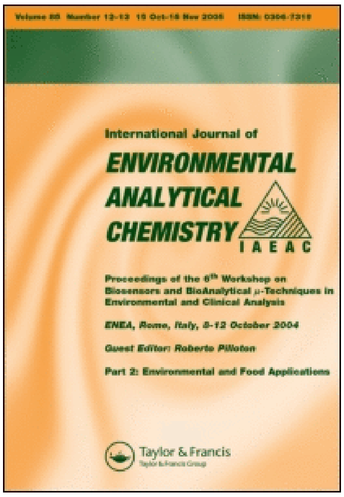

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# Determination of Alkaline Earth Metals in Japanese Rain and Snow by ICP Emission Spectrometry

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Alkaline earth metals such as magnesium, calcium, strontium and barium were easily determined in rain and snow samples by a sequential ICP emission spectrometry, when appropriate instrumental conditions and solution matrices were chosen. In this study, 1 N $HNO_3$ solution was used, without any preconcentration or separation, in a regular determination mode by a sequential ICP emission spectro-photometer. The amount of monthly deposition of magnesium, calcium, strontium and barium was determined at 11 stations in Japan in 1984 and 1985. The seasonal variation of Sr(excess) was served as a good index for the characterization of Japanese rain, evaluating the contribution rate of sea salt.

KEY WORDS: ICP emission spectrometry, calcium, magnesium, strontium, barium, Japanese rain and snow.

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## INTRODUCTION

Alkaline earth metals have been widely determined in rain and snow samples from geochemical and environmental interests. The concentration of calcium and magnesium could be easily determined by atomic absorption spectrometry and flame emission spectrometry because of their appropriate concentrations in the rain and snow samples as well as their good sensitivities in these analytical methods. Strontium and barium, however, could not be determined so easily as calcium and magnesium mainly owing to their low concentrations in the samples.

ICP emission spectrometry is known to be most efficiently applied to alkaline earth metals because they have ionic lines of high intensities in an appropriate wavelength range. Another characteristic of ICP method is the wide dynamic range of analyte elements, which is very suitable for the natural samples such as rain and snow samples whose concentration range of metals is fairly wide.

In this study, a simple sequential determination of magnesium, calcium, strontium and barium was examined using a sequential type ICP emission spectrophotometer. Monthly total deposition amount of these elements were determined in the rain and snow samples at 11 stations throughout Japan for two years. The results suggest that the relative concentration of strontium can serve as a good index for characterization of Japanese rain.

## EXPERIMENTAL

### 1. Sample collection and pretreatment

Monthly total depositions were collected in stainless steel samplers of $0.5\,m^2$ at eleven sampling stations in Japan, the locations and brief descriptions of their environmental situations are summarized in Table 1. A known amount of distilled water was added to each sampler for the period when no rain was observed, in order to keep the wet surface. At the end of each month, the sample solutions were transfered into flexible polyethylene bottles and sent to Meteorological Research Institute at Tsukuba Science City.

Each 250 ml aliquot of the sample was filtered through Millipore filter (pores size; $0.45\,\mu m$) and $HNO_3$ was added to 0.1 N. The

**Table 1** Location of the sampling stations

| *Sampling station* | *Locations* | | *Description* |
|---|---|---|---|
| | *N* | *E* | |
| Wakkanai | 45 25′, | 141 41′ | Near the sea shore, weak traffic |
| Sapporo | 43 03′, | 141 20′ | In a big city, moderate traffic |
| Akita | 39 43′, | 140 06′ | Area of government offices, moderate traffic |
| Sendai | 38 16′, | 140 54′ | Near a main road, heavy traffic |
| Wajima | 37 23′, | 136 54′ | Near the sea shore, weak traffic |
| Tsukuba | 36 03′, | 139 30′ | Area of res. institutes, moderate traffic |
| Tokyo | 35 41′, | 139 36′ | In a big city, very heavy traffic |
| Yonago | 35 26′, | 133 21′ | Near the sea shore, moderate traffic |
| Osaka | 34 41′, | 135 31′ | Near a highway, very heavy traffic |
| Fukuoka | 33 35′, | 130 23′ | Near a park, moderate traffic |
| Ishigaki | 24 20′, | 124 10′ | On the coral reef, weak traffic |

Millipore filters were also digested in $HNO_3$-$HClO_4$ solutions and adjusted to 0.1 N $HNO_3$ solution. Both solutions were used for the determination by ICP emission spectrometry.

## 2. Instrument and analytical conditions for ICP

A sequential ICP emission spectrophotometer, Plasma 100 of Instrumentation Lab. Co. Ltd. was used with a peristeric pump to maintain a constant flow rate. The flow rate of 10 ml/min was adopted in this study.

*2.1. Ionization interferences* In ICP emission spectrometry ionization is known to be high but stable. Since sodium and potassium exist at significant amounts in the precipitation samples, the effect of them on the ionization of analyte was examined adding various concentrations of sodium chloride to the standard solution of alkaline earth metals. The results for strontium are shown in Figure 1, for the atomic line and ionic line. The effect of the position in the plasma was also examined changing the observation height above the coil.

As seen in Figure 1a, the emission intensity of strontium in the ionic line was scarcely affected by the addition of NaCl up to 0.1 M at most of the positions in the plasma examined. On the other hand,

