# Transboundary and local air pollutants in western Japan distinguished on the basis of ratios of metallic elements in size-segregated aerosols

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**ABSTRACT**

Trace metals in aerosols were observed at an urban site (Kumamoto, Kyushu, Japan) and a rural site (Cape Hedo, Okinawa, Japan) to investigate the relative contributions of transboundary air pollutants from mainland Asia and local air pollutants in western Japan. We used a cascade impactor to collect aerosols in five size classes. We apportioned the sources of the air masses on the basis of elemental components. Transboundary and local air pollutants were distinguished by use of the Pb/Cu and V/As ratios in selected size fractions of aerosols. The contribution of Pb (primarily from coal combustion in China) to total anthropogenic elements was greatest in spring, autumn, and winter in the 0.5–1 μm size fraction at both collection sites. The atmospheric environment at both sites was affected by this transboundary air pollutant. The contribution of Cu (primarily from local vehicle traffic) to total anthropogenic elements was greatest in all seasons in the 2.5–10 μm fraction at Kumamoto. Local air pollutants such as road dust, automobile brake abrasion, and waste incineration affected ambient air quality in Kumamoto. Because these pollutants resided mainly in the coarse aerosol fraction (>2.5 μm), most of them were not transported to Cape Hedo in air bodies that we were able to trace to Kumamoto by backward projection. Based on our data the ambient air quality at Cape Hedo was little affected by local air pollutants emitted in the Kumamoto area.

Keywords: Size-segregated aerosol analysis; Chemical composition of metallic elements; Difference in transboundary and local pollution; Elemental ratios.

# INTRODUCTION

Severe air pollution has been caused by rapid economic growth in Asia (Chan and Yao, 2008, Deng *et al*., 2012). Emissions of gaseous pollutants and particulate matter (PM) from both industries and residents have increased in this area (Ohara *et al.*, 2007), while the emission of $SO_2$ and $NO_x$ in China have decreased since 2006 and 2011, respectively (Xia *et al.*, 2016). PM is transported from East Asian countries to Japan and Korea with prevailing westerly winds in the winter and spring (Kaneyasu and Takada, 2004; Kim *et al.*, 2009, Itahashi *et al*., 2010; Hatakeyama *et al*., 2014). Many studies have reported on the occurrence of transboundary air pollution in western Japan (Kaneyasu *et al.*, 2014). Coal combustion is a major source of fine particulate matter (PM) in China (Han *et al.*, 2005). Concentrations of PM smaller than 2.5 μm ($PM_{2.5}$) derived from coal combustion are highest during the winter heating period in China. $PM_{2.5}$ has significant impacts on climate and human health (Shaheen *et al.*, 2005).

Toxic trace elements are often contained in PM (Shah *et al.*, 2006). In $PM_{2.5}$, these can cause lung and cardiopulmonary injuries in humans (Shaheen *et al.*, 2005, IARC, 2012). The concentrations and size distributions of trace elements in PM are mainly governed by the natural and anthropogenic emission sources in the atmosphere (Samara and Voutsa, 2005). Major natural emission sources are sea salt, soils, and forest fires. Major anthropogenic emission sources are fuel combustion, waste incineration, and road traffic. In particular, traffic emissions consist of various sources such as combustion products from fuel and lubricating oil, abrasion products from brake pads and tires, and resuspension of road dust (El-Fadel and Hashisho, 2001).

The objective of this study was to determine the contribution of transboundary air pollution transported from China to western Japan. In order to investigate the contributions of transboundary air pollutants and local air pollutants in western Japan, we conducted observations simultaneously at an urban site and a remote site, more than 1500 km southeast of Beijing. The urban site was at Kumamoto University in Kumamoto City, on Kyushu Island, and the remote site was the Cape Hedo Atmosphere and Aerosol Monitoring Station (CHAAMS) on Okinawa Island. Takami *et al.* (2007) reported that the ambient air quality at Cape Hedo is influenced by air pollutants transported by the northwest winter monsoon and the prevailing westerlies.

Cape Hedo usually receives air masses directly transported from eastern China, which pass over the East China Sea. At times air masses from China that pass over the city of Kumamoto and its vicinity are affected by locally emitted air pollutants on their way to Cape Hedo (Tatsuta, 2017).

This study focused on distinguishing between local pollutants and pollutants transported across national boundaries. This was done by conducted measurements of toxic metallic elements in different aerosol size fractions with four objectives: (1) to evaluate seasonal variation of trace elements at Kumamoto and Cape Hedo; (2) to evaluate the size distribution of anthropogenic

trace elements in aerosols at the two sites; (3) to use of elemental ratios to determine the contribution of transboundary and local air pollutants at both sites; and (4) to compare the elemental compositions of aerosols transported directly to Cape Hedo from China and aerosols transported to Cape Hedo from China by way of Kumamoto.

# METHODS

### *Observations*

Sampling at Kumamoto City was conducted at the top of a nine-story building (32.81°N, 130.73°E) in Kumamoto University. Kumamoto is a city of 740,000 inhabitants on Kyushu Island in western Japan, approximately 1500 km southeast of Beijing (Fig. 1). The city contains no heavy industries; however, the sampling site was adjacent to a central arterial road with heavy traffic. Furthermore, the location is in the eastern part of the city. We collected a total of 38 daily samples during spring (13–17 March 2015 and 1–7 March 2016), summer (27 July to 2 August 2015), fall (14–21 October 2014 and 26–31 October 2015) and winter (17–21 December, 2014).

In Okinawa, sampling was conducted at CHAAMS (26.87°N, 128.25°E; 60 m above sea level), located at the northern end of Okinawa Island, approximately 100 km north of Naha, the largest city on the island, and approximately 1800 km southeast of Beijing (Fig. 1; details of the station are reported in Takami *et al.*, 2007). There are no large industrial or residential areas nearby. Air masses reaching Cape Hedo are transported from China, Korea, Japan, Southeast Asia, or the Pacific Ocean, depending on weather conditions. We collected a total of 33 daily samples during spring (13–17 April 2014 and 12–16 March 2015), fall (17–21 October 2014 and 26 October to 7 November 2015) and winter (13–17 December 2013).

Sampling was carried out by a five-stage cascade impactor (Nanosampler Model 3180, Kanomax, Japan) operated with 40 L $min^{-1}$ air flow at 1 atm air pressure (Otani *et al.*, 2007). Each sample was collected for 24 h from 10:00 am to 10:00 am the next day. Aerosols of particle diameter (Dp) > 10 μm, 10 > Dp > 2.5 μm, 2.5 > Dp > 1 μm, 1 > Dp > 0.5 μm and 0.5 μm > Dp were collected on PTFE filters 55 mm in diameter (PF020, Advantec, Japan). After sampling, filters were cut into two pieces for analyses of trace metal elements and ionic components.

