



Comparison of Online and Offline Methods for Measuring Fine Secondary Inorganic Ions and Carbonaceous Aerosols in the Central Mediterranean Area

Antonella Malaguti^{*}, Mihaela Mircea, Teresa M.G. La Torretta, Chiara Telloli, Ettore Petralia, Milena Stracquadanio, Massimo Berico

ENEA - National Agency for New Technologies, Energy and Sustainable Economic Development, via Martiri di Monte Sole 4, 40129 Bologna, Italy

ABSTRACT

Online hourly concentrations of nitrate (NO_3^-), sulphate (SO_4^{2-}) and ammonium (NH_4^+), and two hourly concentrations of organic carbon (OC) and elemental carbon (EC) were compared with the daily concentrations determined offline from filter samples. The comparison was performed over two months (May and June 2010) at a coastal site characterized by low local pollution, located in the Southern Italy (Central Mediterranean basin). The online measurements of the above inorganic ions and carbonaceous components of the aerosols were carried out using an Ambient Ion Monitor-Ion Chromatograph (AIM IC URG 9000-D) and a Sunset Laboratory Model-4 Semi-Continuous OCEC Field Analyzer, respectively, while the offline analyses were performed with two ion chromatographs instruments (Dionex DX-120 and Dionex 500) and a Sunset Laboratory Dual-Optical Carbonaceous Analyzer (Sunset Laboratory). The collocation of instruments allowed to evaluate the differences between online and offline daily concentrations and to interpret the origin of positive and negative sampling artefacts. As an example, the offline OC concentrations are constantly higher than online concentrations and this is explained by positive artefacts of offline measurements. The analysis was performed separately for days with and without transport of Saharan dust and revealed significant enhancement of concentrations for both inorganic ions and carbonaceous aerosols in the presence of dust. The increase of EC concentrations during dust events may be explained by an increase of emissions transport from sea traffic to the site.

Moreover, the results showed that the online instruments may be used at a low polluted site for the acquisition of high temporal resolution data.

Keywords: Coastal background site; Online and offline methods; Secondary inorganic aerosol; Carbonaceous aerosol.

INTRODUCTION

In the last two decades an increasing interest for understanding the relationship between atmospheric aerosol and population health had led to the development of online techniques and instruments able to quantify the concentration of specific chemical with a high time resolution (one hour or less) (Chow, 1995). The high time resolved and fast response measurements (online measurements) allow for identifying connections between the variability of aerosol chemical composition and concentration with meteorological conditions and/or with time of day (Wittig *et al.*, 2004; Brink *et al.*, 2007; Timonen *et al.*, 2010). The datasets are large enough to conduct source/receptor modeling for assessing the variability of sources and ambient levels (Gao

et al., 2011; Park *et al.*, 2013), and for assessing the human exposure (Morishita *et al.*, 2011), over short periods of time, weeks or months (Wexler *et al.*, 2008). The effective identification of emission sources and, thus, a better characterization of environmental exposure is fundamental for decision-makers to individuate and implement emission reduction actions. Due to their fast response to ambient changes, the online methods are suitable for measurements on moving platforms like airplanes, trains or cars (Ma *et al.*, 2004; Sorooshian *et al.*, 2006; Kuokka *et al.*, 2007). In addition, the online measurements are less costly than the offline ones consisting in collecting aerosol on filter, transport and refrigeration followed by laboratory analysis, and give real-time data. The offline methods have time resolutions ranging from few hours to days, depending on the level of pollution at the site. Moreover, these measurements are subject to positive or negative artefacts due to volatile species that may change during sampling, transport, storage and analysis (Chow, 1995; Tsai and Perng, 1998; Pathak and Chan, 2005; Viana *et al.*, 2006; Vecchi *et al.*, 2009; Cheng *et al.*, 2010). Errors and uncertainties in offline measurements

^{*} Corresponding author.

Tel.: 39-051-6098090; Fax: 39-051-6098675
E-mail address: antonella.malaguti@enea.it

have been extensively studied during the last decades (Pathak and Chan, 2005; Viana *et al.*, 2006) but the online methods are relatively novel and pose new problems (Wu and Wang, 2007). For example, due to the short integration times the online measurement are often close to the determination limits of the analyzing methods when the ambient concentrations are very low (Lee *et al.*, 2008; Malaguti *et al.*, 2013). Moreover, some online measurements require daily operator intervention and maintenance, especially when continuous long data series are intended to be obtained in AQ monitoring networks. Up to now, the performances of the online instruments have been evaluated at urban (Jeong *et al.*, 2004; Wu *et al.*, 2007; Godri *et al.*, 2009; Aurela *et al.*, 2011; Park *et al.*, 2013; Rumsey *et al.*, 2014) and background sites (Aurela *et al.*, 2011; Makkonen *et al.*, 2012). However, further tests of the online methods are still needed for assessing their performances in environments with different/ various aerosol mixtures and concentrations in order to gain a deeper understanding of the limitations and strengths of instruments in different atmospheric conditions (Bauer *et al.*, 2009; Nie *et al.*, 2010; Markovic *et al.*, 2012). Other operation performance factors such as maintenance requirements and easy-to-use have to be assessed by field testing. This study shows a comparison between online and offline measurements at a site characterized by low levels of local pollution, close to the coast and affected by dust transport from Saharan desert in spring/summer atmospheric conditions. Online measurements of inorganic water-soluble ions and carbonaceous compounds obtained with an Ambient Ion Monitor-Ion Chromatograph (AIM-IC) system and an OCEC Semi-Continuous analyzer were compared with offline filter measurements on daily basis when the monitor data completeness was fulfilled. The comparability and correlations between the monitor and filter-based data is also shown.

METHODS

The field campaign was carried out at Trisaia ENEA Research Centre (Italy) (40°09'58.23"N–16°38'25.95"E, 25 m altitude) from 3rd May to 30th June 2010. Information on site description and meteorological conditions can be found in Malaguti *et al.* (2013, 2015). The monitors have operated continuously and simultaneously with daily aerosol sampling for comparison over 59-days.

During this period four Saharan dust events were identified, three in May (3–5, 11–14, 27–29) and one in June (11–19) on the basis of AERONET data (<http://www.esrl.noaa.gov/gmd/obop/mlo/programs/coop/nasa/aeronet/aeronet.html>), MODIS maps (http://modis-atmos.gsfc.nasa.gov/MOD04_L2/index.html) and air mass back trajectories (Malaguti *et al.*, 2015) computed with NOAA HYSPLIT model (<http://ready.arl.noaa.gov/HYSPLIT.php>). Therefore, the online and offline data were divided in two periods: dust period, that contains the days with significant dust contributions (19), and non-dust period that includes the remaining days (40).

The concentrations of nitrate, sulphate, chloride, sodium, ammonium, potassium, calcium and magnesium (NO_3^- , SO_4^{2-} , Cl^- , Na^+ , NH_4^+ , K^+ , Ca^{2+} , Mg^{2+}) in the fine fraction

($\text{PM}_{2.5}$) were measured with a 60-min time resolution using the Ambient Ion Monitor-Ion Chromatograph (AIM-IC) developed by URG Corp., Chapel Hill, NC/Dionex Inc., Sunnyvale, CA. The instrument configuration includes a sample collection unit (URG 9000-D) for the collection of water-soluble gases and particles into aqueous solution and a sample analysis unit (two Ion Chromatographs, Dionex ICS-1100) for the analysis of both anions and cations.