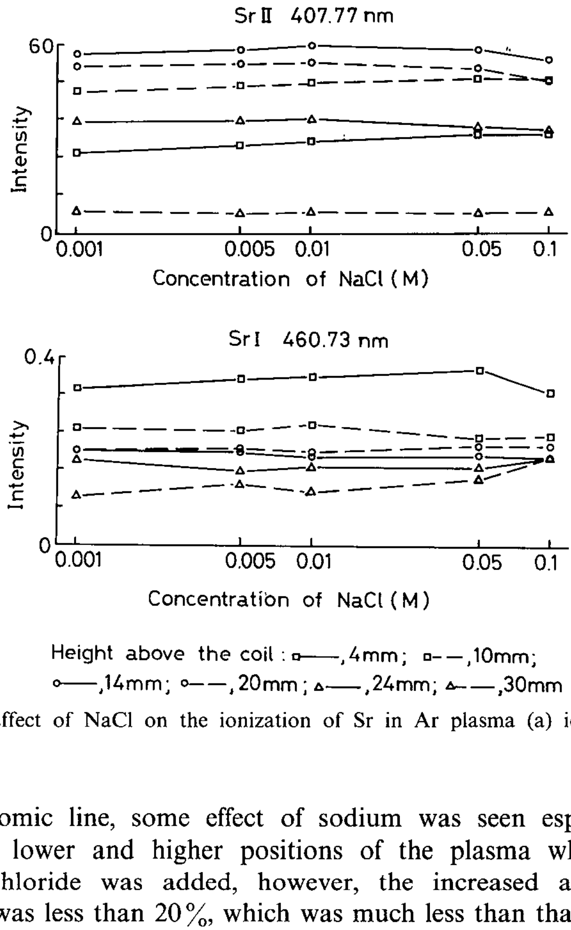


**Figure 1** Effect of NaCl on the ionization of Sr in Ar plasma (a) ionic line (b) atomic line.

in the atomic line, some effect of sodium was seen especially at extremely lower and higher positions of the plasma when 0.1 M sodium chloride was added, however, the increased amount of intensity was less than 20%, which was much less than that found in the nitrous oxide acetylene flame. For calcium, magnesium and barium similar tendencies were also found.

From this data, the effect of alkali metals in the rain samples for the ionization of alkaline earth metals could be negligible, when the proper measuring position in the plasma was used in the high intensity ionic lines.

*2.2. Acid interferences* The interferences of acids are well known in the determination of metals by ICP emission spectrometry. The main cause of them was known to be the increment of viscosity of the sample solution by the addition of acids, which changes the aspiration rate.[1] At the lower concentrations such as 0.1 to 2.0 N, however, it was found that the major effect of acids were found to be the lowering of the plasma temperature in our system.[2]

The effects of the addition of acid on the emission intensities of magnesium, calcium, strontium and barium were examined, adding various concentration of $HNO_3$ to the sample solution. It was found that the addition of $HNO_3$ decreased the emission intensities when the concentration of acid increased (0.1–0.5 N). But at the concentration range of 1 N–2 N, the intensity of these metals remained fairly constant at the 80–90% of the initial intensities when no acid was added. This means that the interference of $HNO_3$ could be negligible when the concentration of $HNO_3$ were adjusted to be 1 N–2 N for both the sample and standard solutions. In the further determination, the concentration of $HNO_3$ was adjusted to be 1 N.

*2.3. Recovery of standard solutions added to the sample* Known amounts of standard solution of magnesium, calcium, strontium and barium were added to the actual rain sample and the concentrations of them were determined by a single sequential determination described above. The recovery rate was calculated and summarized in Table 2. It is shown that the recovery rate was 90–110% for all the elements, which is supposed to be sufficient for these field samples.

**Table 2** Recovery of known amounts added to rain samples in the sequential determination of Mg, Ca, Sr and Ba by ICP emission spectrometry

| | *Analytical line (nm)* | *Rain sample (ug/ml)* | *Recovery (%)* |
|---|---|---|---|
| Mg(I) | 285.21 | 0.5–10 | 104 |
| Ca(II) | 315.89 | 0.1–1.5 | 106 |
| Sr(II) | 407.77 | 0.001–0.02 | 95 |
| Ba(II) | 455.40 | 0.001–0.02 | 93 |

## RESULTS AND DISCUSSIONS

### 1. Concentrations of alkaline earth metals found in the solution and the suspended matter

The concentrations of alkaline earth metals in the samples of 11 stations in Japan for July, 1984 are shown in Table 3 as an example of the determination. The concentrations of elements in the filtrate are shown in the column of Af and those of acid digested filter are shown in the column of As, the concentration of which is calculated as the original amount in the sample solutions. Multiplying the sample amount with the sum of Af and As, the monthly total deposition of alkaline earth metals were obtained as shown in the column B. In the column C, the monthly mean concentrations of elements in the precipitation samples are shown, dividing B by the monthly precipitation amount of each sampling station. These numbers are 20–50% higher than the concentration in the actual rain or snow, because they include the amount of these metals in dry deposition during the period when no precipitation was observed.

As seen in the table, more than 95% of the calcium was found in the filtrate and the amount which remained on the Millipore filters was negligible. But for magnesium, about 10% was left on the filter. For strontium and barium 20–30% was left on the filter. This result might be explained by the difference in the solubility of sulfates of these alkaline earth metals, which could be one of the main chemical forms of them.

For strontium and barium, the amount of insoluble fraction varied widely. It might be owing to the environmental conditions such as sand storm in spring time, pollen fallout in the early summer and etc. The evaluation of insoluble fraction in the distribution of alkaline earth metals might be of interest if the seasonal or local variations are observed, however, in this study, because of the lack of more detailed local information, the discussions were limited to the total deposition amount (Af+As) of these elements in each month.

### 2. Monthly deposition of alkaline earth metals at 11 stations in Japan

The monthly total deposition amounts of the precipitation, magnesium, calcium, strontium and barium are shown in Figures 2, 3, 4, 5 and 6. (These values were reported with those of other elements elsehwere.[4])

**Table 3** Distribution of alkaline earth metals in soluble and suspended matter in the rain (Monthly total deposition of June, 1984)

