIN 1974). The pathway of these pollutants in an ecosystem is very complex and not yet known. For the investigation of the accumulation mechanism the radiochemical tracer method is the most efficient one. In model experiments we have investigated the direct uptake (excluding the food chain) of different dissolved mercury compounds by female species of "poecilia reticulata".

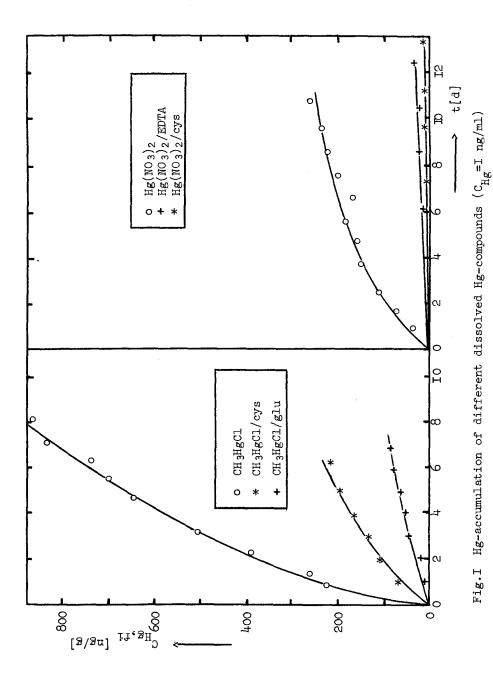
Hg-203 labelled $\rm Hg(NO_3)_2$ and $\rm CH_3HgCl$ were dissolved in deionised water resulting in concentrations of 0.I / I / 5 / I0 / and 20 ng Hg/ml. The temperature was constant within 24-26°C. There was a continuous decrease of the Hg-concentration because of the adsorption of mercury on the glass walls; this was compensated by adding small amounts of mercury or by changing the whole solution daily. The fish were measured in vivo, using a 3"x3" NaI(T1)-well-typedetector. In some experiments a complexing agent was added.

In particular we have investigated

- a) accumulation rates (ng ${\rm Hg/g_{fi}\cdot d}$) as a function of the chemical form of the dissolved mercury compounds,
- b) accumulation rates as a function of the mercury concentration in the water.
- c) the release of incorporated mercury in deionised water as a function of the mercury compound and the incorporation time.

RESULTS and DISCUSSION

In Fig.I the mercury concentration in the fish is plotted versus the incorporation time for different Hg-compounds. In these experiments the mercury concentration in the water was I ng/ml. The concentration of the complexing agents was about 10^{-7} mol/ml. The accumulation curves show that the uptake of mercury by the fish in a CH₃HgCl-solution is about four times as fast as in a Hg(NO₃)-solution. In the presence of EDTA, cysteine or glutathione the accumulation rates decrease.



These effects can be explained as follows:

- a) The lipid solubility of CH₃HgCl is much better than the lipid solubility of inorganic mercury (REICHERT and MALINS 1974)
- b) In the case of the complex compounds the complexing groups may have a screening effect, so that adsorption at the surface of the cells is insignificant or does not take place at all. Only the mercury which is not complexed is accumulated; (the concentration is determined by the equilibrium constants). That means that the accumulation rate should depend very strongly on the concentration of the "free mercury" in the water.

The latter statement was checked in another set of experiments, the results of which are summarized in Tab.I.

TABLE I

Accumulation of mercury(as CH3HgCl)for different Hg-concentrations

C _{Hg,H2} O	after IO days C _{Hg,fi} [ng/g]	accumulation rate [ng/g _{fi} ·d]	rel.accumulation rate $\frac{[{\rm ng_{Hg,fi}}\cdot{\rm ml_{H_2O}}]}{[{\rm g_{fi}}\cdot{\rm d\cdot ng_{Hg,H_2O}}]}$
0.1	185	17.4	174
I	1200	II3	II3
5	4000	400	80
10	9500	950	95
20	17600	1760	88

The higher the Hg-concentration in the water, the higher the contamination of the fish (column 2). The accumulation rate increases with increasing Hg-concentration in the water(column 3), whereas the relative accumulation rate decreases with increasing contamination of the water(column 4). This is illustrated in Fig.2. It is to be expected, that the curve will become flat and run into saturation at very high mercury concentrations. However, this region is not accessible experimentally, as the lethal dose for the fish is attained very soon (>30 ng/ml).

