

## OCCURENCE AND TRANSPORT OF MERCURY WITHIN A SMALL CATCHMENT AREA

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**ABSTRACT.** To contribute to the understanding of Hg flow to forest lakes the storage of Hg in the soil of a catchment was quantified, the transport of Hg from the recharge area to the discharge area was studied and a mass balance for different soil horizons was calculated. The transport of Hg in soil, ground and stream water was estimated using water flows from a hydrological model and by determining Hg in water sampled with a clean procedure. The estimate for the annual Hg flux out of the till overburden in the catchment was  $3.4 \text{ g km}^{-2}$ . The annual flux was reduced to  $1.3 \text{ g km}^{-2}$  in the stream, indicating interception in a lake. The transport was predominantly taking place in the upper 50 cm of the soil. The storage of Hg in the soil was  $8.8 \text{ kg km}^{-2}$ , which is large compared to the flux. A net accumulation, amounting to 80% of the Hg deposition, is almost entirely located to the mor layer.

### 1. Introduction

This work is a contribution to the understanding of the Hg flow to lakes in forest areas. Concern about increasing concentrations of Hg in fish in forest lakes, which are not situated in the immediate neighbourhood of point sources is the direct motive for the investigation.

Air-borne Hg is deposited either on the recharge area, the discharge area or the lake itself within a catchment area of a lake. The Hg fall-out on the recharge area has to percolate through the unsaturated zone of the soil to the groundwater to be able to be transported horizontally towards the discharge area and finally the lake.

In till slopes with broken topography recharge and discharge areas can, on a local scale, repeatedly occur. Some areas are temporarily discharge areas during episodes of high groundwater tables. This condition enables a very shallow horizontal waterflow close to the ground surface.

The main objects of the investigation were:

- to quantify the pool of Hg in the soil of a catchment area
- to study the transport of Hg from recharge area to discharge area within a catchment area.
- to make a balance of the Hg flows for different soil horizons.

The investigation has been carried out in a part of lake Storesjön catchment area at the Tiveden National Park in South Central Sweden.

## 2. Methods and Materials

The small forested catchment in the Tiveden National Park chosen for the investigation is one of the localities used in the Swedish Environmental Monitoring Programme (PMK). The area has a very broken topography with granitic outcrops. The valleys are filled with till or peat, while the elevated parts have a very shallow cover of till and humus. Most of the area supports a pine and spruce forest of low productivity, interspersed with tree-less bogs in the depressions. The soils are podsoles. The mor layer is characterized by extremely low pH, with an average of 3.8 in water extracts, resulting in a very acid percolate collected underneath the layer. However, the pH-values and high concentrations of exchangeable and dissolved Al in the mineral soil layers are usual for acid forest soils in South Sweden. The site has an unusually large pool of soil organic material, in the form of a thick mor layer, 12 cm on the average, and a C content of 5.6% in the B-horizon. The Hg budget was worked out in detail for a till formation on a slope, making up a funnel-shaped minicatchment of 0.014 km<sup>2</sup>, which drains into a fen. The fen in its turn drains into lake Storesjön. In the minicatchment, surfacewater appears occasionally during episodes of high groundwater level at some spots along the slope and at the outlet into the fen. Mercury was also monitored in the stream leaving the lake.

### 2.1. CALCULATION OF THE MERCURY STORE

For the calculation of the Hg stores, the investigated till slope has been divided into one area with shallow soils (43% of the area, defined by soil depth <20 cm), one intermediate area and one waterlogged area (6% of the area, defined by mor layer >25 cm). The volume of the soil layers was determined for each of these areas separately, using a frequency distribution for soil depths. The waterlogged area was considered to have a profile of a peat layer and an underlying C-horizon only. Mercury contents determined for different horizons (Table I) were multiplied

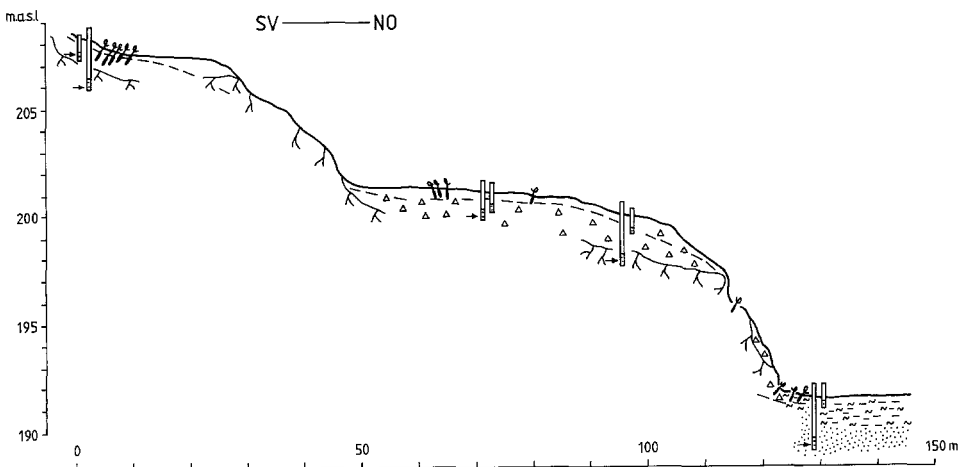


Fig 1. The investigated slope in the Tiveden National Park with installations of suction lysimeters and ground water tubes. m. a. s! = meter above sea level.