| | *Amt. of sample (kg/m²)* | *Amt. of ppt. (mm)* | *Mg* | | | | *Ca* | | | | *Sr* | | | | *Ba* | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | *Af ug* | *As ml* | *B mg/m²* | *C ug/ml* | *Af ug* | *As ml* | *B mg/m²* | *C ug/ml* | *Af ng* | *As ml* | *B mg/m²* | *C ng/ml* | *Af ng* | *As ml* | *B mg/m²* | *C ng/ml* |
| Wakkanai | 22.0 | 37.0 | 0.8 | 0.016 | 18.0 | 0.49 | 12.0 | 0.026 | 264.6 | 7.15 | 26 | 1 | 0.59 | 16.1 | 19 | 1 | 0.44 | 11.9 |
| Sapporo | 24.0 | 44.5 | 0.45 | 0.016 | 11.2 | 0.25 | 9.5 | 0.018 | 228.4 | 5.13 | 28 | 1 | 0.70 | 15.6 | 27 | 3 | 0.72 | 16.4 |
| Akita | 126.0 | 208.0 | 0.09 | 0.13 | 29.9 | 0.14 | 0.7 | 0.06 | 100.6 | 0.48 | 2 | 7 | 1.22 | 5.9 | 5 | 9 | 1.90 | 9.2 |
| Sendai | 68.0 | 110.0 | 0.17 | 0.015 | 12.6 | 0.11 | 1.0 | 0.006 | 66.4 | 0.60 | 2 | 3 | 0.34 | 3.1 | 2 | 3 | 0.34 | 3.1 |
| Wajima | 81.0 | 146.5 | 0.12 | 0.044 | 13.3 | 0.09 | 0.05 | 0.03 | 41.5 | 0.28 | 2 | 1 | 0.24 | 1.7 | 3 | 1 | 0.32 | 2.2 |
| Tsukuba | 13.0 | 85.5 | 0.56 | 0.12 | 8.8 | 0.10 | 1.5 | 0.004 | 18.9 | 0.22 | 8 | 4 | 0.16 | 1.8 | 13 | 6 | 0.25 | 2.9 |
| Tokyo | 43.0 | 81.5 | 1.95 | 0.007 | 84.2 | 1.03 | 12.5 | 0.028 | 538.7 | 6.61 | 45 | 1 | 1.94 | 23.7 | 19 | 2 | 0.90 | 11.1 |
| Yonago | 18.0 | 95.5 | 0.27 | 0.006 | 5.0 | 0.05 | 2.6 | 0.016 | 47.1 | 0.49 | 8 | 1 | 0.14 | 1.5 | 17 | 1 | 0.31 | 3.2 |
| Osaka | 107.5 | 138.5 | 0.11 | 0.004 | 12.2 | 0.09 | 1.3 | 0.016 | 144.0 | 1.04 | 5 | 1 | 0.54 | 3.9 | 5 | 1 | 0.54 | 3.9 |
| Fukuoka | 12.0 | 22.5 | 0.36 | 0.16 | 6.2 | 0.28 | 10.0 | 0.052 | 120.6 | 5.26 | 16 | 4 | 0.24 | 10.7 | 8 | 10 | 0.22 | 9.6 |
| Ishigaki | 30.0 | 117.5 | 0.49 | 0.02 | 15.3 | 0.13 | 1.9 | 0.2 | 63.0 | 0.54 | 37 | 5 | 0.13 | 1.1 | 2 | 3 | 0.15 | 1.3 |

Af: concentration of element in the sample: filtrate.

As: concentration of element in the sample: suspended matter.

B: total deposition per month in 1.0 m$^2$.

C: monthly mean concentration of element in the rain, including dry fallout.

It can be seen from Figure 2, that the amount of precipitation in 1984 ranged from 724.5 of Sapporo to 2232.5 mm of Ishigaki. The amount of precipitation in 1984 was generally smaller compared with normal years especially at the north-east part of the Pacific side of Honshu Island, where the amount of precipitation were recorded to be 40–60% of the normal years.[3]

On the other hand, in 1985 the amount of precipitation was mostly normal ranging from 1045.5 of Sapporo to 2953.5 mm of Ishigaki.

The deposition amount of magnesium was high at Wakkanai, Tokyo, Akita and Wajima. At Wakkanai, Akita, Wajima and Yonago, the deposition amount of magnesium was higher in winter time than in summer. These sampling stations are known with heavy snow in winter.

The deposition of calcium was somewhat different from that of magnesium seen in Figure 3. The deposition amount of calcium was highest at Tokyo followed by Sapporo, Sendai and Osaka. These stations are in big cities. In most stations the deposition of calcium was high in spring months when local and continental dust might have added to the dry fallout (Figure 4).

For strontium the deposition pattern resembled that of calcium, except for the higher amount in winter time at the stations especially on the Japan Sea side (Figure 5). As seen in Figure 6, the deposition of barium were generally low at these stations. Since some significant amount was found in the suspended particle rather than in the solution, the partial utilization of the whole sample (each 250 ml samples from 10–20 l) might have caused the loss of solid part which were stuck to the walls of the polyethylene containers during the storage though they were throughly mixed prior to the separation of sample solutions. So, the amount shown here could be somewhat underestimated ones, though the rate should be small.

The deposition of alkaline earth metals showed almost no correlation with the amount of precipitation. The deposition magnesium showed good correlation with that of strontium at Wakkanai, Wajima and Tokyo. Deposition of calcium generally showed good correlation with that of strontium.

## 3. Estimation of the rate of sea salt origin and other origins for the deposition of strontium

The concentration of alkaline earth metals in sea salt and average soil materials are summarized in Table 4. The following equations were used for the calculation of Sr(excess), meaning the strontium originated from other sources than sea salt, provided barium came solely from the soil.

$$Mg^* = Mg - Ba \times Mg(soil/Ba(soil)$$

$$Sr(excess) = Sr - Mg^* \times Sr(sea\ salt)/Mg(sea\ salt)$$

The rate of Sr(excess) in the total strontium was calculated and plotted for each month for each sampling station as shown in Figure 7 for 1984. Some typical patterns can be seen in the seasonal variation of the rate of Sr(excess), which can be summarized as follows.

i) Low in winter and high in other seasons, seen at Wakkanai, Akita, Wajima and Yonago. The stations are all located on the Japan Sea side and known with heavy snow in winter.

