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Methylmercury production and distribution in aquatic systems

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Abstract

Mercury methylation and partitioning between sediment, water and fish were studied in river sediment spiked with mercuric chloride at levels of 1, 5 and 10 ppm as Hg. Maximum methylmercury production in the sediment occurred during the first week of incubation, with concentrations reaching 45.5 ng/g (dry wt.). Equilibrium conditions were established 3–4 weeks after the contamination of the sediment with mercury. Methylmercury partitioning between sediment and water yielded methylmercury levels of 25–154 ng/l in the fish aquariums and 0.26 ng/l in the fish-free control after 1 week of incubation. Equilibrium levels were 1.5–5.5 ng/l and 0.53 ng/l, respectively, during the 7th week. Over 50% of the methylmercury in whole water were in soluble form or associated with colloidal particulate < 1 μm. Mercury concentration in fish increased almost exponentially from 30 ppb to an average of 345 ppb within 3 weeks. Mercury uptake rates by fish were in the range of 10–18 ng/g per day during the 2nd and 3rd weeks, high rates occurring in water with methylmercury to total mercury ratios > 0.45. The partition coefficients for total mercury and methylmercury between fish and water (K_{f-w}) were 5000–7000 and 10 000–22 000, respectively. Large differences were observed in methylmercury production in sediment–water incubation with fish and the fish-free control. Equilibrium methylmercury concentrations in sediment were in the range 15–32 ng/g in the aquariums containing fish and 3–4.5 ng/g in the fish-free control. The significance of fish in mercury methylation in the aquariums still remains to be clarified as fish itself cannot methylate mercury in vivo. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Our knowledge of mercury transformation, distribution and accumulation in aquatic environments has improved significantly in recent years because of advancements in analytical techniques for detection of mercury species in environmental matrices. With modern techniques it is now possible to measure mercury concentrations as low as picogram levels (Liang et al., 1996), which were impossible to detect before the 1980s. The improvement of analytical methods and renewed

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interest in environmental mercury research triggered by the discovery of high mercury levels in fish from pristine remote lakes in US, Canada and Scandinavia (Stephens, 1995; Andersson et al., 1995) and the increase of mercury pollution from gold mining in developing countries, has made it necessary to re-evaluate the existing data on the biogeochemistry of mercury. For example, recent studies have shown that mercury concentrations in sea water and freshwater bodies are much lower than previously reported (WHO, 1990).

Although accurate determinations of total mercury concentrations in sediment, water, and biota are now available from laboratory and field studies (Driscoll et al., 1994; Wang and Driscoll, 1995), reliable methylmercury data are still scarce. The difficulty in analysing extremely low methylmercury concentrations, especially in water, and poor recoveries of methylmercury from sediment and biological samples are the main reasons limiting the availability of reliable data. A better understanding of mercury distribution in aquatic systems not only requires knowledge of total mercury, but also the amount of mercury that exists in methylated form which is much more available for bioaccumulation. Previous studies have used radiochemical methods to investigate the speciation and distribution of mercury in aquatic systems (Kudo et al., 1977; Akagi et al., 1979). Other researchers have used analytical methods based on the Westoo (1968) procedure to extract mercury from environmental samples followed by the analysis of methylmercury by gas chromatography with electron-capture detection (ECD-GC) (Jacobs and Keeney, 1974; Olson and Cooper, 1975; Shin and Krenkel, 1976; Bartlett et al., 1977). In most of these and other early studies, methylmercury extraction efficiency and the results of certified reference materials were not reported. Also, the presence of interfering organic compounds reduced the accuracy of methylmercury analyses. This limited the reliability of methylmercury data for evaluation of methylmercury production and partitioning in various compartments of aquatic systems. In the present study, highly precise and accurate analyses for total mercury and methylmercury have been used to constrain levels of methylmercury production in laboratory experiments involving sediment–water systems with or without fish. The results of the experiments have important implications regarding the production, distribution and accumulation of methylmercury in aquatic environments, especially in areas affected by mercury pollution from gold mining.

