MERCURY IN THE SURFACE WATER OF SWEDISH FOREST LAKES — CONCENTRATIONS, SPECIATION AND CONTROLLING FACTORS

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ABSTRACT. Concentrations of total Hg and five operationally defined Hg species were determined in the surface water of 25 Swedish forest lakes of different type. Regional and seasonal variations were studied during the ice-free season of 1986. The concentration of total Hg was usually in the range of 2 to 10 $\mu g\ m^{-3}$. Hg concentrations were highly correlated to the concentration of humic matter measured as water color. Hg concentrations were about twice as high in acidic lakes (pH 5) than in circumneutral lakes, which is attributed basically to the acidity of humic compounds acting as Hg carriers in boreal waters. Significant seasonal variations were caused by hydrological processes. During periods of high water flow, Hg concentrations increased dramatically, especially in humic lakes. Between spring and autumn, chemically reactive Hg compounds were gradually replaced by more inert species. Hg/C ratios were higher than in surface runoff from forest watersheds, indicating a significant impact of direct deposition of Hg on lake surfaces during summer. Regional differences were small despite differences in Hg contamination.

1. Introduction

Hg concentrations in fish in Swedish lakes exceed health advisory limits (0.5 to 1.0 $mg\ kg^{-1}$, wet weight) in thousands of lakes with no obvious source of contamination (Håkanson *et al.*, 1988; Chapter 12 in Lindqvist *et al.*, 1991). The Hg contamination of aquatic organisms is presumably related to the concentrations in the water column. However, only limited data on Hg concentrations in lake waters are presently available, and the existing information is too scattered to allow a thorough study of underlying mechanisms. This lack of data is due to the high risk of sample contamination and analytical difficulties in measuring concentrations at the $\mu g\ m^{-3}$ level as they occur in natural waters (e.g. Chapter 3 in Lindqvist *et al.*, 1991). In inland waters, special attention has to be paid to interferences by suspended and dissolved organic matter. Improvements of sampling, handling and analytical techniques have lead to a dramatic decrease of the values reported for lake and sea water (Fitzgerald and Watras, 1989). Earlier values referring to systems without known contamination were usually on the order of 10 to 100 $\mu g\ m^{-3}$ or higher (Fitzgerald, 1979; Wrembel, 1983; Glass *et al.*, 1986). In recent years, several groups using different methods have reported values from inland waters which usually are in the range of 1 to 10 $\mu g\ m^{-3}$ (Iverfeldt and Johansson, 1988; Fitzgerald and Watras, 1989; Schintu *et al.*, 1989; Lee and Iverfeldt, 1991). These groups have also succeeded in performing fractionations of Hg into different chemical species at these low concentrations.

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In this study, the Hg concentrations in the surface water of 25 Swedish forest lakes are compiled and related to environmental variables which were monitored simultaneously. The study is based on 450 analyses conducted in 150 samples from a broad spectrum of lake types with respect to morphology, hydrology and water chemistry. The data set covers a wide geographical range and includes seasonal variations as well as a chemical Hg speciation. Factors controlling Hg concentrations and speciation are identified and their influence quantified.

2. Study sites

The study area covers a large part of the Swedish boreal forest region (Figure 1). The lakes are located in four counties (G=Kronoberg, T=Örebro, X=Gävleborg, Y=Västernorrland), which are evaluated separately. The lakes cover a fairly wide range of lake types representing the majority of Swedish forest lakes (SNV, 1986). Most of the lakes are small, oligotrophic soft-water lakes with varying degrees of humicity and acidity. The catchments of these drainage lakes are mainly covered with coniferous forest (ca. 70 to 100%) and a minor proportion of mire (ca. 0 to 25%). The selection criteria and the

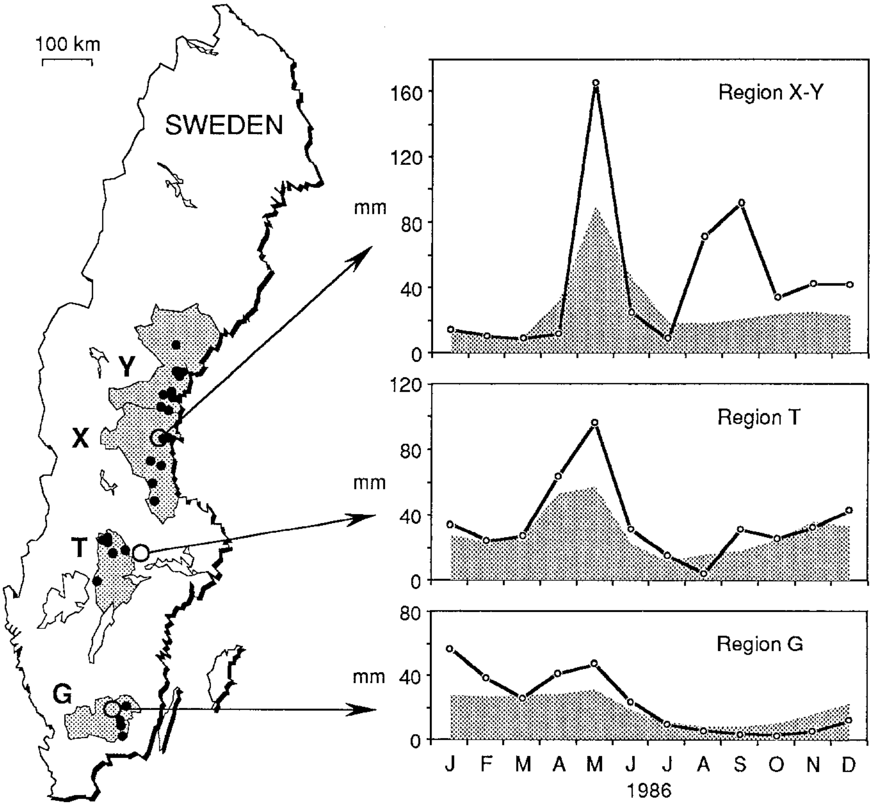


Figure 1. Location of the 25 study lakes (•) in four counties (Y = Västernorrland, X = Gävleborg, T = Örebro, and G = Kronoberg), and seasonal variations of water discharge at three hydrological stations (O) in the study regions in 1986 (lines) and mean values from 1931 to 1960 (shaded areas).

