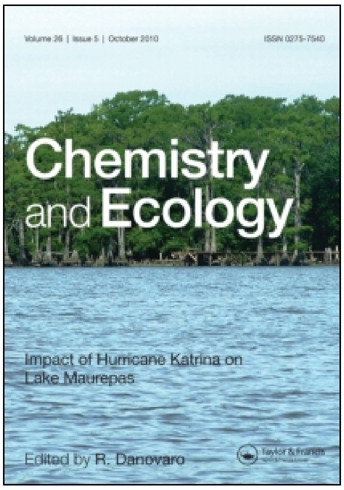

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Inorganic and methyl-mercury speciation in sediments of the Swarzędzkie Lake

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Sediment samples were analysed for mercury and methylmercury content in different parts of the bottom sediment of Swarzędzkie Lake, which were influenced by different external pollution sources. The results of determination with two methods of mineralization using two separate media (HNO_3/H_2O_2 and HF) were compared. The accuracy of the studied methods was analysed using certified reference material IAEA 405 of river sediment. The recovery of mercury was satisfactory and ranged from 97.5 to 98.8%. Methylmercury compounds in the studied sediments were found in limited concentrations. Their concentrations ranged from 0.26 to 58.1 $\mu g\,kg^{-1}$, i.e. 1.0–7.4% of the total mercury content. The depth profile displayed high values of both total and methylmercury content at a depth of 10–20 cm, related to the heavy pollution of the lake in the 1980s. Canonical analysis displayed the relationship of both total mercury and methylmercury concentrations with organic matter and phosphorus content in bottom sediments.

Keywords: Inorganic mercury; Methylmercury; Speciation; Lake sediment; Organic matter

1. Introduction

Increasing industrialization and the use of agriculture chemicals are potential sources of toxic metals in the environment. Mercury is one of the most poisonous and accumulative metals in biological systems. Natural mercury arises from the degassing of the earth's crust through volcanoes and by evaporation from the oceans and by the burning of fossil fuels. The chloralkali, electrical equipment, paint, and wood-pulping industries are the largest consumers of mercury, accounting for 55% of the total consumption. Mercury has a wide variety of other uses in military applications, batteries, medicine, and dentistry. Some mercury compounds have been used in agriculture, principally as fungicides [1]. Because of the adverse toxic

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effects of mercury compounds, their accurate determination in environmental samples has received great attention [2]. Concern over environmental pollution with mercury has intensified the search for analytical methods that require minimal sample preparation, and give contaminant-free analysis and good analytical sensitivity.

The problem of losing mercury through volatilization during sampling digestion at high temperatures precludes the use of fusion and dry ashing procedures [3]. Since the introduction of microwave digestion [4], there has been significant interest in using microwave heating to replace conventional heating during acid digestion. The major advantages of microwave digestion using a closed-vessel container are that the digestion time is significantly reduced, and problems caused by contamination and losses through volatilization are also minimized [5]. Numerous techniques have been developed for the determination of low mercury levels in environmental samples. One of the most widely used techniques for the determination of mercury is the cold vapour generation method followed by atomic absorption spectrometry [6]. Either stannous or borohydride compounds are used to reduce the mercury compounds to elemental mercury, followed by sweeping the free mercury atoms into an absorption cell and subsequent detection by an appropriate mercury line.

After entering an aquatic system, mercury can be transferred (from water to sediment) and transformed (Hg^{2+} to CH_3Hg, etc.) [7]. From a biological and health-protection point of view, the production of toxic CH_3Hg^+ is the most important process. Both inorganic and organic mercury tend to be accumulated in sediments [8]. Methylmercury compounds can subsequently be adsorbed by fish and accumulated in their tissues [9, 10]. Contaminated food is the major way of exposure for humans to methylmercury [11, 12]. Once contaminated food is ingested, about 95% of methylmercury is absorbed from the gastrointestinal tract into the blood. Kidney damage, cardiovascular collapse, and death may occur if 10–60 mg CH_3Hg/kg is consumed within a short period of time, while neurotoxicity results when smaller concentrations of methylmercury are absorbed over a long period of time [11].