The operation principle of AIM-IC is described in details by Markovic *et al.* (2012). Briefly, the sample collection unit mainly consists of a diffusion-based Parallel-Plate Wet Denuder (PPWD), a Particle SuperSaturation Chamber (PSSC) and a sample syringe pump with four 5 ml syringe. Ambient air was drawn (flow rate of 3 L min^{-1} , $0.17 \text{ m}^3 \text{ h}^{-1}$) through an Teflon[®] Coated Aluminium 3 m sample inlet equipped with a $\text{PM}_{2.5}$ cyclone (URG Corporation), passing then along the PPWD where the water-soluble gases are collected by diffusion through two cellulose membranes (one per plate) and by dissolution in a hydrogen peroxide solution. After the PPWD, the airflow continues into the PSSC that consists of a steam generator, a mixing/condensation chamber and a cyclone. The particles hygroscopic growth is activated by the steam and the grown particles are collected passing through the cyclone; then, the solution containing dissolved particles is split in two subsamples. After 55 min of air sampling, the collected samples are injected by the syringe pump toward the corresponding ion concentrators and the analyses of the loaded samples start immediately. The sample loading time is 5 min and the new sample collection with the syringe pump re-starts every hour. The sample analysis unit is composed by an anion and a cation ion chromatographs (Dionex ICS-1100). The anion IC was equipped with a concentrator (IonPac[®] TAC-ULP1), a guard column (IonPac[®] AG9CH) and an analytical column (IonPac[®] AS9CH $250 \times 4 \text{ mm}$); the suppressor was an ASRS 300 Self-regenerating Suppressor 4mm. The anion analyses were performed by an isocratic elution using Na_2CO_3 8 mM + NaHCO_3 1.5 mM (running at 1 mL min^{-1}). The cation IC was equipped with a concentrator (IonPac[®] TCC-ULP), a guard column (IonPac[®] CG12A) and an analytical column (IonPac[®] CS12A $250 \times 1 \text{ mm}$); the suppressor was a CSRS300 Self-regenerating Suppressor 4mm. The cation analyses were performed by an isocratic elution using methane sulfonic 20 mM (running at 0.25 mL min^{-1}). The manufacturer's limit of detection (LOD) was $0.08 \mu\text{g m}^{-3}$ for NH_4^+ and $0.1 \mu\text{g m}^{-3}$ for each other ions (Table 1); the ion concentrations lower than the corresponding LOD threshold were excluded from the statistical calculations.

Simultaneous ambient $\text{PM}_{2.5}$ samples for inorganic ions analysis were collected with an atmospheric particles monitor sampler (FAI SWAM 5A Monitor, flow rate $2.30 \pm 0.05 \text{ m}^3 \text{ h}^{-1}$) on a daily basis, over 24 hours, with start time at 00:01 UTC. Particles were collected on quartz fiber filters (Pall 2500-QUAT-UP Ø47 mm) and preserved at -20°C until the IC laboratory analysis; more details can be found in Malaguti *et al.* (2015). AIM-IC and filter-based method LOD values for each ion (expressed as $\mu\text{g m}^{-3}$) are resumed in Table 1.

Total carbon (TC), organic carbon (OC) and elemental

Table 1. Calculation of the AIM and ECOC daily Limit of Detection (LOD) and comparison to laboratory IC and thermal optical LOD.

	AIM LOD		IC Laboratory LOD
	$\mu\text{g m}^{-3}$		$\mu\text{g m}^{-3}$
NH ₄ ⁺	0.08		0.012
SO ₄ ²⁻	0.10		0.133
NO ₃ ⁻	0.10		0.010
Cl ⁻	0.10		0.015
K ⁺	0.10		0.024
Na ⁺	0.10		0.012
Ca ²⁺	0.10		0.027
Mg ²⁺	0.10		0.010
	OCEC online LOD		OCEC offline LOD
	$\mu\text{gC cm}^{-2}$	$\mu\text{gC m}^{-3}$	$\mu\text{gC cm}^{-2}$
Th-OC	0.058	0.096	0.0480
Opt-OC	0.067	0.112	
Th-EC	0.026	0.043	0.0002
Opt-EC	0.009	0.015	

carbon (EC) mass concentrations in PM_{2.5} fraction were measured with 2-h time resolution using a Sunset Laboratory Model-4 Semi-Continuous OCEC Field Analyzer (Malaguti *et al.*, 2013). The ambient air was sampled into a 3 m long piece of 3/8" of Stainless Steel Tubing equipped with a PM_{2.5} cyclone inlet (flow rate of 8 L min⁻¹) and then passed through a carbon parallel plate diffusion denuder in order to avoid the absorption of any remaining organic vapours on the sampling filters (positive artefacts) (Turpin *et al.*, 2000). Ambient aerosols were collected on a quartz fiber filter mounted in a central part of an oven, inside the instrument. The analyzer provides measurements with the EUSAAR_2 thermal optical transmittance (TOT) protocol (Cavalli *et al.*, 2010) of OC and EC and optical measurements of EC; an internal standard (5% methane in helium mixture) is automatically injected, through a sample loop of 1 ml, at the end of each TOT analysis. OC and EC determined with the thermo-optical method are defined as Thermal OC and Thermal EC and their sum represents the Total Carbon (TC); the optical measurement of EC (amount of the EC on the filter) is defined as Optical EC and is calculated using the laser transmission data through the quartz filter monitored throughout the sampling time; the Optical OC is calculated by subtracting Optical EC from TC. Details on the monitor and the OC and EC environmental concentrations recorded during the Trisaia campaign can be found in Malaguti *et al.* (2013). The LOD for thermal and optical OC and EC, expressed as $\mu\text{gC cm}^{-2}$ and $\mu\text{gC m}^{-3}$ (Table 1) were calculated as three times the standard deviation (3σ) of the 90 min dynamic blanks. The OC and EC values lower than the corresponding LOD threshold were excluded from the statistical calculations.

The AIM-IC system and the OCEC Semi-Continuous analyzer were placed in an environmentally controlled cabin designed for field deployment of instruments: Fig. 1 shows an external view of the trailer at the Trisaia site, with the monitor inlets located on top of the trailer. The reference samplers were positioned approximately 10 m from the trailer, as shown in Fig. 1(a).

Installation, start-up procedure and calibration required about 2–3 days for the AIM and 1–2 days for the OCEC field analyzer. Calibrations of the AIM sampler and of the AIM sample analysis unit (anion and a cation ion chromatographs) were performed before to start the campaign. The AIM sampler calibration was performed in the following order: temperature sensor calibration, pressure sensor calibration and flow rate calibration. The sample analysis unit was calibrated using multi-point external standard solutions (Dionex Corporation, six cation standard for cation and seven anion standard for anion). During the campaign the AIM required routine maintenance consisting in changing the denuder cellulose membrane and performing an instrument blank and a single point external standard every two weeks, performing a multipoint external standard set and cleaning the cyclone inlet monthly. The calibration of the OCEC field analyzer was performed using a multi point Sucrose Check (Sucrose, Sigma-Aldrich). A 90 min dynamic blank was performed for one day placing a filter pack with 47 mm Teflon filter between the stainless steel tubing and the PM_{2.5} inlet. The routine maintenance of the OCEC field analyzer consisted in changing the quartz fiber filters used for sample collection and then performing an instrument blank and a single point external standard weekly, cleaning the cyclone inlet and performing a multipoint external standard set monthly. During the routine operations the monitors did not acquire ambient data.

Ambient PM_{2.5} samples for OC and EC analysis were collected on a daily basis over 24 hours, with start time at 00:01 UTC. Particles were collected on quartz micro-fibre filters (Pall 2500-QAT-UP 7204 8 × 10 in) using a high volume sampler with flow rates of $68 \pm 1 \text{ m}^3 \text{ h}^{-1}$ (Dust sampler High Volume, Tisch-Analitica). The filters were stored in a freezer (at -20°C) until the analysis was performed with a Sunset Laboratory Dual-Optical Carbonaceous Analyzer (Sunset Laboratory) following the EUSAAR_2 thermal optical transmittance protocol (Cavalli *et al.*, 2010). More details can be found in Malaguti *et al.* (2015).



Fig. 1. External view of the trailer and of the reference sampler at the Trisaia site (a), the AIM and Sunset inlets (red circles) located on top of the trailer (b), AIM (c) and Sunset (d) monitors inside the trailer.

Comparison of Online Monitor with Offline Filter-Based Measurements

The percentage difference (%diff) between the online and offline concentrations was computed for each day as follows:

$$\%diff = [(24\text{hrs average online} - \text{offline})/\text{offline}] \times 100 \quad (1)$$

The percentage differences are reported as mean, minimum and maximum for each aerosol species investigated. It should be noted that the percentage differences are sensitive to the magnitude of the concentration: little difference between the measurements can correspond to large percentage difference at low ambient concentration.

The completeness of monitor data was determined for the entire campaign on hourly and daily basis: the former was

calculated as the percentage of online valid data divided by the total numbers of campaign hours while the latter was calculated as the percentage of days with online valid data for at least half of the 24 hours divided by the total numbers of campaign days

Achievement of comparability between the two measurements was also investigated in this study. The comparability was evaluated for each inorganic species and carbonaceous aerosols by applying the linear regression using offline data as the independent variable and the online data as the dependent variable:

$$Y_i = mX_i + b \quad (2)$$

where Y_i is the daily average of online data and X_i is the offline data for each day. The slope (m), the intercept (b)

and the coefficient of determination (R^2) values of the linear regression allow assessing the comparability and the degree of correlation.