2. Materials and methods

2.1. Experiment setup

Fresh river water and sandy sediment were collected from Minamata river approximately 5 km upstream from Minamata City in Kumamoto Prefecture, Japan. The temperature of river water was 25–27°C during sampling. The sediment (Table 1) was immediately sieved in the laboratory to remove gravel and coarse fragments; the < 840-μm fraction was used for the methylation experiment. After sieving, the sediment was thoroughly mixed and then split into four equal aliquots, each weighing 3.25 kg, and placed into four glass aquariums ($45 \times 30 \times 30$ cm) labelled AQ1, AQ2, AQ3 and AQ4. The sediment was then spiked with mercuric chloride aqueous solution at a level of 1 ppm Hg in AQ1, 5 ppm in AQ 2 and AQ3, respectively, and 10 ppm in AQ4 on a dry weight basis. The mercury concentration in the spiked sediment (1–10 ppm) was within the range of concentrations found in areas affected by mercury pollution from gold mining, such as the Brazilian Amazon (Larcerda and Salomons, 1991) and Tanzanian (Ikingura, 1998) gold fields. The spiked sediment was thoroughly mixed by stirring to achieve a more or less uniform mercury concentration in each aquarium. Six thin sampling boats were then immersed in the sediment in each aquarium to facilitate sediment sampling during the course of the experiment. A screen was placed above the sediment in each aquarium to prevent the disturbance of the sediment by fish. Fresh river water was then carefully added to the aquariums using a siphon tube, making sure not to stir up the sediment. A total of 25 l of water was added in each aquarium. Ten gold-fish

Table 1
Properties of river sediment used in the experiment

Grain size (μm)	< 840
Organic matter (%)	5.6
T-Hg (ppb)	49
MeHg (ppb)	0.45

(*Carassius auratus*), each weighing approximately 5–7 g, were added in each of the aquariums AQ1, AQ3 and AQ4, leaving AQ2 as a fish-free control for the first 3 weeks of the experiment. Each aquarium was covered on top to reduce water loss by evaporation. The aquariums were also sheltered from direct sunlight. Aerobic conditions were maintained in all four aquariums by bubbling air through the water, at a rate of 100 ml/min. The incubation temperature was 27 ± 3°C. The above setup constituted Part I of the experiment.

At the end of the 3rd week all fish were removed from the aquariums so that AQ1, AQ3 and AQ4, previously containing fish, and the fish-free control (AQ2) all remained without fish from the beginning of the 4th week to the end of the 7th week. The 4th–7th-week period constituted Part II of the experiment.

Ten new gold-fish (*Carassius auratus*) were introduced into each of the four aquariums, including aquarium AQ2 (which never had fish before), at the beginning of the 8th week. The 8th week formed Part III and the last part of the experiment.

2.2. Sample collection

Fish, water and sediment samples were collected from the aquariums at the end of 1st and 3rd weeks of the experiment. More water and sediment samples were collected for analysis at the end of 5th and 7th weeks; no fish samples were collected this time as there were no fish in the aquariums during the 4th–7th week of the experiment. Fish, water and sediment samples were collected again together at the end of the 8th week of the experiment. The total number of samples collected for mercury analysis were 36 for sediment, 45 for fish and 20 for water. Glass-fibre filter papers (1 μm) were used for water filtration.

2.3. Mercury analysis

Total mercury (T-Hg) and methylmercury (MeHg) in fish, sediment and water samples were extracted and analysed using reliable, highly sensitive and accurate techniques developed at the National Institute for Minamata Disease (NIMD, Japan) by Akagi and Nishimura (1991) and subsequently modified by Akagi (1997). An overview of the analytical methods is only given here, a more elaborate procedure of methods can be found in the cited references. For total mercury analysis, up to 1 g of sediment or 0.5 g of fish muscle tissue are placed in a thick-walled 50-ml volumetric flask and digested with 2 ml of HNO_3–$HClO_4$ mixture (1:1) plus 5 ml of H_2SO_4 for 20 min at 230–250°C on a hot plate. After cooling, the digested sample is made up to 50 ml by adding mercury-free water to the volumetric flask. The flask is then capped with a glass stopper and shaken to homogenise the sample solution. Analysis of T-Hg in the solution is done by cold vapour atomic absorption (CVAA) using a semi-automated mercury analyser (Model Hg 4000) developed at NIMD in collaboration with Sanso Seisakusho Co. Ltd., Japan.

In water total mercury analysis, 2 l of water sample are treated with 10 ml of 20 N H_2SO_4 and 5 ml of 0.5% $KMnO_4$. The treated sample is neutralised with 20 ml of 10 N NaOH and mixed with 5 ml of 10% NH_2OH–HCl and 5 ml of 10% EDTA–4Na solution. Mercury is extracted from the treated sample using 10 ml of 0.01% dithizone–toluene solution. Of the dithizone–toluene extract, 5 ml are placed in a 50-ml volumetric flask and evaporated to dryness under reduced pressure. The extract residue is then digested with a mixture of HNO_3–$HClO_4$–H_2SO_4, and analysed for T-Hg using the same procedure described earlier for sediment and fish samples.

The procedure for MeHg analysis in sediment and fish samples involves digesting the sample with 1 N KOH solution in ethanol (1 N KOH–EtOH), slight acidification with 1 N HCl, and extraction of MeHg by 10 ml of purified 0.01% dithizone solution in toluene (Dz–Tol).

