

Accumulation and Distribution Pattern of Mercury in Soil Profile in Kyushu (Japan) as Related to Man's Impact

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Due to its acute toxicity, and its tendency to bioaccumulate, mercury (Hg) has been of prime interest.⁵⁾ Mercury is widely distributed in nature, almost always in such a quite low concentration as in ppb (parts per billion) level.⁷⁾ However, indeterminable, yet potentially large source of environmental Hg contamination results from natural processes as well as inadvertent release of HG through the exploitation of the world's mineral resources other than Hg.⁷⁾ Furthermore, Hg is lost into the environment as a result of man's utilization of Hg, and Hg-related technology.⁵⁾ In this category, the agricultural use of organic mercury fungicides including phenylmercuric acetate contributed widely to the Hg burden to the soil environment, especially to paddy fields in Japan.⁵⁾ Nose gave total consumption figure for the agricultural use of the fungicides in this country, 2,416 tons as Hg, from the year 1953 to the ban of their use in 1968.⁹⁾

Field sampling of soils has generally indicated only slight movement of Hg in undisturbed soils.⁵⁾ However, information has been needed concerning the Hg distribution in soil profile, together with its amounts, as affected by long-term movement of Hg added to soils. Like other heavy metals, Hg which accumulated in the root zone could be absorbed by plants to constitute a hazard to the food chain. On the other hand, a possible drastic movement of added Hg through soil

profile may lead to its translocation into the ground water. Recently, soil contamination was also disclosed due to the burial of used Hg batteries derived from the domestic use.

In view of the increasing public awareness of Hg contamination described above, the present study was undertaken to investigate a feature of the amounts and distribution pattern of total Hg in soils of Kyushu under a range of land use. This study was also associated with the determination of the natural background level of Hg in the soil. This report makes a final remark on the basis of the previous several relevant publications.²⁻⁶⁾

Materials and methods

Forty-six soil profiles mostly from northern and southern parts of Kyushu were investigated for total Hg (Fig. 1). In terms of Soil Classification System of Japan, included were 7 Yellow soils, 3 Gley soils, 16 Gray Lowland soils, 3 Brown Forest soils, 1 Brown Lowland soil, 2 Red soils, 9 Andosols, 3 Volcanic Regosols, and 2 Wet Andosols. Also from the land use viewpoint, collected soil samples were from 24 paddy soils, 8 upland soils, 8 forest soils, 4 orchard soils, and 3 virgin soils (Table 1). Soil samples were taken by horizon with a core sampler to the maximum possible depth, and were combined making a composite. The determination of Hg was made with dry-combustion method by the use of a Shimadzu High Sensitivity Mercury Analyzer UV-201. All results are based on at least 3 samples, and reported as an average on a dry weight basis.

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Results and discussion

1) Hg accumulation in soil related to natural background level

The Hg distribution in soil leads to alteration related to older and current episodes of natural activity such as background category of Hg. Most soils retain Hg by formation of chelates, by adsorption on clays, or by ion exchange. Soil characteristics like pH, clay content and organic matter content therefore influence the amounts and distribution of Hg in the soil, but man's impact introduces Hg in sufficient amounts to overwhelm local background variations. The background levels determined in the different parts of the world are frequently incomparable as reflected by different environmental conditions. On the basis of generalization of extensive published data, however, Jonasson and Boyle⁷⁾ proposed the background Hg level in soils ranging from 20 to 150 ppb.

From our soil profile data (n=282), it was found that Hg content of the soil ranged from 3 to 473 ppb with an average of 78 ppb. Mercury is therefore considered a trace element in the soil under study. In conjunction with the horizontal values, cumulative frequently plot of Hg can be helpful in defining abnormal boundaries, and can aid in the selection of contaminated site location. From total Hg content of all the horizon samples, a three-fold distribution pattern was clearly observed, and classified into native (A), natural background (B), and abnormal (C), as shown in Fig. 2. Native values vary between 3 and 48 ppb, natural background between 49 and 104 ppb, and abnormal from 105 to the maximum of 473 ppb. The native data show a