RESULTS AND DISCUSSION

Online Measurements

The hourly AIM measurements of NH_4^+ , SO_4^{2-} and NO_3^- during the whole campaign are plotted in Fig. 2(a). The hourly time series of these secondary inorganic ions show periods of high concentrations lasting from several hours to few days, rather than hourly spikes.

SO_4^{2-} was the most abundant ion followed by NH_4^+ , and NO_3^- . The peak concentrations of NH_4^+ , and often that of NO_3^- as well, coincided with peak concentrations of SO_4^{2-} . Moreover, it can be noticed that all the highest peak concentrations occurred during the periods with Saharan dust transport. The enhancement of the secondary inorganic ions during Saharan dust events has been observed also in the southeastern Spanish Mediterranean coast (Galindo *et al.*, 2008; Nicolas *et al.*, 2009) and in the French Alps (Aymoz *et al.*, 2004).

SO_4^{2-} hourly concentrations were always above the LOD and ranging from 0.34 to 5.28 $\mu\text{g m}^{-3}$ with an average value of 1.87 $\mu\text{g m}^{-3}$, while the NH_4^+ concentrations had 29 hourly values below the LOD and, consequently, they were excluded from the analysis; the readings under the LOD occurred on June 1 (7 readings), June 2 (3 readings), June 4 (2 readings), June 17 (8 readings) and June 21 (9 readings). NH_4^+ hourly concentrations above the LOD ranged from 0.11 to 3.36 $\mu\text{g m}^{-3}$ with an average value of 1.03 $\mu\text{g m}^{-3}$.

As for SO_4^{2-} , NO_3^- hourly concentrations were always above the LOD and ranging from 0.13 to 2.03 $\mu\text{g m}^{-3}$ with an average value of 0.52 $\mu\text{g m}^{-3}$.

Due to the routine maintenance operations of the monitor, a total of 28 readings have been lost for the three ions, thus the data completeness of the AIM was 98% both for SO_4^{2-} and NO_3^- and 96% for NH_4^+ during the campaign. The hourly concentrations of the primary ions (Na^+ , Cl^- , K^+ , Ca^{2+} and Mg^{2+}) were frequently closed or below the LOD values of AIM monitor, therefore they were not analyzed in this study.

Measuring the carbonaceous species with high time resolution allows a better understanding of their relationship with natural/anthropogenic sources and/or meteorological conditions. Up to now the few studies based on high time resolution measurements refer to urban areas (Venkatachari *et al.*, 2006; Lin *et al.*, 2009; Yu *et al.*, 2009; Sciare *et al.*, 2011; Timonen *et al.*, 2014).

A two-hourly cycle for OCEC field measurements was decided for the Trisaia site based on the very low local EC mass loadings observed with an hour cycle measurements performed during a test week conducted before the beginning of the campaign. Figs. 2(b)–2(d) shows the temporal evolution of OCEC field analyzer two-hourly readings for TC, thermal and optical OC and thermal and optical EC respectively. As for the AIM, OCEC field analyzer measured high concentrations for periods lasting from several hours to few days. The statistics of these measurements and the

comparability between the thermal and optical OC and the thermal and optical EC measurements has been discussed in Malaguti *et al.* (2013). Briefly, for TC the two-hourly concentrations ranged from 0.26 to 6.34 $\mu\text{gC m}^{-3}$ with an average value of 2.11 $\mu\text{gC m}^{-3}$. OC was the most abundant carbonaceous fraction. Figs. 2(b) and 2(c) also shows that TC and OC concentrations were similar and the peak concentrations always coincided.

Thermal and optical OC two-hourly concentrations were always above the corresponding LOD, their values were similar and ranged from 0.26 to 5.38 $\mu\text{gC m}^{-3}$ (1.69 $\mu\text{gC m}^{-3}$ average concentration) and from 0.20 to 5.56 (1.76 $\mu\text{gC m}^{-3}$ average concentration) respectively.

Thermal EC two-hourly concentrations were under the LOD value for 134 times; this occurred from May 7 to May 23 (56 readings) and from June 1 to June 30 (78 readings) and it is not related to the presence of dust (Fig. 2(d)). The thermal EC concentrations ranged from 0.04 to 1.55 $\mu\text{gC m}^{-3}$ with an average value of 0.44 $\mu\text{gC m}^{-3}$. Optical EC two-hourly concentrations were always above the LOD and ranging from 0.04 to 1.27 $\mu\text{gC m}^{-3}$ with an average value of 0.34 $\mu\text{gC m}^{-3}$.

Due to the routine maintenance operations of the monitor, a total of 39 readings have been lost for TC, thermal and optical OC and thermal and optical EC. The data completeness of the OCEC online measurements was 75.5% for thermal EC and 94.4% for the other measurements. The optical EC measurements are considered more reliable at sites with low concentrations (Timonen *et al.*, 2014) since their data completeness is higher than for thermal EC measurements.

The carbonate carbon (CC) measurements were performed only on offline samples since the hourly Ca^{2+} and Mg^{2+} concentrations in $\text{PM}_{2.5}$ were below LOD. On the other hand, the estimations of CC based on the thermal optical sunset OCEC analyzer software may introduce high errors due to the low peaks of online concentrations. More details about this issue may be found in Malaguti *et al.* (2015).

Comparison of Online and Offline Measurements

Comparison between inorganic soluble ions concentrations of filter-based analysis and online instruments were shown in very few studies. Generally, sulfate and ammonium concentrations measured with online methods showed a good correlation with filter based measurements but the agreement was poor for nitrate (Orsini *et al.*, 2003).

Table 2 shows the daily mean, maximum and minimum of online and offline measurements during dust and non-dust periods for NH_4^+ , SO_4^{2-} and NO_3^- concentrations. Figs. 3(a)–3(c) shows the daily average concentrations from AIM and from the corresponding daily-integrated filter-based samples. The comparability and correlation between the measurements assessed based on the Eq. (2) is shown in Figs. 3(d)–3(e) and in Table 3 are summarized the number of measurements used, the slope and the intercept with their associated 95% CI values and the R^2 values.

Most of the times, high and low concentrations measured by the online and offline methods occurred simultaneously for NH_4^+ (Fig. 3(a)). It can be noticed that the highest levels of ammonium concentrations were observed on May

