Short Communication

A compact semi–continuous atmospheric aerosol sampler for elemental analysis: a preliminary result

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ABSTRACT

A compact semi–continuous atmospheric aerosol sampler has been developed for subsequent elemental analysis by inductively coupled plasma mass spectrometry (ICP–MS). The sampler is basically a downsized and simplified version of the University of Maryland Semi–continuous Element in Aerosol Sampler–II (SEAS–II) and is hereafter referred to as the Korean version of SEAS (KSEAS). It has four major components: a steam generator, a particle growth chamber, a particle impactor, and a fractional XY collector. The air flow rate of this sampler is 16.7 L min^{-1}, roughly one fifth of the flow rate of SEAS–II. Due to the lower volume sampling rate, a virtual impactor is not needed, which makes it simple to fabricate and use. The absence of a virtual impactor also improves sample collection efficiency. Ambient air is withdrawn to a particle growth chamber where it mixes with a hot steam flow. As the resulting supersaturated air flows downward, its temperature decreases due to heat loss to the lower part of the water–chilled glass wall. Finally, air–flow is directed to a particle impactor where moisturized aerosol–laden droplets accumulate at the bottom as an aqueous solution, which is withdrawn periodically to a fraction collector. To evaluate the validity and field applicability of our sampler, we used it and SEAS–II to collect $PM_{2.5}$ and PM_{10} in Seoul, Korea over the period of a month. Collected samples were analyzed for several key elements using ICP–MS. Elemental analysis results showed good to excellent correlation coefficients, ranging from 0.3~0.9 (n = 586), between the two samplers, confirming the validity of KSEAS. Due to the lower volume sampling rate, the detection limits of KSEAS is higher than those of SEAS–II (2~5 times higher). However, lower sampling volume needs lower power for operation and provides a better field applicability.

1. Introduction

High time–resolved ambient aerosol chemical composition data are essential to understand rapidly changing atmospheric phenomena such as emission source intensity, gaseous reactions, intermediate/precursor variations, and physicochemical changes in response to sub–hourly changing weather parameters such as air temperature, air pressure, and mixing depth, among others. In response to this demand, various aerosol composition analysis techniques have been developed in recent years. Techniques have been developed for organic carbon (Lim and Turpin, 2002), elemental carbon (Lim et al., 2003a; Lim et al., 2003b; Park et al., 2005a), and ionic species such as nitrate (Park et al., 2005b), sulfate, and ammonium (Simon and Dasgupta, 1995; Weber et al., 2001; Orsini et al., 2003; Lee et al., 2008). These chemical species are relatively abundant in ambient aerosols, making it possible to measure these species using small volume samples. However, for minor to trace elements such as As, Se, Co, Cu, V, Ni, Cd, and Pb, a large volume sampling is mandatory for subsequent quantitative analysis. Manual filter–based sampling for several hours to days is required to measure the concentrations of these minor and trace elements. The only method that allows sub–hourly measurements of trace elements in $PM_{2.5}$ is the one developed by a research group based at the University of Maryland (Kidwell and Ondov, 2001; Kidwell and Ondov, 2004). This group developed an automatic $PM_{2.5}$ sampler called the Semi–continuous Element in Aerosol Sampler (SEAS–II) for trace element analysis. SEAS–II was successfully used at four US air monitoring "Supersites" (Baltimore, Pittsburgh, and St. Louise in 2001 and 2002 and Tampa in 2002)

(Weber, 2003; Harrison et al., 2004). High frequency elemental data have been used for multivariate receptor model development and emission source apportionment (Park et al., 2005c; Park et al., 2006). SEAS–II is now commercially available from Ondov Enterprise Inc. USA (http://ondoventerprises.com/).

SEAS–II consists of an aerosol concentrator mated to an automated sample collector. Particles as small as 0.08 µm in diameter are grown to a size of 3 – 10 µm by condensation of water vapor using steam injection. Ambient air is sampled at 90 L min^{-1} and samples are collected automatically in polyvials of a fraction collector. The sampling interval can be adjusted to less than an hour, with sampling generally performed for 30 minutes. Collected samples can then be subjected to elemental analysis using multi–element electrothermal atomic absorption spectro–metry. In the study by Pancras et al. (2005) using SEAS–II, concentrations of 11 marker elements were determined.

