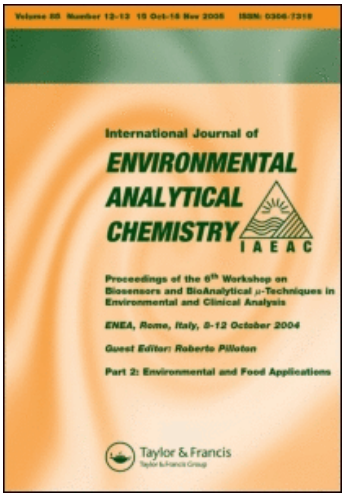

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Speciation of Mercury in two Dimictic Lakes of North-East Germany During a Period of 600 Days

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SPECIATION OF MERCURY IN TWO DIMICTIC LAKES OF NORTH-EAST GERMANY DURING A PERIOD OF 600 DAYS

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The speciation of mercury was studied with respect to (a) dissolved atomic mercury, (b) dissolved ionic mercury, and (c) total mercury in two dimictic lakes of North-East Germany. Differential pulse anodic stripping voltammetry was used for the analyses. The results show that biological processes dominate the speciation. They are responsible for high concentrations of atomic mercury and also organomercury compounds. The oxidation of atomic mercury under environmental conditions in lake water is very slow, so that the equilibrium between Hg^{0}_{aq} and Hg^{2+}_{aq} can only be established during long periods of decreased bioactivity, as in wintertime. The sedimentation of the detritus during summer leads to a very pronounced decrease of the overall mercury concentration in the entire water body of the lakes.

Keywords: Mercury; mercury speciation; freshwater; differential pulse anodic stripping voltammetry

INTRODUCTION

The environmental cycles of mercury are complex and involve chemical, biological and physical processes.[1,2] Speciation analysis of mercury is of utmost importance for the elucidation of the fate of mercury in the environment. During the last years many electrochemical methods have been published in which the determination of ionic mercury in aquatic solutions is described.[3–6] The present study is an application of a novel electrochemical method for mercury speciation. This method is based on the anodic stripping voltammetry of mercury in a thiocyanate electrolyte with the application of a glassy carbon electrode.[7,8]

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TABLE I Characteristic properties of the investigated lakes *Haussee* and *Krüselin*.

	Lake Haussee	*Lake Krüselin*
Area [m^2]	1 300 000	657 500
Volume [m^3]	8 152 565	4 408 850
maximum depth [m]	12	18
above sea level [m]	84.5	74.5

The method allows a speciation of mercury into: (i) dissolved atomic mercury (DAM), (ii) dissolved ionic mercury (DIM) and (iii) total mercury concentration (TM). In this study no attempt was made to specify the different organomercury compounds.

The *Feldberg* Lake Territory Reserve in North-East Germany was selected for this study. This area has a number of interconnected lakes which are isolated from the surrounding territory and which have only one common drain to the river *Havel* (see Figure 1). The entire territory and its surroundings has no industry and the overall pollution is at a very low level. We have chosen two lakes, lake *Haussee* and lake *Krüselin*, for a study of mercury speciation. In the past, agriculture was the main contributor to pollution (esp. nutrients like phosphate and nitrate). The small town of *Feldberg* had a share in the pollution of lake *Haussee* as, until the early 70's, the sewage water of this town was released into the lake. This lake is presently polytrophic while lake *Krüselin* is mesotrophic. The latter lake is situated at a rare geological site: It has no surface connection with any other lake of the *Feldberg* Lake Territory Reserve. Its surface level is situated approximately 9.5 to 9.75 m below that of all other lakes. The only water influx is a subterranean flow from the near lake *Dreetssee* through gravel, clay and loam over a distance of 250–300 m. The characteristic properties of the two lakes are summarized in Table I.

EXPERIMENTAL

Reagents and Equipment

For the preparation of standard solutions, ion-exchanged bidistilled water and a certified AAS mercury standard solution of 1 g/l (Merck/Germany) were used. NaSCN (pro analysi Merck/Germany) and HNO_3 (suprapur Merck/Germany) were of the highest available purity. All solutions, with the exception of samples, were stored in glass vessels. For all diluted mercury standard solutions, i.e. for solutions below 10^{-9} M, the same vessels have been always used. All glass vessels were cleaned by leaching them with 30% HNO_3 followed by thoroughly washing them with bidistilled water. The samples were stored in 250 ml vessels

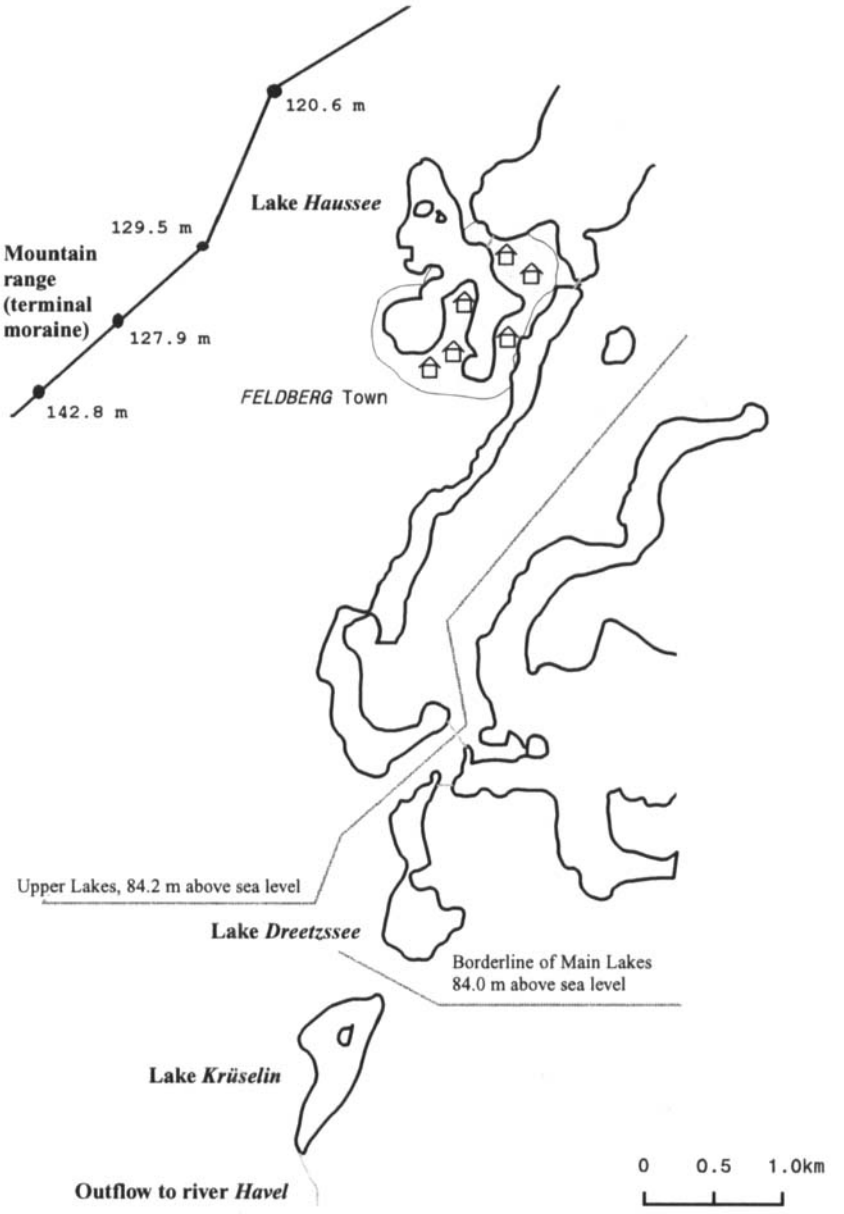

FIGURE 1 Map of *Feldberg* Lake Territory Reserve.

made of Nalgene (polyproylene). All DPASV experiments were carried out in electrolyte solutions containing 0.25M NaSCN. To remove oxygen we used high-purity nitrogen (Messer Griesheim/Germany) with a mercury content below 4 ng m^{-3}.