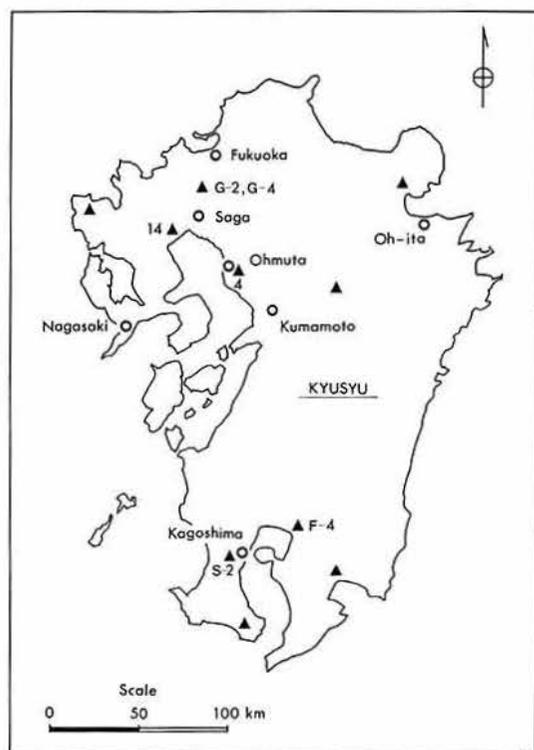


Fig. 1. Location map showing geographical distribution of groups of soil sampling sites

Each group is indicated by a solid triangle. Numbers inserted in the figure correspond to those of soil sampling sites involved in the respective groups, and relevant to Fig. 3.

Table 1. Summary of total Hg data in the surface horizon samples (ppb)

Hg data	Paddy	Upland	Forest (A0)	Forest (A1)	Orchard	Virgin	Total*
n	24	8	7	8	4	3	46
Range	86-473	21-235	40-318	25-141	21-90	25-75	21-473
Mean	228	83	180	69	57	44	173
Median	208	64	205	63	30	33	162
s.d.	104	68	53	37	36	27	112
c.v. (%)	46	82	53	54	64	61	65

* Calculated excluding Forest (A0) samples.

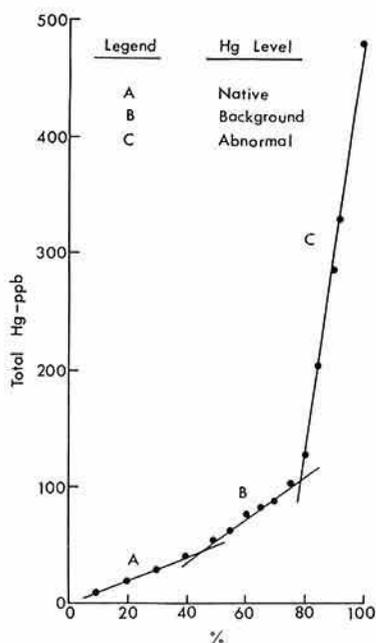


Fig. 2. Cumulative frequency plot of total Hg content for all soil horizon samples

Appropriate random selection is adopted for dotting from which three lines are delineated in relation to soil Hg contamination.

geometric mean of 25 ppb, natural background with 71 ppb, and abnormal at 212 ppb.

The distribution of total Hg content in the soil showed a tendency to vary with profile depth, as will be described later. It is notable that the Hg content was generally highest in the surface soil, and decreased with increasing depth. Table 1 shows a summary of total Hg data in the surface horizon samples. Almost all surface features in paddy soils were accompanied by abnormal values of Hg, which is definitely explained by the strong Hg accumulation attributable to the application of organic mercury fungicides. It is also remarkable to note that, while only small amounts of Hg were accumulated per unit area, enough remain to form an abnormality in the humus-rich horizon of forest. This is

most likely influenced by the transport of Hg from root zone through biocycle Hg accumulation. The virgin soil sampling did not indicate any Hg abnormalities, on the other hand.

2) Distribution pattern of Hg in the soil profile

In natural ecosystem, Hg content of the soil approaches an equilibrium value. The magnitude of this value may depend upon such factors as type of vegetation, nature of the terrain, and chemical and physical characteristics of the soil. The soil environment as a natural system is a dynamic one, hence any alteration in the environment could lead to a new equilibrium level of soil Hg. As stated earlier, disruption of the equilibrium via the activity of man produces some appreciable changes in the Hg content of the soil, leading to different Hg distribution pattern in the soil profile.