Being SEAS–II used in various applications, it is highly desirable to have a smaller version because the existing instrument is rather voluminous and heavy, and requires a large amount of power to operate, limiting its field deployment. Furthermore, to pump air samples at a flow rate of 90 L min^{-1}, a high power pump is required; however, the loud noise and vibrations that emanate from the high power air pump can potentially interfere with delicate instruments.

To address these limitations of SEAS–II, we developed a compact ambient aerosol sampler as an alternative to SEAS–II,

which we refer to as the Korean version of SEAS, abbreviated as KSEAS. This instrument samples air at a flow rate of 16.7 L min^{-1}, roughly one fifth of the flow rate of SEAS–II. Due to the lower volume sampling rate, the power required for operation is also lower. There is no virtual impactor in this sampler, which makes it simple to fabricate and to use. The absence of a virtual impactor also improves sampling efficiency.

From a theoretical perspective, lower sampling volume will lead to a lower sample concentration factor, thereby increasing the limits of elemental detection. Assuming the same volume of condensed liquid sample, the aerosol concentration factor of our sample would be one fifth of that of SEAS–II. This may limit the number of elements measurable using this sampler; in particular, elements of low natural abundance and/or of low analytical sensitivity may be difficult to detect. Nevertheless, this sampler has many practical applications in atmospheric aerosol studies, and as we describe below, no element detection limit issues arose in the Seoul aerosol study that we have performed.

2. Experiments

2.1. Sampling Apparatus

We modeled our sampler for semi–continuous collection of atmospheric aerosol for elemental analysis after Kidwell and Ondov's (2001) device, SEAS–II. A schematic diagram of KSEAS is provided in Figure 1. KSEAS was designed and fabricated to achieve a reduced air–flow rate of 16.7 L min^{-1}. The device has four major parts: a steam generator, a particle growth chamber, a particle impactor, and a fractional XY collector. There is no virtual impactor in KSEAS in contrast to SEAS–II, because of the reduced airflow rate of KSEAS.

The air sample is drawn in with a pump (GAST MODEL DOA–P101–AA) at a flow rate of 16.7 L min^{-1} through PFA tubing (10 mm id) to the top of the particle growth chamber. There may be some particle loss on to the PFA tubing inner wall due to electrostatic attractions. Yet we still chose PFA tubing rather than metallic one for two reasons. Firstly, PFA tubing is better choice in contamination control respects especially for metallic element analysis: our target elements are mostly metallic ones. Secondly, water vapor condensation can be problematic when high humidity warm air is withdrawn to the sampler placed in air conditioned room by using heat conductive metallic tubing. Actually, we believe the particle loss on the tubing wall is not significant from the fact

that no visible deposited particles or tubing darkening is observed whereas impactor needs to be cleaned periodically due to carbon soot particle deposit. The sample air is then mixed with hot steam, which becomes super–saturated at approximately 45 °C. The particle growth chamber comprises a cylindrical borosilicate glass tube with an internal diameter of 45 mm and a length of 520 mm. The lower portion of the tube is inwardly water–jacketed using a 300 mm long glass tube (36 mm internal diameter, 180 mm long). The unjacketed upper glass tube serves as a steam and air–mixing chamber. A precision–machined PTFE cylindrical block plugs the top end of the tube. There are two straight holes: one at the center and the other at off–center. The center hole, which is 12 mm in diameter, serves as an air inlet, while the other off–center hole with a diameter of 3.5 mm serves as a hot steam inlet. A glass funnel is pressure–fitted downward through the center hole. The funnel stem end is connected to the PFA tubing of sample air. Another 3 mm hole that was drilled diagonally is used for steam introduction. The air inlet glass funnel has a 3.5 mm hole in the middle mouth for positioning of the PFA tubing for steam injection. The funnel mouth is 41 mm in diameter. The reason that we used a glass funnel as an air inlet was to prevent any steam condensate from dropping downward to the aerosol catching funnel. Any water droplets falling down from the PTFE block wall will be caught by upside of the glass funnel mouth wall. The lower part of the glass tube is connected to an aerosol impactor via another glass funnel. This funnel mouth is also 41 mm in diameter, but its stem is 5 mm OD. A machined PTFE block is used to connect the funnel to the aerosol impactor.