The DPASV measurements were performed with an AUTOLAB (ECO-Chemie, Netherlands) in conjunction with an electrode stand VA 663 (Metrohm, Switzerland) and an IBM compatible computer 386SX16 PC with 1 MB RAM. The glassy carbon electrodes (GCE) used were either from VEB Elektrokohle Berlin (former GDR) or Tokay (Japan). The glassy carbon rods with diameters of 5 and 3 mm were pressed and sealed into Teflon. The auxiliary electrode (Metrohm, Switzerland) was a glassy carbon rod and the reference electrode (Metrohm, Switzerland) an Ag/AgCl electrode with 3.0 M KCl (E = 0.208 V vs. SHE).

Sampling and Sample Handling

Sampling was made from a rowing boat at the deepest points of the lakes. A sonar (Bauer/Germany) was used to spot the same position each time. Before the water sampling was started the depth profiles of the temperature and of the oxygen concentration were measured with an oxymeter Oxi 196 (WTW/Germany). After that three or four samples were collected from different depths. Samples were taken within the epilimnion (i.e. in a depth of 0.25 m), the metalimnion and the hypolimnion (near to the bottom). The used bailer was homemade from a acrylic glas tube (Grünberg/Germany). The bailer samples a volume of 3.0 L. One liter of each sample was stored in a Nalgene (polypropylene) vessel. Since the degree of pollution in these two lakes considerably differs, the same vessels were always used for the same lake.

The determination of visibility, i.e. the visual range from the surface down into the water, was carried out by letting down a white porcelain disc (diameter: 28 cm) fixed on a tape measure.

Sample Preparation

After the transfer to the laboratory (4–5 hours), the mercury speciation analysis was performed within 24 hours. Before the analysis, the samples were divided into two parts. One part of the sample was filtrated by use of a filtration system SM 1753 (Satorius/Germany) with two filters having pore sizes of 8 μm and 0.45 μm (Satorius/Germany). In the filtrated part, the amount of free dissolved ionic mercury was determined.

TABLE II ASV deposition time as a function of mercury concentrations.

Concentration range	*deposition time*
$5 \cdot 10^{-14}$ to 10^{-12} mol l^{-1}	2400 s
10^{-12} to 10^{-9} mol l^{-1}	1800 s
10^{-9} to 10^{-7} mol l^{-1}	1200 s

In the unfiltrated sample, the total amount of mercury was determined after an UV digestion. The UV digestion was carried out using a 250 W UV lamp (Heraeus, Germany) in the following way: 10 ml of the sample were filled into a quartz test tube and 0.25 ml concentrated HNO_3 were added to the samples from lake *Krüselin* and 0.5 ml concentrated HNO_3 to the samples from lake *Haussee*. One hour was found to be sufficient for the UV irradiation of the samples from lake *Krüselin* and two hours for samples from lake *Haussee*.

The dissolved atomic mercury (DAM) was purged out of the sample with high-purity nitrogen. The DAM is carried by the nitrogen gas stream to a gold wool trap and there it is absorbed. Then the absorbed mercury can be determined by DPASV after anodic dissolution of the trapped mercury in an electrolyte solution.[7,8]

Additionally, the pH of every sample and also the biological oxygen demand (BOD-5) were measured.

Determination of Mercury by DPASV

Ionic mercury concentrations in solutions were determined by differential pulse anodic stripping voltammetry (DPASV), using a 0.25 M NaSCN electrolyte at a pH value between 3.6 and 3.8. The adjustment of the pH is very important. A lower pH value leads to a partial decomposition of the thiocyanate electrolyte and finally to a complete loss of detectable ionic mercury, probably due to the formation of HgS. The thiocyanate ions form complexes with ionic mercury. This complexation allows a reproducible determination of mercury of very low concentrations down to 5×10^{-14} M Hg^{2+}.[7,8] However, a very long deposition time is necessary. The usual deposition times corresponding to the mercury concentrations are given in Table II. The parameters of the DPASV method are summarized in Table III.

RESULTS

The present results were obtained from April 1995 to August 1996. In this period, weather conditions were remarkably different from each other and also from the usual average. Spring and summer 1995 (April to August) were ex-

TABLE III Parameters for the DPASV method:

Parameter	value
purging time [s]	300
deposition potential [mV]	−1500
deposition time [s]	see Table II
equilibration time [s]	5
modulation time [s]	0.07
interval time [s]	0.5
step potential [mV]	3.2
modulation amplitude [mV]	35
initial potential [mV]	−650
final potential	100

tremely hot and dry. The water temperatures of all lakes exceeded the normal annual average. The winter of 1995/96 was extraordinary cold and a compact ice layer of 45–65 cm thickness covered all lakes in the *Feldberg* Lake Territory Reserve for 8–10 weeks during December to February. The spring 1996 was very warm during two to three weeks, which was followed by a long lasting cold period with plenty of rainfall.

The two investigated lakes are very different as can be seen from oxygen and temperature profiles (see Figures 2 and 3). Lake *Haussee* has periodically a thick layer with an absence of oxygen (see Figure 2**A**). During this period the concentration of H_2S was in the range of 3 to 8 mg/l in the summer of 1995 and up to 14 mg/l in the summer of 1996. The temperature profiles (see Figure 3) show that almost no spring turn-over took place in 1996 as a result of fast stratification. The spring weather in 1996 was too warm for allowing the spring turn-over to occur. This means that the last oxygen input into the deep water body of the lakes *Haussee* and *Krüselin* took place in the autumn of 1995. Although the bioactivity in 1996 was lower than in 1995, the higher concentration of H_2S in summer 1996 can be explained by the absence of the spring turn-over period. The anoxic layer of the *Haussee* ranged up to a depth of 4–4.5 m during the summers of 1995 and 1996 (see Figure 2**A**). The amount of dissolved oxygen in lake *Krüselin* is different from that of lake *Haussee* (see Figure 2**B**). In lake *Krüselin*, the oxygen deficit layer is confined to the very bottom and a H_2S concentration was measured only once in August 1996 (2 mg/l).

Figure 4 shows the visibility and the biological oxygen demand (BOD-5) for lake *Haussee* and lake *Krüselin*. The Figure proves that the bioactivity, which limits the visibility, is much higher in lake *Haussee* than in lake *Krüselin*. Another indication of that is the oxygen supersaturation in different depths. In lake *Haussee* the supersaturation of oxygen was confined to a surface layer, the thickness of which was almost identic with the measured visibility. The mesotrophic lake *Krüselin* has an oxygen supersaturation in a depth between 2.5 and 6 m.

