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## SORPTION AND MOBILIZATION OF MERCURY IN PEAT SOIL

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The sorption, leaching and evaporation of mercury was studied in peat lysimeters. Most of the mercury was adsorbed at the top of the peat soil columns. The leaching of mercury was increased by irrigation or chloride addition and reduced by the addition of acid rain or fertilizers.

### Introduction

The construction of man-made lakes and the control of the water level causes a mobilization of mercury from the inundated soil, which is revealed as elevated mercury contents in fish and people who eat fish<sup>1-5</sup>. High mercury contents have also been found in fish from unregulated lakes without any known mercury discharge. It has been assumed that mercury may be mobilized from the soil by ditch digging in forests and bogs and related operations<sup>6-7</sup>.

Fish with high mercury contents are often from lakes with low pH-values and high humus contents<sup>8-9</sup>. In man-made lakes the mercury content of fish is influenced by the age of the basin, the amplitude of the regulation and the amount of organic matter<sup>4</sup>. The water quality of Finnish man-made lakes differs significantly from that of natural lakes: pH and oxygen values are lower, the suspended solids, iron, chloride and nutrient values are higher<sup>10-11</sup>.

Mercury is strongly but reversibly adsorbed to the organic matter in soil and water<sup>12-14</sup>, but little is known about the factors affecting the sorption and leaching of mercury in peat soils. The results presented here are preliminary and the investigation will be extended to cover several physico-chemical parameters.

### Material and methods

The peat used in our experiments originated from Torrnsuo in south west Finland and was slightly humificated white Sphagnum peat (v. Post H2, pH 3.3 directly from the samples, extractable chloride  $12 \text{ mg l}^{-1}$  d.w.). The sample was taken from the top layer of the bog and deep-frozen. Peat was applied into 16 polyethylene lysimeter columns, the length of which were 40 cm and diameter 6.3 cm. 900 g of peat was pressed into a volume of 0.8 l in each column.

$^{203}\text{Hg}$ -mercuric acetate (code HBS 2; Amersham Co., England) was used as tracer.  $10.5 \mu\text{Ci}$  was added superficially to 12 columns. The tracer was mixed with inactive mercuric acetate and the total mercury addition was  $100 \mu\text{g}$  per column. To four columns no additions were made in order to detect any possible contamination<sup>15</sup>. The experiment was performed in room temperature (approximately  $20^\circ\text{C}$ ).

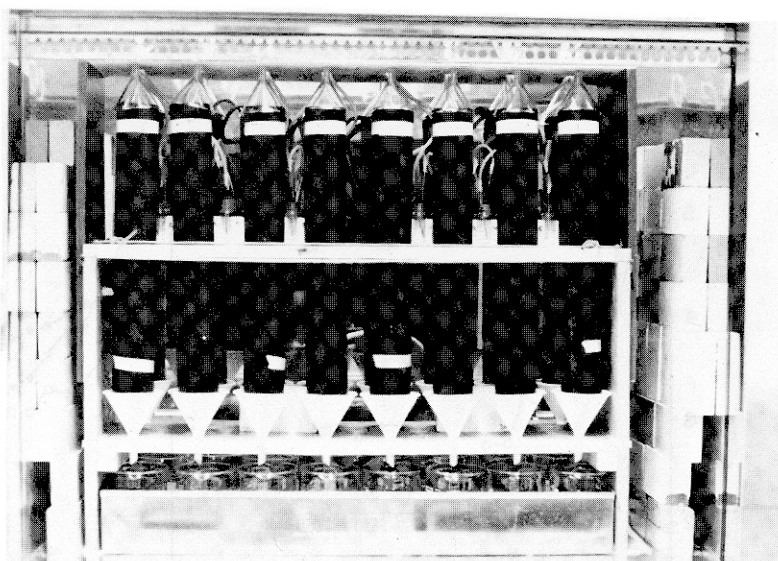
1.5 g KCl was added to four columns to get a 0.02 M chloride concentration in which the formation of mercury-chloride complexes is theoretically possible in the pH-range of peat soils<sup>16</sup>. The chloride addition was a thousandfold that of Scandinavian precipitation. Phosphorous ( $\text{Ca}_3(\text{PO}_4)_2$ ), potassium and nitrogen ( $\text{KNO}_3$ ) were added to four columns in amounts corresponding to the amounts recommended for the forest fertilizing of Finnish mires (5.5 mg P, 10.1 mg K and 26.4 mg N per column).