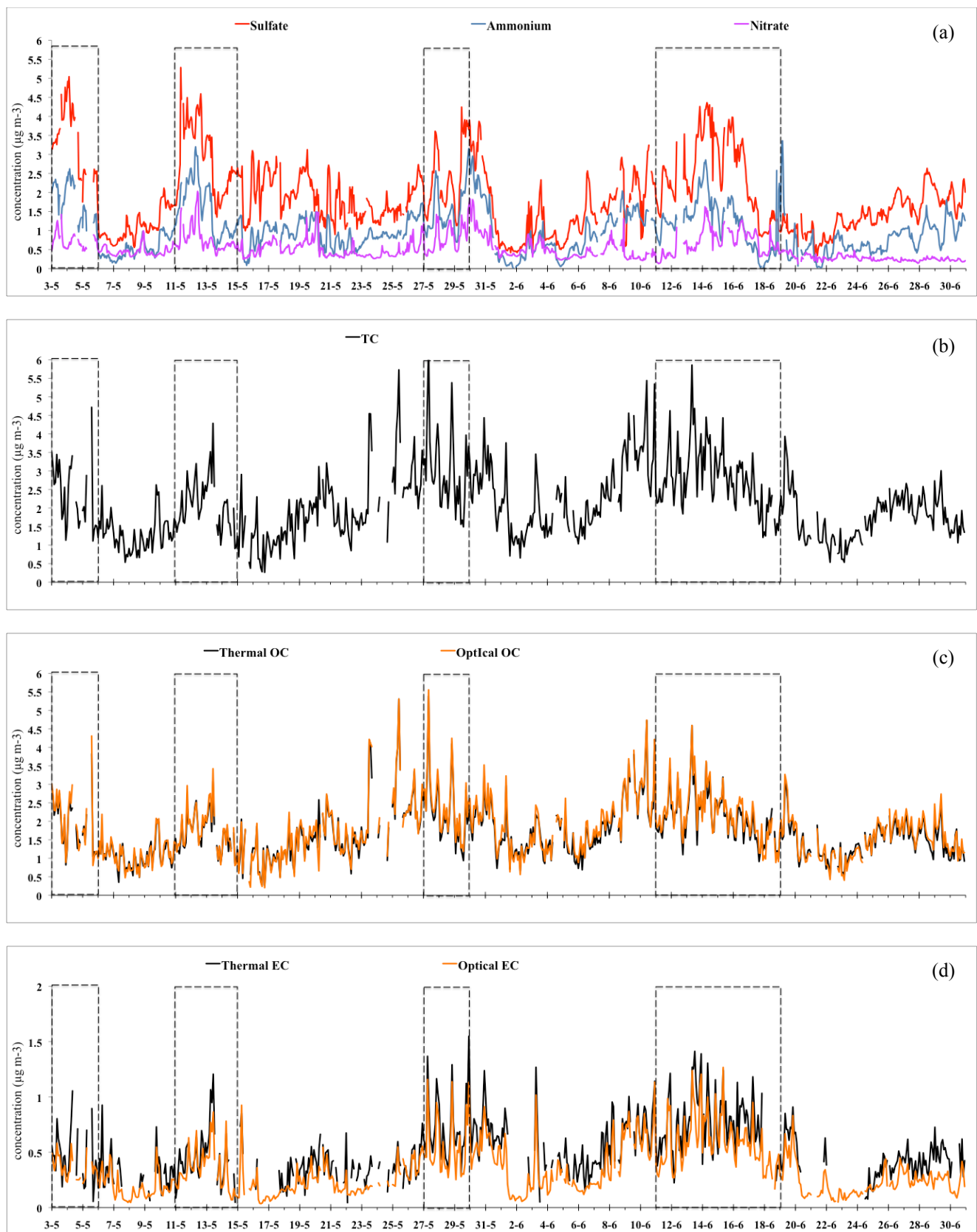


Fig. 2. AIM hourly measurements (a) for ammonium (1358 readings), sulfate (1387 readings) and nitrate (1387 readings), during the whole campaign (1415 total readings); OCEC field analyzer two-hourly measurements for TC (669 readings) (b), Thermal (669 readings) and Optical (669 readings) OC (c) and Thermal (535 readings) and Optical EC (669 readings) (d) during the whole campaign (708 total readings). Periods with Saharan dust transport are identified by the rectangles.

Table 2. Mean and range of the daily values of ions and carbonaceous fractions reported by the filter-based methods (off) and by the AIM and the OCEC field analyzer (on) during non-dust (40 days) and dust (19 days) periods. The grey shadows lines are referred to monitor data.

	Mean $\mu\text{g m}^{-3}$		Maximum $\mu\text{g m}^{-3}$		Minimum $\mu\text{g m}^{-3}$	
	non-dust	dust	non-dust	dust	non-dust	dust
NH ₄ on	0.82	1.42	2.28	2.23	0.14	0.41
NH ₄ off	0.88	1.54	2.18	2.42	0.24	0.50
SO ₄ on	1.54	2.60	3.15	3.78	0.54	1.08
SO ₄ off	2.12	4.32	5.98	7.21	0.55	1.26
NO ₃ on	0.43	0.72	1.17	1.11	0.20	0.30
NO ₃ off	0.08	0.12	0.16	0.24	0.04	0.07

	Mean $\mu\text{gC m}^{-3}$		Maximum $\mu\text{gC m}^{-3}$		Minimum $\mu\text{gC m}^{-3}$	
	non-dust	dust	non-dust	dust	non-dust	dust
Th-OC on	1.62	1.85	2.94	2.74	0.82	1.12
Opt-OCon	1.68	1.94	3.04	2.95	0.84	1.04
Th-OC off	2.46	2.68	4.21	3.66	1.26	1.48
Th-EC on	0.35	0.57	0.77	1.04	0.01	0.22
Opt-ECon	0.27	0.46	0.71	0.82	0.11	0.20
Th-EC off	0.28	0.45	0.66	0.80	0.09	0.20

3–4, May 12, May 30 and June 14, both for online and offline measurements. It can be observed that the average concentrations were higher during the dust period (1.42 and 1.54 $\mu\text{g m}^{-3}$ for online and offline, respectively) than during the non-dust one (0.82 and 0.88 $\mu\text{g m}^{-3}$ for online and offline, respectively) (Table 2). The mean values of the percentage difference between the AIM and the filter-based data were $-6.09 \pm 14.14\%$ and $-2.33 \pm 30.49\%$ for non-dust and dust periods, respectively (Table 3). The larger percent differences during non-dust period with respect to dust one were mostly related to the small concentrations of the filter-based data during non-dust period rather than due to a significant difference in measured concentrations (Fig. 3(a)). The comparability and correlation of NH₄⁺ measurements were good, particularly during non-dust period, as showed by the slope value close to 1 (0.959 ± 0.084), the intercept close to zero value (-0.015 ± 0.082) and a regression coefficient of determination (R^2) of 0.930 (Fig. 2(d)); similar agreement was observed at rural sites during warm season by Bae *et al.* (2007). The AIM and the filter-based measurements differ during the dust period occurred in June (Fig. 3(a)) and their comparability is characterized by a slope of 0.732 ± 0.158 , a positive intercept $+0.289 \pm 0.263 \mu\text{g m}^{-3}$ and a coefficient of determination values (R^2) of 0.833 (Table 4). This may be due to reactions between sulfuric acid (H₂SO₄) formed on smaller particles and surface-adsorbed or gas-phase ammonia (NH₃) to form (NH₄)₂SO₄ (Zhang *et al.*, 2000). The reaction explains the increase of both ammonium and sulfate concentrations in aerosols in the presence of dust (Nicolas *et al.*, 2009).

The maximum values filter-based measurements of SO₄²⁻ were higher than those from the AIM instrument mainly during the dust events (Fig. 3(b)), as confirmed by the mean and maximum concentrations reported in Table 2. The minimum concentrations are similar for both methods independently from the presence of dust. The mean values

of the percentage difference between the two methods (Table 3) were $-21.03 \pm 15.09\%$ and $35.47 \pm 12.69\%$ for non-dust and dust periods, respectively. Higher SO₄²⁻ concentrations on filter-based samples with respect to online measurements could be due to positive sampling artefact of the filter because of the absorption of sulphur dioxide (SO₂) by the alkaline particles collected on filter (Nie *et al.*, 2010) or, as already mentioned, because of the reactions between sulfuric acid formed on smaller particles and gas-phase ammonia (Nicolas *et al.*, 2009). The linear regression slope less than 0.5 and the intercept values significantly higher than 0 (0.47 ± 0.065 and $+0.547 \pm 0.155 \mu\text{g m}^{-3}$ for non-dust data; 0.446 ± 0.058 and $+0.672 \pm 0.275 \mu\text{g m}^{-3}$ for dust data) show significant differences between measurements as already discussed in Witting *et al.* (2004). However, the online and offline SO₄²⁻ measurements showed a good correlation, as indicated by R^2 ranging from 0.844 to 0.931 (Table 4) for non-dust and dust periods, respectively.

