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Accumulation and distribution of mercury in Dutch soils

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Summary

Eleven Dutch soils have been sampled up to a depth of 1 m and the total amount of mercury has been determined. The soils selected differ widely in characteristics, location and farming practice. Included are foreland soils from the river Rhine, at Millingen, Valburg and the Biesbos, which show a mercury content in the top 20 cm layer of 0.10, 3.35 and 10.4 ppm, respectively. Soils in the bulb culture area, at Hillegom and Anna Polowna Polder, show a mercury content of about 0.15 ppm in the top 20 cm layer. Permanent pastures have been choosen as references. No profile disturbances have occurred in these soils for the last 20 years. Sampling sites are at Biesbos, Alkmaar, Hilversum, Amersfoort, Anna Polowna Polder and Schoonebeek. They show with one exception a mercury content of about 0.09 ppm in the top 20 cm.

Introduction

Insufficient information is available on the behaviour of mercury in soils to allow predictions to be made concerning the fate of mercury compounds added to soils. Eleven soils were therefore selected, differing widely in characteristics, location and farming practice. The total amount of mercury in these soils was determined up to a depth of 1 meter.

Material and methods

Sampling sites, grouping

The soils selected can be divided into three groups:
Group I. Soils known as foreland soils from the river Rhine. The Rhine is heavily contaminated with pollutants; about 70 000 kg of mercury are discharged into the North Sea annually. The foreland soils are frequently flooded, usually in winter. The sampling sites are placed in such a sequence that the clay content increases as the sites become closer to the North Sea.
Group II. Soils situated in areas used for bulb culture. Mercury compounds are applied as fungicides in these areas.
Group III. Soils permanently used as pastures. No profile disturbances have occurred for the last 20 years. These series of soils have widely differing soil characteristics and include calcareous and non-calcareous soils, a variation of clay content from 2 to 40% and a peat soil with an organic matter content of more than 95%.

Description of the profiles of the sampling sites

Group I

1. *Millingen.* Area frequently flooded with Rhine water, foreland soil, pasture, distance to the North Sea about 200 km.

0-25 cm	clay sand	clay 5%	organic matter 4%	calcareous
> 25 cm	clay poor sand	clay <2%	organic matter <1%	calcareous

2. *Valburg.* Area frequently flooded with Rhine water, foreland soil, pasture, distance to the North Sea about 150 km.

0-15 cm	heavy 'zavel'	clay 22%	organic matter 6%	calcareous
15-25 cm	heavy 'zavel'	clay 24%	organic matter 2.5%	calcareous
> 25 cm	heavy 'zavel'	clay 20%	organic matter <1%	calcareous

3. *Biesbos.* Area frequently flooded with Rhine water, reed culture, distance to the North Sea about 50 km.

0-15 cm	heavy clay	clay 40%	organic matter 8%	calcareous
> 25 cm	heavy clay	clay 40%	organic matter 2%	calcareous

Group II

4. *Hillegom.* Area used for bulb culture.

0-50 cm	clay poor sand	clay 3%	organic matter 3%	calcareous
> 50 cm	clay poor sand	clay 2%	organic matter <1%	calcareous

5. *Anna Polowna Polder.* Area used for bulb culture.

0-50 cm	clay poor sand	clay 3%	organic matter 2.5%	calcareous
50-70 cm	clay poor sand	clay 2%	organic matter <1%	calcareous
70-90 cm	light 'zavel'	clay 14%	organic matter <1%	calcareous
> 90 cm	light clay	clay 25%	organic matter <1%	calcareous

Group III

6. *Biesbos.* Area reclaimed since 50 years, previously frequently flooded with Rhine water, permanent pasture.

0-25 cm	heavy clay	clay 40%	organic matter 7%	calcareous
> 25 cm	heavy clay	clay 40%	organic matter 2%	calcareous

7. *Alkmaar.* Agricultural area, permanent pasture.

0-25 cm	heavy 'zavel'	clay 20%	organic matter 8%	calcareous
> 25 cm	heavy 'zavel'	clay 20%	organic matter <1%	calcareous

8. *Hilversum.* Agricultural area, permanent pasture.

0-20 cm	slightly loamy sand	clay 5%	organic matter 5%	non-calcareous
20-60 cm	clay poor sand	clay 2%	organic matter 1.5%	non-calcareous
> 60 cm	clay poor sand	clay 2%	organic matter <1%	non-calcareous

9. *Amersfoort.* Agricultural area, permanent pasture.

0-30 cm	slightly loamy sand	clay 5%	organic matter 8%	non-calcareous
30-80 cm	slightly loamy sand	clay 5%	organic matter 1.5 %	non-calcareous
> 80 cm	loam poor sand	clay 2%	organic matter <1%	non-calcareous

10. *Anna Polowna Polder.* Bulb-growing area, permanent pasture.

