

## Input of Atmospheric Heavy Metals to the Kushiro Marsh in East Hokkaido

その他（別言語等） のタイトル	北海道東部釧路湿原における大気重金属降下量
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# Inputs of Atmospheric Heavy Metals to the Kushiro Marsh in East Hokkaido

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Concentrations of selected chalcophile metals and Ni were analyzed by IDMS for a dry deposition and fresh waters in the Kushiro marsh, east Hokkaido so as to understand current heavy metal contaminations of ecosystems. Atmospheric inputs of toxic metals, Ag, Cd, Cu, Ni, Pb, Tl and Zn to the marsh area were estimated to be 0.005, 0.07, 2.6, 1.1, 2.2, 0.009 and 8.8 kg/km<sup>2</sup>/yr, respectively. These elemental precipitations except Cd are distinctly larger than those in Muroran city that is the heartland of the highly industrial area in Hokkaido. The elemental ratios and lead isotopic characteristics studied revealed that the dry deposition in the marsh area is incorporated substantially with eolian lead from distant sources, in part from the highly industrial area in southwest Hokkaido. Furthermore, the surface water of Takkobu lake which is a reservoir of the Kushiro river was contaminated by industrial lead more than the running water of the Kushiro river in the marsh region.

Key words: Kushiro marsh, Dry deposition, Toxic chalcophile elements, Lead isotope ratios

## 1. INTRODUCTION

There are many marshes in Hokkaido, the northern main island of the Japanese islands and the sum of their areas is 200000 ha which reach to 96 % of the total marsh area in Japan<sup>(1)</sup>. The Kushiro marsh is located in the eastern part of Hokkaido(Fig. 1) and has the widest area among the marshes in Japan. Local and national governments of Japan have tried to preserve wildlife especially unique aquatic vegetation and freshwater fishes, and animals inhabiting in this pristine marsh region specially since it was assigned as the 28th national park of Japan on July 31, 1987. In fact, the marsh is covered by the typical aquatic vegetation such as a *Kita* reed, *Phragmites communis* and a sedge, *Carex*<sup>(2)</sup>. Moreover, it offers the inhabitat for the *Ezo*-salamander, *Salamandrella keyserlingi*, the Japanese huchen (or the Sakhalin taimen), *Hucho perryi* and the *Ezokahojiro*-dragonfly, all of which are relic animals survived since the ice age<sup>(1)</sup>. A red-crested white crane, *Grus japonensis*, a specially protected bird designated by the Japanese Government inhabits in the marsh region. The 5th conference for the contracting parties of the Ramsar Convention held in Kushiro city contributed greatly to accelerating the protection of wildlife in the Kushiro marsh as well as other wetlands in Japan<sup>(3)</sup>. As a result, the Kushiro marsh has become not only a sanctuary for aquatic birds but also one of the most important bases for migratory birds.

It is essential for the conservation of this animal and plant kingdom to properly understand current environmental conditions about the Kushiro marsh area. Furthermore, this preserved area is suitable for studying bioaccumulation of toxic heavy metals such as

lead and cadmium in ecosystems. In particular, current environmental conditions of the atmosphere and fresh water in the marsh area are necessary to be disclosed because elemental species in the atmospheric and aquatic environment affect essentially to plants and animals living there.

As the first step for understanding bioaccumulation of heavy metals in ecosystems, we focused to reveal the input of chalcophile elements, Ag, Cd, Cu, Pb, Tl and Zn and Ni from the atmosphere into the Kushiro marsh region because they are considered to be potentially toxic species to wild animals as well as human beings. In fact, bioconcentration and/or food chain accumulation of these atmospheric pollutants have been reported on birds, voles, ducks, rats, and grouses from Canada, Japan, USA and other countries<sup>(4)</sup>. Furthermore, positive relations were observed between air pollutants of chalcophiles and death of birds<sup>(5)</sup> and also decline in antler quality of deers<sup>(6)</sup>. Besides, we have tried to see potential sources of atmospheric lead that is deposited on the marsh area, based on its isotopic characteristics. Although analytical data have been not accumulated enough to clearly understand environmental conditions in the study area today, the present paper reports atmospheric inputs of the selected heavy metals and the existence of eolian lead of distant sources in the Kushiro marsh.

