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The Presence of Heavy Metals in Urban Snow

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Abstract

Manganese, zinc, lead, copper, chromium and cadmium concentrations in snow collected in an urban area and its environs and snow dumping stations were determined for the snow from an area along the basin of the Toyohira River which runs through Sapporo City in Hokkaido.

These elements were chosen because they can be commonly found in municipal, industrial and mining effluents. We studied the relationship of heavy metal concentrations against a background level, to see whether the heavy metal concentrations in the snow could be used as an available indicator of urban pollution.

The heavy metal concentrations in the snow clearly increased as the river approached the center of the city. The maximum value of the Mn, Zn, Cu, Cr and Cd in the snow were 161.3, 22.3, 11.2, 9.74, 1.21 and 0.13 μg/l, respectively. These values were influenced by local pollution in the industrial area of the city and by the effect of the seasonal wind from the northwest. The heavy metals except Mn had a high correlation with each other.

Key Words: Heavy metal, Snow, Snow dumping station, Background level, Air pollution.

1. Introduction

Recently, promoted by a rapidly developing technology, hectic economic activity has stimulated industrialization, urbanization and motorization, and has begun to destroy the human, animal, botanical and bacteriological ecosystem. Environmental pollution by heavy metals has become one of the world's most serious problems. By analyzing the geochemistry of polar snow, Murozumi et al. (1969) certified that lead in the atmosphere had spread around the world, while Airey (1982) identified a special case of air pollution by measuring concentrations of mercury in the air, rainwater and snow caused by mercury in materials produced by the coal industry.

Air, water and soil pollution has also spread throughout the total area of Japan, a country where industry has developed markedly. Hence the occurrence of Minamata disease caused by industrial mercury (Fujino and Itai, 1982) and Itai-

itai disease caused by the outbreak of cadmium from the Kamioka mine (Kobayashi, 1969., Mckenzie, 1972). Now, although the industrial nations have begun to attempt to reduce the amount of heavy metals released into their environments, the damage caused by heavy metals released into their environments, the damage caused by heavy metals around the world is increasing because of the released heavy metals which have accumulated in the marine, river and lake food chain.

At the same time, the solution of the problem of locating the presence of air pollutants in urban dust, SO_x, NO_x, CO, heavy metals and the chemical carcinogens in areosol has advanced from a study of quantity to one of quality. In this study, we aim to capture the essential characteristics of air pollution in an area of heavy snow. Air pollutants result mainly from street dust caused by spiked tires, the burning of fossil fuel for heating and the effluents of automobiles and so on. In Sapporo, a serious social problem has arisen because of the yearly damage to roads and human health during the period before the onset of snow and during the melting period. First, we determined the presence of heavy metals in snow and analyzed its distribution along the Toyohira River where it runs through urban area of Sapporo City and its environs in Hokkaido, as illustrated in Figure 1. And we also analysesed the contamination ratio that the presence of heavy metals from air pollution loaded up the river pollution. We then considered whether the heavy metal concentrations of Mn, Zn, Pb, Cu, Cr and Cd in snow were suitable for use as an index of air pollution. Finally, we discuss a simple and effective