Since the studied Swarzędzkie Lake was under the influence of pollution sources from many human activities and has been provided for restoration measures, it was necessary to survey the ecosystem functioning under stress of different variables. Municipal waste-water discharges into aquatic systems without proper treatment are frequently major contributors of different pollutants, among them also mercury. Pesticides and fungicides with mercury content were also widely used in agriculture for a long period of time. This resulted in high concentrations of mercury in intensively cultivated soils [13]. As Swarz ędzkie Lake was affected by both these pollution sources, it was very important to search for the concentrations of mercury in the different parts of the ecosystem of this lake. This paper presents one aspect of multidirectional studies of Swarz ędzkie Lake.

The main aim of the present study was to determine the spatial variability of mercury and methylmercury content in different parts of the bottom sediment of Swarz ędzkie Lake, which have been under diverse influence of external pollution sources. The methodological aspect, the test of the accuracy of mercury determination with sample mineralization using two separate media (HNO_3/H_2O_2 and HF), was also of primary importance.

2. Materials and methods

2.1 *Site description*

Swarz ędzkie Lake is a shallow post-glacial lake, located between two towns, Poznań and Swarz ędz. Its main inflow is the Cybina River, which below the lake flows into the Warta

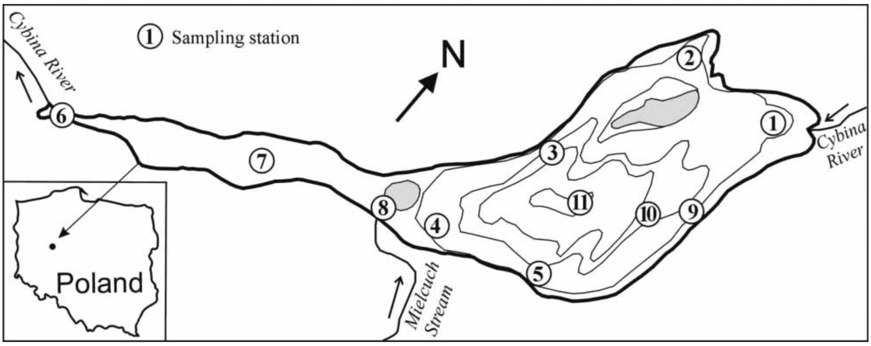

Figure 1. Map of the Swarzędzkie lake, showing the positions of the sampling stations (according to Kowalczewska-Madura [20], modified).

River as its right tributary [14]. The Mielcuch is a stream which flows through the built-up area of Swarzędz and reaches Swarzędzkie Lake at its middle part (figure 1). The total catchment area of the lake is 17 230 ha, but its direct part is only 452 ha [15]. The total catchment area contains mostly farmland (75.5%), woodland (18%), and built-up areas (5.3%) [16]. The water supplying the lake is very rich in nutrients. Every year, the Cybina River carries 139 923 kg of nitrogen and 1945 kg of phosphorus, mainly from non-point sources (farmland, fishponds, and villages without a sewage system), while the Mielcuch Stream carries 10 932 kg N and 829 kg P, mainly from point sources (stormwater and some domestic sewage) [17]. In the 1980s, the lake was contaminated with untreated municipal wastewater from Swarzędz (population 20 000). Sewage was diverted in 1991, and over subsequent years the water quality has improved [15–17].

The area of the lake is 79.4 ha, the volume is approximately 2 million m^3, and the maximum depth is 7.2 m (average depth 2.5 m). The lake is elongated in shape and has a maximum length is 2940 m and width of 560 m [18]. It consists of two parts: a deep and wide north-east basin, and a narrow and shallow south-west basin (with a depth not exceeding 2 m).

2.2 *Sampling strategy*

Sediments samples were collected from 11 stations, four times (in every season) during 2002. The stations were located in the deep zone (the deepest place in the lake – station 11), in the littoral zone (water depth 1.5–3.0 m – stations 1 and 9) and in the intermediate zone (between the littoral and the deep zone) (depth 4 m, station 10); see Figure 1. The deeper sites (stations 10 and 11) were characterized by organic sediments of plankton origin, with oxygen depletion in the summer period. A large content of organic matter in sediments (15–25%) was recorded at the majority of the stations. Only in the case of station 9 does the bottom have a typically mineral composition.

The top 10 cm of sediments was collected using the Kajak core sampler, designed for soft sediments [19]. In September 2002, the mercury content was additionally analysed down to a depth of 30 cm in the sediments (divided into four layers: 0–5, 5–10, 10–20, and 20–30 cm) in the deepest part of the lake (station 11). 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 was passed through a no. 20 sieve.

