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SWEDISH WATER AND AIR POLLUTION RESEARCH LABORATORY

INSTITUTET FÖR VATTEN- OCH LUFTVÅRDSFORSKNING

TELEPHONE 08-22 25 40
TELEGRAMS WATERRESEARCH

DROTTNING KRISTINAS VÄG 47 D
S-114 28 STOCKHOLM SWEDEN

SOME ASPECTS OF THE MERCURY PROBLEM

A Review of current knowledge at the end of 1972

Arne Jernelöv

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A B S T R A C T

Available information is summarized on the local aquatic and global circulation of mercury and a short exposé is given of the methods proposed for restoration of mercury contaminated water bodies.

In relation to medical aspects of the mercury problem, the latest development with regard to inter-action between mercury and selenium and concerning a certain number of subclinical effects of mercury poisoning on man is discussed.

At present mercury contamination of the environment is a very well known problem. Mercury is likely to appear on more or less any list of chemicals posing environmental health hazards. However, the concern about environmental mercury contamination does not go back very far. It is only about 15 years ago that methyl mercury was identified as the cause of Minamata disease (1) and 8 years that it was recognized that mercury discharged into the aquatic environment would appear in fish as methyl mercury regardless of the form in which it was discharged (2). Biological formation of methyl mercury was not demonstrated til 1967 (23).

During this period a large number of studies were carried out covering almost every aspect of the mercury problem. This does not in any way mean that our knowledge of the situation is complete today, as will be apparent from this article, but we have started to illustrate most aspects of it. This article will be an attempt to summarize our knowledge as it stands at the end of 1972 in relation to mercury turnover in local aquatic and in the global ecosystem and to the state of the art on methods for restoration of mercury contaminated bodies of water. Some comments will also be given on a few aspects of the medical mercury problem.

With regard to the medical aspects of environmental contamination of mercury a very comprehensive and - at the date of issue - close to complete review exists in the form of a report on a Swedish expert group entitled "Methyl Mercury in Fish.. A Toxicological Epidemiological Evaluation of Risks". (3)

The evaluation of risks to man from exposure to organo-mercury compounds was expressed in the report and has largely been confirmed by the tragedies of the last two years, where human beings in developing areas have suffered from poisoning by agricultural organo-mercurials. The safety factors proposed

in the report and applied in many countries today by the means of different administrative measures seen to give satisfactory protection against clinical effects of mercury poisoning also in the light of new findings.

The main concern today is, as it was when the report was issued the subclinical effects, e.g. of the genetic type or connected with loss of brain cells.

The effects of loss of brain cells caused by methyl mercury exposure on learning ability, memory capacity, etc., are sometimes hard to distinguish from those arising from social and psychological factors. This is the case in studies of e.g. on school failure rates in relation to mercury hair levels in school boys in a primitive roral village that suffered severely from mercury poisoning. With total mercury levels in hair ranging from 5 - 435 ppm, a correlation between mercury levels (grouped < 100; 100-200; 200-300 and > 300) and failure rates was obtained. Evidently, the boys with higher mercury levels are more likely to have dead, dying or severely affected family members at home. This would naturally affect their school performance.

The available information on these and other subclinical effects to date in too insufficient for a reasonable evaluation of risks from low level methyl mercury exposure.

Another aspect of the medical problems connected with environmental mercury contamination that was not considered in the "blue book" is the possible inter-action between mercury and selenium.

Discussions on this problem started in Czechoslovakia during the late sixties. Studies of persons exposed to mercury in mining dust revealed some inconsistency in the occurrence of protein-urea as a function of mercury exposure. Correlation analyses carried out with other environmental factors like co-exposure to other elements, dietary habits, age etc., demonstrated that a significant negative correlation between protein-urea in relation to exposure of inorganic mercury and exposure to selenium was present. Laboratory experiments on rats showed that acute toxicity of both mercury and selenium was released in the presence of the other element (4, 5, 6).

An antagonistic inter-action was proposed besed on the formation of a certain number of less biologically active mercury-selenide. The possible use of selenium in the treatment of mercury intoxication has also been discussed.