This is followed by the clean-up of the Dz–Tol extract and the analysis of MeHg by ECD-GC. The clean-up procedure for a biological sample normally involves washing the extract with 1 N NaOH and back-extraction of MeHg into 5 ppm Na_2S solution in 0.1 N NaOH–EtOH (1:1). The aqueous solution is then slightly acidified with 1 N HCl and bubbled with N_2 to remove excess sulphide ions. The solution is adjusted to pH 3 using Walpole's Buffer, before re-extraction of MeHg into 0.5 ml of 0.01% Dz–Tol solution in the final step. This clean-up procedure removes organic materials in the sample solution which otherwise would interfere with MeHg analysis by ECD-GC. In the clean-up of the Dz–Tol extract of a sediment sample, the extract is first passed through a Florisil column (0.5 g Florisil, topped with 0.5 g Na_2SO_4) and washed twice with 1 N NaOH before the extract is subjected to back-extraction with Na_2S following the procedure outlined above. For MeHg analysis in water, the extraction procedure, which is the same as that for T-Hg extraction in the water sample, is followed. The Dz–Tol extract of the water sample is then carried through the same clean-up procedure as for fish analysis, followed by MeHg analysis by ECD-GC.

Inter-laboratory comparison (Kehring et al., 1998) and the analysis of certified reference materials (e.g. TORT-1) have repeatedly verified the accuracy and precision for T-Hg and MeHg analytical methods employed in this study. Also our methods have been used in the certification of the reference materials from the International Atomic Energy Agency (IAEA) (Horvat et al., 1997). The detection limits are 5 ng/g for T-Hg and 5 ng/g for MeHg in biological and sediment samples, and 0.5 ng/l for T-Hg and 0.1 ng/l for MeHg in water samples.

3. Results

3.1. Methylmercury production

Net methylmercury production in sediment was in the order of 39.7–45.5 ng/g (dry wt.) in the fish aquariums (AQ1, AQ3, AQ4) and about 8.9 ng/g in the fish-free control (AQ2) at the end of the 1st week of the incubation. These concentrations correspond to net methylation rates of 5.7–6.5 ng Hg/g per day and 1.3 ng/g per day, respectively. Methylmercury production was slightly lower in sediment with a low mercury concentration (1

Table 2
Average T-Hg (ppb) and MeHg (ppb) concentrations (dry wt.) in river sediment spiked with mercuric chloride at the level of 1 ppm (AQ1), 5 ppm (AQ2, AQ3), and 10 ppm (AQ4) as mercury[a]

Week no.		Aquarium			
		AQ1	AQ2	AQ3	AQ4
0	T-Hg	1049	5049	5049	10 049
	MeHg[b]	*(0.42)*	*(0.42)*	*(0.42)*	*(0.42)*
1		1044	3764	4376	8710
		(39.73)	*(8.94)*	*(45.01)*	*(45.51)*
3		866	3975	4185	8409
		(17.62)	*(3.53)*	*(31.61)*	*(31.49)*
5		907	4129	4121	8270
		(18.97)	*(4.58)*	*(28.74)*	*(25.64)*
7		760	4567	4514	8357
		(15.00)	*(3.33)*	*(28.77)*	*(26.88)*
8		726	3889	4269	8375
		(20.51)	*(19.35)*	*(40.08)*	*(35.72)*

[a]Aquariums AQ1, AQ3, AQ4 contained fish during 1st–3rd weeks, whereas AQ2 was kept as a fish-free control. All aquariums remained without fish between the 4th–7th weeks. New fish were introduced into the aquariums, including AQ2, at the beginning of the 8th week. Ambient mercury concentration in river sediment was 49 ppb.
[b]Numbers in italics indicate MeHg concentration.