0-10 cm	clay poor sand	clay 2%	organic matter 12%	calcareous
10-30 cm	clay poor sand	clay 2%	organic matter 1.5%	calcareous
30-80 cm	clay poor sand	clay 2%	organic matter <1%	calcareous
> 80 cm	heavy 'zavel'	clay 22%	organic matter <1%	calcareous

11. *Schoonebeek.* Agricultural area, permanent pasture.

0->100 cm peat soil organic matter > 95%.

Sampling technique

A sampling technique has been developed for obtaining soil samples from each desired and known depth, even from below the soil water level. Fig. 1 presents this technique schematically. Sampling is done by means of a perspex tube with a length of 150 cm and an inner diameter of 2.3 cm. A hollow augerhead of hardened stainless steel is screwed into the bottom end of this tube (situation 1). The tube is gently knocked into the soil

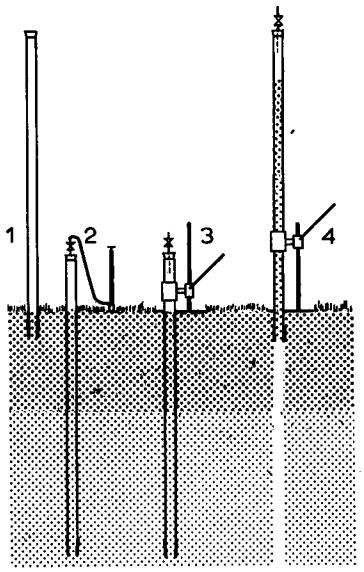

Fig. 1. Schematic presentation of a technique to obtain soil samples from each desired and known depth, even from below the soil water level.

with a wooden hammer. The top of the column is closed by a rubber stop with valve and underpressure is applied by means of a small pump (situation 2). The tube is lifted from the soil with a jack (situation 3), taking the soil core with it even from below the phreatic level (situation 4). The augerhead is unscrewed and the soil core pushed out and cut into pieces.

Analytical technique

The total mercury content is determined according to Melton et al. (1971), by applying flameless atomic absorption spectrophotometry. The soil is treated with a mixture of $HNO_3/H_2SO_4/K_2S_2O_8$. After a reducing solution has been added the mercury is blown from the solution into a closed system containing a quartz cell located in the beam path.

Results

The mercury content was determined to a depth of up to 100 cm. Each 5-cm layer was analysed up to a depth of 30 cm and from then on each 10-cm layer. The values measured are averages of duplicates. The results are shown in Fig. 2 and Table 1.

Discussion

The soils of Group I – foreland soils from the river Rhine – show an increasing amount of mercury in the top soil (0-20 cm) when placed in a sequence of increasing clay content. The soil at Millingen, about 200 km from the sea, with a clay content of about 2%, shows a mercury content of only 0.10 ppm. At Valburg, 50 km closer to the sea and with a clay

