Notes

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

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A simple digestion method for a mixed cellulose membrane filter in order to analyze trace elements in aerosols was examined. The 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 the contribution from the Asian continent was larger in the winter and spring than the summer. Systematic changes in the 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 the mountain areas. For aerosols in Tokushima City and near to the mountain areas, 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 considered based on the Pb/Cd ratio.

Introduction

Trace elements in atmospheric aerosols play an important role on concerning to transport 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, the distribution of Pb as a toxic element was also investigated for surface water in the open ocean.[10] It is well known that these trace elements are included not only in crustal aerosols, but also in anthropogenic aerosols, mainly derived from coal, petroleum, and domestic waste combustion and industrial activities.[11,12] The 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 exist, to the ocean.[11-15]

Because the solubility of the trace elements in the ocean, which depends on the chemical state, affects to the bioavailability for marine microbe, the solubility of trace elements in aerosols is important.[16,17] Evaluating the solubility of trace elements was conducted by determining the chemical state of trace elements using XAFS.[17-21] Extraction experiments of trace elements were also used to evaluate the solubility.[11,22] In the latter case, the decomposition of aerosols on the sampling filter is required in order to determine the fraction of the water-soluble contents to the whole content. The Ministry of the Environment and the National Institute for Environmental Studies proposed a sampling method using a PTFE filter for inorganic components due to a low abundance of impurities.[23] However, the decomposition of a PTFE filter requires hydrofluoric acid and pressure vessel for microwave assisted decomposition instrument. Therefore, procedure of the pretreatment for PTFE filter is complicated. The aim of this study is to simplify the pretreatment method for the analysis of inorganic component in aerosols. We conducted sampling using a mixed cellulose ester (MCE) membrane filter, because a 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 a neighboring rural mountain, which are located in a channel from Kansai Area to the Kuroshio Current in the Northwestern Pacific Ocean. To discuss the solubility of trace elements, both the acid-soluble and water-soluble fractions were measured. Environmental aerosol samples were collected from a local city at a low altitude (15 m) and a rural mountain area at a high altitude (700 and 850 m) to understand the distribution of each trace element. At a lower altitude point, aerosol samples were collected every month to understand the seasonal variation.

Experimental

Location and sampling
  Figure 1 shows the sampling sites. St. 1 is located at the top

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of a 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, where no anthropogenic emission source exists nearby. St. 2 and St. 3 were selected as high-altitude rural sites in the atmospheric boundary layer, which were 17 and 35 km distance 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 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. An aerosol sample was collected by a low-volume air sampler (SHIBATA C30) with a 0.45-μm MCE membrane filter (ADVANTEC, diameter 47 mm), placed at a height of 1 m above the ground level. This sampler has an availability of 100% cut-off above 10 and 7.07 μm particles at 30 and 9.6 L min⁻¹, respectively. In this study, air flow of 20 L min⁻¹ was used, corresponding to 8.24 μm of the cut-off diameter. Aerosol samples were collected from Jul. 2012 to Dec. 2013. The sampling period, air volume and average wind speed are given in Table 1. Here, the periods of Nov. – Feb., Mar. – May and Jun – Oct. were defined as the winter, spring and summer seasons, respectively. The 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 amounts of anthropogenic aerosols from the Asian continent were found in our samples.
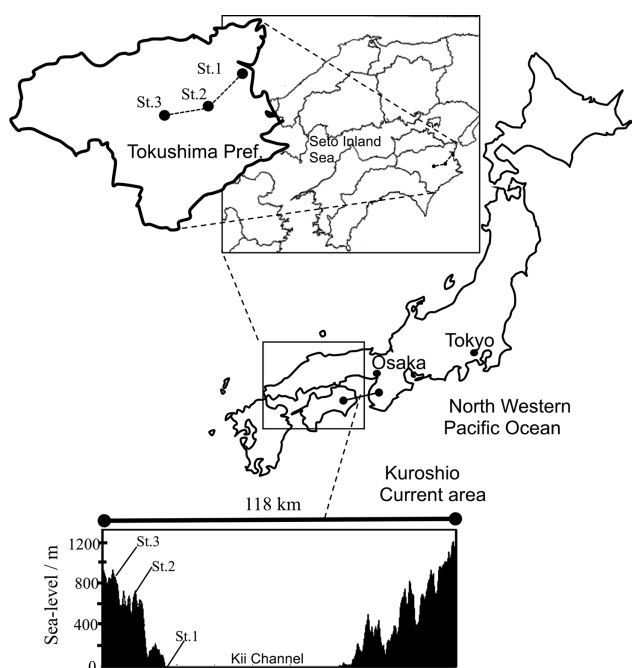
HNO₃–H₂O₂ digestion

