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SIZE-DISTRIBUTIONS OF WATER SOLUBLE COMPONENTS OF ATMOSPHERIC AEROSOL MEASURED WITH A MOUDI IMPACTOR

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Abstract: Understanding climate and health effects of atmospheric aerosol is an important aspect of research. These effects are strongly related to the size-distribution of particles and of chemical components contained in aerosol. In this work aerosol was collected, in an urban background site in Lecce, using a 10-stages Micro-Orifice Uniform Deposit Impactor (MOUDI). Collected samples were analysed to evaluate the size-segregated composition of water soluble ions (Ca^{2+}, Mg^{2+}, K^{+}, NH_4^{+}, Na^{+}, SO_4^{2-}, NO_3^{-} and Cl^{-}), using High Performance Ion Chromatography (HPIC), and of water soluble organic (WSOC) and inorganic (WSIC) carbon, using a TOC analyzer. Collected data were used to estimate the losses in the impactor, to characterise the size distributions of the different species and to obtain information on the main aerosol sources acting on the studied area.

Keywords: MOUDI, aerosol size-distributions, size-segregated composition, losses in impactor.

1. INTRODUCTION

Atmospheric aerosol is an important component of earth atmosphere playing a relevant role in determining visibility [1], in deterioration of air quality and human health [2-3], in deposition of pollutants to ecosystems and on direct and indirect effects on the radiative balance and on the climate system [4]. These phenomena are strongly related to the life-cycle of particles that depends on their size distribution and on their chemical composition. Thereby, the knowledge of the size distribution is a necessary step for the accurate analysis of the short- and long-term effects of aerosol. The aims of this work were to characterise the size distributions of aerosol and of the water soluble species (main ions, organic and inorganic carbon) in an urban background site in south-east Italy. The samples were collected using a 10-stages Micro-Orifice Uniform Deposit Impactor. Collected samples were statistically analysed to evaluate the losses in the impactor and to characterise the size distributions of aerosol and of the chemical species analysed. This also allowed to gather information on the main aerosol sources acting on the area studied.

2. EXPERIMENTAL EQUIPMENT USED AND MEASUREMENT SITE

The site chosen was the University Campus in Lecce, located in the Apulia region about 4 km SW of the town of Lecce (SE of Italy, coordinates 40°20'N, 18°06'E). The site could be considered an "urban background" station not strongly influenced by traffic or industrial emissions [5-6]. Aerosol samples were collected at 2.5m above the ground using a Micro-Orifice Uniform Deposit Impactor (MOUDI II, MSP, Model 120R) operating at 30 l/min. The MOUDI is a cascade impactor which allows air to be drawn through a series of micro-orifice nozzles and particles of different aerodynamic diameters are collected on to a series of different impaction plates. The MOUDI is equipped with rotating stages (Figure 1) to obtain a uniform distribution of aerosol on the collection substrate minimizing the blow-off of particles.

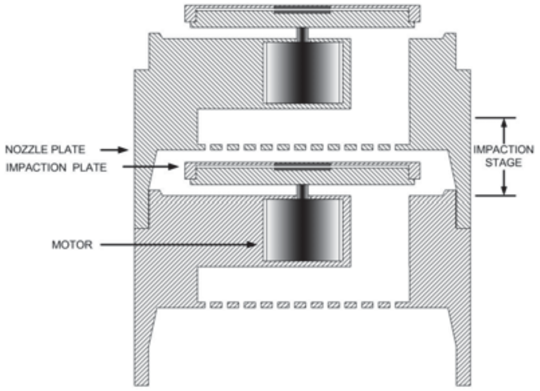

Figure 1) Typical stepper motor operated impaction stage.

The principle of operation of MOUDI is the same as any inertial cascade impactor with multiple nozzles. At each stage, jets of particle-laden air are impinged upon an impaction plate and particles larger than the cut size of each stage are collected on the impaction plates. By rotating this stage relative to the stage above and the stage below, the impaction plate is rotated relative to the upper nozzle plate and the nozzle plate is rotated relative to the lower impaction plate. Rotation of alternate stages of the impactor, while the other stages are held stationary, results in every nozzle plate having rotation relative to its corresponding impaction plate [7]. Smaller particles with less inertia follow the air stream lines and proceed on to the next stage. The nozzles of each succeeding stage are smaller than the prior stage, giving a higher velocity through the nozzles, and a smaller particle size cut. The air flow continues through a series of impactor stages until the smallest particles are removed by the back-up filter [8].

