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THE PRESENT CONDITION OF SOIL CONTAMINATION WITH HEAVY METALS AT PARKS IN HONSHU AND KYUSHU

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Abstract

The concentration of heavy metals and other elements in the soil at 157 locations in Honshu and Kyushu were determined using the three different extraction methods. High concentration of Cr and Co was found in urban areas. Pb was also found a high concentration at one location. Concentration of Cr, Co, and Cu were correlated with population density, while the concentration of Cr, As, Se, Cu, and Zn were correlated with the distance from a waste incinerator plant. The data should provide a basis for pollution prevention measures.

KEYWORDS: *heavy metal, soil contamination, extraction method, park soils*

1. Introduction

Soil pollution is a serious problem not only in agricultural lands but also in residential area. It is sometimes difficult to clear the relationship between the present land owner and the soil pollution in the site where factories and plants are constructed in residential area. However, an effective soil pollution survey is required in order for a company to acquire ISO 14001 certification or to redevelop a factory, etc. There are many cases where soil pollution has been found by investigation and groundwater monitoring for such surveys. In addition, soil pollution is affected by the landfill problem and the increasing amount of waste produced by society. Table 1, which is the summary of soil pollution investigation results in Japan, shows that both the investigations and the excess pollution have increased from 1990 to 2000. Table 2 shows that about half of the soil pollution cases involved heavy metals.

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Table 1. Environmental survey of soil pollution, from1990 to 2000

	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000
number of investigation	26	38	35	44	44	44	58	62	199	206	179
number of excess	0	8	13	13	25	36	50	48	118	129	134

Source: Ministry of the Environment of Japan(2000)

Table 2. Soil pollution due to heavy metals

(contain duplicate data)

	2000		total (1975-2000)	
	number of survey points	number of points exceeding the soil environmental standard	number of survey points	number of points exceeding the soil environmental standard
Cadmium	27	6	234	33
Lead	72	45	384	170
Hexavalent Chromium	41	26	189	95
Arsenic	60	40	300	143
total Mercury	39	19	257	77
Arkyl Mercury	0	0	2	0
1.1-dichloroethylene	14	4	80	24
Cis-1.1-dichloroethylene	43	24	186	105
1,1,1-Trichloroethane	21	4	181	15
Trichloroethylene	66	38	398	178
Tetrachloroethylene	50	37	319	152
Benzene	20	9	48	25

Source: Ministry of the Environment of Japan(2000)

Pollutants such as heavy metals and dioxins accumulate in soils, and cannot be removed easily. These pollutants migrate slowly through soil and may leach into groundwater, and become absorb into agricultural products. There is little risk of taking polluted soil directly into the body by direct ingestion, dermal adsorption, and inhalation of fugitive dusts. For this reason, many countries such as Germany (1998), the Netherlands (1997), and Sweden (1996) have established guidelines for dioxin based on direct ingestion from soils. In addition, the U.S. EPA (1998) has also set a provisional level for direct ingestion of dioxin-contaminated soil. In Japan, the Ministry of the Environment has established the environmental standard for dioxin measured by the content test, and later established the environmental standards for heavy metals measured both by the elution tests and content test in order to estimate health risks due to direct ingestion and indirect ingestion.

Various studies of soil pollution have demonstrated the relationships between the soil pollution and human activities such as a factory, a refinery and heavy traffic. Al-Chalabi and Hawker (2000) showed that lead concentration extracted nitric acid decreased inversely with the distance from roads, and accumulated over the depth of five centimeters. Valery Barcan and Eugene Kovnatsky (1998) researched the heavy metal soil pollution caused by operation of copper and nickel refineries in Russia. These studies focused on areas near factories, refineries, waste incinerator plants, and heavy traffic roads. However, there are few studies on soil pollution that has been influenced by unspecified industrial activities in a large area. In this study, we surveyed park soil over a wide region of Japan. The reason we investigated children's parks is that children may take soil directly into the body when playing in the park. Characteristics of a park soil depend on the history of park (preparation and soil dressing), however, the chemical properties of the soil in each park were similar in terms of the ratios of principal component elements, pH, etc. We have analyzed the relation between soil contamination and industrial activity. This study offers basic data for developing measures for pollution prevention.

2. Methodology

Heavy metal content in soil is dependent on various factors such as the chemical properties of the soil, the influence of artificial pollution, and the influence of sea and climate. We selected on soil sampling areas in the Honshu and Kyushu regions of Japan in order to investigate the influence of industrial activity. As shown in Figure 1, we conducted soil investigations in the Sanyo (1998), Kyushu and Sanin (1999), Chubu (2000), and Tohoku areas (2001) for three days during the months of November and December. For this investigation, soil samples were gathered from children's parks. Each park locates at intervals of 7-20 kilometers in Sanyo, Kyushu, Sanin, 35-40 kilometers in Chubu, Tohoku.