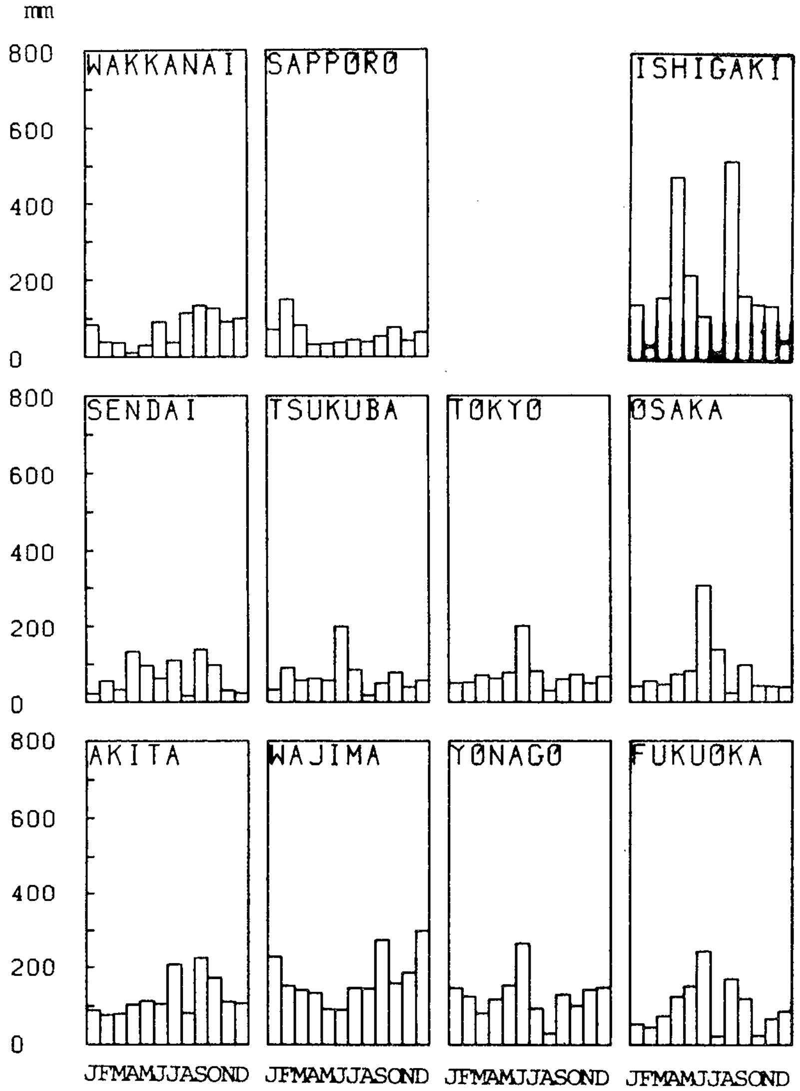
ii) High almost throughout the year, seen at Tokyo, Osaka and Fukuoka.

iii) Mostly high with a low value in autumn, seen at Sapporo, Sendai and Tsukuba.

As seen in Figure 7, it is very clear that the pattern (i) is seen only at the stations on Japan Sea side where heavy snow is known in winter time. The mechanism of heavy snow is assumed that the cold westerly from the Continent gets moisture above the Japan Sea forming the thick cloud to give the heavy snow fall at the coasts of Japan Sea, when the clouds hit the mountainous area in the middle of islands. The fact that the strontium of sea salt origin was high only in winter time at the stations on Japan Sea side is consistent with this mechanism.

The stations showing the pattern (ii) include the big cities on the Pacific side. There, the strontium in the deposition might come mainly from the soil and anthropogenic sources.

For the explanation of pattern (iii), the heavy rain of 12–13 October 1984 was examined. The rain was reported to be affected by the typhoon 8419, which means that the sea salt could be enriched in the rain. In 1984, no typhoon was reported to land on the Honshu Island, which was rather an exceptional pattern of rainfall in Japan. Thus the amount of precipitation in October 1984 was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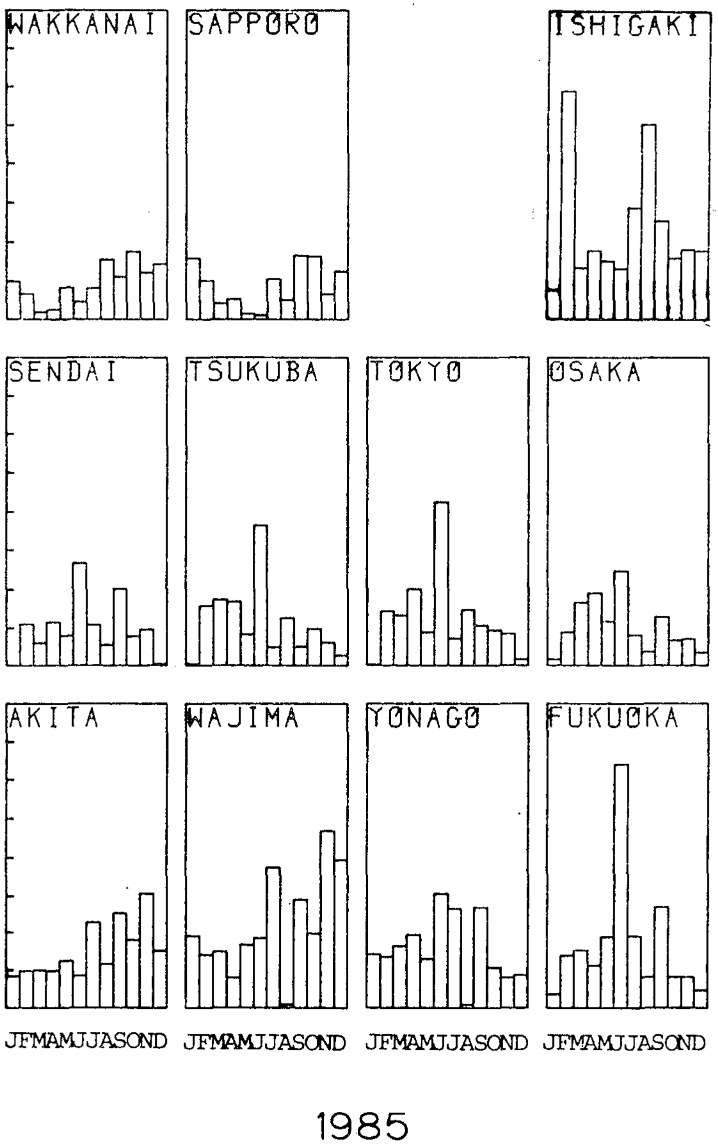
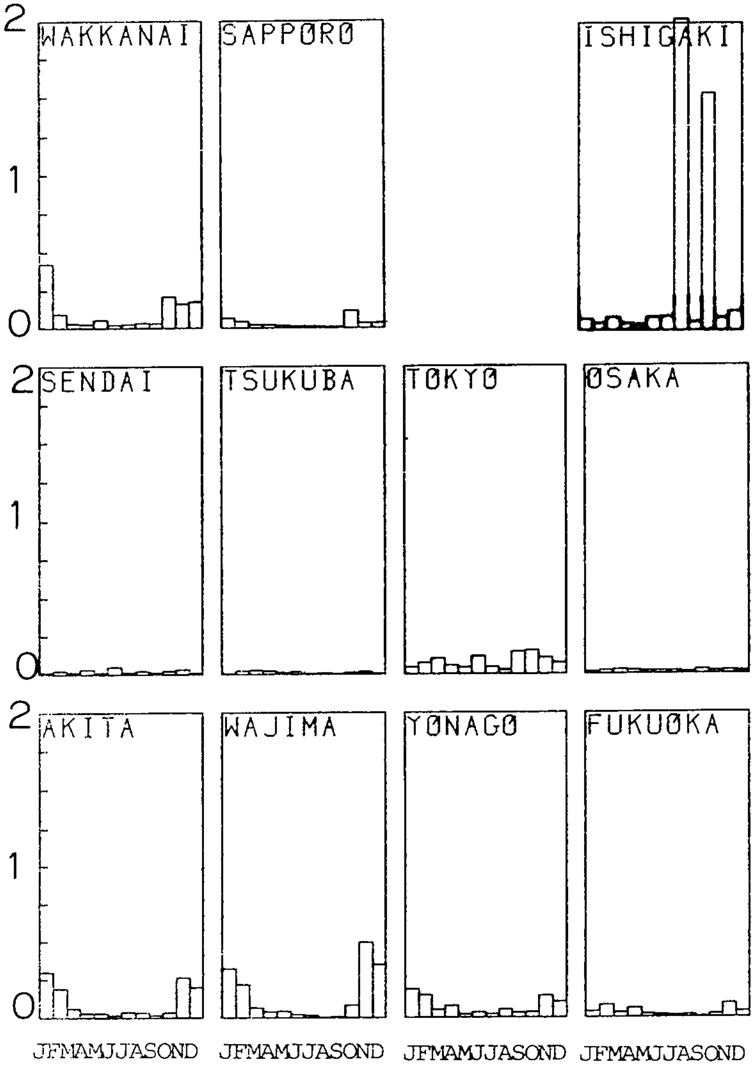


