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Comparison of techniques and measurement methods for determination of the water-soluble carbon and nitrogen in atmospheric particulate matter

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ABSTRACT

The water-soluble fraction of particulate matter (PM) is the most bio-accessible and potentially harmful component due to its ability to be absorbed through the respiratory tract. This study evaluates the content of water-soluble organic carbon (WSOC) and water-soluble total nitrogen (WSTN) in $PM_{2.5}$ and PM_{10} filters collected in the Lecce area (Italy), focusing on monthly samples from different site typologies and daily samples from a single background site. WSOC was quantified using two methods on aqueous extracts with a TOC-L CPH analyser: (1) the total organic carbon (TOC) method, which determines WSOC as the difference between total carbon (TC) and inorganic carbon (IC); and (2) the non-purgeable organic carbon (NPOC) method, which removes inorganic carbon by acidification and air purging before TC measurement. The analytical parameters of the NPOC method were optimized using a Design of Experiment (DoE), while WSTN, equivalent to total soluble nitrogen in the extract, was measured simultaneously using the NPOC method in N-mode. Results showed a strong correlation and high consistency between the two WSOC methods, with overall combined averages of $WSOC_{TOC} = (3.3 \pm 0.5)\ \mu g/m^3$ and $WSOC_{NPOC} = (3.2 \pm 0.4)\ \mu g/m^3$. OC solubility was high and similar in both PM fractions, averaging 65 % in $PM_{2.5}$ and 66 % in PM_{10} but demonstrated a clear seasonal variability, with higher WSOC/OC ratios in the cold season. Furthermore, the NPOC approach facilitates the simultaneous quantification of WSTN with a reduced sample volume, and the data confirmed the limited content of water-soluble organic nitrogen (WSON) in this dataset, thus enhancing analytical efficiency for routine monitoring.

1. Introduction

The climatic, environmental, and human health impacts of atmospheric aerosols are largely determined by particle size and chemical composition [1]. In addition to a wide range of inorganic compounds, a significant portion (20–50 %) of aerosol mass consists of carbonaceous material, which influences its toxicity [2] and optical properties [3]. Total carbonaceous aerosol (TC) is typically classified into elemental carbon (EC), organic carbon (OC), and inorganic carbon (IC) [4,5]. The latter is primarily composed of carbonate carbon, often found in small or negligible amounts, especially in the region studied in this work [6,7]. EC is typically a tracer of primary emissions of anthropogenic sources, directly emitted from incomplete combustion processes [8], while OC is a complex mixture of organic species originating from both anthropogenic and biogenic sources. OC can be directly emitted as primary OC or formed in the atmosphere through the oxidation of volatile organic compounds (VOCs), leading to the condensation of semi-volatile or non-volatile compounds to form secondary OC [9,10]. Organic carbon is further divided into two categories: water-soluble organic carbon (WSOC) and water-insoluble organic carbon (WIOC) [9]. WSOC accounts for 20–70 % of total OC and plays a crucial role in aerosol hygroscopicity and cloud condensation nuclei (CCN) activity, thereby influencing cloud formation and climate change [10]. It includes various compounds containing functional groups such as carboxyl ($-COOH$), hydroxyl ($-OH$), carbonyl ($C{=}O$), nitrate esters ($-ONO_2$), nitro ($-NO_2$), and amino ($-NH_2$) groups. These functional groups directly impact aerosol hygroscopicity and CCN activity, affecting cloud microphysics and the Earth's radiative balance [11].