In each park, we sampled soil from five different locations. This sampling method is based on the Handbook of Soil and Groundwater Pollution Measurement from the Ministry of the Environment in Japan. In this method, the sampling density of the soil is five points in 1000 m^2: one point is the center of the area and the other four points are 5-10 meters from the center in two perpendicular directions. If the area or shape of the park did not allow us to apply this method, we located five suitable sampling points separated mutually by a few meters, (Kiuchi et al. (2000)). The surface soils were taken from the ground down to a depth of 5.0 centimeters, and the five samples in each park were mixed into one sample. Ikenouchi et al. (1998) showed that surface soil concentration of Cr and Ni has varied according to the depth within 5.0 centimeters. In Chubu (2000) and Tohoku (2001), each sample from a sampling point was divided into two fractions: the upper soil sample (0-2.5 centimeters depth) and the lower soil sample (2.5-5.0 centimeters depth). The

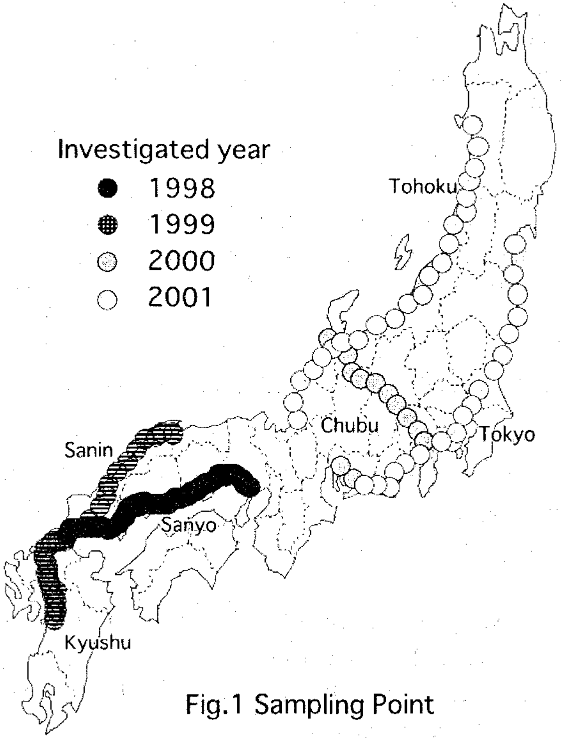

Fig.1 Sampling Point

average concentration of the upper soil and the lower soil was regarded as the concentration for that sampling location. Soil samples were dried in a desiccator for 12 hours, keeping the temperature at 60℃. Soil samples were passed through the sieve of 2.0 millimeters mesh.

3. Measurement

In this study, trace elements and heavy metals were extracted from the soil and the concentrations contained in the extraction solutions were determined. Target elements were Na, Mg, Al, K, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Y, Zr, Cd, Sn, Sb, Cs, Hg, and Pb. These elements accumulate in soils in various forms such as metallic oxides, ion combinations and cation exchangers. Thus, the content of an extraction solution depends on the extraction method. The soils were extracted using three different methods in order to measure the concentrations of the target elements and determine the forms of their accumulation. In this study, we used the three extraction methods, hydrochloric acid extraction, nitric acid extraction, and exchangeable cation extraction.

3.1 Hydrochloric acid extraction method

This method provides for hydrochloric acid extraction in a closed vessel using a shaker and incubator. Hydrochloric acid exchanges trace elements adsorded on organic group, stabilizes trace elements in a liquid phase by ion-pair formation reaction between chloric ion and extracts trace elements absorped by Fe and Al oxide and hydroxide. The method extracts the trace elements adsorbed on soil particles in the metal oxide forms or exchangeable cation form.

Procedure

1. Weigh 10 gram of soil sample into each vessel. Add 50 ml HCl (0.1 mole per liter) to each vessel.
2. Shake vessels (150 rpm) for 12 hours at a temperature of 60℃.
3. Centrifuge (2500 rpm) for three minutes and filter through a 0.45 micrometer acetate filter.
4. Dilute the extraction solution with deionized water to 25 times dilution.

3.2 Nitric acid extraction method

This method provides for nitric acid extraction in a closed vessel using pressure controlled microwave heating for the determination of metals. Nitric acid desolves most part of soil particles in order to extract total amount of trace elements. This method extracts almost all trace elements adsorbing onto soil particles.

Procedure

1. Weigh 0.5 grams of soil sample into each vessel. Add 15 ml HNO_3 (60 percent of body weight) to each vessel.
2. Operate MDS2000 (Microwave Digestion System, CEM Corporation) under conditions as shown in Table 3.
3. Filter through 0.45 micrometer acetate filter.

4. Dilute the extraction solution with deionized water to 25 times dilution.

Table 3. Operating conditions for HNO_3 microwave digestion

Stage	1	2	3
Power [%]	100	100	100
Pressure [atm]	40	80	120
Time [min]	10	15	20
Time at Pressure[min]	5	8	10
Fan Speed [%]	100	100	100

3.3 Exchangeable cation extraction method

This method provides for the ammonium acetate extraction in a closed vessel using a shaker. It extracts trace elements that have adsorbed onto cation exchangers in soil particles.

