

Arsenic Levels in Soil of a Town Polluted 35 Years Ago (Nakajo, Japan)

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Endemic arsenic poisoning occurred in Nakajo Town, Niigata Prefecture, Japan, in 1959 (Niigata Prefectural Office 1966). Of 454 residents who took medical examinations organized by the Prefectural office and the School of Medicine Niigata University, 93 residents (20.5%) had symptoms of chronic arsenicism. Chronic arsenicism was found for the first time when a 11 year-old boy consulted a doctor because of white spots, hyperpigmentation and hyperkeratosis of the skin. The other members of his family had the same symptoms. His family lived near a factory producing arsenic sulfide ($\text{As}_2\text{S}_3 + \text{As}_2\text{S}_5$) and drank well water containing 2.0 ppm of arsenic. Most of the patients lived within 500m of the south-west side of the factory.

Waste water containing arsenic from the factory had been running into underground water since about 1920. The situation aggravated from 1951 to 1957 when the bed of a river was fixed with concrete, with the result of which the flow of underground water decreased and the arsenic level in well water increased. The waste water from the factory finally contained 400 ppm of arsenic. The use of well water in the polluted zone were banned two days after the first chronic arsenicism was diagnosed. Temporary tap water service was implemented one month later.

While the toxicological problems of arsenic were thus overcome, those related to the environmental contamination might persist. Inorganic arsenic is a suspected carcinogen (WHO 1981). Inorganic arsenic compounds are evaluated as skin and lung carcinogens in humans (IARC 1987). Some epidemiological studies reported that the two cancers were causally associated with exposure to arsenic (Pershagen 1985; Frost et al. 1987; Chen and Wang 1990; Smith et al. 1992). We were interested in the current environmental arsenic contamination in Nakajo in terms of assessing the effects of arsenic on human health. To examine the geographical distribution of arsenic, we sampled soil for determination on the assumption that soil is the most directly polluted environmental medium by the contaminated well water. In fact, well water was used for agriculture and livestock husbandry in the

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town. Once soil is contaminated with toxic substances, such substances are not easily lost or decomposed and remain in soil for a long period of time. Well water is an ideal material for environmental arsenic determination, but wells are now closed. Sampling of agricultural products and human blood were rejected by the town office for fear that they would cause unnecessary public concern. This study was conducted as a part of investigations into health effects of the arsenic poisoning caused 35 years ago by waste water contaminated with arsenic in Nakajo. The purpose of this work is to determine the current soil arsenic levels and assess the possible influence of arsenic on human health.

MATERIALS AND METHODS

The location of Nakajo Town in Niigata Prefecture, Japan, is shown in Figure 1.

Experiment 1 was designed to determine soil arsenic levels in an area of 2 km² covering the polluted zone. Because underground water ran from north-east to south-west (Niigata Prefectural Office 1966), we set the former factory site in the north-east of the area. We drew 7 lines vertically and 4 horizontally by 300m on the map of the area to get 28 intersections as sampling points. One point (No.14) belonged to the premises of the factory. Four samples of earth at a depth of 15cm were collected at each of the sampling sites with plastic instruments and mixed in a 100ml polyethylene bottle (Tokyo Metropolitan Government Office, 1980). The soil sampled was air-dried at room temperature, ground in a glass mortar and then sieved through a 0.25mm screen. The finely powdered soil was decomposed by the sulfuric acid - nitric acid - hydrofluoric acid - perchloric acid method. The determination of arsenic concentrations was carried out by the hydride generation - atomic absorption spectrophotometric technique according to the Japan Industrial Standard (Japan Industrial Standard Committee, 1986). The standard calibration curves were prepared. All samples and standards were measured in triplicate.

Experiment 2 was performed to define the pattern of arsenic contamination in a smaller area than Experiment 1 so as to determine whether arsenic levels were high restrictedly in and around the former premises of the factory. The area was 0.36km² (600m × 600m) with the old industrial site in its center. On the map of the area, three lines were drawn vertically and as many horizontally 50m, 150m, and 300m away from the center of the map. Among the intersections obtained, twenty five were selected as sampling points. There were two points within the former factory site (No.12 and 13) and three on the margin of the site (No.11, 17 and 18). Soil was sampled as described in Experiment 1. Two different decomposition procedures were used; one was the method described in Experiment 1 and the other the sulfuric acid - nitric acid - perchloric acid method as defined by the Ministry of Environment (1973). Soil analysis was performed using the same method as Experiment 1. All samples and standards were measured in duplicate.