### *Size-Segregated Aerosol Analysis*

The metallic elements in the aerosol samples were quantitatively analyzed after digestion of the samples with a mixture of 1.5 mL hydrofluoric acid, 2.5 mL nitric acid, and 0.5 mL hydrogen peroxide in a Teflon vessel in a microwave oven operated at 200 W for 10 min. After digestion, the hydrofluoric acid was removed by evaporation at 200°C on a hot plate in a hood. Sample solutions were prepared by the addition of nitric acid solution and filtration. The atomic species $^{23}Na$, $^{24}Mg$, $^{27}Al$, $^{39}K$, $^{51}V$, $^{55}Mn$, $^{57}Fe$, $^{63}Cu$, $^{75}As$, $^{82}Se$, $^{88}Sr$, $^{111}Cd$, $^{121}Sb$, $^{137}Ba$, $^{208}Pb$ and $^{209}Bi$

were analyzed by inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7500, Agilent Technologies, USA).

Ionic components were measured by the method described in Tatsuta *et al.* (2017, this volume).

***Backward-trajectory Analysis***

To identify the transport pathways of air masses, backward trajectories for 72 hours starting from a height of 500 m above sea level were calculated using the HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model (Stein et al., 2015) from the U.S. National Oceanic and Atmospheric Administration (http://ready.arl.noaa.gov/hypub-bin/trajtype.pl) based on GDAS (Global Data Assimilation System) global weather data by 1 degree.

## RESULTS AND DISCUSSION

***Source Identification of Metallic Elements Based on Enrichment Factors***

To determine the extent to which aerosols were emitted from natural or anthropogenic sources, enrichment factors (EFs) for elements in each aerosol size fraction were calculated (Tables S1 and S2). The sea salt enrichment factor ($EF_{sea\ salt}$) and the crustal enrichment factor ($EF_{crust}$) are defined by

$$EF(X)_{sea\ salt} = (X/Na)_{aerosol}/(X/Na)_{sea\ salt} \quad (1)$$

and

$$EF(X)_{crust} = (X/Al)_{aerosol}/(X/Al)_{crust}, \quad (2)$$

respectively, where X is the target element. EF < 10 typifies mainly natural sources, and EF > 10 suggests strong enrichment from non-natural sources (Waheed *et al.*, 2011). In this study, we assumed that all Na originated from sea salt and all Al originated from the crust. In these equations, we used the average chemical profile of sea salt from Chester (2009) and of continental crust from Taylor and McLennan (1995).

The average $EF_{sea\ salt}$ values for Mg in all size ranges at both sites were lower than 10, indicating a source in sea salt. The average $EF_{crust}$ values for Fe, Sr, and Ba in all size ranges at both sites were lower than 10, indicating a crustal source. Average $EF_{sea\ salt}$ and $EF_{crust}$ values were much higher than 10 for Cu, As, Cd, Sb, Pb and Bi in all size ranges, indicating emission from anthropogenic sources. Enrichment factors for K, V, Mn, and Se had mostly anthropogenic values (>10) in fine particles (<2.5 μm), but mostly crustal values (<10) in coarse particles (>2.5 μm).

From the resulting EF values, we determined the proportional contributions to total elements from sea salt, crustal, and anthropogenic sources (Fig. 2). Here, total elements mean the sum of mass concentrations of 16 elements in all size fractions sampled in this study in each season. At Kumamoto, sea salt, crustal, and anthropogenic sources accounted for roughly 45%, 45%, and 10% of total elements in aerosols in spring, autumn and winter, respectively; however, these percentages were about 73%, 21%, and 6%, respectively, in summer (Fig. 2a). At Cape Hedo, sea salt, crustal, and anthropogenic sources accounted for about 86%, 12%, and 2%, respectively, in the three seasons we took samples (Fig. 2b).

The influence of sea salt at Cape Hedo was greater than at Kumamoto, because Cape Hedo is surrounded by the sea. At Kumamoto, the contribution of sea salt sources was much greater in summer than in other seasons. Backward-trajectory analyses for the days on which we took samples showed clearly that most air masses in summer were transported to Kumamoto primarily over the ocean (Fig. S1).

These results suggest that the contribution of natural sources to the total elements was dominant at both sites. The annual average contribution of anthropogenic sources was small, although it was greater at Kumamoto (8%) than at Cape Hedo (2%).

***Seasonal Variation of Anthropogenic Trace Elements***

Total concentrations of eight elements (V, Cu, Cd, As, Se, Sb, Pb, and Bi) are shown for each aerosol size class in Fig. 3. Their EF values show that all of these elements, except V and Se, were derived from anthropogenic sources in all size ranges at both sites (Table S1 and S2). Concentrations were higher at Kumamoto than at Cape Hedo in all size ranges and seasons (Fig. 3). At both sites, the highest concentration was observed in the 0.5–1 μm fraction. At Cape Hedo, the highest concentrations in the 0.5–1 μm, 1–2.5 μm, and 2.5–10 μm fraction were observed in winter, indicating greater transboundary air pollutants in winter (Takami *et al.*, 2007).

As for anthropogenic sources, Waheed *et al.* (2011) attributed high metal concentrations in the Dp = 0.2–1 μm fraction of Shanghai aerosols to coal and fuel oil combustion. Other studies have attributed high metal concentrations in the Dp = 2–4 μm fraction at other localities to mechanical abrasion of brake pads and tires (Gietl *et al.*, 2010; Oakes *et al.*, 2016). We show the proportions of the eight anthropogenic elements at our sites in the 0.5–1 μm and 2.5–10 μm fractions for each season in Fig. 4.

In the 0.5–1 μm fraction at both sites, Pb was the greatest contributor to total anthropogenic elements in spring, autumn, and winter. Shimada *et al.* (2015) inferred that the source of Pb, As, Se, and Cd in $PM_{2.5}$ at Cape Hedo may have been coal combustion in China on the basis of a statistical analysis using positive matrix factorization. Tian *et al.* (2010, 2012) reported that trace elements such as Pb, As, Se, and Cd in emissions from China were mainly derived from coal combustion. Among these four elements, Cd made the smallest contribution to total

anthropogenic elements in spring, autumn, and winter at both sites, and As and Se were roughly equal contributors at intermediate concentrations. In spring, autumn, and winter, most air masses were transported to Kumamoto and Cape Hedo from China judging from back trajectories (Fig. S1). The contributions of these four elements were in the order Pb>As>Se>Cd at both sites in these seasons. The contributions of those four elements are in the same order of volume in emissions in China (Tian *et al.*, 2010, 2012). These results indicate that the anthropogenic elements in 0.5–1 μm aerosols at Kumamoto and Cape Hedo were derived from coal combustion in China.

