Mercury Residue in Paddy Fields of Japan

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The phenylmercuric fungicide was widely used in paddy fields for rice-blast control since 1953 and the use lasted until 1968 when other fungicides not containing mercury replaced completely the mercury fungicide. For a period of these 16 years, 2,416 tons of metalic mercury were converted into the fungicide most of which was consumed in paddy fields. Total area of paddy field in Japan is approximately three million hectares. If that amount of mercury was mixed with the top layer (0–10 cm) of all the paddy soil, mercury content in the soil would increase by 800 ppb. By other calculation that one application causes increase of mercury content in the soil by 50 ppb and that farmers had applied the fungicide commonly three times a year, an increase of mercury content by 2,400 ppb would be caused in 16 years. Since these figures may not be neglected compared to the value of naturally existing mercury, the actual content in paddy soils was determined and the possible effect of the residual mercury on the mercury content of rice grains was estimated.

Progress of mercury determination

The colorimetric method by dithizone complex so far used can detect only microgram order of mercury, but recently introduced atomic-absorption method enables the detectable limit of mercury to reduce down to nanogram. This improvement of mercury analysis provides an easy way to trace the small amount of mercury.

1) *Dry method*

A weighed soil or rice (less than 1 g) is combusted in an oxygen stream in a quarts tube and the combution products are absorbed into a $KMnO_4$ solution. The absorbing solution is decolorized with a NH_2OH–HCl solution and the mercury is extracted with a dithizone chloroform solution. An aliquot of the chloroform solution is taken into a ceramic boat containing a small amount of BAL (2,3-dimercapto-1-propanol). The chloroform is evaporated at room temperature remaining the mercury in the form of mercuric dithizonate. The boat with the mercuric dithizonate is inserted in the furnace of vaporizer unit for the determination.[1,2]

2) *Wet method*

In spite of having a disadvantage of the high blanck value, the wet method is useful for a variety of reasons. Organic mercury can not be atomized by the acidic reduction, but can by an alkaline reduction. Both

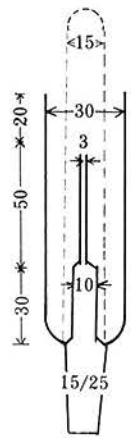

Fig. 1. An Hg trap for the rice digestion

inorganic and organic mercuries can be atomized by the alkaline reduction. This provides a good way to determine organic mercury separately from inorganic mercury. Second, soluble mercury content in soil seems to be an important factor for the study on mercury uptake of plant. Third, any expensive equipments except a mercury meter are not required.

(1) Total mercury content in soil and rice

A weighed rice is soaked over night in a mixture of nitric acid and sulfuric acid in a flask with a ground grass joint. A reflux condenser fitted with a trap containing 2 N sulfuric acid, as shown in Fig. 1, is attached to the flask, and the mixture is heated under reflux until the evolution of yellow fume subsides. A urea solution is added to destroy the formed nitrous oxid. The subsequent procedure is operated in the usual way (Fig. 2). In the case of soil, sulfuric acid and the trap can be omitted. Suitable amounts of soil and rice for operation are 0.5 g and 1 g, respectively.

One gram of rice+5 ml of HNO_3+2 ml of H_2SO_4
↓
allowing to stand overnight
↓
reflux for 1 hr with a trap containing 5 ml of 2N H_2SO_4
↓
+1 ml of 10% urea solution and 5 ml of water
↓
reflux for 10 min
↓
+1 g of $KMnO_4$
↓
+5 ml of 10% hydroxylamine sulfate solution
↓
to 50 ml with water
↓
+1 ml of 10% $SnCl_2 \cdot 2H_2O$ Solution
↓
determination

Fig. 2. Determination of total Hg in rice.

(2) Thiomalic acid soluble mercury content in soil

Mercury in soil is hardly eluted with a mild reagent such as a salt solution, a dilute acid, an alkaline solution etc., but a part of mercury can be eluted with a thiomalic acid solution. Methylmercuric and phenylmercuric compounds are eluted with the thiomalic acid solution, too. A weighed soil is added to a thiomalic acid solution and the mixture is stirred and then filtered. Sodium hydroxide is added to an aliquot of the filtrate so as to obtain finally 3 N solution, and then hydrogen peroxide is added. The mixture is allowed to stand at 70°C for 1 hr. After cooling, the mixture is made up a definite volume with water. The determination is carried out in the presence of cupper sulfate in 3 N alkaline condition (Fig. 3).