The steam generator consists of a water reservoir, a peristaltic pump (PP2, Gilson Miniplus–3), stainless tubing (1/16" id. x 60 cm) coiled around a quartz rod heater (12 mm od x 20 cm, 500 W), and an ion exchange cartridge (D8901 HOSE NIPPLE–type, Barnstead). The temperature of the quartz rod is maintained at 160 ± 1 °C by using a temperature controller (Atonics TEMP controller TZ4ST). Steam is generated by delivering deionized water (18.2 MΩ cm) at a flow rate of 1.2 mL min^{-1} to the heated stainless tubing. The flow rate can be changed, but lowering it below 0.5 mL min^{-1} may cause large variability in condensate liquid volume and particle collection efficiency. At 1.2 mL min^{-1}, the changes of sample air temperature and humidity did not significantly affect on the condensate liquid volume. The steam is then injected through Teflon® tubing (1 mm id. x 150 mm) at an angle of about 10° to the air stream. Turbulence within the steam introduction funnel results in rapid mixing. The super–saturated sample air then enters the particle growth chamber, which is maintained at 4 °C by cooling water
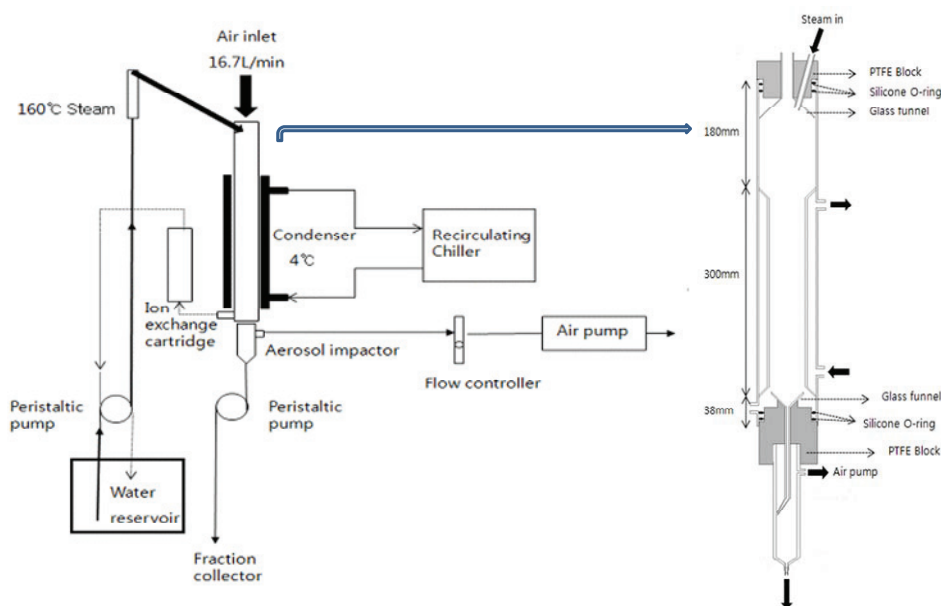

Figure 1. Detailed schematics for semi–continuous atmospheric aerosol sampler developed in this study.

using a chiller (SIBATA COOLMAN PAL C–302). Upon traveling through the chamber, the air cools rapidly to about 8 – 20 °C depending on the axial position and aerosol growth. The maximum theoretical saturation ratio for our device, derived from the ratio of the actual vapor pressure to the saturation vapor pressure at a given temperature, ranges from 4.2 to 7.8 depending on the temperature. Vapor loss occurs due to condensation on the condenser walls, reducing the actual saturation ratio, but the saturation ratio is still much larger than the theoretically calculated saturation ratio of 1.25, which is needed to grow hydrophobic particles as small as 0.01 μm by condensational growth (Hinds, 1982; Kidwell and Ondov, 2001). The residence time within the chamber is about 1.1 seconds, which is much longer than the theoretically predicted time for particles to grow from 0.01 to 5 μm at a saturation ratio of about 1.25 (Kidwell and Ondov, 2001).

