HEALTH IMPACTS OF MERCURY CYCLING IN CONTAMINATED ENVIRONMENTS IN CHINA STUDIED BY NUCLEAR TECHNIQUES

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Abstract

Mercury is a highly toxic non-essential element. The mercury cycling in natural environments is a complex process. In recent years, the stable mercury isotope tracer and related analytical techniques have been developed. They offer unique possibility to understand the biogeochemistry of mercury in various environmental conditions. So a new co-ordinated research project (CRP), on health impacts of mercury cycling in contaminated environments studied by nuclear techniques, has been supported by the IAEA. This paper introduces the research project which IAEA research contract number is CPR-10874. It includes the scientific background, scope of the project, methods, some results related this CRP and the plans for future work.

1. INTRODUCTION

Mercury as a global pollutant has concerned worldwide since the end of the 1980s. It emitted to atmosphere from both anthropogenic and natural sources. Important source of the former is discharged from the combustion of fossil fuels as well as production and use of Hg [1]. When coming back to earth's surface with wet and dry deposition, 93.7% of it entered terrestrial ecosystem [2]. While the terrestrial food chains would be polluted by mercury.

In the past 20 years, China's economy was forging rapidly ahead. The combustion of fossil fuels was increasing year after year, especially in some industrial cities. For example in Chongqing, which is an important industrial city in southwest China and is located at the subtropical zone, it was reported that about 7 million tons of coal was consumed in 1980 but more than 15 million tons of coal was used in 1995[3].

For this and other reasons, about 5000 kg Hg was emitted to the atmosphere there per year. In 1995, for example, about 5680.3 kg mercury was emitted, 87.8% of which was from coal combustion. It was found that Hg contents in soils, edible parts of some vegetables were increasing up to unacceptable level in Chongqing area [4]. Moreover, the fishponds, which produce the main aquatic production in the area, were also affected by the mercury deposition. So, it is important that finds out the laws of atmospheric Hg depositing into soil-plant system, fishponds and terrestrial food chains. So a new co-ordinated research project (CRP), on health impacts of mercury cycling in contaminated environments studied by nuclear techniques, has been supported by the IAEA.

In the first research year (1999/10/01~2000/10/01), according to the contract (PRC-10874) our work included:

- Collection of environmental samples such as air, soil and sediments, plants, fish, and water, at selected sampling sites;

- Analysis of the mercury content in the collected samples using CVAFS (or CVAAS), ICP-MS;
- Collection and analysis of human biological material samples, for example hair and urine.

During the second research year (2000/10/01~2001/10/01), according to the contract (PRC-10874 R1) our work included:

- Investigating the transformation of atmospheric mercury deposition in soil-plant-water system studied by stable isotope trace.
- Study the rate of mercury uptake of vegetables from atmosphere or from soil.

2. METHODS

2.1. Selection of Research Sites

In the investigation, we selected Chongqing for the research field of the CRP in China. Chongqing is located at subtropical zone (28°27'49''N~30°26'28''N and 105°17'2''E~107°27'30''E), it is an important industrial city in southwest China. Three fixed research sites have been selected in difference atmospheric mercury conditions in Chongqing. They were heavy pollution site, medium pollution site and control site. The heavy pollution site was near a clinic thermometer factory, the medium pollution site was near a fire power plant and the control site was a rural site.

For this project, the samples were mainly collected in the fixed research sites. Furthermore, some samples of water, sediment and fish were also collected from other sites, for example mainstream of the Yangtze River and its branches and some reservoirs in Chongqing, and some samples of fish were collected from the markets.

2.2. Methods of sampling and collection of samples

Air samples were collected by amalgamation on gold trap; soil samples were collected at the depths of 0~20 cm; plant samples were collected in the edible part; sediment samples were collected with the sediment collector; water samples were collected at the center of fishponds; fish samples included the difference feeding habits fishes that the research site had; hair and urine samples were the local residents'.

