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**Determination of Trace Elements in Aerosols at Rural Mountainous area and Local City of Eastern Shikoku Region, Japan**

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Abstract

Simple digestion method for mixed cellulose membrane filter in order to analysis of trace elements in aerosols was examined. Determination of Cu, Fe and Ni in the certified reference materials of China loess (CJ-1) could be conducted using the digestion method. Trace elements in aerosols smaller than 10 µm size collected at Tokushima City and near mountain areas for each season were determined as a water-soluble fraction and all components by the digestion method. Back trajectory analysis implied that contribution from Asian continent was larger in winter and spring than summer. Systematic changes in trace element compositions for each season were not observed, except for Fe, Th and U. Water-soluble components in aerosols at Tokushima City showed higher concentrations of all trace elements than those of mountain area. For aerosols in Tokushima City and near mountain area, As, Bi, Cd, Cu and Pb were mainly derived from anthropogenic sources, whereas Ba, Co, Cs, Ga, Mn, Rb, Sr, Th, U and V were derived from natural crustal sources. The origin of Pb and Cd was discussed based on the Pb/Cd ratio.

**Keywords:** Aerosols, filter digestion, trace elements, water-soluble
Introduction

Trace elements in atmospheric aerosols play an important role on transportation of biogeochemical micronutrients for marine ecosystems, such as Fe\(^{1,2}\), Co\(^{3,4}\), Mn\(^{5}\), Ni\(^{6,7}\) and Cu\(^{8}\). In the ocean, the distribution and behavior of these micronutrients have been investigated for such trace elements\(^{8,9}\). On the other hand, distribution of Pb as a toxic element was also investigated for surface water in open ocean\(^{10}\). It is well known that these trace elements are included not only in crustal aerosols but also anthropogenic aerosols, mainly derived from coal, petroleum, and domestic waste combustion and industrial activities\(^{11,12}\). Long range transport of aerosols is important as a transport process of trace elements from the Asian continent, where the dominant emission source of crustal and anthropogenic aerosols, to the ocean\(^{11-15}\).

Because solubility of the trace elements in the ocean, which is depending on chemical state, is affected to bioavailability for marine microbe, solubility of trace elements in aerosols is important\(^{16,17}\). Evaluation of solubility of trace elements was conducted by determination of chemical state of trace elements using XAFS\(^{17,21}\). Extraction experiments of trace elements were also used for evaluation of the solubility\(^{11,22}\). In the latter case, decomposition of aerosols on the sampling filter is required in order to determine the fraction of the water-soluble contents to the whole content. Ministry of the Environment and National Institute for Environmental Studies proposed a sampling method using PTFE filter for inorganic components due to low abundance of impurities\(^{23}\). However, decomposition of PTFE filter requires hydrofluoric acid and pressure vessel for microwave assisted decomposition instrument. Therefore, procedure of the pre-treatment for PTFE filter is complicated. The aim of this study is simplification of the pre-treatment method for analysis of inorganic component in aerosols. We conducted sampling using a mixed cellulose ester (MCE) membrane filter, because MCE filter can be decomposed without hydrofluoric acid, pressure vessel and microwave digestion. To evaluate the new method, trace elements were determined for certified reference materials of China loess (CJ-1),
which is the origin of Kosa, and environmental aerosol samples collected from Tokushima City and neighboring rural mountain, where is in the channel from Kansai Area to the Kuroshio Current in the Northwestern Pacific Ocean. To discuss solubility of trace elements, both acid-soluble and water-soluble fractions were measured. Environmental aerosol samples were collected from local city with a low altitude (15 m) and rural mountain area with a high altitude (700 and 850 m) to understand the distribution of each trace element. At lower altitude point, aerosol samples were collected at every month to understand the seasonal variation.