In 1970-71 some research workers in USA and elsewhere reported that certain fish, besides containing mercury and other "well known" contaminants, also contained high concentrations of selenium (7, 8, 9).

In 1972 a group at the Wisconsin University reported that mercury and selenium concentrations in tuna fish were very well correlated, so well, in fact, that the relation appeared close to toechiometric with two molecyles of selenium per molecyle of mercury in the high-mercury tuna. The increment in mercury content between the low and high mercury tuna was in an approximative 1:1 molar ratio with the increment in selenium. The group also carried out some feeding experiments. Two groups of Japanese quails were given 20 ppm of mercury as methyl mercury in their diet. One of the groups of quails got a diet containing 17% of tuna fish and the other a diet containing 17 % corn-soya. The quails fed with methyl mercury added to the diet of tuna fish survived considerably longer than those fed on the same amount of methyl mercury added to the corn-soya diet. The authors suggest that the higher selenium content in the tuna diet is the cause of the sensitivity difference to methyl mercury and that the stochiometric relation between mercury may be caused by the natural accumulation process leading to an automatic reduced toxicity both for mercury and selenium in the fish. (10)

Correlation between mercury and selenium has also been found in the brains of seals from the Dutch coast. (11)

Evidently, there is a gap between the rat and the quail experiments. The former deals with inorganic mercury and the latter with methyl mercury. Also, selenium was given in an inorganic form in the case of the rats while selenium given in tuna fish is probably present in association with organic molecyles.

If there is an uptake mechanism regulating the relation between mercury (as methyl mercury) and selenium in sea fish giving the lowest toxicity of both, it may seen surprising that not only did this reduce the toxicity of the methyl mercury accumulated in fish together with the selenium, which would meen that "excess" selenium some how must be present.

The discussions on the possible antagonistic inter-action between mercury and selenium and on the possibility of an uptake mechanism in fish leading to a balance between the two elements are connected with earlier discussions in Sweden on the possible toxicity difference between chemically synthetized methyl mercury and that which was biologically formed and incorporated in natural fish. (12)

These discussions ended when it was deminstrated that fish caught in the water system Delångerån caused symptoms of methyl mercury poisoning in cats at the same exposure as that of chemically methylated mercury added to low mercury pike from Lake Hjälmaren. (13)

Then these past Swedish discussions are reviewed in the light of the mercury-selenium inter-action question, it is found that River Delångerån is situated in a region with an unusually low selenium content. To what extent this "naturally contaminated" pike used in cat experiments is typical is therefore unknown.

Present knowledge can be summerized as follow:

1. There is toxicological evidence of an antoginistic action between inorganic mercury and selenium and indication of a similar inter-action between methyl mercury and selenium in fish.

2. A clear correlation between mercury (predominantly as methyl mercury) and selenium exists for certain marine organisms. This may be due to a regulation accumulation mechanism for the two elements.

Whether this is significant for mercury toxicity in marine fish is still not known. Doubtless, more studies are needed and some are underway.

The mercury turnover in a local aquatic ecosystem is comparatively well known and includes the following principal steps: (14, 15, 16)

1. Release of mercury into the watercourse.
2. Accumulation of mercury in organic particles in the sediment or in suspention.

3a. Gradual biological (chemical) conversion to mono- or dimethyl mercury. The former will be released to the water and the latter may evaporate into the atmosphere, alternatively

3b. Conversion to mercuric sulphide under anaerobic conditions and/or binding to ferrioxides under serobic conditions. In these forms mercury will remain inactive as long as the anaerobic or the aerobic conditions remain unchanged. These forms can be regarded as temporary sinks for mercury.

4. Mercury converted into dimethyl mercury may be degradeted into monomethyl mercury in contact with acid conditions (pH appr 5.6) or converted into elementary mercury in contact with UV-light.
5. Methyl mercury released to the watermass will be accumulated in water-living organisms.
6. A further accumulation will take place along the food chain. however, the intake will be of larger or similar importance to the direct uptake only for the top predators.
7. (Methyl) mercury will be returned to the sediment with dead organisms or removed from the water body with the organisms through catch or migration. (Naturally, mercury will also be removed when in solution and when attached to suspended particles through water and mass transport).