with horizon volumes and bulk densities. A reduction factor for stone and boulder volume was applied to mineral soil horizons, a factor that is very difficult to determine precisely.

The mercury stores for the investigated minicatchment was calculated on a general  $\text{km}^2$ -basis. The calculated result is directly applicable to terrain of the shallow soils in Tiveden. The mor layer and upper mineral soil horizons are representative for other forest sites also.

## 2.2. SAMPLING EQUIPMENT AND INSTALLATIONS

Soilwater for chemical analysis was sampled with ceramic (P80) suction lysimeters. These were installed in the E, B and C horizons of the podsol profiles at two sites along the slope.

Groundwater was sampled from acrylic plastic tubes installed in three groups along the till slope and one additional group in the fen. In each group groundwater was sampled from two levels. The groundwater was sucked through ceramic cups in order to obtain comparable Hg analyses with soilwater. The installations of the sampling devices are shown in Figure 1. A logger for continuous recording of groundwater level was installed to calibrate the simulation of the water flows.

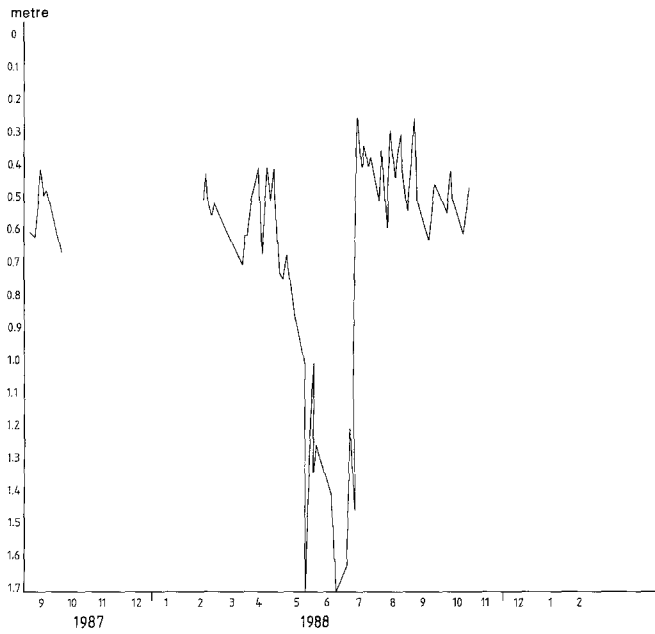
## 2.3. THE SOIL MODEL

The water and heat model, SOIL, (Jansson and Halldin 1979) is based on fundamental physical principles solved by two coupled partial differential equations. Standard meteorological data are used as driving variables to govern processes such as snow-melt, interception of precipitation and evapotranspiration. Soil properties, such as water tension, unsaturated and saturated hydraulic conductivity as well as thermal conductivity and heat capacity, are considered and accounted for in each soil layer as well as each boundary between layers. The two differential equations for water and heat flow are solved with an explicit numerical method in which the Darcy law for gradients in water potential is a part. Accuracy with which precipitation and evapotranspiration can be determined is crucial to such a model and the best way of calibrating the output seems to be against measurements of groundwater fluctuations (Figure 2). The model describes the flow of heat and water in one dimension in a soil profile. By combining simulation from two profiles a quasi-three dimensional picture of the water flow was obtained.

Simulations were made for the three subperiods, i.e. autumn 1987, spring 1988 and autumn 1988 as well as for the whole investigation period. The period called autumn 1987 has a duration of 4 mo, while spring as well as autumn 1988 extend over 6 mo. The whole investigation period was thus 16 mo.

The calculation of water flow with a hydrologic model is a theoretical exercise with many pitfalls. The climatic data used as driving variables are taken from stations situated away from the investigation area. The physical parameters of the soil have only to a small extent been determined in the investigation area itself, and there is a large spatial variation for these parameters. The geometry of the soil profiles in the slope is incompletely known. The assumption that the boundaries of the soil layers run parallel and are persistent is dubious. Possible seepage through fissures in the bedrock have been neglected. However, as the simulations have been calibrated against a continuous recording of groundwater level, the total quantity of horizontal flow as well as the overall distribution between different soil layers should be roughly correct.