Up to the present, 161 fish samples, 81 water sample, 81 sediment samples, 37 soil samples, 62 plant samples, 143 hair samples, 49 urine samples and 158 air samples have been collected and been analyzed, respectively (Table I).

2.3. Methods of samples analysis

Items of samples analysis: total mercury of whole samples; organic mercury or methyl-mercury of fish, water, sediment, hair samples; isotopic abundance ratio of mercury of some important samples; pH of water, sediment and soil samples; EC of water and sediment.

Pretreatment of samples: soil and sediment samples were digested with HNO_3-H_2SO_4-$KMnO_4$ for total mercury measured; plant and fish samples were digested with HNO_3-H_2SO_4-V_2O_5; mercury of water samples were accumulated using sulfhydryl cotton fiber (SCF); extraction of methylmercury in samples using 2N HCl, separated by SCF.

Mercury measured: total mercury in the samples was analyzed using CVAFS (or CVAAS); distribution of mercury isotopes in the samples were analyzed using ICP-MS; methylmercury were analyzed using GC (ECD).

TABLE I: SAMPLES SAMPLING IN THE INVESTIGATION

Samples		Numbers of sample
(1) Fish samples	Fish samples of fishponds	84
	Fish samples of river or reservoirs	56
	Fish samples from markets	21
(2) Water samples	Water samples of fishponds	53
	Water samples of river or reservoirs	28
(3) Sediment samples	Sediment samples of fishponds	53
	Sediment samples of river or reservoirs	28
(4) Soil samples		37
(5) Plant samples		62
(6) Hair samples		143
(7) Urine samples		49
(8) Air samples		158

2.4. Experiment design for studying the transformation

Two treatments of B_1, which 3 kg air-dry (<3 mm) was put in a 16x12 cm plastic pot.), and B_2 (B1+1% humic substances) were put in a room with an average air Hg concentration of 796.4±186.3 ng/m^3 under constant moisture for 60 days. Furthermore, two treatments P_1 and P_2 were set up according to the same design as B_1 and B_2, respectively, but the soils of P_1 and P_2 were applied 2 mg/kg Hg (II) with $HgCl_2$ solution. After mixing thoroughly, the soils of P_1 and P_2 were incubated in the laboratory under constant moisture for two months. The P_1 and P_2 were regarded as the treatments that were polluted by contain-Hg waste water and the B_1 and B_2 were regarded as the treatments that were polluted by atmospheric Hg. After 60 days, the soil samples of P_1, P_2, B_1 and B_2 were collected. Then the various forms of Hg of native soil (CK), P_1, P_2, B_1 and B_2 were determined immediately according to the sequential extraction procedure [5][6] listed at Table II.

2.5. Experiment design for studying the uptake rates of mercury by vegetable

Two groups of pot experiments, the high air Hg condition with an average air Hg concentration of 57.6±14.7 ng/m^3 and the low air Hg condition with an average air Hg concentration of 22.8±3.7 ng/m^3, were carried out at the simulated experiment. Two same treatments were adopted in each group (Table III). Neutral purple soil (Table IV) was taken for the study.

The experiments were carried out from 09/1999 to 08/2000. Four kinds of vegetables, radish, capsicum, lettuce and kidney bean, were planted at different seasons. Every vegetable sample was collected and was analyzed after its seedling was cultured for 50 days in the experiment soil according to above mention treatments. The soil samples were also collected and analyzed at the same time.

2.6. Quality assurance and quality control

- Fields investigated, sampling collected with standard operating procedures;
- Quality control of analysis using standard geochemical samples and reference materials.