Table I. Hydrographical and chemical characteristics of the 25 study lakes in 1986, and Hg concentrations in different ecosystem compartments. Leading values in parentheses show ranges from which single untypical values were excluded.

		Median	Mean	Min.	Max.
CATCHMENT					
Area	(km^2)	8.6	12.0	0.4	(28) 44
Forest	(%)	83	82	(73) 63	97
Mire	(%)	11	12	(3) 1	(24) 33
Cultivated	(%)	1	4	0	(12) 21
Lakes	(%)	1	2	0	(5) 10
LAKE MORPHOMETRY AND HYDROLOGY					
Area	(km^2)	0.25	0.32	0.04	(0.8) 1.5
Max. depth	(m)	11.2	11.7	2.4	25.2
Mean depth	(m)	4.0	4.1	1.3	8.7
Mean water residence time	(yr)	0.4	0.7	(0.1) 0.02	(1.9) 3.8
WATER CHEMISTRY					
Water color (summer)	($g\ Pt\ m^{-3}$)	73	85	(35) 15	(200) 300
P (summer)	($mg\ m^{-3}$)	13	16	(8) 5	(24) 46
TOC (estimated, spring-autumn)	($g\ m^{-3}$)	10	11	(6) 3	(14) 32
pH (summer)		6.2	6.2	5.0	7.0
Hg CONCENTRATIONS					
Pike (*Esox lucius*), 1 kg	($\mu g\ g^{-1}$ (ww))	1.3	1.4	0.6	2.0
Perch (*Perca fluviatilis*), 5-10 g	($\mu g\ g^{-1}$ (ww))	0.17	0.19	0.08	0.30
Sediment traps, growing season	($\mu g\ g^{-1}$ (dw))	0.31	0.39	0.15	(0.65) 0.99
	($\mu g\ g^{-1}$ (C))	1.6	2.1	0.7	(2.6) 7.1
Surface sediment, 0-1 cm,	($\mu g\ g^{-1}$ (dw))	0.21	0.24	0.15	(0.32) 0.46
mean of n=3	($\mu g\ g^{-1}$ (C))	1.4	1.9	0.9	(2.5) 7.5
Surface water (Hg-tot)	($\mu g\ m^{-3}$)	4.6	4.7	1.9	7.8
mean of n=6, spring-autumn	($\mu g\ g^{-1}$ (C))	0.41	0.43	0.21	0.63

morphometric, hydrological and chemical characteristics of the study lakes and their catchments are shortly described in Håkanson (1986a, b). Details about the lakes in each region are given in Jönsson *et al.* (1987, 1988), Grahn *et al.* (1987, 1988), Johansson *et al.* (1987, 1988) and Bengtsson *et al.* (1987, 1988). A summary of these data is shown in Table I.

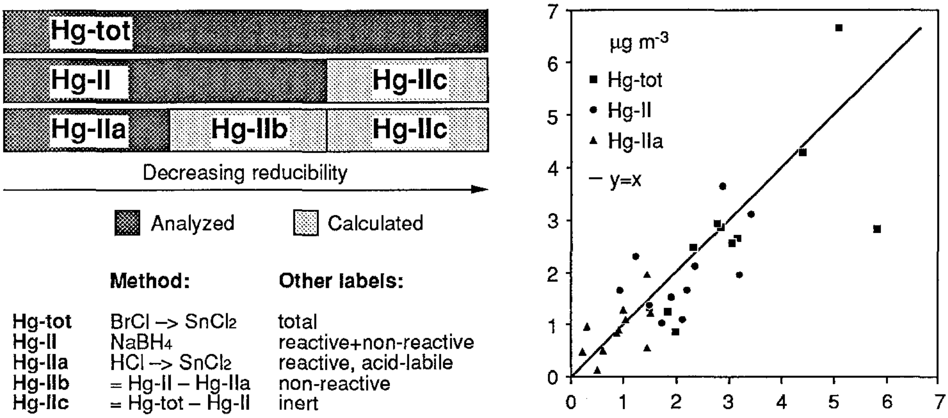
3. Sampling and analytical methods

All lakes were sampled six times during the ice-free period of 1986. For the determination of Hg concentrations, surface water samples (0.5 m depth) were collected and analyzed according to an ultra-clean protocol to avoid contamination (cf. Iverfeldt, 1988; Iverfeldt, 1991a, 1991b). All parts of the sampling equipment in contact with the water sample including sampling and storage bottles were constructed in borosilicate glass. The cleaning procedure for new bottles involved the following sequential steps: acid leaching (3 M HNO_3 during 1 week; 0.1 M HNO_3 during 1 week), a two-days redox treatment with 5 mL L^{-1} BrCl in 6 M HCl, washing with 12% $NH_2OH \cdot HCl$, and an extensive Milli-Q water rinsing. For the cleaning of used bottles, only the redox treatment, washing and rinsing steps were applied.

Samples were taken by hand on the upwind side of a fiberglass boat, using arm-long plastic gloves. A capped sampling bottle was passed across the water surface and opened beneath. The samples were immediately sent to the laboratory, where they were processed in a class-100 clean-air bench in a laboratory with a controlled, near-ambient gaseous Hg level in air (cf. Iverfeldt, 1991a).

The samples were routinely subjected to a chemical fractionation procedure based on the chemical reactivity (e.g. reducibility) of various Hg compounds in aqueous solution. In three different analyses the concentration of purgeable Hg was analyzed after treatment either with $SnCl_2$ in acidified samples, or with $NaBH_4$, or with $SnCl_2$ after strong oxidation with BrCl. This procedure resulted in five operationally defined species: Hg–tot, Hg–II, Hg–IIa, Hg–IIb and Hg–IIc (Figure 2). The samples were preserved in the laboratory by addition of HCl (5 mL L^{-1}; Merck, suprapur), after the analysis of the fraction Hg–II but before the analysis of Hg–IIa and Hg–tot. Freshly prepared reagent solutions were always used: 10% $SnCl_2$ in 3% H_2SO_4 (prepared from $SnCl_2 \cdot 2\,H_2O$, Merck, p.a.) for determination of the Hg–IIa fraction, 10% $NaBH_4$ (Fluka, purum p.a.) for the Hg–II fraction, while Hg–tot was determined using BrCl in 6 M HCl and a prereducing 12% $NH_2OH \cdot HCl$ solution (Merck, p.a.) according to the method described by Bloom and Crecelius (1983). After each treatment, volatilized Hg was determined by direct current helium plasma atomic emission spectrometry after preconcentration by double amalgamation (Iverfeldt and Lindqvist, 1986). The remaining fractions described in this study, Hg–IIb and Hg–IIc, are calculated differences according to Figure 2. The analytical procedure, including a description of the laboratory, equipment, calibration methods, detection limits, precision, reproducibility and intercomparisons, has been described elsewhere in detail (Iverfeldt and Lindqvist, 1986; Iverfeldt, 1988; Brosset and Iverfeldt, 1989; Iverfeldt, 1991a). The analytical precision (coefficient of variation) is typically ±2 to 5 %. The reproducibility of the whole procedure, including sampling, handling, analysis and natural variations within a lake, was tested by repeated parallel sampling in different parts of one lake which indicated a coefficient of variation on the order of ±20% (Figure 2).