The grown droplets are collected directly in a real impactor, which improves the collection efficiency by avoiding the loss of particles in a virtual impactor (Kidwell and Ondov, 2001). A glass single–jet real impactor is used to separate the droplets from the air–flow. The droplets accumulate in the bottom of the real impactor as an aqueous slurry at a rate of about 0.1 mL min^{-1}. After a 60 minute collection period, the slurry is hydraulically delivered to a fractional collector (ADVANTEC SF–2120) and collected in pre–cleaned polyvials. The volume of the liquid remained in the impactor after delivery was less than 0.2 mL. No impactor washing step was employed to minimize carryover effect. If needed, one can change liquid delivery program between sampling steps.

2.2. Elemental analysis

A 100 μL aliquot of 70% trace metal–free nitric acid (semiconductor grade) was added to the sample vials removed from the fraction collector, typically within 24 hours after sampling. The vials were capped tightly and then stored at room temperature until chemical analysis. Sample volume was measured by weighing the sample slurry. ICP–MS (Elan DRC–e, Perkin Elmer) was used for the elemental analysis. A 200 μL aliquot of mixed standard solutions of 200 ppm indium and 200 ppm bismuth as an internal standard was dispensed into each sample vial just before analysis. The concentrations of Pb, Cd, Cr, Cu, Ni, Zn, Fe, Al, Ca, Mg, K, As, and V were measured. An autosampler (AS 10, Dionex, USA) was used to minimize sample contamination during the analytical process. Detailed analytical conditions for the ICP–MS measure–ments are presented in Table 1.

Table 1. ICP–MS operating parameters

ICP–MS Instrument	Perkin–Elmer Elan DRC–e
ICP system	
RF power	1 300 W
Plasma gas flow rate	18.3 L min^{-1}
Nebulizer gas flow rate	0.97 L min^{-1}
Auxiliary gas flow rate	1.2 L min^{-1}
Mass spectrometer	
Interface cone	standard Nickel
Sample cone orifice	1.1 mm
Skimmer cone orifice	0.9 mm
Lens setting	Auto lens dynamically scanned
Detector mode	Dual
Detector voltage	1 250 V
DRC mode NEB	0.99
DRC mode QRO	−5
DRC mode CRO	0
DRC mode CPV	−17

2.3. Collection efficiency

Mono–dispersed fluorescent polystyrene latex (PSL) particles (Polysciences, Inc., Warrington, PA) were used to determine KSEAS

particle collection efficiency. Suspensions of 0.075, 0.2, 0.43, 0.92, 1.0, 1.9 and 4.8 μm diameter PSL were prepared by diluting a 1.2 mL aliquot of each stock solution to 100 mL with deionized water (18.2 MΩ cm). Test aerosols were generated by using an atomizer (Model 9302, TSI) with dried air at a flow rate of 6.6 L min^{-1}. The aerosol was then mixed with filtered (3 μm pore capsule filter) air at a flow rate at 10.1 L min^{-1} in a mixing chamber. The generated particles were alternately collected on a reference filter (Filta–Max Filter membrane, FMC 10800, IDEXX Laboratones Inc., USA) and KSEAS. The sampled particles were dried in an oven at 60 °C for over an hour. The fluorescent dye on the reference filter and sampled particles were extracted with 4 mL ethyl acetate. The fluorescent intensity of each sample extract was measured with a spectrophotometer ($\lambda_{excitation}$ = 468 nm, $\lambda_{emission}$ = 508 nm, Model FS–5301PC, SIMADZU, Japan). The system blank was measured with deionized water as atomizer solution without any PSL particles. The collection efficiencies were calculated as F_S/F_R, where F_S and F_R are the fluorescent intensities of the sample extract and the reference filter extract, respectively.