Twenty-one samples were collected in randomly chosen periods between February and October 2011. Eighteen samples were collected for 48 h and three samples were collected for 72 h. The MOUDI impactor was equipped with aluminium substrates (47 mm in diameter, MSP Corporation) in the 10 stages. The inlet of the impactor had a nominal cut-off (50% efficiency) size of 18 μm and the nominal cut-off size of the 10 stages were: 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.10 and 0.056 μm. Teflon filters (47 mm in diameter, Pall Corporation R2PJ047) were used as back-up filters in the impactor and as sampling filters for simultaneous collection of PM10 using a low-volume sampler(2.3 m^3/h, TCR-Tecora BRAVO HPLUS) for comparison purposes. Collected samples were stored in petri dishes and kept refrigerated at 4 °C until analysed. The back-up filters were not included in the statistical analysis of aerosol composition because the collection mechanism is filtration which differs from impaction, similarly to what has been done, for example, in [9].

Gravimetric analysis was performed using a microbalance (Sartorius CP2/F, sensitivity 1 μg) after 48h stabilisation of the samples in the same room in which the microbalance was operating. The uncertainty in gravimetric data was evaluated using field blanks and it was typically 4 μg on aluminium substrates and 6 μg on teflon filters (in terms of one standard deviation of blank filters).

The aluminium foils collected with MOUDI and the teflon filters collected with the low-volume sampler were analyzed for the evaluation of concentration of soluble ionic species (SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, Na^+, K^+, Mg^{2+} and Ca^{2+}) via High Performance Ion Chromatography (HPIC, Dionex DX-500 System). Each sample was extracted in Milli-Q water: two successive extractions of 20 min in an ultrasonic bath were needed for a nearly complete recovery, with the renewal of the water at each step [6]. In each of the 2 extraction steps 10 ml of Milli-Q water was used for teflon filters while 5 ml of Milli-Q water was used for aluminium foils. The extracted solutions were analyzed by HPIC for major ionic species. Anions determination was performed by means of a Ion Pac® AS14A column (Dionex) using 1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$ as eluent at 2 ml/min flow-rate and, for the detection, a conductivity system equipped with a ASRS®-ULTRA suppression mode (Dionex). Cations determination was performed by means of a Ion Pac® CS12A column (Dionex) using 20 mN H_2SO_4 as eluent at 1 ml/min flow rate and, for the detection, a conductivity system equipped with a CSRS®-ULTRA suppression mode (Dionex).

The concentrations of water soluble organic carbon (WSOC) and of water soluble inorganic carbon (WSIC) were measured, in the same solutions used for ions determination. The water-extracts were analyzed for WSOC on a Shimadzu TOC analyzer, model 5050 (Shimadzu corporation), using high temperature (680 °C) Pt-catalyzed oxidation coupled to non-dispersive infrared (NDIR) gas detection of CO_2. In an optimized analytical procedure, 50 μl of water-extract was injected into the furnace. The CO_2 evolved was used to assess the total carbon (WSTC) content. Another aliquot of the solution was acidified with 25% phosphoric acid (25% H_3PO_4, vol/vol) and the evolved CO_2 (measured using the NDIR as above) was interpreted as inorganic carbon (WSIC).The difference between the two sets of measurements (i.e. WSTC and WSIC) was used as a measurement of water soluble organic carbon (WSOC) in the aerosol samples. Mean response areas of three replicate injections for each sample were calibrated to a potassium hydrogen phthalate ($C_8H_5KO_4$) standard curve for WSTC and sodium carbonate and bicarbonate mixture (Na_2CO_3+$NaHCO_3$) standard curve for WSIC. The average standard deviation for the triplicate measurements was 3% at maximum.

Results of analytical determinations were obtained with the removal, for each chemical species, of the average level present in the blank samples. For each samples, the calculated concentration for a specific species was quantified if it was larger than the standard deviation σ_B of the blank filters, otherwise a threshold value equal to σ_B was considered. In cases in which concentration was below the method detection limit (MDL), or not detectable above the average variability of the field blanks, a concentration value equal to the maximum between the MDL and σ_B was assumed.

