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Sorption of Mercury in Soils with Different Humus Content

Martin Lodenius, Ari Seppänen, and Sari Autio

Department of Environmental Conservation, University of Helsinki,
SF-00710 Helsinki, Finland

The strong sorption of mercury to humic matter in soil and water has raised the question about the influence of organic matter of different soil types on the mobilization of mercury from soil. Mercury is normally bound to humic and fulvic acids, which may be released in connection with flooding, draining and ditching (Rekolainen et al. 1986, Verta et al. 1986). High mercury contents in fish from man-made lakes have been reported mainly from temperated regions (e.g. Lodenius et al. 1983a, Bodaly et al. 1984). This has been assumed to be a result of the slower metabolism of methyl mercury in cool water but the effect of temperature on the mobilization process is still poorly known.

The sorption and leaching of mercury in three different soils was studied in vitro using mercury concentrations near the natural level. Soil lysimeters were watered with distilled water or artificial acid rain at two temperatures

MATERIAL AND METHODS

The experiments were performed using polyethylene lysimeter columns (length 40 cm, ϕ 6.3 cm; Lodenius et al. 1983b) filled with soil (900g, 0.8 l). The soils were slightly humified Sphagnum peat, sand (< 2 mm) with a low content of humic matter and fine sand of pure quartz (0.05 - 0.2 mm, 99.5 % SiO₂). Some properties of the peat and sand soil samples are given in Table 1. The high E₄/E₆-ratios indicate a high portion of small-molecular-weight material (fulvic acids). In one lysimeter set a peat layer (5 cm at 20 cm depth) was inserted within the quartz sand column.

Send reprint requests to M. Lodenius at the above address.

Table 1. Some properties of the peat and sand samples used in the experiments.

	pH ¹	C (%) ²	N (%) ²	E ₄ /E ₆ ³
peat	3.6	44	1.4	12
sand	4.4	0.47	-	8.5

¹ from 0.02 N CaCl₂, ² Hewlett-Packard 185B C-N-analyzer, ³ ratio of absorbances at 465 and 665 nm in 0.05 N NaHCO₃-leachate

Mercury was added superficially as ²⁰³Hg-acetate. 10.5 µCi (389 kBq) of the tracer was added to each column mixed with the carrier so that the total amount of added mercury was 100 µg. Two parallel columns were used for all lysimeters. The leaching from peat and mineral soil samples were studied at two temperatures: + 5°C and + 20°C (Table 2). The acid rain was obtained as described earlier (pH 3.9, 43 µM SO₄⁼/l, 40 µM NO₃/l; Lodenius et al. 1983b). The amount of water added to each column was 1920 ml (12x160 ml). The length of the experiment was 50 d.

The leachates were collected periodically during the experiments and the volume, pH, colour (absorbance at 420 nm) and ²⁰³Hg-activities were measured. The mercury contents of the columns were measured externally from two directions using a one channel gamma-sample counter connected to a printer. External scanning has also been successfully used by Semu et al. (1985). The measurements from different soils are not directly comparable and for this reason no unit is given for the distribution of mercury in different soil columns (Figs 1-3).

Table 2. Scheme for the experimental treatments (duplicate columns).

Columns	Acid rain (20°C)	H ₂ O (5°C)	H ₂ O (20°C)
peat	A	B	C
sand	D	E	F
quartz sand	G	H	I
quartz-peat-quartz	J	K	L

RESULTS AND DISCUSSION

Significant differences were detected between the different soils analysed (Figs 1-3). As there was a good agreement between the duplicate columns and between the two scanning measurements all the results reported in Figs 1-4 are means of four determinations. After addition of distilled water the mercury was leached deeper in the sand columns than in the peat or in the quartz sand (Figs 1 and 3). In the peat columns two distinct peaks were obtained at + 20°C (Fig. 1) indicating that the mercury may have been bound as two different compounds. Only one peak appeared at + 5°C (Fig. 3) or after addition of acid rain (Fig. 2). In the peat and sand columns the mercury had leached into deeper layers at + 5°C than at + 20°C (Figs 3 and 1).

Even in the quartz sand columns significant amounts of mercury were bound (Figs 1-3). In the quartz-peat-quartz columns the mercury peak never reached the peat layer and the distribution of mercury resembles that of the pure quartz sand columns.