2.4. Application of KSEAS to Seoul air analysis

We used KSEAS to perform an analysis of Seoul air during two campaign events: from 19 February through 4 March, 2009 and from 10 March through 1 April, 2009. Sampling was performed for 60 minutes. For comparison, air samples were collected simultaneously using SEAS–II for 30 minutes. Sampling was performed from a five story high building of the National Institute of Environmental Research, located 15 km northwest of Yonsei University campus. KSEAS was operated automatically. The sampled vials were recovered and the status of the sampler was checked every morning.

3. Results and Discussion

During the five week field campaign period, about 82% of aerosol samples were successfully collected using our newly developed aerosol sampler. The corresponding sample success rate of SEAS–II was 75%. The principle reasons for KSEAS sample collection failure were leaks in the peristaltic pump tubing and for SEAS–II were malfunctioning of the temperature controller of the steam generator. The samplers were operated unattended from a distant site, so liquid leaks and malfunction of the temperature controller were not detected immediately. The sampling success rate is likely to be higher if the sampler is operated by an operator for the whole study period. The limits of detection calculated by 3σ of the system blank levels are presented in Table 2, where σ is the standard deviation of six measurements. Over the entire study period, the atmospheric concentrations of Fe, V, Al, K, Zn, Ca, and Mg were higher than the detection limits of the sampler at all times. For Cr, Ni, As, Cd, Cu, As, and Pb, ~1% of the hourly samples showed concentrations below the limit of detection (LOD).

Table 2. Limits of detection ^{a}

Element	LOD (ng m^{-3})
Cr	0.028
Ni	0.027
As	0.031
Cd	0.006
V	0.003
Al	0.200
K	0.330
Fe	0.460
Cu	0.018
Pb	0.037
Zn	0.037
Ca	0.420
Mg	0.170

^{a} *3σ of 6 measurements of system blank*

The collection efficiencies of various sizes of input particles are shown in Table 3. The collection efficiencies for input particles <1.0 µm in diameter were 55 – 60% without any obvious dependence on particle size. For particles larger than 1.0 µm, collection efficiencies increased with particle size to 99% for 4.8 µm diameter input particles. These collection efficiencies are higher than those reported in a previous study (Kidwell and Ondov, 2001), but particle losses were still significant for particles <1.0 µm in diameter. The results of the mass balance test using 0.075 µm PSL particles for the entire system are summarized in Table 4. Each component was washed before and after the tests to determine losses. The collection efficiency for grown droplets in a real impactor was 55%. The condenser was the major source of loss, accounting for 31% of the loss of input particles. Particle deposition in the sample outlet tube, which is connected to the air pump, was also significant and accounted for 11% of the loss of input particles. This supports the hypothesis of Kidwell and Ondov (2001) that the lower collection efficiencies of smaller particles are due to incomplete growth of these particles. Atmospheric particles from combustion sources are generally smaller than 1.0 µm. Therefore, quantitative collection of $PM_{1.0}$ is important to improve our understanding of the chemical composition of particles produced as a result of human activities. Even though the collection efficiencies of our newly–developed sampler were slightly higher than those of SEAS–II, further experiments for the improvement of the collection efficiency are needed.

Table 3. *Collection efficiency*

Particle size (µm)	Collection efficiency (%)
0.075	54.8 ± 2.5
0.20	56.0 ± 0.6
0.43	55.4 ± 0.6
0.92	61.4 ± 0.8
1.0	77.3 ± 0.7
1.9	79.1 ± 0.5
4.8	99.0 ± 1.0

Table 4. *Mass balance for condensational growth and collection of 0.075 µm particles*

Collected	
Real impactor	55%
Lost	
Condensers	32%
Pump-out line	11%
Tubing	2%
Ref. filter (total)	100%

The elemental compositions of the samples collected using our sampler and SEAS–II were analyzed in the same way. The analytical results of aerosol samples collected by the two aerosol samplers showed a statistically significant correlation at p<0.01 for all elements. The correlation coefficients are summarized in Table 5. The concentrations of As, Cd, V, Al, and Pb were more strongly correlated (r>0.80) between the two samplers than the other elements.