2.3 *Reagents and standard solutions*

All solutions were prepared from analytical-grade reagent with Millipore distilled and deionized water and stored in polyethylene bottles. Analytical-grade reagents of nitric acid (Merck), sulfuric acid (Merck), hydrogen peroxide (30%, BDH), and hydrofluoric acid (Merck) were used. The reduction solution, stannous chloride (10% w/v), was prepared by dissolving it in 10% (v/v) HCl. Mercury stock solutions were prepared from 1000 mg l^{-1} standard solutions. Standards were prepared daily from the stock solution by serial dilution using 0.001% L-cysteine for mercury (II) chloride and benzene for methylmercury chloride. The L-Cysteine–sodium acetate mixture was prepared by dissolving 1 g of L-cysteine hydrochloride, 0.8 g of sodium acetate 3-hydrate, and 12.8 g of sodium sulfate (anhydride) in 100 ml of water. Certified reference material IAEA 405 river sediment was used to validate the procedures.

2.4 *Analytical methodology*

The dry sample was accurately weighed (1 g) directly into a digestion vessel, to which 5 mL of HNO_3 was added, and then left to stand for several minutes; then 3 ml of H_2O_2 was added carefully (to prevent vigorous reactions and loss of volatile Hg). After being left to cool for several minutes, the vessels were tightly capped using the capping station and vented into a collecting container holding water to trap excess acid fumes that might escape. The vessels were then placed in a microwave oven and heated. The microwave operational parameters applied are listed in table 1. The vessels were cooled in ice water for 20 min. When HF for digestion was used, it was added very carefully into the digestion vessel in two doses: 1 mL and 2 mL. Methylmercury compounds were leached with 5 mL of 6 M HCl from 1 g of sediment. After the centrifugation and washing of the residue with 2 mL of HCl, the combined acid phases were extracted twice with 5 mL of benzene. Finally, methylmercury chloride from the combined benzene layer was back-extracted into an aqueous phase with a 2-mL mixture of L-cysteine–sodium acetate.

Mercury in the digested samples was analysed using an atomic absorption spectrophotometer by the cold-vapour technique, using the Automatic Mercury Analyser Ra-3000 (Nippon Instruments Corporation) following stannous chloride reduction. The reproducibility and accuracy were determined by means of the five lectures and analyses of the certified reference standard IAEA 405. The detection limit of methodology was determined as 0.1 $\mu g\,kg^{-1}$. Only ACS-grade reagents were utilized in this study.

2.5 *Statistical analysis*

In order to verify the relationship of mercury and methyl-mercury content with other characteristics of sediments, a canonical analysis was applied. For this analysis, published

Table 1. Microwave heating programme for sediment digestion.

Step	Time (min)	Pa (N/m^2)	Power (%)
1	5	275800	80
2	5	586075	80
3	10	861875	80
4	10	1103200	80

data regarding the organic matter and total phosphorus content in the sediments and soluble reactive phosphorus concentrations in the porewaters were used [20–22]. Analyses of these parameters were made from the same samples, which were used for Hg and Me–Hg analyses. To estimate the significance of the spatial variability of mercury and methylmercury content in the lake sediments, the ANOVA test with a post-hoc Tukey test was used. All statistical analyses were done using STATISTICA software, version 7.1.

3. Results and discussion

3.1 *Effect of acid mixture*

The efficiency of acid mixtures for sediments microwave digestion was investigated by comparing the recoveries of mercury from samples collected from the 11 stations in the lake. The results of these experiments are reported in table 2. Samples from the vertical profile are numbered as follows: 11 for the layer 0–10 cm, 12 for the 10–20 cm layer, and 13 for the 20–30 cm layer. These data show that both mineralization mixture (HNO_3 with H_2O_2) and HF alone may give satisfactory results. The mixture of HNO_3 and H_2O_2 has been used by Tinggi and Craven [3] to mineralize seafood, while applying different parameters of microwave digestion. They had not obtained satisfactory results, which could be explained by the fact that biological samples are extremely difficult to mineralize. Mohd *et al.* [23] have determined that the efficiency of microwave digestion is affected by several parameters which need to be optimized. These include the amount of sample to be used, the type and amount of acid used, the microwave power applied, and the time of dissolution. The efficiency of this digestion methodology was evaluated by measuring the recoveries known certified mercury values. It can be seen from table 2 that the recovery of mercury was satisfactory and ranged from 97.5 to 98.8%.

Table 2. Content of total and organic mercury in the Swarzędzkie Lake (average values ± standard deviation, $n = 5$, $P = 95\%$).