The NO₃⁻ concentrations measured by AIM were higher than the filter-based data during the whole campaign (Fig. 3(c)). The differences are shown in Table 2 and Table 3 for non-dust and dust periods, respectively. In spite of the high mean percentage difference between the measurements ($490.9 \pm 205.57\%$ and $521.8 \pm 229.33\%$ for non-dust and dust periods), the filter data peaks occurred simultaneously to the AIM peaks concentration: from May to June 8 (Fig. 3(c)). After, June 9 the offline concentrations were low and almost constant until the end of campaign. Nitrate concentrations measured by high time resolution systems higher than filter-based concentrations were reported in other studies (Kuokka *et al.*, 2007; Chow *et al.*, 2008) and were explained by nitrate evaporation from the filter samples (Pakkanen and Hillamo, 2002; Schaap *et al.*, 2004; Kuokka *et al.*, 2007). Evaporation loss of aerosol nitrate from the quartz filters may be severe during the initial stage of sampling, particularly when upstream particles concentrations

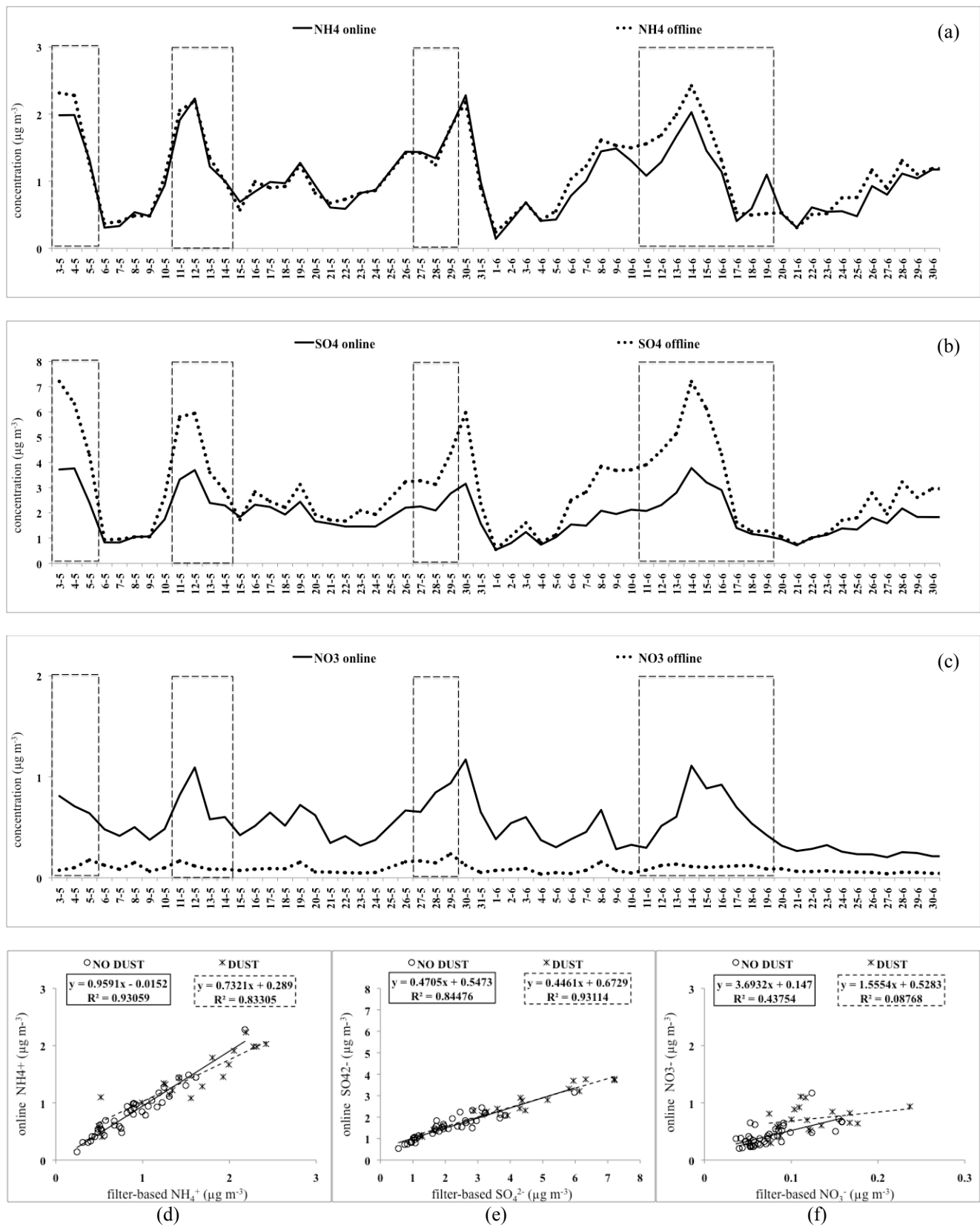


Fig. 3. Temporal trends and linear regressions of the daily average results from AIM and of the corresponding daily-integrated filter based samples for NH_4^+ (a, d), SO_4^{2-} (b, e) and NO_3^- (c, f). The hourly concentrations of the AIM were averaged to match the 24-hr filter-based samples; periods with Saharan dust transport are identified by the rectangles. Linear regressions were calculated by fitting online and offline data for the dust and non-dust events.

Table 3. Difference percentage of monitor results relative to filter-based results for non-dust and dust periods.

	Number of data points	Difference % Mean (\pm SD)
NON-DUST NH ₄	40	-6,09 (\pm 14.14)
DUST NH ₄	19	-2,33 (\pm 30.49)
NON-DUST SO ₄	40	-21,03 (\pm 15.09)
DUST SO ₄	19	-35,47 (\pm 12.69)
NON-DUST NO ₃	40	490,90 (\pm 205.57)
DUST NO ₃	19	521.80 (\pm 229.33)
NON-DUST Th-OC	40	-32.50 (\pm 18.45)
DUST Th-OC	19	-29.19 (\pm 19.08)
NON-DUST Opt-OC	40	-30.02 (\pm 19.01)
DUST Opt-OC	19	-26.34 (\pm 19.65)
NON-DUST Th-EC	40	25.62 (\pm 42.49)
DUST Th-EC	19	31.79 (\pm 35.04)
NON-DUST Opt-EC	40	-1.20 (\pm 22.70)
DUST Opt-EC	19	6.79 (\pm 30.53)

Table 4. Results of linear regression of the monitor daily average versus the corresponding reference results for non-dust and dust periods. For each parameter the number of data points in the regression, the slope and intercept of the regression line and the R² value are shown. The slope and intercept results are reported with their associated 95% CI values.

	Number of data points	Slope (\pm 95% CI)	Intercept ($\mu\text{g m}^{-3}$) (\pm 95% CI)	Coefficient of determination (R ²)
NON-DUST NH ₄	40	0,959 \pm 0.084	-0.015 \pm 0.082	0.930
DUST NH ₄	19	0.732 \pm 0.158	+0.289 \pm 0.263	0.833
NON-DUST SO ₄	40	0.470 \pm 0.065	+0.547 \pm 0.155	0.844
DUST SO ₄	19	0.446 \pm 0.058	+0.672 \pm 0.275	0.931
NON-DUST NO ₃	40	3.693 \pm 1.358	+0.146 \pm 0.113	0.437
DUST NO ₃	19	1.555 \pm 2.433	+0.528 \pm 0.315	0.087
NON-DUST Th-OC	40	0.537 \pm 0.179	+0.298 \pm 0.461	0.483
DUST Th-OC	19	0.406 \pm 0.297	+0.760 \pm 0.817	0.304
NON-DUST Opt-OC	40	0.587 \pm 0.182	+0.241 \pm 0.468	0.520
DUST Opt-OC	19	0.495 \pm 0.325	+0.607 \pm 0.892	0.353
NON-DUST Th-EC	40	1.274 \pm 0.208	-0.001 \pm 0.064	0.797
DUST Th-EC	19	1.016 \pm 0.316	+0.116 \pm 0.153	0.707
NON-DUST Opt-EC	40	1.011 \pm 0.153	-0.008 \pm 0.047	0.819
DUST Opt-EC	19	0.779 \pm 0.272	+0.112 \pm 0.131	0.657

are low (Cheng *et al.*, 1997). This increases with the decrease of humidity and the increase of temperature (Moya *et al.*, 2001; Takahama *et al.*, 2004; Chow *et al.*, 2005; Chow *et al.*, 2006). Complete evaporation was observed at temperature exceeding 25°C (Schaap *et al.*, 2004). Also Chow *et al.* (2008) reported that the volatilized NO₃⁻ loss from quartz-fiber filter accounted for more than 80% during warm season sampling for measurements taken in central California.

During the sampling period of May and June in Trisaia, the temperatures were higher than 20°C and therefore promoted the loss of nitrate from filter by evaporation (as in Wu and Wang, 2007; Chow *et al.*, 2008). Shaap *et al.* (2004) suggested that losses during a 24-h sampling period is not only a function of ambient conditions and sampling apparatus, but also depend on the sampling strategy. The filters changed in the morning will sample night nitrate and the losses may have occurred at the higher temperatures in the afternoon of the previous day, while the filters changed in the afternoon or evening may lost the nitrate sampled during the night since the evaporation increases with the

increase of temperatures during the day. In our case, sampling time was from 0:00 to midnight. Therefore, the offline measurements might be affected by a negative sampling artefact due to the volatilization of nitrate collected during the first part of the day in all the days with temperatures higher than 20–25°C.

For all the above reasons, the regression data for NO₃⁻ (Table 4) showed a better correlation during non-dust period (R² = 0.437) than during dust period (R² = 0.087).