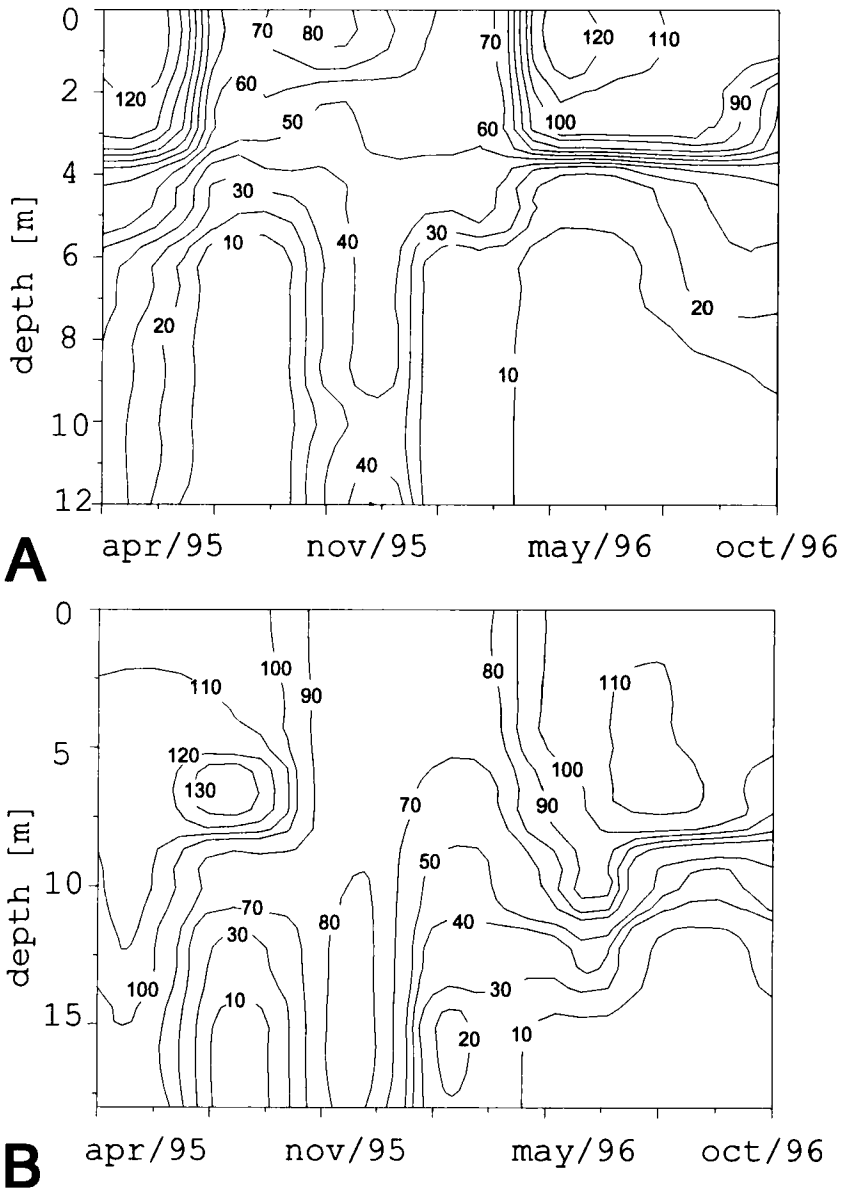

FIGURE 2 The profiles of oxygen saturation in percent; **A** for lake *Haussee* and **B** for lake *Krüselin*.

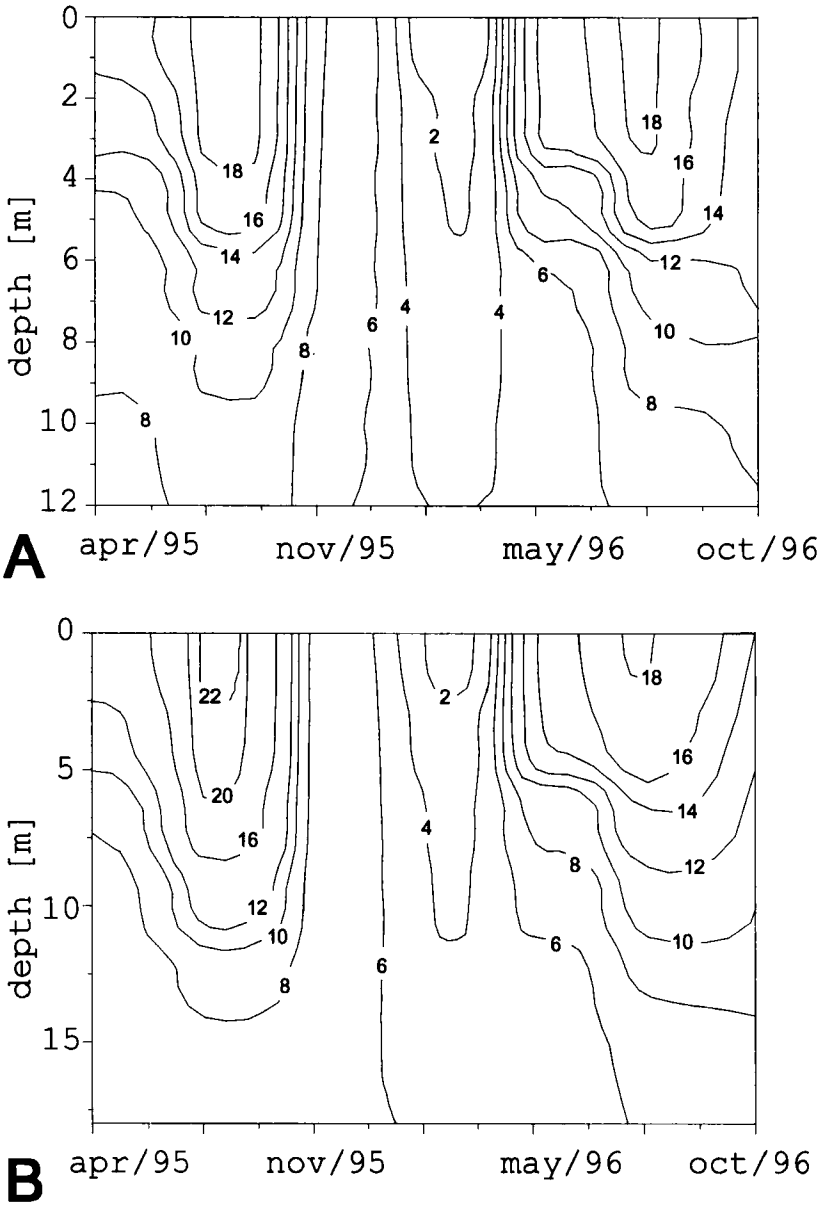

FIGURE 3 Temperature profiles; **A** for lake *Haussee* and **B** for lake *Krüselin*. The temperature is given in [°C].