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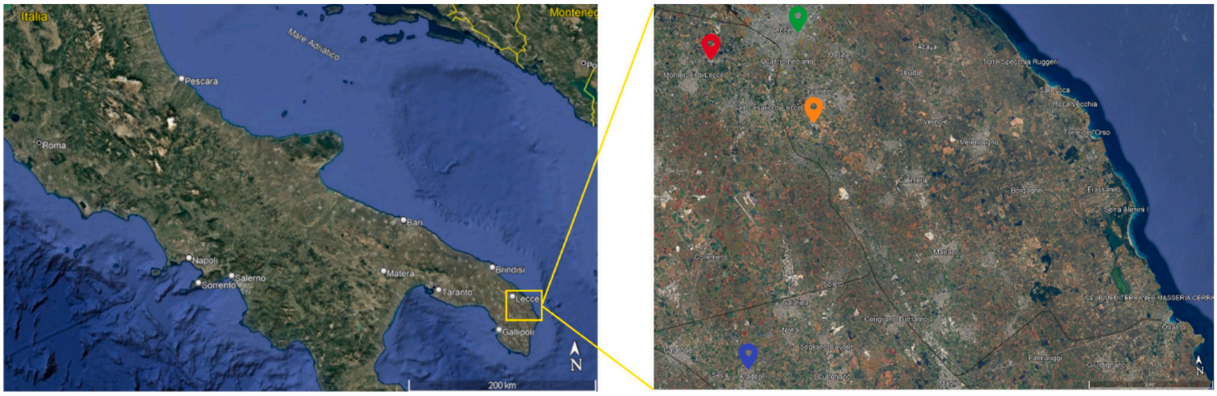

Fig. 1. Map of the measurement area, including the 4 different types of sites in the Lecce area: FU/S or ECO (red), TU (green), I/CS (orange), PR (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The atmospheric load of WSOC arises from both primary emissions and secondary formation processes. Primary sources include direct emissions from anthropogenic activities (e.g., fossil fuel combustion and biomass burning) and natural sources (e.g., plant emissions). Secondary WSOC forms through the oxidation of VOCs, producing more polar, water-soluble species that partition into the aerosol phase [12]. Understanding the relative contributions of these sources is essential for assessing WSOC's role in atmospheric chemistry and its environmental impact [13]. In addition, accurate quantification of WSOC is crucial for characterizing PM chemical composition and evaluating its potential effects on air quality and human health.

Various analytical techniques have been developed to measure WSOC concentrations in aerosol samples, each with its advantages and limitations. Two commonly used methods are the Total Organic Carbon (TOC) method and the Non-Purgeable Organic Carbon (NPOC) method. The TOC method measures the total carbon content of a sample, including both organic and inorganic carbon species. To quantify WSOC, inorganic carbon (IC) is first removed by acidification, which converts it to carbon dioxide (CO_2). The remaining carbon, assumed to be organic, is then oxidized to CO_2 and quantified, providing a measure of TOC. This method is widely used due to its simplicity and ability to provide comprehensive carbon content information. In contrast, the NPOC method specifically targets the organic carbon fraction that remains after purging volatile components. The sample is acidified to convert IC to CO_2, which is then removed via inert gas purging. The remaining non-volatile OC is oxidized and quantified. This approach is particularly advantageous for samples containing volatile organic compounds, as it minimizes their loss during analysis. In the literature, both TOC and NPOC protocols have been used for the determination of WSOC concentrations. For instance, the TOC method was applied in the study by Contini et al. [6] while the NPOC approach was used in Besis et al. [14]. However, a comprehensive comparison between the two methods is yet lacking, and a limited number of studies have systematically evaluated the differences in WSOC concentrations obtained using these distinct analytical protocols [15]. This highlights the importance of comparative assessments to understand the potential biases introduced by the selected methodology and to support the development of standardized approaches for WSOC analysis. Since TOC measurements were performed using a TOC analyser equipped with a TNM-L unit, which applies catalytic thermal decomposition at 720 °C combined with chemiluminescence detection for total nitrogen (TN) analysis, it was also possible to determine water-soluble total nitrogen (WSTN) simultaneously. An additional advantage of this approach is that WSTN can be quantified without requiring additional sample volume or separate analytical procedures. Compared to other methods for TN determination, the TNM-L system offers high sensitivity and selectivity, enabling accurate quantification of both organic and inorganic nitrogen species in aqueous samples. While nitrogen in atmospheric aerosol particles is often analysed through more detailed chemical speciation, which requires dedicated instrumentation and complex analytical protocols, WSTN measurements still provide valuable insights into atmospheric chemistry and air quality, as they include the organic nitrogen fraction and its significant contribution to the atmospheric nitrogen deposition budget.