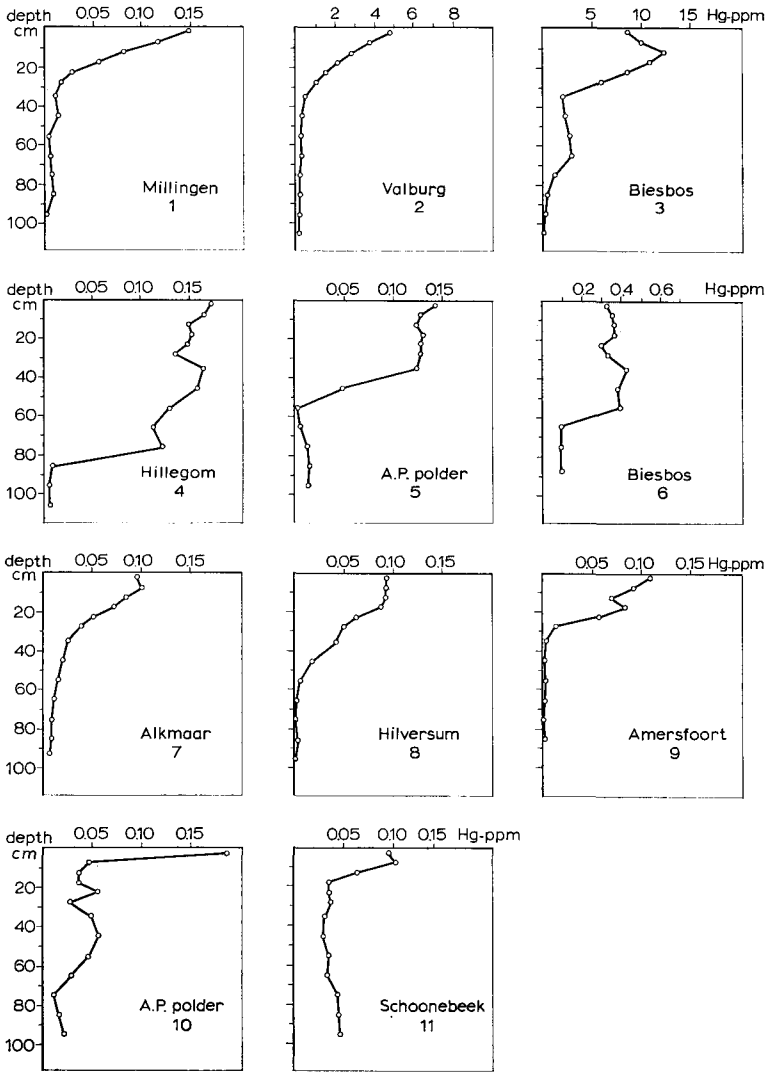

Fig. 2. The content of mercury in some Dutch soils in relation to depth. Note that the horizontal axes of graphs 2, 3 and 6 differ from each other and from the horizontal axes of the other graphs.

content of about 22%, the mercury content has increased to 3.35 ppm, whereas at Biesbos with a distance of about 50 km from the sea and a clay content of about 40%, the mercury content has increased to 10.43 ppm. Obviously the mercury stems from the river Rhine and it is strongly adsorbed by clay.

The soils of Group II, used for bulb culture, show a mercury content of about 0.15 ppm. Mercury compounds have been applied as fungicides on these soils for many years. These applications have not resulted in an excessive accumulation of mercury in these soils.

Table 1. The mercury content in the 0-20 and 20-100 cm layer of Dutch soils, respectively.

Soil No	Location	Hg content (ppm) 0-20 cm	20-100 cm
I-1	Millingen	0.10	0.01
I-2	Valburg	3.35	0.45
I-3	Biesbos	10.43	2.60
II-4	Hillegom	0.16	0.10
II-5	Anna Polowna Polder	0.13	0.05
III-6	Biesbos	0.35	0.26
III-7	Alkmaar	0.09	0.02
III-8	Hilversum	0.09	0.02
III-9	Amersfoort	0.09	0.01
III-10	Anna Polowna Polder	0.08	0.03
III-11	Schoonebeek	0.07	0.04

About 50 g of mercury is introduced annually into the soil per hectare (Scholte Ubing, 1971), which equals about 0.02 ppm per year in the top 20 cm.

The soils of Group III, all of them used as permanent pastures for over 20 years, show, with one exception, all the same mercury content, about 0.09 ppm, irrespective of their widely differing soil characteristics. Even the peat soil with an organic matter content of over 95% is no exception in this group of soils. The only exception is soil No 6, which is from a sampling site in a polder situated in the Biesbos area (see No 3), reclaimed about 50 years ago. One must conclude that even 50 years ago the river Rhine was already polluted with mercury.

The soils of this group were introduced as references. They show a mercury content in accordance with soils in other parts of the world.

The oldest data about the mercury content in soils are from Stock and Cucuel (1934), who analysed a number of German soils and found a mean content of 0.07 ppm. Martin (1963) reports the natural mercury content in soils to be 0.05-0.06 ppm. Klein (1972a) estimates the background level of mercury in uncontaminated soils to be 0.05 ppm. Andersson (1967) analysed 273 Swedish soils and found the mean Hg content to be 0.06 ppm. Recently an extended monitoring programme has been carried out in the USA. In a region of 300 square miles (768 km^2) 264 soil samples have been taken and analysed for different elements. The area used for agricultural purposes showed an average Hg content of 0.11 ppm, the industrial area 0.10 ppm, and the residential area 0.14 ppm (Klein, 1972b).

As mentioned the 5 Dutch reference soils showed a Hg content in the top 20 cm of about 0.09 ppm (profiles 7 to 11). The question arises whether these soils may be considered to be contaminated with mercury. A positive answer includes the fact that Hg fallout does exist. This point of view is strengthened when regarding the distribution of the mercury over the profiles of these soils. Below 10 cm depth a strong decrease of the mercury content is obvious. A deposition of mercury seems the only way of explaining this effect.