(3) Organic mercury content

An aliquot of the thiomalic acid extract is taken in a 1 *l* round bottom flask. To the flask nitric acid and stannous chloride are added. Then, inorganic mercury is removed by bubbling air on the bottom of the flask. Sodium hydroxide and hydrogen peroxide are added to the mixture. The subsequent procedure is same as the preceding section (Fig. 3).

Accumulation of mercury

1) *Upland soil*

Since little mercury fungicides have been sprayed on the upland farms, the mercury content of upland soil supposedly represents the level which is not contaminated with the fungicides. From the data about several volcanic ash soils, characteristic features of mercury distribution in the environment have been found as follows. First, the mercury content of top soil is larger than that of subsoil. Second, a city soil (Nishigahara, Tokyo as shown in Table 1[3]) shows a high mercury level. Third, the soil developed in an old age contains more mercury than that in a recent age (Shinmyo–Ike *vs* Oyama, Miyake). These suggest that mercury content in soil tends to increase year by year, some of which are irrelevant to the artificial contamination.

2) *Paddy soil*

There are still many paddy fields which are free from the mercury fungicide, though the fungicide had widely been used in paddy fields in Japan. Residue of the mercury

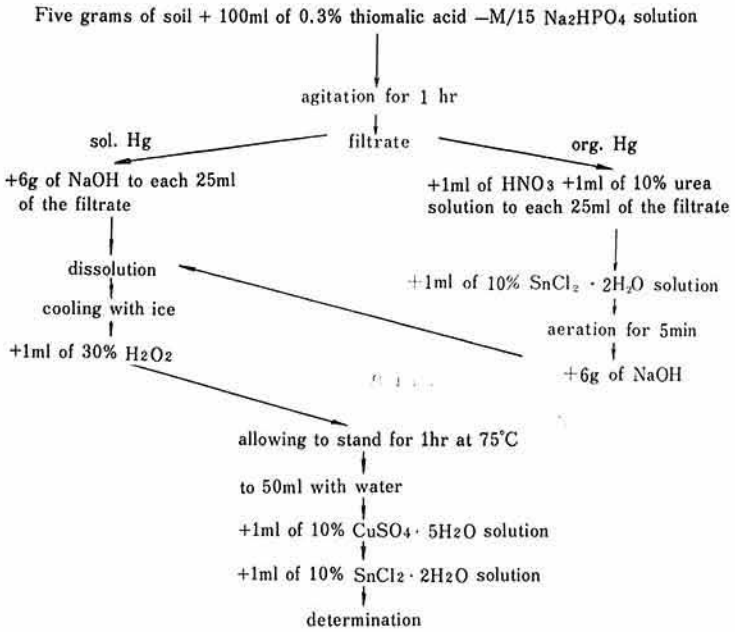

Fig. 3. Determination of soluble Hg and organic Hg in soil

Table 1. Mercury content (ppb) in several volcanic ash soils

Location (sampling date)	Top or sub-soil	Total Hg	Soluble Hg
Tokyo (Sept. 1974)			
Nishigahara	t	340	75
Nishigahara	s	290	63
Hachijo Island (March 1975)			
Botanical garden	t	110	14
Nago	t	160	48
Hattoriyashiki	s	53	< 4
Miyake Island (March 1975)			
Shinmyoike	t, exploded in 1835	110	37
Oyama	t, active volcano	73	7
Ibaraki (March 1975)			
Mawatari	t	160	51
Iwase	t	190	60
Agr. Exp. Sta.	t	71	35
Nakadai	t	110	28
Johoku	t	98	35
Kashima	t	190	46
Kumamoto (March 1976)			
Daikanbo	t	152	78

Note: Ibaraki soils were obtained from cultivated fields; the others from non-agricultural lands