Experiment 3 was to determine arsenic levels in uncontaminated soil in Niigata

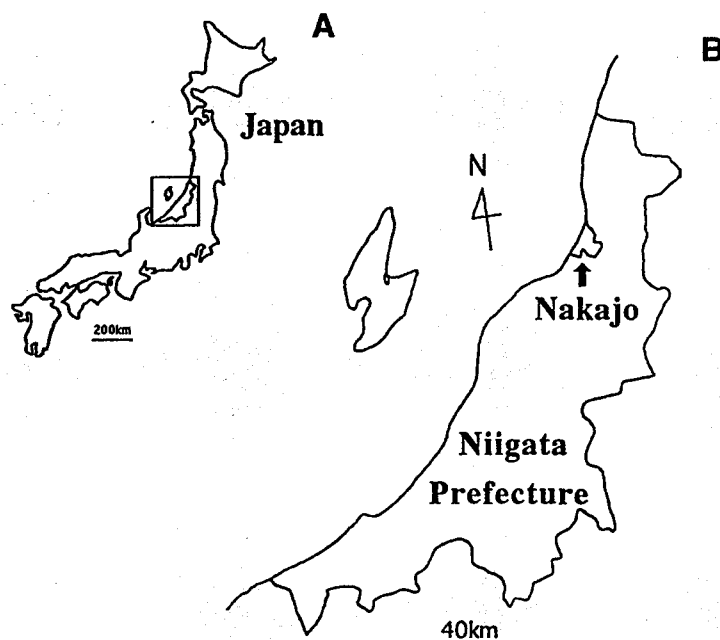


Figure 1. A. Map of Japan indicating the location of Niigata Prefecture.
B. Map of Niigata Prefecture with the location of Nakajo.

Prefecture for comparison. Six samples of soil were collected as described in Experiment 1 from 4 cities and 2 towns where arsenic pollution had not been known. The finely powdered soil was decomposed by the sulfuric acid - nitric acid - perchloric acid method. The hydride generation-atomic absorption spectro - photometric technique was used for arsenic determination in the same manner as Experiment 1 and 2. All samples and standards were measured in duplicate.

RESULTS AND DISCUSSION

In Experiment 1, of the 28 sampling points, 9 were at housing sites, 3 in school yards, 1 by the roadside, 6 in vegetable gardens and 9 in rice fields. The concentrations of arsenic at each sampling point are listed Table 1. The mean \pm SD was $15.17 \pm 13.049 \mu\text{g g}^{-1}$. The maximum and minimum concentrations were $72.73 \mu\text{g g}^{-1}$ and $2.44 \mu\text{g g}^{-1}$, respectively, with the range of 70.29. The highest value was at No.14 sampling point which belonged to the former factory site. This value exceeded the standard limit ($50 \mu\text{g g}^{-1}$) in the guideline for soil pollution (Ministry of Environment 1990). No.15 exceeded the standard limit for rice fields ($15 \mu\text{g g}^{-1}$). The mean concentrations by activity at the sampling points are indicated in Table 2. By the Mann-Whitney U test (Armitage and Berry 1987), the differences between the mean concentrations in rice fields and vegetable gardens and in rice fields and housing sites were both significant ($p < 0.05$).

Table 1. Arsenic levels^a ($\mu\text{g g}^{-1}$ dry weight) in soil of an area near the former premises of a factory which caused arsenic poisoning 35 years ago in Nakajo, Niigata Prefecture, Japan <Experiment 1>

Sampling point ^b	Arsenic level	Sampling point	Arsenic level
1	7.56	15	17.18
2	12.52	16	6.65
3	10.05	17	23.33
4	24.90	18	8.17
5	15.57	19	14.47
6	19.70	20	15.29
7	2.44	21	4.57
8	8.54	22	7.66
9	4.86	23	11.47
10	30.29	24	15.18
11	8.17	25	17.02
12	12.37	26	18.86
13	17.01	27	11.64
14	72.73	28	6.67

^a Mean of three measurements.