Procedure

1. Weigh 2.0 grams of soil sample into each vessel. Add 30 ml ammonium acetate (1.0 mole per liter).
2. Shake vessels (250 rpm) for 15 minutes.
3. Centrifuge (2500 rpm) for three minutes. Skim 10 ml of extraction solution and add 10ml ammonium acetate (1.0 mole per liter) to the remaining extraction solution. Save 10 ml of extraction solution.
4. Repeat the operation 2 and 3 for two times on the slurry (vessels are shaken by hand for 30 minutes) and mix 10 ml of skimmed extraction solutions.
5. Filter through 0.45 micrometer acetate filter.

3.4 ICP/MS Measurement

The concentration of metals in extraction solutions was measured by inductively-coupled plasma mass spectrometry (ICP/MS) using a Hewlett Packard instrument (HP4500). Concentration was determined using a calibration curve method that used standard solutions for each trace element. In this investigation, Sn, Sb and Hg in the extraction solutions were contained under the detection limit of identification for most samples. Thus, each concentration was measured for Na, Mg, Al, K, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Y, Zr, Cd, Cs, and Pb. The concentration in the soils was calculated from the extraction solutions, was shown in the unit of milligram-elements per kilogram-dry soil.

4. Results

4.1 Concentration of heavy metals

The results of the investigation of soil pollution at 157 children's parks in Honshu and Kyushu are shown in Table 4. Samples in Tohoku were not extracted using the exchangeable cation extraction method. The table shows the concentration of the elements, and indicates the 5, 50, and 95 percentile values for concentration of each element by the extraction method. Al, Sc, V, Cr, Co, Y, Zr, and Pb were not measured with the exchangeable cation extraction method. The element found in the highest concentration was Mg, Al, K, Mn, and Fe. These elements were measured at median concentrations of more than 1000 mg per kg-dry soil. It is possible that the hydrochloric acid extraction method captured trace elements due to local pollution that adsorbed weakly onto soil particles. In contrast, the nitric acid extraction method allowed measurement of trace elements contained in the soil particles themselves. Comparing the values obtained from these two methods, the concentration by the hydrochloric acid extraction distributes in larger ranges than the range by the nitric acid extraction, except for Mg and As. Also, the concentration by the nitric acid extraction was higher than those from the hydrochloric acid extraction. For Al, K, Sc, V, Cr, Fe, As, Zr, and Cs, the ratios of hydrochloric acid extraction concentration to nitric acid extraction concentration were under 10 percent. Only the ratio for Na, Mg, Mn, Co, Ni, Cu, Zn, Se, Y, Cd, and Pb were greater than 10 percent.

Table 4. Concentration values found for elements in the soil samples

	HCl extraction [mg/kg-soil]			HNO_3 extraction [mg/kg-soil]			Exchangeable Cation extraction[mg/kg-soil]		
percentile	5	50	95	5	50	95	5	50	95
Na	6.1E+00	3.3E+01	2.6E+02	4.5E+01	1.3E+02	8.6E+02	8.3E+00	2.4E+01	1.5E+02
Mg	8.3E+01	4.4E+02	2.4E+03	9.0E+02	4.1E+03	3.1E+04	2.8E+01	9.5E+01	3.7E+02
Al	3.3E+01	1.3E+03	4.2E+04	1.3E+04	3.2E+04	3.0E+05	-	-	-
K	1.4E+01	4.9E+01	1.3E+02	5.1E+02	1.9E+03	4.8E+03	1.1E+01	2.4E+01	1.1E+02
Sc	1.3E-02	1.6E-01	7.1E-01	1.6E+00	3.7E+00	9.5E+00	-	-	-
V	2.9E-02	2.5E-01	1.5E+00	4.9E+00	2.2E+01	1.0E+02	-	-	-
Cr	2.1E-02	1.9E-01	8.4E-01	9.6E-01	7.1E+00	3.7E+01	-	-	-
Mn	3.3E+01	9.6E+01	2.4E+02	1.8E+02	5.1E+02	1.0E+03	6.9E-01	3.8E+00	4.3E+01
Fe	1.6E+01	2.6E+02	9.8E+02	8.5E+03	2.8E+04	1.4E+05	1.8E+00	4.6E+00	1.2E+01
Co	1.2E-01	8.0E-01	2.1E+00	1.4E+00	4.2E+00	1.3E+01	-	-	-
Ni	1.2E-01	1.1E+00	3.7E+00	9.7E-01	4.4E+00	2.9E+01	2.1E-02	5.6E-02	2.0E-01
Cu	1.4E-01	7.1E+00	2.6E+01	3.7E+00	1.4E+01	6.4E+01	1.4E-01	8.6E-01	2.6E+00
Zn	1.8E+00	1.5E+01	3.7E+01	1.8E+01	4.3E+01	9.2E+01	1.6E-01	6.0E-01	2.6E+00
As	1.3E-02	5.7E-02	1.5E-01	4.2E-01	1.4E+00	6.8E+00	3.2E-03	2.4E-02	3.1E-01
Se	3.4E-02	1.8E-01	5.3E-01	2.8E-01	6.5E-01	1.4E+00	6.1E-03	2.2E-02	3.3E-01
Y	3.4E-01	4.3E+00	2.2E+01	4.5E+00	1.0E+01	2.9E+01	-	-	-
Zr	4.3E-04	1.2E-02	7.4E-02	1.3E+00	4.5E+00	3.0E+01	-	-	-
Cd	1.5E-02	6.8E-02	4.3E-01	4.5E-02	1.6E-01	5.0E-01	2.9E-03	1.1E-02	6.3E-02
Cs	4.5E-04	2.4E-03	2.6E-02	6.8E-01	2.3E+00	6.2E+00	2.1E-03	1.1E-02	1.3E-01
Pb	5.8E-02	2.3E+00	1.4E+01	3.2E+00	8.6E+00	4.2E+01	-	-	-