Most physical, chemical and biological factors in the water system will affect the process of biological conversion and accumulation of mercury.

As a brief summary and general rule, it can be said that the rate of biological formation of methyl mercury is directly related to microbiological activity in the sediment of in the suspension where the inorganic (divalent) mercury is present.

A few special cases should, however. be noted:

1. When mercury is in the form of mercuric sulphide, the methylation rate (also under aerobic conditions) will be significantly reduced.
2. When mercury containing organic matter is exposed to air and water, e.g. drying land deposed dredged material and tidal areas, the biological methylation may be very much accelerated.
3. Differences in the net result (mono- or dimethyl mercury) of the biological methylation process (where ph is a determining factor) may be of great importance to the mercury contamination of local water living organisms.

One important and troublesome aspect of mercury contamination of lakes and rivers is that unless an effective flushing system exists and a high rate of sediment transport accurs, the mercury deposits in the sediments are likely to continue to release methylated mercury and maintain an elevated mercury level in aquatic organisms for a very long time. Estimates of "ecological half-life" for mercury levels in contaminated Swedish lakes after a hypothetical stop of discharge from all sources has given figures of 10 to 100 years.

The recovery process will be much faster in eutrophic lakes with high production, high sedimentation rates, high ph and anaerobic conditions in the sediments than in oligatrophic acid areas with well oxygenated sediments.

During the last five years, a research programme has been carried out in Sweden with the purpose of finding methods for restoration of mercury contaminated water bodies. The following methods have been suggested for field and/or laboratory tests. (17)

1. Removal of mercury.
2. Conversion of mercury into mercuric sulphide with a low availability for biological methylation.
3. Binding of mercury to inorganic material - like silica minerals - where availability for methylation is low. Under aerobic conditions, ferric ions and manganese ions bind heavy metals including mercury when forming oxides and crystallizing.
4. Covering of mercury deposits with mercury binding or inert material that decreases the release of methylated mercury to water.
5. Increase of pH so that the biological methylation process will give volatile dimethyl mercury rather than monomethyl mercury and thereby lead to a lower accumulation rate of methyl mercury in fish in the primary recipient.

No direct restoration attempts have been carried out in Sweden so far. The laboratory tests, pilot field studies and observation of effects of mercury turnover on dredging performed for other reasons indicate that technically at least, the methods 1), 2) and 4) are feasible.

However, from an economic point of view, the costs for restoration measurements according to any of these principles, will outrange - in general with orders of magnitude - the value of the fishing that may be restored.

From an ecological point of view, all the methods, specially 2), 3), 4) and 5) will have adverse effects on the ecosystems concerned. Naturally, before any attempt is made, it has to be evaluated from the local conditions how severe these adverse effects may be in relation to the advantages of reducing mercury contamination of fish.

In view of these facts, direct restoration measurements, according to any of the methods presented, seem unlikely to be carried out in Sweden in the near future, except perhaps in very localized areas with very high recreational values.

During the last two years, restoration techniques have been studied intensively, also in USA and Canada. The principles of the suggested methods, however, have to a large extent been those originally suggested and tried out in Sweden. (18) The technical experience in North America is not very different from that reported above from Sweden. However, in connexion with certain courtcases, very divergent opinions exist on the cost benefit relation of large scale dredging and covering operations.

During the last few years, a few mathematical models have been presented that describe the turnover of mercury in global and local ecosystems. Naturally, mathematical models do not in themselves create any new knowledge, they only help to organize existing information. From a restoration point of view, those describing local ecosystems are interesting as they through sensitivity analyses - where different factors can be tested as to their effect on the end result in the form of mercury levels in fish, can screen possibilities of new principles and techniques.

One alternative method of controlling mercury levels in fish populations, that has recently resulted from sensitivity tests of a mathematical model for methyl mercury accumulation in limnic food chains, (19), and that may deserve more attention, is the possibility of using fish population management as a means of controlling maximum and average mercury concentrations in fish.