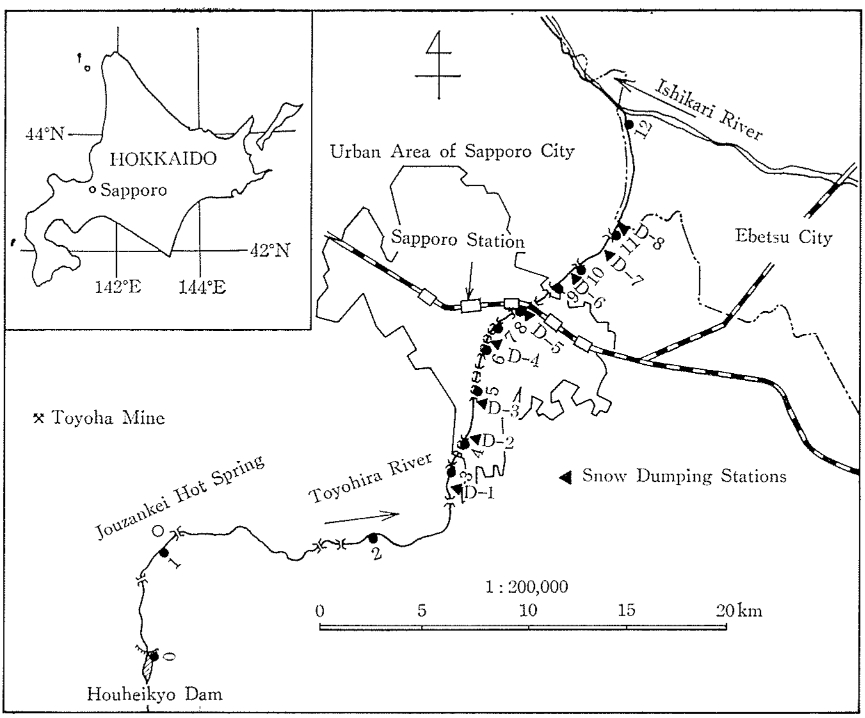

Figure 1. Sampling Stations along the Toyohira River Basin.

method for assessing air pollution in Sapporo City its population of about 1,500,000 people.

2. Materials and Methods

Sample collection

Snow samples were collected from 21 sites (including 8 snow dumping stations) along the Toyohira River basin in March 4–5, 1982. The sites were located within a stretch of 48.2 km along the main stream of the Toyohira River ; the locations are illustrated in Figure 1. The snow sampling method used a cylinder (1 m long, the inside diameter of 8 cm) made of an polyvinyl chloride (method of Saito, 1981). The snow samples were stroed in polyethlene bottles (3 L) and returned to the laboratory.

Sample preparation and analysis

The pH in the water of melted snow was measured immediately after melting. To prevent chemical precipitation forming in the samples to be used for the determination of the heavy metals, the pH was adjusted to less than 1.0 by adding conc. HCl. After the samples has been filtered, the metal solutions were analyzed by the conventional atomic absorption methods for Mn, Zn, Pb, Cu, Cr and Cd, using a Hitachi 170-70 type Zeeman Flameless Atomic Absorption Spectrophotometer.

3. Results and Discussion

Heavy metal concentrations in snow

Suzuki (1982) has shown that during the melting period, the concentration of the chemical constituents of the total snow cover decreased and pH increased in Sapporo during the winters of 1978–1980. We thought that the appropriate time to sample the snow was just before the melting period. Table 1 indicates the

Table 1. Concentrations of heavy metal in snow along the Toyohira River basin

Site No.	pH	Element ($\mu g \cdot l^{-1}$)					
		Mn	Zn	Pb	Cu	Cr	Cd
0	4.8	2.5	3.4	2.3	0.60	0.14	0.05
1	5.3	6.3	8.6	5.0	1.69	0.22	0.06
2	4.7	3.3	4.6	3.3	0.75	0.14	0.06
3	6.3	39.5	11.3	5.4	2.06	0.43	0.04
4	6.3	14.1	7.8	4.2	2.25	0.31	0.06
5	6.5	17.3	9.2	5.6	2.90	0.26	0.06
6	6.4	20.1	15.2	7.0	3.22	0.59	0.09
7	6.1	11.1	14.6	5.9	2.40	0.37	0.10
8	5.9	14.2	14.8	6.8	4.03	0.47	0.08
9	6.2	161.3	22.3	9.5	5.81	0.73	0.10
10	6.4	67.2	18.5	11.2	9.74	1.21	0.13
11	6.1	53.8	12.5	7.2	3.42	0.56	0.10
12	4.8	41.8	11.3	4.4	1.87	0.31	0.09