**Figure 2** Amount of precipitation at eleven stations in Japan.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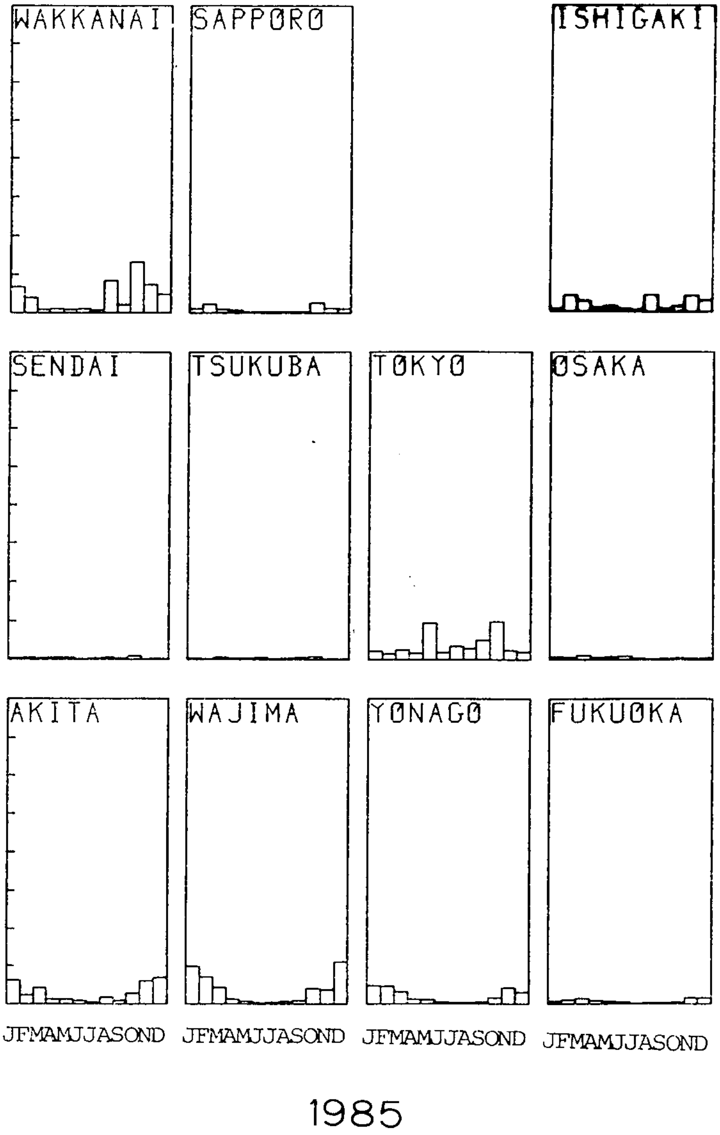
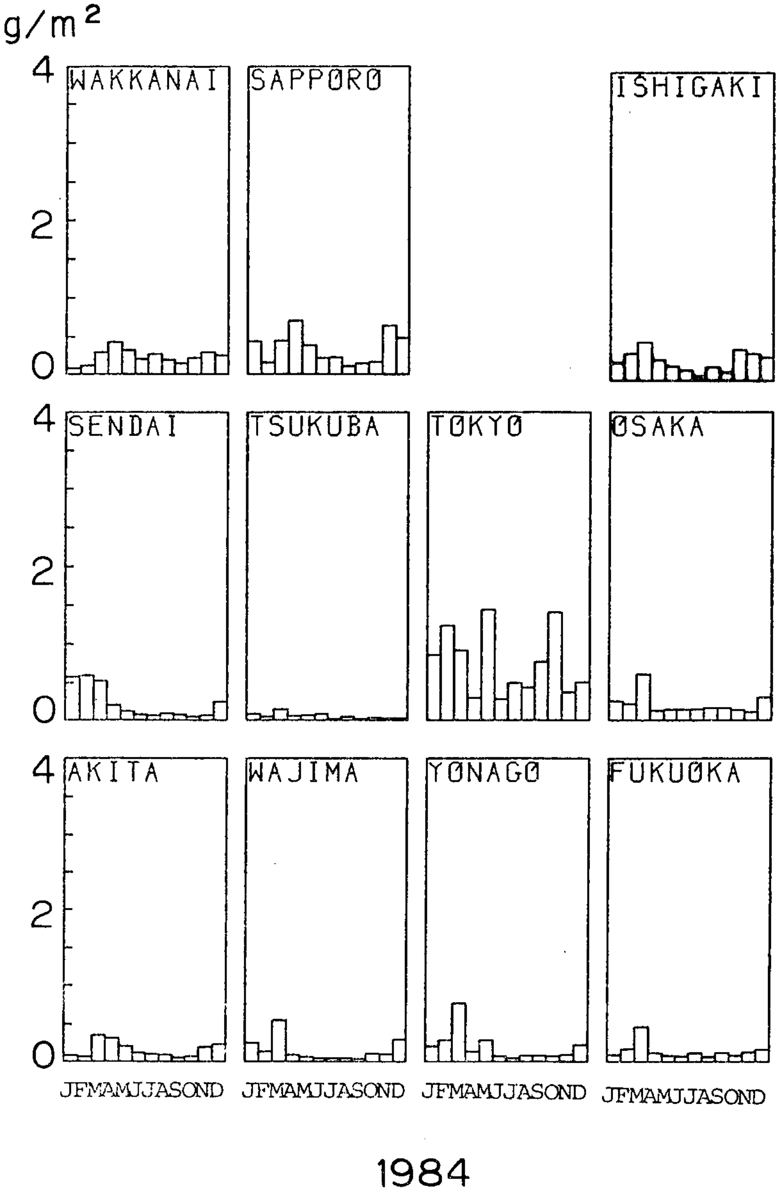