Table 2. Mercury content (ppb) in paddy soils

Location (sampling date)		Total Hg	Soluble Hg	Organic Hg
Shonai Agr. Exp. Sta.	(Nov. '74)	440	48	< 4
Shonai Agr. Exp. Sta.	F. (Nov. '74)	320	43	< 4
Fukushima Agr. Exp. Sta.	(Nov. '74)	140	< 4	< 4
Fukushima Agr. Exp. Sta.	F. (Nov. '74)	150	< 4	< 4
Gunma Agr. Exp. Sta.	(March '75)	150	47	< 4
Gunma Agr. Exp. Sta.	F. (March '75)	90	29	< 4
Kumamoto Agr. Exp. Sta.	(March '75)	780	81	59
Kumamoto Agr. Exp. Sta.	F. (March '75)	490	57	44
Aso Agr. Exp. Sta. (old)	(March '76)	313	47	< 4
Aso Agr. Exp. Sta. (new)	(March '76)	57	33	< 4
Shiozawa, Niigata	(May '74)	250	86	10
Nago, Okinawa	(Oct. '75)	1,060	55	< 4
Tamagusuku, Okinawa	(Oct. '75)	165	32	< 4
Ishigaki, Okinawa	(Oct. '75)	183	45	< 4
The following soil is contaminated by mining.				
Oguchi, Kagoshima	(Dec. '75) No. 1	7850	280	< 4
	No. 2	9470	260	5
	No. 3	6570	270	9
	No. 4	4180	480	5
	No. 5	6630	410	9
	No. 6	4840	470	< 4

Notes (1) F.: Forcasting field for rice blast where no fungicide has been used.
(2) Aso Agr. Exp. Sta. (new) was constructed in 1971 and the mercury fungicide has never been used in the field.

fungicide can hardly be estimated from mercury contents of farmers' paddy fields because the past use of the fungicide is not clear. On the other hand, each prefectural agricultural experimental station has the rice blast forecasting field where the fungicide had never been used. Mercury content in soil of the forecasting fields was found lower than that of the adjacent experimental fields of the same stations (Table 2[3]). But, the difference was at most 300 ppb which is only one-eighth of the calculated value based on 16 years application. Similar difference was observed in soils between the old Aso Agricultural Experimental Station and the new one which was founded in 1971.

Organic mercury was detected in several soils. Most of them seem to be phenylmercury because methylmercury tends to decompose in the paddy fields[4]. But, organic mercury in the forcasting field of Kumamoto Agricultural Experimental Station should be further investigated (Table 2). Any correlation was not observed among total, soluble, and organic mercuries.

The Saga polder land in the northern Kyushu has a long history of reclamation and therefore a series of lands with different ages after reclamation can be found within a limited area. Gotoh and Koga[2] selected one of those areas and determined mercury contents of soil and rice as shown in Table 3 and Fig. 4. A series of fields from site no. 3 to 7, consisted of fields reclaimed successively in a period from 1954 to 1971 showed the effect of mercury fungicide application because the fungicide had been commonly used from 1953 to 1968. A linear relationship was observed between the mercury content in the top soil (Apg horizon, Table 3) and the number of years subjected to the fungicide application, with annual increase of mercury con-

Table 3. Total mercury content (ppb) of soil and rice in the Saga polder land having various ages after reclamation
(Rearranged from Gotoh and Koga[2])

Site No.	Reclaimed age	Horizon (depth, cm)		Rice	
		Apg	G	Unhulled rice	Straw
1	sea sediments	243 (—)	—	—	—
2	exposed land	208 (0—18)	220 (40+)	—	—
3	1971	91 (0— 7)	106 (30+)	10	26
4	1969	86 (0— 7)	91 (20+)	10	29
5	1965	162 (0— 9)	73 (70+)	12	26
6	1959	289 (0—11)	74 (70+)	10	28
7	1954	297 (0— 9)	54 (74+)	11	32
8	40 years ago	154 (0— 9)	57 (99+)	29	198
9	70 years ago	197 (0—10)	76 (86+)	10	35
10	100 years ago	212 (0— 8)	59 (93+)	8	33
11	150—200 years ago	210 (0—10)	95 (95+)	11	34
12	300—500 years ago	235 (0—10)	90 (100+)	15	33
13	500—700 years ago	307 (0— 9)	116 (102+)	14	31
14	500—700 years ago	333 (0—10)	104 (120+)	13	33
Average (Nos. 3—14)		214	83	13	45
(without No. 8)		—	—	11	31

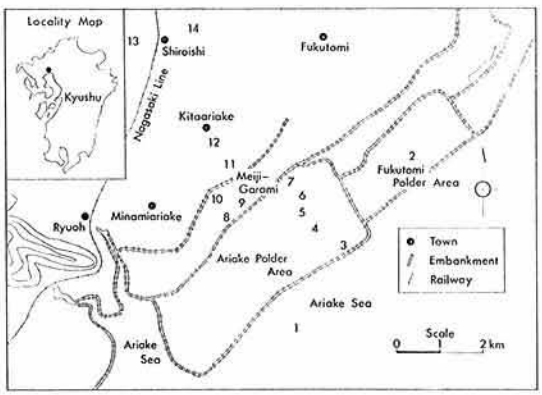

Fig. 4. Map of the Saga poler land. Numbers indicate the location of sampling sites

tent by 13.7 ppb. This value is less than one-tenth of the calculated one based on an assumption that the application rate was uniform through all the area during this period and that the fungicide was not used after 1969. A series of site no. 8 to 14 shows a feature of mercury accumulation by year. Because all these sites had received the fungicide application uniformly, the effect of fungicide itself can be neglected. The older the time of reclamation the higher the mercury content is. The mercury content of top soil is higher than that of sub-soil (G horizon). These features of mercury accumulation are similar to those found with upland soils.