## 2. SAMPLE AND METHOD

### 2.1. Sampling location and method

The Kushiro marsh is one of the national parks of Japan, whose lateral dimensions were designated to be 26861 ha, is located ca. 5 Km northwest from Kushiro city in east Hokkaido. The marsh is spread over the drainage area of the Kushiro river, the Akan river, the Settsuri river and the Kuchyoro river(Fig. 1). There are three lakes in the eastern side of the marsh region; Touro, Shirarutoro and Takkobu. all of which are a reservoir of running water of the Kushiro

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river. River and lake waters were sampled for a study of geochemical characteristics of fresh water running through the marsh area. Running and surface waters were collected at the Iwahogi floodgate of the Kushiro river and at Takkobu lake, respectively. A dry deposition was also received at the Iwahogi floodgate.

A polypropylene container(0.1426 m<sup>2</sup> in inner dimension) in which 1000 ml of 0.5 % nitric acid solution was pooled was employed to receive dry deposition. The container was placed on a stainless steel structure whose surface was coated with clear acrylic resin so as to minimize metal contamination by the structure itself. The container on the structure was set at a height of 50 cm from the ground and was exposed for 12 hours to receive atmospheric aerosol depositions. The dilute nitric acid solution in the container was then put into an acid-cleaned FEP teflon bottle after exposure to the atmosphere. Low density polyethylene bottles were used to sample fresh waters for the analysis of major ions and heavy metals. The polyethylene bottles for the major ion analysis were previously cleaned with acetone and subsequently were washed with purest water thoroughly. The bottles for heavy metals were rigorously acid-cleaned by the same method as wet depositions(7). The cleaned polyethylene bottles were triply wrapped with polyethylene bags in order to prevent contamination during transportation to the sampling sites. These plastic vials were handled with polyethylene-gloved hands through sample collection.

## 2.2. Analytic method

The river and lake waters collected were filtered through a nitrated cellulose membrane filter(0.45 μm in pore size) into an FEP teflon bottle. The membrane filter used was previously washed by soaking a dilute hydrochloric acid solution(1 part of HCl + 2 parts of H<sub>2</sub>O) and was rinsed with purest water thoroughly, followed by drying at a room temperature under laminar flow filtered air. The filtrate was prepared to be 0.5 % acid solution by adding an appropriate amount of HNO<sub>3</sub> to shortly store for further chemical treatments. An aliquot was taken from this stock solution and was mixed with a known amount of the multi-spike solution of <sup>62</sup>Ni, <sup>65</sup>Cu, <sup>66</sup>Zn, <sup>109</sup>Ag, <sup>114</sup>Cd, <sup>203</sup>Tl and <sup>206</sup>Pb. The dilute nitric acid solution received dry deposition was also filtered by the same method as the water samples and a part of the filtrate was mixed with a known amount of the multi-spike solution. These spiked solutions were allowed to stand for several days in order to ensure the equilibrium between the artificially enriched isotopes added and the corresponding natural ones in the sample solution.

The dithizone-chloroform extraction method was applied to separate the heavy metals of interest from other species in the spiked sample solution. Ag and Cu were extracted from the sample solution under the pH value of 2 and subsequently Cd, Ni, Pb, Tl and Zn were concentrated under the pH value of 9. The metal species separated and concentrated were loaded with a mixture of silica-gel and phosphoric acid onto a Re-filament to analyze on a high resolution surface thermal ionization mass spectrometer(Finnigan MAT 262). Chemical processes for the samples were performed in a ultra-clean laboratory at the Muroran Institute of Technology, where the air is controlled to be Class 10 of the Federal Standard of the United States. Teflon laboratory wares were rigorously pre-cleaned by soaking in warm (ca.60 °C) acid baths in the following sequence: a dilute nitric acid(3 parts of HNO<sub>3</sub> + 1 part of H<sub>2</sub>O) for 3 days, 1 % high purity nitric acid for 1 day and 0.1 % purest nitric acid for 1 day or more, respectively. The acid-soaked wares were thoroughly