**Experimental**

*Location and Sampling*

Figure 1 shows sampling sites. St.1 located at the top of building of Tokushima University in Tokushima City, Tokushima Prefecture (34°4′39″ N, 134°33′38″ E: altitude 15 m) as a local city area, where some anthropogenic emission sources exist. St.2 and St.3 were Ogawara Kohgen (33°57′32″ N, 134°25′18″ E: 700 m) and Gakujin no Mori (33°55′32″ N, 134°16′16″ E: 850 m) in the eastern part of Shikoku Island, Japan, in where no anthropogenic emission source exist nearby. St.2 and St.3 were selected as high-altitude rural site in atmospheric boundary layer, which were 17 km and 35 km far from St.1, respectively. Tokushima City is about 100 km distance from Osaka, where many anthropogenic emission sources exist, and about 100 km distance from Tokushima City to the north end of Kuroshio Current through Kii Channel. Only the aerosols smaller than 10 μm such as PM$_{10}$ and PM$_{2.5}$ could be transported over 30 km during convectional air circulation in the boundary layer. Aerosol sample was collected by a low volume air sampler (SHIBATA C30) with a 0.45μm of MCE membrane filter (ADVANTEC, diameter 47 mm), placed at a height of 1 m above ground level. This sampler has an availability of 100% cut off above 10 μm and 7.07 μm particles at 30 L min$^{-1}$ and 9.6 L min$^{-1}$, respectively.
In this study, air flow of 20 L min\(^{-1}\) was used, corresponding to 8.24 \(\mu m\) of cut off diameter. Aerosol sample was collected from Jul. 2012 to Dec. 2013. The sampling period, air volume and average wind speed were shown in Table 1. Here, the period of Nov.-Feb., Mar.-May and Jun-Oct. were defined as winter, spring and summer seasons, respectively. Concentration of PM\(_{2.5}\) in China was maximum during the sampling period\(^{24}\) due to the largest amount of coal consumption in the past. It is likely that large amount of anthropogenic aerosols from Asian continent was found in our samples.

\textit{HNO}_3\text{-H}_2\text{O}_2\text{ digestion}

Acid-soluble fraction in aerosol sample was digested by a HNO\(_3\)-H\(_2\)O\(_2\) solution without HF, where a reagent grade of those reagents were used. A 1/8 cut portion of filter after sample collection was digested in a 20 mL of PFA vessel (ASONE). An aliquot of sample was digested using a mixture of 3 mL of 69\% HNO\(_3\) and 3 mL of 30\% H\(_2\)O\(_2\) heating up to 160\(^\circ\)C on a hot plate with the PTFE evaporation chamber (SAN-AI Kagaku A-1) equipped with a clean air pomp (SAN-AI Kagaku Clean Air Z) after 10 hours immersion. No residual particles were observed in the digested solutions. After drying on the hot plate, the dried sample was dissolved by 6 mL of 2\% HNO\(_3\). After this procedure, trace elements were determined by ICP-MS. The filter blanks were obtained according to the identical procedure for a whole filter before use at each sampling period. In order to examine the accuracy, concentrations of Al, Si and Fe as major components more than 2wt.\% and those of Co and Ni as minor components less than 100 mg kg\(^{-1}\) in the certified reference material of China loess (CJ-1) were determined by the GFAAS technique after different procedures of the HNO\(_3\)-H\(_2\)O\(_2\) digestion with and without HF. After the HNO\(_3\)-H\(_2\)O\(_2\) digestion, coarse alminosilicate particles may exist in the sample solution because CJ-1 contains refractory alminosilicate minerals. These particle could not be detected by ICP-MS due to the sample introduction mechanism. Therefore, the sample solution of CJ-1 was
measured by GFAAS.

**Water extraction**

A 1/8 cut portion of filter and the volume of water diluted sample solution in a 50 mL polypropylene centrifuge tube (TPP®) were calibrated by weight. The water-soluble component was obtained from a supernatant solution after centrifuge with 1000 rpm for 20 min of 15 hours extracted sample by 20 mL of Milli-Q water (Millipore Milli-Q academic). The supernatant solution was prepared to 2% HNO₃ matrix after removing the filter. After that, trace elements were determined by ICP-MS. The filter blanks were obtained according to the identical procedure for a whole filter before use. Concentrations of trace elements in the supernatant solution were reached to a constant value independently on time between 6 and 32 hours. The water-extraction time of 15 hours was selected. Fraction extracted from aerosol by water was defined as “water-soluble” fraction ([M]ₜₚₑₚₕ).