Seven types of distribution pattern of total soil Hg along the soil profile could be distinguished from the data of the present study, as depicted in Fig. 3.

Type 1 (Site no. 14 at Saga polder rice soil).²⁾ There was the Hg distribution with a surface maximum resulting in steep concentration gradient down the profile. This pattern of the distribution could be found in the polder rice soil with smectite type of clay mineral in combination with the previous application of organic mercurials.

Type 2 (Site no. G-2 from granite-derived rice soil).³⁾ Maximum value of total Hg occurred in the surface horizon, which was followed by a gradual decrease with increasing depth. This was a trend we could see most often in the soil, regardless of the soil type and land use.

Type 3 (Site no. G-4 from granite-derived forest soil).³⁾ In the forest soil, the Hg concentration was extremely high in the top few mm humus-rich horizon with 200-300 ppb Hg, and then quickly decreased to low values below that horizon. Accumulation of Hg in the organic horizon through the biocycle of plant-root system is often invoked to explain the vertical distribution of Hg in the forest soil

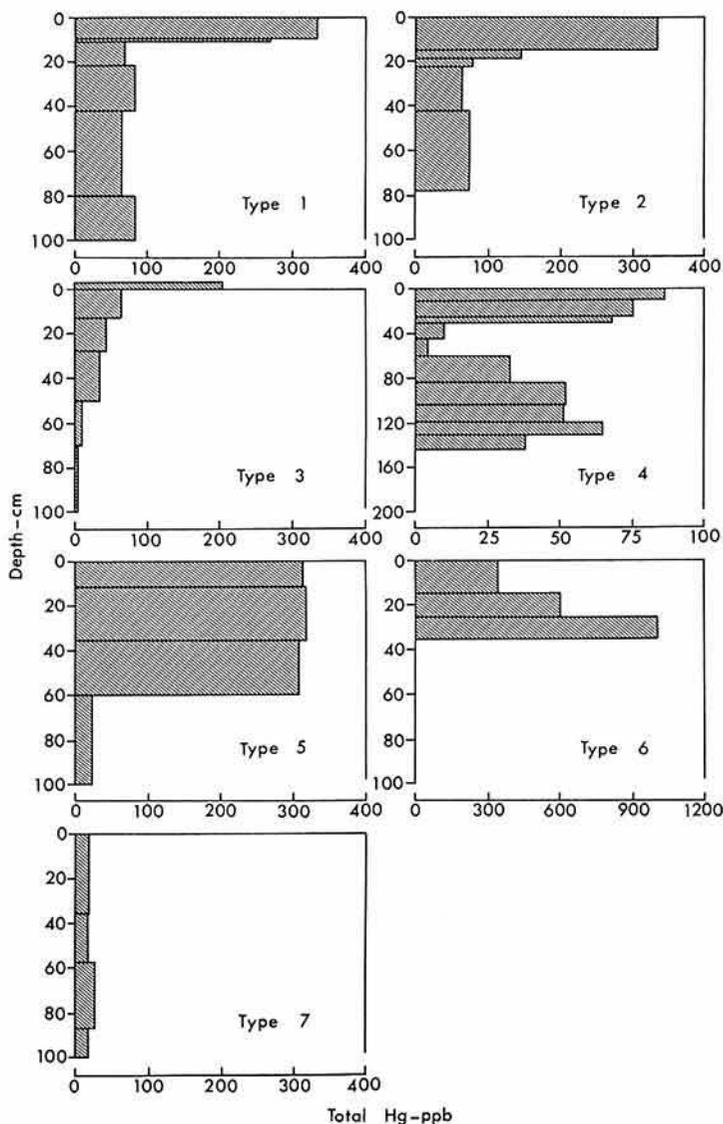


Fig. 3. Distribution pattern of total Hg content in selected soil profiles

environment.