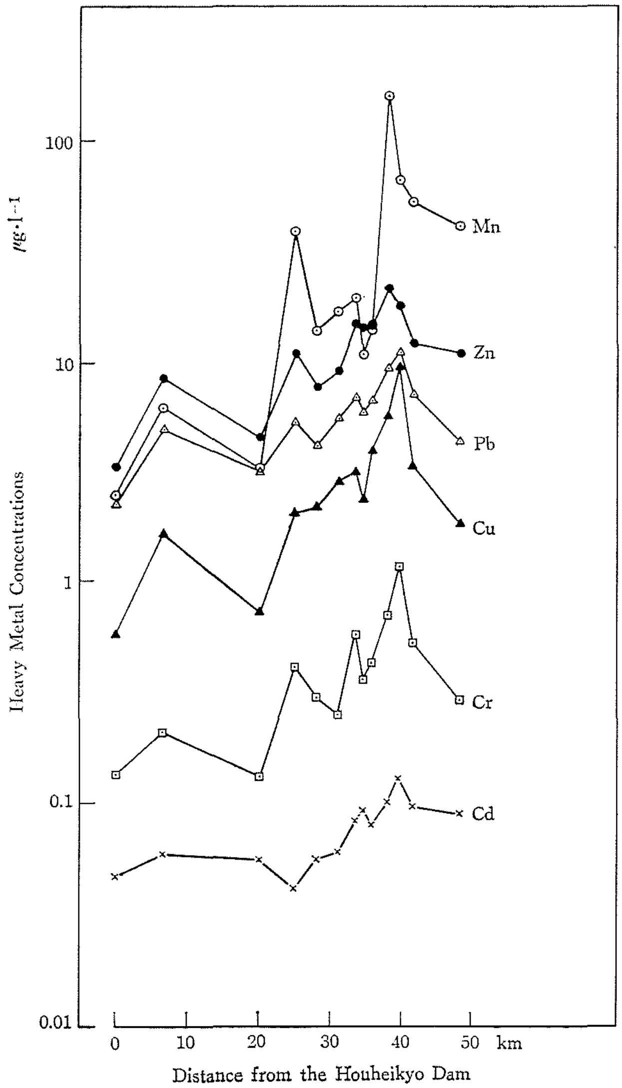

Figure 2. Distribution of Heavy Metal Concentrations in Snow of the Toyohira River Basin.

results of the analysis of heavy metal concentrations in the snow from 13 sites in the basin of the Toyohira River. Figure 2. indicates the relationship of each heavy metal concentration in the snow and the distance from the site No. 0. The concentrations of heavy metal in the snow showed a minimum value for the site No. 0 (the Houheikyo Dam), while the concentration of every element in the snow increased as the river approached the center of the city. At the site No. 9 which runs through the urban area, Mn and Zn showed their maximum value, and at the site No. 10, Cu, Pb, Cr and Cd showed their maximum value. These values were influenced by local pollution in the industrial area and by the effect of the seasonal winds from the northwest. Labarre et al. (1973) and Grandstaff and Myer (1979) have shown that lead aerosols are introduced into the atmosphere by the combustion of lead-containing fuels in internal combustion engines (automobiles) and result in the lead pollution of snow. Moreover, the pollution of snow is related to the distance from the site No. 0. In Sapporo City, our results were consistent with these previous findings, but in Sapporo the pollutants result not only from combustion fuels but also from street dust and industrial effluents.

Table 2 indicates the results of the measurement of heavy metal concentrations in the snow collected from the snow dumping stations (8 sites). Table 3 indicates that concentrations in these areas are comparable to data published in other reports. It compares the mean value of the urban examples (61 sites) from Sapporo City made by Saito (1981), the mean value of the examples used in this study and mean value of the examples from the snow duming stations. In this table, a comparison between our study and Saito's shows the same pH value, but the concentrations of each element expect Pb, Cu and Cr are clearly higher in our study than in his. Pb, Cu and Cr concentrations were almost the same in the both. The values of our examples from the snow dumping stations also indicate much higher levels to (except for Cd) when compared with the urban areas and the river basin. This phenomenon may have occurred as a result of the accumulated and disturbed matter of the variable pollutants.