**ICP-MS analysis**

Determination of trace elements was subsequently performed using Thermo Fisher Scientific X-2 series ICP-MS equipped with He/H₂-collision cell unit, which is placed in the room providing atmosphere cleaned by HEPA filter. For the operating parameters of the ICP-MS measurement, RF power of 1.4 kW, Ar cool gas of 13.0 L min⁻¹, auxiliary gas of 0.80 L min⁻¹ and nebulizer gas of 0.85 L min⁻¹ were employed. Number of repetitions was four. The standard operation mode was employed for $^{137}$Ba, $^{209}$Bi, $^{111}$Cd, $^{59}$Co, $^{133}$Cs, $^{65}$Cu, $^{69}$Ga, $^{55}$Mn, $^{208}$Pb, $^{85}$Rb, $^{88}$Sr, $^{232}$Th, $^{238}$U and $^{51}$V. The collision cell mode was employed for $^{75}$As and $^{57}$Fe in order to reduce the molecular ion forming interference. The He/H₂ mix gas flow rate was 3.5 mL min⁻¹, which gave cerium oxide to cerium ratios ($^{140}$Ce$/^{160}$O:$^{140}$Ce) of < 0.1%. A 10 μg L⁻¹ of Ge and Rh solution was used as internal standard. Calibration standards were prepared by serial
dilution of a multi-elemental standard (XSTC-13, SPEX) with 2% (v/v) HNO₃ matrix. Water was prepared by a system of Milli-Q academic after Elix-5 (Millipore). Detection limits were defined here as the equivalent concentration of three times the standard deviation on the five measurements of blank solution. Although the detection limits varied from day to day, concentration of the above elements in most of the digested sample solution surpassed the detection limits of ICP-MS and could be determined without further pre-concentration. The mean value of detection limits of the ICP-MS were shown in Table 2.

Results and Discussion

Backwards trajectory analysis

Backwards trajectory analysis of air mass were conducted by NOAA HYSPLIT(archive trajectories) system for 48 hours of trajectory run time at every 12 hours. The height of starting point was 500 m for St.1 and 1000 m for St.2 and St.3. Figure 2 shows typical examples of backwards trajectory analysis. Atmospheric aerosols transported from the Asia continent such as anthropogenic emissions and natural mineral dust could affect in winter (Nov.-Feb.) and spring (Mar.-May) and relative contribution of aerosols derived from Japan including ship emissions from the neighborhood become larger in summer (Jun.-Oct.).

Acid soluble fractions in reference materials

Table 3 shows analytical results of trace elements such as Fe, Co and Ni. The observed values were in agreement with the certified values within the experimental errors. However, unsatisfactory analytical results of Al and Si were obtained, suggesting that alminosilicate in CJ-1 could not be completely decomposed. This acid digestion technique could provide all contents of trace elements in aerosols, except for Al and Si. Concentrations of trace elements in aerosols were defined as “all component” ([M]ₐ₁) in aerosols.
Concentrations and enrichment factor of trace elements in aerosols

The average concentrations of trace elements in acid-soluble and water-soluble fractions were shown in Table 4 after conversion to the concentration in the atmospheric volume (ng m$^{-3}$ or pg m$^{-3}$). The insoluble component ($[\text{M}]_{\text{insoluble}}$) were estimated by the difference of $[\text{M}]_{\text{all}}-[\text{M}]_{\text{ws}}$.