An acid-soluble fraction in an aerosol sample was digested by a HNO_3–H_2O_2 solution without HF, where a reagent grade of those reagents were used. A 1/8 cut portion of a filter after sample collection was digested in a 20-mL of a PFA vessel (ASONE). An aliquot of the sample was digested using a mixture of comprising 3 mL of 69% HNO_3 and 3 mL of 30% H_2O_2 heating up to 160°C on a hot plate with a PTFE evaporation chamber (SAN-AI Kagaku A-1) equipped with a clean air pump (SAN-AI Kagaku Clean Air Z) after 10 h of immersion. No residual particles were observed in the digested solutions. After drying on a hot plate, the dried sample was dissolved in 6 mL of 2% HNO_3. After this procedure, trace elements were determined by ICP-MS. The filter blanks were obtained according to an identical procedure for a whole filter before use at each sampling period. In order to examine the accuracy, the concentrations of Al, Si and Fe as major components more than 2 wt.% 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 HNO_3–H_2O_2 digestion with and without HF. After HNO_3–H_2O_2 digestion, coarse alminosilicate particles may exist in the sample solution because CJ-1 contains refractory alminosilicate minerals. These particles could not be detected by ICP-MS due to the sample introduction mechanism. Therefore, the sample solution of CJ-1 was measured by GFAAS.

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

Table 1 Sampling date, air volume and average wind speed

Site	Season	Start – end (yy.mm.day; h:min)	Time/min	Volume/m³	Wind/m s⁻¹
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

Water extraction

A 1/8 cut portion of the 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 being centrifuged at 1000 rpm for 20 min of a 15-h extracted sample by 20 mL of Milli-Q water (Millipore Milli-Q academic). The supernatant solution was prepared to a 2% HNO_3 matrix after removing the filter. After that, trace elements were determined by ICP-MS. The filter blanks were obtained according to an identical procedure for a whole filter before use. The concentrations of trace elements in the supernatant solution reached to a constant value independently at times between 6 and 32 h. The water-extraction time of 15 h was selected. The fraction extracted from aerosol by water was defined as the "water-soluble" fraction ($[M]_{ws}$).

ICP-MS analysis

The determination of trace elements was subsequently performed using a Thermo Fisher Scientific X-2 series ICP-MS equipped with a He/H_2-collision cell unit, which was placed in the room providing atmosphere cleaned by HEPA filter. Concerning the operating parameters of ICP-MS measurements, an RF power of 1.4 kW, Ar cool gas of 13.0 L mim^{-1}, auxiliary gas of 0.80 L min^{-1} and nebulizer gas of 0.85 L min^{-1} were employed. The 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 any molecular ion forming interference. The He/H_2 mix gas flow rate was 3.5 mL min^{-1}, which gave cerium oxide to cerium ratios ($^{140}Ce^{16}O$:^{140}Ce) of <0.1%. A 10 μg L^{-1} of Ge and Rh solution was used as the internal standard. Calibration standards were prepared by the serial dilution of a multi-elemental standard (XSTC-13, SPEX) with 2% (v/v) HNO_3

matrix. Water was prepared by a system of Milli-Q academic after Elix-5 (Millipore). The detection limits were defined as the equivalent concentration of three times the standard deviation on five measurements of a blank solution. Although the detection limits varied from day to day, the concentration of the above elements in most of the digested sample solution surpassed the detection limits of ICP-MS, and could be determined without any further preconcentration. The mean value of the detection limits of the ICP-MS are given in Table 2.