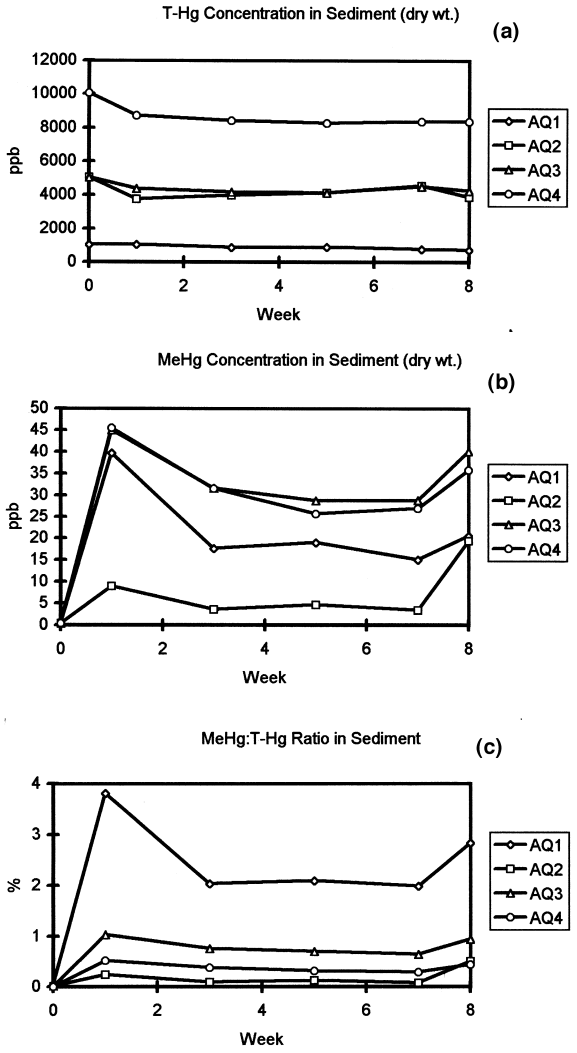


Fig. 1. Total mercury (T-Hg) and methylmercury (MeHg) concentrations and MeHg:T-Hg ratio in river sediment spiked with different mercury concentrations and incubated for 8 weeks in four aquariums (AQ1, AQ2, AQ3, AQ4). (See Table 2 for details.)

ppm) than in sediment with high mercury concentration (5 ppm or 10 ppm) in the fish aquariums (Table 2). No significant difference was, however, observed in net methylmercury production in sediment containing 5 ppm (AQ3) or 10 ppm (AQ4) mercury (Fig. 1a,b). Hence, increasing mercury concentration above 5 ppm did not result in any increase in net methylmercury production in the sediment.

Methylmercury levels in the sediments were much lower at the end of the 3rd week than those recorded at the end of the 1st week. This indicated that net demethylation had occurred in the sediments. No significant changes were observed in methylmercury levels in the sediments from the end of the 3rd week to the end of 7th week, suggesting that equilibrium was possibly attained within the sediments. The average equilibrium methylmercury concentrations in the sediments were 17.2 ng/g (dry wt.) in AQ1, 3.8 ng/g in AQ2, 29.7 ng/g in AQ3, and 28.0 ng/g in AQ4 during the 3rd–7th-week period. Re-introduction of fish in all aquariums at the end of the 7th week resulted in an abrupt increase in methylmercury levels both in sediment (Fig. 1b,c) and water (Fig. 2b,c) by the end of the 8th week. More significant is the sixfold increase in methylmercury level in the sediment in aquarium AQ2 which was originally a fish-free control during the 7 weeks of the experiment.

3.2. Methylmercury distribution

The patterns of methylmercury concentrations in whole water at the end of the 1st and the 3rd weeks were exactly similar to those of the sediments in the fish aquariums. After 1 week, methylmercury concentrations in water were 97.41 ng/l in AQ1, 154.4 ng/l in AQ3, and 25.66 ng/l in AQ4 (Table 3). The concentrations were lower at the end of the 3rd week, being 34.29, 13.71, and 19.15 ng/l, respectively. In contrast, a twofold increase in the methylmercury concentration in water, from 0.26 to 0.57 ng/l, was attained in the fish-free control (AQ2) between the 1st and the 3rd week. A definite equilibrium was reached in the fish-free control as the methylmercury level remained almost constant from the 3rd to the 7th week of the experiment. In the aquariums which originally contained fish, methylmercury levels in water showed a declining trend from the 3rd to the 7th week despite the removal of all the fish at the end of the 3rd week (Fig. 2b,c). The average ratio of methylmercury in filtered water (< 1 μm) to that in whole water varied from 58% to 90% during the 3rd–7th-week period of the experiment. The highest ratio was attained in the 7th

Table 3
T-Hg (ng/l) and MeHg (ng/l) concentrations in whole water

Week no.		Aquarium			
		AQ1	AQ2	AQ3	AQ4
0[a]	T-Hg	1.09	1.09	1.09	1.09
	MeHg[b]	–[c]	–	–	–
1		115.38	826.92	230.77	246.15
		(97.41)	*(0.26)*	*(154.40)*	*(25.66)*
3		48.83	367.06	57.65	70.89
		(34.29)	*(0.57)*	*(13.71)*	*(19.15)*
5		47.73	46.82	76.82	331.00
		(10.67)	*(0.53)*	*(9.60)*	*(3.20)*
7		36.67	70.00	67.00	81.67
		(5.55)	*(0.53)*	*(4.80)*	*(1.40)*
8		47.31	32.38	105.40	22.86
		(44.87)	*(12.04)*	*(73.78)*	*(8.15)*

[a] Beginning of experiment, initial T-Hg concentration in river water: 1.09 ng/l.
[b] Numbers in italics indicate MeHg concentration (see Table 2 for the aquarium set up).
[c] MeHg below detection.

week or 4 weeks after the removal of the first batch of fish from the aquariums. Re-introduction of new fish in the aquariums at the end of the 7th week resulted in the sudden increase of methylmercury levels both in the filtered water and whole water (threefold to 17-fold, Fig. 2b,c) as well as in the sediment by the end of the 8th week.