Atmospheric aerosols consist of a mixture of particles derived from various sources such as crustal and anthropogenic (coal and petroleum combustion, industrial waste, domestic waste and urban dust) sources. The enrichment factor (EF) of specific element M is an indicator for the contribution of anthropogenic constituents. In this study, EF value was calculated as follows:

$$\text{EF} = \frac{([\text{M}]_{\text{all}}/ [\text{Fe}]_{\text{all}})_{\text{aerosol}}}{([\text{M}]/[\text{Fe}])_{\text{crust}}}$$

where M was an element evaluated in this study, and $([\text{M}]/[\text{Fe}])_{\text{crust}}$ was a reference value of surface crust proposed by Rudnick et al. An EF value higher than 100 indicates significantly the presence of particles derived from anthropogenic sources, whereas an EF value lower than 10 indicates less contribution from anthropogenic sources. In the case of pollutant elements, such as, Bi, Cd, Cu and Pb, the EF value of Bi (EF: 375 to 827), Cd (686 to 1398) and Pb (164 to 287) were higher than 100, and that of As (54 to 93) and Cu (41 to 129) were more than 10. The EF values of Ba, Co, Cs, Ga, Mn, Rb, Sr, Th, U and V were less than 10.

Concentration ratios of trace elements

Figure 3a shows concentration ratios of trace elements in acid-soluble fraction ($[\text{M}]_{\text{all}}$) between seasons at Tokushima City. The average value of the ratio of $[\text{M}]_{\text{all}}$ for winter/summer was 1.3±0.3, except for Fe, Th and U, whereas that for spring/summer was 2.0±0.5. The ratio for Th and U were higher than those for other elements, suggesting that increase rate of Th and U concentrations in acid-soluble fraction in winter and spring was larger than other elements.
compare to summer. In the case of Fe, the increase rate for winter/summer was similar to those of other elements, whereas the increase rate for spring/summer was larger than those of other elements. Figure 3b shows concentration ratio in water-soluble fraction ([M]ws) between seasons at Tokushima City. The average value of the ratio of [M]ws for winter/summer was 1.1±0.4, except for Th and U, whereas that for spring/summer was 2.3±0.5. The ratio for Th and U were higher than those for other elements. Increase rate of Th and U concentrations in water-soluble fraction in winter and spring was larger than other elements compare to summer, as similar as the acid-soluble fraction. Figure 3c shows concentration ratios of trace elements between mountain area and Tokushima City at winter. In the case of the acid-soluble fraction, the ratios of Co, Cs, Cu, Fe, Rb, Sr, Th and U were larger than 1. These elements had a small EF value less than 10, except for Cu, suggesting that trace elements derived from natural mineral aerosols were enriched in mountain area relative to Tokushima City. In the case of water-soluble fraction, the ratios of all trace elements were smaller than 1, suggesting that trace elements in water-soluble fraction in Tokushima City were enriched relative to mountain area. The total amount of trace elements, which can be micronutrients such as Co, Cu and Fe, was abundant in mountain area, but the water-soluble fraction for such elements was enriched in Tokushima City. In general, trace elements in anthropogenic aerosols through the burning process show a high water-solubility due to the much generation of fine particles. It is likely that aerosols in Tokushima City were affected from the Osaka-Kobe urban and the Setouchi industrial areas having a short distance from Tokushima City, implying that trace elements in aerosols at Tokushima City had higher bioavailability than those at mountain area. Our results were consistent with report by Kurisu et al.\textsuperscript{17} that water-solubility of Fe became higher in the aerosol fraction with large contribution from anthropogenic sources.

