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5.8 Mercury in Canadian Rivers

D. R. MILLER

5.8.1 INTRODUCTION

The general history of the problem of mercury in the environment, and mercury as a toxic chemical generally, has been told many times, and we will not repeat here any details of the tragic poisoning in Japan, Iraq, and elsewhere. It is the purpose of this brief report to describe the environmental mercury problem specifically in Northwestern Ontario, in the English–Wabigoon river system.

In view of what was known about mercury intoxication at the time, and particularly in the light of the observation that its effects are extremely unpleasant and that therapy, at least at the stage of clinical expression, is almost totally unavailable, it is not surprising that the reaction to the discovery that mercury concentrations in certain Canadian foodstuffs were at dangerous levels produced something akin to a panic response. In retrospect, it is generally agreed that the issue was not handled in a particularly effective way; however, some important lessons were learned about the institutional frameworks and procedures that ought to have been in place to deal with such a problem. In addition, the story serves as a good example of how Northern systems may be especially delicate. In a sense that goes beyond what we think of as the ecosystem, it was found that reliance on a single resource, narrowness of the food chain, specialization in food and livelihood at the highest level (in this case, man), and difficulty in dealing with the problem in a holistic fashion led to profoundly serious consequences.

The lessons learned were quite expensive, in the sense that much irrelevant work was done, and in the sense that the victims were not quickly relieved of their most serious problems. The consequences were at the social and economic level; we can at least be satisfied to observe that no actual human deaths caused by clinically demonstrable mercury poisoning have been documented.

5.8.2 BACKGROUND

Historically, mercury has entered the Canadian environment in five ways (Hocking, 1979). They are:

(i) The use of mercury-containing chemicals as fungicides on certain seed grains;
(ii) The use of mercury compounds, most often phenylmercuric acetate, as a general-purpose antibiotic (a so-called 'slimicide') in the pulp and paper industry;
(iii) The use of mercury as an electrode in the chemical preparation of chloralkali products;
(iv) As a by-product of smelting operations directed at the production of other metals; and
(v) The general, diffuse input caused by the presence of mercury as an impurity in fossil fuels.

The first three of these have been discontinued in Canada. The other two are unavoidable in the short term. The fourth is particularly difficult to deal with, since the mercury in stack gases is normally in the form of elemental mercury vapour, and standard scrubbing devices are of limited use. However, some methods are available (Stuart and Down, 1974). The fifth will in fact increase as the fossil fuel consumption continues to rise in North America and, of course, throughout the world. It is not yet clear how soon this will result in a demonstrable danger on a wide scale (see below).

The first indication that mercury was a problem in Canada was the observation that mercury was present in the tissues of birds that had eaten fungicide-treated grains after they had been distributed as seeds. This was a relatively easy situation to correct, particularly since the source was the same as that responsible for the large number of deaths of humans in Iraq, where seed grains had been diverted into the making of bread for human consumption (Bakir *et al.*, 1973). This direct and widespread danger to human life made it very easy to justify the resources to identify and use alternative fungicides, as is now done. This, together with the imposition of more stringent controls on the disposition of such seed grains, should make it possible to avoid the problem in the future.

The second and third activities, although now discontinued, resulted in large quantities of mercury being released into river systems, much of which is still present and is still a source of considerable concern and, indeed, outright danger (Hocking, 1979). It is this collection of reservoirs of mercury, generally contaminated sediments in rivers, with which we are primarily concerned in what follows.

5.8.3 PHYSICAL BEHAVIOUR OF MERCURY

Most of the mercury released into Canadian rivers was in a relatively innocuous form in terms of toxicity, typically elemental mercury from chloralkah plants or phenylmercuric acetate from pulp and paper mills (Miller, 1977). The contaminant generally adhered to fine-grained sediments, especially to richly organic sediments. Initially it was thought that this mercury would be permanently trapped in the sediment, and completely unavailable on purely chemical grounds, since the sediments are rich in sulphur and the solubility of mercuric sulphide is so low (the solubility product in water is 10^{-53}). It was assumed therefore that virtually none would ever dissolve and appear as a chemically available ion in the water column, particularly in the cold waters of Canadian rivers.