Effect of residual mercury on mercury content in rice grains

No correlation was observed between total mercury content of soils and that of rice grains produced on these soils (Tables 3 and 4). The mercury content of rice grains was less than one-tenth that of rice roots as shown in Table 4 . Perhaps, only few mercury may move or translocate in rice plants. A slight rise in mercury uptake of rice grain induced by the residual mercury was experimentally demonstrated (Fig. 5). Phenylmercuric acetate was sprayed to a field at the rate of 0 g, 30 g, and 150 g per are, which are equivalent to the total

Table 4. Determination of mercury in soil and rice, obtained in 1973
(from Kushizaki[13])

soil		rice		
soil class	total Hg (ppb)	variety		total Hg (ppb)
FSL	272	Fujiminori		10
SiCL	299	Toyonishiki		9
FSCL	325	Sachinishiki		7
CL	231	Toyonishiki		8
CL	423	Kiyonishiki		11
CL	360	Sasanishiki		12
FSL	651	Kiyonishiki		4
CL	321	Sasanishiki		7
Li CL	368	Sasanishiki		6
CL	207	Gohyakumangoku		7
		Echigowase		6
LiC	321	Koshihikari		6
SL	397	Koshihikari		11
LiC	175	Honenwase		4
SL	231	Fuko No. 60	rice	32
			straw	32
			root	455
CL	388	Honenwase		30
		Honenwase	rice	19
			immature	19
			chaff	13
			straw	27
			root	121
CL	1, 160	Kinmaze		25

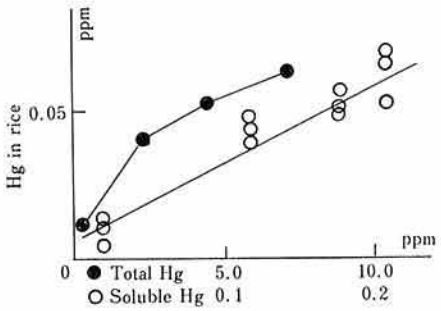

Fig. 5. Relationship of Hg contents (ppm) between rice and soil in the field treated 9 years ago with phenylmercuric acetate at the rate of 0, 30, and 150 g Hg/a, which corresponds to the amount to be applied in 0, 20, and 100 years period, respectively.
The regression equation is $y=0.255x+0.007$ where y is Hg content (ppm) in the brown rice and x is soluble Hg content (ppm) in the soil.

amount of mercury fungicide applied in the periods of 0, 20, and 100 years, respectively. The soil was mixed with the fungicide by using a plow before the transplanting of rice plants in July 1965. Each block had been separated with sheets of plastic plate, which were removed after the harvest of the first year crop. In October 1974, soils and rice grains were sampled in these fields and mercury contents of them were determined (Fig. 5). The soil in the 0 year block, which was not treated with the fungicide, showed a high mercury content as compared with other fields not treated with the fungicide. Total mercury content in soils disclosed that an appreciable movement of soil was caused by plowing, but the characteristic of each blocks still remained. Thus, the field was characterized by four levels of mercury contents in

soil.

The mercury content of rice increased with the increase of both total and soluble mercury contents in soil as shown in Fig. 5. The highest mercury content of rice was 62 ppb which was obtained from the 100 years block, and total and soluble mercury contents in the soil were 7200 and 210 ppb, respectively. The mercury content in rice grains was determined for each stumps and the significant difference of mercury content in rice grains between stumps was 13.7 ppb at 5% level of significance. On the basis of a regression line between mercury content in rice grains and soluble mercury content in soil, 13 ppb of difference between rice grains is derived from 51 ppb of difference between soils. Such a large difference was not observed between soils obtained from fields where the fungicide was used or not used as shown in Table 2.

This suggests that the mercury fungicide sprayed in past days gives little effect on the mercury content of rice grains.

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