During 34 days water was added superficially to the peat columns seven (8 columns) or fifteen times (8 columns). Each addition was 160 ml, which corresponds to 60 mm of precipitation. Half of the columns got distilled water and the other artificial acid rain (pH 3.9,  $43 \mu\text{M SO}_4^{2-} \text{ l}^{-1}$ ,  $40 \mu\text{M NO}_3^- \text{ l}^{-1}$ ). The lysimeter columns were placed on funnels collecting the leachates, which were measured and analysed 4-5 times during the experiment (Fig. 1). The absorbances of the leachates were measured at the wavelength 270 nm (Spektrofotometer SF-16) using distilled water as blanks. A leachate from a separate experiment was fractionated in samples of 20 ml using gel filtration (Sephadex 100).

The columns were covered with glass funnels collecting the evaporated gases into a cysteine trap and a HgBr-KBr-trap. An acid  $\text{KMnO}_4$ -trap ensured that no mercury passed to the sewage system. The 1% cysteine-hydrochloride solution was made in a 0.2 M Tris (hydroxi-methylaminomethane)-buffer<sup>17</sup>. The bromide solution contained  $100 \text{ g KBr l}^{-1}$  and  $15 \text{ g HgBr l}^{-1}$ . The volume of the traps was kept at 10 ml by compensating the evaporated water daily. The cysteine trap was intended to collect the evaporated  $\text{Hg}^{2+}$  and  $\text{CH}_3\text{Hg}^+$ , and the bromide trap to collect the evaporated  $\text{Hg}^0$  and  $(\text{CH}_3)_2\text{Hg}$ <sup>18</sup>.

At the end of the experiment the columns were deep-frozen and samples of  $3.7 \text{ cm}^3$  were taken at distances of 2 cm. The trap solutions, the leachates and the peat samples were measured by a gamma-sample counter (Ultragamma 1280;

Fig. 1.  
The lysimeter  
columns used in  
the experiments.



Wallac Co., Finland). The volume of the samples was 5 ml, the measuring time 300 s and the counting efficiency  $43 \pm 1.3$  %. Samples with the same activity as that added to the columns were used as standards.

### Results

In the four columns without any tracer additions no activity was found in the peat samples, trap solutions or leachates. Nor was any labelled mercury adsorbed to the walls of the polyethylene columns.

Most of the added mercury was strongly adsorbed to the uppermost 3.5 cm layer of the peat columns (Fig. 2). The chloride addition caused an increased leaching of mercury and the fertilizing a decreased leaching. The acid rain enhanced the adsorption of mercury to the peat soil. Mercury was leached from all of the columns to which 900 mm water was added except the fertilized ones. At the smaller water addition (420 mm) the leaching decreased significantly and mercury was leached only from the columns to which chloride was added.

A significant correlation ( $r=0.563$ ,  $n=28$ ) was found between the absorbance (270 nm) and the activity ( $^{203}\text{Hg}$ -content) in the leachates, which implies a binding of mercury to the humic substances. Most of these substances were small-molecular fulvic acids while most of the mercury was adsorbed to the large-molecular humic acid fraction (Fig. 3).

From all columns, to which mercury was added, mercury was evaporated. A low but measurable activity (about 0.01% of the total addition was accumulated in the cysteine traps (Fig. 4). More mercury (0.01 - 1 % of the total addition)