In this work a detailed intercomparison of the two methodologies was done on both daily and monthly $PM_{2.5}$ and PM_{10} samples simultaneously collected at four different sites located in south Italy. The samples cover a period of one year allowing to investigate eventual seasonal effects as well as potentially site-specific effects. In addition, the samples were analysed for OC and EC allowing to estimate solubility of organic carbon at the different sites. Finally, the WSTN was compared with ion chromatography determination of inorganic nitrogen. Results will be useful for guiding the selection of optimal methodologies for WSOC analysis helping to further enhance our ability to characterize this complex atmospheric component.

2. Materials and methods

2.1. Measurement sites and sampling

The atmospheric particulate matter filters were collected using two distinct sampling strategies: daily samples were collected over a 24-h duration to capture short-term variability, while monthly samples were collected over a calendar month to represent monthly averaged concentrations.

Twelve daily PM_{10} samples plus twelve daily $PM_{2.5}$ samples were selected, one for each month, being collected at the Environmental Climate Observatory (ECO) of Lecce, national facility of the ACTRIS network and regional station of the Global Atmosphere Watch network (GAW/WMO) [16] located inside the University Campus of Lecce in south-east of Italy. The site can be considered as an urban background site [17,18] because it is influenced by vehicular traffic within the University Campus but also by the integrated contributions of different sources, such as emissions of Lecce town and of the other small villages located nearby, and the industrial settlements not so far of Taranto and Brindisi. Particulate matter was collected on pre-fired (2 h at 700 °C) quartz fiber filters (Whatman Q-grade, 47 mm) using a low-volume (2.3 $m^3\ h^{-1}$) dual-channel sequential sampler (SWAM, Fai Instruments S.r.l.), operating with automatic detection of aerosol mass concentration by the β-ray attenuation method, a standardized approach (EN 16450:2017) based on the attenuation of β radiation through the particle-loaded filter [18,19]. This instrument was compared with the reference gravimetric method in a previous study [18,20] showing average uncertainties of 2.5 % for $PM_{2.5}$ and 3.2 % for PM_{10}.

Simultaneously collected monthly samples of PM_{10} and $PM_{2.5}$, representative of an annual period (2022), were also selected. They were collected on the above-mentioned filters, using HSRS (High Spatial Resolution Sampler; Fai Instruments S.r.l.) intelligent samplers, operating at low flow (2 L/min) and distributed in 4 different types of sites in the Lecce area (Fig. 1): urban/suburban fund FU/S; TU of urban traffic; I/CS suburban industrial/commercial; PR Province. These were selected as being influenced by different local sources.

2.2. Analytical procedures

$PM_{2.5}$ and PM_{10} concentrations on daily samples were determined using the β-attenuation method having average estimated uncertainties of 2.5 % for $PM_{2.5}$ and 3.2 % for PM_{10} [20]. The monthly samples were weighted before and after sampling with an analytical balance (Sartorius CP2/F, reading precision 1 μg) after stabilizing for 48 h, in a room with controlled temperature and humidity. The variability observed between pre-sampling and post-sampling weighing were usually within 1 °C and relative humidity differences within 10 %. The uncertainty in the gravimetric data was evaluated using field blanks [21] and was on average 3.2 %.

Determination of OC and EC was done on 1 cm^2 punches obtained by a quarter of each sampled filters. The analysis was done via thermo-optical method by Sunset OC/EC Analyser (Sunset Laboratory Inc., Tigard OR, USA), following the EUSAAR2 protocol [22]. A multi-point calibration curve was obtained using a standard sucrose solution as detailed in Merico et al. [23]. In addition, blank filters were also analysed, and all concentration values were blank corrected. An extensive analysis of repeatability, done on different punches obtained by the same filter sample, showed an experimental uncertainty on final concentrations of approximately 5 % for OC and 10 % for EC [23].