HCl extraction	157 samples
HNO_3 extraction	157 samples
Exchangeable Cation extraction	103 samples

Figure 2 shows the distributions of Cu concentration and its logarithm in the soils by the nitric acid extraction, in the semilog scale. The distributions of logarithmic concentration was approximated to normal distribution in semilog scale. The distributions for the other trace elements were similar. Concentration values were transformed into logarithms in order to prepare a distribution type for statistical analysis. Figure 3 shows the distributions of As concentration in the soils after the hydrochloric acid extraction and nitric acid extraction. As we have seen, nitric acid extraction concentration was higher than hydrochloric acid extraction values. This suggests that the amount of newly accumulated trace element (loosely adsorbed to soil particles) is lower than the amount of trace element contained within the soil particles.

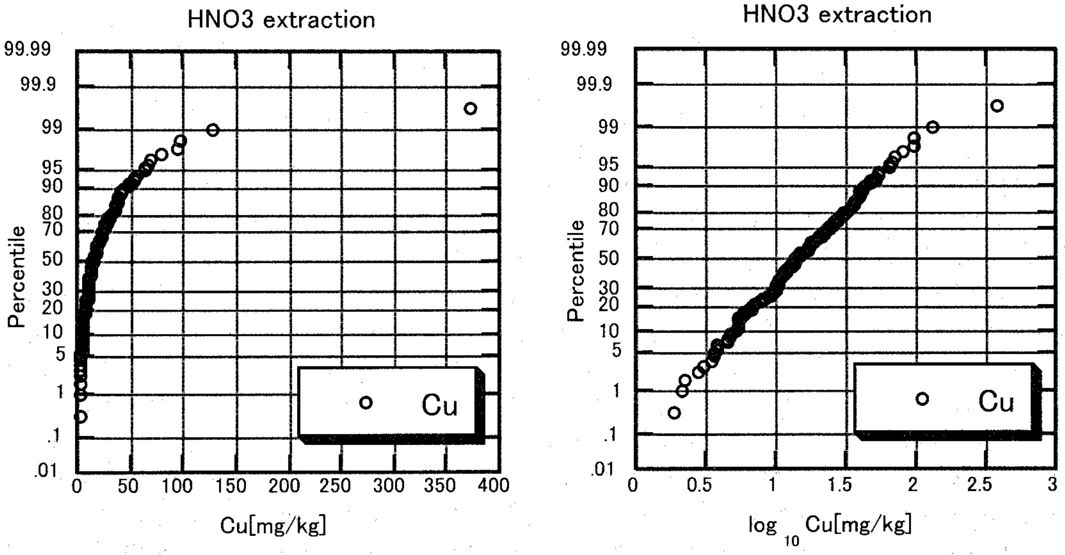

Fig. 2: Distribution in semilog scale of Cu concentration by HNO_3 extraction

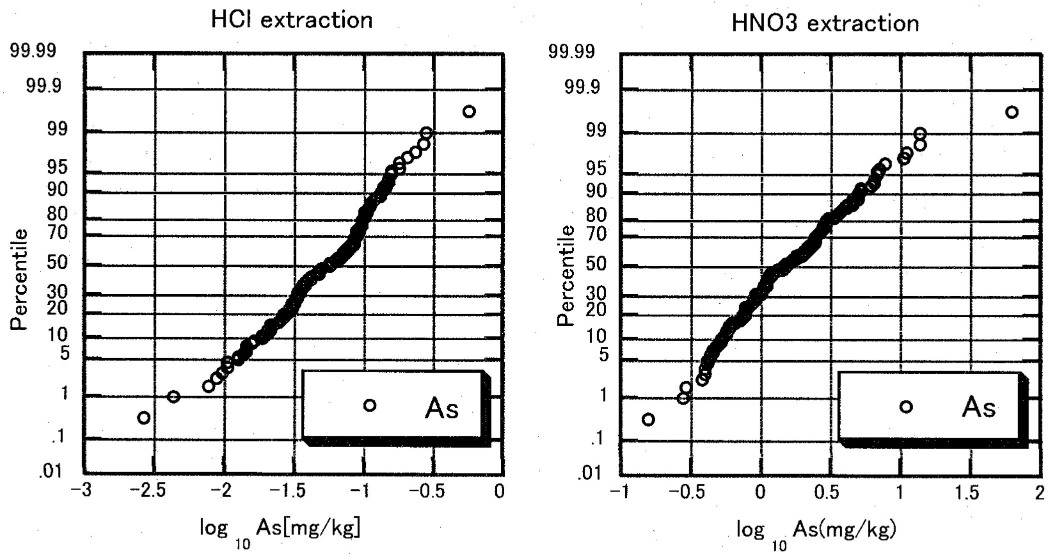

Fig. 3: Distribution of HCl extraction and HNO_3 extraction for As

