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

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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...
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., 2000; Godri et al., 2009; Aurela et al., 2011; Park et al., 2013; Runsey 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 Research Centre (Italy) (40 °09'58.23"N–16°38'25.95"E, 25 m altitude) from 3rd May to 30th June 2010. Information

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/programs/coops/aerosol/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 (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 m$^3$ h$^{-1}$) through an Teflon® Coated Aluminium 3 m sample inlet equipped with a PM$_{2.5}$ cyclone (URG Corporation), passing then along the PPWD were 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 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 × 4 mm); the suppressor was an ASRS 300 Self-regenerating Suppressor 4mm. The anion analyses were performed by an isotropic elution using Na$_2$CO$_3$ 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 × 1 mm); the suppressor was a CSRS300 Self-regenerating Suppressor 4mm. The cation analyses were performed by an isotropic elution using methane sulfonic 20 mM (running at 0.25 mL min$^{-1}$). The manufacturer’s limit of detection (LOD) was 0.08 µg m$^{-3}$ for NH$_4^+$ and 0.1 µg 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 PM$_{2.5}$ samples for inorganic ions analysis were collected with an atmospheric particles monitor sampler (FAI SWAM 5A Monitor, flow rate 2.30 ± 0.05 m$^3$ 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 047 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 µg m$^{-3}$) are resumed in Table 1.

Total carbon (TC), organic carbon (OC) and elemental
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 EC 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 µg C cm$^{-2}$ and µg C 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 ± 1 m$^{-3}$ 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).

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

<table>
<thead>
<tr>
<th></th>
<th>AIM LOD µg m$^{-3}$</th>
<th>IC Laboratory LOD µg m$^{-3}$</th>
<th>OCEC online LOD µgC cm$^{-2}$</th>
<th>OCEC offline LOD µgC cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4^+$</td>
<td>0.08</td>
<td>0.012</td>
<td>0.096</td>
<td>0.0480</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>0.10</td>
<td>0.133</td>
<td>0.112</td>
<td>0.0002</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>0.10</td>
<td>0.010</td>
<td>0.043</td>
<td></td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>0.10</td>
<td>0.015</td>
<td>0.015</td>
<td></td>
</tr>
<tr>
<td>K$^+$</td>
<td>0.10</td>
<td>0.024</td>
<td>0.027</td>
<td></td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.10</td>
<td>0.012</td>
<td>0.012</td>
<td></td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.10</td>
<td>0.027</td>
<td>0.027</td>
<td></td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.10</td>
<td>0.010</td>
<td>0.010</td>
<td></td>
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</tbody>
</table>
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:

\[
\text{%diff} = \left( \frac{\text{24hrs average online} - \text{offline}}{\text{offline}} \right) \times 100
\]  

(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:

\[
Y_i = mX_i + b
\]  

(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 (R²) values of the linear regression allow assessing the comparability and the degree of correlation.

RESULTS AND DISCUSSION

Online Measurements

The hourly AIM measurements of NH₄⁺, SO₄²⁻ and NO₃⁻ 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.

SO₄²⁻ was the most abundant ion followed by NH₄⁺, and NO₃⁻. The peak concentrations of NH₄⁺, and often that of NO₃⁻ as well, coincided with peak concentrations of SO₄²⁻. 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).

SO₄²⁻ hourly concentrations were always above the LOD and ranging from 0.34 to 5.28 µg m⁻³ with an average value of 1.87 µg m⁻³, while the NH₄⁺ 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). NH₄⁺ hourly concentrations above the LOD ranged from 0.11 to 3.36 µg m⁻³ with an average value of 1.03 µg m⁻³.