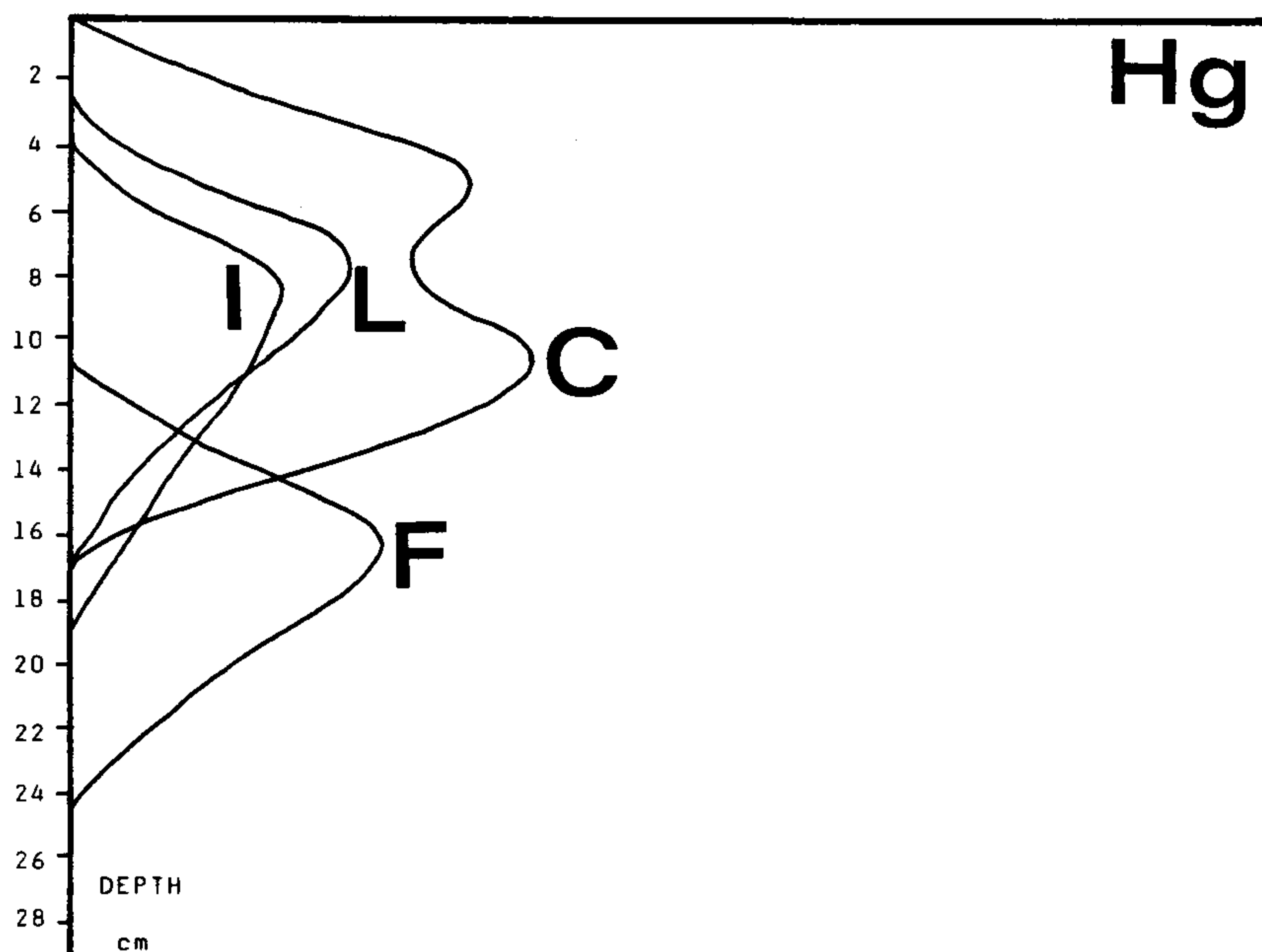


Figure 1 Sorption of mercury in + 20°C after watering with distilled water. C = peat, F = sand, I = quartz sand, L = quartz-peat-quartz.