TABLE II: THE SEQUENTIAL EXTRACTION PROCEDURE OF ANALYSIS OF MERCURY SPECIES IN SOIL SAMPLES

Step	Extracting method	Mercury species
I	1.00 g of soil sample was weighed into a 50 ml plastic centrifugal tube, and 20 ml of 0.1 mol/L $CaCl_2$ (pH=7) solution was added in. Vibrate the tube for 30 min at room temperature, and centrifuged it at 3500 r.m.p for 10 min. The aqueous phase was transferred to a 25 ml volumetric flask. Adopt CVAFS method to analyze Hg content.	Active Hg (include soluble Hg and exchangeable Hg)
II	20 ml of 1mol/L HCl and 0.5 ml of 1% $CuSO_4$ solution was added into the residue above. Vibrate the tube for 30 min at room temperature, and centrifuged it at 3500 r.m.p for 10 min. The aqueous phase was transferred to a 25 ml volumetric flask. Bromized the solution, then adopt CVAFS method to analyze Hg content.	HCl-dissoluble Hg
III	20 ml of 1% KOH solution was added into the residue above. Vibrate the tube for 30 min at room temperature, and centrifuged it at 3500 r.m.p for 10 min. The aqueous phase was transferred to a 25 ml volumetric flask. Bromized the solution, then adopt CVAFS method to analyze Hg content.	Organic-bound Hg
IV	10 ml of 2 mol/L HNO_3 was added into the residue above. Vibrate the tube for 30 min at room temperature, and centrifuged it at 3500 r.m.p for 10 min. The aqueous phase was transferred to a 25 ml volumetric flask. Adopt CVAFS method to analyze Hg content.	Hg° form
V	10 ml of aqua regia was added into the residue above, heated at 90°C in a water bath for 4 h, and centrifuged it at 3500 r.m.p for 10 min. The aqueous phase was transferred to a 25 ml volumetric flask. Adopt CVAFS method to analyze Hg content.	Residual Hg

TABLE III: EXPERIMENT DESIGN FOR STUDYING THE MERCURY UPTAKE RATES BY VEGETABLES

Air treatment	Air Hg content (ng/m^3)	Soil treatments	Treatment mark	Soil Hg content (mg/kg)
Low air Hg conditions	22.8±3.7	Native soil	A	0.0973
		Native soil applied Hg	B	0.199
High air Hg conditions	57.6±14.7	Native soil	C	0.0973
		Native soil applied Hg	D	0.199

TABLE IV: PROPERTIES OF EXPERIMENT SOIL

Soil	pH (H_2O, 1:2.5)	O.M. (g/kg)	CEC (c mol/kg)	Clay(<1μm) (g/kg)	Hg (mg/kg)
Neutral purple soil	6.92	10.4	18.4	149	0.0973

3. RESULTS AND DISCUSSION

3.1. Content of mercury in atmosphere in Chongqing

The results from the investigation indicated that the Hg concentration in atmosphere in Chongqing was in the range of 9.2 to 101.5 ng/m^3 and its average concentration was 34.4±12.7 ng/m^3. Table V shows that the average concentration of atmospheric mercury in the research sites. The Hg emitted source in heavy pollution site was the clinic thermometer factory, in medium pollution site was the fire power plant. The concentrations of air Hg in heavy and medium pollution sites were much higher than that in control site.

TABLE V: CONCENTRATION OF AIR HG IN THE RESEARCH SITES

	Heavy pollution site	Medium pollution site	Control site
Air Hg (ng/m^3)	61.6±27.9	42.6±6.9	11.4±4.2

3.2. Content of mercury in fish, water and sediment in Chongqing

Table VI showed the mercury in fishpond systems in the research sites. From these data, they indicated that the accumulation of mercury in fishponds in polluted sites was much higher than that in control site. So the contents of mercury in muscle of fish in polluted sites were higher than that in control site. The contents of mercury in all the muscles of fish in heavy pollution site exceeded the limit of Food Health Standard Value (FHSV) for Hg (of China) in fish (0.3 mg/kg FW).

TABLE VI: CONTENTS OF MERCURY IN FISHPONDS IN THE RESEARCH SITES

	Heavy pollution site	Medium pollution site	Control site
In water (ng/L)	96.8~1789	55.3~935	20.0~53.2
In sediment (mg/kg DW)	0.531~13.5	0.275~2.68	0.0950~0.189
In muscle of fish (mg/kg FW)	0.307~2.46	0.107~0.417	0.0268~0.0941

Table VII showed that the contents of mercury in Yangtze River and some reservoirs in Chongqing. The contents of mercury in muscle of fish from the Yangtze River were lower than the FHSV, but some data from the reservoirs were higher than the FHSV.