Measured groundwater level (metres below top of the tube)



Simulated groundwater level (metres below ground surface)

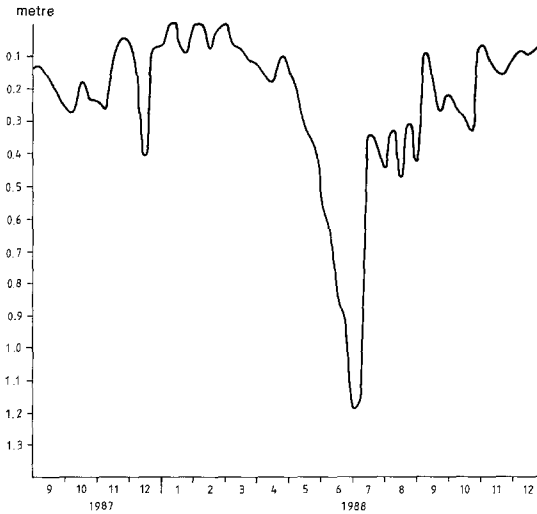


Fig 2. Ground water levels continuously recorded and groun 1 water levels simulated by the hydrological SOIL water and heat mc. lel.

## 2.4 ANALYSES

To avoid contamination, water samples were collected in extensively cleaned borosilicate bottles (cf. Iverfeldt 1991, Lindqvist *et al* 1991). A two-step acid leaching procedure (3 M HNO<sub>3</sub> during 1 week; 0.1 M HNO<sub>3</sub> during 1 week) combined with a redox-treatment step (5 ml L<sup>-1</sup> BrCl in 6M HCl during 2 weeks, washing with 12% NH<sub>2</sub>OH · HCl, and rinsing with milli-Q water) was applied for new bottles. Only the redox treatment was performed in the case of used bottles.

The soilwater and groundwater samples were collected using closed systems consisting of ceramic cups in soil or groundwater, sample bottles and tube connections. For sampling, the systems were subjected to an underpressure of 0.3 atm by manual pumping. Samples were taken with great care to avoid contamination and were thereafter immediately sent to the laboratory for analysis. Operationally defined Hg fractions were determined according to an ultra-clean analytical protocol (e.g. Iverfeldt 1988, Iverfeldt 1991).

One fraction was obtained by reduction of Hg with 10% SnCl<sub>2</sub> in 3% H<sub>2</sub>SO<sub>4</sub> (prepared from SnCl<sub>2</sub> · 2H<sub>2</sub>O, Merck p.a.), another fraction by reaction of Hg with 10% NaBH<sub>4</sub> (Fluka, purum p.a.). Total Hg was analyzed after oxidation with BrCl in 6M HCl followed by prereduction with 12% NH<sub>2</sub>OH · HCl (Merck p.a.) and reduction with SnCl<sub>2</sub> solution. The fraction recovered by SnCl<sub>2</sub> treatment is named Hg-IIa, while NaBH<sub>4</sub> treatment results in a larger fraction denoted Hg-II (cf. Iverfeldt 1991, Lindqvist *et al* 1991). After purging, the volatilized Hg was preconcentrated on a gold trap and detected by double amalgamation direct current plasma atomic emission technique. Detailed information on procedures, precision, detection limits etc can be found elsewhere (Iverfeldt and Lindqvist 1986, Brosset 1987, Iverfeldt 1988, Brosset and Iverfeldt 1989, Iverfeldt 1991 and Lindqvist *et al* 1991)

The soilwater and groundwater were also analysed for the major ions, heavy metals and organic content according to the current programme of the Swedish Environmental Monitoring. The groundwater samples for analyses of metals were filtered through 0.45 µm filter and preserved with nitric acid. All other analyses were made on unfiltered samples.

The organic content was analysed as TOC in the soilwater and COD-Mn in the groundwater. On one sampling occasion groundwater was analysed for TOC on samples which were collected through the lysimeter cups as well as on samples completely unfiltered.

The soil samples were analysed by the Swedish Agricultural Laboratory. Total concentration of Hg was determined on the organic soil samples and the acid-soluble (2M HNO<sub>3</sub>) on the mineral soil samples.

## 3. Results and Discussion

### 3.1 THE SOIL STORAGE OF MERCURY

The total Hg storage of mor layer, 3.6 kg km<sup>-2</sup> (Table I), is in the upper part of the range found in Sweden (Lindqvist *et al.*, 1991). This is due to the large thickness of the layer. Of the total soil Hg in Tiveden, 41% was found to be retained in the mor.

