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Chemistry and Ecology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455114>

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To cite this Article Baralkiewicz, Danuta , Gramowska, Hanka and Gołdyn, Ryszard(2006) 'Distribution of total mercury and methyl mercury in water, sediment and fish from Swarzędzkie lake', *Chemistry and Ecology*, 22: 1, 59 – 64

To link to this Article: DOI: 10.1080/02757540500393935

URL: <http://dx.doi.org/10.1080/02757540500393935>

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Distribution of total mercury and methyl mercury in water, sediment and fish from Swarzędzkie lake

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(Received 23 May 2005; accepted 28 September 2005)

Concentrations of total mercury and methyl mercury were determined in water, sediment and fish collected from Swarzędzkie lake in order to understand their distribution and partitioning which are not well known. Samples of water and sediments were collected at 11 locations. Water THg (total mercury) concentrations ranged from 155 to 342 ng l⁻¹ and MeHg (methyl mercury) ranged from 21.7 to 36.5 ng l⁻¹. Total mercury concentrations in sediments ranged from 76 to 880 µg kg⁻¹ dry wt. Methyl mercury accounted for, on average, 1.32 % of total mercury in sediment. The concentrations of total mercury in fish muscle were between 0.25 and 2.95 µg kg⁻¹ wet wt, with methyl mercury contributing 87.3 % of total mercury. Methyl mercury concentrations in fish muscle were directly proportional to total mercury concentrations and ranged between 0.18 and 2.63 µg kg⁻¹ wet wt.

Keywords: Inorganic mercury; Methylmercury; Lake sediment

1. Introduction

Mercury is a hazardous environmental contaminant. Mercury species can undergo a variety of transformations in the environment. Toxicology studies also proved that mercury, especially methyl mercury (MeHg), is very toxic to humans. In aquatic systems, mercury exists in elemental, inorganic and organic forms. The main form of mercury in sediment is probably the highly insoluble mercury sulfide. Microorganisms in the bottom mud, however, can convert several mercury compounds into methylmercury [1]. In aquatic systems, bioaccumulation through the food chain may cause high levels of mercury contamination in fish from even very low concentrations of MeHg in water [2]. The uptake routes, which may be through the food chain, directly from water, or both, are not fully understood yet. A large assortment of microorganisms are capable of converting inorganic Hg²⁺ into CH₃Hg⁺ [3–6]. The rate of CH₃Hg⁺ production depends on a complex interaction of a variety of environmental variables. Little is known about the biogeochemical cycling of mercury compounds in Swarzędzkie lake. The goal of this work is recognizing the distribution, concentration and partitioning of mercury between water, sediment and fish from this lake.

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2. Materials and methods

2.1 Site description

The Swarzędzkie lake is a shallow post-glacial lake. It is situated on the border of two towns, Poznań and Swarzędz. Its main tributary is the Cybina river which below the lake, flows into the Warta river as its right tributary. The Mielcuch is a stream which flows through the built-up area of Swarzędz and reaches Swarzędzkie lake at its mid-section (figure 1). The water supplying the lake is very rich in nutrients. Every year the Cybina river carries 139923 kg of nitrogen and 1945 kg of phosphorus, mainly from non-point sources (farmlands, fishponds and villages without a sewage system), while the Mielcuch stream carries 10932 kg N and 829 kg P, mainly from point sources (storm water and some domestic sewage) [7]. The Swarzędzkie lake is exposed to pollution coming from the tributary. In this eutrophic lake the nutrient content depends on the season of the year, ranging from 1.66 to 15.64 for nitrogen and from 0.037 to 0.864 for phosphorus.

2.2 Sampling

Samples of water and sediment were collected from 11 sampling stations, 4 times (in each season) during the year 2002. The stations were situated in the profundal zone (the deepest place in the lake – station 11), in the littoral zone (water depth 1.5–3 m – stations 1–9) and in the intermediate zone (between the littoral and the profundal zone) (depth 4 m – station 10) (figure 1).

The top 10 cm of sediments were collected with the Kajak core sampler, designed for soft sediments [8]. After collection, the samples were placed in polyethylene zippered bags and stored at 4°C until analysis (<30 d). Prior to analysis, sediment samples were air-dried and ground to a fine powder that passed through a number 20 sieve.

Water samples were collected into cleaned Teflon bottles from the depth of 30 cm under the water mirror. When the depth was higher than 5 m the samples were collected from 1 m above the lake sediment and they were combined with previously collected samples. Samples were stored in a refrigerator.