TABLE VII: CONTENTS OF MERCURY IN YANGTZE RIVER AND RESERVOIRS

	Main stream	Branches	Reservoirs
In water (ng/L)	48.3~71.2	55.3~89.8	36.5~119
In sediment (mg/kg DW)	0.0847	0.0622~0.128	0.0913~0.130
In muscle of fish (mg/kg FW)	0.0174~0.122	0.0383~0.258	0.0231~0.414

3.3. Mercury in soil-plant system

Because of serious air pollution by Hg in some places in Chongqing, the soil-vegetable system had been polluted. It was found that the content of mercury in the edible part of some vegetables, for example lettuce, Chinese cabbage, green pepper and so on, had exceeded the national limits (Food Health Standard Value, FHSV) for Hg of China (GB 2762-82, 0.01 mg/kg FW), especially in heavy polluted area. Table VIII appeared that the contents of mercury in all the vegetable samples were higher, 91.7% of which was in excess of the FHSV. In the medium polluted site, the contents of mercury in the vegetable samples exceeded FHAV with 28.6%, while in the control site, which was far from Hg emission sources, the vegetables were in good quality there.

TABLE VIII: MERCURY IN SOIL AND VEGETABLE IN THE RESEARCH SITES

Sites of sampling	Soil (mg/kg)		Vegetables (mg/kg FW)	
	range	mean	range	mean
Heavy pollution site	0.247~0.433	0.310	0.0027~0.213	0.083
Medium pollution site	0.098~0.214	0.174	0.0017~0.093	0.014
Control site	0.043~0.075	0.065	0.00086~0.0098	0.0033

3.4. Content of mercury in hair and urine

In the investigation, some hair and urine samples of human were collected and were analyzed for studying the health impacts of mercury cycling in different contaminated environments. The data of analysis were presented in Table IX and Table X. The contents of mercury in hair and urine from the pollution sites were higher than that in the control site. It indicated that the crowd in mercury-polluted area had been impacted by mercury.

TABLE IX: CONTENTS OF MERCURY IN HAIR (MG/KG)

Sites of	Men			Women		
Sampling*	number	range	mean	number	range	mean
H. P. site	31	0.393~8.78	3.22	28	0.303~12.4	4.17
M. P. site	24	0.289~6.16	1.84	25	0.523~6.55	2.03
Control site	18	0.177~4.45	0.971	17	0.261~5.14	1.12

*H. P. site = Heavy pollution site; M. P. site = Medium pollution site.

TABLE X: CONTENTS OF MERCURY IN URINE (MG/L)

Sites of	Men			Women		
Sampling	number	range	mean	number	range	mean
H. P. site	8	11.3~40.8	28.1	11	6.38~45.7	22.5
M. P. site	9	1.26~19.4	9.16	9	0.925~23.4	11.4
Control site	6	0.845~8.33	3.14	6	0.637~10.2	3.46

3.5. Relationship between atmospheric mercury and plant leaves mercury content

The results of investigation indicated that the bioaccumulation of Hg in plant leaves was related to the concentration of atmospheric Hg, which was linearly correlated as Figure I showed, with correlation coefficients of 0.925** (n=39).

Hg in plants came both from soil and the atmosphere. On the whole, Hg contents in plant leaves increased with the increase of air-Hg, the correlation equation was:

$$y = 0.0173x-0.3204$$

Calculation from this equation showed that the accumulation of Hg in plants stemmed mainly from soil rather than atmosphere when air-Hg was lower than 18.5 ng/m^3, however contribution of air-Hg to plant Hg accumulation was increasing with the increase of Air-Hg when its concentration was higher than 18.5 ng/m^3. Similar to the variation of air-Hg with the distance from the Hg emission source, the Hg contents in leaves of banyan-tree and lettuce were decreased as the increase of the distance from the Hg emission source in a thermometer factory, their relations could described by following equations:

$$y_b = 88.806x^{-0.8365} \quad R^2=0.9502$$

$$y_l = 2.2677x^{-0.5778} \quad R^2=0.9209$$

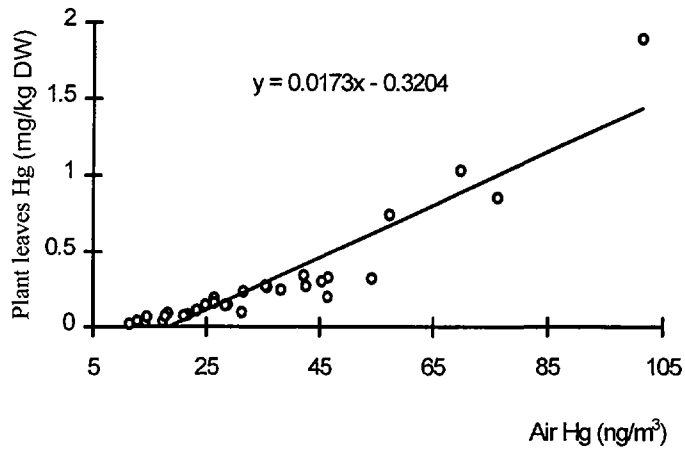

FIG 1: Relationship between plant leaves and air Hg

3.6. Transformation of atmospheric Hg in soil

The distribution of various forms of Hg in native soil (CK), B1, B2, P1 and P2 were listed in Table XI.

TABLE XI: DISTRIBUTION OF VARIOUS FORMS OF HG IN SOIL OF VARIOUS TREATMENTS

Treatment		Active Hg	HCl-dissoluble Hg	Organic-bound Hg	Hg° form	Residual Hg	Total Hg
CK	Content (mg/kg)	ND	0.0240	0.0194	0.0148	0.1748	0.2330
	% in total	/	10.30	8.34	6.35	75.01	
B_1	Content (mg/kg)	0.0003	0.0677	0.0214	0.0722	0.3039	0.4665
	% in total	0.06	14.54	4.60	15.51	65.28	
B_2	Content (mg/kg)	0.0004	0.0821	0.0427	0.1220	0.3849	0.6321
	% in total	0.06	12.97	6.74	19.27	60.81	
P_1	Content (mg/kg)	0.0026	0.6249	0.0707	0.1882	1.2625	2.1489
	% in total	0.12	29.08	3.29	8.76	58.75	
P_2	Content (mg/kg)	0.0022	0.6633	0.1843	0.2654	1.3747	2.4899
	% in total	0.09	26.64	7.40	10.66	55.21	

Contrasting with the CK, the percentage of Hg° form in total Hg increased in the polluted soil by atmospheric Hg, and so did the HCl-dissoluble Hg. But the percentage of organic-bound Hg and residual Hg decreased. The distribution of various Hg forms in the polluted soil by contain-Hg wastewater had the same variation as the polluted soil by atmospheric Hg.

The contents of various Hg forms in the polluted soil subtracted by that in the CK were their net contents (Table XII).

TABLE XII: NET INCREASING CONTENTS OF VARIOUS HG FORMS IN THE POLLUTED SOIL

Treatment		Active Hg	HCl-dissoluble Hg	Organic-bound Hg	Hg° form	Residual Hg	Total Hg
B_1	Net increasing(mg/kg)	0.0003	0.0437	0.0020	0.0574	0.1291	0.2335
	% in total	0.12	18.75	0.86	24.58	55.29	
B_2	Net increasing(mg/kg)	0.0004	0.0581	0.0233	0.1072	0.2101	0.3991
	% in total	0.10	14.56	5.84	26.86	52.64	
P_1	Net increasing(mg/kg)	0.0026	0.6009	0.0513	0.1734	1.0877	1.9159
	% in total	0.14	31.36	2.68	9.05	56.77	
P_2	Net increasing(mg/kg)	0.0022	0.6393	0.1649	0.2506	1.1999	2.2269
	% in total	0.10	28.71	7.40	11.25	53.88	