A probable initial value for Hg in parent materials originating from igneous rocks is 0.007 µg g<sup>-1</sup> a conclusion based on the content of C-horizons from different profiles (Lindqvist *et al.*, 1991). The content of the C-horizon in Tiveden is close to this value (Table I). The initial concentration of mor layers has been given as 0.075 µg Hg g<sup>-1</sup>, which is calculated as the residual concentration after subtracting the estimated contribution from pollution in a national survey (Lindqvist *et al.*, 1991). These initial contents applied to Tiveden means that the initial store of

TABLE I.

Contents of total soil Hg and C as well as stores of Hg in soil horizons of the investigated till slope in Tiveden. The stores are given as total amounts for the 0.014 km<sup>2</sup> investigation area and as generalized figures for the terrain of Tiveden on a km<sup>2</sup> basis. N=number of determinations, mv=mean value, cv=coefficient of variation.

Soil layer	Total-C (%)	Hg-content( $\mu\text{g g}^{-1}$ )			Hg/C-ratio		Hg-stores	
		N	mv	cv(%)	mv	cv(%)	in area (g)	general (kg km <sup>-2</sup> )
mor	48	18	.25	17	2.7	17	50	3.6
E-horizon	5.6	10	.027	35	2.2	22	9	.6
upper B-hor.	6.3	10	.058	36	4.6	16	34	2.4
lower B-hor.	3.0	9	.023	49	4.3	32	23	1.6
C-horizon	1.0	13	.006	62	3.4	43	8	.6
Total store							124	8.8

the mor layer was 1.1 kg km<sup>-2</sup> and that of the mineral soil 1.6 kg km<sup>-2</sup>. The difference to the present day store is 6.1 kg km<sup>-2</sup> for the soil profile as a whole and 2.5 kg km<sup>-2</sup> for the mor layer, this being the net input from natural and/or anthropogenic sources.

### 3.2. CHEMICAL PROPERTIES OF THE SOILWATER AND GROUNDWATER

Soilwater and groundwater of the investigated till area are characterized by a low salt content and low pH. The dominating anion is sulphate and the Al concentrations are extremely high. Of most interest for the mobility of Hg is the high content of organic matter compared to most soilwaters and groundwaters in Sweden. The chemical composition of soilwater and groundwater is given in Table II.

The analyses of filtered (P80, 1  $\mu\text{m}$  pores) and unfiltered samples for TOC revealed that the lysimeter cups in the superficial groundwater in the upper part of the till slope retained a great part of the organic material. Downslope this effect became less pronounced and in the deep groundwater, no organic matter was retained. This is taken as evidence of large organic particles occurring in the upper layers. Larger particles are known to be the main carriers of Hg in lakes (Lodenius and Seppänen, 1984).

TABLE II.

The chemistry of soilwater and groundwater in the investigation area. The concentrations are given in  $\mu\text{eq L}^{-1}$

Level	pH	SO <sub>4</sub>	Cl	Na	K	Ca	Mg	H	Al(III)	TOC mg L <sup>-1</sup>	COD-Mn mg L <sup>-1</sup>
soilw. E	4.05	268	134	149	6	28	32	89	210	25.5	
soilw. B	4.62	310	98	147	4	19	28	24	244	7.7	
soilw. C	4.74	202	69	107	5	28	28	18	132	7.4	
groundw. shallow	4.53	252	105	125	7	110	47	29	178		140
groundw. deep	4.80	259	111	146	12	185	75	16	105		18

## 3.3. MERCURY CONCENTRATIONS IN SOILWATER AND GROUNDWATER

Sampling of soilwater and groundwater has been carried out at nine occasions from September 1987 until November 1988. The Hg concentrations in water were found to be very variable in time. From one sampling occasion the concentrations were so divergent from the rest, that the data from this occasion are omitted in the calculations. The mean values for all samples were 11.9 ng L<sup>-1</sup> for Hg-tot, 3.6 ng L<sup>-1</sup> for Hg-II and 1.2 ng L<sup>-1</sup> for Hg-IIa. The waters (soilwater and groundwater) from the mor layer, the eluvial E and the illuvial B-horizon had mean Hg-tot concentrations of 11 to 15 ng L<sup>-1</sup>. The concentrations decreased to 7 ng L<sup>-1</sup> in the deep C-horizon. The corresponding concentrations for Hg-II were 0.4 ng L<sup>-1</sup> and 0.9 ng L<sup>-1</sup>, which can be

TABLE IIIa.

Hg-tot concentrations in ng L<sup>-1</sup> in soilwater and groundwater.