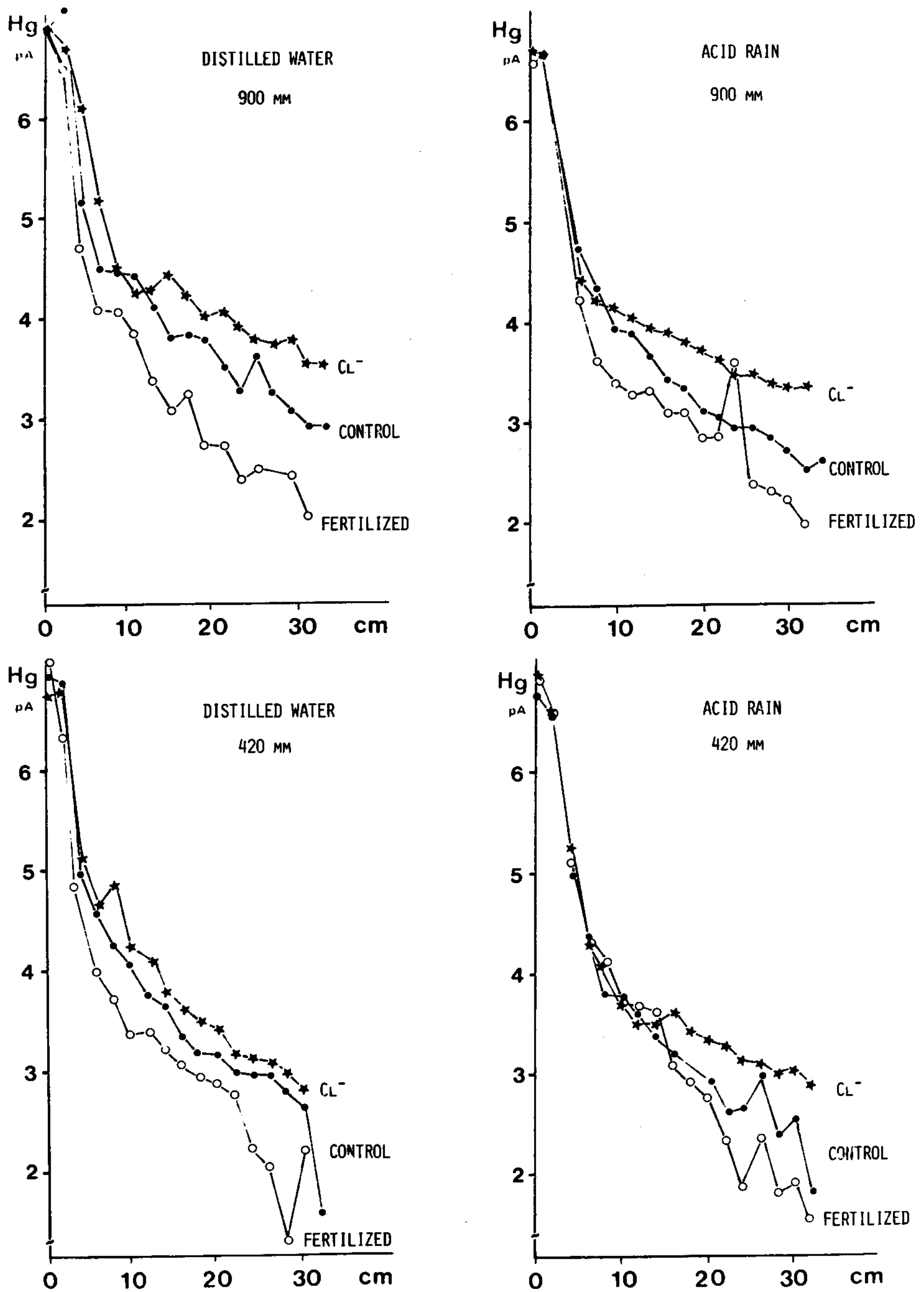


Fig. 2. The amount of mercury (as a logarithm of the activity (cpm) of  $^{203}\text{Hg}$ ) at different depths of the peat columns at the end of the experiment. The activity of the  $^{203}\text{Hg}$ -addition was 6.7 pA.

was usually found from the bromide traps. The addition of chloride or fertilizers increased the amount of mercury trapped by the bromide solutions.