At every sampling occasion, samples were collected with a Ruttner sampler at a depth of 2 m for the determination of physical and chemical water characteristics according to Håkanson *et al.* (1990a).



	Method:	Other labels:
Hg-tot	BrCl -> $SnCl_2$	total
Hg-II	$NaBH_4$	reactive+non-reactive
Hg-IIa	HCl -> $SnCl_2$	reactive, acid-labile
Hg-IIb	= Hg-II – Hg-IIa	non-reactive
Hg-IIc	= Hg-tot – Hg-II	inert

Figure 2. Operationally defined speciation of Hg in natural waters. The Hg–IIb fraction includes MeHg, and Hg–IIc is probably associated to particulate matter. The figure also shows the correlation of Hg concentrations obtained from repeated duplicate sampling (n=11) at two sites within one of the study lakes (Kinnen, lake area 1.5 km^2), illustrating both the reproducibility of Hg sampling and analysis and natural variations in lake waters.

4. Results and discussion

4.1. HYDROLOGICAL CONDITIONS

Biogeochemical processes are strongly influenced by lake hydrology, which is a product of local climatic conditions and lake morphometry. As most of the study lakes are small and shallow, but are part of a comparably large drainage area, the water residence time is usually rather short, typically on the order of a few months (Table I). In Sweden, especially in the north, the snow melt in spring leads to a distinct seasonal discharge pattern with a peak in April or May. In addition, increased discharge in autumn often leads to a bimodal flux pattern (Falkenmark, 1979). All the data in this study were collected in 1986, which was a year characterized by a late but rapid snow melt leading to exceptionally high water discharge, by a rather dry summer, and by a high precipitation in autumn (Figure 1). In late August, large parts of central Sweden, including many of the study lakes, were affected by a short period of very high rainfall leading to flooding and heavy soil erosion (SMHI, 1986).

4.2. WATER CHEMISTRY

In this study, water color was used as a measure of the concentration of humic matter (SNV, 1986; Meili, 1991c). The median value in the study lakes was about 80 g Pt m^{-3} in all regions (Tables I and II), which is typical of Swedish forest lakes (SNV, 1986). Water color is highly dependent on the ambient hydrological conditions (Andersson *et al.*, 1989; Rasmussen *et al.*, 1989). Similar to the water discharge, the seasonal pattern is often bimodal, with a maximum in spring and a lower peak in autumn. It should be pointed out that in 1986, the water color was unusually high in many Swedish lakes (cf. Andersson *et al.*, 1989). Water color increased dramatically during periods of high water flow (cf. Figure 1).

pH varied from 5.0 to 7.0 (Table I), indicating that most lakes were slightly acidic, which common for lakes in these regions (SNV, 1985). No significant differences between lakes from regions were observed.

The concentrations of total P were typically 8 to 24 mg m^{-3} (Table I). Total P is often used as a substitute variable representing autochthonous bioproduction in lakes, as P availability in many lakes is a limiting factor for the production of plankton organisms. In humic lakes, however, a significant proportion of P is recalcitrant and associated with humic substances (Jones *et al.*, 1988).

The biogeochemical cycle of Hg is coupled to the cycle of organic matter (Meili, 1991a). Knowledge of the TOC concentration in lake waters is therefore desirable. For reasons of compatibility with various Swedish monitoring programs, the analysis of TOC concentrations was not included in this study, but substituted by measurements of water color and total P. TOC in forest lakes can, however, be estimated from water color and P concentrations (Meili, 1991c). In lake water, organic matter is basically composed of strongly colored allochthonous humic matter and weakly colored but more nutrient-rich autochthonous matter such as algae and little stained DOC. Relationships in 18 lakes of the same character as the study lakes provide the following TOC estimate for lake surface water during the actual period (Meili, 1991c, revised equation):

$$\mathrm{TOC} \approx 0.095\ \mathrm{WC} + 0.35\ (\mathrm{TP} - 0.05\ \mathrm{WC}) \qquad (1)$$

where TOC = total organic carbon (g m^{-3}), WC = water color (g Pt m^{-3}) and TP = total phosphorus (mg m^{-3}). The first term in Equation (1) refers to allochthonous matter, the second to autochthonous matter. Estimated TOC was typically 3 to 17 g m^{-3}, but values up to 42 g m^{-3} were calculated in some lakes. Estimated mean values from the ice-free period were 6 to 14 g m^{-3} in most lakes (Table I).

In the study lakes, the overall median P concentration was about 10 to 15 mg m^{-3}, and the water color about 70 to 80 g Pt m^{-3}, corresponding to a TOC concentration of 9 to 11 g m^{-3} (Table II). From the second term of Equation (1), the proportion of autochthonous organic C in the water column can be roughly estimated at 3 g m^{-3}, which is about 30% of TOC. This indicates that the majority of TOC in a typical forest lake is of allochthonous origin (Meili, 1991c).

4.3. MERCURY CONCENTRATIONS AND SPECIATION

Hg–tot in single samples usually varied from 2 to 10 μg m^{-3}. Lake mean values from the ice-free period ranged from 2 to 8 μg m^{-3} (Table I).

Generally, Hg–IIa, Hg–IIb and Hg–IIc occurred in similar proportions of Hg–tot when considering annual median values. However, the proportions varied considerably with season (Table II). In spring, the dominating single species was Hg–IIb, in summer Hg–IIa, and in autumn Hg–IIc. The internal correlations of all Hg species are shown in Figure 3.