This turns out to be largely true, but not exactly. At any time, a small fraction (one or two per cent) of the mercury in the sediment exists in the form of monomethyl mercury ion, which is of course much more soluble. Just how the conversion to this chemical form takes place has never been made clear; initially (Jensen and Jernelov, 1969) it was thought to be bacterially mediated, and there was even a detailed process suggested in which the methylmercury would be the result of an incorrect biological synthesis of methylcobalamine (Landner, 1971). Recently, the idea of a rate-determined process has fallen into disfavour, and the concept of a quickly re-established equilibrium between the organic and inorganic forms seems to be the consensus opinion (Miller, 1977; Beijer and Jernelov, 1979). Whether the equilibrium is essentially chemical or whether there is a balance between biologically-mediated demethylation as well as methylation steps is not clear. Certainly a demethylation process of some sort is occurring, since mercury released into the atmosphere from a sediment–water system contaminated with a mercuric salt appears to be exclusively in the form of elemental mercury vapour (Miller, D. R., unpublished data).

One thing that is abundantly clear is that the monomethyl mercury does leave the sediment and enter the water column and ultimately the biota. This removal from the sediment allows more to be produced as natural processes tend to re-establish the equilibrium in the sediment. Although the level of the organic form at any time is low (Akagi *et al.*, 1979), as long as it continues to be effectively removed from the sediment–water system by the biota, more will continue to be produced. The end result is that, although the proportion of organic mercury in the sediment is only one or two per cent, and although the partition coefficient for mercury between water and sediment is around 5000:1 in favour of the sediment (less for organic mercury) (Kudo, 1977), nevertheless the large fish in a contaminated river will typically have a tissue concentration of the same order as the sediment concentration of mercury, except that in the fish the mercury is almost all in the highly toxic methylmercury form (Miller, 1977). We might also note that the clearance rate of methylmercury from fish is slow; the half-life of mercury is somewhat more than one year in a relatively large (say, one kilogram) fish (Norstrom *et al.*, 1979).

As was noted above, the release of mercury into the atmosphere from a contaminated aquatic system appears to take place after a demethylation process rather than the reverse, and this may have important environmental consequences. Elemental mercury vapour would not be expected to adhere to a particulate, even one with high organic content, but would be transported in the vapour phase (Miller and Buchanan, 1977). Thus, dry deposition would not be an effective clearance mechanism. This is quite consistent with what is observed; numerous reports have indicated that soil samples taken in the immediate vicinity of a known mercury source contain far less mercury than would be expected if dry deposition were dominant (Miller and Buchanan, 1977). It should be noted that this is quite contrary to the traditional wisdom of the field, in which it was supposed that mercury was methylated twice and released into the atmosphere as the volatile dimethyl form (Jernelov, 1969). The dimethyl form would have a substantial affinity for organic particulates, and would be expected to be found in soil samples. This appears not to be the case.

The more important implication for environmental concerns is, of course, that mercury in the elemental form may be expected to be transported over long distances indeed. Even when removed from the atmosphere by wet deposition through a precipitation event, a resuspension of the substance through volatilization will allow the mercury to re-enter the global atmospheric circulation pattern, contributing again to the long-range transport that seems consistent with environmental observations (Miller, 1979).

This widespread distribution is reflected in several ways, for example in game fish in areas like Ontario, Canada, where fish of large size (a kilogram or so) almost invariably contain substantial body burdens of mercury, even when caught in locations far removed from known sources of mercury pollution.

We might also point out that this recycling of mercury in the atmosphere due to resuspension or volatilization means that if we attempt to estimate the global atmospheric content of mercury by precipitation sampling, we will be counting the same mercury several times. Thus, we would be led to significantly overestimate the amount in general circulation. The conclusion is that a larger fraction of the mercury in general circulation is due to man's operations than is generally thought, and therefore a fractional increase in anthropogenic mercury generation will significantly increase the overall global atmospheric levels (Miller, 1979).