Soil layer	Mean	Sd	min	max	cv%	N
0 - 8 cm	11.9	12.7	1.9	39.6	113	7
8 - 20 cm	13.6	13.7	1.9	48.4	101	23
20 - 50 cm	15.1	12.9	0.6	52.1	85	29
50 - 100 cm	9.9	8.8	0.7	39.2	89	39
100 - 155 cm	6.8	3.7	1.5	12.5	55	8

TABLE IIIb.

Hg-I concentrations in ng L<sup>-1</sup> in soilwater and groundwater.

Soil layer	Mean	Sd	min	max	cv%	N
0 - 8 cm	4.1	3.7	0.9	10.3	90	7
8 - 20 cm	4.3	4.8	0.5	20.2	112	23
20 - 50 cm	4.1	4.6	0.1	19.5	111	32
50 - 100 cm	3.3	4.9	0.0	27.6	147	39
100 - 165 cm	0.9	0.5	0.3	1.7	63	8

TABLE IIIc.

Hg-I a concentrations in ng L<sup>-1</sup> in soilwater and groundwater

Soil layer	Mean	Sd	min	max	cv%	N
0 - 8 cm	1.4	1.1	0.5	3.4	79	6
8 - 20 cm	1.5	1.1	0.0	4.2	70	22
20 - 50 cm	1.3	0.8	0.0	3.8	64	31
50 - 100 cm	1.1	0.9	0.0	3.8	75	40
100 - 155 cm	0.5	0.4	0.0	1.4	89	8

compared with an earlier investigation of the Hg concentrations of deep groundwater sampled from springs. That investigation showed that Hg-II concentrations generally were less than 1 ng L<sup>-1</sup> (Aastrup, 1987).

The concentrations of Hg-tot, Hg-II and Hg-IIa of the waters of the different soil layers included in the modeling are presented in Table III.

The relations between the mercury fractions varied during the investigation period, the ratios Hg-IIa/Hg-II/Hg-tot being 1:2:8 in the autumn 1987, 1:2:20 in spring 1988 and 1:4:8 in autumn 1988. The increase in the total Hg in spring implies a pronounced peak in the occurrence and transport of Hg during this period.

The variation of Hg level in time was found to be greater than the variation of most other constituents. As Hg is transported in association with organic material there should have been good covariation between these two compounds. In some sampling points, there was a fair covariation, but for most sampling points the covariation was not consistent. In the case of groundwater this might depend on the fact that Hg was analyzed in a filtered (P80) sample, while the organic material was analyzed in an unfiltered sample. Another cause of weak covariation might be variation in time in the size distribution of the organic particles, which lead to variations in the amount of Hg per unit amount of organic matter.

Contamination of samples is probably contributing to some of the variation and the weak covariation with organic material. Contamination may come from the porous ceramic lysimeters. If proper cleaning of the porous material is carried out before installation, porcelain material should give acceptable low bias even for trace metals, although a risk prevails for all materials (Rasmussen *et al.*, 1986; Creasey and Dreiss, 1988). Teflon samplers were tested parallelly with the ceramic cups and were found to yield much higher Hg concentrations than porcelain samplers in the present investigation. This is probably because the larger pores in the teflon allow the passage of larger organic particles associated with Hg. The pore size is 3 µm in the teflon cup, while it is 1 µm in the porcelain (P80) ceramics. However, dissolved and colloidal humus and some larger particles will pass both types of materials. As larger particles are less mobile in soil and groundwater, it may be argued that the exclusion of the biggest particles is desirable (c.f 4.2).

### 3.4. TRANSPORT OF MERCURY

Some generalizations have been made of the geometry of the investigated till area to be able to make the water flow simulations. The soil depth varies greatly along the till profile, but a constant soil depth of 165 cm has been chosen for the simulations. The same subdivisions of the soil were made for the recharge and discharge area.

As mentioned above simulations were made for three subperiods as well as for the whole investigation period. The dominating water flow occurred during spring 1988. The specific flow (L m<sup>-2</sup> yr<sup>-1</sup>) during that period was more than double the flow during autumn 1988 and about 1.5 times the flow during autumn 1987. More than 25% of the flow during the spring 1988 took place as surface run-off in the discharge area compared with 10 to 12% during the other periods.

The simulated water flow and fluctuation of groundwater level were calibrated against the recorded groundwater level (Figure 2.)

The magnitude of the simulated flows, horizontal along the soil layers, vertical crossing the borders between the soil layers, evaporation and root uptake is illustrated in Figure 3 for the whole investigation period. In the simulation a soil profile in the recharge area is coupled to a corresponding profile in the discharge area or rather the temporary discharge area.