**Figure 3** Deposition of Mg at eleven stations in Japan.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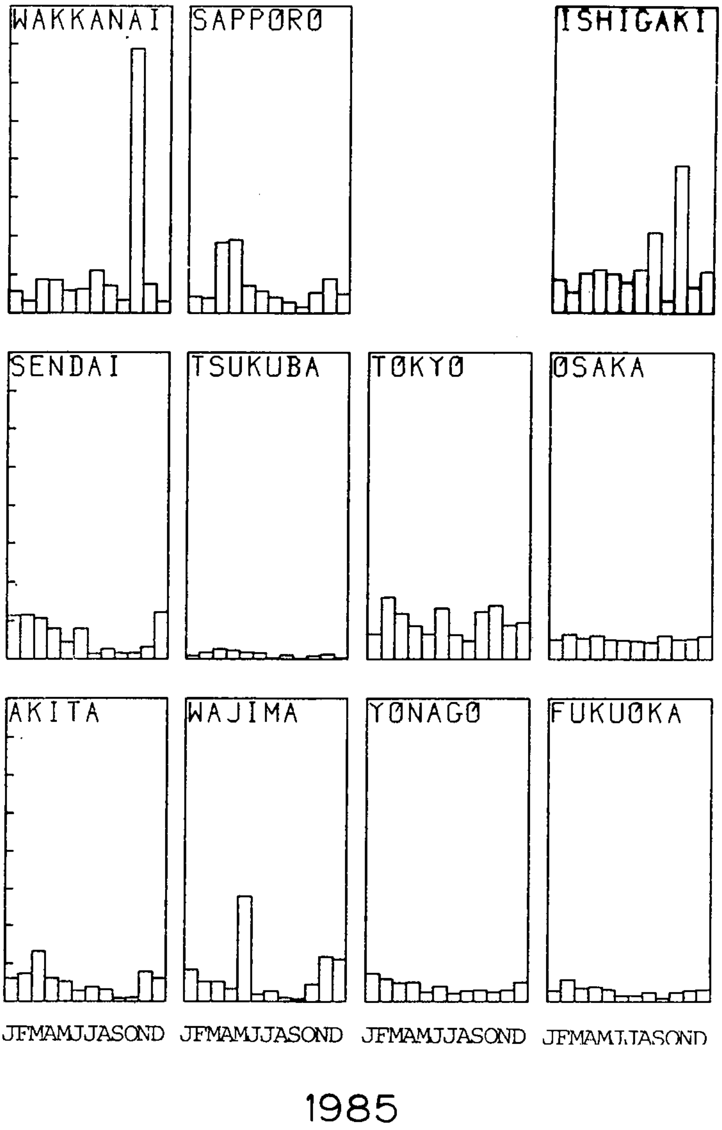
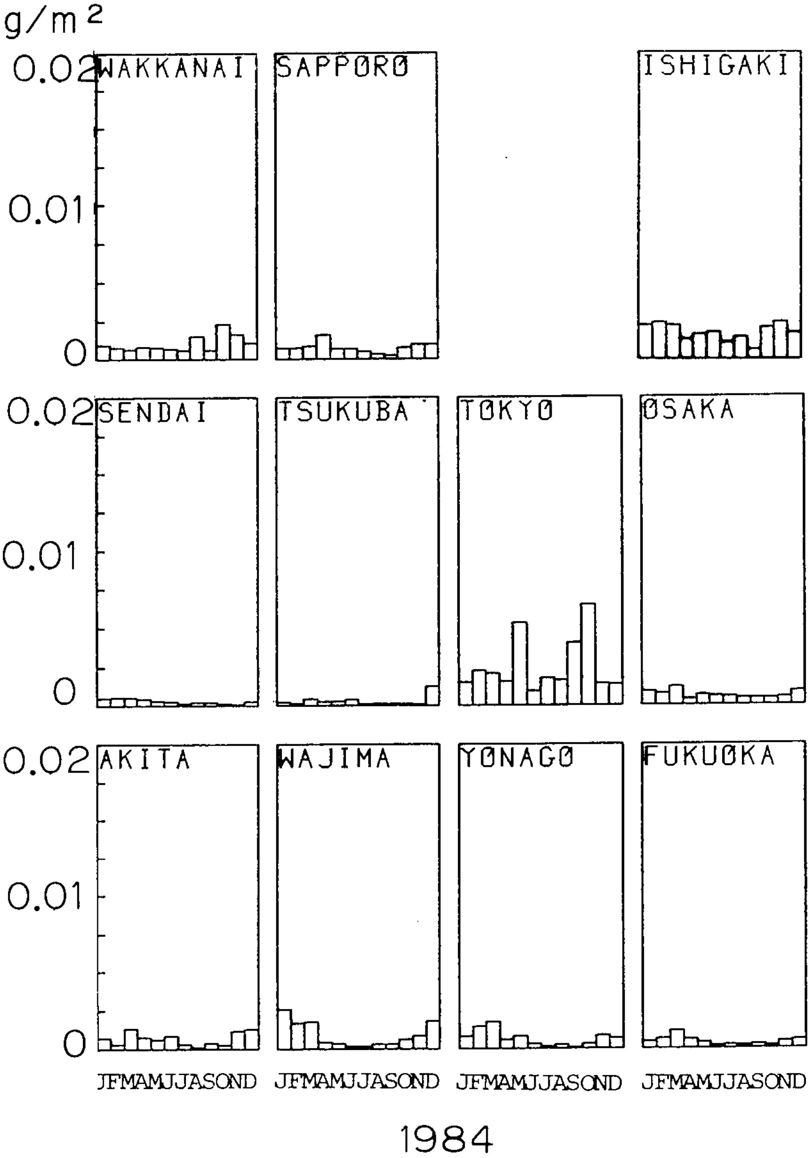