	Total Hg ($mg\,kg^{-1}$)			
	Mineralization in medium			
Sample	$HNO_3+H_2O_2$	HF	MeHg ($\mu g\,kg^{-1}$)	Contribution of MeHg to total Hg (%)
1	0.60 ± 0.04	0.58 ± 0.05	6.03 ± 0.15	1.01
2	0.082 ± 0.007	0.106 ± 0.009	1.12 ± 0.17	1.35
3	0.31 ± 0.05	0.34 ± 0.06	3.23 ± 0.17	1.03
4	2.12 ± 0.04	2.06 ± 0.04	26.1 ± 3.1	1.23
5	1.70 ± 0.07	1.68 ± 0.07	2.34 ± 0.42	1.35
6	0.69 ± 0.10	0.75 ± 0.08	8.25 ± 0.32	1.19
7	1.17 ± 0.06	1.23 ± 0.06	15.1 ± 1.03	1.28
8	2.11 ± 0.03	2.21 ± 0.04	23.4 ± 2.3	1.09
9	0.20 ± 0.04	0.20 ± 0.05	3.18 ± 0.26	1.60
10	0.38 ± 0.04	0.44 ± 0.07	5.12 ± 0.12	1.34
11	0.20 ± 0.05	0.19 ± 0.06	2.63 ± 0.10	1.30
11a	0.78 ± 0.06	0.75 ± 0.05	58.1 ± 4.2	7.43
11b	0.29 ± 0.11	0.27 ± 0.13	10.18 ± 0.56	3.50
IAEA 405*	0.79 ± 0.05	0.80 ± 0.05	5.01 ± 0.22	0.63

*Certified value w IAEA 405. Hg− : 0.81 ± 0.04 $mg\,kg^{-1}$; MeHg: 5.49 ± 0.53 $\mu g\,kg^{-1}$.

3.2 *Spatial variability*

The range of total mercury content in the sediments of Swarz ędzkie Lake was 0.082–2.21 mg kg^{-1} (figure 2), and values changed significantly at particular stations (table 3). The spatial variability of total mercury was very high, and only in four cases were differences not statistically significant. Similar values were mainly observed between stations located nearby (stations 3 and 10, stations 4 and 8, stations 9 and 11, respectively) and only in one case were similar values reported for stations located at the opposite sides of the lake (stations 1 and 6). Among three pairs of stations, the differences were rather indistinct, and in the case of the rest of the stations (48 pairs), the differences were very important ($p < 0.01$). The lowest concentration of this element was observed at station 2, located in the northern part of the lake, in a bay sheltered from the influence of the catchment area by a wide belt of rush vegetation (0.082 mg kg^{-1}). Grosheva *et al.* [24] obtained a similar mercury concentration in the unpolluted Baikal Lake. Station 1 was located in the vicinity of station 2 but in the mouth of the Cybina River. The mercury concentration recorded was almost 10 times higher. This provides evidence that mercury compounds flow into the lake with the waters of the Cybina River. As the pollution was spread within the north-east basin of the lake, the mercury content recorded at the stations situated in its middle part (stations 3, 9, 10, and 11) was much lower and displayed a limited spatial variability among these stations (the mercury content was 0.31, 0.20, 0.38, and 0.20 mg kg^{-1}, respectively). A similar level of mercury content was also observed in other lakes located in urbanized area [25, 28]. A very high and similar mercury concentration was recorded in sediments at stations 4 and 8, located near the area where the Mielcuch Stream flows into the lake (2.12 and 2.11 mg kg^{-1}, respectively). This stream carried pollution from the built-up area of the town of Swarz ędz to Swarz ędzkie Lake. The effect of the pollution could also be observed at other stations, located along the water flow, i.e. stations 7 and 6. The concentrations decreased with increasing distance from the Mielcuch Stream discharge (1.17 and 0.69 mg kg^{-1}, respectively). Some pollution, however, had been transported within the lake in the opposite direction, probably due to the action of the wind. Thus, the mercury concentration at station 5 was also high (1.70 mg kg^{-1}). Kishe and Machiwa [29] observed the same diversity in mercury content in Victoria Lake sediments (0.1–2.8 mg kg^{-1}). This pollution also probably affected other stations, located in the middle of the north-east basin (i.e. stations 3, 9, and 10), mentioned above.

