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学位授与の題目	Impurities in Winter Precipitation on the Japan Sea Side of Japan （冬季の日本海側地域における大気汚染降下物に関する研究）
論文審査委員	（主査）　平井英二 （副査）　山本善一 （副査）　林　良茂 （副査）　寺田喜久雄 （副査）　宮崎元一

学位論文要旨

ABSTRACT

Daily snowfall was collected on polyethylene sheets at six sites along the coast, in city areas and in the inland mountains. The samples were analyzed for EC, pH, soluble and insoluble amounts of Al, Cd, Cr, Cu, Fe, Mn, Pb, and Zn; Cl^-, NO_3^-, SO_4^{2-}, Ca^{2+}, K^+, Mg^{2+}, and NH_4^+. Experiments were conducted to estimate the below-cloud scavenging, the wet and dry deposition, the propagation of impurities in a snowpack, and their final release in meltwater.

Contrary to coastal snowpacks which released meltwater almost daily, most of the impurities in mountain snowpacks were retained until spring; the first fraction of meltwater released between 50 and 90 percent of the total amount of water-dissolved impurities. The last meltwater fraction contained the maximum of water-undissolved metals.

1. INTRODUCTION

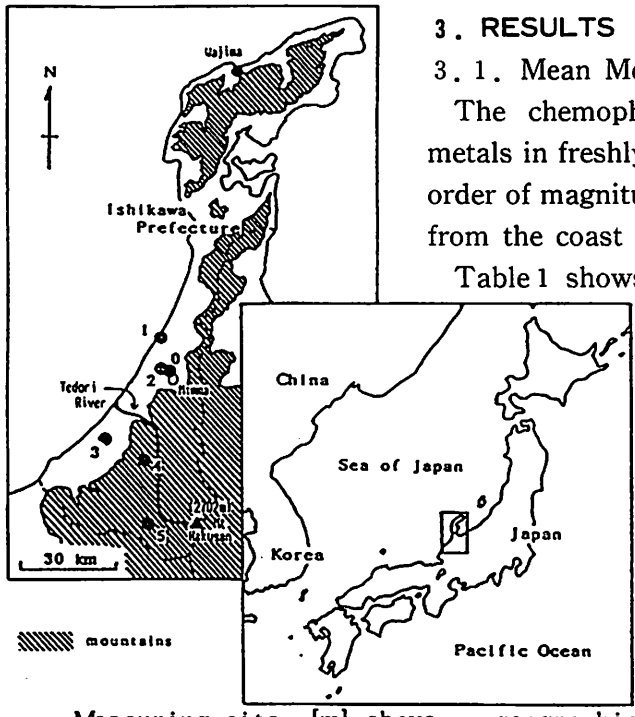
In Japan, numerous field surveys have studied the ionic composition of wet deposition intensiveiy. However, few information is available on the deposition of trace metals. Data concerning their deposition and release in and from snowpacks are lacking; such data are especially important for the estimate of

long-range transport from the Asian continent to the snow-rich Hokuriku area along the Japan Sea side of central Japan.

This thesis presents an analysis of the concentration of trace metals, anions and cations in wet deposition and meltwater released from snowpack in the area during the winters of 1986-1988.

2. METHODS

Daily snowfall was collected on polyethylene foils (50×50cm) at six sites along the coast, in city areas, and in the inland mountains (Fig. 1). Experiments were conducted to estimate wet and dry deposition, local background concentrations, and the final release in natural meltwater. Meltwater was collected in lysimeters embedded in the ground before the first snowfall accumulated to a snowpack. Samples were analyzed for EC, pH, and soluble and insoluble amounts of Fe, Mn, Pb, Cd, Cr, Cu, Zn, and Al; Cl^-, NO_3^-, SO_4^{2-}, Ca^{2+}, K^+, Mg^{2+}, Na^+, and NH_4^+.



3. RESULTS

3.1. Mean Metal Concentration

The chemophysical properties of various metals in freshly fallen snow were of the same order of magnitude at all six sampling stations from the coast to the inland mountains.

Table 1 shows the average concentrations in wet-deposited snow of concurrent snowfall at the six sites. It should be noted that the average values, calculated as arithmetic means, are overestimates, considering the most frequently occurring (median) values at a particular site.