Table 2. Concentrations of heavy metal in snow from the snow dumping stations

Station No.	pH	Element ($\mu g \cdot l^{-1}$)					
		Mn	Zn	Pb	Cu	Cr	Cd
D-1	6.7	34.4	39.3	9.4	7.18	4.67	0.05
D-2	6.6	280.0	41.0	27.4	27.75	9.72	0.39
D-3	6.6	49.6	50.3	13.1	13.06	4.86	0.10
D-4	7.2	87.4	28.8	15.1	14.69	4.11	0.08
D-5	6.8	87.4	28.8	20.8	9.79	4.11	0.10
D-6	6.2	62.0	225.6	35.1	13.71	7.85	0.28
D-7	6.1	30.3	63.0	9.7	8.87	1.87	0.07
D-8	6.6	373.4	25.3	16.4	22.67	4.67	0.13

Table 3. Comparison of heavy metal concentrations in snow

	pH	Element ($\mu g \cdot l^{-1}$)						References
		Mn	Zn	Pb	Cu	Cr	Cd	
Urban Area of Sapporo (61)	5.8±0.2	40.8± 7.0	37.0± 3.4	14.1±1.6	12.7±2.0	4.3±0.7	0.30±0.03	Saito
Toyohira River Basin (13)	5.8±0.2	34.8±12.0	11.8± 1.5	6.0±0.7	3.1±0.7	0.4±0.1	0.08±0.03	This study
Snow Dumping Station (8)	6.6±0.1	120.0±46.0	62.7±22.7	18.4±3.2	14.6±2.5	5.2±0.9	0.15±0.01	This study

mean±S.E.

Table 4. Comparison of heavy metal concentrations in snow of unpolluted area

	pH	Element ($\mu g \cdot l^{-1}$)						References
		Mn	Zn	Pb	Cu	Cr	Cd	
Mt. Kitanomine	—	2.1	1.5	1.6	N.D.	0.2	N.D.	Saito
Nebraska	—	4.0	12	7.8	4.0	—	0.63	Struempler
Houheikyo	4.8	2.5	3.4	2.3	0.6	0.1	0.05	This study

Table 4 indicates a comparison of the mean values of snow collected from an unpolluted area on Mt. Kitanomine at Furano City in Hokkaido (measured by Saito, 1981), from Nebraska in the U. S. A. (measured by Struempler, 1976) and from the Houheikyo Dam (the site No. 0). At the site No. 0, heavy metal concentrations in the snow were almost the same as for Mt. Kitanomine and lower than the mean value for the Nebraska sites. That is, heavy metal concentrations in the snow of the Houheikyo site has not yet been influenced by pollution from the urban area. We therefore regarded its concentrations as giving a background level against which to judge the snow from Sapporo City.

Assessment of air pollution from heavy metals in snow

The concentrations of heavy metal in show will vary according to different meteorological situations, and it is insufficient to show only that heavy metal concentrations increase with time in the yearly layers of snows, for this could result from a number of different factors, some of them unrelated to general increases of heavy metal in the atmosphere. Heavy metal concentrations in snow can be related to atmospheric concentrations with more confidence if it can be shown against the background level of their concentrations in snow from an urban area. The National Institute for Environmental Studies (NIES), Ambe (1984), has also been trying to measure and evaluate the background level of air pollution. Nevertheless the geocycles of pollutants in the atmosphere will depend on a variety of mechanisms as well as the uniqueness of each area, so that the assessment of the background has been thought to be difficult. There have been reports of atmospheric precipitation sampling procedures, application and chemical properties, or chemical composition data for the estimation of the composition of background aerosol (Petrenchuk 1977; Middleton et al., 1984; Uno et al., 1984).

