Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Electronic Supplementary Information

Determination of oxoanions and water-soluble species of arsenic, selenium, antimony, vanadium, and chromium eluted in water from airborne fine particles ($PM_{2.5}$): effect of acid and transition metal content of particles on heavy metal elution

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1. Back trajectory analysis for each sampling period.

2. Recovery of the water extraction

3. Limits of detection (LODs) in the three analysis modes

1. Back trajectory analysis for each sampling period.

Back trajectory analysis was performed by CGER METEX at http://db.cger.nies.go.jp/metex/index.jp.html
Trajectory from Kumamoto (the University campus), E 130.43, N 32.48, Altitude 50 m
Analyzed for 5 days back.

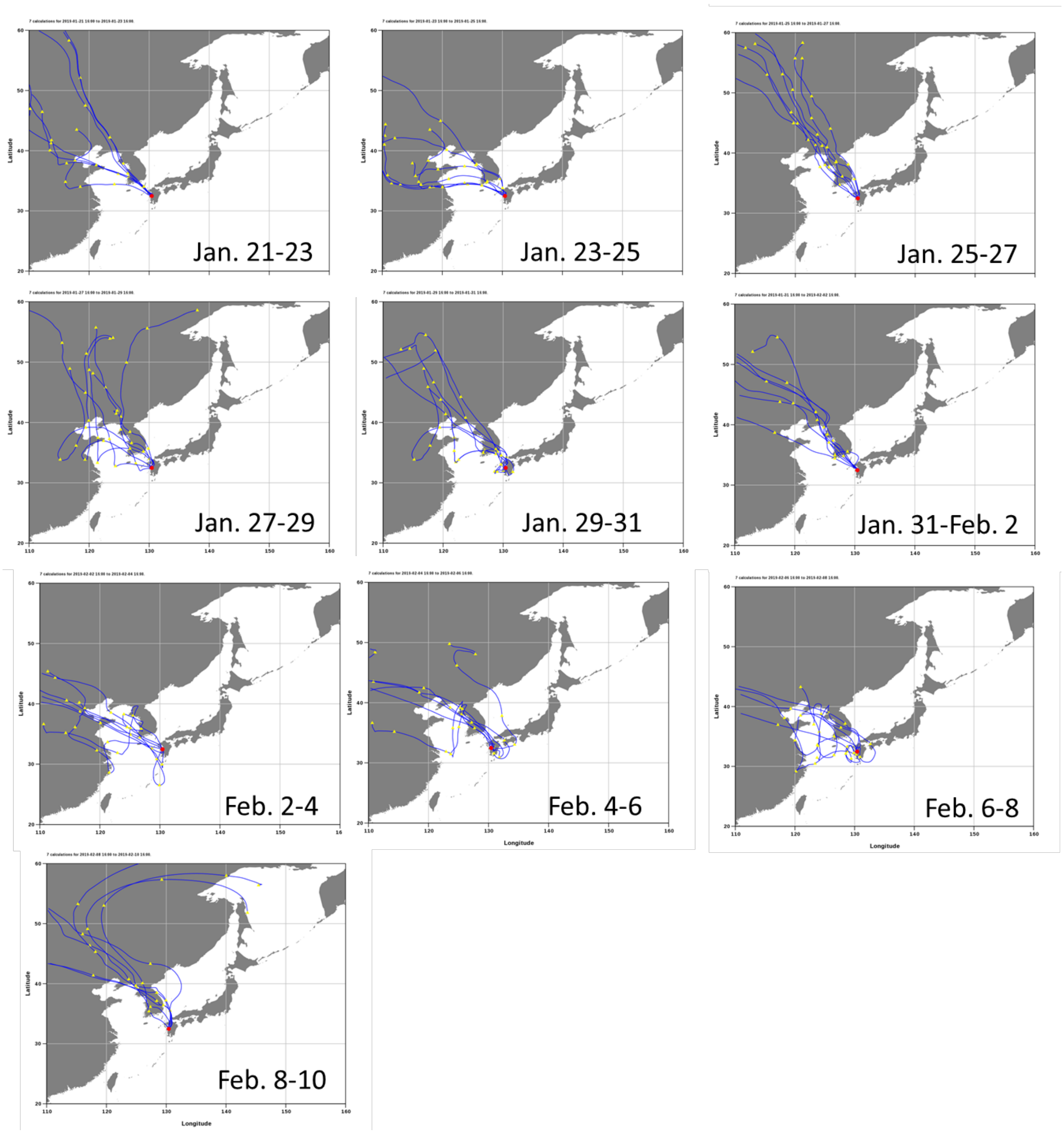

Fig. S1 Back trajectories for the winter campaign period. Each panel shows back trajectory data for each sampling period. Trajectory traces every 8 h in each panel are for 16:00 and 24:00 of the first day, 8:00, 16:00 and 24:00 of the second day, 8:00 and 16:00 of the third day, and total 7 traces are shown for the 48 h period.