Results and Discussion

Backwards trajectory analysis

A backwards trajectory analysis of the air mass was conducted by the NOAA HYSPLIT[25] (archive trajectories) system for 48 h of the trajectory run time at every 12 h. The height of the

Table 2   Average values and the standard deviation of limit of detection by blank runs

	Solution[a]/ ng dm^{-3}	Atmospheric[a]/ pg m^{-3}		Solution/ ng dm^{-3}	Atmospheric/ pg m^{-3}
As	63 ± 39	46 ± 10	Ga	1.0 ± 0.7	0.7 ± 0.2
Ba	9.1 ± 8.8	6.6 ± 1.4	Mn	4.5 ± 2.7	3.3 ± 0.7
Bi	0.77 ± 0.80	0.6 ± 0.1	Pb	2.5 ± 2.7	1.8 ± 0.4
Cd	1.6 ± 0.9	1.2 ± 0.2	Rb	2.2 ± 1.7	1.6 ± 0.3
Co	1.0 ± 0.5	0.7 ± 0.2	Sr	2.1 ± 2.5	1.5 ± 0.3
Cs	0.34 ± 0.32	0.2 ± 0.1	Th	0.49 ± 0.41	0.4 ± 0.1
Cu	13 ± 12	9.2 ± 1.9	U	0.13 ± 0.1	0.1 ± 0.0
Fe	110 ± 30	82 ± 17	V	8.3 ± 11	6.0 ± 1.3

a. Statistic calculation were carried out by using L.O.D. values at every sampling event.
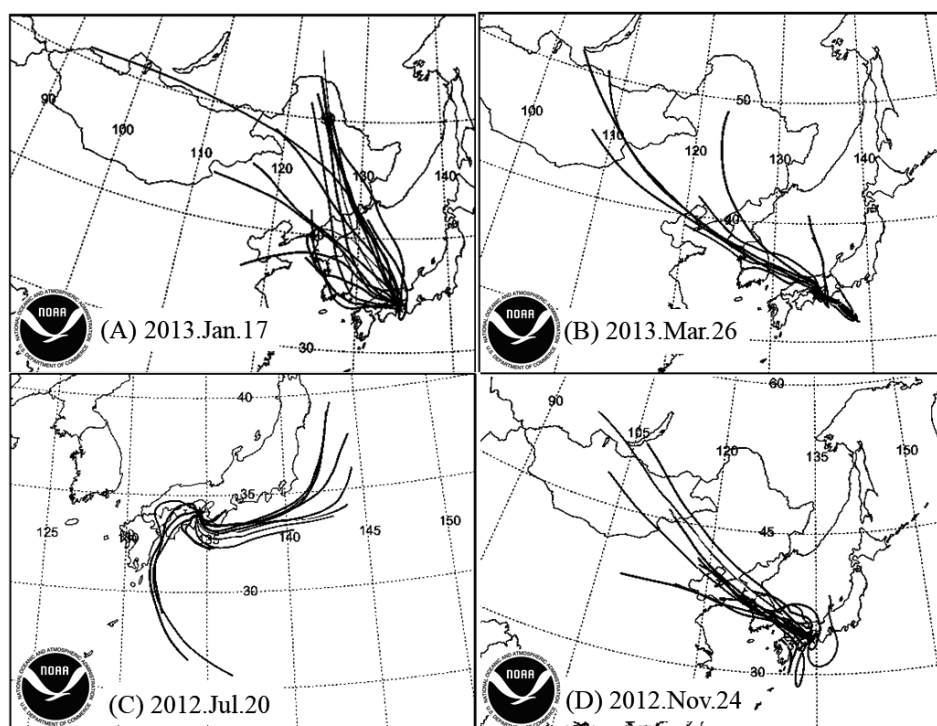

Fig. 2   Typical examples of backward trajectories at 500 m (A, B, C) and 1000 m sea level (D) during sampling. A, St. 1 in winter; B, St. 1 in spring; C, St. 1 in summer; D, St. 3 in winter.