3.SIZE DISTRIBUTIONS OF MEASURED AEROSOL AND OF WATER SOLUBLE COMPONENTS

The average size distribution of measured aerosol was reported in Figure 2. The statistical chi-square test showed that this distribution could be described (at 5% probability) with a combination of two log-normal distributions (the fit is also reported in Figure 2). Measured aerosol concentrations were on average 20 μg/m^3 (standard deviation 5.3 μg/m^3) and were characterised by two modes.

The first mode was the accumulation mode, that had a Mass Median Diameter (MMD) of 0.35 ± 0.02 μm and represented, on average, 51 ± 4 % of collected aerosol. The second mode was the coarse mode that had a MMD=4.5 ± 0.4 μm and represented, on average, 49 ± 4 % of collected aerosol. The size distribution of each collected sample was also fitted with a combination of two lognormal distributions to obtain the mass median diameter associated to the accumulation mode (D_1) and the mass median diameter associated to the coarse mode (D_2). Results were reported in Figure 3 together with the percentage weight associated to the accumulation mode.

During sample 5 there was an event of strong sea-spray accompanied to an intrusion of African dust. This was characterised by large particles (aerodynamic diameters larger than 2 μm) that decreased the weight of the accumulation mode. Results indicated that D_1 was relatively constant during the sampling period but D_2 was larger during summer and the beginning of autumn period.

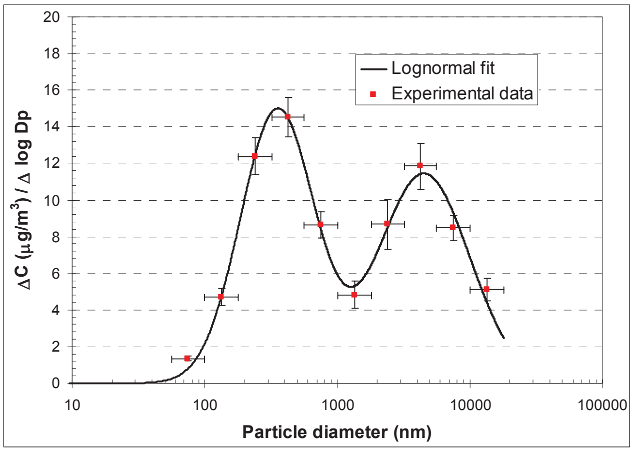

Figure 2) Average size distribution and fit with a combination of two log-normal distributions.

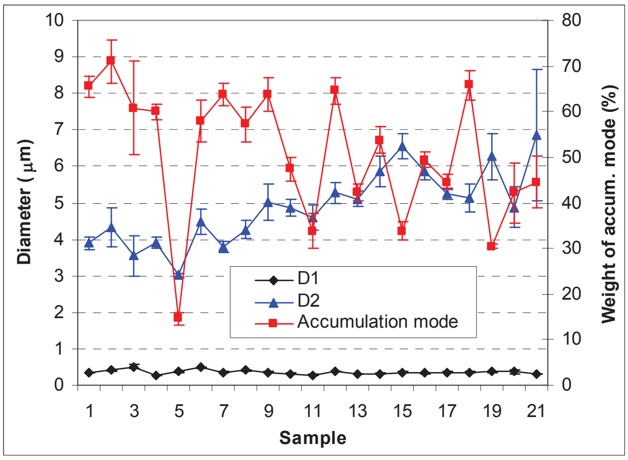

Figure 3) Calculated values of D_1 and D_2 for the different samples and calculated weight of the accumulation mode on collected aerosol.

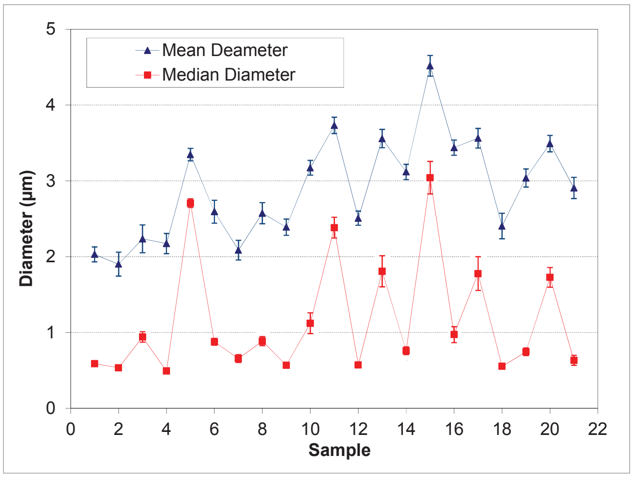

Figure 4) Aerodynamic mean and median diameters for the different samples.