The proportion of Hg–IIc in lake waters is usually in the range 0 to 50% (Table II), similar to forest runoff (Johansson *et al.*, 1991). The proportion is higher in soil water (Aastrup *et al.*, 1991) and in precipitation (annual median values 40 to 80%; Iverfeldt, 1991a), where Hg occurs mainly in a particulate or colloidal phase. The values are also elevated in lake waters after heavy rainfall. Hg–II on the other hand is very well correlated to the concentration of organic matter measured as water color or TOC, both in runoff water (Johansson and Iverfeldt, 1990) and lake water (see below). Hence it can be hypothesized that in lake waters, Hg–IIc is mainly associated with inorganic and/or organic particles, and Hg–II (Hg–IIa and Hg–IIb) with dissolved organic matter. Dissolved methylmercury is included in the Hg-IIb fraction.

4.3.1. *Organic matter.*

The concentration of all Hg species was positively correlated to water color, although to a varying degree (Figure 4). The correlation parameters ($n=150$, values in parentheses for Hg–IIc) were $R = 0.34$ to 0.50 (0.14) and $p<0.0001$ (0.2) for Hg and color, $R = 0.44$ to 0.67 (0.29) and $p<0.0001$ (0.002) for log(Hg) and log(color). These correlations are in agreement with the high affinity of Hg to organic matter in soils and natural waters (Ramamoorthy and Kushner, 1975; Benes and Havlik, 1979; Andersson, 1979; Schnitzer and Kerndorff, 1981; Lodenius and Seppänen, 1984; Johansson and Iverfeldt, 1990). They also indicate that a large part of the Hg in the lakes originates from the catchment. The observed correlation coefficients are probably underestimates due to the procedural variability in both Hg and color analyses (Figure 2; Håkanson *et al.*, 1990a). In addition, water color is a complex parameter, and may not only reflect the

Table II. Hg concentrations and some chemical characteristics in the surface water of 25 Swedish lakes in the boreal forest region (seasonal median values for all lakes, 2 analyses in each lake and period). Mean values of Hg were generally about 130% of the median due to skew frequency distribution (cf. Figure 4).

		spring (Apr.-Jun.)		summer (Jul.-Aug.)		autumn (Sep.-Nov.)	
Water color	(g Pt m^{-3})	80		70		80	
P	(mg m^{-3})	15		10		10	
TOC (estimated)	(g m^{-3})	12.1		9.5		10.4	
pH		6.0		6.2		6.1	
Hg-tot	(μg m^{-3})	3.7	(100%)	3.1	(100%)	6.2	(100%)
Hg-II	(μg m^{-3})	3.4	(92%)	2.1	(68%)	3.4	(55%)
Hg-IIa	(μg m^{-3})	1.5	(41%)	1.3	(42%)	1.1	(19%)
Hg-IIb	(μg m^{-3})	1.9	(51%)	0.8	(26%)	2.2	(36%)
Hg-IIc	(μg m^{-3})	0.3	(8%)	1.0	(32%)	2.8	(45%)
Hg-tot/C (estim.)	(μg g^{-1})	0.31		0.31		0.57	

concentration of humic matter. Thus the data may obscure the probably stronger causal link between Hg and organic matter.

In eutrophic lakes, Hg levels in fish are usually comparatively low (D'Itri *et al.* 1971; Håkanson, 1980). This may partly be the result of a more efficient sedimentation of Hg associated with planktonic particles, which would result in a lower Hg concentration in the water column. Bioproduction and total P would then probably be negatively correlated with Hg concentrations in the water. In contrast, weak positive correlations were found in the study lakes (Figure 4). In these lakes, however, which are

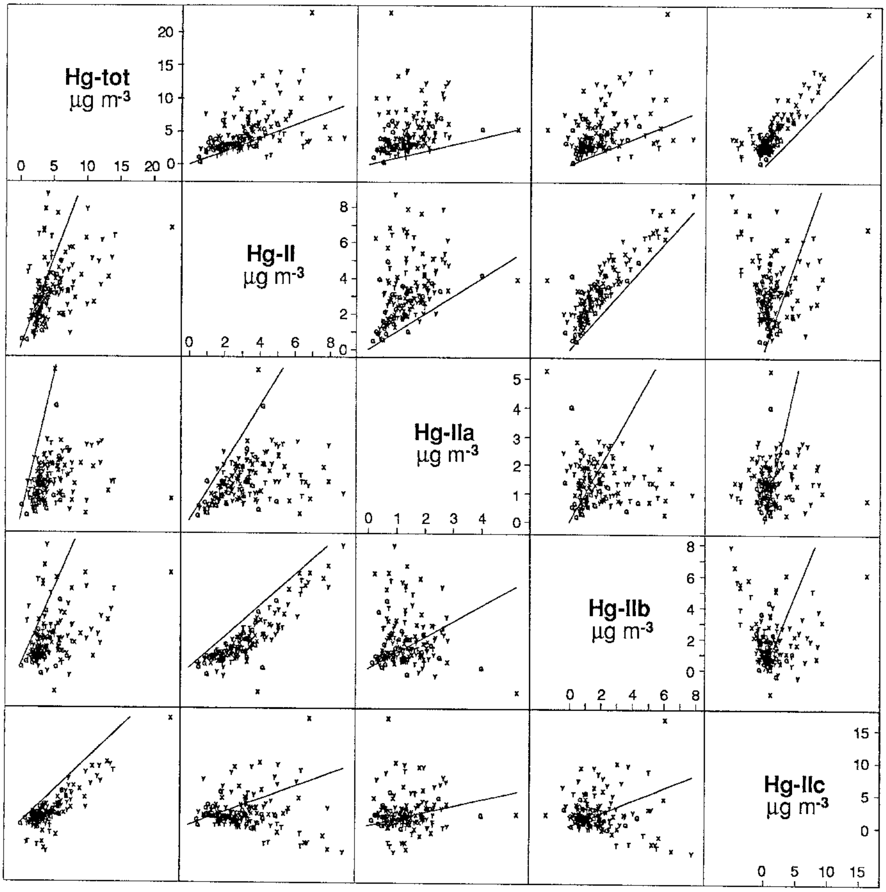


Figure 3. Graphical correlation matrix of the concentrations of five operationally defined Hg species in surface water from 25 Swedish lakes in the boreal forest region in 1986. Horizontal and vertical axes are given for each column and row of plots, respectively. Symbols denote regions (G, T, X, Y), lines denote 1:1 ratios starting from the origin.