In the 2.5–10 μm fraction at Kumamoto, Cu was the greatest contributor to total anthropogenic elements in all seasons (Fig. 4a); however, this was not the case at Cape Hedo (Fig. 4b). This indicates that Cu in the coarse particles was a local pollutant, mainly derived from abrasion of vehicle brake pads (Sternbeck *et al.*, 2002).

The contribution of V to total anthropogenic elements in the 0.5–1 μm fraction was greatest in summer at Kumamoto, where summer air masses were usually transported from the East China Sea (Fig. S1). According to Eyring *et al.* (2010), the activity at large Chinese ports creates a very high density of shipping traffic in the East China Sea, and Celo *et al.* (2015) reported that V in fine particles is a tracer of fuel oil combustion. Thus, fuel oil combustion in ships appears to have affected the summer air quality in Kumamoto. Likewise, ship emissions have been shown to account for V in aerosols measured at Fukue Island, west of Kumamoto, and at Cape Hedo (Shimada *et al.*, 2016).

***Identification of Transboundary and Local Air Pollutants based on Metallic Element Ratios***

The next task was to characterize air sources on the basis of ratios of metal concentrations in aerosols. We evaluated two ratios: Pb/Cu and V/As.

The Pb/Cu ratio was used as a means of identifying transboundary air pollution, using the Pb concentration in the fine (0.5–1 μm) fraction and Cu in the coarse (2.5–10 μm) fraction. Coal combustion in China is the predominant source of Pb in aerosols. Annual coal consumption in China increased by 2.4 times from 2000 to 2010, at which time it amounted to 50% of worldwide coal combustion (BP Statistical Review of World Energy, 2016). Coal combustion is the main source of toxic elements such as Pb, Cd, As, and Se in aerosols. In particular, the concentration of Pb emitted from coal combustion is larger than that of any other toxic element (Li *et al.*, 2012). On the other hand, Fe, Ba, Cu, and Sb are derived from abrasion of vehicle brake pads and tires (Hulskotte *et al.*, 2014). Among these, Fe and Ba are not suitable tracers of vehicle-brake abrasion, because they are also abundant in soil; therefore Cu was used a tracer of vehicle abrasion at Kumamoto. Cu in coarse particles is emitted from abrasion of vehicle brakes (Sternbeck *et al.*, 2002), whereas Cu in fine particles is derived from combustion (Font et al., 2015). Cu concentrations in the coarse size range were considerably higher at Kumamoto than at

Cape Hedo, because Kumamoto had much more vehicle traffic. Furthermore, because $PM_{10}$ has a much shorter residence time in the atmosphere than $PM_{2.5}$ (Shin *et al.*, 2009), we can expect that little or no Cu in coarse particles emitted in Kumamoto reached Cape Hedo.

The size distribution of Cu concentrations at Kumamoto differed from that at Cape Hedo (Fig. 5b). At Kumamoto, Cu concentrations were highest in the coarse fraction owing to the contribution of vehicle abrasion in Kumamoto. At Cape Hedo, Cu concentrations were lowest in the coarse fraction and highest in the fine fraction. We attributed this difference to the more rapid deposition of coarse particles than fine particles during long-range transport (Allen *et al.*, 2001).

Pb/Cu ratios were higher in all seasons at Cape Hedo (Fig. S2a). The ratio in winter was particularly high at both sites. Similar to the results of Shimada *et al.* (2014), the contribution of coal combustion at Cape Hedo is greater in winter than in other seasons. V/As ratios were also used as a means of distinguishing among transboundary pollutants. Fuel oil combustion releases V in aerosols (Viana *et al.*, 2014), and concentrations of V are often used as a tracer of ship emissions. Coal combustion releases As (Tian *et al.*, 2010), and almost all As observed in western Japan originates from China (Sakata *et al.*, 2014) as coal is little used in Japan. Therefore the V/As ratio should effectively distinguish ship emissions from coal emissions. Because particles derived from fossil fuel combustion dominate the 0.2–1 μm aerosol fraction (Waheed *et al.*, 2011), we used the elemental concentrations of the 0.5–1 μm fraction to determine V/As (Fig. S2b).

The V/As ratio at Kumamoto was particularly high in summer (Fig. S2b), when air masses are transported to Kumamoto from the East China Sea (Fig. S1), indicating large contributions of V from ship emissions. The ratio was low at both sites in spring, autumn, and winter, but was particularly low in winter. This is attributed to the large contribution of As from coal combustion in China, because air masses reaching Kumamoto in winter were largely derived from China (Fig. S1).

***Comparisons of Aerosols in the Same Air Masses at Kumamoto and Cape Hedo***

In two cases, backward-trajectory analysis showed that the same air mass was observed at both Kumamoto and Cape Hedo (Fig. S3). The air mass reaching Cape Hedo on 17 October 2014 passed over Kumamoto on 16 October, and the air mass reaching Cape Hedo on 31 October 2015 passed over Kumamoto the same day. Fig. S4 compares the mass proportions of the 16 metallic elements in coarse particles at our two measurement sites. The correlation between sites was very strong ($r^2 = 0.97$, $p<0.05$), and the regression-line slope was 0.93. That most of the elements plotted on the 1:1 line indicated that they did not increase or decrease during transport from Kumamoto to Cape Hedo. However, percentages of Cu, Sb, and K departed greatly from the 1:1 line, with Cu and Sb being higher at Kumamoto and K being higher at Cape Hedo.

Looking in detail at Sb (Fig. 5a) and Cu (Fig. 5b), we found the highest concentrations in the 0.5–1 μm fraction at Cape Hedo, but at Kumamoto, Cu had its peak concentration in the 2.5–10 μm fraction, and Sb had a bimodal distribution, with peaks in the 0.5–1 μm and 2.5–10 μm fractions. Sb and Cu are found in coarse particles emitted from the abrasion of vehicle brakes (Hulskotte *et al.*, 2014), as brake pads contain 1–5% $Sb_2S_3$ (Varrica *et al.*, 2013), and brake linings contain Cu (Sternbeck *et al.*, 2002). Furthermore, particles produced by mechanical abrasion are mainly in the 2–4 μm size range (Gietl *et al.*, 2010). According to Pio *et al.* (2013), Cu/Sb ratios in material derived from vehicle abrasion range from 7.1 to 12.1, and in our results the annual average Cu/Sb ratio at Kumamoto was in the same range (10.3). The sum of the evidence indicates that Cu and Sb are enriched in coarse aerosols at Kumamoto that settle out from air bodies before reaching Cape Hedo.