The mean value of water-soluble fraction ([M]ws) against acid-soluble fraction ([M]all) was listed in Table 4. For anthropogenic elements such as [As]ws, [Bi]ws, [Cd]ws, [Cu]ws, [Pb]ws,
the [M]ws/[M]all value at Tokushima City was remarkably larger than that at mountain area. For crustal elements with a low EF value less than 10, the seasonal variations were also not clear. The [Fe]ws/[Fe]all values in Tokushima City were 0.06 in winter, 0.08 in spring and 0.15 in summer, respectively. Kurisu et. al.\textsuperscript{17} also reported that the simulated rain-soluble Fe fraction of aerosols collected in Hiroshima, Japan was increased from 0.07 to 0.14 and 0.06 to 0.27 with the decrease in particle size from 5 μm (coarse) to 0.45 μm (fine) in March and August, respectively. Backward trajectory analysis suggested that spring samples was influenced by aerosols from East Asia, whereas summer sample had a weak contribution from East Asia. Nishikawa et al.\textsuperscript{22} also reported the [M]ws/[M]all values of aerosols with a particulate size larger than 2 μm at Nagoya. According to the study, the [M]ws/[M]all values of Fe (0.02), Pb (0.27) and V (0.52) at Nagoya were close to those at mountain area rather than Tokushima City. The [M]ws/[M]all value of Cd (0.99) at Nagoya was close to that at Tokushima City, whereas Cu (0.36), Mn (0.52) and Sr (0.63) showed intermediate values between Tokushima City and mountain area.

**Correlation between trace elements in water-soluble fraction**

Figure 4 shows typical correlation between [Fe]ws and [M]ws at Tokushima City in summer. A liner correlation was found for [Bi]ws, [Co]ws, [Mn]ws, [Pb]ws and [Rb]ws, suggesting that these trace elements in water-soluble fraction were derived from identical source. Since contribution from Asian continents was small in summer, the emission source was likely located around Tokushima City. In contrast, [Fe]all and [M]all for such elements at Tokushima City in summer did not show a liner correlation, except for [Rb]all, suggesting that [Fe]insoluble, [Bi]insoluble, [Co]insoluble, [Mn]insoluble and [Pb]insoluble were derived from difference sources. It is likely that [Rb]all was derived from the same sources with [Fe]all.
Origin of trace elements based on Pb/Cd ratio

Based on the differences in Pb/Cd ratio for aerosol samples between Japan and China, the Pb/Cd ratio can be an index to discuss the origin of Pb and Cd. Imai et al.\textsuperscript{13,14} reported that aerosols in Chinese cities show a high Pb/Cd ratio more than 30 due to coal burning, and that aerosols in remote areas of Japan also show a high Pb/Cd ratio more than 30 when air mass came from China, whereas the Pb/Cd ratio in Osaka was 18. In this study, the $[\text{Pb}]_{\text{all}}/[\text{Cd}]_{\text{all}}$ ratios were 36-39 in Tokushima City and 36 in mountain area, suggesting that Pb and Cd in aerosols of both sampling points mainly came from China. In contrast, the $[\text{Pb}]_{\text{ws}}/[\text{Cd}]_{\text{ws}}$ ratios were 19-22 in Tokushima City and 26 in mountain area, suggesting that $[\text{Pb}]_{\text{ws}}$ and $[\text{Cd}]_{\text{ws}}$ partially came from Japan, and that the contribution of $[\text{Pb}]_{\text{ws}}$ and $[\text{Cd}]_{\text{ws}}$ from Japan was larger in Tokushima City relative to mountain area. In the case of summer, although the typical back trajectories did not come from China as shown in Fig 2, the $[\text{Pb}]_{\text{all}}/[\text{Cd}]_{\text{all}}$ ratio in Tokushima City was 39. Around 2013, July 20 and Aug. 10, migratory cyclone and air mass flow from the southeast part of China were observed even in summer.\textsuperscript{27} Therefore, the high Pb/Cd ratio more than 30 in summer was affected by aerosols originated from China.