The average methylmercury concentrations in fish in the aquariums AQ1, AQ3 and AQ4 were 334, 308 and 275 ppb, respectively, at the end of the 3rd week in comparison with 80, 41 and 33 ppb at the end of the 1st week of the experiment (Table 4). Therefore, methylmercury levels in the fish were 4–8 times higher at the end of the 3rd week in comparison with the 1st week. Equilibrium partition coefficients for methylmercury between fish and whole water were 10390 in AQ1, 22487 in AQ3 and 14337 in AQ4 at the end of the 3rd week of the incubation. The partition coefficients for methylmercury between fish and filtered water were much higher, being in the range 21 000–32 000.

Total mercury concentrations in the fish varied from 55 to 200 ppb at the end of the 1st week, and from 272 to 389 ppb at the end of the 3rd week. The proportion of methylmercury to total

Table 4
Average T-Hg (ppb) and MeHg (ppb) concentrations in fish

Week no		Aquarium		
		AQ1	AQ3	AQ4
0	T-Hg	30.55	30.55	30.55
	MeHg[a]	*(29.40)*	*(29.40)*	*(29.40)*
1		85.60	56.15	198.97
		(79.85)	*(40.95)*	*(33.30)*
3		342.40	321.00	341.80
		(333.70)	*(308.30)*	*(274.60)*

[a] Numbers in italics indicate MeHg concentration (see Table 2 for the aquarium set up).

mercury was generally $>70\%$, indicating that most of the mercury accumulated by the fish was methylmercury. The partition coefficients for total mercury between fish and whole water (K_{f-w} = 5000–7000) were significantly lower than those for methylmercury (10 000–22 000).

4. Discussion

4.1. Effect of mercury concentration in sediment on methylmercury production

The transformation of mercury to methylmercury in aquatic environment is mediated by biological processes (Shin and Krenkel, 1976; Jensen and Jernelov, 1969), although abiotic methylation has also been suggested (Rogers, 1976). A positive relationship between methylmercury and mercury concentration in sediments has been demonstrated in several studies (Jacobs and Keeney, 1974; Olson and Cooper, 1975), although the relationship is not linear. It is still uncertain which levels of inorganic mercury concentration in sediment result in maximum methylmercury production and its transfer to the water column, and hence posing a greater hazard because of the high toxicity of methylmercury. In the present study, equilibrium methylmercury concentration in sediment spiked with inorganic mercury at a level of 5 ppm was almost 1.75 times higher than that in sediment containing mercury spike of 1 ppm in the fish aquariums. However, there was no significant difference in equilibrium meth-

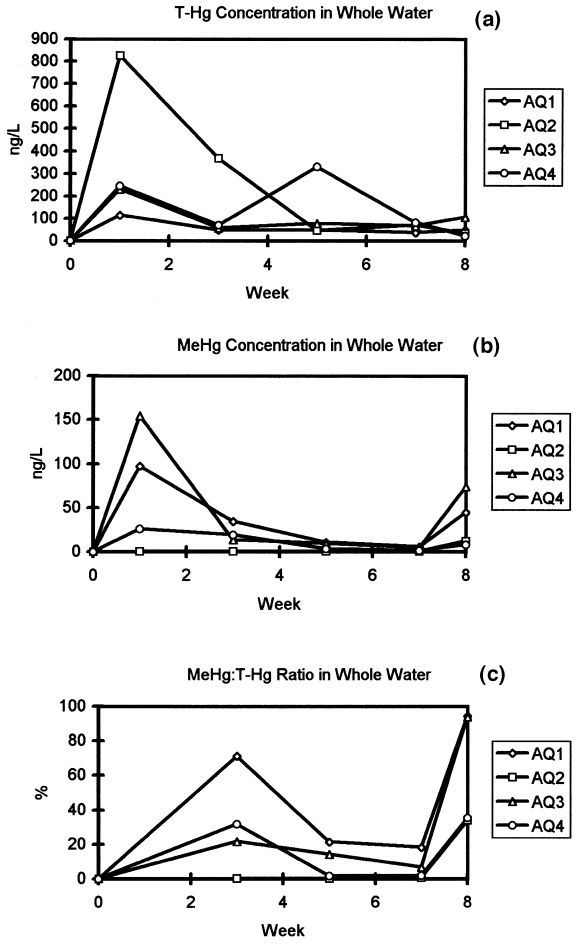


Fig. 2. Total mercury (T-Hg) and methylmercury (MeHg) concentrations and MeHg:T-Hg ratio in whole water in equilibrium with mercury-spiked sediment in the aquariums (AQ1, AQ2, AQ3, AQ4). (See Table 3 for details.)