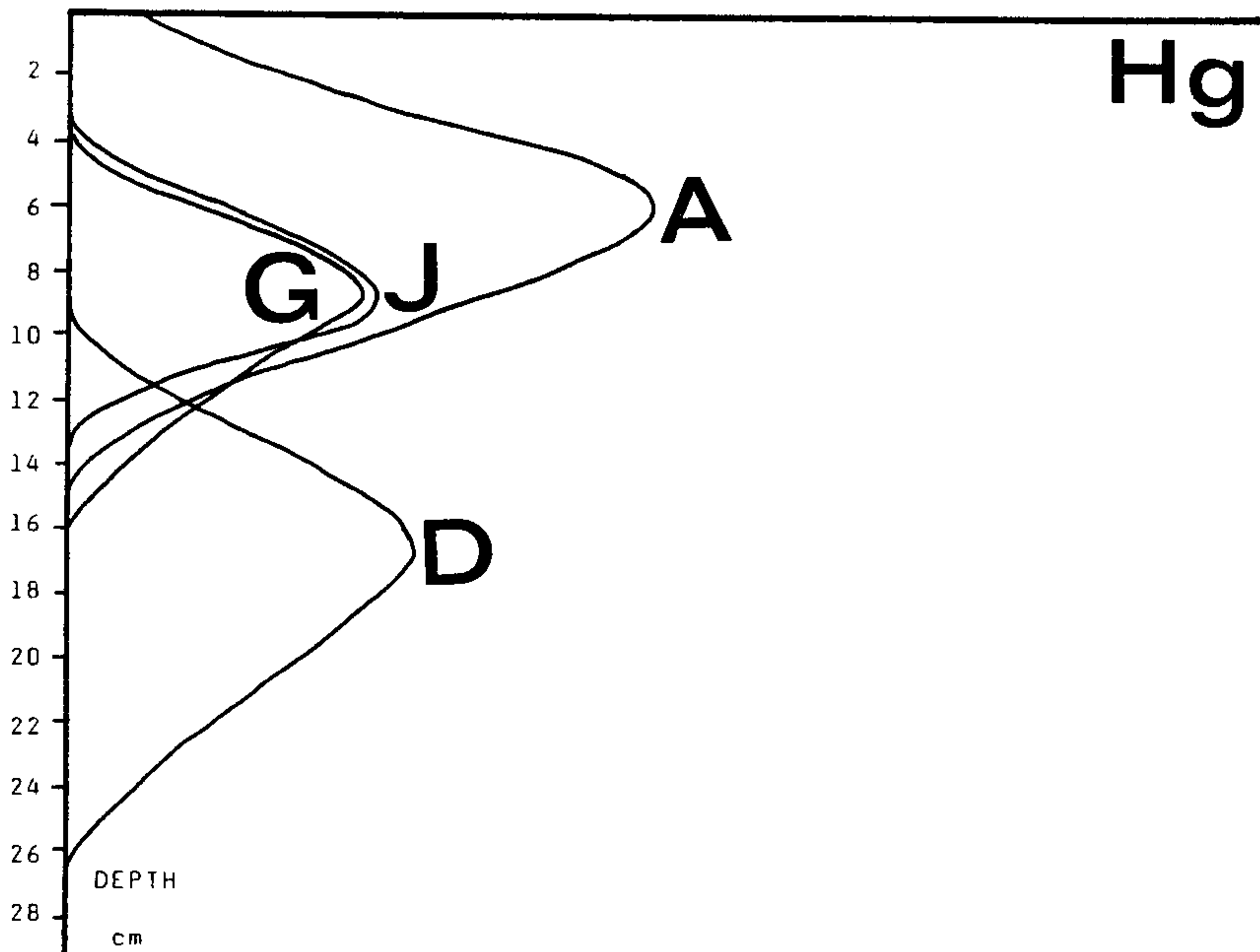


Figure 2 Sorption of mercury in + 20°C after watering with acid rain. A = peat, D = sand, G = quartz sand, J = quartz-peat-quartz.

