

**Mission Report - Investigation into Suspected Mercury Contamination
at Sihanoukville, Cambodia**

National Institute for Minamata Disease

(This Mission Report was prepared in collaboration with the following Study Group)

Study Group for WPRO-Project Proposal (1998)

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control, 5 hair samples of villagers working in the center of the Sihanoukville about 5 km away from the site were selected for the purpose of comparison. All the samples were analyzed at the NIMD to determine the mercury concentrations. Waste samples were further analyzed for cadmium, manganese and nickel. In addition, Dr K E Mony and Dr P P Raingsey from the Ministry of Health interviewed health conditions of the port and site workers. This report summarizes the results of the findings.

2. Mission objectives

The objectives of the mission are as follows:

- I to make preliminary recommendations to avoid possible risks from the waste in Sihanoukville.
- II to carry out analyses of the waste samples for mercury and some other metals.
- III to carry out analyses of the water samples for mercury.
- IV to carry out an health assessment of the port workers and soldiers to ascertain whether they are suffering from mercury poisoning.
- V to make further recommendation to avoid possible risks from the waste in Sihanoukville standing on the results analyzed in NIMD.

3. Survey

3-1. Samples for the study

Sihanoukville is about 10 km south of the dumping site of the waste. About 3,000 tons of the waste was dumped on the hill. We collected two slightly different properties gray solids, which were main component of the waste, two black solids and sand-like waste. Water samples from the wells and tap water near the dumping site were collected. Hair, urine and blood samples of 9 port workers who have complaints after the work of unloading or cleaning the waste were collected. Hair, urine and blood samples of 5 workers/soldiers involved in the clean-up operation at the site were also collected. Hair samples from 5 villagers at the center of Sihanoukville were collected as a control.

Waste

About 100 g of waste samples was collected into pre-cleaned plastic bottles and stored in icebox with ice cubes.

Property and color of taken were:

- ① Fragile and gray solid (A part of main component of the waste)
- ② Fragile and gray solid (A part of main component of the waste)
- ③ Hard and back solid (Pieces found in the main waste)
- ④ Hard and back solid (Pieces found in the main waste)
- ⑤ Sand-like brown waste (A small part of the waste)

① and ② occupy more than 95% of the waste.

Water

Samples were collected in a 100ml pre-cleaned bottle. The samples were stored in an icebox, avoiding sunlight exposure until analysis.

Samples of water were taken from:

- ① the well water 200-300m below the site (supplies both drinking and washing for woodcutters).
- ② the tap water in Pagoda (supplies both drinking and washing for priests and soldier working in the site).
- ③ the well water 200m below the Pagoda (supplies both drinking and washing for inhabitants of a small village)
- ④ the tap water for inhabitants living 1.5km far away from the site; another side across a Road no.4. (As a control without the contamination of the waste).

Blood

About 10 ml of blood sample were collected by syringe and transferred into sample tube including heparin. All the samples were stored in icebox with ice cubes.

Urine

Urine was collected in a paper cup. From that cup, 5 ml of the urine was transferred into sample tube. All the samples were stored in icebox with ice cubes.

Hair

About 0.5 g of hair samples were cut with scissors from the root and taken into small sealed bag.

Health condition

Two doctors from Ministry of Health of Cambodia also interviewed workers at the port and site for their health conditions.

3-2 Mercury analyses

Total mercury

(a) Biological samples

A known amount of samples (1 - 10 mg of human hair, 0.5 g or less blood, fish) is placed in a 50 ml volumetric flask, to which 2 ml of nitric acid-perchloric acid (1+1), 5 ml of sulfuric acid 1 ml of water are added and heated at 230 - 250°C on a hot plate for 20 minutes. In the case of urine sample, the mixture of these acids are placed first in the 50 ml volumetric flask, to which 1 - 5ml of urine sample is added dropwise with stirring the mixture and then digested in the same manner as described above. After cooling, the digest samples is made up to 50 ml with mercury free water. An aliquot of the sample solution is introduced into automated circulating airflow system with addition of 10 % stannous chloride solution. After air circulating for 30 seconds, the circulating air is measured with a cold vapor atomic absorption spectrometry. The detection limit is around 1 ng/g for 0.5 g samples.