Table 2 summarize the mean, maximum and minimum of online and offline OCEC measurements during dust and non-dust periods. Figs. 4(a)–4(b) shows the daily evolution of OC and EC online and offline concentrations.

For EC, the online and offline methods gave quite similar results (Fig. 4(a)), as confirmed also by the statistic values reported in Table 2. This good agreement suggests that the shedding of denuder material (activated carbon which would be classified as EC in TOT analysis) was negligible. The daily variation of EC offline measurements was more comparable with the online optical EC than with the online

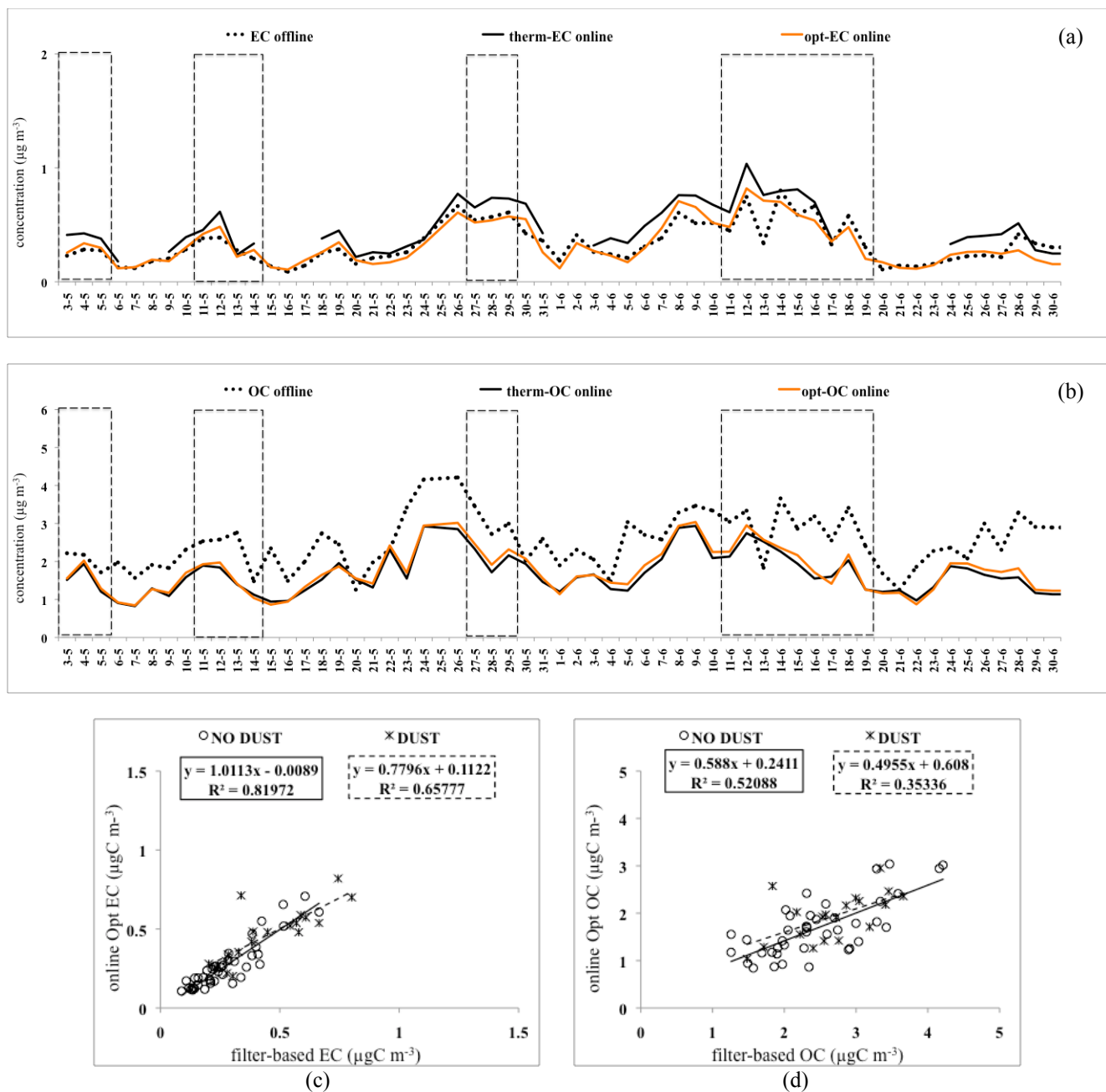


Fig. 4. Temporal trends and linear regressions of the daily average results from the OCEC field analyser and of the corresponding daily-integrated filter based samples for EC (a, c) and OC (b, d). The two-hourly concentrations of the field analyser were averaged to match the 24-hr filter-based samples; periods with Saharan dust transport are identified by the rectangles. Linear regressions were calculated by fitting online and offline data for the dust and non-dust events.

thermal EC. The low offline concentration occurred on June 13 could be explained as a negative artefact related to the filter sampling and/or handling (e.g., non-uniform particles deposit or particles lost during sample handling). The lack of online thermal EC data corresponded to days with monitor readings less of half data relative to 24-hours sampling. As discussed above, at this site, the thermal EC has a data completeness lower (80%) than for the optical (100%) EC readings and therefore, the optical data (optical EC and optical OC) were used for assess the comparability between methods (Figs. 4(c)–4(f) and Table 3).

The mean, minimum and maximum EC concentrations (Table 2) are similar for both methods with little difference between non-dust and dust periods as confirmed also by the mean values of the percentage difference showed in Table 3 ($-1.2 \pm 22.70\%$ and $6.79 \pm 30.53\%$ for non-dust and dust periods, respectively). The correlation (Fig. 4(c)) was better for non-dust (R^2 0.819) than dust (R^2 0.657) data, as showed by the slope and intercept values resumed in Table 4.

OC filter-based measurements were higher than those from the field analyser for the whole campaign (Fig. 4(b))

as confirmed by the mean, minimum and maximum concentrations resumed in Table 2 and by the mean values of the percentage difference of $-30.02 \pm 19.01\%$ and $-26.34 \pm 19.63\%$ for non-dust and dust periods respectively (Table 3). The good agreement between online and offline data for EC indicates that the difference in OC measurements may be due to positive artefacts on the filters and not due to errors in flow rate measurements or other systematic differences in sampling and analysis technique.

The OC regression was better for non-dust (R^2 0.819) than dust (R^2 0.657) data (Fig. 3(d)). The slope values ranging from 0.587 ± 0.182 to 0.495 ± 0.325 and the intercept values significantly higher than zero (Table 4) were related to the higher filter concentrations respect to the online readings.

The high concentrations detected on the undened filters might be related to the positive sampling artefact due to the absorption of gases on filters (Mader et al., 2003; Viana et al., 2006; Vecchi et al., 2009; Cheng et al., 2010). Aurela et al. (2011) estimated the amount of gaseous compounds absorbed on the bare filter using a tandem filter method showing that the amount of gaseous OC absorbed on the filter, on annual basis, ranged from 3 to 39% in a background area of Southern Finland and was higher during summer than winter and independent of OC concentration. The positive OC artefact estimated by Vecchi et al. (2009) in Milan ranged from 39% in summer to 23% in winter. Similar percentage of differences between OC online and offline measurements are also reported in Table 3.

CONCLUSIONS

This study shows a first comparison between online and offline methods of measuring secondary inorganic ions and carbonaceous aerosols at low polluted site influenced by dust transport from Saharan desert. During the two months investigated (May and June 2010), it was observed the same daily evolution of online measurements with respect to the offline ones: both methods exhibited high concentrations in the presence of Saharan dust. This behaviour was less evident for NO_3^- concentrations measured offline since these concentrations were very low probably due to negative sampling artefacts. The significant differences between the concentrations of NO_3^- , NH_4^- and SO_4^{2-} measured during the days with dust transport with respect to those measured in days without dust suggested that the enhancement of concentration may be due to the advection of more polluted air mass from the Mediterranean sea (due to naval traffic) or due to more uptake of inorganic gases by the dust particles. The online measurements of AIM-IC show similar values with NH_4^- offline concentrations, lower values than SO_4^{2-} offline concentrations in the presence of dust and much higher values than NO_3^- offline concentrations, in particular, in the presence of dust.