Measuring site		[m] above sea level	geographical coordinates	
0:	Kodatsuno	75	136°41'06"	36°32'44"
1:	Uchinada	25	136°38'31"	36°38'58"
2:	Hondamachi	25	136°40'00"	36°33'05"
3:	Komatsu	5	136°28'08"	36°24'16"
4:	Torigoe	190	136°36'27"	36°21'13"
5:	Shiramine	480	136°37'33"	36°09'40"

Fig. 1 Sampling site locations

3．2．Metal Solubility

All examined elements occurred in both soluble and insoluble fractions. Fig. 2 show the average soluble fractions of the metals which were obtained by the ratios of (soluble fraction)/(total amount) of each metal. Given the pH values involved, the low solubility of some elements can only be explained by the incorporation of water-soluble compounds into insoluble material[1].

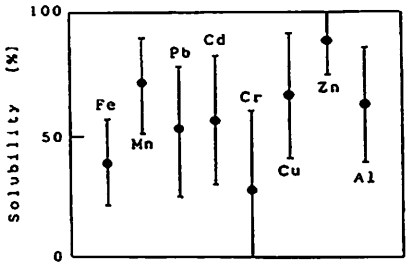


Fig. 2 Average percent solubility (●) and standard deviation (I) in wet-deposited snow.

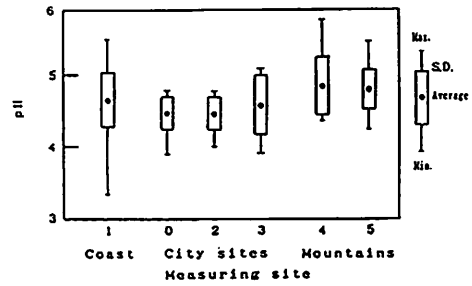


Fig. 3 Average pH (●), standart deviation (□) and extrema (I) in wet-deposited snow

3．3．Local Distribution of pH

Fig. 3 shows the average and standard deviations in pH of melted, wet-deposited snow samples at each sampling site. Average pH values were lowest at the urban and suburban sites and generally higher at the remote sites. It is interesting to note that standard deviations occurred within a narrow range from pH4.2 to pH5.2 at every site, especially as the pH values of rainwater at the same sites occurred within a wider range during other seasons of the year. Investigation of this phenomenon included the analysis of a range of anions and cations and finally led to the conclusion that local washout of acidic ions exceeded that of alkaline ions[2]. Weekly deposition samples with high pH values appeared to be inflated by excess Ca^{2+}, which was emitted from road dust. Except for these samples contaminated by road dust, pH values of weekly deposition were conform with the daily wet deposition samples.

The average annual pH remained nearly constant during the five winters of the study.

3．4．Regional Background Concentrations of Trace Metals

All concentrations of airborne impurities exhibited fairly similar distributions. Relatively high concentrations at the begining of a snowfall event declined to nearly constant, low values with increasing snow quantities and snowfall duration. These lower values were accepted as the local background concentration. Absolute regional background concentrations (the sum of the insoluble and soluble) for trace metals were deriveed for each element (Table 2).

Table 1 Average Concentrations of Trace Metals in Wet-Deposited Snow at the Various Sites and Number(#)of Samples(1986-1988)

Concentration [μg/l]

Measuring site		Fe	Mn	Pb	Cd	Cr	Cu	Zn	Al	#
0	Kodatsuno (suburb)	77.1	2.9	3.5	0.17	5.9	1.9	4.3	20.5	31
1	Uchinada (ocean)	72.9	4.9	3.7	0.17	8.5	2.1	4.6	9.6	19
2	Hondamachi (city)	82.6	3.1	3.4	0.19	4.7	2.3	5.7	17.7	24
3	Komatsu (city)	85.2	2.4	4.1	0.18	6.8	2.0	5.2	25.8	20
4	Torigoe (mountain)	68.7	3.0	3.1	0.15	11.0	1.8	3.1	11.3	23
5	Shiramine (mountain)	63.2	2.1	2.6	0.15	8.7	1.9	2.7	17.3	22

Table 2 Regional Background Concentrations in Wet-Deposited Snow

Cd :	0.02 - 0.04	μg/l
Cr,Cu,Mn,Pb :	0.1 - 0.5	μg/l
Zn,Al :	0.5 - 2.0	μg/l
Fe :	10.0	μg/l

3.5. Long-range Transport

To understand long-range transport mechanisms, it is important to determine local and regional sources which might contribute to the background. Besides local anthropogenic emission sources, the analysis of background values on the Japan Sea side of Japan must account for natural sources such as sea spray components and the so-called "Kosa" (loess aerosol) from the Asian continent.