(b) Water

For water analysis, preconcentration is carried out by dithizone extraction. 100 ml of a water sample in a separately funnel is mixed with 0.5 ml of 20 N sulfuric acid and 0.25 ml of 0.5 % potassium permanganate and allowed to stand for 5 minutes. The treated sample is then neutralized with 1 ml of 10 N sodium hydroxide and 0.25 ml of 10 % hydroxylamine hydrochloride and allowed to stand for 20 minutes. After addition of 5 ml of 10 % ethylenediamine tetraacetic acid tetrasodium salt, the sample is extracted with 0.5 ml of purified 0.01 % dithizone in benzene. The sample was left until it separated and the water layer is discarded. A known volume of benzene layer is transferred into a 10 ml volumetric flask and evaporated to dryness using a rotary evaporator. The residue in the volumetric flask is digested with nitric acid - sulfuric acid - perchloric acid system, diluted and measured by cold vapor atomic absorption spectrometry in the same manner as described in above.

(c) Others

Total mercury in other environmental materials (0.5 g or less of biota, 1 - 2g of sediment) is measured by the same method as outlined for biological samples.

(2) Methylmercury

The procedure for methylmercury analysis developed in our laboratory is based on the combined techniques of dithizone extraction and ECD gas chromatography. For hair

a flow rate of 100 ml/min., after acidified with hydrochloric acid. The sample was then mixed with 2 ml of 20 % hydroxylamine hydrochloride and 2 ml of 20 % ethylenediamine tetraacetic acid tetrasodium salt and extracted with 5 ml of purified 0.05 % dithizone in benzene followed by cleanup procedure using sodium sulfide solution, re-extraction with purified dithizone in benzene, and ECD gas chromatography.

Determination other metals in waste

Powdered samples of 0.200g were exactly measured and placed in sample tubes. Samples were digested with 3 ml of HCl and 1 ml of HNO₃. The digested samples were diluted to 1/500. Manganese, lithium, zinc, lead, iron and copper were measured by the method of ICP-emission spectrometry (ICP-Emission Spectroscopy Optima 3000XL, Perkin-Elmer Co. Ltd.). Cadmium and nickel were measured by flame-less atomic absorption method (Atomic Absorption Spectroscopy, Z-5100, Perkin-Elmer Co. Ltd.). Background absorbance was corrected by done with

Conversion factors

1 ppm (parts per million) = 1 µg/g

1 ppb (parts per billion) = 1 ng/g

4. Results and discussion

4-1 Total and methylmercury concentrations in waste samples.

As shown in Table 1 total mercury concentrations in the gray samples were 496 µg/g and 726 µg/g, respectively. Total mercury concentrations in the black samples were 2497 µg/g and 3984 µg/g, respectively. Total mercury concentrations in the brown sample was 97 µg/g.

Mercury concentrations in soils and sediments are summarized in Mercury Contamination in Man and his Environment (International Atomic Energy Agency, Vienna, 1972) as follows; In Sweden the mercury concentration in the soil ranged from 20 to 920 ng/g, with a mean of 70 ng/g (Anderson 1967). Stock and Cucuel (1934) regarded 100 ng/g as normal but gave ranges 100-290 ng/g for forest soils, 140-1000 ng/g for cultivated soil, 30-34 ng/g for clay soil and 1-29 µg/kg for sand. In vicinity of gold, molybdenum and base-metal deposits, soils were found to contain 50-250 ng/g but sometimes 2000 ng/g. Thus, mercury concentrations in the waste was very high compared with the environmental levels.

Methylmercury concentrations in the waste samples, except the sand-like waste, were lower than detective level (0.01 ng/g). Methylmercury concentration in the sand-like sample was 33.7 ng/g, suggesting the contamination of surface soil or some other organic matters.

4-2 Metals in waste samples

Table 2. shows cadmium, manganese, nickel, lithium, zinc, lead, iron and copper concentrations in the waste samples. Cadmium concentrations in black samples were below 1.0 ng/g. Cadmium concentrations in the other samples were 9-26 ng/g. The other metals concentration were as follows; Manganese 83.3-1779.6 µg/g. Nickel 10.6 -76.7 µg/g. Lithium 7.5-147.6 µg/g. Zinc 101.8-698 µg/g. Lead 35.1-499 µg/g. Iron 23058-87525 µg/g. Copper 35.1-323.3 µg/g.

Cadmium, manganese and nickel concentrations in natural soils and sediments are summarized in Trace Elements in Biochemistry (Bowen 1966) as follows; Cadmium 0.01-0.7 µg/g. Manganese 100-4000 µg/g. Nickel 10-1000 µg/g. Lithium 7-200 µg/g. Zinc 100-300 µg/g. Lead 2-200 µg/g. Iron 7000-550000 µg/g. Copper 2-100µg/g. Thus, almost all the cadmium, manganese, nickel, lithium, zinc, lead, iron and copper concentrations in the waste samples were within the natural soils level. However, lead concentration in sample 2 was slightly higher than natural soil and sediments.