Conversely, the content ratio of K at Kumamoto was smaller than at Cape Hedo (Fig. S4), meaning that the K content in fine particles was larger at Kumamoto than at Cape Hedo. Concentrations of K were highest in the coarse (2.5–10 μm) fraction at both sites (Fig. 5c). Our analysis of EF values showed that particles in this size range originated from sea salt or soil dust (Table S1 and S2). Because the concentration of K in coarse particles was higher at Cape Hedo than at Kumamoto, some addition of K must have occurred during transport, presumably from sea salt. On the other hand, K concentrations were also high in the 0.5–1 μm fraction at Kumamoto. Waste incineration (Oakes *et al.*, 2016) and biomass burning (Chen *et al.*, 2013) are known generators of high K concentrations in fine aerosols. We attributed the K content in fine aerosols from Kumamoto to this cause.

Chloride is also emitted from waste incineration and biomass burning (Kaneyasu *et al.*, 1999). The correlation of $Cl^-$ and K concentrations in fine aerosols was poor ($r^2 = 0.0038$) at Cape Hedo, but was appreciable at Kumamoto ($r^2 = 0.82$, $p<0.05$); we therefore attributed both K and $Cl^-$ in fine aerosols at Kumamoto to emissions from waste incineration or biomass burning (Fig. 6a, 6b). We determined the correlation between $Na^+$ and $Cl^-$ concentrations in coarse particles (Fig. 6c, 6d) and fine particles (Fig. 6e, 6f) at Kumamoto and Cape Hedo during the observation period. As expected, $Na^+$ in both size ranges originated from sea salt. As for $Cl^-$, the correlation was good at both sites in the coarse particle size range, consistent with sea salt, but the correlation was poor at both sites in the fine particles (Fig. 6e, 6f). Furthermore, the average concentrations of $Cl^-$ in fine particles were higher at Kumamoto (0.91 neq/$m^3$) than at Cape Hedo (0.14 neq/$m^3$). It appears that local emissions such as waste incineration or biomass burning contributed more to the ambient air quality in Kumamoto than at Cape Hedo.

In sum, our results showed that Cu and Sb in coarse aerosols can be tracers of local emissions from vehicle brakes and tires, and K in fine aerosols can be a tracer of local emissions from waste incineration or biomass burning.

## CONCLUSIONS

At the Kumamoto site, local air pollutants, including elements derived from abrasion of vehicle brakes, affected ambient air quality. However, because these pollutants resided mainly in coarse aerosol particles, most of them were not transported long distances, and air quality at the Cape Hedo site was relatively unaffected by them. This means that in air masses from China that arrive at Cape Hedo after passing over Kumamoto, almost all trace elements in the fine aerosol particles were from China. Our results show that the contribution of most anthropogenic elements in transboundary air pollutants, particularly in fine particles, is greater than that of local air pollutants at Kumamoto. Therefore, transboundary air pollutants are of special concern when assessing the effects of ambient trace elements on human health in western Japan. Trace element concentrations and their ratios, specifically Pb/Cu and V/As, are effective in distinguishing transboundary air pollutants from local air pollutants. In particular, Cu and Sb are useful indicators of local emissions from vehicle brake abrasion, and K is an indicator of local emissions from waste incineration or biomass burning.

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472
473

## Figure Captions

**Fig. 1.** The location of two observation sites: KM and HD.

**Fig. 2.** Average proportions of sea salt, soil, and anthropogenic sources in total metallic elements for each season at Kumamoto (a) and Cape Hedo (b).

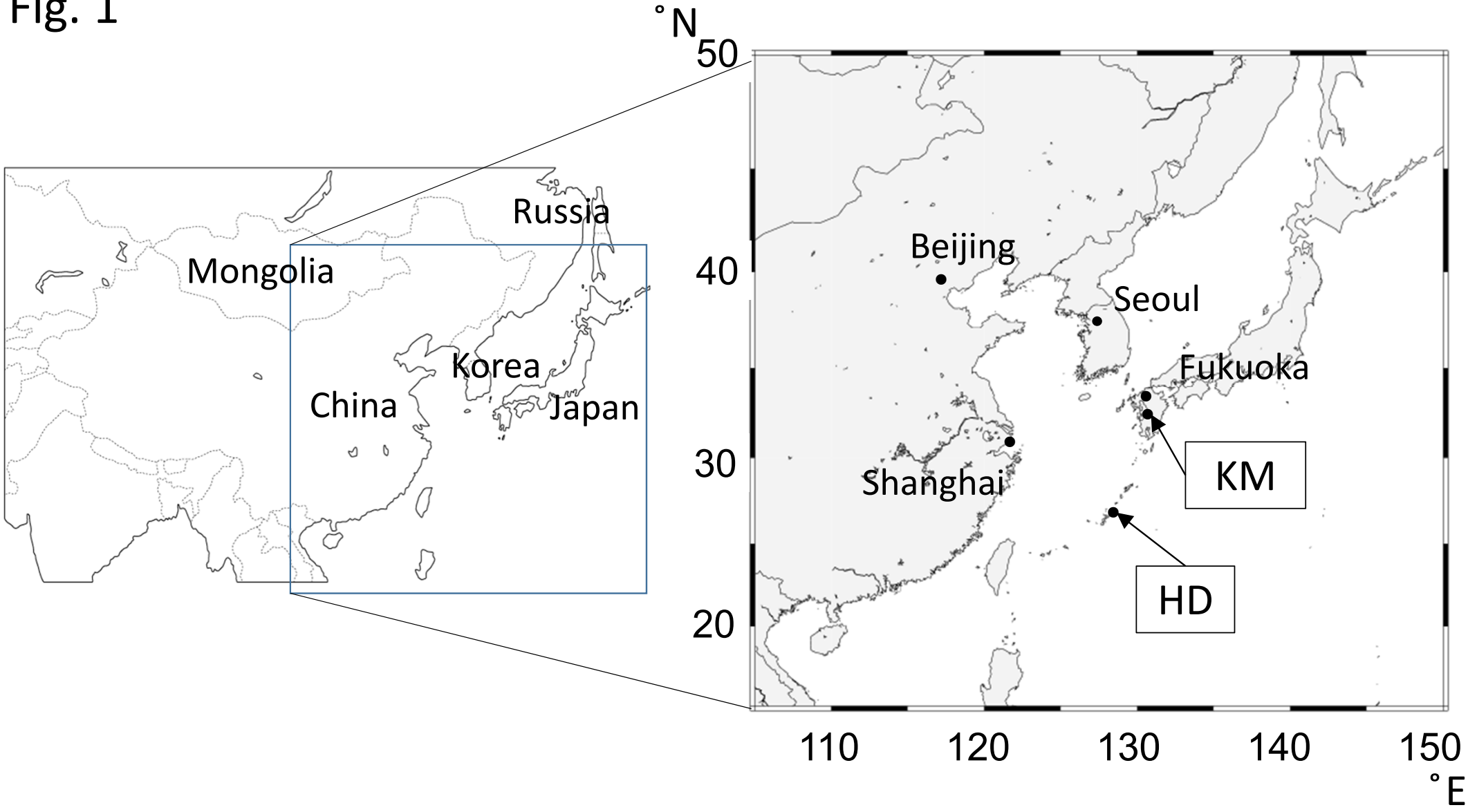
**Fig. 3.** Average concentrations of total anthropogenic metallic elements (V, Cu, As, Se, Cd, Sb, Pb, Bi) by particle size in each season at Kumamoto (a) and Cape Hedo (b).