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
HNO$_3$ + H$_2$O$_2$	19.0 ± 0.4	0.90	34.0 ± 1.4	1.10	2.78 ± 0.23	1.03
HNO$_3$ + H$_2$O$_2$ + HF	22.4 ± 0.5	1.07	32.5 ± 1.9	1.05	2.91 ± 0.17	0.98

Table 4   Average concentrations trace elements in acid-soluble and water-solublefractions

		Tokushima City (winter)			Tokushima City (spring)		
		$[M]_{all}$	$[M]_{ws}$	$[M]_{ws}/[M]_{all}$	$[M]_{all}$	$[M]_{ws}$	$[M]_{ws}/[M]_{all}$
As	ng m^{-3}	1.67 ± 0.67	1.30 ± 0.7	0.78	2.53 ± 0.98	2.46 ± 1.41	0.97
Ba	ng m^{-3}	3.62 ± 0.41	1.20 ± 1.22	0.33	5.96 ± 2.53	4.12 ± 1.82	0.69
Bi	pg m^{-3}	404 ± 109	86 ± 55	0.21	514 ± 200	121 ± 60	0.24
Cd	pg m^{-3}	431 ± 152	301 ± 140	0.70	529 ± 143	477 ± 220	0.90
Co	pg m^{-3}	59 ± 24	24 ± 6	0.41	72 ± 25	47 ± 21	0.65
Cs	pg m^{-3}	124 ± 42	92 ± 54	0.74	163 ± 93	123 ± 68	0.75
Cu	ng m^{-3}	4.27 ± 2.86	2.01 ± 0.53	0.47	3.73 ± 1.77	2.53 ± 0.71	0.68
Fe	ng m^{-3}	146 ± 18.9	8.70 ± 2.9	0.06	336 ± 188.7	26.0 ± 13.6	0.08
Ga	pg m^{-3}	382 ± 206	255 ± 110	0.67	305 ± 94	289 ± 114	0.95
Mn	ng m^{-3}	5.65 ± 1.37	3.39 ± 1.03	0.60	7.24 ± 2.43	7.68 ± 4.36	1.0
Pb	ng m^{-3}	15.8 ± 3.98	6.40 ± 3.82	0.41	253 ± 877	9.51 ± 5	0.38
Rb	pg m^{-3}	508 ± 107	405 ± 174	0.80	734 ± 391	584 ± 308	0.80
Sr	ng m^{-3}	0.860 ± 0.19	0.660 ± 0.16	0.77	1.40 ± 0.75	1.36 ± 0.81	0.97
Th	pg m^{-3}	26.8 ± 13.7	6.8 ± 7.8	0.25	67.5 ± 47.3	10.8 ± 6.8	0.16
U	pg m^{-3}	12.6 ± 2.6	4.3 ± 3.5	0.34	23.1 ± 15.6	5.1 ± 4.0	0.22
V	pg m^{-3}	1.50 ± 0.23	1.06 ± 0.32	0.71	2.43 ± 0.56	3.26 ± 1.48	1.0

		Tokushima City (summer)			Mountain area (winter)		
		$[M]_{all}$	$[M]_{ws}$	$[M]_{ws}/[M]_{all}$	$[M]_{all}$	$[M]_{ws}$	$[M]_{ws}/[M]_{all}$
As	ng m^{-3}	1.03 ± 1.00	1.05 ± 0.97	1.0	0.87	0.39	0.45
Ba	ng m^{-3}	3.77 ± 2.02	2.13 ± 1.77	0.56	1.22	0.34	0.28
Bi	pg m^{-3}	321 ± 291	76 ± 118	0.24	245	4	0.02
Cd	pg m^{-3}	305 ± 210	233 ± 212	0.76	276	101	0.37
Co	pg m^{-3}	46 ± 19	20 ± 17	0.43	71.0	10	0.14
Cs	pg m^{-3}	72 ± 59	50 ± 47	0.69	119	46	0.39
Cu	ng m^{-3}	3.75 ± 3.38	2.82 ± 2.86	0.75	8.87	0.440	0.05
Fe	ng m^{-3}	95.0 ± 85.5	14.4 ± 14.8	0.15	119	4.60	0.04
Ga	pg m^{-3}	236 ± 142	158 ± 109	0.67	160	53	0.33
Mn	ng m^{-3}	4.35 ± 1.17	3.19 ± 2.03	0.73	4.20	1.67	0.40
Pb	ng m^{-3}	11.9 ± 13	5.33 ± 6.25	0.45	1.01	2.68	0.26
Rb	pg m^{-3}	300 ± 179	246 ± 204	0.82	444	207	0.47
Sr	ng m^{-3}	0.770 ± 0.48	0.660 ± 0.57	0.86	0.880	0.460	0.52
Th	pg m^{-3}	10.3 ± 11.6	1.6 ± 4.2	0.16	28.2	I.I	0.04
U	pg m^{-3}	4.8 ± 5.1	0.5 ± 0.8	0.10	12.4	1.4	0.11
V	pg m^{-3}	2.13 ± 0.92	2.44 ± 2.33	1.0	0.680	0.35	0.51