4-3 Total mercury concentrations in water samples.

Total- and methyl-mercury concentrations in water samples are shown in Table 3. The mercury concentrations in water samples in wells and tap water were from 4 to 6 ng/l. Even the water of the well near the site was 4 ng/l. Tap water from 1.5 km far from the site and another side across Road no.4 was 6 ng/l, which was considered as a control.

Representative values for dissolved total mercury are: open ocean, 0.5-3 ng/l; coastal seawater, 2-15 ng/l; fresh water rivers and lakes, 1-3 ng/l (WHO, 1990). The concentration range for mercury in drinking water is the same as in rain, with an average of about 25 ng/l (Lindqvist *et al.* 1984, in WHO, 1990). All the water samples around the site showed natural levels of total mercury suggesting no leakage of mercury from the site. Dry weather at the present in Cambodia may be a redeeming feature in a tragic affair.

4-4 Total and/or methylmercury in red blood cells and serum

Total and/or methylmercury concentrations in red blood cells and serum are shown in Table 5. Total mercury concentrations in red blood cells were 13.1-25.5 ng/g for port workers and 10.5-17.0 ng/g for site workers, respectively. Methylmercury concentrations in red blood cells were 11.8-22.4 ng/g for port workers and 7.5-14.0 ng/g for site workers, respectively. Total mercury concentrations in serum were 1.96-3.59 ng/g for port workers and 3.26-4.58 ng/g for site workers, respectively.

Methylmercury concentration in red blood cells is one of the best indicators of the methylmercury pollution. It is said that certain groups with a high fish consumption may attain a blood methylmercury level (about 400ng/g) associated with a low (5%) risk of neurological damage to adults (WHO, 1990). Methylmercury level of non-exposed

neurological damage to adults (WHO, 1990). Fish consumption is the main source of mercury accumulation in human. Since the people of this area eat fish daily, methylmercury accumulation of these populations was similar to that of Japanese. The mean mercury concentrations corresponds to fish consumption patterns as follows: once or less a month, 1.4 $\mu\text{g/g}$; once every 2 weeks, 1.9 $\mu\text{g/g}$; once a week, 2.5 $\mu\text{g/g}$; and once or more day, 11.6 $\mu\text{g/g}$. (Airey, 1983 in WHO, IPCS, Environmental Criteria 101: Methylmercury, 1990). The mercury concentrations were similar to normal levels (0.8-2.5 $\mu\text{g/g}$) in Southern Hemisphere.

4-7 Complaints of the port and site workers

Complaints of port and site workers were shown in Tables 4 and 5. The health conditions of most of the port worker were becoming better.

Inorganic mercury poisoning should be first considered because the symptoms were occurred after transportation and unloading of the waste that contains high mercury. However, mercury concentrations in blood, urine and hair of port and site workers. Therefore, the symptoms should be different from those of mercury poisoning. Also, there should be little possibility that poisoning was caused by organic solvent and Cl^- because the condition of the wastes was solid

From the complaints listed in tables 4 and 5, dizziness, visual trouble, headache and weakness were common in the patients. Judging from the working environment, heat stroke and hypoxia must be thought as the differential diagnosis. The symptoms of abdominal pain, diarrhea and chest pain may be also explained by the cause. Temperature, blood pressure, pulse, findings of electrocardiogram and chest X-ray film, minerals of blood and urine, hematocrit would help the diagnosis, but it is impossible to get these findings. The symptoms should be caused by the severe physical work in the dusty and hot environment.

But the above-mentioned differential diagnosis is within an analogy. Also, the further investigation will not give us the answer of the cause of the symptoms because the samples of urine and blood and the findings of body condition at the time of the accident are impossible to get.

6. Preliminary recommendations from the investigation of the waste site in Sihanoukville by Dr M Sakamoto, WHO temporary adviser, National Institute for Minamata Disease, Japan and Dr G Petersen, WHO Representative to Cambodia, 25th and 26th December 1998.

Samples were taken of various parts of the waste for further analysis in Japan. The site was tested for radioactivity (alpha- and beta rays). A test was also done for mercury vapor. Water Samples from water sources in neighboring village and a well used by woodcutters just 200 meters from the site were taken and tested. The preliminary tests of air and water showed no abnormal level of radioactivity or mercury. The result of tests on the soil samples will not be available before Dr Sakamoto returns.

Results from analysis of a soil sample taken previously and sent to Singapore for testing was given to the team. It showed high level of mercury (675 µg/g) but does not specify if it is inorganic mercury and/or methyl-mercury.

Samples of hair, blood and urine were collected from port workers complaining of sickness after handling the waste and of soldiers engaged in the Clean up operation.