The results clearly demonstrated that the Hg transferred from air into soil had been transformed in two months in the pot experiment, 0.10~0.12% of which was in active Hg, 14.56~18.75% in HCl-dissoluble, 0.86~5.86% in organic-bound and 52.64~55.29% in residual, respectively. The Hg° form-the main form of atmospheric Hg was only kept for 24.58~26.86% in soil. Additionally, the total net increasing content of Hg and the transforming rate of organic-bound Hg and the maintaining rate of Hg° forms in the treatment with humus (B_2) were higher than that in the treatment without humus (B_1). The result indicated that humus application could promote the Hg accumulation in soil.

After applied in soil, the H_2O-dissolutable $HgCl_2$ would be transformed. In the pot experiment, after incubated in two months, only 0.10~0.14% of active Hg that applied with $HgCl_2$ solution remained in the soil. The rest had been transformed to other forms, 28.71~31.36% of which was in HCl-dissoluble, 2.68~7.40% in organic-bound, 7.05~11.25% in Hg° form, and 53.88~56.77% in residual, respectively.

3.7. Uptake rates of mercury by vegetable from atmosphere and soil

The uptake Hg amount of vegetables in the pot experiments was listed in Table XIII.

TABLE XIII: UPTAKE HG AMOUNT OF VEGETABLE PLANT IN POT EXPERIMENTS

Treatment mark	capsicum		Kidney bean		Lettuce		Radish	
	biomass (g/pot)	uptake Hg (μg/pot)	biomass (g/pot)	uptake Hg (μg/pot)	biomass (g/pot)	uptake Hg (μg/pot)	biomass (g/pot)	uptake Hg (μg/pot)
A	5.4	0.0451	15.2	0.0600	41.4	0.123	25.7	0.198
B	5.6	0.0623	15.0	0.0911	41.0	0.235	25.4	0.295
C	5.6	0.261	14.8	0.140	39.9	0.481	26.3	0.524
D	5.2	0.289	15.0	0.180	39.1	0.631	26.4	0.620

According to below expressions, the contribution rates of air-Hg to plant and soil-Hg to plant were showed in Table XIV.

$$AMCR(\%) = \frac{M}{D-A} \times 100 \qquad M = \frac{[(C+D)-(A+B)]}{2}$$

$$SMCR(\%) = \frac{N}{D-A} \times 100 \qquad N = \frac{[(B+D)-(A+C)]}{2}$$

Where AMCR means the contribution of air-Hg to plant, SMCR means the contribution of soil-Hg to plant.

TABLE XIV: CONTRIBUTION RATES OF AIR-HG TO PLANT AND SOIL-HG TO PLANT (%)

	Capsicum	Kidney bean	Lettuce	Radish
AMCR	90.7	70.4	74.2	77.1
SMCR	9.3	29.6	25.8	22.9

The results of the experiments showed that the four tested vegetables absorbed Hg came both from soil and the atmosphere, 70.4%~90.7% of it came from the atmosphere and 9.3%~29.6% came from the soil.

4. PROGRAMME OF WORK AND EXPECTED OUTPUT FOR 2002

During 2002, we plan to take the study of Cycling of Mercury in Vegetable Land Systems in Different Acid Deposition Areas.

It will select three fixed monitoring sites at vegetable land in different acid deposition areas. The area of the land will be about 150 m^2, lysimeters will be set up in each land for collecting the soil water samples and the water sample will be imbibed out for analysis mercury content at intervals of 15 days. Each rainwater will be collected and will be determined pH, EC and mercury content. Furthermore, the samples of air, soil, plant, soil-sorption-water will be collected and be analyzed at fixed intervals, respectively. After one-year monitoring, the input value and sendout of mercury in the vegetable land systems will be calculated, the cycling of mercury will be described in vegetable land systems in different acid deposition areas and the reasons of mercury pollution of soil and vegetable will be proved up in acid deposition area.

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