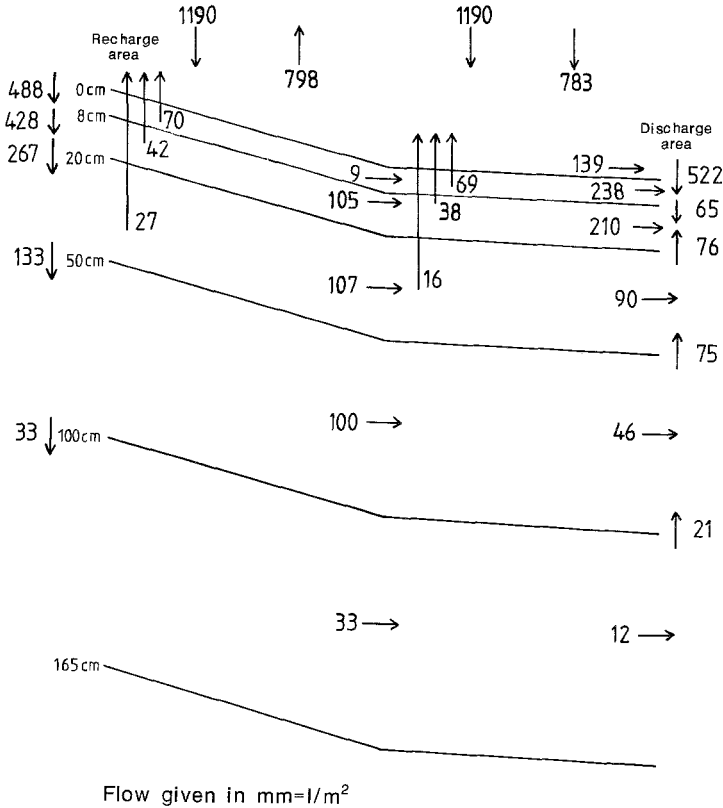


Fig. 3. Annual water flows in the forested slope resulting from simulations with the SOIL model in the recharge and discharge areas. The areal size relations between these two parts of the terrain are not considered in this representation, i.e. all water flows are expressed on an areal basis for each part separately.

When considering the flow of the minicatchment the magnitude of the flow in the discharge area becomes much smaller as the contribution to this area by precipitation is proportional to its portion of the whole minicatchment, which is 6%. The relative distribution of the flow between the different soil layers remains the same as illustrated in Figure 3. The horizontal flow in the discharge area of the minicatchment is presented in Table IV.

The Hg flow has been calculated using the simulated values of flow and the analysed concentrations of Hg. Mean values of the concentrations of the different periods have been used. The horizontal flow of the different Hg fractions during the different simulation periods are presented in Table V. More than 75% of the transport of total-Hg occurred during the 6 mo period spring 1988. The differences in transport between the time periods are not so pronounced for the other fractions.

TABLE IV.

Horizontal water flow in the discharge area in mm = L m<sup>-2</sup> in the minicatchment, where the discharge area amounts to 6%.

Period/layer(cm)	-0	0-8	8-20	20-50	50-100	100-165	total
whole	71	122	108	46	24	6	377
autumn 1987	9	27	34	16	7	2	94
spring 1988	55	67	48	20	8	3	201
autumn 1988	10	24	27	14	7	2	84

TABLE V.

Horizontal mercury flow in the discharge area.

Period	Hg-tot		Hg-II		Hg-IIa	
	g km <sup>-2</sup>	g km <sup>-2</sup> yr <sup>-1</sup>	g km <sup>-2</sup>	g km <sup>-2</sup> yr <sup>-1</sup>	g km <sup>-2</sup>	g km <sup>-2</sup> yr <sup>-1</sup>
whole	4.5	3.4	1.5	1.2	0.5	0.4
autumn 1987	0.5	1.5	0.1	0.4	0.06	0.2
spring 1988	6.3	12.7	0.8	1.5	0.3	0.6
autumn 1988	1.3	2.6	0.7	1.3	0.2	0.3

The transport of Hg-tot and flux balance for each soil horizon are illustrated in the schematic picture in Figure 4. The flux balance for Hg-tot during the whole investigation period show a large accumulation in the mor layer, 15 g km<sup>-2</sup> yr<sup>-1</sup> in the recharge area. The accumulation per unit area is of the same magnitude in the discharge area, but the figures shown in Figure 4 refer to a catchment where the recharge and discharge areas were calculated on a joint km<sup>-2</sup> basis in proportion to their respective size. The accumulation in the mor layer is based on the assumption of an atmospheric deposition of 20 g km<sup>-2</sup> yr<sup>-1</sup>, which is an approximate figure for South Sweden based on measurements in precipitation. The concentration in the moss carpet at Tiveden was 0.12 mg kg<sup>-1</sup> in 1983, a number that may be multiplied by the dry weight production of mosses, 150 g km<sup>-2</sup> yr<sup>-1</sup>, to yield an independent estimate of deposition (Tyler, pers. comm.). The resulting 18 g km<sup>-2</sup> yr<sup>-1</sup> roughly supports the deposition figure used in the flux balance.