Results, however, indicate that neither Kosa nor sea spray contribute significantly to the local trace metal background in winter. Also, the immission patterns of the soluble and insoluble fractions of the various metals at six sites demonstrated that the concentration levels were directly related to local sources.

The cities of Kanazawa and Komatsu represent major sources of insoluble metal compounds. In the case of Cr, a major source can be assumed in the vicinity of Torigoe (Fig. 1).

3.6. Release of Meltwater

The concentrations of the 'soluble/insoluble' fractions found in wet deposition samples were distributed around an arithmetic mean (Fig. 2). The meltwater samples during winter, however, revealed separate releases of soluble and insoluble components. (Fig. 4). At the coastal sites, lysimeter samples showed a release of meltwater from the snow-pack to the ground all winter. The

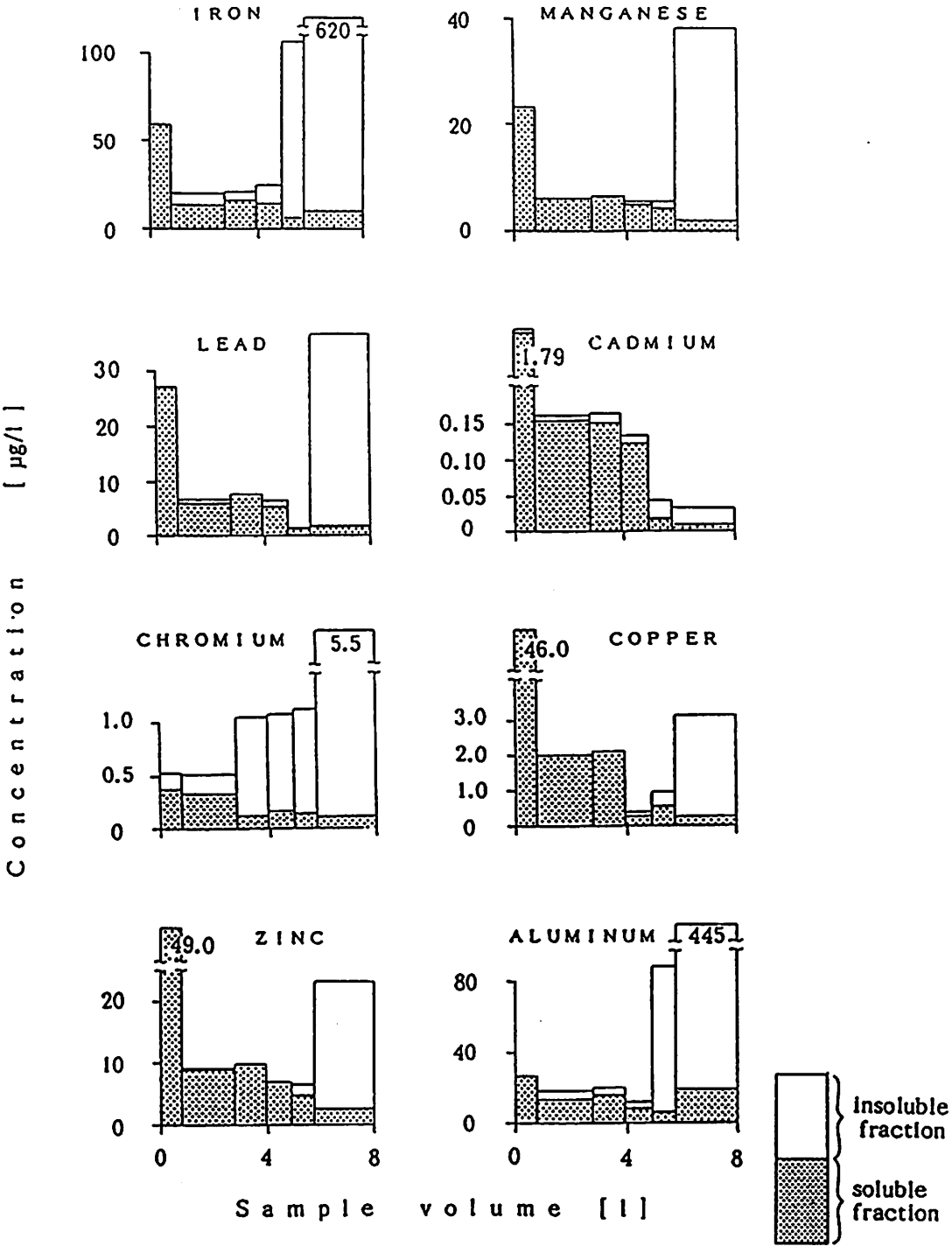


Fig. 4 Concentration of trace metals in lysimeter samples at Shiramine in 1988

concentrations of the insoluble and soluble fractions, the EC and pH values of consequent samples, though they exhibited a preferential release of dissolved impurities, were in the order of magnitude of wet deposition samples. At the remote mountain site, however, meltwater breakthrough was delayd into late March and was restricted to a relatively short period. The first meltwater fraction carried an enriched (50-90% of the total meltwater concentration) load of water-soluble material and was characterized by low pH (3.97) and high EC (420μS/cm) values, a magnitude never measured during any other, prior snowfall event. Compared to the soluble concentrations, the insoluble fraction of all trace metals was negligible in the first meltwater samples. During the later meltwater discharges, the soluble fraction rapidly fell off while the insoluble quantities increased to a maximum in the last sample. The high ionic strength (EC, pH) and the enrichment of bio-available (i.e., water-soluble) heavy metals in this first meltwater breakthrough was caused by preferential elution; this impurity-laden first release undoubtedly reaches aquatic systems and may affect aquatic biota.