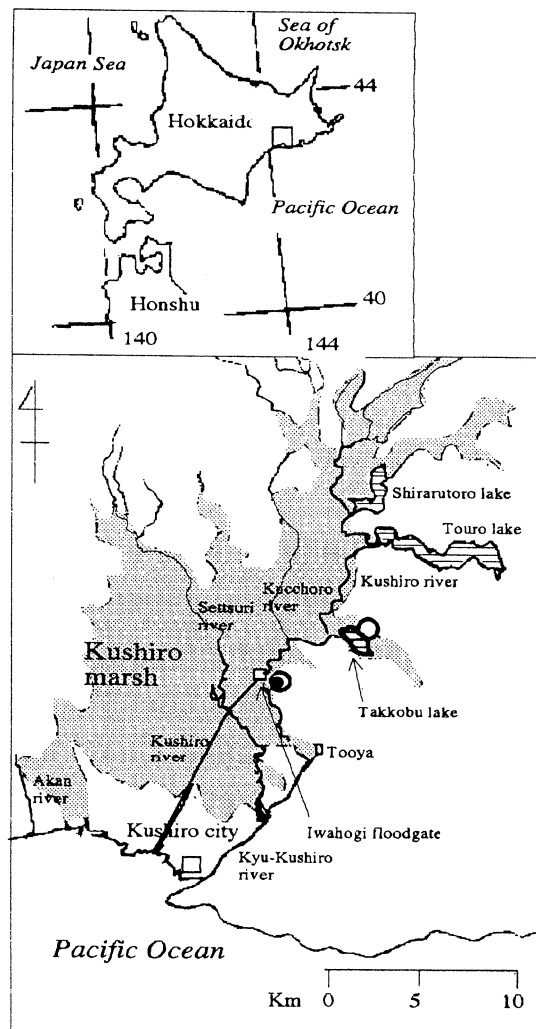


Fig. 1 Distribution of the Kushiro marsh and sampling sites.

Open circle: Sampling location of fresh water.  
Solid circle: Sampling location of dry deposition.

rinsed with purest water between baths. Polyethylene and polysulfone wares were cleaned by the similar way as the Teflon wares except heating of the acid baths. The acids and ammoniacal water used were doubly purified by subboiling techniques(8) from ultra-pure grade reagents commercially available and chloroform was doubly distilled with a borosilicate glass apparatus. Pure dithizone was obtained by recrystallization techniques(9). Ammonium citrate and potassium cyanide were repeatedly purified by solvent extraction. Laboratory vessels were handled with polyethylene-gloved hands

Table 1. The annual input of atmospheric heavy metals to the Kushiro marsh.

Sample No.	Tl	Ag	Cu	Cd	Ni	Pb	Zn
DDKU9801	0.009	0.005	2.6	0.066	1.1	2.2	8.4
DDMU9701	0.011	0.003	0.46	0.29	0.16	2.3	4.8

Unit : kg/km<sup>2</sup>/yr

DDKU9801: Dry deposition collected at the Iwahogi floodgate of the Kushiro river.

DDMU9701: Dry deposition collected at Muroran city(Unpublished data).

Table 2. Heavy metal contents in river and lake waters in the Kushiro marsh.

Sample No.	Tl	Ag	Cu	Cd	Ni	Pb	Zn
KU971001-1	0.0128	0.00032	0.335	0.0695	0.143	0.0104	0.296
KU971001-2	0.0048	0.00012	0.291	0.0437	0.147	0.0233	0.321
River water*			1.4				5
River water**			1.5	0.02-0.1	0.3	1	4

Unit: ng/g for KU971001-1 and KU971001-2; ng/ml for river water.

KU971001-1: Water collected at the Takkobu lake.

KU971001-2: Running water collected at the Iwahogi floodgate of the Kushiro river.

\* Sugawara K.(1967)<sup>(15)</sup>.

\*\*Kitano Y.(1979)<sup>(16)</sup>.

through the sample preparation and chemical treatments in the ultra-clean laboratory. A lint-free combination suit was put on in the laboratory.

### 3. RESULTS AND DISCUSSION

On the basis of 30 and 50 measurements of each ratio of the selected isotopes, concentrations of Ag, Cd, Cu, Ni, Pb, Tl and Zn were determined for the samples of a dry deposition, a running water of the Kushiro river and a surface water of Takkobu lake in the Kushiro marsh area. The within-run precision for these elements in the samples was better than 0.3 % in relative standard deviation ( $2\sigma$ ). Table 1 represents the annual precipitation of the seven metals of the dry deposition, which was calculated based on the analytical results and the exposure duration. As seen in Table 1 the Kushiro marsh area received annually the amounts of atmospheric Tl, Ag and Pb comparable with those of Muroran city. In particular, the Cu, Ni and Zn dry depositions on the marsh area were distinctly larger than those on Muroran city.