starting point was 500 m for St. 1 and 1000 m for St. 2 and St. 3.   Figure 2 shows typical examples of the backwards trajectory analysis.   Atmospheric aerosols transported from the Asia continent, such as anthropogenic emissions and natural mineral dust, could have an effect in the winter (Nov. – Feb.) and the spring (Mar. – May), and relative contribution of aerosols derived from Japan, including ship emissions from the neighboring regions become larger in the summer (Jun. – Oct.).

Acid soluble fractions in reference materials

Table 3 gives the 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 for Al and Si were obtained, suggesting that aminosilicate 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.   The concentrations of trace elements in aerosols were defined as the "all component" ($[M]_{all}$) in the aerosols.

Concentrations and enrichment factor of trace elements in aerosols

The average concentrations of trace elements in the acid-soluble and water-soluble fractions are shown in Table 4 after converting to the concentration in the atmospheric volume (ng m^{-3} or pg m^{-3}).   The insoluble component ($[M]_{insoluble}$) was
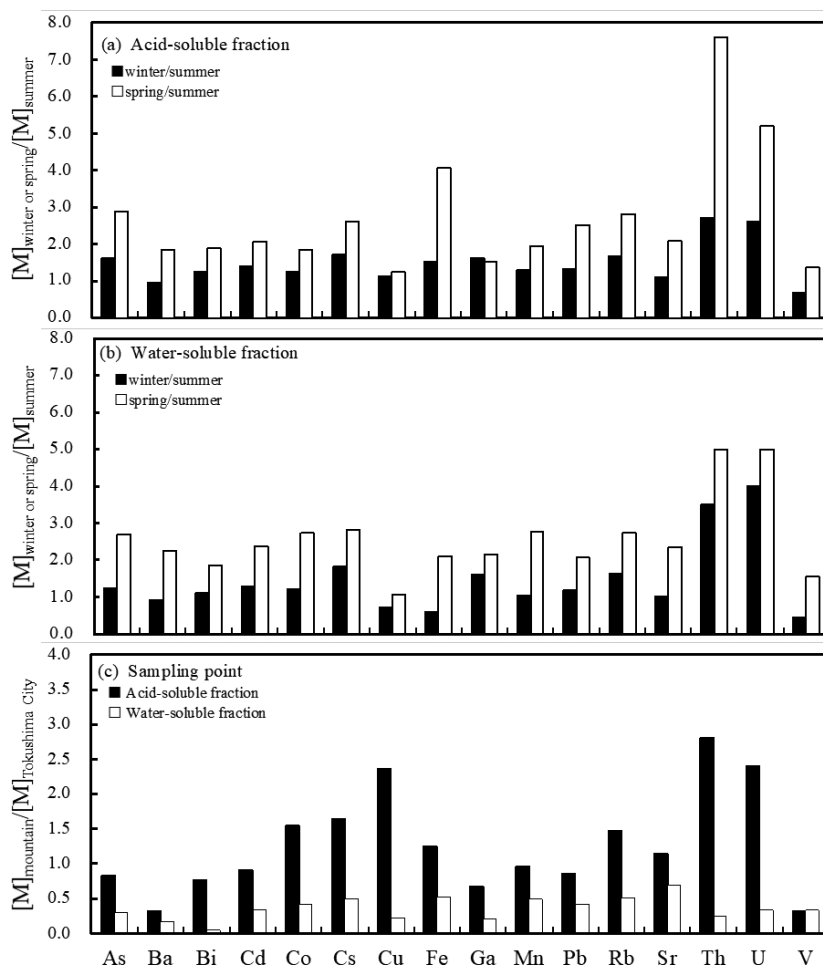
Fig. 3   Concentration ratios of trace elements for each season and sampling point: (a) The black column corresponds to the concentration ratios for the acid-soluble fraction between the winter and summer in Tokushima City, whereas the white column corresponds to that of the spring/summer. (b) The black column corresponds to the concentration ratios for the water-soluble fraction between the spring and summer in Tokushima City, whereas the white column corresponds to that of the spring/ summer. (c) The black column corresponds to the concentration ratios for the acid-soluble fraction between the mountain areas and Tokushima City in the winter, whereas the white column corresponds to that for the water-soluble fraction.

estimated by the difference of $[M]_{all} - [M]_{ws}$.