**Fig. 4.** Average chemical compositions of anthropogenic metallic elements (V, Cu, As, Se, Cd, Sb, Pb, Bi) in the 0.5–1 μm and 2.5–10 μm size fractions in each season at Kumamoto (a) and Cape Hedo (b).

**Fig. 5.** Average concentrations of Sb (a), Cu (b), and K (c) by particle size in the autumn observation period at Kumamoto and Cape Hedo.

**Fig. 6.** Correlation between $Cl^-$ and K in fine particles (<2.5 μm) at Kumamoto (a) and Cape Hedo (b). Correlation between $Na^+$ and $Cl^-$ in coarse particles (>2.5 μm) at Kumamoto (c) and Cape Hedo (d). Correlation between $Na^+$ and $Cl^-$ in fine particles (<2.5 μm) at Kumamoto (e) and Cape Hedo (f).

Fig. 1


°N
50
40
30
20
110
120
130
140
150
°E
Russia
Mongolia
China
Korea
Japan
Beijing
Seoul
Fukuoka
Shanghai
KM
HD

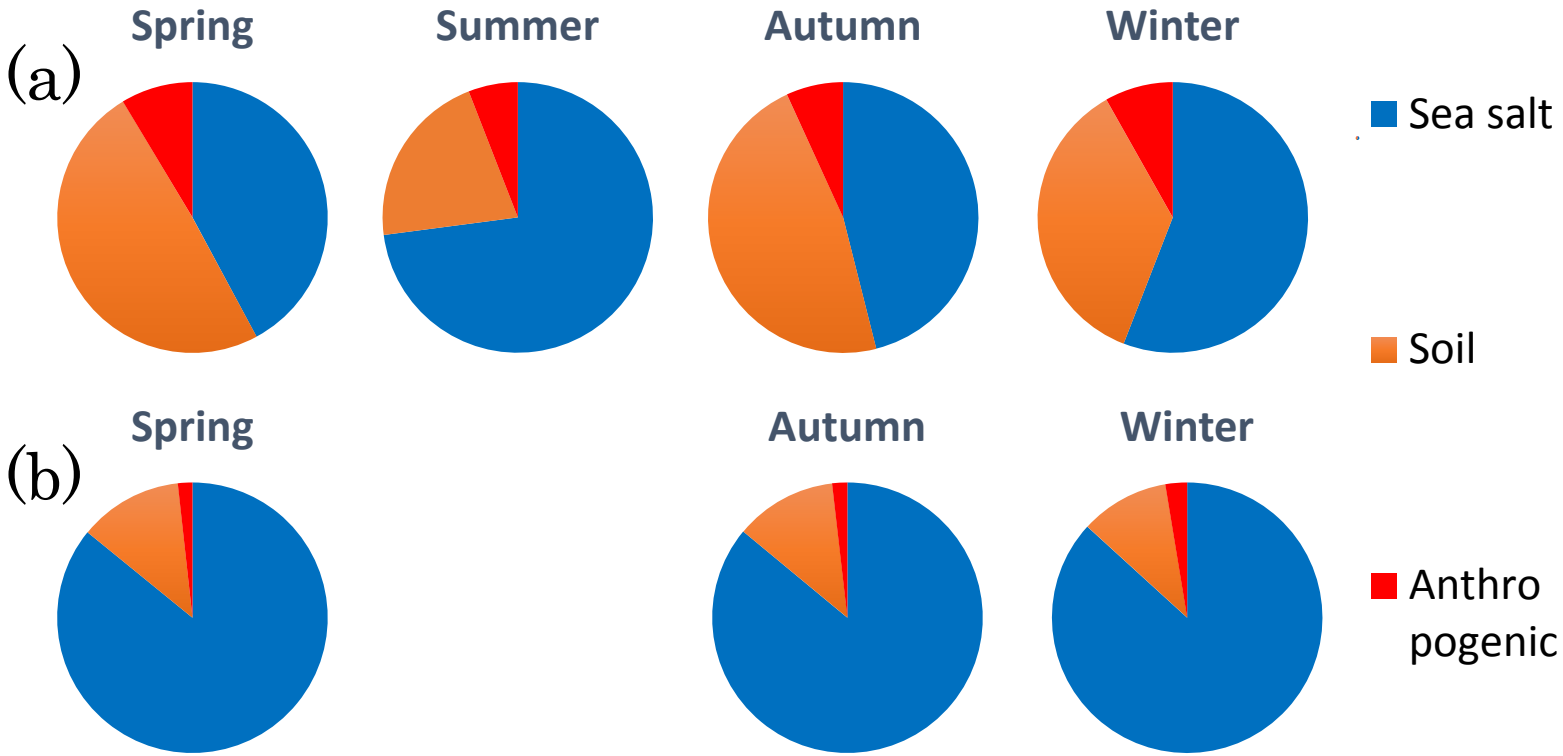
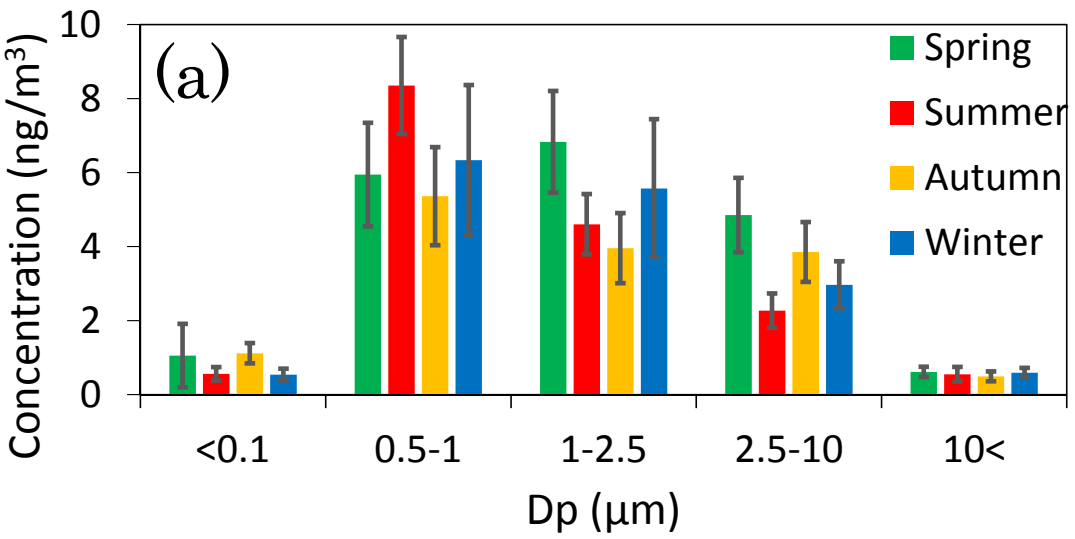