It is significant that the elemental ratios of Cu to other metals in the dry deposition from the marsh are closer to that of urban atmospheric aerosols in Muroran city rather than Sapporo city and Rishiri island except Ni/Cu (Fig. 2). Because the Kushiro marsh area is located in the eastern district of Hokkaido, the atmosphere above the area probably receives heavy metal aerosols transported by westerly, specially in the spring season. Therefore, it is predictable that heavy metal aerosols emitted from the Muroran-Tomakomai industrial area in southwest Hokkaido are transported in part to east Hokkaido. This assumption seems to be supported by the fact that the dry deposition from the marsh area is plotted between the urban atmospheric aerosol of Kushiro city and one of Muroran city on the diagram of  $^{208}\text{Pb}/^{206}\text{Pb}$  vs  $^{207}\text{Pb}/^{206}\text{Pb}$  (Fig. 3). The existence of such an airborne metal as lead occurring in a distant source is not a few case. In fact, it was revealed on the basis of lead isotopic investigations that eolian lead generated in industrial and populated areas in east Asia incorporated with the wet deposition in the Muroran-Tomakomai industrial area in southwest Hokkaido<sup>(10)(11)</sup>.

The atmospheric lead aerosol is characterized by its isotopic composition that is essentially subjected to that of anthropogenic lead besides natural sources. Consequently, the isotope ratios of lead in the dry deposition observed in this study are ascribed to result from significant contributions of urban atmospheric lead aerosols emitted from the highly industrial area of southwest Hokkaido and from Kushiro city where is located close to the marsh area. On the other hand, lead aerosols of natural sources can be expected to insignificantly contribute to the isotopic composition of the dry deposition in the Kushiro marsh. This claim is based on the fact that rock and soil from the Hidaka mountain region have distinctly different isotope ratios of lead<sup>(12)</sup> from the dry deposition as seen in Fig. 3. The argument mentioned above, however, still remains somewhat obscure since it is not due to lead isotope ratios of the basement rock of the Kushiro marsh and surrounding areas. Actually, geology of this particular areas is quite different from the Hidaka mountain region. The Kushiro marsh area is widely covered by the Alluvium that consists mainly of peat, fine-grained gravel,

clay and gravel beds from surface to depth<sup>(13)</sup>. Nevertheless, it is estimated that the constituents of the Alluvium there have isotopic ratios of 0.84-0.85 in  $^{207}\text{Pb}/^{206}\text{Pb}$  and 2.06-2.10 in  $^{208}\text{Pb}/^{206}\text{Pb}$  ratios, respectively, based on data listed by Doe(1970)<sup>(14)</sup>. Furthermore, the  $^{208}\text{Pb}/^{206}\text{Pb}$  and  $^{207}\text{Pb}/^{206}\text{Pb}$  ratios in the running water of the Kushiro river, which would be substantially

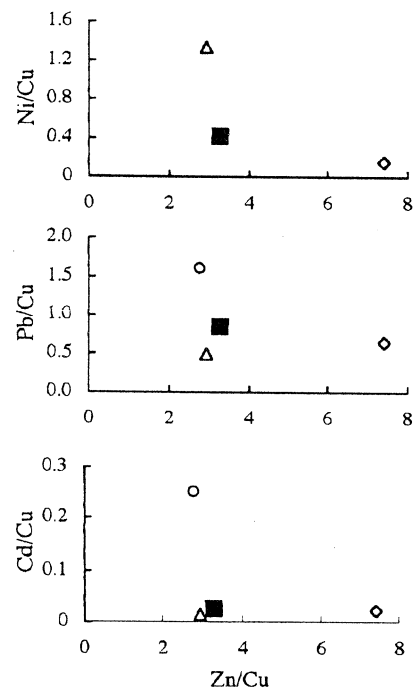


Fig. 2. Relations of elemental ratios between dry depositions and aerosols.

- Solid square: Dry deposition in the Kushiro marsh.
- Open triangle: Aerosol in Muroran, SW Hokkaido (Average of 85 analyses, unpublished data).
- Open diamond: Aerosol in Sapporo, Hokkaido (Data from National Air Monitoring Stations).
- Open circle: Rishiri island, the northernmost Hokkaido (ibid).

contributed by natural lead leached from the basement rock forming the marsh area, are similar to the estimated values (Fig. 3). Thus, it is likely that the isotope ratios of lead in the dry deposition are not affected by natural lead to a large degree.

Very similar contents of the heavy metals analyzed were found between the surface water of Takkobu lake and the running water of the Kushiro river, both of which were sampled in the marsh area (Table 2). Although these concentrations are markedly low in comparison with the mean values for river waters in Japan (Table 2), it does not always denote that the fresh water in the marsh area remains pristine. Evidently Cu and Cd in the fresh water in the marsh area showed respectively 3 and 30 times higher in content than a running water in a pristine region of the Hidaka mountains (12).