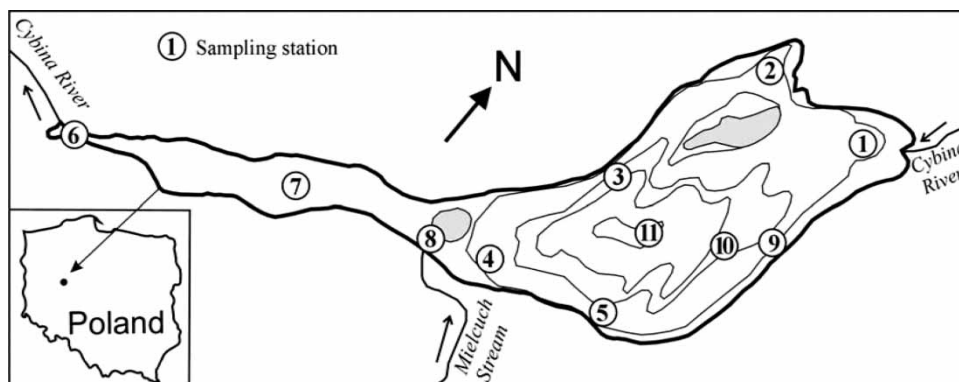


Figure 1. Map of Swarzędzkie lake indicating sampling sites.

Fish samples were of roach (*Rutilus rutilus* (L)). They were collected only during the summer and placed in polyethylene bags and frozen. Whole fish were weighed, measured, the skin removed, and equal amounts of muscle fillets were homogenized and analyzed.

2.3 Mercury analysis

The determination of mercury in water was performed using the Automatic Mercury Analyzer RA-3000 System (Nippon Instruments Corporation) based on reducing vaporization with stannous chloride into an atomic fluorescence spectrometer. Methyl mercury was determined after the addition of hydrochloric acid, extraction with benzene and back extraction into an aqueous phase with L-cysteine. The detection limit of both form mercury in water was 50 pg l^{-1} .

Total mercury in sediment and fish tissues was analyzed after microwave digestion with acid mixture ($\text{HNO}_3 + \text{H}_2\text{O}_2$). Detection limits of both form Hg in sediment and in fish were $0.1 \text{ } \mu\text{g kg}^{-1}$ dry wt.

Analytical quality control was verified by the analysis of certified reference material for water ORMS-2 (THg $30.6 \pm 2.3 \text{ ng l}^{-1}$) and sediment IAEA 405 (THg $0.81 \pm 0.04 \text{ mg kg}^{-1}$ dry wt; MeHg $5.49 \pm 0.53 \text{ } \mu\text{g kg}^{-1}$). Similarly, for fish tissues, BCR-463 ($2.85 \pm 0.16 \text{ mg kg}^{-1}$ dry wt for total mercury and $3.04 \pm 0.16 \text{ mg kg}^{-1}$ dry wt for methyl mercury) was analyzed.

3. Results and discussion

Mercury concentrations in water varied from 155 to 342 ng l^{-1} . The highest concentration was noted at stations 3, 2 and 7 (342 , 331 and 315 ng l^{-1} , respectively), located in the northernmost part of the lake, whereas the lowest concentration was found at station 11 which was in the deepest part of the lake (155 ng l^{-1}). Mercury was measured in unfiltered water samples because most mercury is attached to particles of suspended sediment [9]. Methyl mercury compounds in the studied waters were in small quantities. Their concentrations ranged from 21.7 to 36.5 ng l^{-1} , i.e. 8.1–11.0 % of the total mercury contents. It was confirmed that levels of methyl mercury are usually much lower than those of inorganic mercury [10]. Recent reports estimate a total mercury concentration in natural waters ranging from 0.2 to 100 ng l^{-1} , while

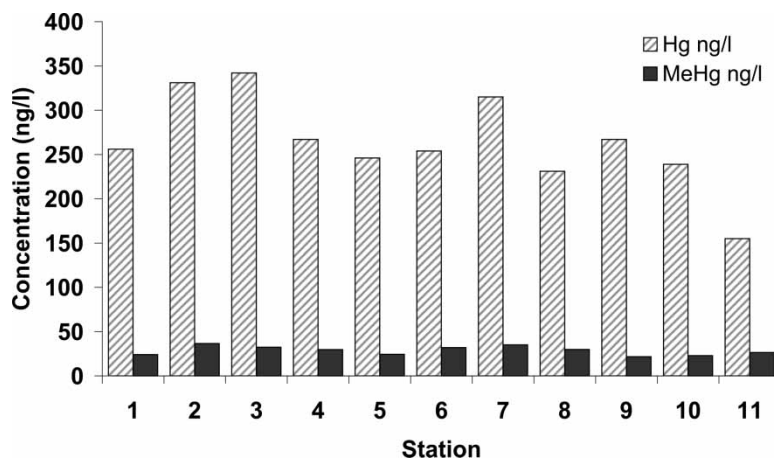


Figure 2. Contents of mercury in water.

Table 1. Concentrations of total mercury and methyl mercury in sediment and fish muscle collected from the Swarzędzkie lake, Poland.

Location	Sediment		Fish ^a	
	THg ($\mu\text{g kg}^{-1}$)	MeHg ($\mu\text{g kg}^{-1}$)	THg ($\mu\text{g kg}^{-1}$)	MeHg ($\mu\text{g kg}^{-1}$)
1	338	2.70		
2	76	0.97		
3	241	1.67	2.95	2.63
4	880	13.5		
5	769	1.67	0.38	0.34
6	410	5.66		
7	812	9.70	0.60	0.59
8	877	15.3		
9	166	3.65		
10	182	3.97		
11	130	1.86	0.25	0.18

^aFish were sampled in the vicinity of marked stations.

methyl mercury levels are much lower, ca 0.05 ng l^{-1} [11]. Certainly, higher values can be found in waters located in heavily industrialized areas.