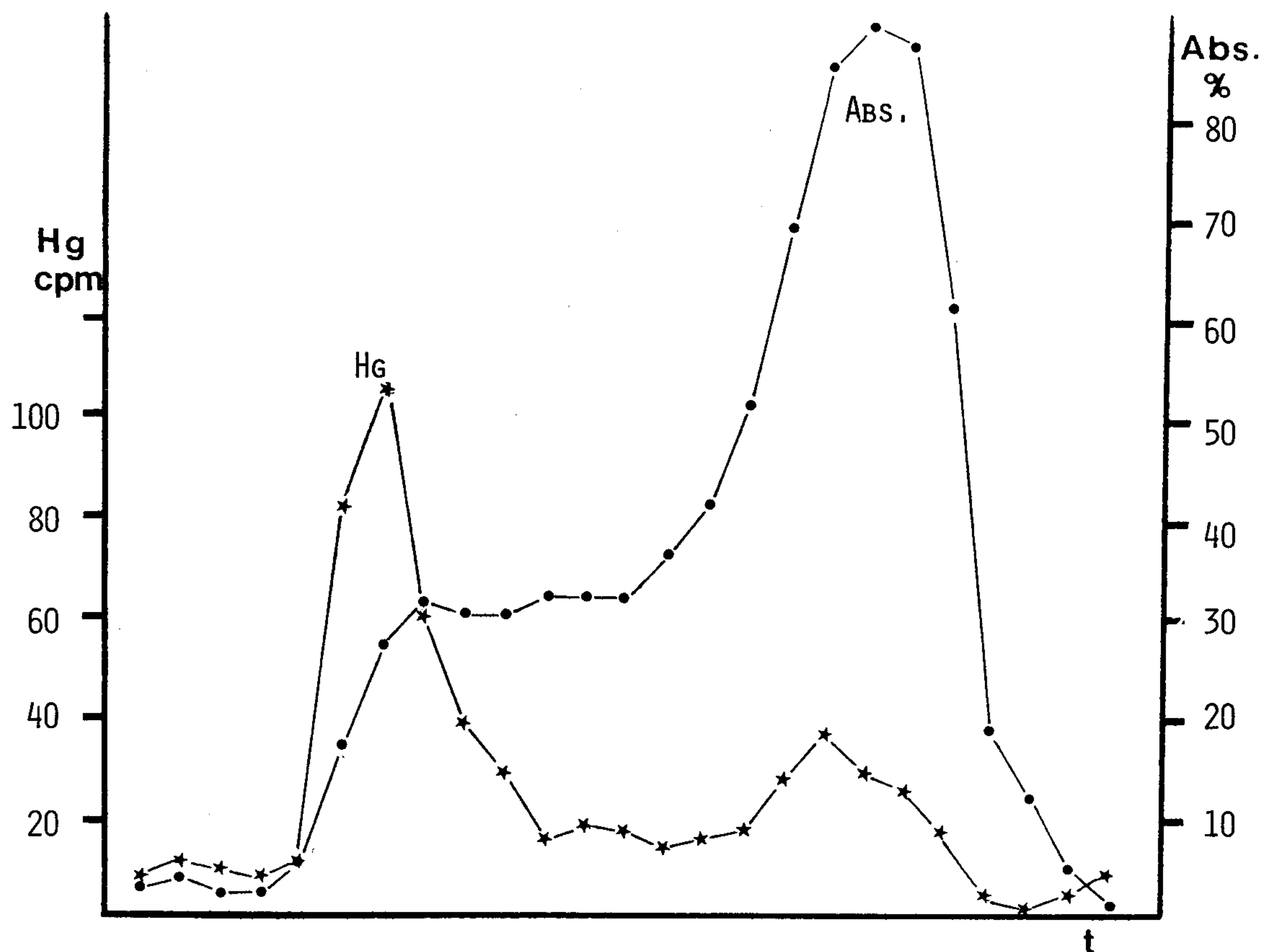


Fig. 3. The differentiation of mercury (cpm  $^{203}\text{Hg}$ ) in the water leached in six days through a peat column in relation to the absorbance (270 nm) of the leachate. The leachate was gel filtrated into samples of 20 ml.

### Discussion

The amount of leached mercury in our experiment correlated positively with the amount of leached organic matter, which implies the essential role of humus in the transport of mercury between soil and water. Humus has been found to both promote the leachability of mercury<sup>17, 19-20</sup> and to cause a non-biological methylation of mercury<sup>21-22</sup>. A high pH-value and chloride content will promote the solubility of mercury<sup>23-24</sup> and an increased acidity obviously causes a stronger binding to the organic matter (soil, water humus and organisms), which promotes the bioaccumulation of mercury. Acid rain reduced the leachability of