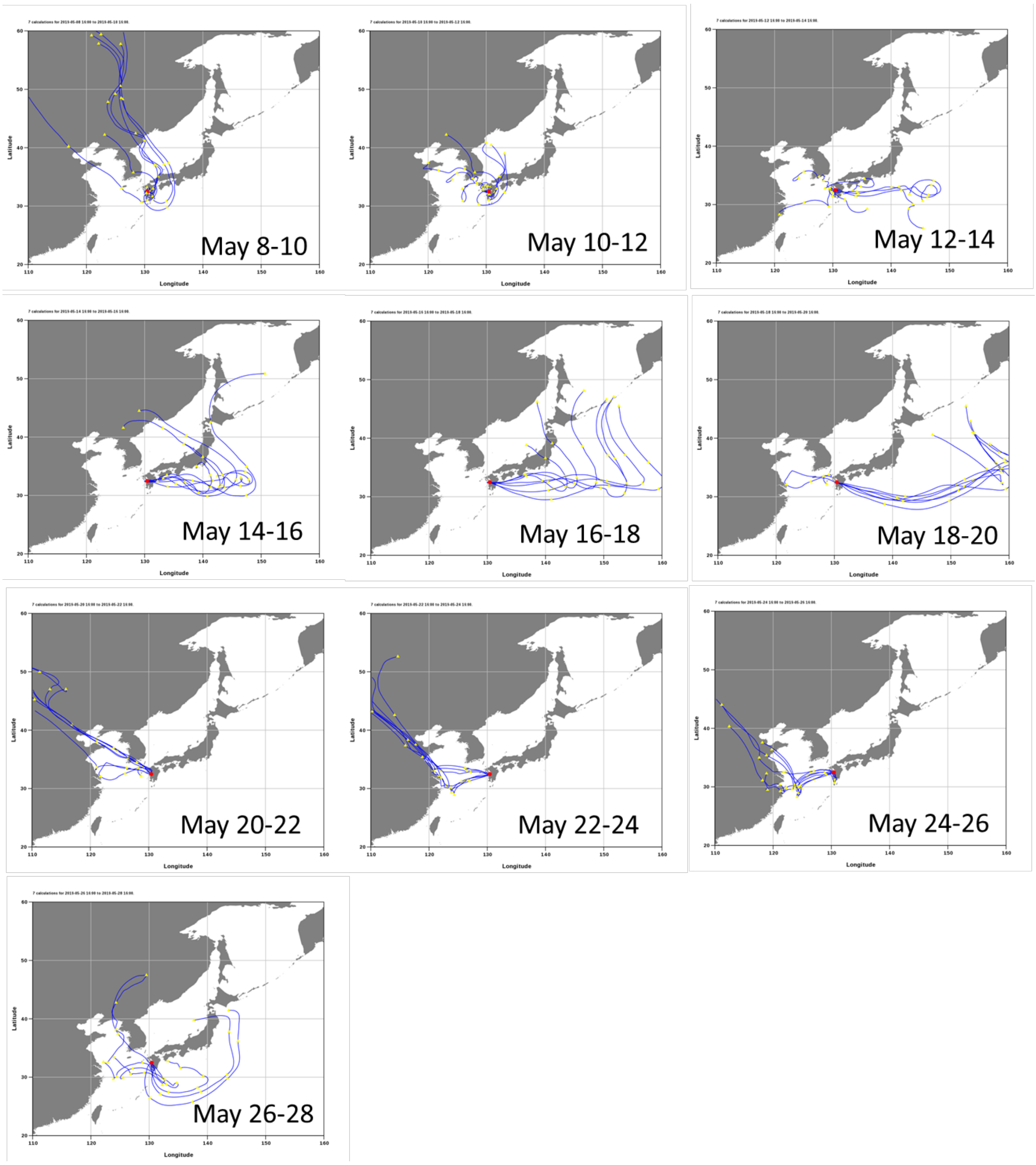

Fig. S2 Back trajectories for the summer campaign. The conditions are same as in Figure S1.