Conclusions

Our proposed method combing aerosol sampling using MCE membrane filter and filter digestion using HNO$_3$ and H$_2$O$_2$ without HF were available for Fe, Cu and Ni, but not for Al and Si. Concentrations of trace elements in acid-soluble fraction of aerosols, those were all components, were determined. The concentrations in water-soluble fractions were also determined by water extraction. As, Bi, Cd, Cu and Pb with a high EF value more than 10 were derived from anthropogenic sources, whereas Ba, Co, Cs, Ga, Mn, Rb, Sr, Th, U and V with a low EF value less than 10 were derived from natural crustal sources. Differences in both acid-soluble and water-soluble fractions for each season were not found in Tokushima City. Due
to the higher water-solubility of trace elements in aerosols at Tokushima City, trace elements in aerosols at Tokushima City may have higher bioavailability than mountain area. The origin of Pb and Cd in aerosols were mainly dominant from China, but water-soluble Pb and Cd were affected by aerosols from Japan.

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| Site              | Season | Start - End | Time | Volume | Wind |
|------------------|--------|-------------|------|--------|------|
| St. 1 Tokushima City | winter | 2013.Jan.17; 18:00-Jan.21; 20:00 | 5880 | 117.6  | 3.8  |
|                  |        | 2013.Jan.22; 18:00-Jan.25; 18:00 | 4320 | 86.4   | 3.6  |
|                  |        | 2013.Feb.01; 18:00-Feb.04; 19:30 | 4410 | 88.2   | 3.6  |
|                  |        | 2013.Nov.18; 18:00-Nov.23; 00:00 | 6120 | 122    | 3.4  |
|                  |        | 2013.Dec.24; 20:30-Dec.28; 00:10 | 4540 | 90.8   | 3.2  |
|                  | spring | 2013.Mar.26; 18:00-Mar.30; 18:00 | 5760 | 86.4   | 2.7  |
|                  |        | 2013.Apr.29; 18:00-May.03; 20:00 | 5780 | 88.8   | 3.1  |
|                  |        | 2013.May.21; 18:00-May.24; 18:00 | 4320 | 86.4   | 2.4  |
|                  | summer | 2012.Jul.20; 15:00-Jul.24; 16:00 | 5820 | 116.4  | 3.6  |
|                  |        | 2012.Aug.10; 15:00-Aug.17; 18:00 | 10260| 199.2  | 2.9  |
|                  |        | 2012.Sep.21; 14:00-Sep.25; 23:00 | 6300 | 126.0  | 3.8  |
|                  |        | 2013.Jun.18; 20:30-Jun.21; 18:30 | 4200 | 84.0   | 2.0  |
|                  |        | 2013.Jul.26; 18:40-Aug.01; 05:50 | 7870 | 157.4  | 2.0  |
|                  |        | 2013.Aug.23; 18:00-Aug.28; 13:30 | 6930 | 138.6  | 2.4  |
|                  |        | 2013.Sep.30; 18:00-Oct.04; 21:00 | 5940 | 118.8  | 3.0  |
|                  |        | 2013.Oct.22; 17:30-Oct.25; 18:00 | 4350 | 87.0   | 4.4  |
| St. 2 Oogawara Kohgen | winter | 2012.Nov.10; 13:00-Nov.14; 12:00 | 5700 | 114.0  | 4.1  |
| St. 3 Gakujin no Mori | winter | 2012.Nov.24; 11:00-Nov.28; 14:00 | 5940 | 118.8  | 3.6  |
Table 2  Average values and its standard deviation of limit of detection by blank run

|    | solution$^a$ | atmospheric$^a$ | solution | atmospheric |
|----|--------------|-----------------|----------|-------------|
| As | 63±39        | 46±10           | 1.0±0.7  | 0.7±0.2     |
| Ba | 9.1±8.8      | 6.6±1.4         | 4.5±2.7  | 3.3±0.7     |
| Bi | 0.77±0.80    | 0.6±0.1         | 2.5±2.7  | 1.8±0.4     |
| Cd | 1.6±0.9      | 1.2±0.2         | 2.2±1.7  | 1.6±0.3     |
| Co | 1.0±0.5      | 0.7±0.2         | 2.1±2.5  | 1.5±0.3     |
| Cs | 0.34±0.32    | 0.2±0.1         | 0.49±0.41| 0.4±0.1     |
| Cu | 13±12        | 9.2±1.9         | 0.13±0.1 | 0.1±0.0     |
| Fe | 110±30       | 82±17           | 8.3±11   | 6.0±1.3     |