(a)
Spring
Summer
Autumn
Winter
(b)
Spring
Autumn
Winter
Sea salt
Soil
Anthro
pogenic

Fig. 2 (a) (b)


(a)
Concentration (ng/m³)
10
8
6
4
2
0
Spring
Summer
Autumn
Winter
<0.1
0.5-1
1-2.5
2.5-10
10<
Dp (µm)

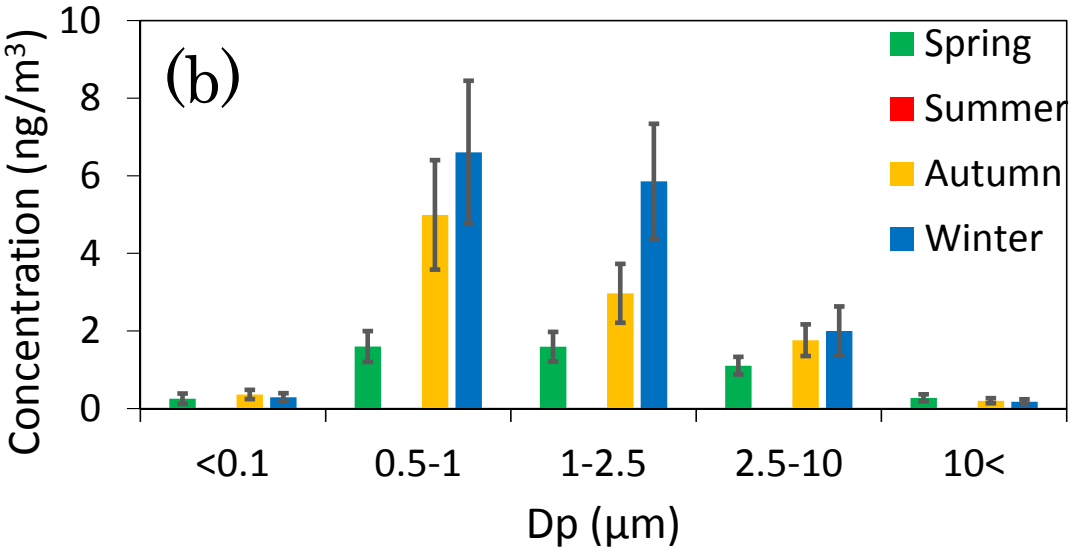

(b)
Concentration (ng/m³)
10
8
6
4
2
0
Spring
Summer
Autumn
Winter
<0.1
0.5-1
1-2.5
2.5-10
10<
Dp (µm)

Fig. 3 (a) (b)

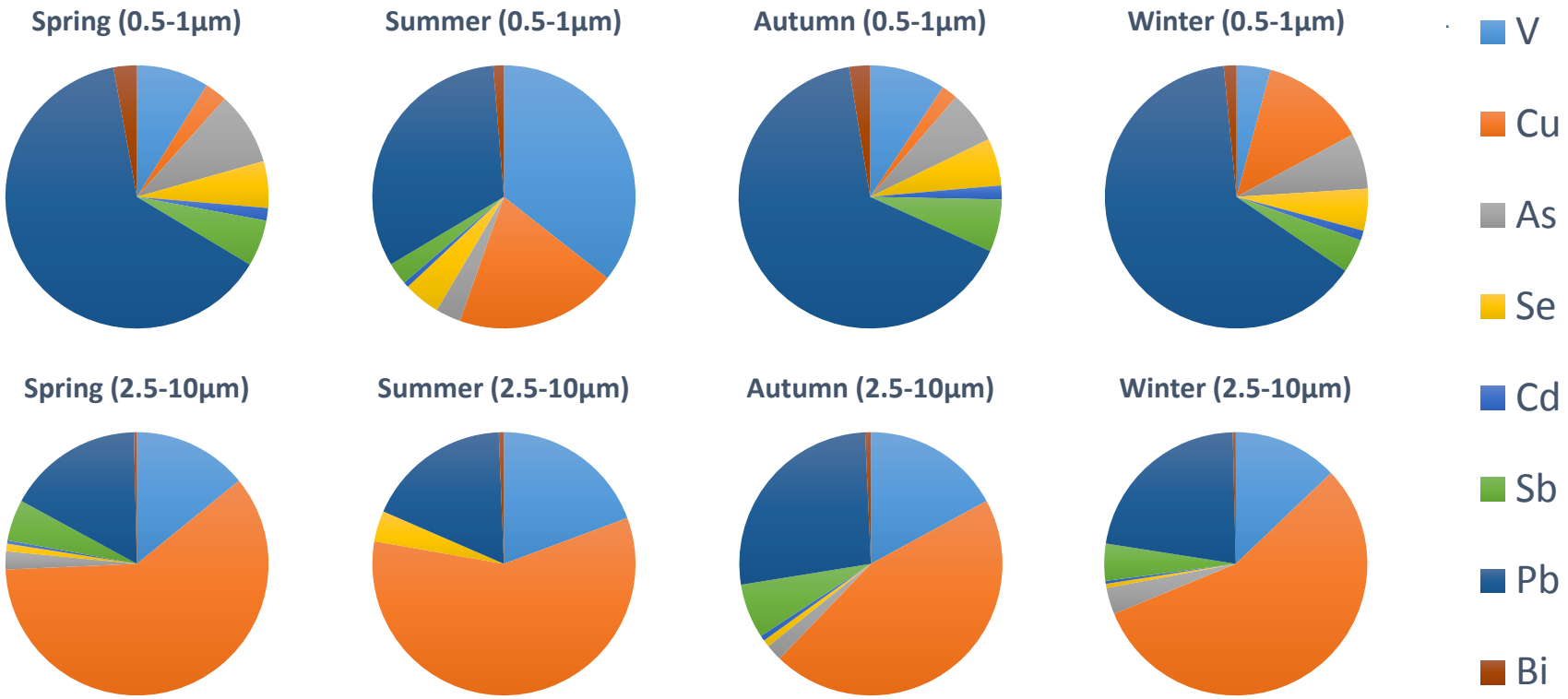

Spring (0.5-1µm)
Summer (0.5-1µm)
Autumn (0.5-1µm)
Winter (0.5-1µm)
Spring (2.5-10µm)
Summer (2.5-10µm)
Autumn (2.5-10µm)
Winter (2.5-10µm)
V
Cu
As
Se
Cd
Sb
Pb
Bi