Figure 4 (a) - (d) show the concentration of Cr, Co, As, and Pb measured using the hydrochloric acid extraction method. Figure 5 (a) - (d) show the concentration of Cr, Co, As, and Pb found after the nitric acid extraction. The area of circle represents the concentrations. The concentration of Cr and As [HNO_3 extraction] is about 100 times larger than the concentration of Cr and As [HCl extraction]. The data in the figures suggests that elements such as Cr and As extracted with nitric acid are contained within the soil particles, whereas the Cr and As extracted with hydrochloric acid accumulate on or adsorb to the soil particles. Figure 6 shows the relationship between the concentration of Co extracted with the hydrochloric acid and population density. The concentration of Co extracted with the hydrochloric acid is higher in urban regions (such as Tokyo and Yokohama area) compared to non-urban areas. In terms of Pb, the concentration by the hydrochloric acid extraction observed at high values, which suggests that the concentration of Pb affected by the peripheral roads because leaded gasoline was used in Japan until 1970.

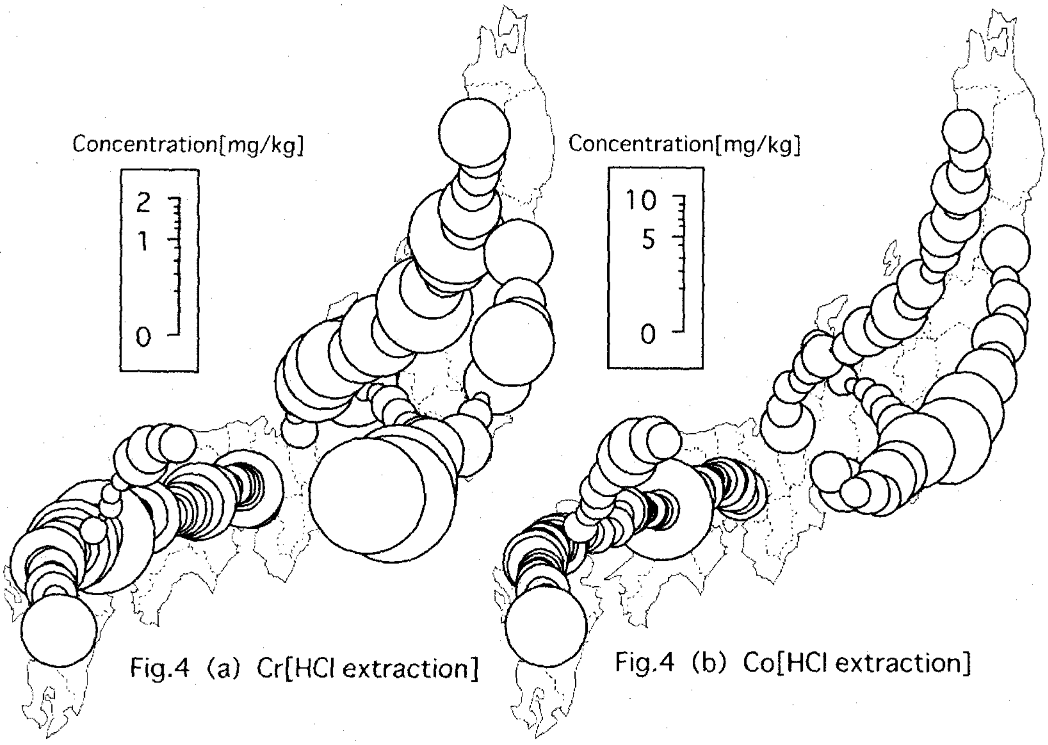

Fig.4 (a) Cr[HCl extraction]

Fig.4 (b) Co[HCl extraction]