Online and offline measurements of EC are in good agreement during the whole period of campaign. The increase of EC concentrations, a primary anthropogenic pollutant mainly emitted by traffic and residential combustion, during the advection of dust is supporting the hypothesis that other anthropogenic pollutants emitted by sea traffic are transported

to the site. The offline OC concentrations are constantly higher than online concentrations, up to ca. 30%, and this is explained by a positive artefacts of offline measurements.

The differences shown in this study are mostly due to the artefacts related to the offline methods; therefore, the use of online instruments (AIM-IC, OCEC field analyser) at such a site is the only alternative to have valuable information for process studies, even if the time resolution decrease to two hours for OCEC field analyser.

REFERENCES

- Aurela, M., Saarikoski, S., Timonen, H., Aalto, P., Keronen, P., Saarnio, K., Teinila, K., Kulmala, M. and Hillamo, R. (2011). Carbonaceous Aerosol at a Forested and an Urban Background Sites in Southern Finland. *Atmos. Environ.* 41: 1394–1401.
- Aymoz, G., Jaffrezo, J.L., Jacob, V., Colomb, A. and George Ch. (2004). Evolution of Organic and Inorganic Components of Aerosol during a Saharan Dust Episode Observed in the French Alps. *Atmos. Chem. Phys.* 4: 2499–2512.
- Bae, M.S., Demerjian, K.L., Schwab, J.J., Weimer, J.H., Zhou, X., Rhoads, K. and Orsini D. (2007). Intercomparison of Real Time Ammonium Measurements at Urban and Rural Locations in New York. *Aerosol Sci. Technol.* 41: 329–341.
- Bauer, J.J., Yu, X.Y., Cary, R., Laulainen, N.S. and Berkowitz, C. (2009). Characterization of the Sunset Semi-Continuous Carbon Aerosol Analyzer. *J. Air Waste Manage. Assoc.* 59: 826–833.
- Brink, H., Otjes, R., Jongejan, P. and Slanina, S. (2007). An Instrument for Semi-continuous Monitoring of the Size-distribution of Nitrate, Ammonium, Sulphate and Chloride in Aerosol. *Atmos. Environ.* 41: 2768–2779.
- Cavalli, F., Viana, M., Yttri, K.E., Genberg, J. and Putaud, J.P. (2010). Toward a Standardised Thermal-optical Protocol for Measuring Atmospheric Organic and Elemental carbon, the EUSAAR Protocol. *Atmos. Meas. Tech.* 3: 79–89.
- Cheng, Y., He, K.B., Duan F.K., Zheng, M., Ma Y.L., Tan, J.H., Du Z.Y., Vartiainen E., Kulmala M., Skorokhod A.I., Elansky N.F. and Belikov, I.B. (2010). Improved Measurement of Carbonaceous Aerosol: Evaluation of the Sampling Artifacts and Inter-comparison of the Thermal-optical Analysis Methods. *Atmos. Chem. Phys.* 10: 8533–8548.
- Cheng, Y.H. and Tsai, C.J. (1997). Evaporation Loss of Ammonium Nitrate Particles during Filter Sampling. *J. Aerosol. Sci.* 28: 1553–1567.
- Chow, J.C. (1995). Measurement Methods to Determine Compliance with Ambient Air Quality Standards for Suspended Particles. *J. Air Waste Manage. Assoc.* 45: 320–382.
- Chow, J.C., Watson, J.G. and Lowenthal, D.H. (2005). Loss of $\text{PM}_{2.5}$ Nitrate from Filter Samples in Central California. *J. Air Waste Manage. Assoc.* 55: 1158–1168.
- Chow, J.C., Chen, L.-W.A., Watson, J.G., Lowenthal, D.H., Magliano, K.A., Turkiewicz, K. and Lehrman, D.E. (2006).

- PM_{2.5} Chemical Composition and Spatiotemporal Variability during the California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS). *J. Geophys. Res.* 111, D10S04, doi: 10.1029/2005JD006457.
- Chow, J.C., Watson, J.G., Lowenthal, D.H., Park, K., Doraiswamy, P., Bowers, K. and Bode, R. (2008). Continuous and Filter-based Measurement of PM_{2.5} Nitrate and Sulfate at the Fresno Supersite. *Environ. Monit. Assess.* 144: 179–189.
- Galindo, N., Nicolas, J.F., Yubero, E., Caballero, S., Pastor, C. and Crespo, J. (2008). Factors Affecting Levels of Aerosol Sulfate and Nitrate on the Western Mediterranean Coast. *Atmos. Res.* 88: 305–313.
- Gao, X., Yang, L., Cheng, S., Gao, R., Zhou, Y., Xue, L., Shou, Y., Wang, J., Wang, X., Nie, W., Pengju, X. and Wang, W. (2011). Semi-continuous Measurement of Water-soluble Ions in PM_{2.5} in Jinan, China: Temporal Variations and Source Apportionments. *Atmos. Environ.* 45: 6048–6056.
- Godri, K.J., Evans, G.J., Slowik, J., Knox, A., Abbatt, J., Brook, J., Dann, T. and Dabek-Zlotorzynska, E. (2009). Evaluation and Application of a Semi-continuous Chemical Characterization System for Water Soluble Inorganic PM_{2.5} and Associated Precursor Gases. *Atmos. Meas. Tech.* 2: 65–80.
- Jeong, C.H., Lee, D.W., Kim, E. and Hopke, P.K. (2004). Measurement of Real-time PM_{2.5} Mass, Sulfate, and Carbonaceous Aerosols at the Multiple Monitoring Sites. *Atmos. Environ.* 38: 5247–5256.
- Kuokka, S., Teinilä, K., Saarnio, K., Aurela, M., Sillanpää, M., Hillamo, R., Kerminen, V.M., Vartiainen, E., Kulmala, M., Skorokhod, A.I., Elansky, N.F. and Belikov, I.B. (2007). Chemical Composition of Atmospheric Aerosols between Moscow and Valdivostok. *Atmos. Chem. Phys.* 7: 4793–4805.
- Lee, T., Yu, X.Y., Kreidenweis, S.M., Malm, W.C. and Collett, J.L. (2008). Semi-continuous Measurement of PM_{2.5} Ionic Composition at Several Rural Locations in the United States. *Atmos. Environ.* 42: 6655–6669.
- Lin, P., Hu, M., Deng, Z., Slanina, J., Han, S., Kondo, Y., Takegawa, N., Miyazaki, Y., Zhao, Y. and Sugimoto, N. (2009). Seasonal and Diurnal Variations of Organic Carbon in PM_{2.5} in Beijing and the Estimation of Secondary Organic Carbon. *J. Geophys. Res.* 114: D00G11.
- Ma, Y., Weber, R.J., Maxwell-Meier, K., Orsini, D.A., Lee, Y.N., Huebert, B.J., Howell, S.G., Bertram, T., Talbot, R.W., Dibb, J.E. and Scheuer, E. (2004). Intercomparison of Airborne Measurements of Aerosol Ionic Chemical Composition during TRACE-P and ACE-Asia. *J. Geophys. Res.* 109.
- Mader, B.T., Schauer, J.J., Seinfeld, J.H., Flagan, R.C., Yu, J.Z., Yang, H., Lim, H.-J., Turpin, B.J., Deminter, J.T., Heidemann, G., Bae, M.S., Quinn, P., Bates, T., Eatough, D.J., Huebert, B.J., Bertram, T. and Howell, S. (2003). Sampling Methods Used for the Collection of Particle-phase Organic and Elemental Carbon during ACE-Asia. *Atmos. Environ.* 37: 1435–1449.
- Makkonen, U., Virkkula, A., Mäntykenttä, J., Hakola, H., Keronen, P., Vakkari, V. and Aalto, P.P. (2012). Semi-continuous Gas and Inorganic Aerosol Measurements at a Finnish Urban Site: Comparisons with Filters, Nitrogen in Aerosol Gas Phases, and Aerosol Acidity. *Atmos. Chem. Phys.* 12: 5617–5631.
- Malaguti, A., Mircea, M., La Torretta, T.M.G., Piersanti, A., Salvi, S., Zanini, G., Telloli, C., Salfi, F. and Berico, M. (2013). Fine Carbonaceous Aerosol Characteristics at a Coastal Rural Site in the Central Mediterranean as Given by OCEC Online Measurements. *J. Aerosol Sci.* 56: 78–87.
- Malaguti, A., Mircea, M., La Torretta, T.M.G., Telloli, C., Petralia, E., Stracquadiano, M. and Berico, M. (2015). Chemical Composition of Fine and Coarse Aerosol Particles in the Central Mediterranean area during Dust and Non-dust Conditions. *Aerosol Air Qual. Res.* 15: 410–425.
- Markovic, M.Z., VandenBoer, T.C. and Murphy, J.G. (2012). Characterization and Optimization of an Online System for the Simultaneous Measurement of Atmospheric Water-soluble Constituents in the Gas and Particle Phases. *J. Environ. Monit.* 14: 1872–1874.
- Morishita, M., Keeler, G.J., Kamal, A.S., Wagner, J.G., Harkema, J.R. and Rohr, A.C. (2011). Identification of Ambient PM_{2.5} Sources and Analysis Pollution Episodes in Detroit, Michigan Using Highly Time-resolved Measurements. *Atmos. Environ.* 45: 1627–1637.
- Moya, M., Ansari, A.S. and Pandis, S.N. (2001). Partitioning of Nitrate and Ammonium between the Gas and Particulate Phases during the 1997 IMADA-AVER Study in Mexico City. *Atmos. Environ.* 35: 1791–1804.
- Nicolas, J.F., Galindo, N., Yubero, E., Pastor, C., Esclapez, R. and Crespo, J. (2009). Aerosol Inorganic Ions in a Semiarid Region on the Southeastern Spanish Mediterranean Coast. *Water Air Soil Pollut.* 201: 149–159.
- Nie, W., Wang, T., Gao, X., Pathak, R.K., Wang, X., Gao, R., Zhang, Q., Yang, L. and Wang, W. (2010). Comparison among Filter-based, Impactor-based and Continuous Techniques for Measuring Atmospheric Fine Sulfate and Nitrate. *Atmos. Environ.* 44: 4396–4403.
- Orsini, D.A., Ma, Y., Sullivan, A., Sierau, B., Baumann, K. and Weber, R.J. (2003). Refinements to the Particle-into-liquid Sampler (PILS) for Ground and Airborne Measurements of Water Soluble Aerosol Composition. *Atmos. Environ.* 37: 1243–1259.
- Pakkanen, T.A. and Hillamo R. (2002). Comparison of Sampling Artifacts and Ion Balances for a Berner Low-pressure Impactor and a Virtual Impactor. *Boreal Environ. Res.* 7: 129–140.
- Park, S.S., Jung, S.A., Gong, B.J., Cho, S.Y. and Lee, S.J. (2013). Characteristics of PM_{2.5} Haze Episodes Revealed by Highly Time-Resolved Measurements at an Air Pollution Monitoring Supersite in Korea. *Aerosol Air Qual. Res.* 13: 957–976.
- Pathak, R.K. and Chan, C.K. (2005). Inter-particle and Gas-particle Interactions in Sampling Artifacts of PM_{2.5} in Filter-based Samplers. *Atmos. Environ.* 39: 1597–1607.
- Rumsey, I.C., Cowen, K.A., Walker J.T., Kelly, T.J., Hanft E.A., Mishoe, K., Rogers C., Proost R., Beachley G.M., Lear, G., Frelink, T. and Otjes, R.P. (2014). An