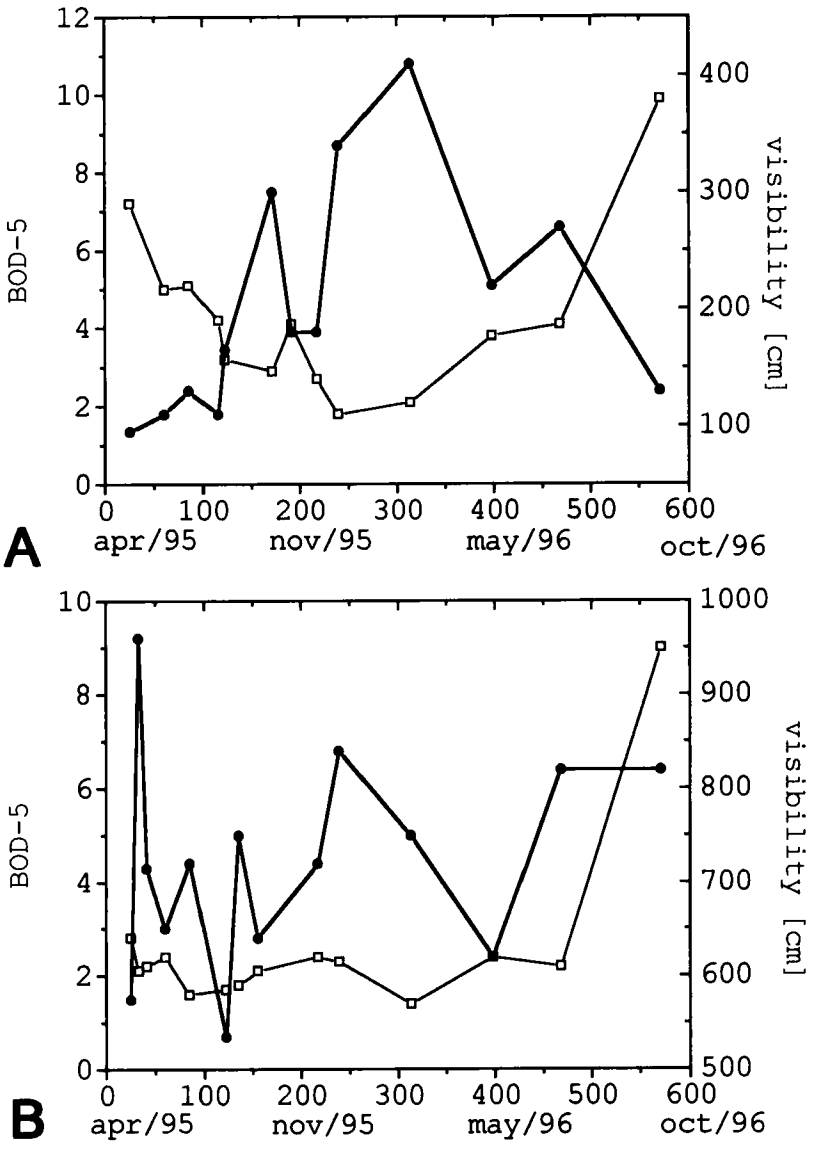

FIGURE 4 Limit of visibility (●) and biological oxygen demand (□) (BOD-5); **A** for lake *Haussee* and **B** for lake *Krüselin*.

Figures 2 to 4 illustrate the differences between the lakes with respect to their content of oxygen, nutrients and their bioactivity.

As the two studied lakes are so different, the experimental results of mercury speciation will be discussed separately and only finally they will be compared. The concentration of mercury differs in the two lakes by a factor of 10^2–10^3. Figures 5 and 6 show the results of mercury speciation, oxygen content and temperature for lake *Haussee*. Part **A** gives the results for the surface layer (epilimnion), **B** gives the results for the interfacial layer (metalimnion) or, in wintertime, for a corresponding depth, and **C** the results for the hypolimnion.

In April 1995, the concentrations of TM in lake *Haussee* were found to be very similar in all depths from the surface down to the bottom. During the summer, the sedimentation processes started as a result of bioactivity. This follows from a decrease of TM, a decrease of visibility and from high BOD-5 values. In July and August, the reduced oxygen content led to decreasing BOD-5 values and increasing visibility. Decreasing TM values in the upper water layers correspond to increasing TM values in the bottom region. A periodically decreasing and increasing of bioactivity is well known to occur in lakes during the summer.[9] From lake to lake the length of these periods is different, because of varying contents of nutrients. The observed decreasing bioactivity goes parallel to a decreasing oxygen content and is not due to deficient nutrients (see Table IV). The resulting decrease in bioactivity again led to an increase of the oxygen content. A growing bioactivity before the autumn turn-over starts may be the reason for the dramatical decrease of TM in the upper water levels, because the biota take up all the mercury. A diminishing solar irradiation and a decreasing temperature will cause the death of the biota. This induces an increase of TM in the bottom region. The bioactivity ceases with the beginning autumn turn-over. This can be deduced from a sudden increase of visibility, having a maximum in February with 400 cm, and also from an increasing content of DIM throughout all layers of the water body. The same processes were observed in summer 1996 but not to the same dramatic extent.

Figure 7 shows the results of mercury speciation and Figure 8 the oxygen and temperature profiles of lake *Krüs*. During the stagnation period in summer 1995, the drop in mercury concentration in lake *Krüselin* was much more pronounced than in lake *Haussee*. In May 1995, a very high mercury input was measured. This event is detectable throughout the whole water body. The mercury input could be detected in the bottom layer with a delay of several weeks. The bioactivity, represented by BOD-5-values, increased at the same time (see Figure 4**B**). The TM concentration decreased very fast to a concentration level no longer detectable with our technique. The mercury decrease can be explained by a sedimentation of dead biota. In the middle of August 1995, the first mercury