The measured size distributions have been used to evaluate the aerodynamic mean diameter and median diameters [10] of collected aerosol and results are reported in Figure 4. The mass mean diameter (D_{mean}) has been calculated as:

$$D_{mean} = \int_{0.056\,\mu m}^{18\,\mu m} x f(x) dx \qquad (1)$$

where f(x) is a step function with constant value in each size-interval I_i, of the MOUDI impactor. The function f(x) is normalised as a probability distribution of the aerosol size:

$$f(x) = \frac{1}{N}\frac{C_i}{\delta_i} \quad x \in I_i \qquad (2)$$

where N is the normalisation factor that makes:

$$\int_{0.056\,\mu m}^{18\,\mu m} f(x) dx = 1 . \qquad (3)$$

I_i is the i-th size-interval of the impactor, δ_i is the extension of the i-th interval and C_i is the measured concentration in the i-th interval. The mass median diameter (D_{median}) has been calculated as the diameter value for which the following equation holds:

$$\int_{0.056\,\mu m}^{D_{median}} f(x) dx = \frac{1}{2} . \qquad (4)$$

To evaluate the uncertainties on the calculation of D_{mean} and D_{median}, it was decided to evaluate both diameters using a statistical procedure in which the probability distribution of aerosol size is defined as:

$$\tilde{f}(x) = \frac{1}{N}\frac{R[C_i, \sigma_i]}{\delta_i} \qquad x \in I_i \qquad (5)$$

where $R[C_i, \sigma_i]$ is a randomly generated number having gaussian distribution centred in C_i and standard deviation equal to σ_i. The values of σ_i represent the experimental uncertainties on measured values of C_i. This function was used to evaluate n-times (with n=500) $D_{mean,n}$ and D_{median} taking at the end the mean of these values as final values for D_{mean} and D_{median}. The standard deviations ahev been used as an estimate of the uncertainties on D_{mean} and D_{median}.

The mass median diameter showed a relatively large value during the sea spray event and, even if strong variability between one sample and the other is observed, it was generally lower than 2 μm and often lower than 1 μm. This indicated that accumulation and coarse mode had often a similar weight on collected aerosol. The mass mean diameter showed an increase in summer and the beginning of autumn period similar to the increase observed in D_2.

The average size-segregated composition of collected aerosol is reported in Figure 5 with specific reference to the water soluble components. Results showed that measured ions accounted, on average, for 39.6% of collected aerosol, WSOC accounts for 13.1%, and WSIC accounts for 1.8%.

Results showed that sulphate, ammonium, WSOC and K^+ were more abundant in the accumulation mode (stages S6-S10) and Na^+, Cl^-, Mg^{2+}, Ca^{2+}, WSIC and NO_3^-were more abundant in the coarse mode (stages S1-S5).

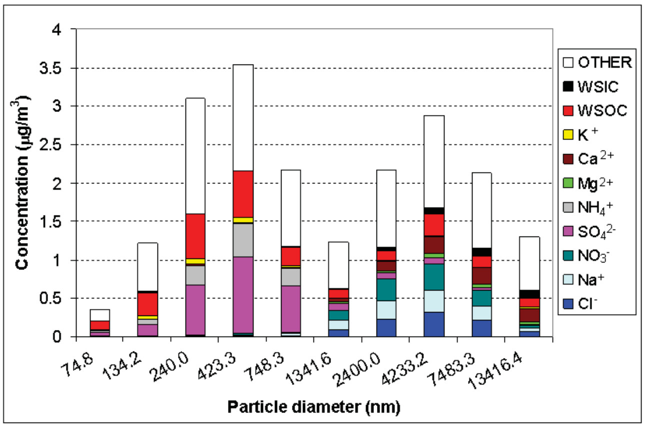

Figure 5) Average size-segregated composition of measured aerosol.