- Assessment of the Performance of the Monitor for Aerosols and Gases in Ambient Air (MARGA): A Semi-continuous Method for Soluble Compounds. *Atmos. Chem. Phys.* 14: 5639–5658.
- Schaap, M., Spindler, G., Schulz, M., Acker, K., Maenhaut, W., Berner, A., Wieprecht, W., Streit, N., Müller, K., Brüggemann, E., Chi, X., Putaud, J.P., Hitztenberger, R., Puxbaum, H., Baltensperger, U. and ten Brink, H. (2004). Artefacts in the Sampling of Nitrate Studied in the “INTERCOMP” Campaigns of EUROTRAC-AEROSOL. *Atmos. Environ.* 38: 6487–6496.
- Sciare, J., d’Argouges, O., Sarda-Estève, R., Gaimoz, C., Dolgorouky, C., Bonnaire, N., Favez, O., Bonsang, B. and Gros, V. (2011). Large Contribution of Water-insoluble Secondary Organic Aerosol in the Region of Paris (France) during Wintertime. *J. Geophys. Res.* 116: D22203.
- Sorooshian, A., Brechtel, F.J., Ma, Y., Weber, R.J., Corless, A., Flagan, R.C. and Seinfeld, J.H. (2006). Modeling and Characterization of a Particle-into-Liquid Sampler (PILS). *Aerosol Sci. Technol.* 40: 396–409.
- Takahama, S., Witting, A.E., Vayenas, D.R., Davidson, C.I. and Pandis, S.N. (2004). Modeling the Diurnal Variation of Nitrate during the Pittsburgh Air Quality Study. *J. Geophys. Res.* 109: D16S06, doi: 10.1029/2003JD004149.
- Timonen, H., Aurela, M., Carbone, S., Saarnio, K., Frey, A., Saarikoski, S., Teinilä, K., Kulmala, M. and Hillamo, R. (2014). Seasonal and Diurnal Changes in Inorganic Ions, Carbonaceous Matter and Mass in Ambient Aerosol Particles in an Urban, Background Area. *Boreal Environ. Res.* 19: 71–86.
- Timonen, H., Aurela, M., Carbone, S., Saarnio, K., Saarikoski, S., Mäkelä, T., Kulmala, M., Kerminen, V.M., Worsnop, D.R. and Hillamo, R. (2010). High Time-resolution Chemical Characterization of the Water-soluble Fraction of Ambient Aerosol with PILS-TOC-IC and AMS. *Atmos. Meas. Tech.* 3: 1063–1074.
- Tsai, C.J., Perng, S.N. (1998). Artifacts of Ionic Species for HI-VOL PM₁₀ and PM₁₀ Dichotomous Samplers. *Atmos. Environ.* 32: 1605–1613.
- Turpin, B.J., Saxena, P. and Andrews, E. (2000). Measuring and Simulating Particulate Organics in the Atmosphere: Problems and Prospects. *Atmos. Environ.* 34: 2983–3013.
- Vecchi, R., Valli, G., Fermo, P., D’Alessandro, A., Piazzalunga, A. and Bernardoni, V. (2009). Organic and Inorganica Sampling Artefacts Assessment. *Atmos. Environ.* 43: 1713–1720.
- Venkatachari, P., Zhou, L., Hopke, P.K., Schwab, J.J., Demerjian, K.L., Weimer, S., Hogrefe, O., Felton, D. and Rattigan, O. (2006). An Intercomparison of Measurement Methods for Carbonaceous Aerosol in the Ambient Air in New York City. *Aerosol Sci. Technol.* 40: 788–795.
- Viana, M., Chi, X., Maenhaut, W., Querol, X., Alastuey, A., Mikuska, P. and Vecera, Z. (2006). Organic and Elemental Carbon Concentrations in Carbonaceous Aerosols during Summer and Winter Sampling Campaigns in Barcelona, Spain. *Atmos. Environ.* 40: 2180–2193.
- Wexler, A.S. and Johnston, M.V. (2008). What Have We Learned from Highly Time-Resolved Measurements during EPA’s Supersite Program and Related Studies? *J. Air Waste Manage. Assoc.* 58: 303–319.
- Witting, A.E., Takahama, S., Khlystov, A.Y., Pandis, S.N., Hering, S., Kirby, B. and Davidson, C. (2004). Semi-Continuous PM_{2.5} Inorganic Composition Measurements during the Pittsburgh Air Quality Study. *Atmos. Environ.* 38: 3201–3213.
- Wu, S.W. and Wang, T. (2007). On the Performance of a Semi-continuous PM_{2.5} Sulphate and Nitrate Instrument under High Loadings of Particulate and Sulphur Dioxide. *Atmos. Environ.* 41: 5442–5451.
- Yu, X.Y., Cary, R.A. and Laulainen, N.S. (2009). Primary and Secondary Organic Carbon Downwind of Mexico City. *Atmos. Chem. Phys.* 9: 6793–6814.
- Zhang, D., Shi, G.Y., Iwasaka, Y. and Hu, M. (2000). Mixture of Sulfate and Nitrate in Coastal Atmospheric Aerosols: Individual Particle Studies in Qingdao (36°04’N, 120°21’E), China. *Atmos. Environ.* 34: 2669–2679.

Received for review, April 15, 2015

Revised, July 8, 2015

Accepted, September 19, 2015