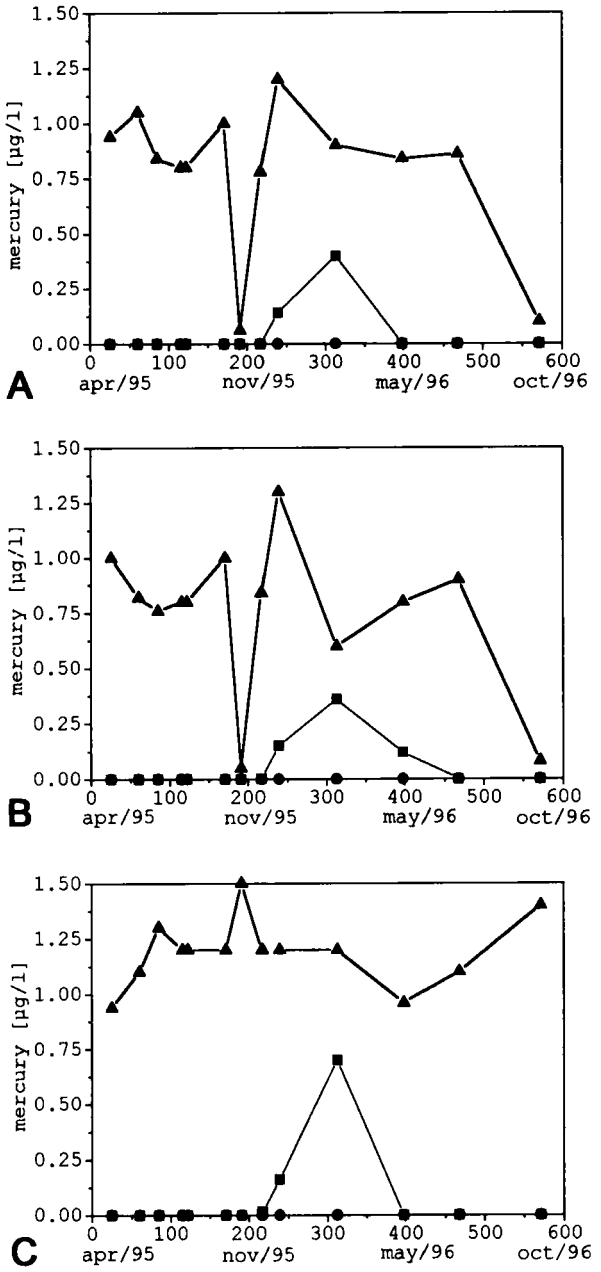

FIGURE 5 Results of the mercury speciation in lake *Haussee* during the project time; **A** epilimnion, **B** metalimnion and **C** hypolimnion. (▲ total mercury, ■ ionic mercury and ● dissolved atomic mercury).

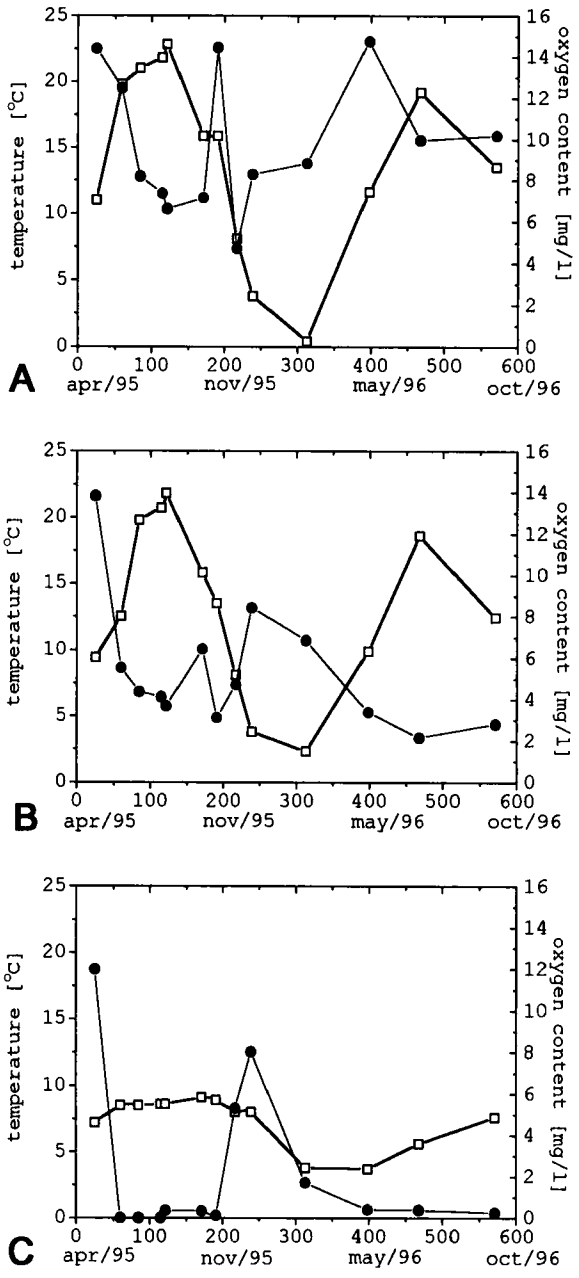

FIGURE 6 The oxygen content and the temperature of lake *Haussee* during the project time. **A** epilimnion, **B** metalimnion and **C** hypolimnion. (□ temperature [°C] and ● oxygen content [mg/l]).

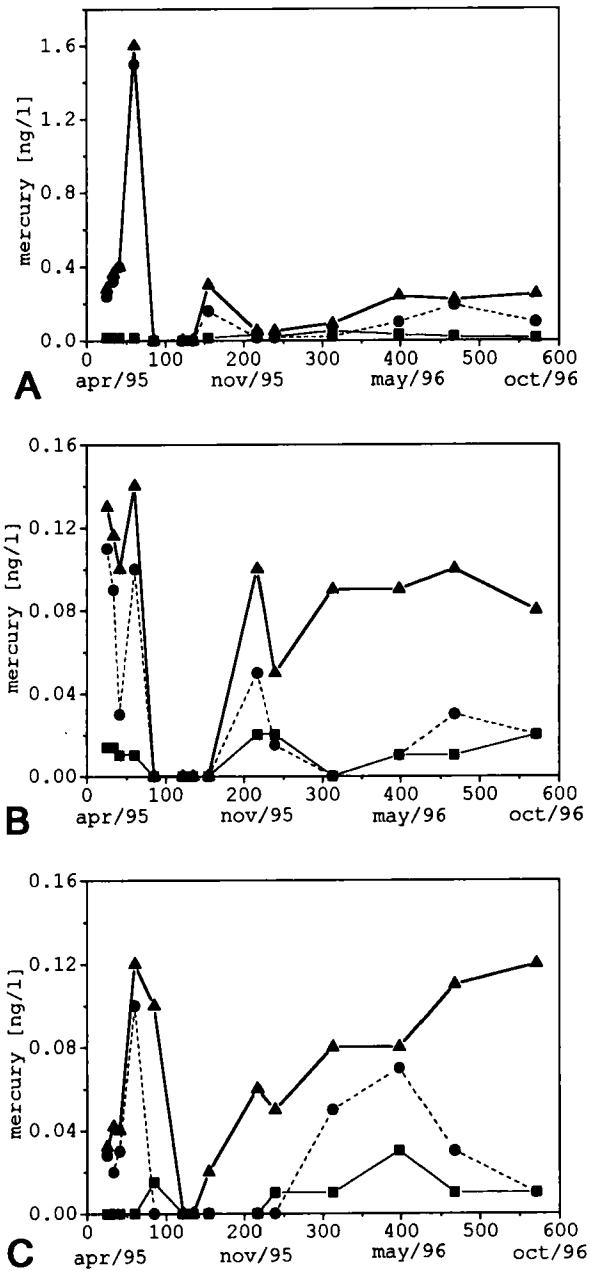

FIGURE 7 Results of the mercury speciation in lake *Krüselin* during the project time; **A** epilimnion, **B** metalimnion and **C** hypolimnion. (▲ total mercury, ■ ionic mercury and ● dissolved atomic mercury).