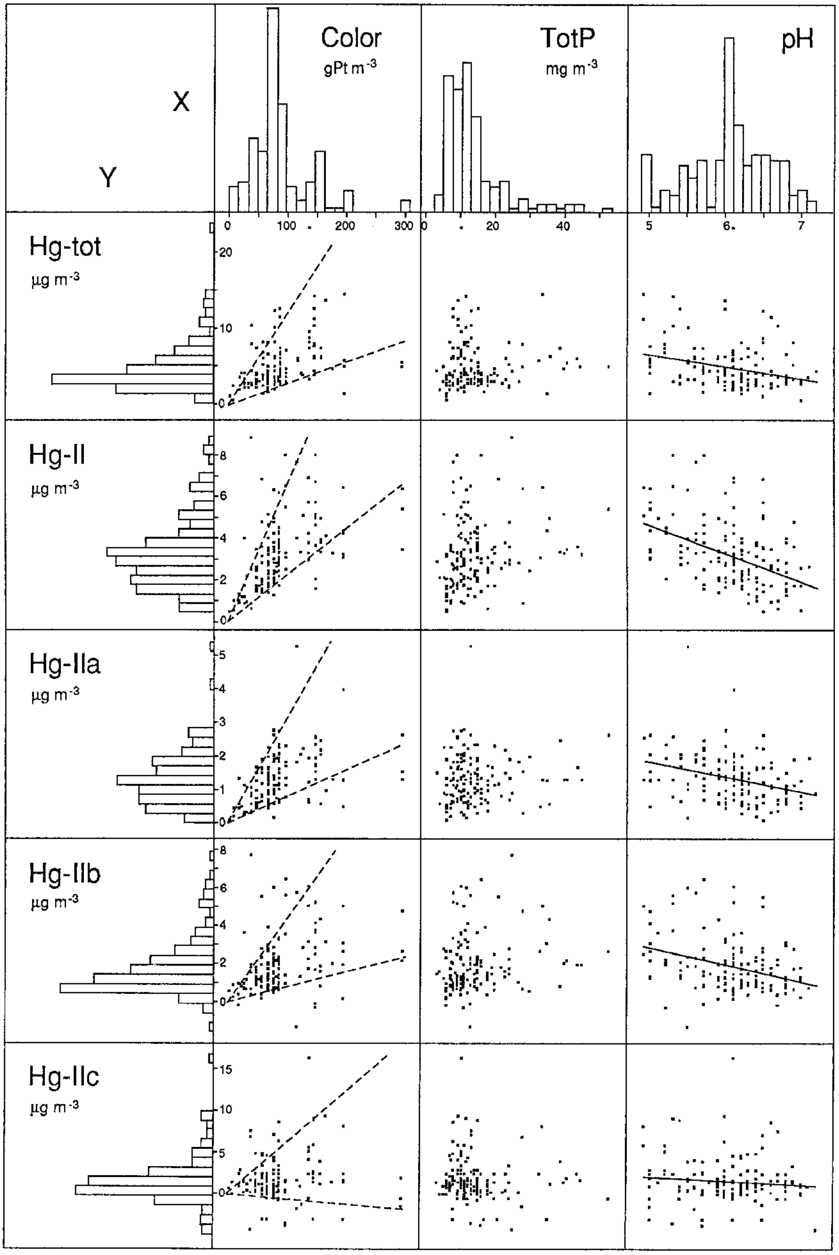


Figure 4. Frequency distribution and correlations of the concentrations of five operationally defined Hg species and some chemical variables (water color, total P and pH) in surface water from 25 Swedish lakes in the boreal forest region in 1986. All samples from four regions and six periods are shown. Solid lines are regression lines, dashed lines denote envelopes of ratio quantiles including 80% of the observations (ERQ80).

predominantly oligotrophic and dystrophic, P concentrations are strongly correlated with water color ($p<0.0001$), indicating a large proportion of P being recalcitrant and associated with humic matter rather than autochthonous matter (Jones *et al.*, 1988; cf. Meili, 1991c), and that the positive correlations of Hg and P concentrations are most probably a result of collinearity with the concentration of humic substances.

To obtain a better insight into the mechanisms of Hg cycling, the association of Hg and organic matter in the biogeochemical cycle should be considered. Biogeochemical fractionation processes are partly reflected by changes in the ratio of Hg and organic matter, which is a useful parameter when comparing different ecosystem compartments, such as lake water and runoff water (Meili, 1991a). In most forest lakes, the organic matter is dominated by colored humic substances transported to the lake from the drainage area (Meili, 1991c). These substances carry a significant amount of Hg to forest lakes (Johansson *et al.*, 1991; Meili, 1991a, b), and correlations between water color and Hg concentrations in fish are common (McMurtry *et al.*, 1989; Håkanson *et al.*, 1990b; Verta, 1990). For these reasons, the ratio of Hg concentrations and water color was calculated for all Hg species. As expected, these ratios showed in most cases less variation between lakes than the concentration values, and are useful to visualize seasonal and regional differences (Figure 6).

4.3.2. *Acidity.*

Figure 4 shows a negative correlation of Hg concentrations with lake water pH, which varied between 5 and 7. At pH 5, all Hg species except Hg–IIc showed on average 2 to 3 times higher concentrations than at pH 7. The correlation parameters ($n=150$, values in parentheses for Hg–IIc) were $R = 0.28$ to 0.47 (0.05) and $p<0.0001$ (0.5) for Hg and pH, $R = 0.31$ to 0.49 (0.18) and $p<0.0001$ (0.05) for log(Hg) and pH. The order of the correlation coefficients for different Hg species was the same as for water color, but the coefficients were considerably lower than those for water color. Moreover, pH and water color were strongly intercorrelated ($p<0.0001$), and in all acid lakes ($\text{pH} \leq 6$) the water color was ≥ 60 g Pt m^{-3}, indicating that the observed acidity is largely caused by humic acids (SNV, 1986). This suggests that the apparent influence of pH on the mobility of Hg and its cycling in natural waters is partly a result of the intercorrelation of pH with water color, which is typical for humic lakes. This is supported by multiple regression of log(Hg) on both pH and log(color), which for all Hg species indicates a far stronger influence of water color ($p<0.0001$ except Hg–IIc: $p=0.01$) than pH ($p=0.02$ to 0.8), also when accounting for the collinearity of the two variables (analysis of covariance). However, even if the turnover of Hg is little influenced by acidity, differences in lake water pH may partly reflect differences in the loading of Hg to lakes, as the annual deposition of Hg in remote areas is well correlated with the annual precipitation of acid (Meili, 1991a). Moreover, acid lakes are often situated in areas with shallow soils where the residence time of both water and organic matter is short, which would favor the export of recently deposited Hg from soils (cf. Meili, 1991a).