Fig. 4 (a)

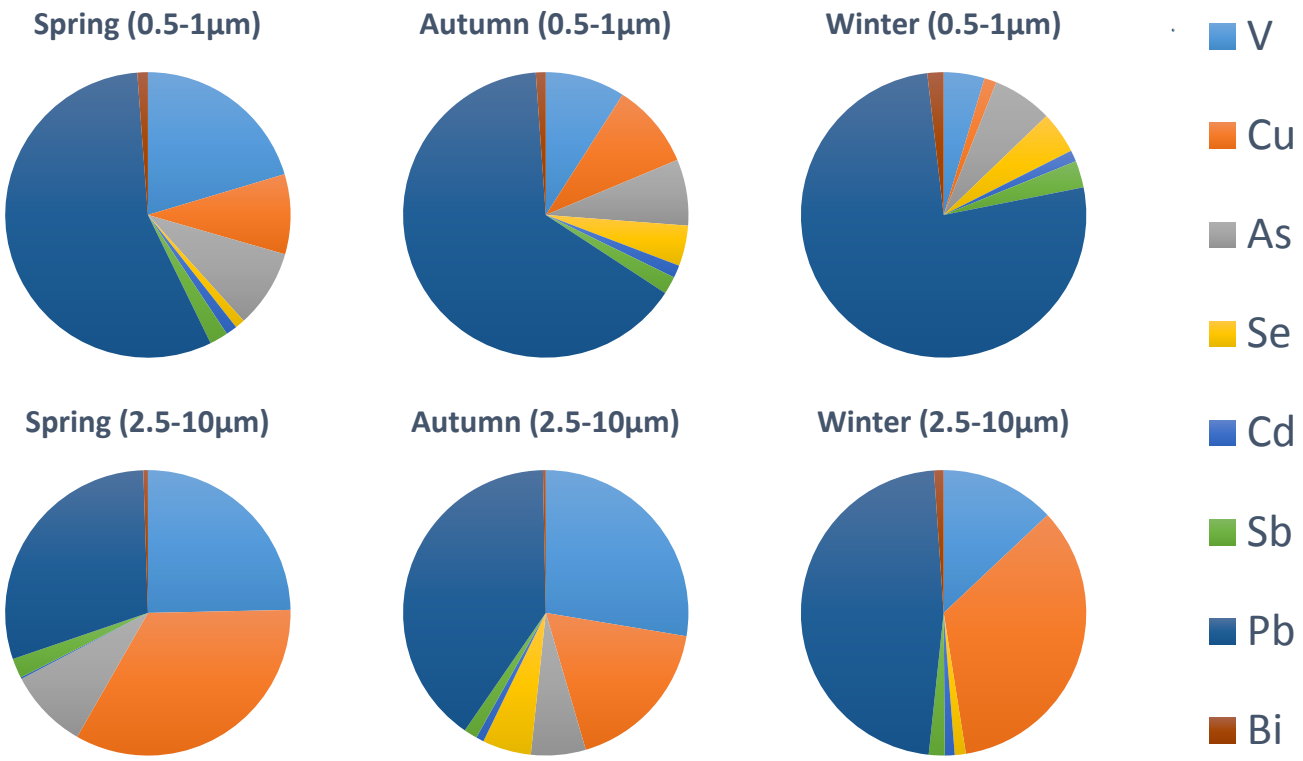

Spring (0.5-1µm)
Autumn (0.5-1µm)
Winter (0.5-1µm)
Spring (2.5-10µm)
Autumn (2.5-10µm)
Winter (2.5-10µm)
V
Cu
As
Se
Cd
Sb
Pb
Bi

Fig. 4 (b)