In most cases, methylmercury compounds displayed low concentrations in the investigated sediments, and their concentrations ranged from 0.26 to 58.1 µg kg^{-1}, i.e. 1.0–7.4% of the total mercury content. The spatial variability of methylmercury in the lake was less distinct than the

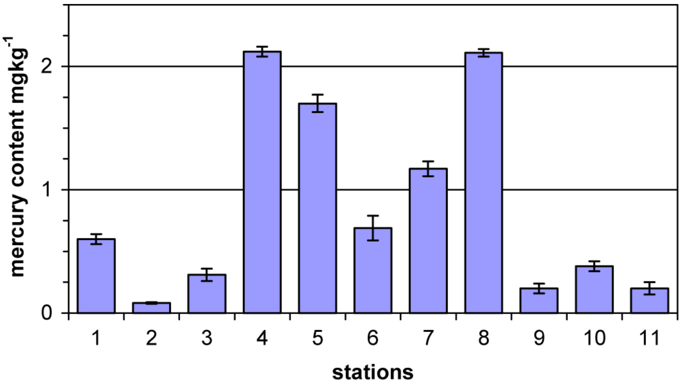

Figure 2. Contents of mercury in the sediments of all sampling stations.

Table 3. ANOVA test for total mercury and methylmercury content in the sediments of Swarzędzkie Lake.

Station	Results for Hg	Results for Me−Hg
1	**6**	3**, 6*, **10**
2	9**, 11*	3*, **5**, **9**, **11**
3	9*, **10**, 11*	2*, **5**, **9**, **10**, **11**
4	**8**	8**
5		**2**, **3**, **9**, **11**
6	**1**	1*
7		
8	**4**	4**
9	2**, 3*, **11**	**2**, **3**, **5**, **10**, **11**
10	**3**	**1**, **3**, 5**, **9**, 11**
11	2*, 3*, **9**	**2**, **3**, **5**, **9**, 10**

Note: Non-significant differences between stations are shown in bold.
$^{*}p < 0.05$; $^{**}p < 0.01$; stations not specified: $p < 0.001$.

total mercury. As many as 12 pairs of stations had similar concentrations, and in two other cases only slight differences were observed (table 3). Nevertheless, a comparison of methylmercury values in 41 cases displayed significant differences. The stations in which the concentrations displayed significant differences were located in the narrow and shallow part of the lake, whereas comparable values were observed in the stations located in the wider and deeper part of the lake. This is probably the result of wind and wave action, leading to resuspension of sediments in the littoral zone and their transfer to other places within the lake. The percentage share of methylmercury was relatively low in the surface layer of bottom sediments (it did not exceed 2%). A larger content was observed only in the deeper layer of sediments (table 2, station 11a). These results are comparable with other literature data [26, 30]. Little is known about background levels for methylmercury compounds in lake sediments. Considering data from recent literature, it seems reasonable to assume a content of $<1\,\mu g\,kg^{-1}$ to be a natural condition [31]. The lowest value reported in this lake was $1.12\,\mu g\,kg^{-1}$ and was recorded only at station 2. The other stations, in particular stations 4 and 8, were strongly influenced by contamination (26.1 and $23.4\,\mu g\,kg^{-1}$, respectively).

The highest mercury content in the vertical profile of bottom sediments from the deepest part of the lake was observed in the 10–20 cm layer (figure 3). This pattern probably originated as a result of the severe contamination of the lake due to untreated sewage from the town

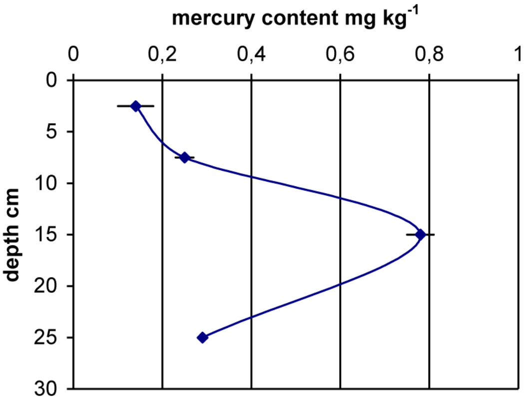

Figure 3. Vertical profile of mercury in the sediment.

of Swarzędz in the 1980s. This is confirmed by the highest organic-matter concentration at the same depth [20] as well as calculation of the mean sedimentation rate in the lake. The estimated thickness of the annual layer of the bottom sediments in 2000–2002 was 0.8 mm [32]. Following the regulation of the sewage system in 1991, the mercury concentration in the newly formed sediments gradually decreased due to the deposition of less contaminated particles. As a result, the maximum content of both mercury and methylmercury was observed in the intermediate layer (table 2), which coincided with the time when the discharge of pollution showed the highest peak. Similar results were previously reported by Marvin *et al.* [33] in Ontario Lake and by Tomiyasu and colleagues [34] in the Yatsushiro Sea.