The available data are not sufficient to make any firm conclusion of the toxicity of the waste. It may contain toxic organic material or toxic metals.

However, based on the size and location of the site, our observations and tests so far and the information given to us by the Department of Health and the Singaporean test results, we make the following preliminary recommendations:

1. The waste site as it is today does not pose any short-term threat to the population of Sihanoukville and there is no need for any special precautions directed towards the general population. There is no need to evacuate anybody. Neither does the waste pose any threat to the water supply of Sihanoukville. There is no danger of contamination of any food produced in the province or any fish or other seafood from the waters outside the province.
2. As the waste may pose a long-term risk for the population in the area, it should be removed as soon as possible in a safe way. To speed up the process more heavy machinery should be employed and the waste stored in larger containers. This will reduce the number of people exposed.
3. The local authorities should do its utmost to calm the population and dispel unfounded rumors about the danger of the waste.
4. The dumpsite must be protected securely from possible scavengers, children and other unauthorized persons.
5. The workers/soldiers employed in the removal of the waste must wear protective clothing: long sleeves, gloves and facemasks. Any solid gloves protecting against direct contact and dust will do. Paper masks plus a tight krama is recommended. After work thorough body wash is needed. Working clothes should be washed every day after use.
6. No special precautions are needed for the population in the closest villages.

Their water source seems safety.

7. The well in the woodcutter's camp very close to the site should be closed.
8. As there may be long term health risks from the waste, anyone possessing ascertained parts of the waste should notify local authorities so it can be collected and disposed of property.
9. Workers and soldiers exposed to the waste should be followed up medically if they develop symptoms of poisoning. Guidelines for this should be developed.
10. Domestic animals should be kept outside the waste area.
11. Fish in the pond next to the site should not be consumed.
12. After removal of the waste a layer of approximately 5cm topsoil should also be removed.

7. Further recommendations after the analysis of samples

- 1 As the mercury concentrations in the waste was very high and it was dumped on the hilly area surrounded with a pagoda and some villages in lower lying land, it should be removed as soon as possible in a safety way. Waste should not be heated in order to avoid the mercury vapor exposure.
- 2 The workers/soldiers employed in the removal of the waste must wear protective clothing: long sleeves, gloves and facemasks in order to avoid the inhalation of the dust and the direct skin contact.
- 3 The contamination of the environment of Sihanoukville would not be worried if the clean up of the site was properly carried. No special precautions are needed for the population in Sihanoukville and in the closest villages, since their water sources close the site were not contaminated with mercury.
- 4 After removal of the waste a layer of approximately 5-10 cm topsoil should also be removed. Check of the mercury contamination would be necessary to know whether the clean up was properly done or not.

5. Conclusion

- 1 The total mercury concentrations in the waste sample was very high. The other metals concentrations in the waste were within the normal concentrations in natural soils.
- 2 The total mercury concentrations in water around the site were normal natural levels.
- 3 ~~The total mercury concentrations in red blood cells, serum urine and hair of port workers and site workers were normal. They were similar to those of the general population in Asia.~~
- 4 Since typical health effects due to mercury exposure were not specified in the complaints of port and site workers and since none of the human samples showed high mercury concentration, it is unlikely that they suffer from mercury poisoning.

So? where's the
'possibly from one
toxic contaminants'?

References

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Acknowledgments

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Table 1. Mercury concentrations in waste samples (dry weight basis)

Number	Property	Color	Moisture (%)	Total Hg (µg/g)	Methyl Hg (ng/g)
1	Solid (fragile)	Gray	28.4	496	-
2	Solid (fragile)	Gray	26.4	724	-
3	Solid (hard)	Black	11.4	2497	-
4	Solid (hard)	Black	1.3	3984	-
5	Sand	Brown	31.1	97	33.7

-: Below 1.0 ng/g

Table 2. Cadmium, manganese, nickel, lithium, zinc, lead, iron and copper concentrations in waste samples (dry weight basis)

Number	Cd (ng/g)	Mn ($\mu\text{g/g}$)	Ni ($\mu\text{g/g}$)	Li ($\mu\text{g/g}$)	Zn ($\mu\text{g/g}$)	Pb ($\mu\text{g/g}$)	Fe ($\mu\text{g/g}$)	Cu ($\mu\text{g/g}$)
1	26	979.0	25.5	111.2	1018.6	194.7	51451	323.3
2	11	1779.6	27.6	448.7	968.3	499.2	87525	306.5
3	-	445.4	10.6	147.0	187.8	87.1	23058	92.6
4	-	83.3	19.9	7.5	102.8	35.1	26834	35.1
5	9	1140.6	76.7	99.5	561.9	134.9	48807	317.9