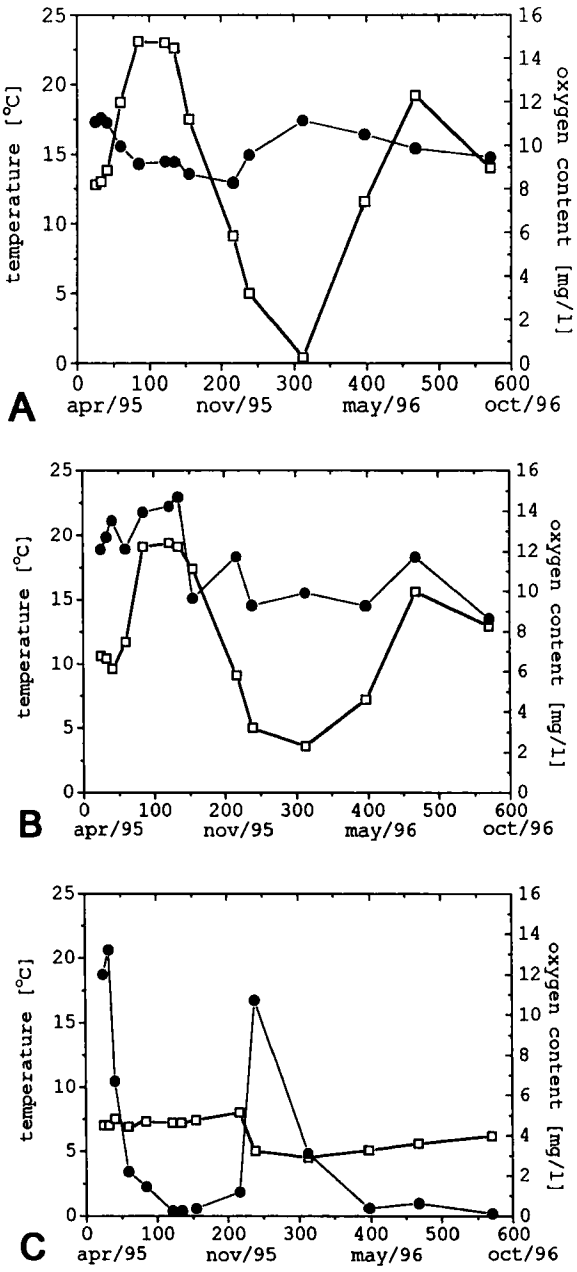

FIGURE 8 The oxygen content and the temperature of lake *Krüselin* during the project time. **A** epilimnion, **B** metalimnion and **C** hypolimnion. (□ temperature [°C] and ● oxygen content [mg/l]).

TABLE IV Contents of nutrients in lake *Haussee* and lake *Krüselin* in [mg/l]: (*) after the spring circulation, (#) in the summer stagnation period and (+) before the autumn circulation.

	lake Haussee			*lake Krüselin*		
	spring (*)	*summer (#)*	*autumn (+)*	*spring (*)*	*summer (#)*	*autumn (+)*
NO_3^-	0.3–0.7	0.5–1.0	0.1–0.9	0.1–0.5	0.1–0.3	0.1–1.2
NH_4^+	0.03–0.3	0.08–1.5	0.1–10.0	0.07–0.1	0.08–0.3	0.1–1.1
PO_4^{3-}	0.08–0.5	0.2–1.0	0.3–5.0	0	0–0.09	0.06–0.1

in the bottom layer was detected after this drastic decrease. During this time the lowest oxygen concentration in the bottom region of this lake was measured and found to be 3% of the saturation. The starting autumn turn-over distributed the mercury throughout the whole water body, as it also occurred in lake *Haussee*. No increase of bioactivity was observed in lake *Krüselin* at the end of the summer as there was a deficit of nutrients (see Table IV). Most probably, the biota had already consumed practically all nutrients during May, June and July. Similar processes were observed in summer 1996 but not to the same dramatic extent.

DISCUSSION

Lake *Krüselin*

In lake *Krüselin*, the concentrations of DIM, DAM and TM always were of the same order of magnitude, whereas in lake *Haussee* the concentration of TM was two or three orders of magnitude higher than the concentrations of DIM and DAM. In lake *Krüselin*, almost always 30–50% of the total mercury were present as atomic mercury.

Figure 9A depicts a plot of the redox potential of the lake water versus the ratio of atomic mercury to mercury(II). The redox potential has not been a directly measured value but it is the potential of the oxygen electrode, calculated from the measured oxygen concentrations and pH values according to the following equations:

$$\frac{1}{4}\,O_2 + H^+ + e^- \rightarrow \frac{1}{2}\,H_2O \tag{1}$$

$$p\epsilon = p\epsilon^{o}_{O_2} + \log[O_2]^{\frac{1}{4}} - pH \tag{2}$$

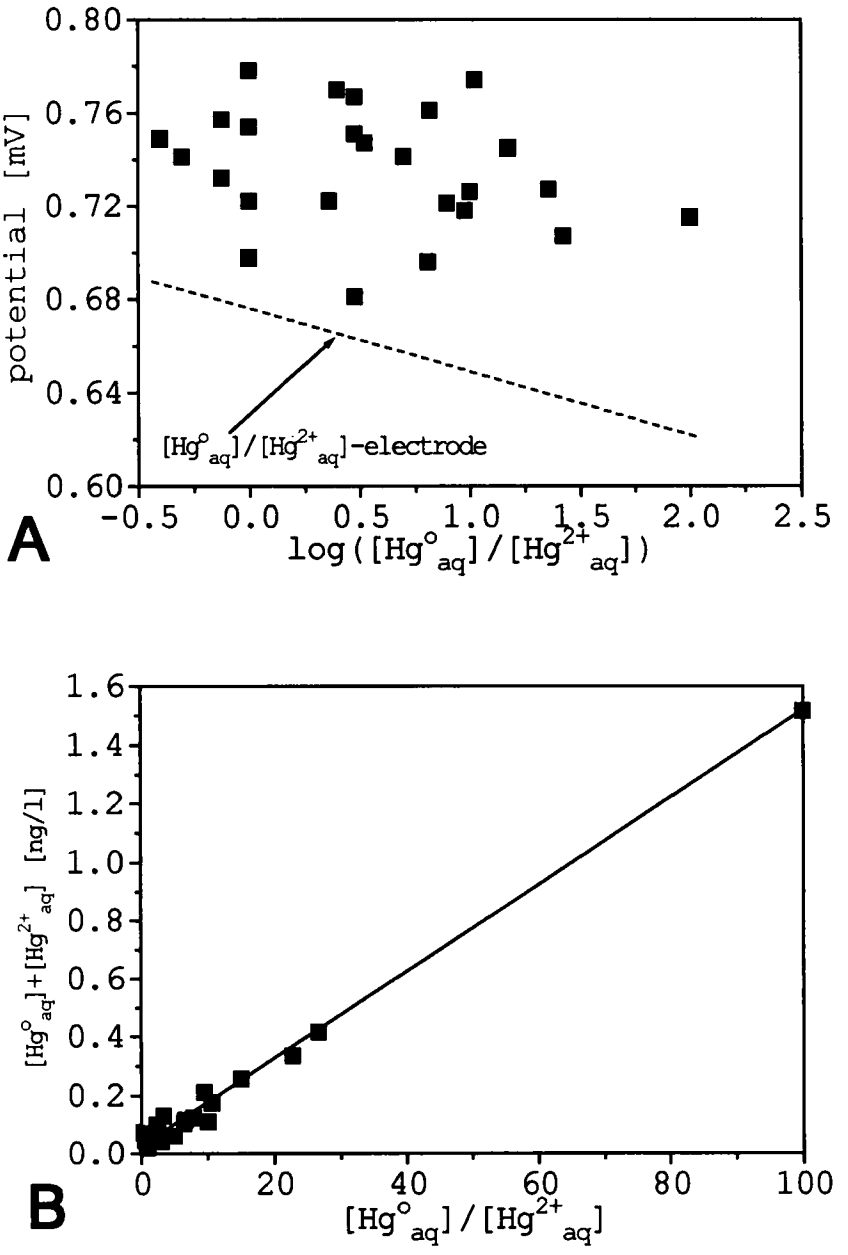

FIGURE 9 **A**: Lake *Krüselin*: The logarithm of the ratio $[Hg^0_{aq}]/[Hg^{2+}_{aq}]$ versus the redox potential of the water sample, as calculated from the O_2 concentration and pH. The dashed line shows the dependence of log $[Hg^0_{aq}]/[Hg^{2+}_{aq}]$ versus the potential for the Hg^0_{aq}/Hg^{2+}_{aq} electrode calculated according to;[10] ■ sample points. **B**: Correlation of the sum $[Hg^0_{aq}]$ and $[Hg^{2+}_{aq}]$ of versus the ratio of $[Hg^0_{aq}]/[Hg^{2+}_{aq}]$.

$$p\epsilon = E\frac{F}{2.3RT} \tag{3}$$

The redox potential of the water was not measured with a platinum electrode as it is well known that such experimentally obtained values are usually mixed potentials caused by different redox reactions. It is more reliable to characterize the redox state of a water by calculating a "theoretical redox potential" according to the O_2 partial pressure and the pH. Figure 9**A** shows that there is no dependence between the oxidizing properties of the water and the mercury(0)/mercury(II) speciation. Figure 9**A** also includes the Nernst plot for the mercury(0)/mercury(II) electrode which has been calculated according to:[10]

$$E = E^{o}_{Hg_{(aq)}}/Hg^{2+}o + \frac{RT}{zF}\ln\frac{[Hg^{o}_{(aq)}]}{[Hg^{2+}]} \tag{4}$$

From the comparison of these two plots, it follows that the lake contained a far too high concentration of atomic mercury compared to the redox potential of the water. This is even more pronounced when one would take into account a possible complex formation of mercury(II), which would shift the formal potential of the system to even more negative values. A complex formation of mercury(0) is very unlikely and has not been described yet. Figure 9**B** shows that there is a strong correlation between the ratio mercury(0)/mercury(II) and the sum of these species. This would also hold if one neglected the one point at the far right of the picture. If the mercury(0)/mercury(II) system had been in equilibrium, the mercury(0)/mercury(II) ratio should not depend on the sum of these species, provided that the redox conditions in the water do not change too much. Thus Figure 9**B** indicates that kinetics plays a decisive role in this system. Figure 10 schematically depicts the situation in the lake. The interpretation of the experimental results is as follows: There is a certain input of ionic mercury, which is incorporated into the biota, where a metabolization to atomic mercury occurs. The atomic mercury is released, probably by diffusion through the cell membranes. In the lake water, the atomic mercury is very slowly oxidized so that the thermodynamic equilibrium is not established. The rate of mercury(II) intake by the biota k_{in} is most probably proportional to the mercury(II) concentration in the water: $k_{in} \approx [Hg^{2+}{}_{aq}]$. The rate of metabolization (k_2) may also be proportional to the mercury(II) concentration inside the cells. This will lead to an increase of the mercury(0) concentration with increasing input of mercury(II):

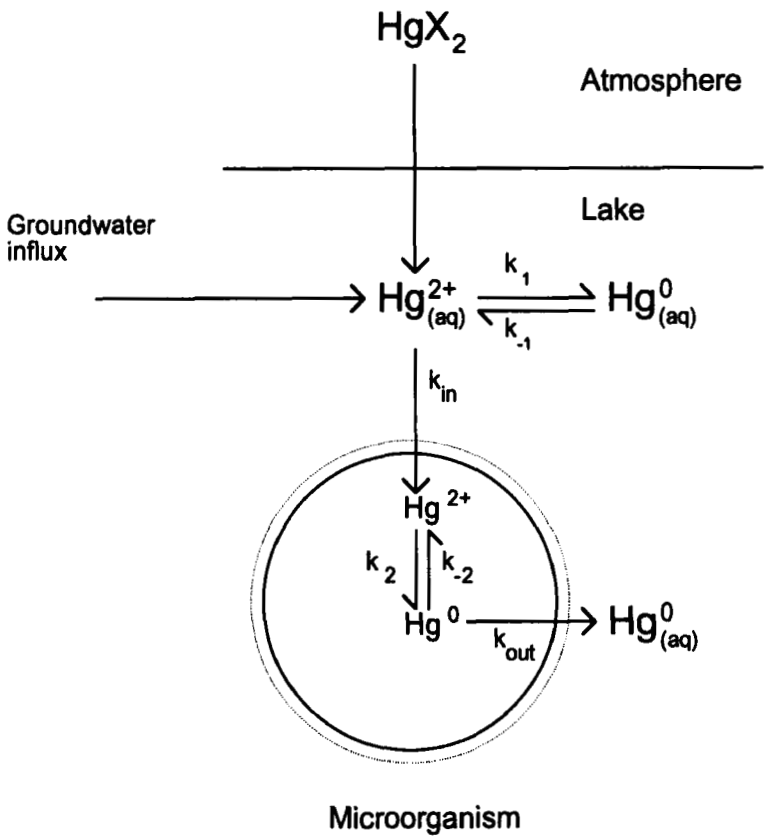

FIGURE 10 Simple scheme of the interconversion of mercury(0) and mercury(II) in lake water.

$$[Hg^0_{aq}] \approx [Hg^{2+}_{aq}]k_{in}\frac{k_2}{k_{-2}}k_{out} \tag{5}$$

Because of the very small rate of the oxidation of atomic mercury in the lake water (k_{-1}), the atomic mercury stays in the lake and can only be released to the atmosphere by partition. This interpretation well agrees with published data.[11,12] In essence, the biota are an irreversible pump which transfers ionic mercury into atomic. The reduction of ionic mercury(II) can occur inside the cells as a result of a shifted redox potential and catalyzed by enzyme systems.

Lake *Haussee*

In lake *Haussee*, the usually measured amounts of TM were between 0.8 and 1.2 μg/l. The DAM fraction was found to be lower than 10^{-4}% of the TM amount. The dissolved inorganic mercury fraction is mostly of the same order

of magnitude as DAM. Thus there is a strong domination of mercury in all other possible forms, i.e. organic mercury compounds and mercury adsorbed at colloid particles or itself in colloidal form. During the autumn turn-over and during the wintertime the DIM concentration can be 40–60% of the TM.