3.3 *Relationship with other environmental parameters*

The relationships between mercury and methylmercury and other parameters (such as organic matter and total phosphorus content in the sediments, and soluble reactive phosphorus concentrations in the porewaters) were analysed using the canonical analysis. Our results suggested that these relationships were significant, albeit not very strong (table 4). The total redundancy for the data obtained from all stations was only 34.5 (table 4). Removal of data from station 4 improved this result, yielding a value of 46.25. The concentrations of Hg and MeHg for station 4 differed considerably from expected values. They were very high, comparable with the data for station 8, while the total phosphorus and organic matter contents were considerably lower. This provided evidence that mercury was much more permanently accumulated in the bottom sediment than phosphorus compounds. In the 1980s, this station was under the direct influence of pollution transported along Mielcuch Stream. Phosphorus was released from sediments in the mean time as a result of the intensive mineralization of organic matter [21, 35], while mercury formed stable complexes with organic matter. According to Lucotte *et al.* [36], mercury is only weakly susceptible to diagenetic remobilization in lake sediments, being strongly bound to refractory organic matter.

The equations for the left and right set of root 1 are:

$$\mathrm{V1} = -0.413\mathrm{Hg} - 0.668\mathrm{MeHg} \tag{1}$$

$$\mathrm{U1} = -0.611\mathrm{TPs} + 0.173\mathrm{SRPint} - 0.481\mathrm{OM} \tag{2}$$

where Hg, MeHg, TPs, and OM are the contents of total mercury, methylmercury, total phosphorus, and organic matter in the bottom sediments, respectively, and SRPint is the concentration of soluble reactive phosphorus in porewaters.

The relatively high canonical weights for total mercury and methylmercury from the left set of variables (1) and total phosphorus and organic matter content from the right set (2) revealed mutual relationships between these parameters. Only the weight for phosphorus in porewaters was low, indicating that this variable has a weak relationship with other parameters.

Table 4. Results of the canonical analyses of the relationship of mercury and methylmercury with other parameters taking into consideration the data from all stations with the exception of data from station 4.

Resultant parameter	Data from all stations ($n = 55$)	Data without station 4 ($n = 50$)
Canonical R	0.63	0.74
χ^2	25.68	36.86
P	0.00026	0.00000
Total redundancy	34.48	46.25

The concentrations of this species of phosphorus are dependent above all on temperature data, thus influencing the mineralization process [35].

Only a few references have reported on the relationship of mercury and phosphorus content. A correlation of total mercury, phosphorus, and organic matter (measured as organic carbon) concentration has been observed in agricultural soils around Lake Victoria [37]. Similar relationships have also been reported in sediments from the southern Baltic Sea (Gulf of Gdańsk) [38]. However, these relationships are rather indirect and are probably a result of the adsorption and compound formation of both mercury and phosphorus with organic matter.

4. Conclusions

The procedures used for the purpose of mineralization (HNO_3/H_2O_2 and HF) turned out to be equivalent, giving both a high efficiency and accuracy in mercury determination in the lake sediments after microwave digestion. Consequently, the application of HF, which requires special safety precautions, to mineralize mercury in sediments is unnecessary. The applied method of methylmercury compound extraction using benzene is rapid and accurate, as has been shown by comparing the collected sediment samples with CRM river sediment IAEA 405. The level of mercury pollution in the bottom sediments of Swarz ędzkie Lake showed a high variability in different parts of the lake. Values reported at stations within the narrow part of the lake (sheltered from the wind) were statistically different from those reported in the other stations. Values observed at stations located in the wider and deeper part of the lake (exposed to wind and wave action) were comparable. The highest mercury content was observed in the stations near the inflows of the Mielcuch Stream and the Cybina River, which carried pollution from the catchment area to the lake. The mercury content in the deepest part of the lake was not representative of the entire lake. However, the analysis of the vertical profile of sediments from the deepest part of the lake provided information on pollution in recent years. A low percentage share of methylmercury in the total mercury content in all the studied samples from the 10-cm surface layer of sediments (not exceeding 2%) suggests that mercury transformation in the studied water is negligible. The distinct relationship of both total mercury and methylmercury with organic matter content confirms other reports, that these variables are strongly mutually dependent. However, the similar relationship found for phosphorus is more likely to be related to the connections of this element with organic matter, not with mercury and methylmercury.