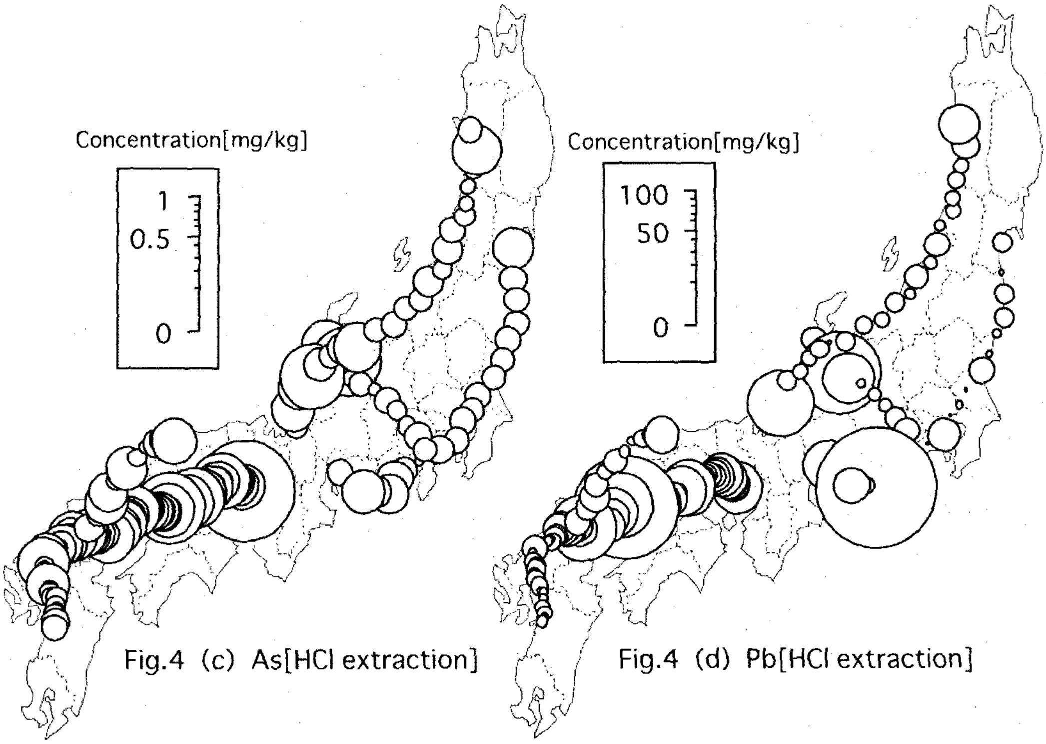

Fig.4 (c) As[HCl extraction]

Fig.4 (d) Pb[HCl extraction]

Fig.4: Concentrations of Cr, Co, As and Pb measured using the hydrochloric acid extraction method

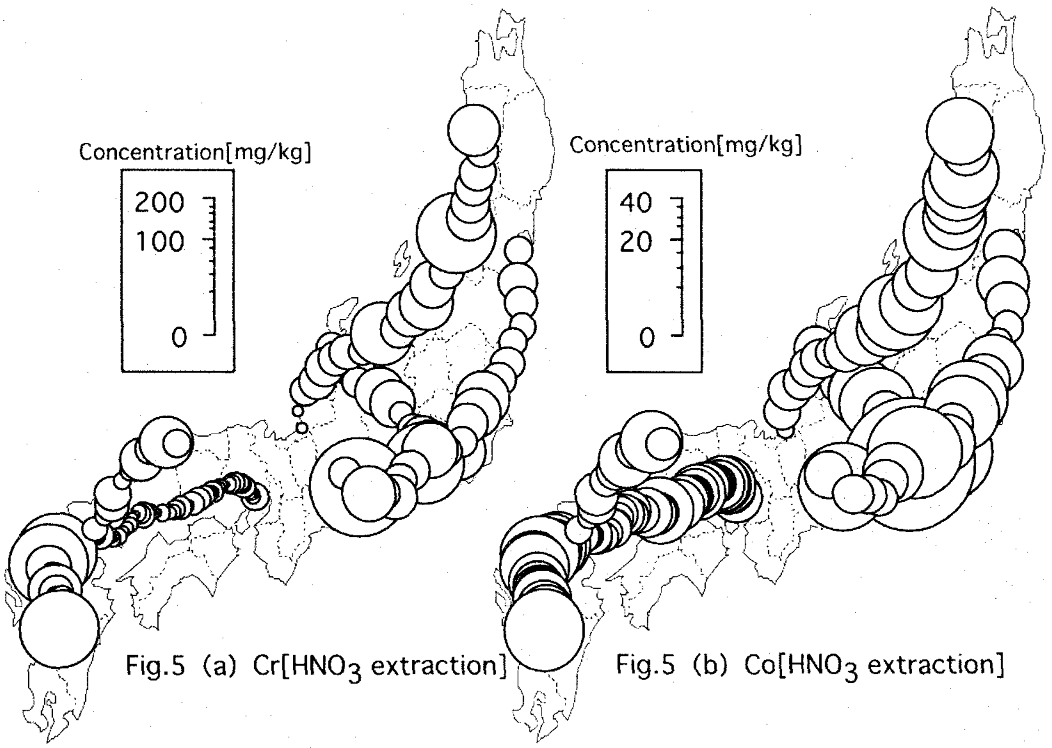

Fig.5 (a) Cr[HNO_3 extraction] Fig.5 (b) Co[HNO_3 extraction]