ylmercury levels between the sediments containing initial mercury concentrations of 5 ppm and 10 ppm. In fact, the methylmercury concentration was slightly lower in the sediment containing 10 ppm mercury (Fig. 1). In this case, it appears that the capacity of the sediment to methylate mercury was almost exhausted at 5 ppm mercury. Hence, increasing the mercury concentration did not result in more methylmercury production in the sediment. Because other studies have reported high levels of methylmercury production in sediment at mercury concentrations as high as 100 ppm (e.g. Olson and Cooper, 1975; Jensen and Jernelov, 1969), it is possible that various types of micro-organisms with different tolerances to inorganic mercury are involved in the methylation of mercury in the sediments in various environments. Also the physical–chemical characteristics of the sediment have a profound effect on the methylation of mercury (Shin and Krenkel, 1976).

It is worth noting that methylmercury production-time course profiles in different studies, including the present study, typically show a sharp rise or gradient within 1 or 2 weeks of the sediment contamination with inorganic mercury, followed by a slight or sharp fall of the profile before levelling at the equilibrium methylmercury concentration in the sediment (Fig. 1b). Methylmercury levels in natural environment, particularly in sediments, are regulated by both methylation and demethylation processes. Net methylation appears to be a dominant process soon after the contamination of sediments with mercury, but the process is reversed when the accumulation of methylmercury presumably exceeds safe levels for the survival of micro-organisms in the sediments. Hence, the methylmercury production profile reflects biogeochemical adjustment within the sediment environment in response to mercury contamination. Methylmercury produced rapidly by the adjustment probably exists in the sediment in a metastable equilibrium until it is degraded to equilibrium levels after the methylmercury production peak.

Average mercury concentrations in river sediments polluted by gold mining activities are in the range of 1–5 ppm in the Tanzanian gold fields (Ikingura, 1998) and up to 20 ppm in the Brazilian Amazon (Larcerda and Salomons, 1991). Mercury spike levels in the sediment used in the methylation experiment were within this range of concentrations. The experiment results could therefore be useful in elucidating methylmercury production and distribution in aquatic systems polluted with mercury from gold mining. In this case, however, mechanisms and factors favouring transformation of metallic mercury (Hg^0) to soluble and reactive mercuric mercury (Hg^{2+}), in order for mercury to get methylated, need also to be carefully evaluated.

4.2. Methylmercury levels in water

The water in contact with mercury contaminated sediments (1–10 ppm Hg) in the present study had highest methylmercury levels (25.7–154.4 ng/l) 1 week after the contamination of the sediments with inorganic mercury. The levels were much lower (13.7–34.3 ng/l) at the end of the 3rd week probably because of net demethylation both in the sediments and water column, but also because of methylmercury uptake by fish from the water. A further decline of methylmercury levels in water between the 3rd and 7th week after the removal of the fish from the aquariums could be attributed to demethylation in water and the removal of methylmercury by particulate matter settling at the bottom of the aquariums. The ratio of methylmercury to total mercury in water decreased from the maximum of 70% in AQ1 to the minimum of 1% in AQ4. Also the ratio showed an inverse relationship with mercury concentration in the sediments. Comparison of methylmercury levels in whole water and filtered water showed that approximately 50–100% of the methylmercury was dissolved in water or associated with the colloidal fraction $< 1\ \mu m$.

It is striking to note that the re-introduction of fish in the aquariums during the 8th week of the experiment resulted in remarkable increase in the methylmercury levels both in water and sediment. Because a small contribution of methylmercury from the fish food could not account for the observed increase in methylmercury, the effect of fish on the methylation process remains to be clarified. Fish cannot methylate mercury in vivo, although slight methylation occurs in the gastrointestinal tract (Spry and Wiener, 1991) and in the external slime layer of fish (Rudd, 1995), presumably by bacteria.