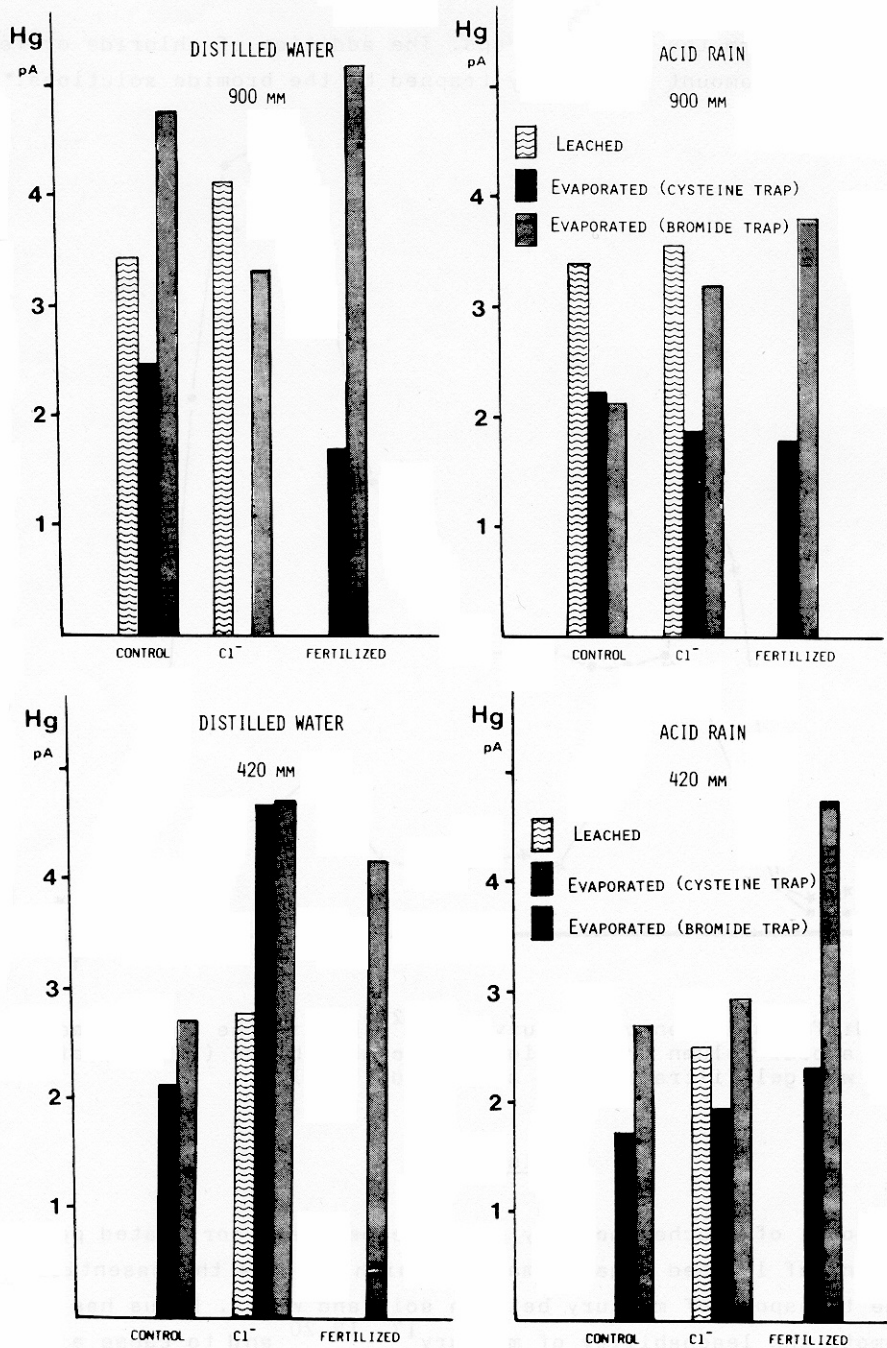


Fig. 4. The amount of mercury (as a logarithm of the activity (cpm) of  $^{203}\text{Hg}$ ) leached through the peat columns or trapped by the cysteine or bromide traps. The activity of the  $^{203}\text{Hg}$ -addition was 6.7 pA.

mercury from our peat soil but it is possible that acid rain could cause a mobilization of mercury from mineral soils<sup>25-26</sup>.

In our experiment the chloride-free fertilizers reduced the leachability but increased the evaporation of mercury. This may be a result of stimulated microbe activity. Our results indicate that the mercury-chloride complexes occurring at the pH and chloride ranges of peat may influence the mobility of mercury despite of the strong binding to the organic matter. The chlorides used as road deicing salts may possibly mobilize mercury from the soil<sup>27</sup>.

#### Acknowledgements

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