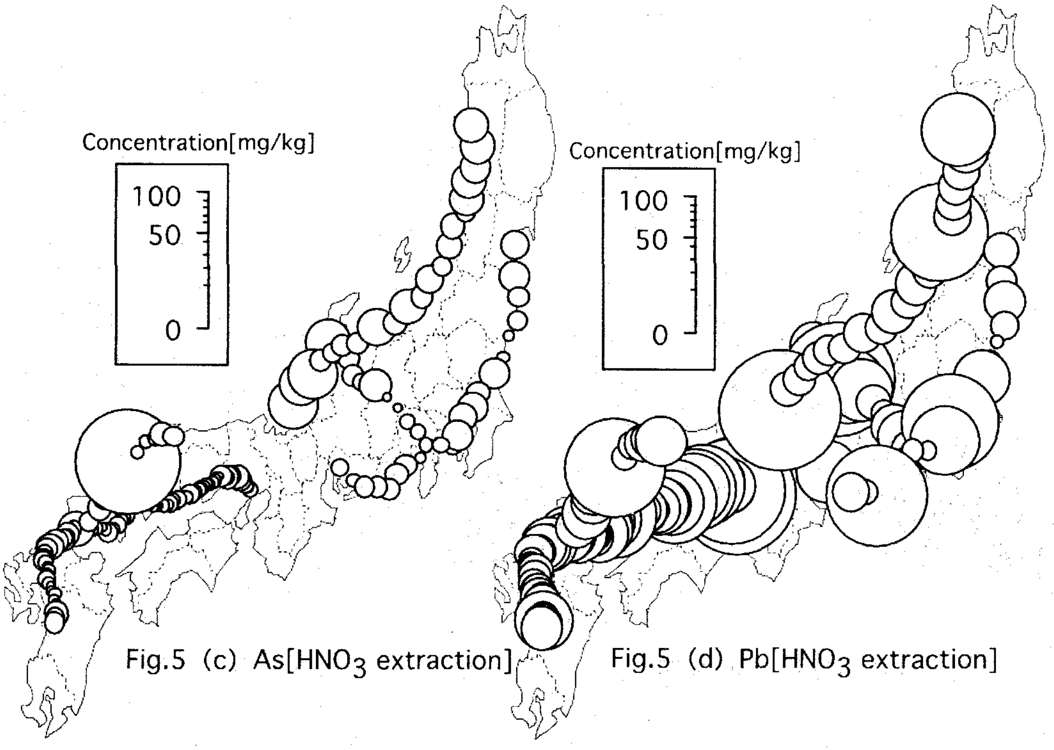

Fig.5 (c) As[HNO_3 extraction] Fig.5 (d) Pb[HNO_3 extraction]

Fig.5: Concentrations of Cr, Co, As and Pb measured using the nitric acid extraction method

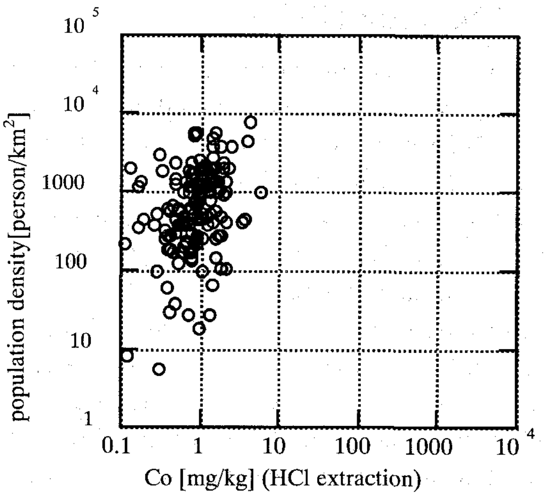

Fig.6: Plot of Co concentration and population density

The Ministry of the Environment in Japan has estimated the risk of taking soil directly into the body (by direct ingestion, dermal adsorption, and inhalation of fugitive dusts) and established allowable heavy metal concentration levels in soil to reduce the health risk due to direct intake of soil in residential districts. The regulation has been established on these heavy metals: Cr, As, Se, Cd, Hg, and Pb. Table 5 lists the levels and measurement data found in this study. The observed maximum Pb concentration by HCl method was 72 times higher than the median value, and the maximum As concentration by HNO_3 method was 38 times higher than the median value. These heavy metals were measured in a high concentration in different locations. Also, the measured Pb concentration exceeded the allowable level at one location.