4.3. Mercury uptake by fish

Mercury concentrations in fish increased exponentially from the initial average concentration of 30 ppb to 56–200 ppb after 1 week, and to 321–342 ppb at the end of the 3rd week (Fig. 3a,b). The partition coefficients for total mercury between fish and whole water (K_{f-w}) were in the range of 5000–7000, whereas for methylmercury the coefficients were much higher at 10 000–22 000. Total mercury uptake rate was calculated to be approximately 18 ng/g per day for fish in aquarium AQ1, 19 ng/g per day in AQ3, and 10 ng/g per day in AQ4, during the 2nd and 3rd weeks of incubation (Fig. 3c). These uptake rates corresponded with average methylmercury concentrations of 65.9, 84.1 and 22.4 ng/l in water, respectively. Methylmercury to total mercury (MeHg:T-Hg) average ratios in the water were 77.32% in AQ1, 45.35%

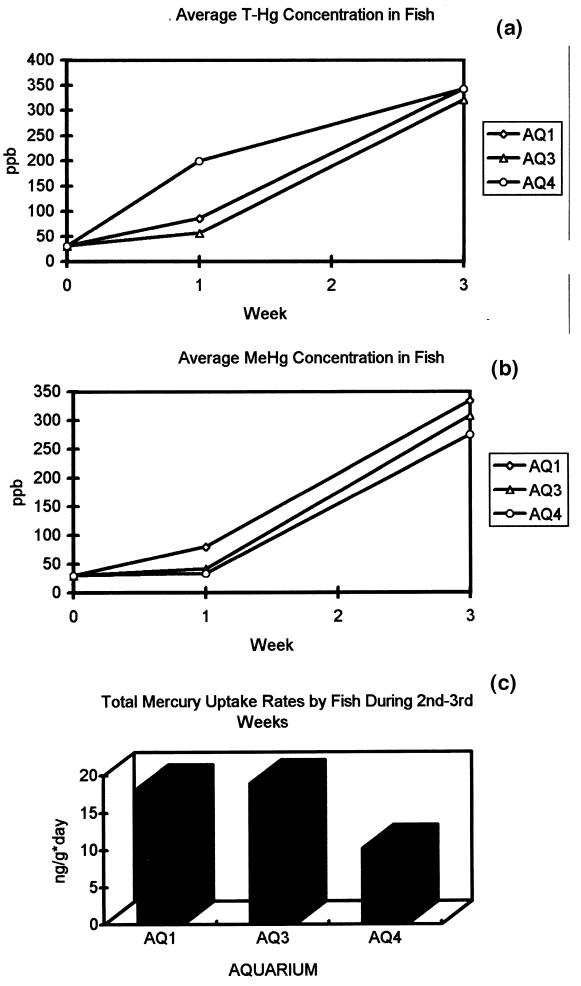


Fig. 3. Average total mercury (T-Hg) and methylmercury (MeHg) concentrations in fish and total mercury uptake rates by fish in different aquariums. (See Table 3 for details.)

in AQ3, and 18.72% in AQ4 in the same period. Relatively low mercury uptake rate by the fish in AQ4 correlated with low methylmercury concentration (22.4 ng/l) in water. This was consistent with the tendency of fish to accumulate methylmercury rather than inorganic mercury.

Studies in Swedish and north American lakes have shown that mercury accumulation by fish is pH dependent, high mercury concentrations being associated with fish from acidic or low pH lakes and vice-versa (Stephens, 1995; Andersson et al., 1995). The water pH was not monitored continuously in the present study but a few measurements taken during water sampling from the aquariums indicated that the pH varied in a narrow range of 6.86–7.10.

5. Conclusions

Maximum methylmercury production in river sediments contaminated with soluble inorganic mercury occurs within a short time interval of 1–2 weeks after the contamination, probably as a consequence of rapid biogeochemical adjustment within the sediment. Methylmercury produced by this adjustment possibly exists in metastable equilibrium in the sediment and hence is quickly degraded by demethylation processes to reach equilibria within 3–4 weeks after the mercury contamination.

Increasing the level of mercury contamination in the sediment will produce more methylmercury only if the methylation potential or capacity of the sediment is not exhausted or overwhelmed by the contamination. Sediments from different environments may have different capacities to methylate mercury and hence methylation studies of one area should be applied to other areas with a lot of caution. The methylation capacity of river sediment used in this study was exhausted by mercury concentration of not more than 5 ppm. Hence there were no significant difference in the amounts of methylmercury produced in the sediments with 5 ppm and 10 ppm mercury, respectively.

The partitioning of methylmercury between the sediment and water column is rapid because methylmercury concentrations in the water exhibit similar patterns as those of the underlying sediments. Comparison of methylmercury concentrations in whole water and filtered water indicated that more than 50% of methylmercury in whole water is in soluble form or associated with colloidal particles < 1 μm.