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References

[1] D.W. Boening. Ecological effects, transport, and fate of mercury: a general review. *Chemosphere*, **40**, 1335 (2000).

[2] J.M. Ombaba. Total mercury determination in biological and environmental standard samples by gold amalgamation followed by cold vapor atomic absorption spectrometry. *Microchem. J.*, **53**, 195 (1996).

[3] U. Tinggi, G. Craven. Determination of total mercury in biological materials by cold vapour atomic absorption spectrometry after microwave digestion. *Microchem. J.*, **54**, 168 (1996).

[4] A. Abu-Samara, J.S. Morris, S.R. Koirtyohann. Ashing of some biological samples in a microwave oven. *Anal. Chem.*, **47**, 1475 (1975).

[5] D.W. Mincey, R.C. Williams, J.J. Giglio, G.A. Graves, A.J. Pacella. Temperature controlled microwave oven digestion system. *Anal. Chim. Acta*, **264**, 97 (1992).

[6] G. Topping, J.M. Pirie. Determination of inorganic mercury in natural waters. *Anal. Chim. Acta*, **62**, 200 (1972).

[7] E.J. Zillioux, D.B. Worcella, J.M. Benoit. Mercury cycling and effects in freshwater wetland ecosystems. *Environ. Toxicol. Chem.*, 12, 2245 (1993).

[8] J.E. Sanchez Uria, A. Sanz-Medel. Inorganic and methylmercury speciation in environmental samples. *Talanta*, **47**, 509 (1998).

[9] S.J. Palmer, B.J. Presley. Mercury bioaccumulation by shrimp (*Penaeus aztecus*) transplanted to Lavaca Bay, Texas. *Mar. Pollut. Bull.*, **26**, 564 (1993).

[10] R.P. Mason, J.R. Reinfelder, F.M.M. Morel. Bioaccumulation of mercury and methylmercury. *Water Air Soil Pollut.*, **80**, 915 (1995).

[11] USEPA. *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories: Volume II*, *Risk Assessment and Fish Consumption Limits*, EPA 823-B-97-009 (1997b).

[12] M. Harada. Minamata disease-methylmercury poisoning in Japan caused by environmental pollution. *Crit. Rev. Toxicol.*, **25**, 1 (1995).

[13] Q. Wang, D. Kim, D.D. Dionysiou, G.A. Sorial, D. Timberlake. Sources and remediation for mercury contamination in aquatic systems – a literature review. *Environ. Pollut.*, **131**, 323 (2004).

[14] D. Baralkiewicz, H. Gramowska, R. Goldyn. Distribution of total mercury and methylmercury in water, sediment and fish from Swarzędzkie Lake. *Chem. Ecol.*, **22**, 59 (2006).

[15] R. Gołdyn, J. Grabia. *Program ochrony wód rzeki Cybiny*, Urzad Miasta Poznania, Wydział Ochrony Środowiska, Poznań, Poland (1998).

[16] H. Szyper, R. Gołdyn, W. Romanowicz. Lake Swarzędzkie and its influence upon the water quality of the River Cybina. *Pozn. Tow. Przyj. Nauk, Pr. Kom. Biol.*, **74**, 7 (1994).

[17] K. Kowalczewska-Madura. Mass balance calculations of nitrogen and phosphorus for Swarzędzkie Lake. *Limnol. Rev.*, **3**, 113 (2003).

[18] J. Jańczak (Ed.). *Atlas jezior Polski.* Inst. Meteorol. i Gosp. Wodnej, Wyd. Nauk., Bogucki, Poznań, Poland (1996).

[19] J.R. Meriwether, W. Sheu, C. Hardaway, J.N. Beck. Coring sampler for chemical analyses of soft sediments. *Microchem. J.*, **53**, 201 (1996).

[20] K. Kowalczewska-Madura. Organic matter in the bottom sediments of the Swarz ędzkie Lake. In Jeziora i sztuczne zbiorniki wodne – funkcjonowanie, rewitalizacja i ochrona [Lakes and man-made reservoirs – functioning, revitalisation and protection], A.T. Jankowski, M. Rzętała (Eds), pp. 125–131, Uniwersytet Śląski, Polskie Towarzystwo Limnologiczne [Silesian University, Polish Limnological Society], Sosnowiec, Poland (2004).