**Figure 4** Deposition of Ca at eleven stations in Japan.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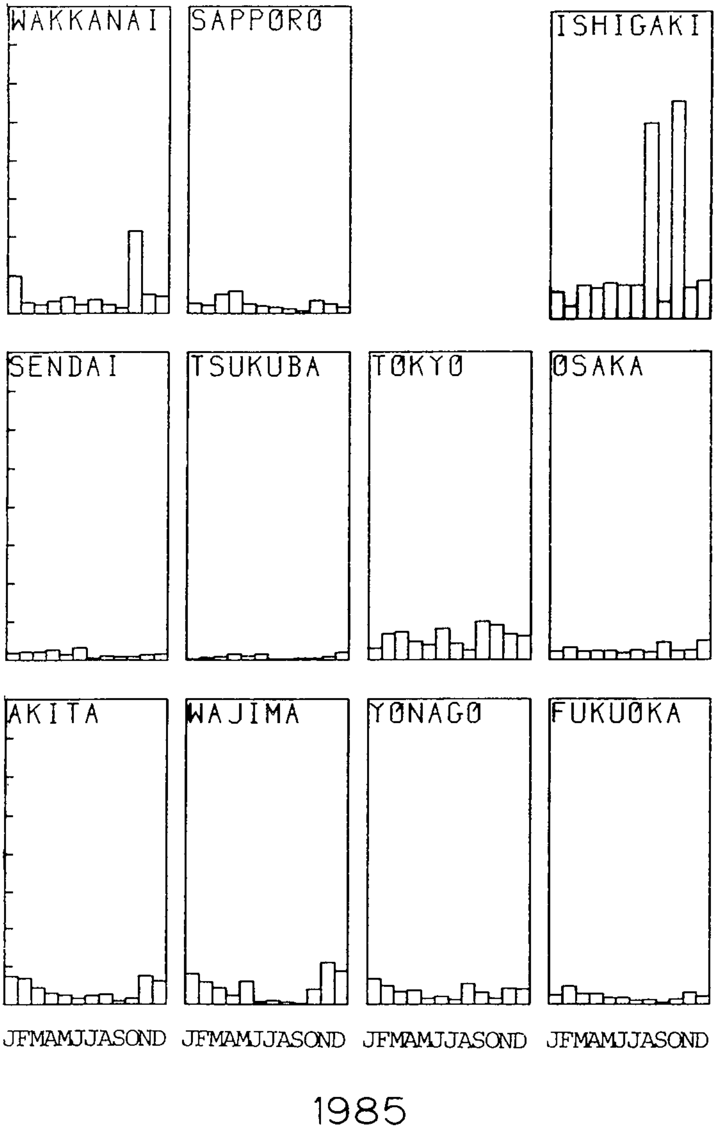
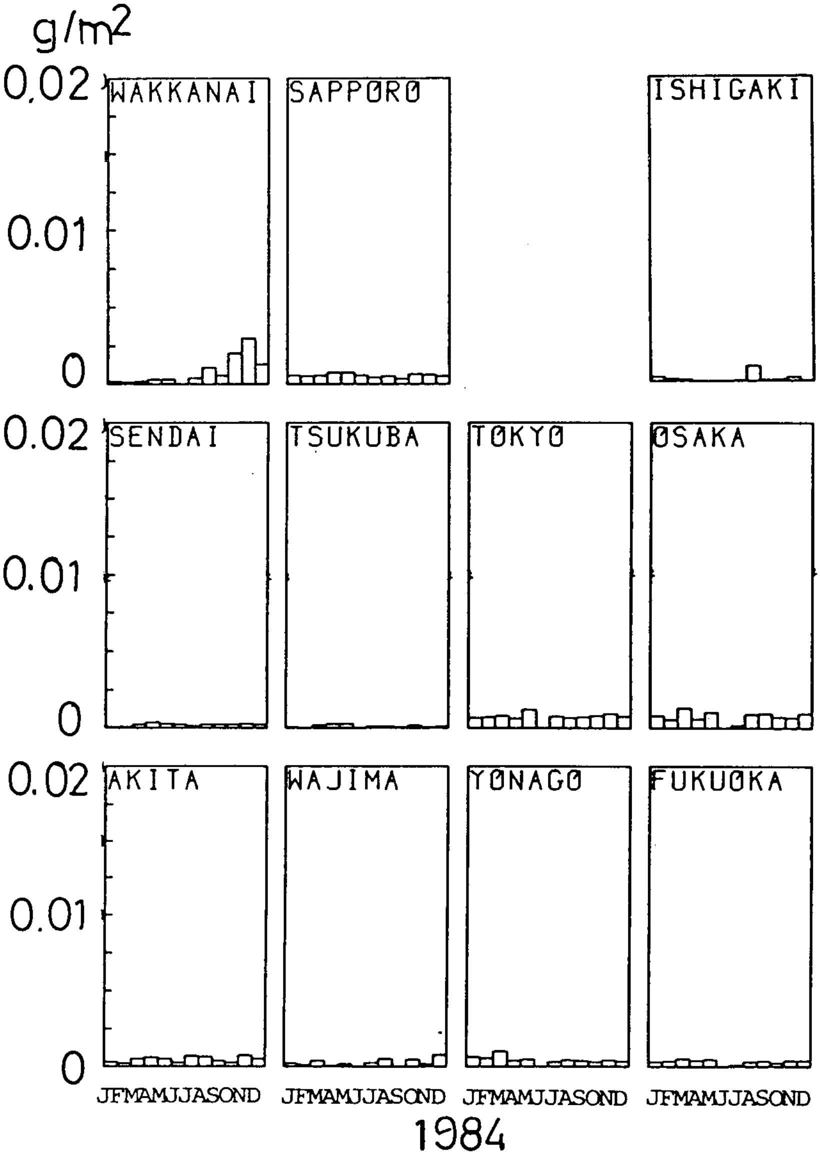