In areas where the present level is approximately 100 % above the acceptable level, fish population management may provide a means of bringing the mercury levels below the critical level at a moderate cost and with the social advantage that those benefiting from the money spent on the measurement would be those suffering most from the loss of the fishing opportunities - the fishermen.

For a study of the global mercury turnover, the oceans represent a natural focus and starting point.

In their classical work, Stock and Cucuel (20) reported mercury concentration in sea surface water of 0.03 - 0.04 ppb. Several later reports have indicated similar figures although others and, in the authors personal opinion, more reliable investigations, have found surface water to contain approximately 0.30 ppb.

Dependent on which group of data is preferred for testing, with a total volume of 1.4×10^{21} l, the oceans would thus contain between 4.5 and 21×10^{13} g of mercury.

Estimates by Goldberg et al. (21) of mercury transports to the sea indicate that rivers may contribute approximately 10^{10} g/year including natural as well as man-released mercury, while the washout with precipitation from the atmosphere could be $(2.5 - 15)10^{10}$ g/year.

The 1.5×10^{11} g/year of mercury in the rain is based on an estimated atmospheric load of 4×10^{9} g, a close to complete washout in connexion with precipitation and an average time between rainfalls of 10 days. It has been argued that the estimate of atmospheric mercury burden is an overestimate of 10 times or more. The alternative figure presented by Goldberg (2.5×10^{10} g) is derived by multiplying the amount of rain falling over the oceans with a low estimate of average mercury concentration in precipitation of 0.06 ppb derived from mercury content in apparent uncontaminated glacial ice. Accepting the idea that 1.5×10^{11} g/year may represent an overestimate and 2.5×10^{10} g/year an underestimate, a compromise of 5×10^{10} g/year will be used by the author for further calculations.

The world production of mercury is in the order of 1×10^{10} g. To this should be added direct release of mercury in connexion with burning of fossil fuels, heating of mercury containing minerals etc. At the very most, the sources could account for a release of mercury equivalent to that from "intentional" production and use. Evidently, as large parts of the man-used mercury will not be released into the environment immediately, but only, if at all, after a considerate lapse of time.

Analyses of the Greenland ice-sheet have demonstrated a tendency to an increase in mercury concentrations during the last decades. (21) When the estimated atmospheric flux of mercury is related to the human production, it is apparent that the observed increase, with roughly a factor of two, that has occured during the last decades cannot be accounted for by the mercury released from mercury handling industries, fossil fuel burning etc.

In "the natural" flux of mercury "degassing from the earth crust" is of dominating importance. Goldberg et al. have estimated it to be in the order of $(2.5 - 44) \times 10^{10}$ g/year.

It is possible that man, through his activities has affected this degassing during the last decades. One way in which such an enhancement could have occurred in through the changed agricultural practice involving more efficient plowing, the use of fertilizers, etc. that have accelerated the biological processes in the soil thereby perhaps increasing the formation rate of volatile mercury compounds like elementary and dimethyl mercury.

The average residue time for mercury in the upper 200 m layers of the oceans has been calculated to be 50-150 years, (22) while for the oceans as a whole the average residue time has been estimated to be 6×10^{4} years (15).

Inorganic mercury, as well as methyl mercury, has a high affinity with organic substances and will therefore in the sea as well as in fresh water tend to accumulate in particulate matter of organic origin and settle with these in the general sedimentation process.

Bioaccumulation and excretion with fecopellets or sedimentation with the dead organisms also contributes to this process. This provides the mechanism for elimination of mercury from seawater and causes the higher mercury concentrations in the bottom water compared with surface water.

In areas with up-welling water and extremely high biological activity, the combination of the higher mercury content in the water and the higher methylation rate could be a natural cause for higher than usual methyl mercury concentrations in marine organisms.

The conclusion of this review of the global mercury circulation is that man, through his activities, may have affected the atmospheric flux of mercury. The main part of this effect may, however, be due to increased degassing from earth crust perhaps through the new agricultural practices and not to his industrial use and release of mercury.

Out of the total amount of mercury present in the sea, man's impact to date is negligible.

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