[21] K. Kowalczewska-Madura, R. Gołdyn. Phosphorus content of bottom sediments in Swarzędzkie Lake. *Verh. Internat. Verein. Limnol.*, **29**, 1063 (2005).

[22] K. Kowalczewska-Madura, B. Jeszke, S. Furmanek, R. Gołdyn. Phosphorus concentrations in the porewaters of bottom sediments of the Swarzędzkie Lake (in press).

[23] A.A. Mohd, J.R. Dean, W.R. Tomlinson. Factorial design approach to microwave dissolution. *Analyst*, **117**, 1743 (1992).

[24] E.I. Grosheva, G.N. Voronskaya, M.V. Pastukhove. Trace element bioavailability in Lake Baikal. *Aquat. Ecosyst. Health Manage.*, **3**, 229 (2000).

[25] A. Szymanowska, A. Samecka-Cymerman, A.J. Kempers. Heavy metals in three lakes in West Poland. *Ecotoxicol. Environ. Saf.*, **43**, 21 (1999).

[26] D.B. Huggett, J.A. Steevens, J.C. Allgood, C.B. Lutken, C.A. Grace, W.H. Benson. Mercury in sediment and fish from North Mississippi Lakes. *Chemosphere*, **42**, 923 (2001).

[27] K. Johansson, A. Andersson, T. Andersson. Regional accumulation pattern of heavy metals in lake sediments and forest soils in Sweden. *Sci. Total Environ.*, **160/161**, 373 (1995).

[28] T. Ristola, J. Pellinen, P.L. Van Hoof, M. Leppanen, J. Kukkonen. Characterisation of Ladoga sediments. II. Toxic chemicals. *Chemosphere*, **32**, 1179 (1996).

[29] M.A. Kishe, J.F. Machiwa. Distribution of heavy metals in sediments of Mwanza Gulf of lake Victoria, Tanzania. *Environ. Int.*, **28**, 619 (2003).

[30] K. Kannan, R.G. Smith, R.F. Lee, H.L. Windom, P.T. Heitmuller, J.M. Macauley, J.K. Summers. Distribution of total mercury and methyl mercury in water, sediment and fish from South Florida estuaries. *Arch. Environ. Contam. Toxicol.*, **34**, 109 (1998).

[31] C.C. Gilmour, E.A. Henry, R. Mitchell. Sulphate stimulation of mercury methylation in freshwater sediments. *Environ. Sci. Technol.*, **26**, 2281 (1992).

[32] K. Kowalczewska-Madura. Influence of changes of nutrients loading on structure and functioning of ecosystem of the Swarzędzkie lake. PhD thesis, Adam Mickiewicz University, Poznań 324, Poland (in Polish).

[33] Ch. Marvin, S. Painter, R. Rossmann. Spatial and temporal patterns in mercury contamination in sediments of the Laurentian Great Lakes. *Environ. Res.*, **95**, 351 (2004).

[34] T. Tomiyasu, A. Nagano, N. Yonehara, H. Sakamoto, Rifardi, K. Oki, H. Akagi. Mercury contamination in the Yatsushiro Sea, south-western Japan: spatial variations of mercury in sediment. *Sci. Total Environ.*, **257**, 121 (2000).

[35] K. Kowalczewska-Madura, R. Gołdyn. Internal loading of phosphorus from the sediments of the Swarzędzkie Lake (in press).

[36] M. Lucotte, A. Mucci, C. Hillaire-Marcel, P. Pichet, A. Grondin. Anthropogenic mercury enrichment in remote lakes of Northern Quebec (Canada). *Water Air Soil Pollut.*, **80**, 467 (1995).

[37] L.M. Campbell, R.E. Hecky, R. Muggide, D.G. Dixon, P.S. Ramalal. Variation and distribution of total mercury in water, sediment and soil from northern Lake Victoria, East Africa. *Biogeochemistry*, **65**, 195 (2003).

[38] S. Uścinowicz, J. Zachowicz, K. Sokołowski. The potential impact of a sewage discharge through the 'Gdańsk-Wschód' sewage-treatment plant collector on the chemical composition of the gulf Gdańsk sediments. *Oceanol. Stud.*, **29**, 4, 67 (2000).