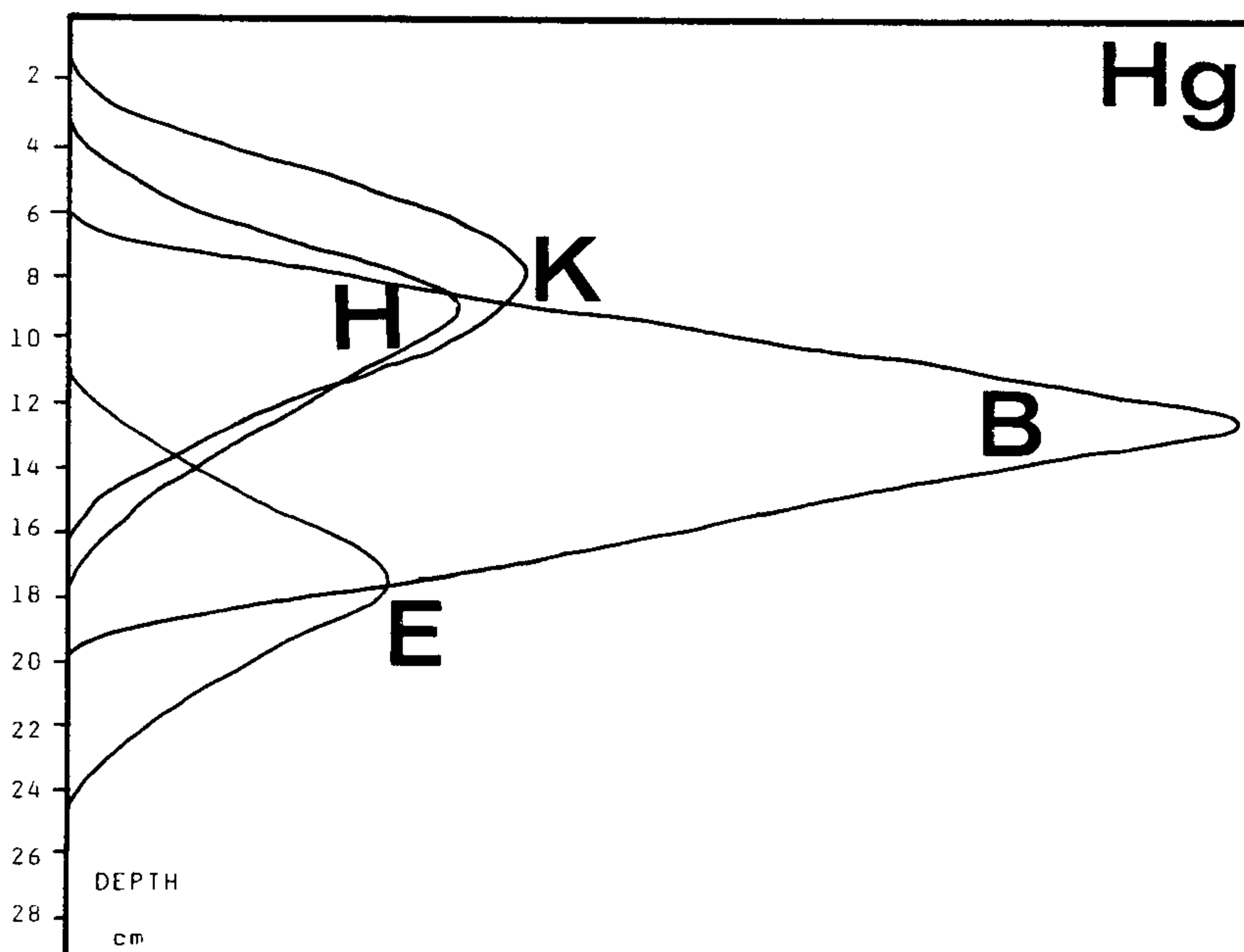


Figure 3 Sorption of mercury in + 5°C after watering with distilled water. B = peat, E = sand, H = quartz sand, K = quartz-peat-quartz.

The addition of acid rain caused a very strong leaching from the pure quartz sand - approximately five times as much as compared with the distilled water (Fig. 4). Low amounts of mercury were leached from the quartz-peat-quartz columns. However, this was not confirmed by any accumulation in the peat layers of these columns. The acidification decreased (approximately three times) the leaching of mercury from sand and peat; the amounts of mercury leached from the sand columns were lower than from the peat columns (Fig. 4).

A decrease of temperature did not affect the leaching of mercury from the peat soil by distilled water but the sorbed amounts were strongly concentrated into one layer about 10 cm from the top of the column (Fig. 3). Contrary to the other experiments no significant amounts of mercury were detected at the top of any column at this temperature. At +5°C the leaching from sand was four times greater and that from quartz sand three times smaller than at room temperature.

The soil type and the content of organic matter seem to be very important for the sorption of mercury. Even a low humus content is enough to sorbe significant amounts of mercury. Zvonarev and Zyrin (1983) found that most of the mercury in organic soils is bound to sites with high bonding energies, which means that the extractability of mercury is low.

In a lysimeter experiment different metal salts added to pure sand columns were easily removed by leaching while metals (including Hg) bound to humic matter were strongly retained (Gomez and Juste 1981). In a clay soil (kaolinite) Semu et al. (1986) found a significant correlation between the mercury sorption capacity and the content of organic carbon and the cation exchange capacity while there was a significant negative correlation with the clay content. All these correlations were insignificant for sandy soils. Aomine and Inoue (1967) found that the soil mineral matter contributed little to the sorption of inorganic mercury even though it was important for the sorption of phenyl mercury. In our pure mineral soil mercury was sorbed but the sorption was weak especially at acid conditions.