**Figure 5** Deposition of Sr at eleven stations in Japan.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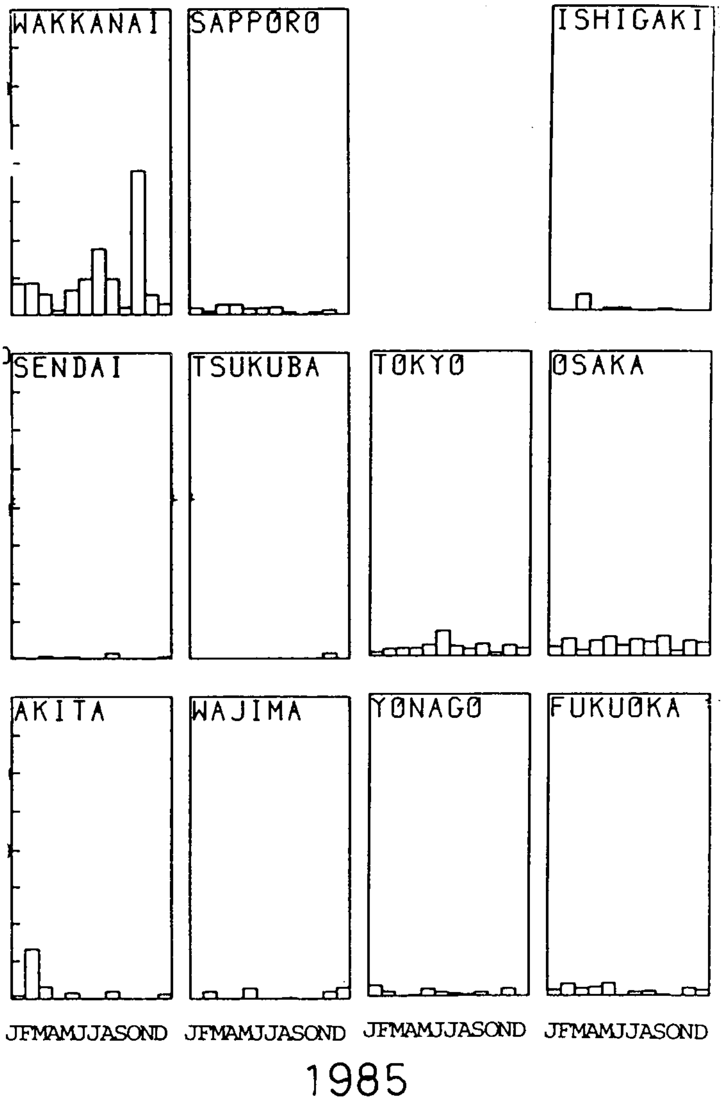

**Figure 6** Deposition of Ba at eleven stations in Japan

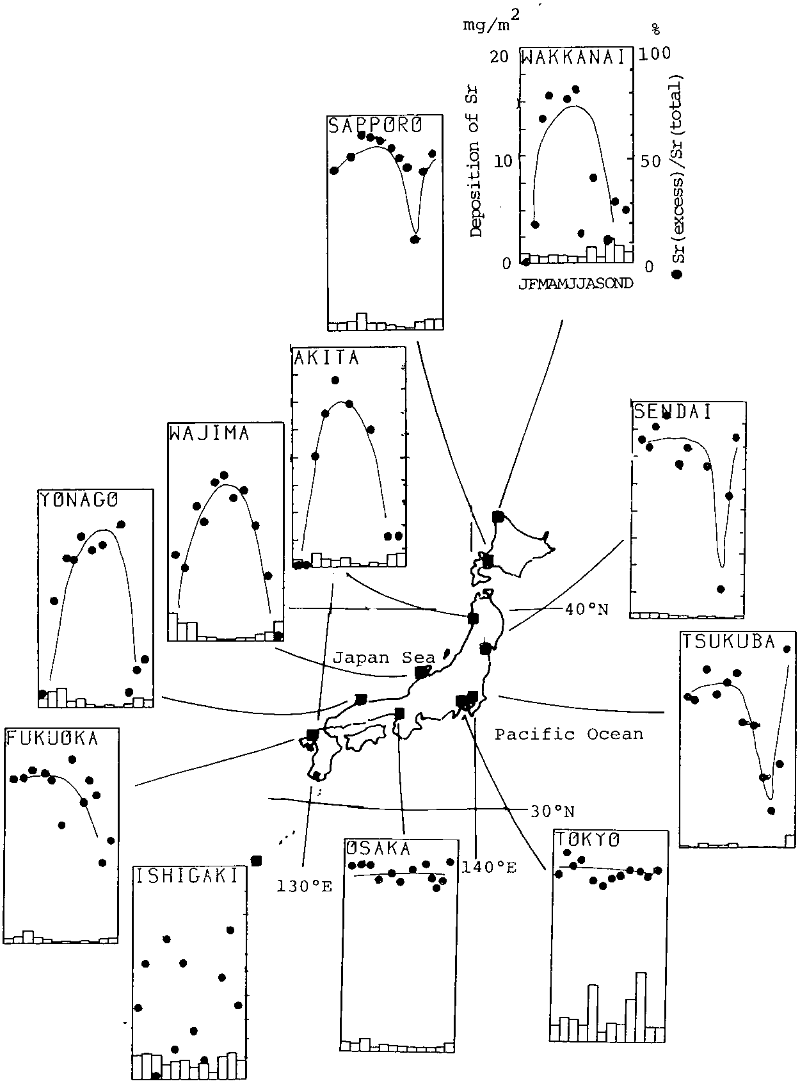

**Figure 7** Monthly deposition of Sr and the % ratio of Sr(excess) in the total Sr in 1984.

**Table 4** Concentrations of alkaline earth metals in sea water and soil

| | *Sea water* | *Soil*[a] |
|---|---|---|
| Ca | 412 | 15 000 |
| Mg | 1290 | 5 000 |
| Sr | 7.9 | 250 |
| Ba | 0.013 | 500 |

[a] H. J. M. Bowen, 1979.

relatively smaller compared with usual years at the stations where pattern (iii) was observed. One example of the chemical components of the rain of 12–13 October 1984 at Tsukuba was examined. It was seen that the concentrations of sodium and chloride were much higher than the average rain at this sampling station. These data suggest that the higher contribution of sea salt strontium in October 1984 at these stations were caused by the rain affected by the typhoon 8419. This could also be observed in the pattern of the rate of Sr(excess) in 1985, though it was less clear than in 1984.

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