As for SO₄²⁻, NO₃⁻ hourly concentrations were always above the LOD and ranging from 0.13 to 2.03 µg m⁻³ with an average value of 0.52 µg 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 SO₄²⁻ and NO₃⁻ and 96% for NH₄⁺ during the campaign. The hourly concentrations of the primary ions (Na⁺, Cl⁻, K⁺, Ca²⁺ and Mg²⁺) 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 Trisara 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 µgC m⁻³ with an average value of 2.11 µgC 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 µgC m⁻³ (1.69 µgC m⁻³ average concentration) and from 0.20 to 5.56 (1.76 µgC 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 µgC m⁻³ with an average value of 0.44 µgC m⁻³. Optical EC two-hourly concentrations were always above the LOD and ranging from 0.04 to 1.27 µgC m⁻³ with an average value of 0.34 µgC 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 Ca²⁺ and Mg²⁺ concentrations in PM₂·₅ 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 NH₄⁺, SO₄²⁻ and NO₃⁻ 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 R² values.

Most of the times, high and low concentrations measured by the online and offline methods occurred simultaneously for NH₄⁺ (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.

<table>
<thead>
<tr>
<th></th>
<th>Mean  µg m⁻³</th>
<th>Maximum µg m⁻³</th>
<th>Minimum µg m⁻³</th>
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<tbody>
<tr>
<td></td>
<td>non-dust</td>
<td>dust</td>
<td>non-dust</td>
</tr>
<tr>
<td>NH₄ on</td>
<td>0.82</td>
<td>1.42</td>
<td>0.14</td>
</tr>
<tr>
<td>NH₄ off</td>
<td>0.88</td>
<td>1.54</td>
<td>0.24</td>
</tr>
<tr>
<td>SO₂ on</td>
<td>1.54</td>
<td>2.60</td>
<td>0.54</td>
</tr>
<tr>
<td>SO₄ off</td>
<td>2.12</td>
<td>4.32</td>
<td>0.55</td>
</tr>
<tr>
<td>NO₃ on</td>
<td>0.43</td>
<td>0.72</td>
<td>0.20</td>
</tr>
<tr>
<td>NO₃ off</td>
<td>0.08</td>
<td>0.12</td>
<td>0.04</td>
</tr>
</tbody>
</table>

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 µg m⁻³ for online and offline, respectively) than during the non-dust one (0.82 and 0.88 µg 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 ± 14.14% and –2.33 ± 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 (R²) 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 ± 0.263 µg m⁻³ and a coefficient of determination values (R²) 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 ± 15.09% and 35.47 ± 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 ± 0.155 µg m⁻³ for non-dust data; 0.446 ± 0.058 and +0.672 ± 0.275 µg 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 R² 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 ± 205.57% and 521.8 ± 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.
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