Figure 11**A** presents the dependence of the redox potential of the lake water on the ratio mercury(0)/mercury(II). The redox potential was again calculated from the measured oxygen concentration and the pH value. Additionally, the theoretical Nernst dependence is given for the logarithm of the ratio mercury(0)/mercury(II) on the potential. From the experimental data, it would be rather difficult to conclude that the redox potential of the water has an effect on the mercury(0)/mercury(II) speciation. Figure 11**B** shows a plot of the sum of mercury(0) and mercury(II) versus the ratio mercury(0)/mercury(II). The interesting result is that the experimental data for the winter season are all situated on one vertical line whereas the experimental data of the summer season are situated on a horizontal line. This means that during the winter season, the ratio mercury(0)/mercury(II) is almost constant for varying concentrations of mercury(0) and mercury(II). This can be explained with an almost equilibrium situation which has been established in the absence of dominating biological processes and in a lake with a well homogenized water body. On the contrary, in summer, there is a strongly dominating biology which prevents any establishment of a thermodynamic equilibrium with respect to mercury speciation. This is further prevented by a pronounced stratification of the entire water body.

Comparable Discussion

In the last years, many papers have been published on mercury and mercury speciation in water. The redox potential, pH value and ligand conditions have been found to be of great importance. Hem[13] and Wollast[14] have published thermodynamic calculations, from which follow that in oxygen rich water the dissolved mercury should exist as a mercury(II) species. Under moderately oxidizing to slightly reducing conditions, mercury should be present as mercury(0) or mercury(II) and under reducing conditions as mercury(0) or as HgS_2^{2-} species. These thermodynamic calculations can hardly be taken as realistic for real environmental systems. The results of our measurements in lake *Krüselin* and lake *Haussee* do not agree with these calculations. Other authors[15–17] discuss the reduction of mercury(II) to mercury(0) by humic acids. It would be imaginable that these reductions occur even in oxic water as there is of course no redox equilibrium between the humic acids and the water in which they are dissolved. However, the concentration of humic acids in lake *Krüselin* is so small that it is improbable that they can reduce all the mercury(II) to mercury(0). The

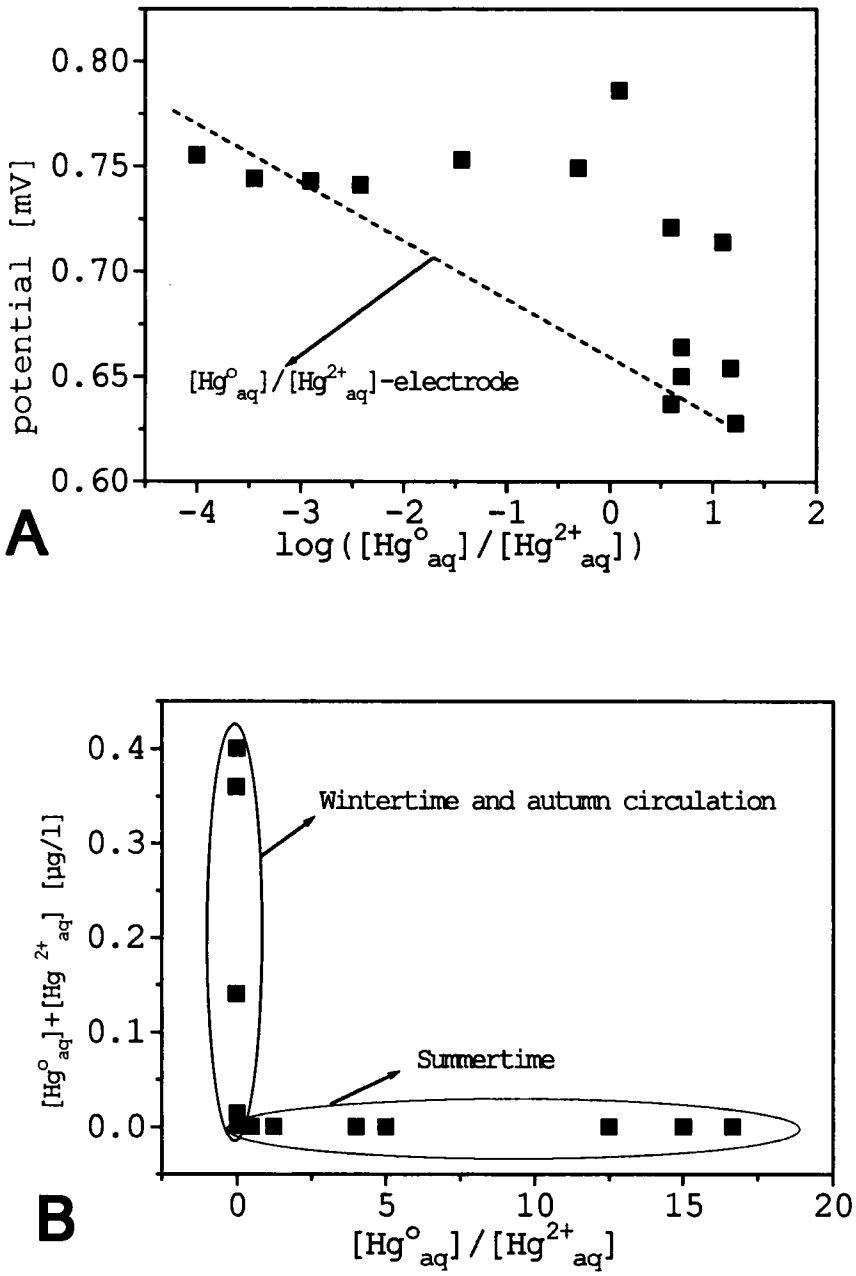

FIGURE 11 **A**: Lake *Haussee*: The logarithm of the ratio $[Hg^0_{aq}]/[Hg^{2+}_{aq}]$ versus the redox potential of the water sample, as calculated from the O_2 concentration and pH. The dashed line shows the dependence of log $[Hg^0_{aq}]/[Hg^{2+}_{aq}]$ versus the potential for the Hg^0_{aq}/Hg^{2+}_{aq} electrode calculated according to;[10] ■ sample points. **B**: Correlation of the sum $[Hg^0_{aq}]$ and $[Hg^{2+}_{aq}]$ of versus the ratio of $[Hg^0_{aq}]/[Hg^{2+}_{aq}]$.

ratios of mercury(0)/mercury(II) are too high for the redox potential in lake *Krüselin* and mostly in lake *Haussee* as well. Thus, it is the biology which has to be made responsible for the reduction of ionic mercury to atomic mercury although the participation of a chemical reduction by dissolved organic matter cannot be fully excluded. Hutzinger[9,18,19], Schlegel[20] and Barkay and coworkers[21] discussed the reduction of mercury by microbiological processes in aquatic media and they also concluded that these are probably the dominating redox processes.

CONCLUSIONS

This study strongly supports the theory that mercury speciation in the aquatic environment is dominated by biological processes. Further, it shows that the oxidation of atomic mercury in lake waters is a very slow process, even under oxic conditions and in cases where the concentration of dissolved organic matter is very low. The measurements show that the overall mercury concentration and also the mercury speciation in two dimictic lakes is subject to fairly fast changes. These changes are partly understandable on the basis of biological and physical (e.g. water turn-over) processes. Some features, esp. the sudden changes of overall concentrations, prompt the idea of a possible influx of mercury. It remains an open question whether this influx is of atmospheric or underground water origin. This study impressively shows how the overall concentration of dissolved mercury is reduced during the summer season, esp. as a result of the sedimentation of biota. This holds also true of other metals, such as copper and lead (see a forthcoming paper). Eventually, this study stresses the capabilities of electrochemical methods of analysis for the speciation of mercury.

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