The two mercury peaks observed in the peat columns (Fig. 1) in this experiment (but not in the previous one; Lodenius et al. 1983b) indicate a partial transformation of the mercury or a binding to two different organic fractions. This transformation is prevented by a low temperature and by addition of acid rain. As pH does not influence the binding of mercury to different organic fractions (Lodenius & Seppänen

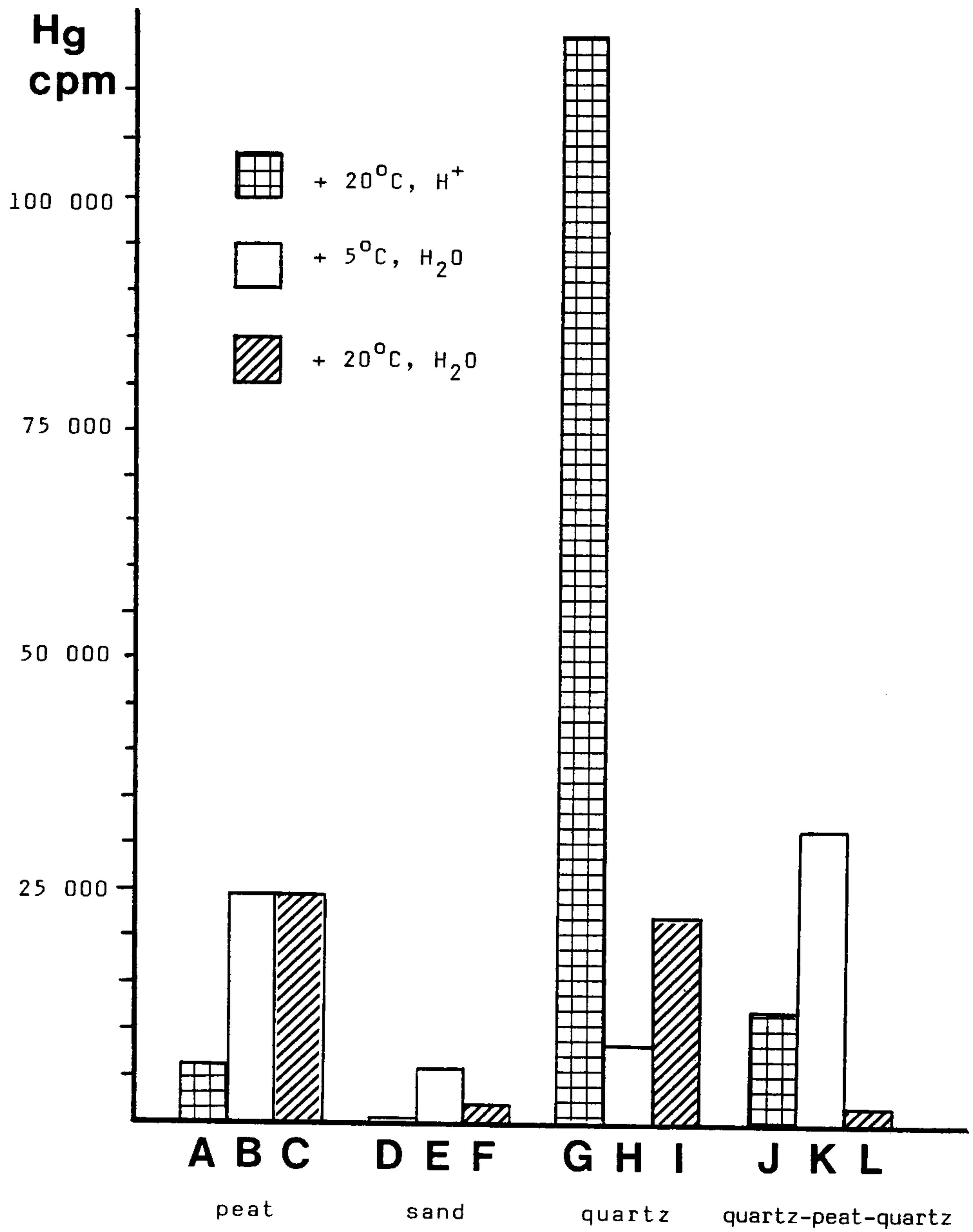


Figure 4 Total leaching of mercury (cpm) from the different columns.

1984) it seems not likely that these peaks would have been caused by binding to different organic fractions. Possibly the lower peak might be methyl mercury which is more soluble than mercury acetate and which may be formed in the presence of humic substances (eg. Lee et al. 1985).

Gomez and Juste (1981) have characterized the humic substances binding heavy metals. The chemical composition of mercury humate differed from those of other metals (Pb, Ni, Cd) having a smaller ash content and a bigger Na-content. The amounts of mercury bound to the humic matter corresponded only partially to the exchange capacity of the soil while it corresponded well to it for the other metals.

The effects of temperature on the leaching of mercury were significant, although opposite, for the sand and quartz columns and not for the peat columns but the reasons for these effects are not known.

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