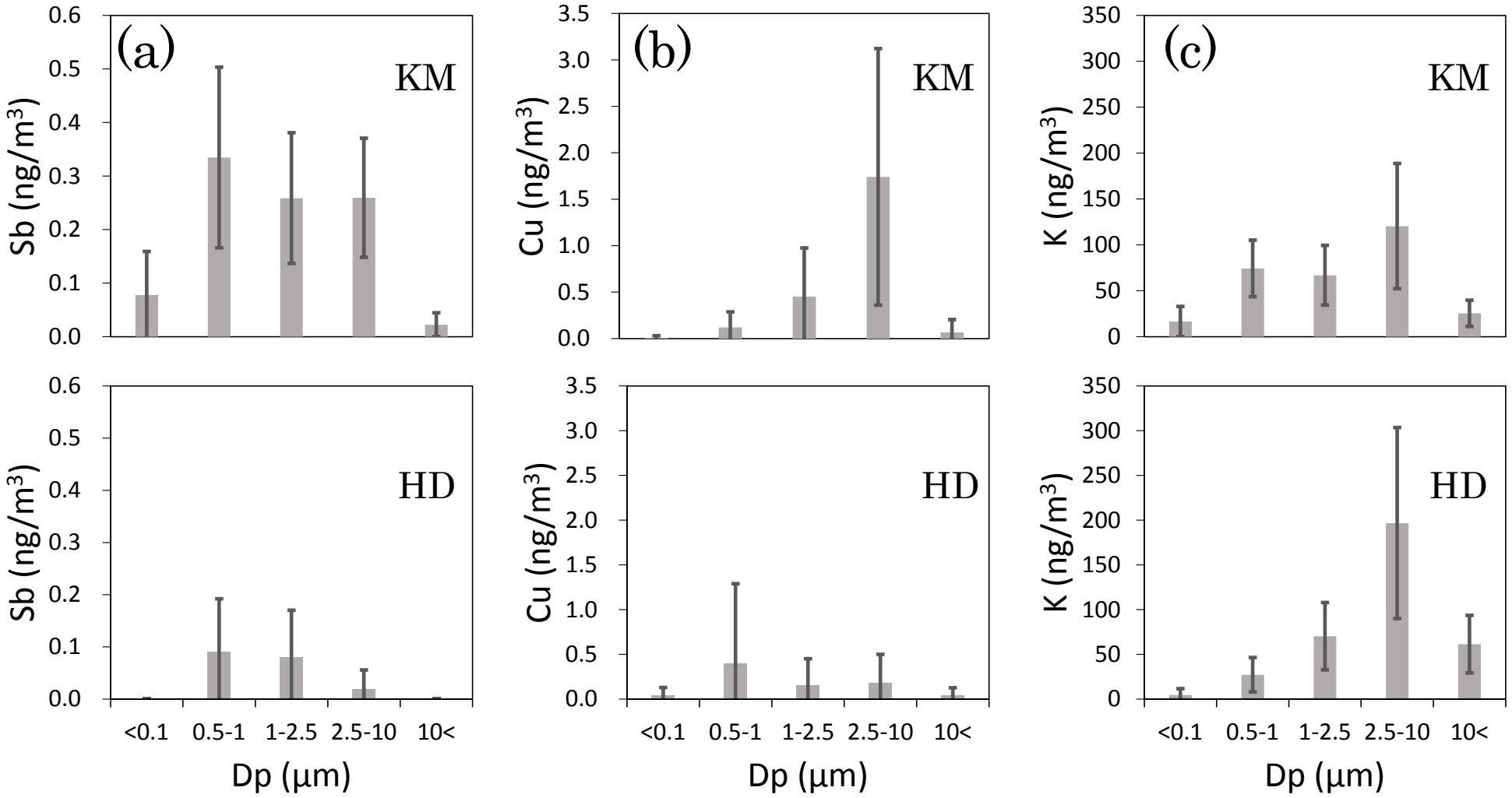
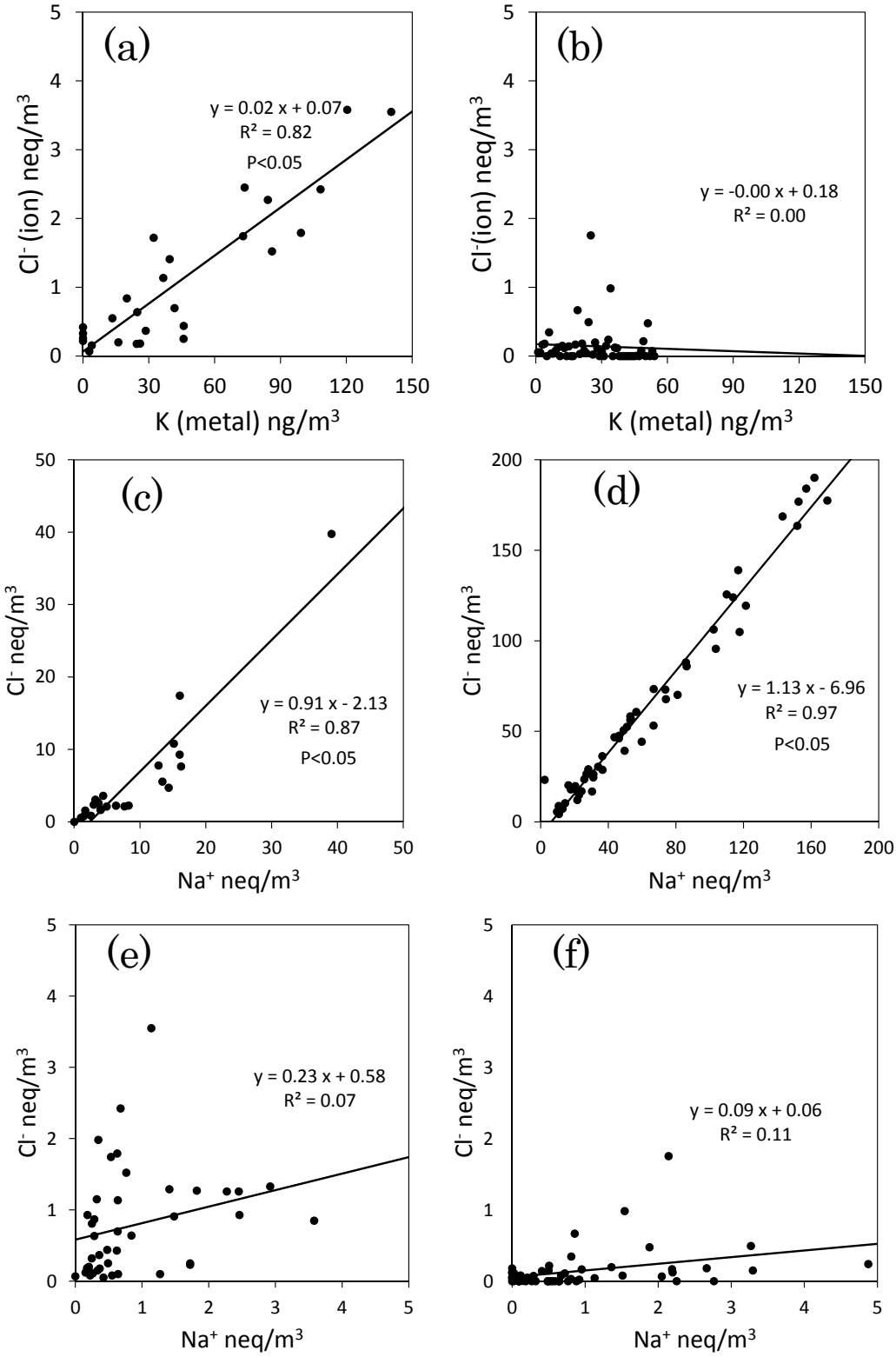

(a)
KM
HD
Sb (ng/m3)
0.6
0.5
0.4
0.3
0.2
0.1
0.0
(b)
Cu (ng/m3)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(c)
K (ng/m3)
350
300
250
200
150
100
50
0
<0.1
0.5-1
1-2.5
2.5-10
10<
Dp (µm)

Fig. 5 (a)(b)(c)


(a)
y = 0.02 x + 0.07
R² = 0.82
P<0.05
Cl⁻ (ion) neq/m³
K (metal) ng/m³
(b)
y = -0.00 x + 0.18
R² = 0.00
Cl⁻(ion) neq/m³
K (metal) ng/m³
(c)
y = 0.91 x - 2.13
R² = 0.87
P<0.05
Cl⁻ neq/m³
Na⁺ neq/m³
(d)
y = 1.13 x - 6.96
R² = 0.97
P<0.05
Cl⁻ neq/m³
Na⁺ neq/m³
(e)
y = 0.23 x + 0.58
R² = 0.07
Cl⁻ neq/m³
Na⁺ neq/m³
(f)
y = 0.09 x + 0.06
R² = 0.11
Cl⁻ neq/m³
Na⁺ neq/m³