Lead isotope ratios of the fresh waters in the marsh area are considered to principally result from mixing of lead from the atmosphere and lead leached from the basement rock and soil. It is worthy to note that the Kushiro river water showed more radiogenic in lead isotope ratio than the surface water of Takkobu lake, as seen in Fig. 3. Whereas, the surface water lead of the Takkobu lake which is a reservoir of the Kushiro river are shifted to less radiogenic sites on the  $^{208}\text{Pb}/^{206}\text{Pb}$  vs  $^{207}\text{Pb}/^{206}\text{Pb}$  diagram. In other words, it is plotted at a more closer site to the dry deposition. This can be explained that the lake water contains much larger amounts of atmospheric lead compared to the running water because of a longer residence time in the lake.

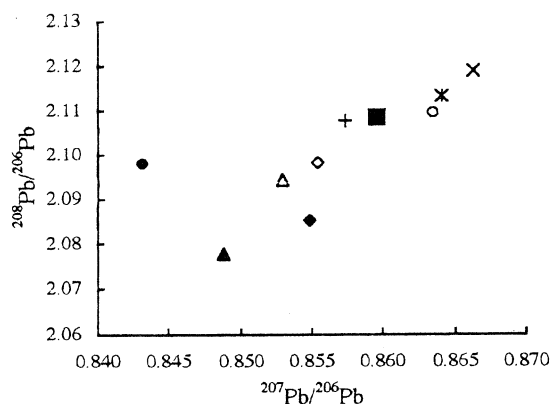


Fig. 3. Pb isotopic characteristics of dry deposition in the Kushiro marsh area.

- Solid square: Dry deposition in the Kushiro marsh area.
- Solid diamond: Surface water of the Takkobu lake.
- Solid triangle: Running water collected at the Iwahogi floodgate of the Kushiro river.
- Solid circle: Rock and soil in the Hidaka mountain region, Hokkaido<sup>(12)</sup>.
- Open circle: Aerosol from Muroran, southwest Hokkaido. (unpublished data).
- Open diamond: Aerosol from Kushiro, east Hokkaido (unpublished data).
- Open triangle: Aerosol from Niseko, southwest Hokkaido (unpublished data).
- Cross: Aerosol from Shenyang, northeast China<sup>(10)</sup>.
- Asterisk: Aerosol from Beijing, China<sup>(10)</sup>.
- Plus: Aerosol from Chengdu, southwest China<sup>(10)</sup>.

## CONCLUSION

Because of not only a sanctuary for a many kind of birds but also an inhabitat for particular aquatic vegetation and animals only living there, it has been required to preserve the nature of the Kushiro marsh as pristine as possible. For this purpose a clear understanding of current environmental conditions of this national park and surrounding areas is essential. The present investigation was done to disclose current pollution of toxic metals on the environment of both the atmosphere and the fresh water in the marsh area. As a result, it was found that the Kushiro marsh area received the dry deposition of substantial toxic metal species such as Ag, Tl, Cd, Cu, Pb, Zn and Ni. Annual precipitations of most of them were comparable or much more than those of the highly industrial area in southwest Hokkaido. Moreover, lead isotopic characteristics revealed that airborne lead originated from distant sources contributed largely to the total lead in the dry deposition in the Kushiro marsh area. The lead isotopic data also enabled us to speculate that industrial lead aerosols generated in the highly industrial area in southwest Hokkaido are likely one of the distant sources.

Thus, the present work revealed the fact that current conditions on the atmospheric and aquatic environment of the Kushiro marsh area are significantly contaminated by anthropogenic heavy metals.

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北海道東部釧路湿原における大気重金属降下量

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概 要

北海道東部に存在する釧路湿原の大気及び淡水の重金属、特に生物に有害なAg、Cd、Cu、Ni、Pb、Tl、Znによる環境汚染について研究した。これら大気重金属の湿原への年間降下量は、Cd以外は室蘭における降下量と同様、又は多い事が判明した。また湿原を流下する河川及び湖水の重金属濃度は低いが、濃度比や鉛同位体比から大気重金属汚染が認められた。更に鉛同位体比の特徴から、釧路湿原に降下する鉛の一部に、西南海道重工業地帯から移送された人類起源鉛が存在すると推定された。

キーワード： 釧路湿原、乾性降下物、有害親銅元素、鉛同位体比

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