On the coastal plain, impurities were released during several midwinter melts in amounts which did not show any significant enrichments compared with other local rain or snow data.

The sea salt aerosol components NaCl and $MgCl_2$ could be well traced from their deposition to the final run-off.

4. FINAL CONSIDERATIONS

In order to deepen the understanding of long-range transport across the Japan Sea, locate sources of trace metals, and follow their path in winter, the measuring net and data-collection program need to be extended. Tracer experiments and case studies need to be performed not only on the rather small coastal line of Japan, but in all countries bordering the Japan Sea.

Further studies also can assess the significance of the sequential snowpack release data in regional ecological models.

5. ACKNOWLEDGMENTS

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6. REFERENCES

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論文審査の結果の要旨

Ecker学位論文審査委員会は，平成2年2月1日と2月9日に第1，第2回論文審査委員会を開催して本学位論文を検討し，2月15日に口頭発表，最終審査会を開催し，意見交換の後に協議の結果，下記の通り判定した。

大気汚染物質は自然界や人為的発生源から大気に放出され，それらは大気循環に伴った輸送や拡散過程をへて，結果として雨及び雪に取り込まれる。よって本論で日本海側における大気汚染物質についての測定と解析を行った。主な内容は下記の通りである。

1) サンプリングの場所について，内灘町から白峰までの間にほぼ南北に6地点を観測点として，降雪のサンプリングを行い，積雪のコアーは白峰と工学部を中心にサンプリングを行った。これらの結果からpHの平均値は都市部が最も低く，海岸や山間部では平均値はやや高いデータが得られた。また，鉄，マンガン，鉛，カドミウム，クロム等の金属濃度として，山間部の鳥越村観測点ではクロムの濃度が都市部より高いことが明かとなった。

2) 降雪量が少ないときは，金属濃度は降雪毎に異なっているが，積雪量が多い程，比較的低い濃度を示し，一定濃度に収束している。

3) 積雪中からの融雪水の濃度であるが，マンガン，亜鉛，カドミウムなどは最初の分画部で高い溶解度を示しているが，その他の不溶解性成分は最終的な分画部でまとめて検出され，溶解成分と不溶解成分とが明確に分離される現象を示している。その他にもpH, EC等についても有益なデータが得られている。

石川県で代表される日本海側は成果でも有名な豪雪地方でもあり，冬季の雨及び雪中の大気汚染物質の定量的評価は環境問題として重要である。この研究によって新しい知見を多く得られている。

本委員会は以上を総合して，提出された本論文が学術博士に値すると判定した。