-: Below 1.0 ng/g

Table 3. Mercury concentrations in water samples

Sampling point	Total mercury (ng/l)
Well (200-300m below the site)	6
Tap water in Pagoda (1km below the site)	4
Well (200m below the Pagoda)	4
Tap water (1.5km far from the site, another side across a road)	6

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Table 4. Complaints of port workers

Object No.	Gender (age)	Exposure period (days)	Exposure period (hours)	Complaints (after the work)	Complaints (present)	Condition (change)
P-1	Male (32)	1	4	Stomatitis, dizziness, cough, weakness	Weakness, stomatitis	Better
P-2	Male (42)	1	5	Visual trouble, weakness	Visual trouble	Same
P-3	Female (40)	4	8	Headache, weakness	Headache, weakness	Better
P-4	Male (34)	2	8	Dizziness, headache, diarrhea	Dizziness, headache, diarrhea, stomachache, cough	Better
P-5	Male (33)	2	5.5	Weakness, stomachache, headache, stomatitis	Weakness, stomachache, headache	Better
P-6	Male (55)	2	4	Dizziness, weakness	Dizziness, weakness	Better
P-7	Male (30)	1	4	Visual trouble, feeling sleepy, chest pain	Weakness,	Better
P-8	Male (31)	1	4	Weakness, cough, body pain	Weakness, pollakiuria, stomachache	Better
P-9	Male (35)	1	4	Weakness, chest pain, headache	Headache, sore throat	Better

Interviewed by Dr K E Mony and Dr P P Raingscy

Table 5. Complaints of soldiers working at the site

Object	Gender (age)	Exposure period (days) (hours)		Protection	Complaints (during the work)	Condition (before working at the site)
S-1	Male (25)	4	16	±	Sore throat, dizzy, chest pain, thoracic oppression,	Healthy
S-2	Male (28)	4	16	±	Chest pain, thoracic oppression, asthenia	Healthy
S-3	Male (26)	4	16	±	Thoracic oppression, dysuria (minor pain and burning during urination), sore throat, headache	Healthy
S-4	Male (28)	4	16	No mask	Sore throat, trouble of vision, chest pain, skin irritation	Healthy
S-5	Male (28)	4	16	-	Thoracic oppression, trouble of vision, headache, skin irritation, Wound on the finger caused by the broken part of the waste	Healthy

Interviewed by Dr K E Mony and Dr P P Raingsey

Table 6. Mercury Concentrations in human samples

Object	RBC (Total Hg) (ng/g)	RBC (Methyl Hg) (ng/g)	Serum (Total Hg) (ng/g)	Urine (Total Hg) (ng/ml)	Hair (Total Hg) (ng/g)	Hair (Methyl Hg) (ng/g)
P-1	19.0	17.1	2.61	3.27	3.87	2.29
-2	16.3	14.3	2.94	1.96	3.39	3.22
-3	22.2	21.0	3.27	1.80	4.45	3.32
-4	19.6	15.7	2.94	1.63	3.63	3.18
-5	20.9	18.1	3.59	3.43	3.39	3.25
-6	25.5	22.4	2.94	1.47	4.79	4.21
-7	13.1	11.8	1.96	2.12	2.17	1.58
-8	17.0	15.7	2.29	0.82	5.08	3.26
-9	19.0	17.7	3.26	3.43	4.68	3.60
S-1	14.7	11.2	3.92	5.56	3.44	2.12
-2	17.0	13.4	3.26	4.41	1.64	1.30
-3	10.5	8.1	3.26	6.53	3.71	2.06
-4	11.7	7.5	4.58	3.84	1.29	1.16
-5	16.0	14.1	3.26	water	4.32	—
C-1					2.27	1.89
-2					2.89	2.84
-3					2.36	2.21
-4					1.68	1.59
-5					3.55	3.37

P: Port worker who has complaints.

S: Site work at the site.

C: Control who works in the center of Sihanoukville

Facsimile

Date: 99/1/11

TO:

Cambodia

FAX: (855) 23-212206

FROM: M. Sakamoto

National Institute for Minamata disease

☎: (0966) 63-3111

FAX: (0966) 61-1145

Message

Dear Sir

This is our latest report. We also got the informatio that the solid was the waste from NaOH production. If it is so, mercury is the most anxious substance and it concentration was very high, but dioxin may not be worried so much. Of corse, all the waste may contain certatin level of dioxin. I suggested to Dr Petersen to ask the National Institute for Environmental Studies if stil he was warring it.

Yours sincerely,