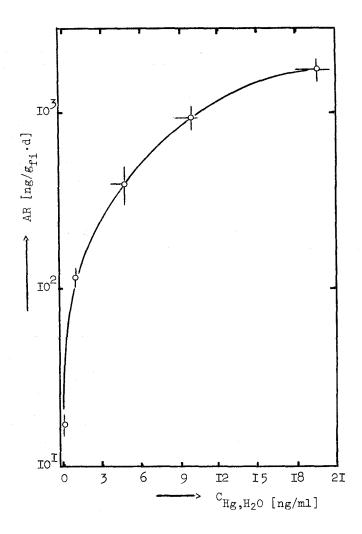


Fig. 2 Accumulation rate (AR) for different Hg-concentrations

The release of accumulated mercury in deionised water after different incorporation times in a ${\sim}10$ ng Hg/ml Hg(NO₃)₂-solution is shown in Fig.3, in which the normalized CHg,fi-values are plotted versus the time of release. The incorporation times were 3.6 h, 46.5 h and 93 h. The release takes place in a two step mechanism. The first, rapid step has a half life of 4.2±I.3 d;the second step has a half life of 67.7±I.8 d. The relative amount of mercury released in the second step increases with increasing time of incorporation.

In the experiments in which CH_3HgCl was used, the incorporation times and the mercury concentrations in the water varied between 40h and 250h and between 0.I and 20 ng Hg/ml resp. The normalized

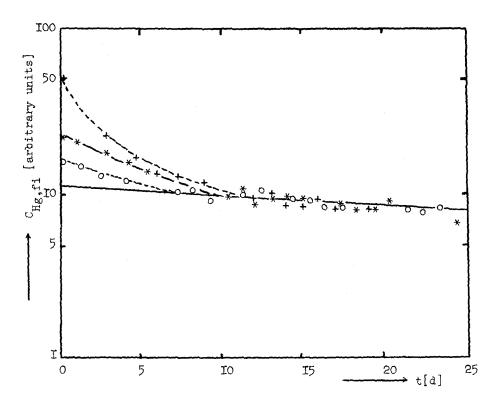


Fig. 3 Hg-release after different incorporation times [Hg(NO₃)₂-solution; ~IO ng Hg/ml]. + = 3.5 h; * = 46.5 h; o = 93 h; drawn line = experiments with CH₃HgCl

values of all experiments with CH3HgCl could be fitted by one straight line. This indicates that the release of incorporated methyl-mercurychloride takes place in one step only, the half life of which is 69.I±2.4 d. The good agreement between the two longer half lives (67.7 d and 69.I d) leads to the following conclusions:

- a) The release of inorganic mercury is about I7 times as fast as the release of incorporated methyl-mercurychloride.
- b) Accumulated inorganic mercury is methylated in the fish (JENSEN and JERNELOV 1969, BERTILLSON and NEUJAHR 1971), and after this the release is identical to that of methyl-mercury-chloride.

We have shown only a small part of the complex biological pathway of mercury in aqueous ecosystems. Other experiments are under investigation, e.g. accumulation by means of the food chain, biological

half life of mercury in the whole system, influence of strange ions (MERLINI et al. 1971) on the accumulation rates and the release etc. All these investigations should lead to a much better understanding of the behaviour of mercury in aqueous ecological systems.

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BERTILLSON,L. and NEUJAHR,H.Y.: Biochemistry 10, 2805 (1971)
FISHBEIN,L.:The science of the total environment 2, 341 (1974)
JENSEN,S. and JERNELOV,A.: Nature 223, 753 (1969)
KECKES,S. and MIETTINEN,J.K.: FAO Technical Conf.on Marine Pollution and its Effect on Living Resources and Fishing,Rome Dec.(1970)
MERLINI,M.,ARGENTESI,F.,BRAZELLI,A.,OREGIONI,B. and POZZI,G.:
Biology Directorate Commission of the European Communities 722,(1971)
REICHERT,W.L. and MALINS,D.C.:Nature 247, 569 (1974)
WOOD,J.M.:Science 183, 1049 (1974)