^b No.1, 7, 8, 9, 15, 16, 21, 27 and 28 are in rice fields. No.5, 10, 13, 14, 17 and 22 are in vegetable gardens. No.2, 3, 6, 11, 18, 19, 23, 24 and 25 are at housing sites. No.12, 20 and 26 are in school yards. No.4 is by the roadside.

Table 2. Concentrations of arsenic ($\mu\text{g g}^{-1}$ dry weight) by activity at the sampling points in Experiment 1.

Activity	Max.	Min.	Mean \pm SD ^a	n
Rice field	17.18	2.44	7.79 \pm 4.384 [*]	9
Vegetable garden	72.73	7.66	27.77 \pm 23.309 [†]	6
Housing site (including school yard)	19.70	8.17	13.61 \pm 3.831 [†]	12
Roadside			24.90 ^{*,†}	1

^a Values with different superscripts are significantly different ($p < 0.05$).

In Experiment 2, of the 25 sampling points, 7 were at housing sites, 2 in school yards, 6 by the roadside, 3 in vegetable gardens and 7 in rice fields. The concentrations of arsenic at the 25 sampling sites by decomposition method are shown in Table 3. In the analysis using the sulfuric acid - nitric acid - perchloric acid method, the mean \pm SD was $11.73 \pm 18.759 \mu\text{g g}^{-1}$. The highest value was $74.30 \mu\text{g g}^{-1}$ at No. 12 sampling site and the second highest was $70.19 \mu\text{g g}^{-1}$ at No.13, both of which belonged to the former factory site. The range was $72.45 \mu\text{g g}^{-1}$. The other sampling points were less than the standard limit. The sulfuric acid - nitric acid - hydrofluoric acid - perchloric acid method gave the average concentration of $18.76 \pm 20.079 \mu\text{g g}^{-1}$. The highest value was $89.13 \mu\text{g g}^{-1}$ at No. 12 sampling point and the second highest was $65.80 \mu\text{g g}^{-1}$ at No.13. The range

Table 3. Arsenic levels^a ($\mu\text{g g}^{-1}$ dry weight) in soil of an area in and around the former premises of a factory which caused arsenic poisoning 35 years ago in Nakajo, Niigata Prefecture, Japan (Experiment 2)

Sampling point ^b	Arsenic level		Sampling point	Arsenic level	
	Method 1 ^c	Method 2 ^d		Method 1	Method 2
1	2.33	2.49	14	6.40	13.64
2	3.43	4.98	15	5.17	11.46
3	2.76	2.42	16	2.13	5.48
4	1.85	5.56	17	9.68	38.13
5	4.95	10.12	18	3.35	10.25
6	4.81	12.70	19	3.81	10.81
7	23.36	37.66	20	3.39	10.74
8	12.49	25.21	21	7.28	20.11
9	7.51	9.14	22	7.03	18.89
10	10.70	11.01	23	7.04	13.51
11	4.09	14.00	24	8.45	13.14
12	74.30	89.13	25	6.67	12.53
13	70.19	65.80			

^a Mean of two measurements.

^b No.2, 5, 16, 21, 22, 24 and 25 are in rice fields. No.3, 8 and 10 are in vegetable gardens. No.1, 4, 9, 11, 12, 13 and 15 are at housing sites. No.20 and 23 are in school yards. No.6, 7, 14, 17, 18 and 19 are by the roadside.

^c Decomposition by the sulfuric acid-nitric acid-perchloric acid procedure.

^d Decomposition by the sulfuric acid-hydrofluoric acid-nitric acid-perchloric acid procedure.

was $86.71 \mu\text{g g}^{-1}$. By Welch's test (Armitage and Berry 1987), there was no significant difference between the mean values in the two groups of data from the two different methods. The correlation coefficient between the sets of data was 0.945 ($p < 0.001$). It is judged that the two pretreatment methods gave principally the same result. The mean concentrations by activity at the sampling points for both methods are shown in Table 4. The differences between the mean values by activity were not significant by the Mann-Whitney U test.