Table 5. Observed Heavy metal concentrations found and allowable concentration levels

	allowable concentration level	HCl			HNO_3		
		max	95percentile	median	max	95percentile	median
Cr	900	1.8	0.8	0.2	108.5	44.7	8.4
As	150	0.6	0.2	0.1	61.6	8.2	1.6
Se	150	1.0	0.5	0.2	3.6	1.4	0.6
Cd	150	2.1	0.4	0.1	2.8	0.5	0.2
Pb	150	185.2	15.2	2.6	619.6	51.8	8.9

unit: mg/kg-soil

HCl extraction	157 samples
HNO_3 extraction	157 samples

4.2 Effects of human activity

It is reasonable to assume that contamination of the park soils are due to human activity such as vehicular traffic and industry. We determine the relationship between the soil contamination and an index of human activity. As indexes, we selected the population density and the distance between the sampling site and the nearest waste incinerator plants.

With population density, it is believed to be an index of the city activities and the area is urbanization. In this study, the population density data of the municipalities around each sampling location was taken from the national census data (1995).

Waste incinerator plants dispose general household garbage. The distance from a waste incinerator plant is considered to represent the influence of exhaust gas emitted by incineration equipments in various districts. Referring to a waste treatment yearbook (1997), we defined an index based on the capacity of the waste incinerator plant (weight of waste treatment [tons/day]) and the distance from the waste incinerator plant to sampling location (distance [kilometers]). The number n=755 was used for locations in prefectures where waste incinerator plants producing more than 30 tons of waste per day were situated.

$$\text{Waste index} = \sum_{i=1}^{n} \frac{\text{weight of waste disposal[tons/day]}}{\text{distance[km]}}$$

In this study, the distribution of concentration of each element and the distribution of the indexes of human activity show lognormal distributions. We took the logarithm of both indexes in order to determine the validity of correlations at a significance level of one percent. Because the measurement method was different in western Japan (Sanyo, Kyushu and Sanin) and eastern Japan (Chubu, Tohoku), we analyzed the two areas separately.

Table 6 shows correlations between the trace elements and the two indexes for human activity. From the results of the hydrochloric acid extraction, it appears that Cr has a correlation with the index of population density (coefficient of correlation is 0.40), and also Cr (0.37), As (0.51) and Se (0.27) have correlations with the index of distance from waste incinerator plants. On the other hand, from the results of the nitric acid extraction, Co (0.30) and Cu (0.36) have correlations with the index of population density, and Cu (0.58) and Zn (0.43) have correlations with the index of distance from a waste incinerator plants. Fig.7 shows the relationship between the concentration of Cr measured in soil in the western Japan by the hydrochloric acid extraction and population density. The figure shows that there is weak correlation between the Cr concentration and population density. The reason why the plot of park soil concentration and human activity indexes has wide dispersion is that park soil has effected by local conditions such as the distance from arterial roads and sampling conditions, in addition the indexes cannot explain the human activities properly.

Table 6. Correlations between elements and indexes of human activity

	HCl		HNO_3	
	west	east	west	east
Index of population density	Cr(0.40)		Co(0.30)	Cu(0.36)
Index of waste	Cr(0.37) As(0.51) Se(0.27)			Cu(0.58) Zn(0.43)

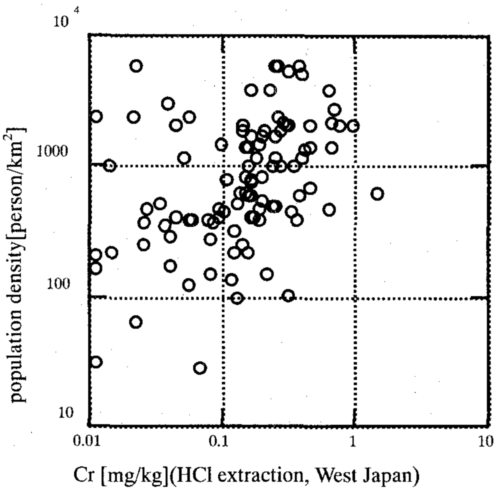

Fig. 7: Plot of Cr concentration and population density

5. Conclusions

The main results obtained in this study are summarized as follows:

(1) On the concentration of Al, K, Sc, V, Cr, Fe, As, Zr, and Cs, the ratios of the hydrochloric acid extraction concentration to nitric acid extraction concentration were less than 10 percent. For Na, Mg, Mn, Co, Ni, Cu, Zn, Se, Y, Cd, and Pb, however, the ratios of the concentrations by the two extraction methods were over 10 percent.

(2) There was a tendency for high concentration of Cr and Co in urban districts. These elements were likely contained in the soil particles originally and were extracted by nitric acid. Also, Concentration of Pb affected by peripheral roads because leaded gasoline was used in Japan until 1970.

(3) Cr (coefficient of correlation 0.40) extracted by hydrochloric acid and Co (0.30) and Cu (0.36) extracted by the nitric acid have correlation with the index of population density. Cr (0.37), As (0.51) and Se (0.27) extracted by hydrochloric acid and Cu (0.58) and Zn (0.43) extracted by nitric acid have correlations with the index of distance from waste incinerator plants.

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