Mercury uptake by fish from water equilibrated with mercury contaminated sediments occurs readily because of the rapid transfer of methylmercury from the sediments to the water column. The uptake rate shows positive relationship with methylmercury (MeHg) concentration and MeHg:T-Hg ratios in water, but the relationship is not linear. Average methylmercury concentration of 66–84 ng/l in water resulted in total mercury uptake rates of approximately 18.5 ng/g per day while a concentration of 22 ng/l resulted in the uptake rate of 10 ng/g per day by fish. These mercury uptake rates gave rise to mercury concentrations as high as 345 ppb in fish within a period of 3 weeks after the contamination of the sediments with 1–10 ppm inorganic mercury. More than 70% of the mercury accumulated by the fish was methylmercury. The mercury partition coefficients between fish and whole water (K_{f-w}) were in the order of 5000–7000 for total mercury and 10 000–22 000 for methylmercury.

Substantially more methylmercury was produced in sediments in the aquariums containing fish than in the fish-free control aquarium sediments. The significance of fish in the methylation of mercury still needs clarification.

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References

Akagi H. Analytical methods for evaluating human exposure to mercury due to gold mining. Proceedings Intern. Workshop: Health and Environmental Effects of Mercury due to Mining Operations. Manila, Philippines: National Institute for Minamata Disease, Japan, 1997:131–141.

Akagi H, Nishimura H. Speciation of mercury in the environment. In: Suzuki T, Imura N, Clarkson TW, editors. Advances in mercury toxicology. USA: Plenum Press, 1991: 53–76.

Akagi H, Mortimer DC, Miller DR. Mercury methylation and partition in aquatic systems. Bull Contam Toxicol 1979; 23:372–376.

Andersson P, Borg H, Karrhage P. Mercury in fish muscle in acidified and limed lakes. Water Air Soil Pollut 1995; 80:889–892.

Bartlett PD, Craig PJ, Morton SF. Behaviour of mercury species in isolated estuarine sediment samples-growth and decay of methylmercury during storage. Nature 1977;267: 606–608.

Driscoll CT, Yan C, Schofield CL, Munson R, Holsapple J. The mercury cycle and fish in the Adrondack lakes. Environ Sci Technol 1994;28:136A–143.

Horvat M, Liang L, Azemard S, Mandic V, Villeneuve J-P, Coquery M. Certification of total mercury and methylmercury concentrations in mussel homogenate *(Mytilus edulis)* reference material, IAEA-142. Fresenius J Anal Chem 1997;358:411–418.

Ikingura JR. Mercury pollution due to small-scale gold mining in Tanzanian gold fields. In: Landner L, editor. Small-scale mining in African countries: prospects, policy and environmental impacts. Sweden: CM Gruppen AB, Bromma, 1998:143–158.

Jacobs LW, Keeney DR. Methylmercury formation in mercury-treated river sediments during in situ equilibration. J Environ Quality 1974;3/2:121–126.

Jensen S, Jernelov A. Biological methylation of mercury in aquatic organisms. Nature 1969;233:753–754.

Kehring HA, Malm O, Akagi H, Guimaraes JRD, Torres JPM. Methylmercury in fish and hair samples from the Balbina reservoir, Brazilian Amazon. Environ Res Sect A 1998;77:84–90.

Kudo A, Akagi H, Mortimer DC, Miller DR. Equilibrium concentrations of methylmercury in Ottawa river sediments. Nature 1977;220:419–420.

Larcerda LD, Salomons W. Mercury in the Amazon: A chemical time bomb. Dutch Ministry of Housing, Physical Planning and Environment, 1991:49.

Liang L, Hovart M, Danilchik P. A novel analytical method for determination of picogram levels of total mercury in gasoline and other petroleum based products. Sci Total Environ 1996;187:57–64.

Olson BH, Cooper RC. Comparison of aerobic and anaerobic methylation of mercuric chloride by San Francisco Bay sediments. Water Res 1975;10:113–116.

Rogers RD. Methylation of mercury in agricultural soils. J Environ Quality 1976;5:454–458.

Rudd JWM. Sources of methylmercury to freshwater ecosystems: A review. Water Air Soil Pollut 1995;80:697–713.

Shin E-B, Krenkel PA. Mercury uptake by fish and biomethylation mechanisms. J WPCF 1976;48/3:473–501.

Spry DJ, Wiener JG. Metal bioavailability and toxicity to fish: Mercury uptake, elimination and distribution in fish. Environ Pollut 1991;71:249–252.

Stephens GR. Mercury concentrations in fish in a remote Canadian Arctic Lake. Water Air Soil Pollut 1995;80: 633–636.

Wang W, Driscoll CT. Patterns of total mercury concentrations in Onodanga Lake, New York. Environ Sci Technol 1995;29/9:2261–2266.

Westoo G. Determination of methylmercury salts in various kinds of biological material. Acta Chem Scand 1968; 22:2277–2280.

WHO (IPCS). Environmental health criteria 101. Methylmercury 1990:35–36.