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

<table>
<thead>
<tr>
<th></th>
<th>Number of data points</th>
<th>Difference % Mean (± SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NON-DUST NH4</td>
<td>40</td>
<td>-6.09 (± 14.14)</td>
</tr>
<tr>
<td>DUST NH4</td>
<td>19</td>
<td>-2.33 (± 30.49)</td>
</tr>
<tr>
<td>NON-DUST SO4</td>
<td>40</td>
<td>-21.03 (± 15.09)</td>
</tr>
<tr>
<td>DUST SO4</td>
<td>19</td>
<td>-35.47 (± 12.69)</td>
</tr>
<tr>
<td>NON-DUST NO3</td>
<td>40</td>
<td>490.90 (± 205.57)</td>
</tr>
<tr>
<td>DUST NO3</td>
<td>19</td>
<td>521.80 (± 229.33)</td>
</tr>
<tr>
<td>NON-DUST Th-OC</td>
<td>40</td>
<td>-32.50 (± 18.45)</td>
</tr>
<tr>
<td>DUST Th-OC</td>
<td>19</td>
<td>-29.19 (± 19.08)</td>
</tr>
<tr>
<td>NON-DUST Opt-OC</td>
<td>40</td>
<td>-30.02 (± 19.01)</td>
</tr>
<tr>
<td>DUST Opt-OC</td>
<td>19</td>
<td>-26.34 (± 19.65)</td>
</tr>
<tr>
<td>NON-DUST Th-EC</td>
<td>40</td>
<td>25.62 (± 42.49)</td>
</tr>
<tr>
<td>DUST Th-EC</td>
<td>19</td>
<td>31.79 (± 35.04)</td>
</tr>
<tr>
<td>NON-DUST Opt-EC</td>
<td>40</td>
<td>-1.20 (± 22.70)</td>
</tr>
<tr>
<td>DUST Opt-EC</td>
<td>19</td>
<td>0.69 (± 30.53)</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th></th>
<th>Number of data points</th>
<th>Slope (± 95% CI)</th>
<th>Intercept (µg m⁻³) (± 95% CI)</th>
<th>Coefficient of determination (R²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NON-DUST NH4</td>
<td>40</td>
<td>0.959 ± 0.084</td>
<td>-0.015 ± 0.082</td>
<td>0.930</td>
</tr>
<tr>
<td>DUST NH4</td>
<td>19</td>
<td>0.732 ± 0.158</td>
<td>+0.289 ± 0.263</td>
<td>0.833</td>
</tr>
<tr>
<td>NON-DUST SO4</td>
<td>40</td>
<td>0.470 ± 0.066</td>
<td>+0.547 ± 0.155</td>
<td>0.844</td>
</tr>
<tr>
<td>DUST SO4</td>
<td>19</td>
<td>0.446 ± 0.058</td>
<td>+0.672 ± 0.275</td>
<td>0.931</td>
</tr>
<tr>
<td>NON-DUST NO3</td>
<td>40</td>
<td>3.693 ± 1.358</td>
<td>+0.146 ± 0.113</td>
<td>0.437</td>
</tr>
<tr>
<td>DUST NO3</td>
<td>19</td>
<td>1.555 ± 2.433</td>
<td>+0.528 ± 0.315</td>
<td>0.087</td>
</tr>
<tr>
<td>NON-DUST Th-OC</td>
<td>40</td>
<td>0.537 ± 0.179</td>
<td>+0.298 ± 0.461</td>
<td>0.483</td>
</tr>
<tr>
<td>DUST Th-OC</td>
<td>19</td>
<td>0.406 ± 0.297</td>
<td>+0.760 ± 0.817</td>
<td>0.304</td>
</tr>
<tr>
<td>NON-DUST Opt-OC</td>
<td>40</td>
<td>0.587 ± 0.182</td>
<td>+0.241 ± 0.468</td>
<td>0.520</td>
</tr>
<tr>
<td>DUST Opt-OC</td>
<td>19</td>
<td>0.495 ± 0.325</td>
<td>+0.607 ± 0.892</td>
<td>0.353</td>
</tr>
<tr>
<td>NON-DUST Th-EC</td>
<td>40</td>
<td>1.274 ± 0.208</td>
<td>-0.001 ± 0.064</td>
<td>0.797</td>
</tr>
<tr>
<td>DUST Th-EC</td>
<td>19</td>
<td>1.016 ± 0.316</td>
<td>+0.116 ± 0.153</td>
<td>0.707</td>
</tr>
<tr>
<td>NON-DUST Opt-EC</td>
<td>40</td>
<td>1.011 ± 0.153</td>
<td>-0.008 ± 0.047</td>
<td>0.819</td>
</tr>
<tr>
<td>DUST Opt-EC</td>
<td>19</td>
<td>0.779 ± 0.272</td>
<td>+0.112 ± 0.131</td>
<td>0.657</td>
</tr>
</tbody>
</table>
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 ± 22.70% and 6.79 ± 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 ± 19.01% and –26.34 ± 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 undenuded 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 it the time resolution decrease to two hours for OCEC field analyser.

REFERENCES


PM$_{2.5}$ Chemical Composition and Spatiotemporal Variability during the California Regional PM$_{10}$/PM$_{2.5}$ Air Quality Study (CRPAQS). J. Geophys. Res. 111, D10S04, doi: 10.1029/2005JD006457.


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