The other components of the flux balance, the percolation, the vertical and horizontal transport, are derived from the measurements of Hg concentrations and the modeling of water flows. Compared to the changes and storage in the mor layer, changes of the storage in the other layers were very small. The Hg flow in the different minerogenic soil layers down to 100 cm depth was of the same magnitude, around 1 g km<sup>-2</sup> yr<sup>-1</sup> in the recharge area, but was only 0.2 g km<sup>-2</sup> yr<sup>-1</sup> in the 100 to 150 cm layer. Due to the upward direction of the flow in the discharge area 75% of the flow occurred in the upper 20 cm. Out of this superficial Hg flow about one quarter took place on the surface. The total Hg flow leaving the till slope was 3.4 g km<sup>-2</sup> yr<sup>-1</sup>. The seasonal variation of the Hg flow was very great as the magnitude in flow volume and Hg concentration more or less coincide. About 75% of the Hg transport during the investigation period occurred during spring 1988. Of the 3.4 g km<sup>-2</sup> yr<sup>-1</sup> leaving the slope, 1.3 g km<sup>-2</sup> yr<sup>-1</sup> left the lake Storesjö. It means that an amount corresponding to the difference between these figure

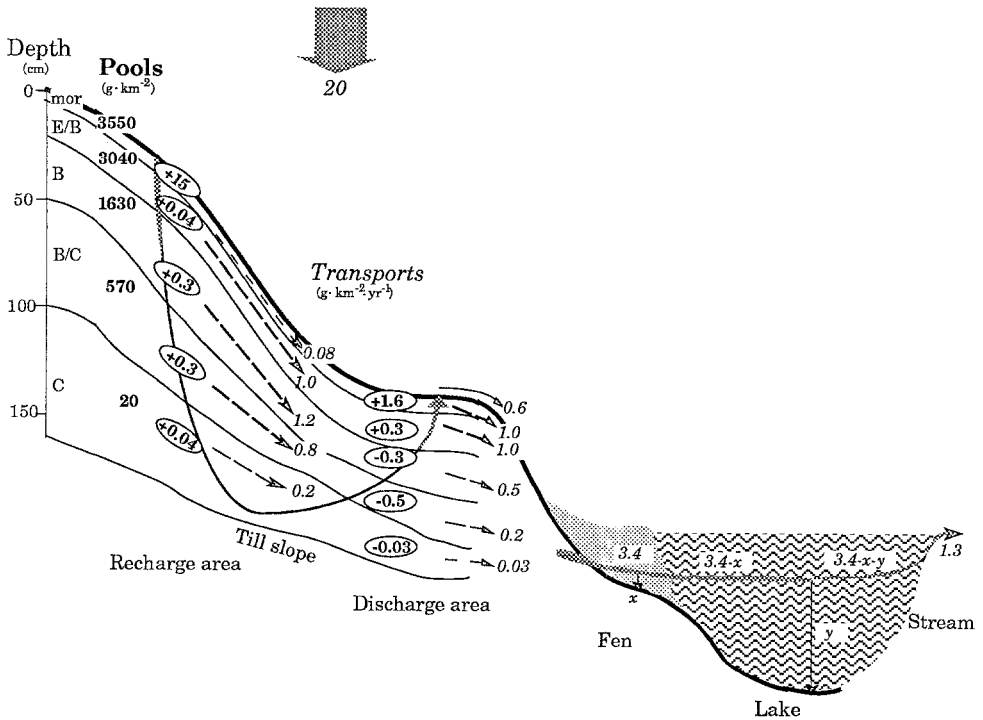


Figure 4. The annual Hg budget for the forested slope, the fen and the lake. Soil pools in different layers, change of pool sizes (shown within ovals) and transports in soil and ground water are expressed per  $\text{km}^2$  of the total forest area, consisting of recharge and discharge areas. The fen and the lake areas are not included in this  $\text{km}^2$ -basis. The discharge area has been estimated to cover 6% of the forest land. The flux out of the lake is expressed on a  $\text{km}^2$ -basis for the catchment as a whole.

was retained in the fen and lake (including the lake sediment). As there were some uncertainties in the result of the Hg analyses, as discussed above, an alternative calculation of the horizontal flow was made. Only the Hg concentrations obtained from the sampling during autumn 1987 were used. These concentrations were the lowest during the investigation period, and thus probably the most reliable with respect to contamination. The mean of these concentrations were multiplied by the flow of the whole investigation period, and thus giving a minimum transport of Hg. The "minimum" transport of Hg was calculated to be  $1.5 \text{ g km}^{-2} \text{ yr}^{-1}$ , which is only  $0.2 \text{ g km}^{-2} \text{ yr}^{-1}$  larger than the Hg transport from the lake Storesjö catchment area.