Table 4. Concentrations of arsenic ($\mu\text{g g}^{-1}$ dry weight) by activity at the sampling points in Experiment 2.

Activity	Max.	Min.	Mean \pm SD	n
[Method 1 ^a]				
Rice field	8.45	2.13	5.70 ± 2.280	7
Vegetable garden	12.49	2.76	8.65 ± 5.181	3
Housing site (including school yard)	74.30	1.85	19.54 ± 29.960	9
Roadside	23.36	3.35	8.57 ± 7.600	6
[Method 2 ^b]				
Rice field	20.11	4.98	12.18 ± 5.913	7
Vegetable garden	25.21	2.42	12.88 ± 11.507	3
Housing site (including school yard)	89.13	2.49	24.65 ± 30.724	9
Roadside	37.66	10.25	20.53 ± 13.506	6

^a Decomposition by the sulfuric acid-nitric acid-perchloric acid procedure.

^b Decomposition by the sulfuric acid-hydrofluoric acid-nitric acid-perchloric acid procedure.

Among the 28 sampling points in Experiment 1, one point which corresponded to the old factory site was the most contaminated. The level of arsenic exceeded the standard limit. In Experiment 2, on the basis of the results from Experiment 1, we analyzed soil from a more limited area in order to examine soil pollution in and around the old industrial site more precisely. It was shown again that the most contaminated was the inside of the old industrial site. The arsenic concentrations in the control soil were shown in Table 5. The mean concentration was $4.19 \pm 1.681 \mu\text{g g}^{-1}$. Because it was not permitted to sample soil at housing sites and vegetable gardens, 5 sampling sites were by the roadside and one in a rice field. In the analysis using the decomposition by the sulfuric acid-nitric acid-perchloric acid

Table 5. Concentrations^a of arsenic ($\mu\text{g g}^{-1}$ dry weight) in uncontaminated soil in Niigata Prefecture, Japan <Experiment 3>

Sampling point ^b	Arsenic level	Sampling point	Arsenic level
1	6.33	4	5.30
2	5.00	5	1.66
3	3.59	6	3.24

^a Mean of two measurements.

^b No.6 is a rice field. No.1~5 are by the roadside.

in Experiment 2, there was no significant difference between the mean concentrations by activity at sampling sites. The mean concentrations were then compared between Nakajo and the control soil by the Mann-Whitney U test and there was no significant difference. These results suggest that the soil pollution by arsenic was restricted to a very small area, only to the old industrial site. The problem is then what influence the arsenic levels determined at the former factory site have on human health. The arsenic levels at the former factory site obtained in the present study is far lower than the those at a mining site which were reported to be higher than 8000ppm (Tsuda et al. 1990), several hundred~1800ppm around a refining and 269ppm at a place about 5 km away from the refining (Yasuda 1981). The former factory site is currently a residential site where wells are closed and no agricultural product are produced. Some arsenic compounds in soils are not in soluble forms. Some clay particles to which arsenic in soils may adsorb are too large to float in the air (Tamaki and Frankenberger Jr 1992). It is thus speculated that the soil pollution had relatively small effects on the health of the residents and the exposure to arsenic in drinking water was the main hazard.

Thirty years after the endemic arsenic poisoning occurred, Tsuda and coworkers (1989) conducted a case-control study in Nakajo, reporting that a significant increase in death due to lung cancer was found in the group of people who drank well water containing high concentration arsenic (≥ 0.5 ppm). Responding immediately to the report, the Niigata prefectural office organized a special committee for the investigation of this matter. The committee reported a positive correlation between arsenic levels in well water and mortality from lung cancer in males who were diagnosed as arsenicism. Causal interpretation of the association between the two factors was made by the committee, which concluded that whether the association was causal or not remained to be evaluated although the strength and consistency of the association were satisfied and the specificity was partially satisfied (Niigata Prefectural Office 1966). It is hence necessary to undertake a long-term cohort study in Nakajo with thorough medical examinations of the residents exposed to arsenic in drinking water to evaluate the biological implications of the arsenic poisoning which occurred 35 years ago.

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