Type 4 (Site no. F-4 from volcanic ash-derived orchard soil).⁴⁾ The distribution of Hg in some soil profiles in the volcanic environment showed somewhat high values in the surface, a decrease below the surface, and an increase in the lower surface horizon, and then a decrease down to the deeper horizon.

Type 5 (Site no. 4 from polder rice soil).⁶⁾ Mercury accumulation extended to the deeper

soil horizon, e.g. 60 cm in the extreme case, forming less marked variation with the profile.

Type 6. The Hg content was high in the low soil horizon so that the profile maximum might be just above the parent material of the soil. We failed to detect this type of the Hg distribution pattern, whereas Aomine et al.¹⁾ reported the presence of this pattern at a paddy soil in Fukuoka.

Type 7 (Site no. S-2 from volcanic ash-

Table 2. Correlation coefficients (r) between total Hg and some soil properties of the profile samples³⁾

Soil sample	Number of samples (n)	Orgainc-C	Clay	CEC	pH
Granite-derived	29	0.5694***	0.4233*	0.5569***	-0.2919
Andesite-derived	23	0.7562***	0.0493	0.1622	-0.4465*
Basalt-derived	20	0.9295***	0.1924	0.7158***	-0.6459**
All samples	72	0.6338***	0.0287	0.6098***	-0.3292**

* Significant at 0.05 level. ** Significant at 0.01 level. *** Significant at 0.001 level.

derived from upland soil.⁴⁾ Throughout the profile, little variation with small amounts of Hg was observed as also the case in non-cultivated virgin soil.

3) Factors determining the status of Hg in the soil profile

Selecting the soil (n=72) derived from igneous rock in northern Kyushu, correlation analysis between the total Hg and the relevant properties of the soil was made, and summarized in Table 2. It is obvious from these results that the total Hg was highly correlated with organic matter, to a lesser degree with CEC, least with clay content, and negatively correlated with pH. A similar high correlation with organic matter was also observed in the soil from other areas in Kyushu.^{3,4,6)} The above information suggests that organic form of Hg constitutes a major portion of total Hg in the soil under study.

There are indications in the literature regarding the formation of extremely strong Hg-organic complexes, and many competing heavy metals are unable to replace Hg bound with organic matter.⁵⁾ The profiles of rice soil from Saga polder were characterized by Hg accumulation restricted in the surface horizon, on the other hand. This may testify to the firm binding of the soil Hg with the clay minerals dominated by smectite.²⁾ From the Hg distribution pattern in the profile (Fig. 3), it seems likely that, though the rate is slow, Hg could migrate in the soil under the control of mass flow and diffusion, apart from its probable vaporization. Fractionation analysis indicates that Hg occurs in the soil exclusively in the form of non-ionic compounds, and may be scarcely migrate in the

ionic form in the soil (unpublished data). Thus, Hg apparently moves in the sorbed state with organomineral and fine colloidal particles.

Summary and conclusion

Most soil profiles are remarkable in that their horizons do not form a homogeneous soil profile. This makes it possible to estimate the magnitude of contamination from Hg, and to trace its behavior in the soil. The natural background level of Hg in the soil (49 to 104 ppb) is around or below results reported by Jonasson and Boyle⁷⁾ for Hg in soils of the world. Seven distribution patterns were detected from the total Hg content within the soil profiles under the present study. In general, soil contamination with Hg was limited to the upper horizons, and does not spread much downward. The total Hg in all the surface soil horizons combined ranged from 21 to 473 ppb with a mean of 173 ppb. Apparently, organic mercury fungicides application in recent years was a principal factor above all regarding the establishment of the elevated Hg levels in the upper soil horizon under cultivation.

Much of the Hg in the soil might be bound with organic matter, and to a lesser degree extent with clay. These properties help the soil to decrease the toxicity of the anomalous Hg concentration by converting Hg into the strongly bound state virtually unavailable to plants and soil microbes as well. Methylmercury is the most toxic of the Hg compounds formed in the soil. According to Van Faassen,¹⁰⁾ methylmercury content in soils is almost always below 1% of the total Hg pre-

sent. Since the soils under study have Hg content less than 500 ppb, methylation would not be expected to be a great concern. Further study is needed in order to ascertain the discrete forms of Hg in the soil of the present study.

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