4.3.3. *Regional variations.*

The lakes are located in four forest regions (Figure 1), which are similar with respect to bedrock, vegetation type, and water chemistry, e.g. the median concentrations of humic matter in the study lakes, measured as water color. The lake waters in all regions had very similar Hg concentrations (Figure 5). Little geographical variation was also found in the Hg/color ratios (Figure 6). This is in contrast to the geographical differences in actual Hg deposition showing a decrease from the south to the north (Iverfeldt, 1991a). This apparent inconsistency may have different causes. Firstly, the growth of forest soils is slower in the colder areas of Sweden, which leads to a less efficient dilution by organic matter of the Hg deposited on vegetation and soils, and is of importance to the Hg/C ratio in surface runoff (Meili, 1991a). Secondly, lakes in southern Sweden have a longer growing season than similar lakes in the north, which may lead to a more efficient sedimentation of Hg. Finally, whereas direct deposition on lake surfaces decreases from the south to the north, the contribution of soil-derived Hg is larger in the northern regions of this study

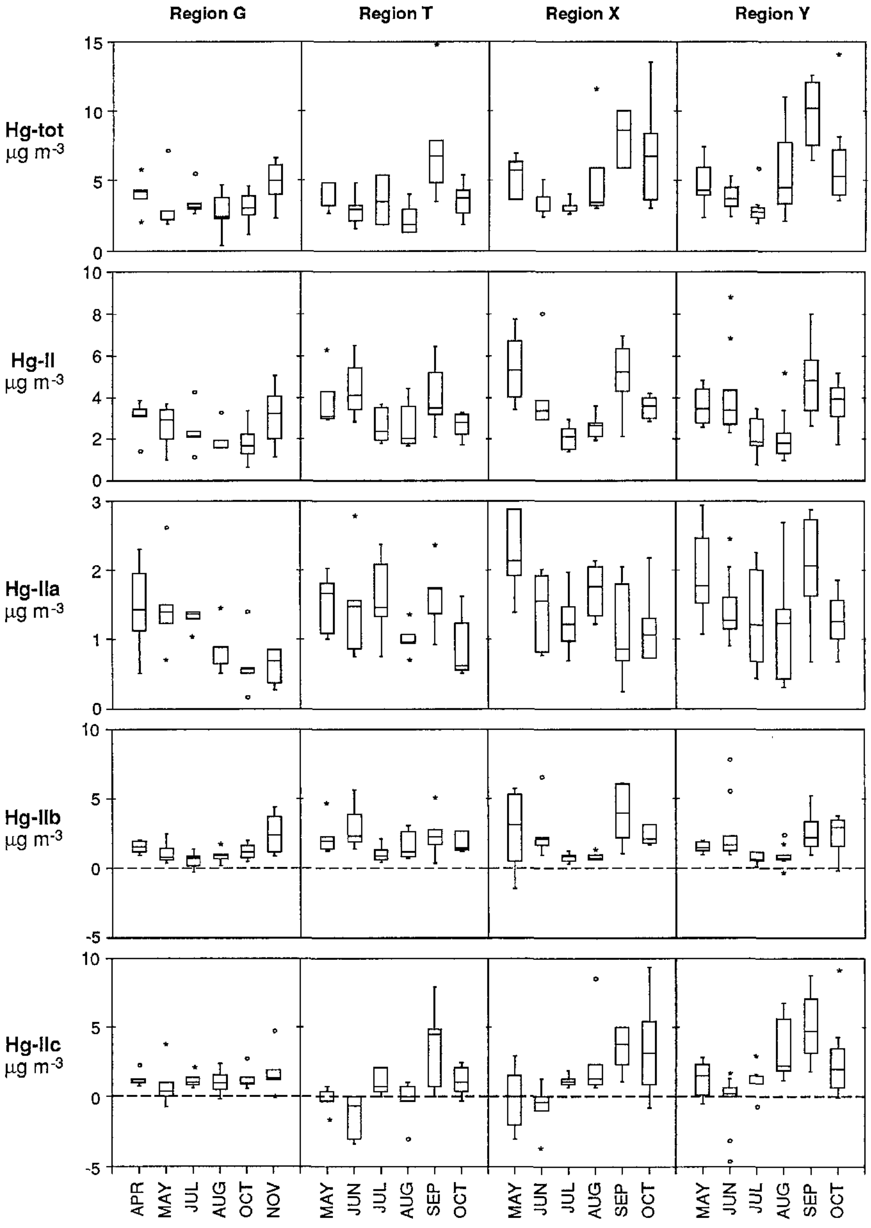


Figure 5. Seasonal variations in concentration of five operationally defined Hg species in the surface water of 25 Swedish forest lakes during the productive period of 1986. The box-and-whiskers plot shows median, lower and upper quartiles (boxes), minimum and maximum values (within 1.5 times the interquartile range from the quartiles), and extreme values (* = within and o = outside 3 times the interquartile range from the quartiles).