Soil ecology of mercury

As stated the soils used for bulb culture show a mercury content of about 0.15 ppm and also a vertical distribution pattern, differing from the reference soils. The mercury content

remains the same to a much greater depth, the decrease starts for profile No 5 below 40 cm, for sampling site No 6 even below 70 cm. Bulb soils are from time to time deeply ploughed to avoid the accumulation of organic matter in the top soil. Compared with the reference soils (Nos 7 to 11) some mercury accumulation does occur. When the 0-50 cm layer is considered the reference soils show a mercury content of about 0.06 ppm, whereas these two soils have a content of 0.15 ppm, a surplus of 0.09 ppm therefore. The application of mercury as a fungicide in these areas is usual already since 50 years, but the use was intensified about 20 years ago. This has led to a dose of about 50 g/ha every two out of three years (Scholte Ubing, 1971). The introduction of this amount of mercury into these soils during 20 years results in a surplus of approximately 0.13 ppm in the 0-50 cm layer. As some mercury was also applied in the period 1920-1950, this calculation shows that some mercury may have disappeared, either by leaching or by evaporation.[1]

There is evidence to assume that organic mercurials as mercury-containing fungicides when added to soils are slowly transformed to metallic mercury, which then escapes from the soil. The mechanisms of these transformations are not clear.

Experiments carried out by Booer (1944) indicated that inorganic and organic mercurials in soils are transformed to metallic mercury. Ethyl and phenyl mercury were more stable than methoxyethyl mercury, but all were ultimately transformed into metallic mercury. Zimmerman and Crocker (1934) noticed that the injuries to roses caused by the vapours of metallic mercury were the same when other mercury compounds, both inorganic and organic, were mixed with soil.

Frear and Dills (1967) have demonstrated that inorganic mercury can be reduced to metallic mercury in soils. Organic matter, temperature, moisture and pH influence the reaction. Increasing pH accelerates the reduction, low moisture content retards it.

It is not clear whether mercurials are directly transformed into metallic mercury by the action of micro-organisms or whether they are first decomposed to inorganic mercury which in turn may be methylated or reduced, both by the action of micro-organisms and by chemical processes.

Kimura and Miller (1964), investigating the degradation of organic mercury fungicides in a sandy soil, found that soil treated with phenyl mercury acetate (PMA) was surrounded by air containing metallic mercury vapour and trace amounts of PMA. When ethyl mercury acetate (EMA) was used about equal amounts of a metallic mercury vapour and a volatile ethyl mercury compound were present. When methyl mercury compounds were used only methyl mercury vapour was present together with trace amounts of metallic mercury vapour.

It is obvious that micro-organisms may exist in the soil which are able to metabolize organo-mercurials. Furukawa et al. (1969) showed that the *Pseudomonas* K62 strain (a bacterium isolated from soil) is able to decompose organic mercurial compounds to form metallic mercury; PMA yields benzene and metallic mercury, EMP ethane and metallic mercury, MMC methane and metallic mercury.

Although organo-mercurials are relatively easily degradable in soils, yielding inorganic mercury, the escape of mercury from soils may take quite a long time. In the experiments carried out by Kimura and Miller (1964) a large portion of the compounds applied (PMA, EMC and MMP and MMC) was still in the organo-mercury form after 50 days.

[1] Our laboratory experiments indicate that leaching of mercury hardly occurs, but that evaporation does occur.

In experiments described by Saha et al. (1970), using Panogene PX, it appeared that about 50% was still present in soil as an unidentified mercury compound after 5 months.

Methylation of mercury may also occur in soils. Most probably Hg^{2+} is the precursor (Jensen and Jernelöv, 1969). Methylation may be the result of the action of micro-organisms (Westlöo, 1966), but chemical methylation of $HgCl_2$ has also been demonstrated (Kim Iong-Yoon et al., 1970). Direct proofs of Hg^{2+} methylation are presented by Wood et al. (1968) and Yamdaa and Tonomura (1972).

The ultimate products of methylation, monomethyl mercury and dimethyl mercury, are both volatile. At high pH the production of dimethyl mercury is probably stimulated (Landner, 1970) but it may also be possible that dimethyl mercury is decomposed to methyl mercury in acid environments, the decomposition being already substantial at pH 4.5 (Ackefors, 1971). Methylation of inorganic Hg is enhanced under anaerobic conditions (Wood et al., 1968). But under complete anaerobic conditions methylation does not occur (Rissanen et al., 1970). It is doubtful whether the mechanism of mercury methylation contributes to the escape of mercury from soils because of its low conversion rate (A. Kaars Sijpesteyn, pers. comm.; H. G. van Faassen, pers. comm.).

It appears from these literature data that mercury compounds, when applied to the soil, will probably decompose, forming volatile products which may then escape from the soil. Our measurements confirm this conclusion, yet it appears that some mechanism exists which retains mercury in soils. The profiles No 4, 5 and 6 show that part of the mercury is rather immobile.

This immobilization is usually attributed to the formation of mercuric sulphide, possibly an end-product of mercury degradation in soils. It is proved that CH_3Hg^+ can also be formed from pure HgS in aerobic organic sediments; but the velocity of this methylation process is so low that it can be neglected (Fagerström and Jernelöv, 1970).

Furher research will be carried out to clarify the mechanisms involved and to predict the fate of the mercury which originates from agricultural application, from fallout or from deposition by mercury-contaminated surface waters.

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