In the calculation of the transport balance, some unknowns were excluded. These are the losses of gaseous Hg and the uptake of Hg into the plant biomass. Mercury volatilization is probably a minor process in acid forest soils, effectively prevented by binding of Hg to humus (MacLean, 1974; Andersson, 1979). However, a few measurements made in Swedish forest sites indicate a flux that may well be important in comparison with deposition (Schroeder *et al.*, 1989). According to these measurements made during a summer month, the emission rate is of the order of  $1 \text{ ng Hg m}^{-2} \text{ hr}^{-1}$ , which corresponds to  $8 \text{ g km}^{-2} \text{ yr}^{-1}$ . This figure would to a great extent influence the net accumulation in the mor layer. The emission from soil is however probably

much lower during other seasons of the year, and it is difficult to estimate a figure of the yearly emission, which could be included in the transport balance of the Tiveden area.

There is evidence from vegetation growing on contaminated soil, that Hg entering the roots is extremely immobile in the plant and will remain in the below ground parts (Rauter, 1976; Fukuzaki *et al.* 1986). Experiments with spruce seedlings show that Hg levels in the whole plants will be proportional to outer solution concentrations, but a magnitude of hundred times lower in the shoots than in the roots (Godbold and Hüttermann, 1988). Furthermore, only a small fraction of the Hg taken up by the shoots is permanently incorporated in the woody parts of the biomass. All this indicates that the permanent storage in biomass is small compared to the fluxes between the soil layers and is disregarded in the transport balance.

#### 4 Conclusions

The total pool of Hg in the investigated minicatchment area corresponds to  $8.8 \text{ kg km}^{-2}$ , divided on the different soil layers accordingly; the mor  $3.6 \text{ kg km}^{-2}$ , the E-horizon  $0.6 \text{ kg km}^{-2}$ , the upper B-horizon  $2.4 \text{ kg km}^{-2}$ , the lower B-horizon  $1.6 \text{ kg km}^{-2}$  and the C-horizon  $0.6 \text{ kg km}^{-2}$ . The total amount is probably somewhat higher in areas with deeper soil cover. The surplus quantity above an initial background level in the mor layer,  $2.5 \text{ kg km}^{-2}$ , corresponds to more than a century of anthropogenic deposition at  $20 \text{ g km}^{-2} \text{ yr}^{-1}$ . The additional  $3.6 \text{ kg km}^{-2}$ , added to the B-horizon of the mineral soil, has probably been accumulated to that amount during a much longer time span when atmospheric deposition was at a much lower level. This Hg has been incorporated in the soil during the build-up of organic material as part of the soil-forming process. The interpretation is supported by our present mass balance showing an almost complete interception of Hg in the mor layer in the high deposition situation of today and only a minute accumulation in the mineral soil.

The Hg concentrations in water were very variable in time. The mean values for all samples were  $11.9 \text{ ng L}^{-1}$  for Hg-tot,  $3.6 \text{ ng L}^{-1}$  for Hg-II and  $1.2 \text{ ng L}^{-1}$  for Hg-IIa. The concentration in soilwater and groundwater tend to decrease with depth, at least below 50 cm depth. The covariation between Hg and organic material in water was not consistent, but the highest Hg concentrations occurred in waters with the highest organic contents. The relations between the Hg fractions varied during the investigation period, the ratios Hg-IIa/Hg-II/Hg-tot being 1:2:8 in the autumn 1987, 1:2:20 in spring 1988 and 1:4:8 in autumn 1988, indicating a pronounced peak in the transport of the least reducible Hg during spring 1988.

The total transport of Hg from the minicatchment was estimated to be  $3.4 \text{ g km}^{-2} \text{ yr}^{-1}$ . About 75% of the transport occurred in the upper 20 cm of the soil in the discharge area, including the surface run-off. The variation in Hg transport with time was great and 75% of the transport of total Hg took place during the 6 mo period of spring 1988. The transport in the stream leaving the larger catchment was estimated to be  $1.3 \text{ g km}^{-2} \text{ yr}^{-1}$ . This indicates that a substantial portion of the Hg is trapped in the fen and in the lake sediments (Figure 4).

The transport balances showed that around 80% of the deposition of Hg was retained in the mor. The downward flux in the recharge area is substantial but there are hardly any changes in the store of the layers of the mineral soil.

A minimum transport, using the lowest concentrations in the data set, has been estimated to be  $1.5 \text{ g km}^{-2} \text{ yr}^{-1}$ .

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