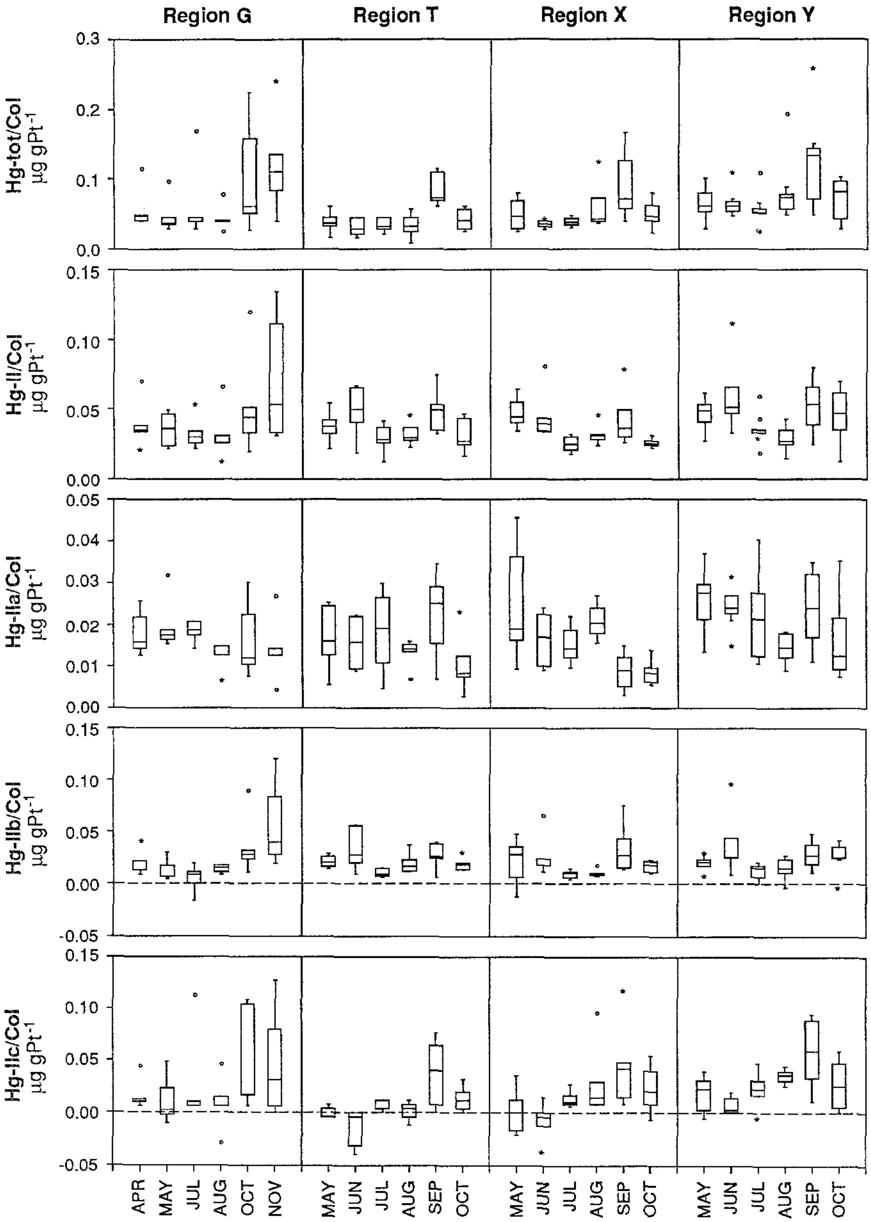


Figure 6. Seasonal variations of the concentration ratios of five operationally defined Hg species and water color (Hg-X/Col) in the surface water of 25 Swedish forest lakes during the productive period of 1986. Symbol description see Figure 5.

where the forest soils are more contaminated due to historical domestic Hg emissions to the air from paper industry (Johansson *et al.*, 1991). This is reflected in the lake water data showing that the Hg–tot/color ratio is elevated in region Y and to a lower degree in region X (Figure 6), which during past decades were the location of several large point sources (Chapter 4 in Lindqvist *et al.*, 1991). Most of the study lakes are located within the influence radius of about 100 km (cf. Håkanson *et al.*, 1990b; Meili, 1991a) from these sources, two of them within <10 km. The deviation is most pronounced for Hg–IIc (Figure 5), even when related to water color as Hg–IIc/color (Figure 6), indicating that the humic matter transported to lakes is more strongly contaminated with Hg, predominantly with chemically inert Hg–IIc.

4.3.4. *Seasonal changes.*

The concentration of all Hg species except Hg–IIa was usually high in spring and autumn, and low in summer. The concentrations covaried with the water color, and their peaks coincided with the maxima of water flow from the drainage area (Figure 1). All these findings are in accordance with the patterns found in runoff water (Iverfeldt and Johansson, 1988) and indicate a close coupling between a lake and its catchment regarding the turnover of both Hg and organic matter (cf. Meili, 1991a).

However, the covariations of Hg concentrations with water color depend strongly on the season. Although both water discharge and water color in autumn reached similar or lower values than in spring, high values of most Hg species were observed in autumn. A comparison of Hg/color ratios shows the variations more clearly. During summer the Hg–tot/color ratios were the same as in spring despite significant changes in water fluxes and color. The Hg–tot/C ratio on the other hand was most probably about 20% higher in spring, as the color/C ratio during this period was higher (Meili, unpubl. data). During autumn rainfall, the Hg–tot/color ratios increased dramatically, mainly due to the Hg–IIc fraction (expressed as Hg–IIc/color ratio) which peaked in autumn in all regions (Figure 6). This implies that both the character of runoff humic matter and its Hg burden varied considerably depending both on season and hydrological conditions (Meili and Håkanson, unpublished data).

While Hg–IIc and Hg–IIc/color increased during the productive period, Hg–IIa and Hg–IIa/color decreased instead (Table II, Figures 5 and 6). This indicates a fractionation of Hg species in the water column where (chemically) reactive Hg was transformed into or replaced by less reactive species during summer and autumn.

4.4. PROCESSES OF MERCURY FRACTIONATION IN THE HYDROLOGICAL CYCLE

In lakes without any known direct discharge of Hg to the lake or its tributaries, Hg is supplied either by direct deposition on the lake surface or via surface runoff from the catchment, and sedimentation is an important removal process (cf. Meili, 1991b).

In studies of fractionation processes in the hydrological cycle, it is advisable to use a common currency of Hg contamination. As the biogeochemical cycle of Hg is closely associated with the cycle of organic matter, the Hg/C ratio is a suitable unit (Meili, 1991a). Variations of this ratio in different compartments of the cycle can provide valuable clues about fractionation processes, especially when data on different Hg species are available which have been determined in a similar manner in all compartments.

The Hg/C ratio (Hg–tot/C) in forest lake waters can be calculated by dividing measured Hg-tot and TOC estimated from Equation (1). In single samples from the study lakes, the Hg/C ratio was 0.1 to 0.8 $\mu g\ g^{-1}$ except in autumn when values up to 1.6 $\mu g\ g^{-1}$ were recorded. The median value was about 0.4 $\mu g\ g^{-1}$ (0.3 $\mu g\ g^{-1}$ in spring and summer, and 0.6 $\mu g\ g^{-1}$ in autumn; Table II).