a. Statistic calculation were carried out by using L.O.D. values at every sampling event.
Table 3 Analytical results of certified reference material of China Loess (CJ-1)

| CJ-1       | Cu / μg g⁻¹ | Ni / μg g⁻¹ | Fe / %  |
|------------|-------------|-------------|---------|
|            | Ave.±SD     | Recovery    | Ave.±SD | Recovery | Ave.±SD | Recovery |
| Certified value | 21±3        | 1.00        | 31±3    | 1.00     | 2.94±0.09 | 1.00   |
| HNO₃ + H₂O₂ | 19.0±0.4    | 0.90        | 34.0±1.4| 1.10     | 2.78±0.23 | 1.03   |
| HNO₃ + H₂O₂+HF | 22.4±0.5 | 1.07        | 32.5±1.9| 1.05     | 2.91±0.17 | 0.98   |
Table 4 Average concentrations of trace elements in acid-soluble and water-soluble fractions

|          | Tokushima City (winter) | Tokushima City (spring) | Tokushima City (summer) | Mountain area (winter) |
|----------|-------------------------|-------------------------|-------------------------|------------------------|
|          | [M]_{lall} | [M]_{lw} | [M]_{ls} | [M]_{lall} | [M]_{lw} | [M]_{ls} | [M]_{lall} | [M]_{lw} | [M]_{ls} | [M]_{lall} | [M]_{lw} | [M]_{ls} |
| As ng m^{-3} | 1.67 ± 0.67 | 1.30 ± 0.7 | 0.78 | 2.53 ± 0.98 | 2.46 ± 1.41 | 0.97 | 1.05 ± 1.00 | 1.05 ± 0.97 | 1.0 | 0.87 | 0.39 | 0.45 |
| Ba ng m^{-3} | 3.62 ± 0.41 | 1.20 ± 1.22 | 0.33 | 5.96 ± 2.33 | 4.12 ± 1.82 | 0.69 | 3.77 ± 2.02 | 2.13 ± 1.77 | 0.56 | 1.22 | 0.34 | 0.28 |
| Bi pg m^{-3} | 404 ± 109 | 86 ± 55 | 0.21 | 514 ± 200 | 121 ± 60 | 0.24 | 321 ± 291 | 76 ± 118 | 0.24 | 245 | 4 | 0.02 |
| Cd pg m^{-3} | 431 ± 152 | 501 ± 140 | 0.70 | 529 ± 143 | 477 ± 220 | 0.90 | 305 ± 210 | 233 ± 212 | 0.76 | 276 | 101 | 0.37 |
| Co pg m^{-3} | 59 ± 24 | 24 ± 6 | 0.41 | 72 ± 25 | 47 ± 21 | 0.65 | 46 ± 19 | 20 ± 17 | 0.43 | 71 | 10 | 0.14 |
| Cs pg m^{-3} | 124 ± 42 | 92 ± 54 | 0.74 | 163 ± 93 | 123 ± 68 | 0.75 | 72 ± 59 | 50 ± 47 | 0.69 | 119 | 46 | 0.39 |
| Cu ng m^{-3} | 4.27 ± 2.86 | 2.01 ± 0.53 | 0.47 | 3.73 ± 1.77 | 2.53 ± 0.71 | 0.68 | 3.75 ± 3.38 | 2.82 ± 2.86 | 0.75 | 8.87 | 0.44 | 0.05 |
| Fe ng m^{-3} | 146 ± 18.9 | 8.70 ± 2.9 | 0.06 | 336 ± 188.7 | 26.0 ± 13.6 | 0.08 | 95.0 ± 85.5 | 14.4 ± 14.8 | 0.15 | 119 | 4.60 | 0.04 |
| Ga pg m^{-3} | 382 ± 206 | 255 ± 110 | 0.67 | 305 ± 94 | 289 ± 114 | 0.95 | 236 ± 142 | 158 ± 109 | 0.67 | 160 | 53 | 0.33 |
| Mn ng m^{-3} | 5.65 ± 1.37 | 3.39 ± 1.03 | 0.60 | 7.24 ± 2.43 | 7.68 ± 4.36 | 1.0 | 4.35 ± 1.73 | 3.19 ± 2.03 | 0.73 | 4.20 | 1.67 | 0.40 |
| Pb ng m^{-3} | 15.8 ± 3.98 | 6.40 ± 3.82 | 0.41 | 25.3 ± 8.77 | 9.51 ± 5 | 0.38 | 11.9 ± 13 | 5.33 ± 6.25 | 0.45 | 10.1 | 2.68 | 0.26 |
| Rb pg m^{-3} | 508 ± 107 | 405 ± 174 | 0.80 | 734 ± 391 | 584 ± 308 | 0.80 | 300 ± 179 | 246 ± 204 | 0.82 | 444 | 207 | 0.47 |
| Sr ng m^{-3} | 0.860 ± 0.19 | 0.660 ± 0.16 | 0.77 | 1.40 ± 0.75 | 1.36 ± 0.81 | 0.97 | 0.770 ± 0.48 | 0.660 ± 0.57 | 0.86 | 0.880 | 0.46 | 0.52 |
| Th pg m^{-3} | 26.8 ± 13.7 | 6.8 ± 7.8 | 0.25 | 67.5 ± 47.3 | 10.8 ± 6.8 | 0.16 | 10.3 ± 11.6 | 1.6 ± 4.2 | 0.16 | 28.2 | 1.1 | 0.04 |
| U pg m^{-3} | 12.6 ± 2.6 | 4.3 ± 3.5 | 0.34 | 23.1 ± 15.6 | 5.1 ± 4.0 | 0.22 | 4.8 ± 5.1 | 0.5 ± 0.8 | 0.10 | 12.4 | 1.4 | 0.11 |
| V ng m^{-3} | 1.50 ± 0.23 | 1.06 ± 0.32 | 0.71 | 2.43 ± 0.56 | 3.26 ± 1.48 | 1.0 | 2.13 ± 0.92 | 2.44 ± 2.33 | 1.0 | 0.680 | 0.35 | 0.51 |
Figure Captions