5.8.4 EFFECTS OF MERCURY CONTAMINATION

In spite of the widespread distribution of mercury and the danger of general environmental contamination that might result, so far in Canada the only identifiable problems have been due to point discharges at a small number of sites, either from chloralkali plants or from pulp and paper manufacturing facilities. The most serious took place in the English–Wabigoon river system in Northwestern Ontario (Parks *et al.*, 1984); other locations of concern were Lake Erie and the Bell River in Northwestern Quebec (Miller *et al.*, 1979).

The English–Wabigoon river system lies in a relatively isolated area, the main inhabitants of which are occupants of two reserves of the Ojibwa Indians, called White Dog and Grassy Narrows Reserves. On these lands, the inhabitants follow to a large extent a traditional life-style, and this includes the consumption of locally caught fish as a dietary staple. Employment in the area is scarce, and many of the inhabitants have historically made most of their real income by serving as guides for tourists who visit one of several local lodges for the purpose of sport fishing (or by working in the lodges themselves).

When it was realized that fish in the area were contaminated, fishing was restricted in the entire system. This had the effect not only of cutting off the population from their main source of protein, but also of removing any possibility of income from the sport fishing industry; the fishing restrictions and the accompanying publicity caused such a slump in the tourist industry that the tourist lodges closed completely in the area. Although government agencies attempted to supply the local inhabitants with imported fish, there were serious problems. Maintenance of the relatively large refrigeration facilities required for such an operation was difficult, and there was no immediate way to replace the lost employment opportunities.

The problem has persisted for many years. The river system has been very slow to clear itself, and at time of writing is still noticeably contaminated, although inputs of mercury to the system have long since stopped. (The offending chloralkali plant changed its operation from the mercury-electrode process to the mercury-free membrane process more than a decade ago.)

The result has been described by the leaders of the Indian Bands themselves as producing a 'complete breakdown of the traditional society'. Incidents of abuse of alcohol and other drugs, and also abuse within the family unit, reached frightening proportions. Truly heroic efforts at the local level were required to deal with the problem. These societal efforts are now succeeding; some new employment has been introduced with extensive government support, and social changes, such as the complete banning of alcohol from the Reserves, has had a noticeable effect.

It is interesting to note that what was initially seen as a corresponding problem in Northern Quebec, specifically on the Bell River, was handled in a quite different fashion. Negotiations among the parties involved, namely the Grand Council of the Cree Indians, the industries involved, and the federal and provincial governments, resulted in a curtailment of the mercury input without anything like the social upset that had taken place in Ontario. It is perhaps necessary to add that even to this day the problem has not been resolved to the satisfaction of all concerned (*Globe and Mail* Newspaper, Toronto, July 13, 1986).

5.8.5 THE FUTURE OF MERCURY IN CANADA

In some previously contaminated Canadian waters, the effective mercury levels have decreased rapidly. In Lake Erie, where sediment is constantly being deposited and remains to some extent undisturbed, the sediments actually in contact with the water column are relatively clean today, and mercury content of the water is low; in other words, the mercury appears to have been effectively buried. The time taken for the fish to become sensibly free of mercury should therefore have depended either on the time taken for an individual fish to clear itself of mercury (the half-life is approximately one year) or should depend on the actual lifetime of a fish (rarely more than ten years). Thus, in the decade or so after the problem was identified and abatement procedures introduced, the situation was seen to greatly improve.

In the Ottawa River, the situation is also much better today than ten years ago, but for a different set of reasons. Like many Canadian (and other) rivers, the Ottawa is subject to greatly increased flow rates during spring melt and runoff (higher than summer flow rates by a factor of at least four, and this in spite of the existence of a number of flood control and hydro-electric dams). This flow causes a great deal of scouring of bottom sediment, which as a result moves far downstream. This is especially true for the very fine-grained sediment, which of course is the kind that preferentially binds most of the mercury; a given particle of clay may move 50 km in one year. Thus the sediment is regularly flushed out of the system and replaced by clean sediment from upstream (Miller *et al.*, 1979). The contaminated sediment is either swept out of the system or settles in front of a large dam to be subsequently buried as more sediment follows in its path. Seen from a single geographical location, the effective result is that sediment in a given location decreases in its mercury content by 30–40% each year (of course it is not the same sediment that is being measured). At a typical location near the city of Ottawa, the sediment concentrations decreased to background levels in four years (1969–1973) (Miller *et al.*, 1979). It is perhaps worthy of note that the problem could reappear if large-scale dredging of reservoirs were to be undertaken in the future.