The ratio of mean values for Hg-tot and estimated TOC during the ice-free period 1986 was normally 0.2 to 0.6 $\mu g\ g^{-1}$ (Table I). These values are higher than the annual mean values found in Swedish runoff waters during the same year, which normally were within 0.15 to 0.5 $\mu g\ g^{-1}$ (typically around 0.25 $\mu g\ g^{-1}$) in forest catchments, with lower values where lakes and bogs were situated upstream, and higher values in areas with shallow soils and close to historical point sources of Hg (calculated from Iverfeldt and

Johansson, 1988, and Johansson and Iverfeldt, 1990; cf. Meili, 1991a). This indicates that the direct deposition of Hg on lake surfaces significantly contributes to the Hg concentration in the lake water during the productive period. This is supported by mass balance calculations (Meili, 1991b) which show that in Swedish forest lakes, both pathways are of importance, and either can dominate, depending on the type and location of a lake. The relative importance of direct deposition is presumably greatest in summer, when many streams are dried out and runoff input of Hg is low.

A large part of the seasonal variations appears to be a result of mechanical fractionation associated with processes such as soil erosion and particle transport in surface runoff and lake waters. In autumn 1986 exceptionally heavy rainfall with subsequent inundations and soil erosion were recorded in region X and part of regions Y and T (Figure 1; SMHI, 1986). A large part of the organic matter entering the lakes during periods of large water flow is most probably particulate as a result of the heavy soil erosion, which would explain the high proportion of chemically inert Hg–IIc. This is supported by the low ratio of color to organic C in other similar lakes during the same autumn period (Meili, unpubl. data), indicating a lower proportion of dissolved humic substances which are responsible for most of the water color (Pennanen, 1988). Heavier humic particles and colloids probably originate from more recent top soil layers which presumably are more contaminated than deeper layers, where older more decomposed dissolved organic substances prevail (Meili, 1991a). The Hg/C ratio in podzolic top soil (raw humus or mor layer) in central Sweden is about 0.4 to 0.8 $\mu g\ g^{-1}$ and in the south about 0.5 to 0.9 $\mu g\ g^{-1}$ (calculated from Figure 6 in Håkanson *et al.*, 1990b; cf. Meili, 1991a), which is higher than the average ratio in surface runoff water. These top soil layers may be eroded during peak-flow episodes in discharge areas near water courses by horizontal water flow in surface layers at events of high groundwater levels (Aastrup *et al.*, 1991; Johansson *et al.*, 1991). This is in accordance with a stratified soil model (Meili, 1991a), where the groundwater table is raised at high water fluxes to a level where soils are more contaminated, as a result of a longer exposure time to Hg deposition due to more rare interference from erosion.

During the spring flood, the patterns were different. Hg–IIc, measured as a proportion of Hg–tot, was lowest in the beginning of the season, although the water discharge was largest, and increased during the summer. At the same time, the ratio of water color/C in comparable lakes decreased steadily, despite the high concentrations of humic matter in autumn, indicating a gradual transition (or replacement) from dissolved to particulate organic matter during summer. These simultaneous changes agree with the hypothesis that Hg–IIc is associated with particles.

The higher loading of Hg in heavier soil particles is also reflected by the Hg/C ratio in sedimenting matter and surface sediments, which generally is around 0.6 to 2.5 $\mu g\ g^{-1}$ in the study lakes (Table I) and other oligotrophic lakes in Sweden (Chapter 11 in Lindqvist *et al.*, 1991; Johansson, 1985). This is considerably higher than the Hg–tot/C ratio in the mor layer of forest soils (0.4 to 0.9 $\mu g\ g^{-1}$; see above), runoff waters from forest soils (annual mean generally 0.15 to 0.5 $\mu g\ g^{-1}$; see above) and lake waters (annual mean generally 0.2 to 0.6 $\mu g\ g^{-1}$; see above). All these ratios can be explained with an intermittent inflow, and subsequent rapid sedimentation, of large amounts of heavy, more contaminated particles from the surface layers of forest soils during short periods of high water flow, in combination with additional contamination of lake waters through direct atmospheric deposition of Hg on lake surfaces.

In precipitation as well as in soil water, the inert Hg–IIc fraction typically accounts for about two third of Hg–tot (Iverfeldt, 1991a; Aastrup *et al.*, 1991), as compared to an average about 20 to 30% in many runoff and lake waters (most observations 0 to 60%; Table II; Johansson *et al.*, 1991). In lake waters, the proportion was elevated after heavy rainfall (see above). These observations indicate that a transformation or segregation of deposited Hg species occurs both in soils and lake waters. Three explanations are at hand: (1) as the measurements of Hg in precipitation only represent net wet deposition, the speciation could have been changed by significant addition of dry deposition on forest canopies with a different composition of Hg species (Iverfeldt, 1991b); (2) due to the presence of organic matter and organisms in both soils and surface waters, a part of the inert Hg is transformed into more reactive species and (3) a large part of Hg in precipitation is associated with aerosol particles (Iverfeldt, 1991a), which may be immobile in soils or settle out in lakes, leaving more soluble (reactive) species behind in the water phase, except in periods of soil erosion. The last hypothesis is supported by the fact that Hg–IIc is the only

Hg species which shows no strong correlation with water color (Figure 4). However, Hg–IIc measured as a proportion of Hg–tot was lowest after snowmelt in the beginning of the season, when large amounts of snow borne aerosol particles should appear in the lakes. These unexpected patterns may be the result of significant dry deposition of Hg in forests (Iverfeldt, 1991b), in combination with an accumulation of wet-deposited Hg by evaporation of rainwater in the canopy in summer, leading to high Hg concentrations in runoff water when the canopy is washed by heavy rainfall, but not during the snow-melt in spring. The low Hg-IIc/Hg-tot ratio in the vernal as compared to the autumnal period of mixing may also result from differences in sediment resuspension which was suppressed in spring 1986 by a very rapid development of a stable stratification of the water column (Meili, unpubl. data). The differences between spring and autumn water are most probably also influenced by other processes preceding hydrological events, e.g. by the higher rate of soil decomposition in summer and the ground frost in winter. Factors such as time delays and integrative processes may be of vital importance for Hg cycling (cf. Bloom and Watras, 1989), but are poorly understood at present and beyond the scope of this paper.

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