Figure 2 shows temporal variations in the concentrations of As and Cd in the atmospheric aerosols collected by the two samplers for the whole study period. So that the relationship between the two results can be shown more clearly, scatter diagrams are also presented in Figure 2. The measured atmospheric concentrations from the two samplers agreed well with each other during the whole study period, as expected from high correlation coefficients for As and Cd. The slope values of 0.97 ± 0.10 are also close to 1, suggesting high accuracy of the two results. There are however, some non–zero offsets in the scatter diagrams for Cd, As and Pb indicating some systematic deviations between the two results.

Causes of these systematic deviations are not known at this time. One possible cause is from sample contamination during sampling. Another cause is from the ICP–MS measurements which are performed KSEAS batch and SEAS–II batch separately. Depending on element and its specific isotope, ICP/MS blank level can be significant and it is variable from batch to batch.

Table 5. *Pearson correlation coefficients of the concentrations of the elements in the aerosol samples collected by KSEAS and SEAS-II*

Element	r
Cr	0.53
Ni	0.43
As	**0.92**
Cd	**0.84**
V	**0.91**
Mg	0.60
Al	**0.86**
K	0.62
Fe	0.39
Cu	0.46
Se	0.62
Pb	**0.82**
Zn	0.31
Ca	0.28
n [a]	586

[a] Number of measurements

The atmospheric concentrations of As varied from 0.43 to 17.3 ng m^{-3}, with an average of 2.96 ng m^{-3}. This variation is dramatic. The concentration of As on February 25, for example, was 1.83 ng m^{-3} at 4:30 in the morning and increased rapidly to 17.4 ng m^{-3} at 9:30 in the morning. The concentrations of Cd varied from 0.11 to 8.30 ng m^{-3} with an average concentration of 0.76 ng m^{-3}. Aerosol Cd on March 17 showed a peak concentration of 4.75 ng m^{-3} at 2:00 in the morning and rapidly dropped to near 1.0 ng m^{-3} within 9 hours. These results suggest that time–resolved aerosol composition data are essential to understand the chemistry of aerosol particulates, and furthermore, indicate that our sampler can be used for this purpose.

Temporal variations in the concentrations of 9 elements for a selected period that we obtained using our sampler are presented in Figure 3 to demonstrate the rapid compositional changes in atmospheric particulate matter.