Specifically a strong correlation is observed in the accumulation mode between sulphate and ammonium with an average ratio SO_4^{2-}/NH_4^+ of 2.5 likely indicating the presence of inorganic ammonium sulphate (characterised by a ratio of 2.66) of secondary origin. In the coarse mode there was a significant correlation (Pearson coefficient 0.97) between Na^+ and Cl^- indicating the presence of a sea salt contribution in collected aerosol. The sea-salt could be estimated as Sea-Salt = Cl^- + 1.4468 Na^+, based on the assumption that all Na^+ and Cl^- were originating from marine contribution [11]. The average contribution in the coarse mode was 22% (±1%) of the aerosol concentration and the average contribution was 1.4% (±0.3%) in the accumulation mode. Further, the correlation between Na^+ and NO_3^- (Pearson coefficient 0.64) likely indicated that marine aerosol was aged and presented a chlorine depletion due to chemical reactions involving NaCl and HNO_3 or H_2SO_4 bringing the formation of $NaNO_3$ and gaseous HCl [12]. The fraction of chlorine depleted was about 40.6% resulting in a Cl^-/Na^+ ratio of 0.93, lower than the expected value of 1.81 in the sea water [13].

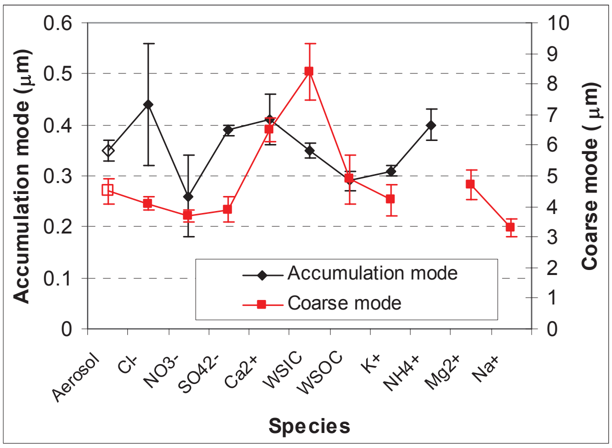

Figure 6) Accumulation and coarse mode diameters for the different species. Open symbols represent aerosol.

The average size distributions for each of the measured species were fitted to lognormal distributions (Figure 6). Results indicated that a combination of two lognormal distributions reasonably described the average distributions of each species, according to the chi-squared test at 5% probability, with the exception of Na^+, Mg^{2+} and NH_4^+. For Na^+ and Mg^{2+} it was not possible to exclude a bi-modality but the uncertainties on measured concentrations did not allow to have a good characterisation of the accumulation mode. Ammonium showed a single mode in the accumulation size range. Nitrate in the accumulation mode presented a large variability with several samples having essentially a mono-modal size distribution with nitrate present only in the coarse mode. The accumulation mode nitrate had a clear correlation with temperature with larger concentrations in autumn and winter at low temperature and lower concentrations in summer time.

This was in agreement with results reported in [14] that showed higher nitrate concentrations in the coarse mode with respect to the accumulation mode with larger concentration in the accumulation mode during winter in the urban aerosol in Madrid (Spain). In [15] it was found that nitrate in a rural site in western Germany was mainly in coarse mode with the exception of few samples associated to winter period. The marked seasonality in the accumulation mode nitrate could be interpreted as a consequence of thermal instability and volatilisation of ammonium nitrate. WSOC and K^+ were more abundant in the accumulation mode, however, they presented a marked bimodal distribution and a good correlation indicating the presence of a contribution to atmospheric aerosol of combustion sources (mainly biomass burning and traffic). The same behaviour for WSOC was observed in [16] and, for K^+, in [17]. The ions typically associated to marine aerosol Na^+, Cl^- and Mg^{2+} presented larger abundances in the coarse mode. The same apply to species typically associated to mineral aerosol (Ca^{2+} and WSIC) that presented the largest coarse mode median diameters.

4. EVALUATION OF AEROSOL LOSSES

The sum of concentrations of aerosol and chemical species measured on aluminium substrates, in the different stages of MOUDI, were compared with the corresponding concentrations measured on the teflon filters collected with the PM10 sampler in order to estimate potential losses in the MOUDI. It is known that some sampling artefacts exists in cascade impactor such as bouncing of particles, interstage losses, blow-off of particles and potential losses of semi-volatile compounds, especially in the final stages of the impactor that have a pressure lower than the atmospheric pressure [10].