The values of mercury concentration in sediment and fish samples are shown in table 1. Mercury concentrations in sediments ranged from 76 to $880 \mu\text{g kg}^{-1}$ dry wt for total mercury and from <1 to $15.3 \mu\text{g kg}^{-1}$ dry wt for methyl mercury (table 1). Sediments collected from stations near the Mielcuch stream, which is one of main pollutants introduced to the lake, contained the highest total mercury and methyl mercury concentrations. Water samples collected from these stations however did not contain high mercury concentrations. Probably mixing of waters resulted in transferring mercury to other stations. Mercury released from sediments takes a very long time and water samples were collected shortly after the introduction of pollutants. The large variation of mercury concentrations determined in this survey reflects the wide diversity of sediment characteristics and pollution intensity. In general, the observed mercury concentrations were within ranges reported for coastal marine sediments [12].

Little is known about background levels for methyl mercury compounds in lake and river sediments. Considering the most recent literature data, it seems reasonable to assume the content $<1 \mu\text{g kg}^{-1}$ to be natural [6]. A comparison of that value with methyl mercury values found in Swarzędzkie lake indicates a high capability of the sediments to produce and/or to accumulate methyl mercury compounds.

The relationship between the concentrations of total mercury and methyl mercury in sediments was shown in figure 3. Total mercury was correlated ($r = 0.78$; $p < 0.05$) with methyl mercury concentrations in sediments. This indicates that mercury is available for methylation under specific conditions. However, under anaerobic conditions most of mercury has high affinity for sulfide, resulting in the formation of insoluble HgS , which is deposited in the sediment [13]. The percentage of methyl mercury in total mercury concentrations in sediments varied between 0.22 and 2.17% .

Concentration of total mercury present in fish muscle was in the range of 0.25 – $2.95 \mu\text{g kg}^{-1}$ dry wt and methyl mercury ranged from 0.18 to $2.63 \mu\text{g kg}^{-1}$. The percent of methyl mercury to total mercury varied between 72% and 98.3% (mean: 87.3). Mercury accumulation by fish depends on the abundance of available inorganic mercury in sediments/water column, trophic interaction and the rate at which microflora transforms mercury into methyl mercury in addition to the species-specific accumulation and seasonal variations [14]. Huggett *et al.* [15] reported that according to the National Bioaccumulation Study (NBS) background concentration in fish around the country was $0.16 \mu\text{g kg}^{-1}$, while fish in agricultural areas averaged

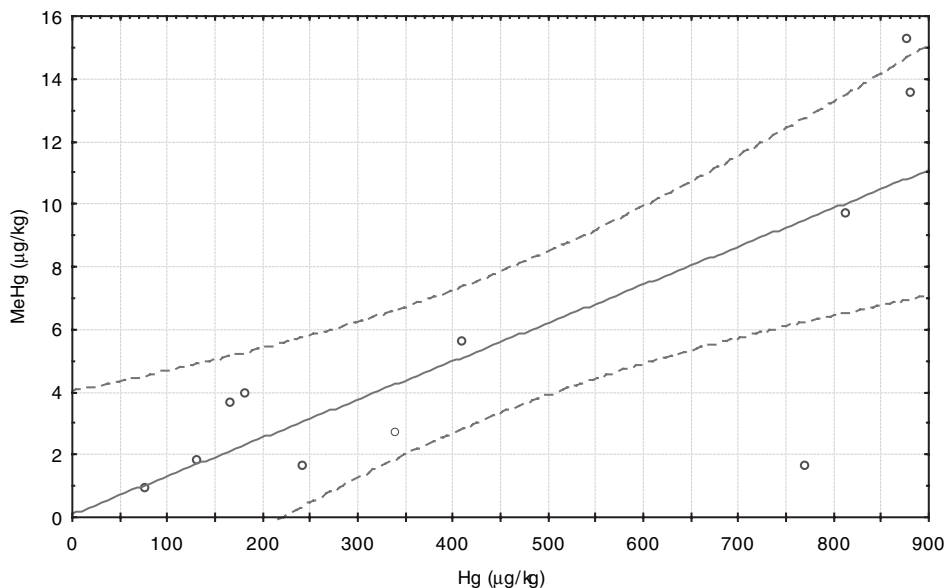


Figure 3. Relation between the concentrations of total mercury and methyl mercury in sediments.

0.17 mg kg⁻¹ [16]. Located in industrial and agricultural area, Swarzędzkie lake fish contained considerably higher mercury concentrations than those observed in the NBS. It may suggest the presence of local inputs.

Acknowledgements

The authors wish to thank Mr Tadeusz Glenc of TESTCHEM company for providing them with access to Automatic Mercury Analyzer RA – 3000, an indispensable tool for the study.

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