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 a specific element, M, is an indicator for the contribution of anthropogenic constituents. In this study, the EF value was calculated as

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

where M is an element evaluated in this study, and $([M]/[Fe])_{crust}$ is a reference value of the surface crust proposed by Rudnick et al.[26] 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 values of Bi (EF: 375 to 827), Cd (686 to 1398) and Pb (164 to 287) were higher than 100, and those 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 gives the concentration ratios of trace elements in the acid-soluble fraction ($[M]_{all}$) between seasons at Tokushima City. The average value of the ratio of $[M]_{all}$ for the winter/ summer was 1.3 ± 0.3, except for Fe, Th and U, whereas that for the spring/summer was 2.0 ± 0.5. The ratios for Th and U were higher than those for other elements, suggesting that the increase rate of the Th and U concentrations in acid-soluble fraction in the winter and spring was larger than other elements compare to the summer. In the case of Fe, the increase rate for the winter/summer was similar to those of other elements, whereas the increase rate for the spring/summer was larger than those of other elements. Figure 3b shows the concentration ratio in the water-soluble fraction ($[M]_{ws}$) between seasons at Tokushima City. The average value of the ratio of $[M]_{ws}$ for the winter/summer was 1.1 ± 0.4, except for Th and U, whereas that for the spring/summer was 2.3 ± 0.5. The ratios for Th and U were higher than those for other elements. The increase rate of the Th and U concentrations in the water-soluble fraction in the winter and spring was larger than other elements compare to the summer, similar to the acid-soluble fraction. Figure 3c gives
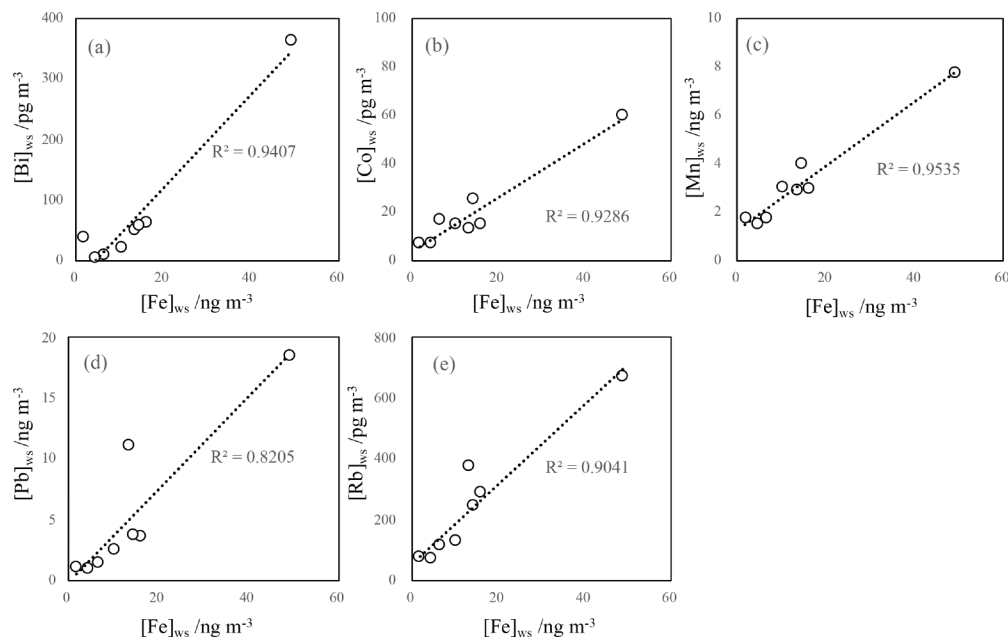
Fig. 4   Correlationship between $[Fe]_{ws}$ and $[M]_{ws}$ for Tokushima City in the summer. (a) Bi; (b) Co; (c) Mn; (d) Pb; (e) Rb. The dotted line is a regression curve for the plots.