Dust storms occurred during the study period. The first dust storm occurred on February 20. During this event, the average PM_{10} level in Seoul, as reported by the Korean Ministry of the Environment (MOE), was 230 µg m^{-3}, which is an order of magnitude higher than the normal PM_{10} level. The other two dust storms occurred on February 25 and 28. The average PM_{10} level of Seoul was about 60 µg m^{-3}, approximately twice as high as the normal level. The aerosol compositions were significantly different for the three dust storms. On February 20, concentrations of all of the elements increased significantly. However, on February 25, the increases in the concentrations of Fe, Mg, Ca, Al, and Zn were not significant, while significant increases in the levels of Cd, As, and Pb were observed. Air mass back trajectory analysis revealed that the air mass was transported from deserts in Asia on February 20. However, the air mass remained near the Seoul metropolitan area for 24 hours on February 25. These findings suggest that hourly or sub–hourly monitoring of the elemental composition of aerosols, combined with meteorological parameters, are essential to improve our understanding of atmospheric chemistry in this region. We are currently evaluating the performance of this sampler as an aerosol collector and are developing an online analyzer that combines an aerosol sampler and ICP–MS.
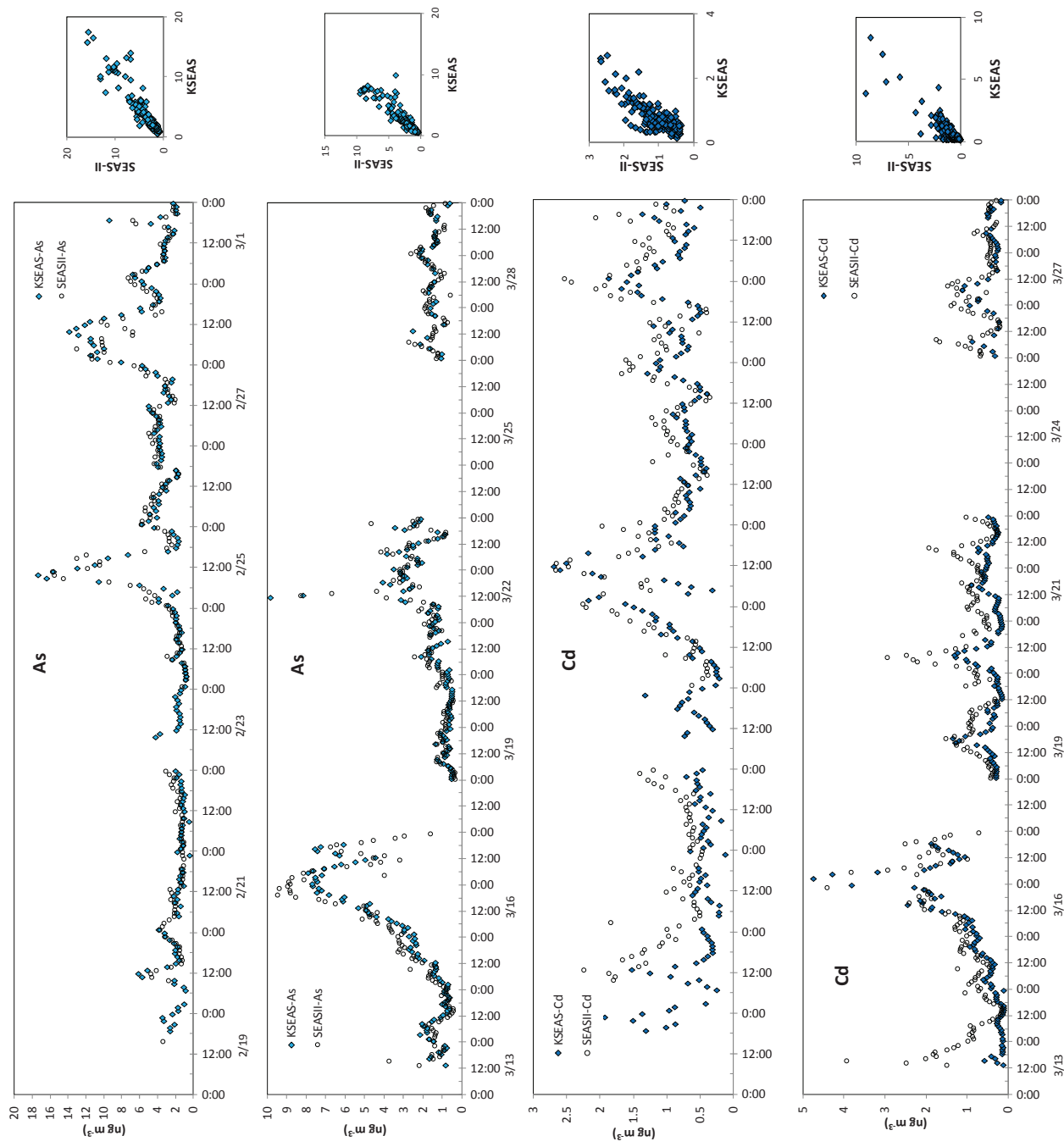
Figure 2. *Temporal variations of As and Cd concentrations in the atmospheric aerosol at Seoul collected by this sampler (◆) and SEAS-II(O).*
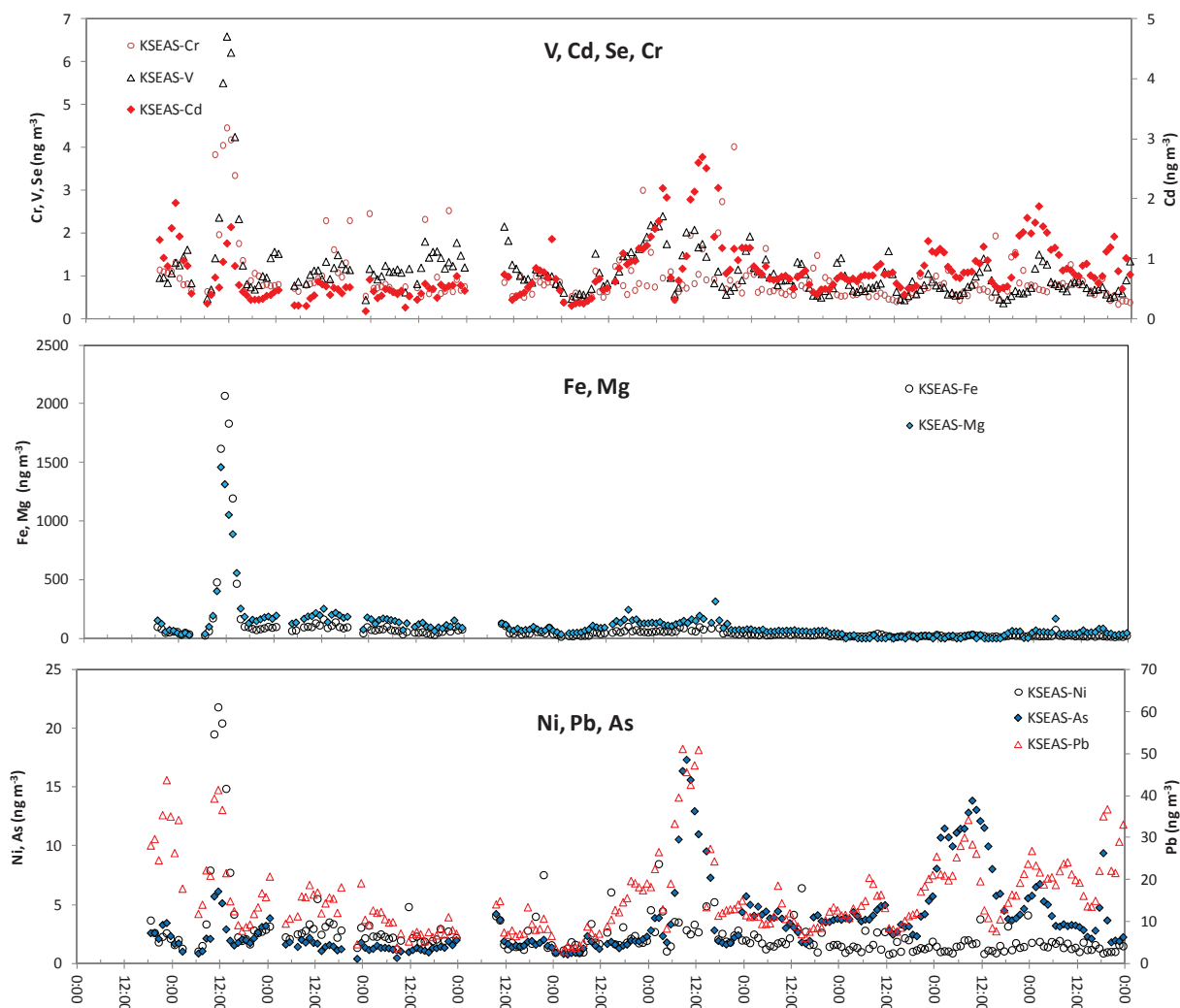
Figure 3. *Temporal variations of the concentrations of the elements in the atmospheric aerosol at Seoul, from February 19 through March 1, 2009.*

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