Comparison of PM10 concentration measurements are reported in Figure 7. Results show that the average loss in PM10 was 19% ± 2%, significantly larger than gravimetric uncertainty and compatible with the losses observed using a Berner impactor in [18] that were evaluated, in average terms, as about 20% of PM10.

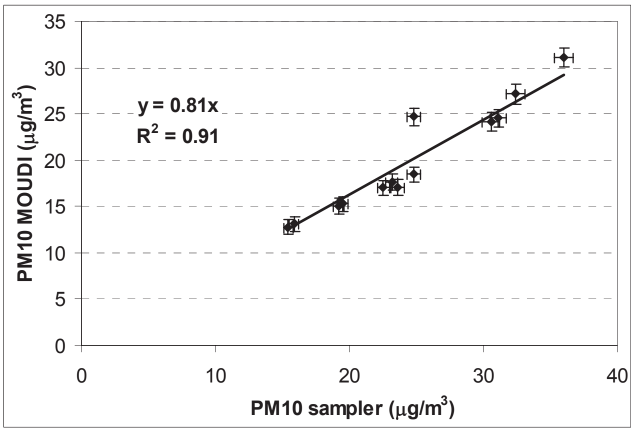

Figure 7) Comparison of PM10 concentrations measured with the MOUDI impactor and with a low-volume sampler including a linear fit.

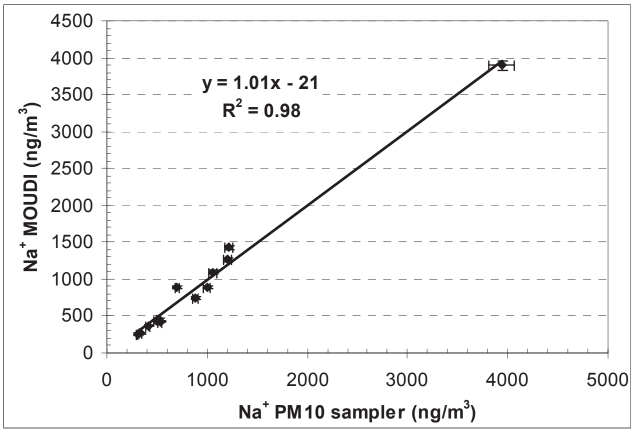

Figure 8) Comparison of Na^+ concentrations in PM10 measured with the MOUDI impactor and with a low-volume sampler including a linear fit.

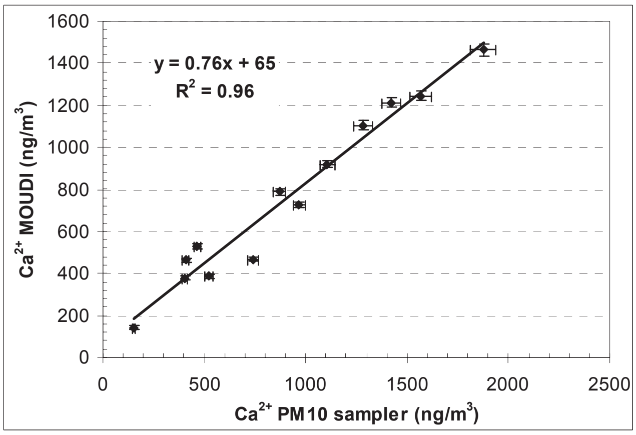

Figure 9) Comparison of Ca^{2+} concentrations in PM10 measured with the MOUDI impactor and with a low-volume sampler including a linear fit.

The average percentage losses for the different species, significantly higher than experimental uncertainties, were: 5.6% ± 7.5% for Cl^-, 35% ± 10% for nitrate, 19% ± 5% for sulphate, 10% ± 4% for K^+, 16% ± 5% for Ca^{2+} and 3% ± 10% for ammonium. The species Na^+ and Mg^{2+} did not show significant losses with respect to experimental uncertainties. The largest loss is observed for nitrate, that is a component with thermal instability, and this was compatible with observations reported in [19] in which an average loss of 70% of nitrate in summer period was estimated.

In Figure 8 it is reported the correlation between concentrations measured with the MOUDI and with the low-volume sampler for a component that did not presented a significant loss (Na^+) and in Figure 9 the same analysis is reported for a component, typical of crustal/dust aerosol (Ca^{2+}) presenting a significant loss. In Both cases the Pearson correlation coefficient is near one.

5. ACKNOWLEDGMENTS

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