Fig. 1  Locations of sampling sites
St.1 Tokushima City; St.2 Oogawara Kogen; St.3 Gakujin no Mori.

Fig. 2  Typical examples of backward trajectories at 500 m (A, B, C) and 1000 m sea level (D) during sampling
A, St. 1 in winter; B, St. 1 in spring; C, St. 1 in summer; D, St. 3 in winter.

Fig. 3  Concentration ratios of trace elements for each season and sampling point. (a) Black column corresponds to the concentration ratios for acid-soluble fraction between winter and summer in Tokushima City, whereas white column corresponds to that of spring/summer. (b) Black column corresponds to the concentration ratios for water-soluble fraction between spring and summer in Tokushima City, whereas white column corresponds to that of spring/summer. (c) Black column corresponds to the concentration ratios for acid-soluble fraction between mountain area and Tokushima City in winter, whereas white column corresponds to that for water-soluble fraction.

Fig. 4  Correlation between [Fe]_{as} and [M]_{as} for Tokushima City at summer. (a) Bi; (b) Co; (c) Mn; (d) Pb; (e) Rb. Dotted line was a regression curve for the plots.
Fig. 1 Locations of sampling sites
Fig. 2  Typical examples of backward trajectories at 500 m (A, B, C) and 1000 m sea level (D) during sampling
Fig. 3  Relative differences in concentrations of trace elements for each season and sampling point.
Fig. 4  Correlation between [Fe]_{ws} and [M]_{ws} for Tokushima City at summer.
(A figure for GI should be inserted in high resolution JPG or TIF format.)