In some cases, as noted above, the situation is not so fortunate. The English–Wabigoon river system is not losing its mercury at anything like the same rate. This is because of geography; the spring flood is not sufficiently strong to scour the sediment significantly, the waterway is not importing new sediment to cover up the old, and the sediment in the first place is of a very fine kind that binds mercury very effectively. Solutions have been proposed, ranging from large-scale dredging and dry-land disposal to the addition of selenium, known to be protective against mercury toxicity, in the hope of providing an antidote at the ecosystem level. So far, attempts to artificially speed up the clearance of the system have met with virtually no success in practical terms (Parks *et al.*, 1984).

In a longer time frame, we should be concerned about mercury as a general environmental contaminant in the future. It is true that all of the recognized problems so far have been due to very local releases. However, levels of mercury sufficient to justify governmental warnings are now found in fish taken from waters far from any known sources, and our new understanding of the atmospheric dynamics of the metal (see above) makes it perfectly understandable that this should be so.

Since one of the significant sources of mercury in the environment is its presence as a contaminant in fossil fuels, and since every prediction is that the consumption of such fuels will markedly increase in the next few years, we should be aware of the potential for mercury to emerge as a more widespread hazard a decade or so from now. The problem of mercury in Canadian waters is by no means over.

5.8.6 INFLUENCE OF A COLD ENVIRONMENT

Geographical and climatological features of Canada have affected the development of mercury problems in the country in several ways. The country has always had an extensive pulp and paper (and hence chloralkali) industry. In many cases the relevant installations have been located in remote areas where pollution control was not thought to be a matter of concern, and the development of such problems went largely unnoticed. (We must always bear in mind that the overall visual impression given by a mercury-contaminated waterway in an isolated northern location is typically that of a rather attractive, unspoiled wilderness environment.) Abatement procedures may have been delayed since the problem had to be not only noticed but also demonstrated from outside; if an outraged local population existed at all, it was often without much political power. Finally, simple considerations of logistics indicate that all kinds of monitoring, abatement, and enforcement procedures are much more difficult in remote areas.

The cold temperature itself is also part of the problem. At depressed temperatures, mercury deposited on the ground does not re-volatilize so rapidly as it does in warmer areas, so we see more ground- and water-level contamination for a given atmospheric burden (Miller and Buchanan, 1977). The generally lower level of biological activity in colder waters, and in particular the lower standing crop of higher plants (which are excellent absorbers of heavy metals in general and mercury in particular, so much so that they have been proposed as one way that mercury can be physically removed from contaminated systems), means that the residence time of mercury in colder waters is longer.

In addition, the significant changes in temperature over the course of the year lead to sudden large concentrations of this and other substances being presented to target organisms at particular times. Over the year, most organisms, at least at the animal level, build up lipid stores which are then called upon and metabolized during short periods of stress, thus effectively presenting a sudden high concentration within the tissues. Similarly, spring runoff brings a sudden load of winter-contaminated snow into the water systems at precisely the time when many aquatic organisms are in the process of reproducing.

The other notable characteristic of cold environments which influences the problem is, of course, the simplicity of the food chain. Animals for which fish constitutes a dietary staple are not only endangered in the vicinity of a point release (it was the appearance of a poisoned domestic animal, specifically a cat, that first alerted people to the problem at Grassy Narrows), but now would seem to be at risk over much larger areas. For example, a population of poisoned wild mink has recently been studied (Wren and Stokes, 1986). Other animals, such as bears and fish-eating birds, may well develop problems in the future. We seem to have been able to prevent human deaths from mercury poisoning (although at the cost of severe social disruption). We will find it much more difficult to protect the rest of the ecosystem.

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