As can be seen in Fig. S1, the air mass came from northeast to carry air of the Ease Asia continent in winter all the periods. In summer, the air masses were from the Pacific Ocean in May 12 – 20 but from China in the other period of the campaign (Fig. S2). The monitoring cite is affected by the Chinese pollutions even in summer.

2. Recovery of the water extraction

Recoveries were obtained from filters where 30 ng (600 µg/L x 50 µL) of each heavy metal was added. After drying in a clean chamber, the filters were treated with water in the same way as the sample filter treatment and the acidified extracted sample solutions were analyzed by ICP-MS. Obtained results are shown in Table S1. Recovery was 85% for V and between 95 and 99% for the other metals. Filter blank for the five heavy metals were negligible in the recovery test.

Table S1 Recoveries of the five heavy metals in the water extraction (*n* = 3).

	As	Se	Sb	V	Cr
ICP-MS results (×10^3 cps)					
Standard	24.8 ± 0.3	2.21 ± 0.05	161 ± 3	84.2 ± 3.7	241 ± 4
Filter blank	0.045 ± 0.014	0.023 ± 0.003	0.238 ± 0.080	0.430 ± 0.118	1.26 ± 0.09
Std added filter	24.0 ± 0.3	2.10 ± 0.03	155 ± 4	71.5 ± 5.7	238 ± 7
Recovery (%)	96.7	94.0	96.3	84.4	98.1

3. Limits of detection (LODs) in the three analysis modes

We have performed IC-ICP-MS analysis for water extractants and direct ICP-MS analysis for water extractants and acid-digested samples. LODs of extracted solution samples (ng/L) were determined for all methodologies from three times deviations of blank signal intensities. LODs in atmospheric concentration (ng/m^3) were calculated from solution's LODs, area ratio of filter used for extraction, and air sampling volume as shown in Eq. S1.

$$\mathrm{LOD_{atmos}}(\mathrm{ng/m^3}) = \mathrm{LOD_{soln}}(\mathrm{ng/L}) \times \frac{f_F \quad V_{\mathrm{soln}}(\mathrm{mL})}{F\,(\mathrm{L/min}) \quad T\,(\mathrm{min})} \qquad \text{(S1)}$$

LOD$_{\mathrm{atmos}}$ and LOD$_{\mathrm{soln}}$ are LODs for atmospheric concentration (ng/m^3) and extractant concentration (ng/L). f_F: area ratio of filter used for extraction, V_{soln}: volume of extractant solution, F: sampling air flow rate, T: sampling time.

Results are shown in Table S2. Acid digestion's LODs were relatively higher (worse) than those of water extraction samples. However, it is shown that sub-ng/m^3 of the total heavy metals can be analyzed. The total soluble-metals and the oxoanions could be determined in one order less concentrations.

Table S2 Limits of detection estimated for three analysis modes

IC-ICP-MS for water extractants								
	As(III)	**As(V)**	**Se(IV)**	**Se(VI)**	**Sb(V)**	**V(V)**	**Cr(III)**	**Cr(V)**
Blank (ng/L)	17 ± 8	31 ± 39	77 ± 109	48 ± 28	ND	15 ± 21	1 ± 1	ND
LOD (ng/L)	25	116	327	142	30*	63	144*	30*
LOD (ng/m^3)	**0.005**	**0.024**	**0.068**	**0.030**	**0.006**	**0.013**	**0.030**	**0.006**

	As	**Se**	**Sb**	**V**	**Cr**
Direct ICP-MS of water extraction sample					
Blank (ng/L)	9 ± 3	52 ± 8	7 ± 2	26 ± 7	26 ± 2
LOD (ng/L)	13*	24	7	21	5
LOD (ng/m^3)	**0.003**	**0.005**	**0.002**	**0.004**	**0.001**
Direct ICP-MS of acid-digested sample					
Blank (ng/L)	133 ± 51	8 ± 6	38 ± 19	33 ± 25	1798 ± 81
LOD (ng/L)	154	17	58	74	242
LOD (ng/m^3)	**0.064**	**0.007**	**0.024**	**0.031**	**0.101**

* LODs for Sb(V), Cr(III) and Cr(VI) were estimated from three times baseline noise of chromatograms because these species were not detected from the filter blank samples or blank value was very small. LOD for As of water extract was estimated from signal to noise ratio of ICP-MS because it was higher than the value estimated from blank value.