the concentration ratios of trace elements between the mountain area and Tokushima City in the 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 of less than 10, except for Cu, suggesting that trace elements derived from natural mineral aerosols were enriched in the mountain area relative to Tokushima City. In the case of the water-soluble fraction, the ratios of all trace elements were smaller than 1, suggesting that trace elements in the water-soluble fraction in Tokushima City were enriched relative to the mountain area. The total amount of trace elements, which can be micronutrients, such as Co, Cu and Fe, was abundant in the mountain area, but the water-soluble fractions for such elements were enriched in Tokushima City. In general, trace elements in anthropogenic aerosols through the burning process show a high water-solubility due to the great 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 the trace elements in aerosols at Tokushima City had a higher bioavailability than those in the mountain areas. Our results were consistent with those report by Kurisu et al.[17] that the water-solubility of Fe became higher in the aerosol fraction with a large contribution from anthropogenic sources.

The mean value of the water-soluble fraction ($[M]_{ws}$) against acid-soluble fraction ($[M]_{all}$) is 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 the mountain areas. For crustal elements with a low EF value of less than 10, the seasonal variations were also unclear. The $[Fe]_{ws}/[Fe]_{all}$ values in Tokushima City were 0.06 in the winter, 0.08 in the spring and 0.15 in the summer, respectively. Kurisu et al.[17] also reported that the simulated rain-soluble Fe fraction of aerosols collected in Hiroshima, Japan increased from 0.07 to 0.14 and 0.06 to 0.27 with a decrease in the particle size from 5 μm (coarse) to 0.45 μm (fine) in March and August, respectively. A backward trajectory analysis suggested that spring samples were influenced by

aerosols from East Asia, whereas summer samples had a weak contribution from East Asia. Nishikawa et al.[22] also reported the $[M]_{ws}/[M]_{all}$ values of aerosols with a particulate size larger than 2 μm in Nagoya. According to the study, the $[M]_{ws}/[M]_{all}$ values of Fe (0.02), Pb (0.27) and V (0.52) in Nagoya were close to those at the mountain areas, 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 the mountain areas.

Correlationship between trace elements in the water-soluble fraction

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

Origin of trace elements based on the Pb/Cd ratio

Based on the differences in the 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.[13,14] reported that aerosols in Chinese cities show a high Pb/Cd ratio of more than 30 due to coal burning, and that aerosols in remote areas of Japan also show a high Pb/Cd ratio of more than 30 when the air mass comes from China, whereas the Pb/Cd ratio in Osaka was 18. In this study, the $[Pb]_{all}/[Cd]_{all}$ ratios were 36 – 39 in Tokushima City and 36 in the mountain areas, suggesting that Pb and Cd in aerosols of both sampling points mainly came from China. In contrast, the $[Pb]_{ws}/[Cd]_{ws}$ ratios were 19 – 22 in

Tokushima City and 26 in the mountain areas, suggesting that $[Pb]_{ws}$ and $[Cd]_{ws}$ partially came from Japan, and that the contribution of $[Pb]_{ws}$ and $[Cd]_{ws}$ from Japan was larger in Tokushima City relative to the mountain areas. In the case of the summer, although the typical back trajectories did not come from China, as shown in Fig. 2, the $[Pb]_{all}/[Cd]_{all}$ ratio in Tokushima City was 39. At around 2013, July 20 and Aug. 10, a migratory cyclone and air mass flow from the southeast part of China were observed even in the summer.[27] Therefore, the high Pb/Cd ratio of more than 30 in the summer was affected by aerosols originated from China.

Conclusions

Our proposed method of combing aerosol sampling using a MCE membrane filter and filter digestion using HNO_3 and H_2O_2 without HF were available for Fe, Cu and Ni, but not for Al and Si. The concentrations of trace elements in the acid-soluble fraction of aerosols, all of components, were determined. The concentrations in the water-soluble fractions were also determined by water extraction. As, Bi, Cd, Cu and Pb with a high EF value of 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 of less than 10 were derived from natural crustal sources. Differences in both the 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 that of the mountain areas. 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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