We have now tried an evaluation of air pollution by analyzing heavy metals in snow. To do so we determined a background level of concentrations for Sapporo City by taking the snow of the Dam as our 'norm'. At the site No. 0, the background level of heavy metal concentrations was at the minimum value; as the river ran through the urban area, however, the element contents continued to rise. The maximum value of Mn, Zn (at the site No. 9), Pb, Cu, Cr and Cd (at the site No. 10) were 161.3, 22.3, 11.2, 9.74, 1.21 and 0.13 μg/l, respectively. The values obtained in our study showed against the background levels that Mn and Zn concentrations were about 65 and 7 times greater at site No. 9, and Pb, Cu, Cr and Cd were about 5, 16, 9 and 3 greater at the site No. 10, respectively. The Mn content was especially marked at the site No. 9. Barrie and Vet (1984) have pointed out that Mn is significantly enriched in the snowpack relative to the crustal rock composition. So a highly Mn content may result from soil or street dust carried by automobiles from rural areas; as a result, at the site No. 9 and No. 10 the content of heavy metals in snow was at its greatest. These areas are located to the southeast and east of the center of the city (Sapporo Rail Way Station) and were influenced most markedly by pollution related to the seasonal northwest wind which blows during the winter. That is, in the southeast area of the city, pollution that results from air pollutants carried from the urban area increases annually. And this occurs relative to the northwest wind, the prevailing wind during the winter. Moreover, we considered that the ratios of heavy metal concentrations at each site and the background levels were suitable for use as index of air pollution.

Table 5 indicates the partial correlation coefficient for the measured elements. We suppose that although the Mn concentration may be related to the source of the other elements, it does have a special property when compared with the others. The heavy metals except Mn, though, had a high correlation with each other. We thought, therefore, that the heavy metal concentrations in the snow were related to and spread from the same sources. Saito (1981) has shown that the mean value of heavy metal concentrations at a distance from the core situation at the center of the city were more variable, and not significant. Inside the urban area, heavy metal concentrations in the snow were complicated owing to many factors; for example, winds created by buildings and human-made pollutants from around the area. We therefore thought that it was important to select conflicting sampling sites to locate the presence of heavy metal in snow as an indicator of air pollution. In our study, the Toyohira River basin, where we selected our sampling sites, runs through the urban area of the city, and the distribution of heavy metal concentrations in the snow may indicate dramatically the nature of air pollution in the city.

At the same time, in a snowy region, the snowmelt has a considerable influence on the quality of surface water and river water. The melted snow causes a sharp drop in the pH of water and this leads to physiological stress in fish and other aquatic organisms (Bell, 1971; Hangen and Langeland, 1973; Leivestad and Muniz, 1976). The snowmelt at snow dumping stations has resulted in the release of

Table 5. Partial correlation coefficient for measured heavy metals

	Mn	Zn	Pb	Cu	Cr
Zn	0.7605**				
Pb	0.6923**	0.9099***			
Cu	0.6105*	0.7900***	0.9460***		
Cr	0.6191*	0.8150***	0.9453***	0.9628***	
Cd	0.5587*	0.7970**	0.8313***	0.8152***	0.8182***

* $p<0.05$ ** $p<0.01$ *** $p<0.001$

many pollutants (especially heavy metals) to the Toyohira River during short periods every year. Scott and Wylie (1980) pointed that both Pb and salt can accumulate in the soil of a dumping site and cause drastic changes in the fertility and physical structure of the soil. They said, moreover, that the movement of a salt-laden runoff from these sites can also affect wells, streams, and lakes. Scott (1980) has also reported that Pb content increases with time as the snow at snow dump sites gradually melts and the Pb-containing particulates accumulate on the snow surface where much of the salt and most of the Pb remains accumulate. Pierstorff and Bishop (1980) have shown that lead analyses performed on sediment samples from a river into which the dumped snow has been pushed indicates that the Pb from the snow may become trapped in the river sediment near the site due to the inhibition of transport of the suspended Pb rich material. So that the ecosystem of the river may be given a large loading shock and may be changed by the dumping of snow that has accumulated many air pollutants from the variable effluent outlets of an urban area.

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