For the determination of WSOC and WSTN, two quarts of each sampled filter were used separately for the water extraction. Each of them was submerged into 15 mL of Milli-Q water (>18 MΩ cm) and extracted for 30 min in an ultrasonic bath at a temperature of 30 °C. The extracts were successively filtered using 0.45 μm PTFE membrane to remove any insoluble particles. The extracts were analysed in a TOC analyser (Shimadzu, model TOC-$L_{CPH/CPN}$, Japan), using both TOC protocol (TC-IC) and NPOC protocol. The TOC method consists of performing TC and IC analysis, separately. In particular, 50 μl of a first aliquot of extracted solution was injected into the combustion tube, where the TC components in the sample undergo catalytic oxidation at 720 °C to carbon dioxide, then detected by a non-dispersive infrared analyser. The TC concentration was calculated using a calibration curve obtained by analysing potassium hydrogen phthalate standard solutions having different concentrations. The measure of IC consists in the quantification of carbon derived by carbonates, hydrogen carbonates and dissolved carbon dioxide. Then, during a second sample injection, a small amount of hydrochloric acid was added ($pH < 3$) directly in the syringe, allowing the chemical conversion of all carbonates in carbon dioxide, that is revealed as previous described and quantified by using a calibration curve of sodium hydrogen carbonate/sodium carbonate standard solutions. WSOC determined by TOC method ($WSOC_{TOC}$) was calculated as the difference between the TC and IC measurements. The NPOC procedure consist of a single sample injection (300 μl) in which, after acidification, air is bubbled to eliminate the inorganic component and purgeable organic carbon (POC). Residual carbon is oxidized and measured as previous described for TC and refers to the non-volatile organic component present in the sample. This measurement is defined as $WSOC_{NPOC}$ (WSOC determined by the NPOC method) Then, $WSOC_{NPOC}$ can be referred to as TOC if the amount of purgeable organic substances is small and negligible with respect to the soluble organic component. Also, to determine $WSOC_{NPOC}$ concentration, a calibration curve was used, built through analysis of potassium hydrogen phthalate standard solutions. Final concentrations are calculated after subtraction of values found on blanks filters. An analysis of repeatability was done using independent extractions, from two different quarters of the same filters, and successive analysis (Fig. S1, supplementary material). This allowed to estimate an average uncertainty of approximately 15 %.

Table 1
Experimental domain of CCF design model.

Factors	Abbr.	Units	Low	High
Sparge Gas Flow	SPG	mL/min	50	120
Sparge Time	ST	min	0.1	1.9
Acid Addition	AA	%	0.2	2.0

The WSTN was determined in both methods, since organic and inorganic nitrogen compounds undergo catalytic oxidation, like carbon compounds. The resulting nitrogen oxides (NOx) were detected by a chemiluminescence analyser. The WSTN concentration was calculated using a calibration curve obtained by analysing potassium nitrate standard solutions at different concentrations. Final concentrations are calculated after subtraction of values found on blanks filters. An analysis of repeatability was done using independent extractions, from two different quarters of the same filters, and successive analysis (Fig. S1, supplementary material). This allowed to estimate an average uncertainty of approximately 11 %.

The determination of water-soluble inorganic nitrogen (WSIN) was done on a quarter of each filter. Extraction was done in two steps, each step lasting 30 min in an ultrasonic bath, utilizing 1.5 mL of ultrapure water (Milli-Q MΩ 18). NH_4^+, NO_2^- and NO_3^- ions concentrations were determined utilizing a Dionex DX600 Ion Chromatography (IC) System, which comprises an AS40 autosampler, a GP50 gradient pump, a LC25 chromatography vessel, and an ED50 conductivity detector equipped with a temperature-compensated conductivity cell featuring a 125 μL injection loop. Anions $\left(NO_2^- \text{ and } NO_3^-\right)$ were separated using a Dionex AS4A-4 mm column in conjunction with an IonPac AG14 guard column, employing 2.7 mM Na_2CO_3 and 1.0 mM $NaHCO_3$ as eluent in isocratic mode. The NH_4^+ ion was separated using a Dionex CS12A-4 mm column paired with an IonPac CG12A guard column and 20 mM MSA as eluent, also in isocratic mode. Self-regenerating suppressors (Dionex ASRS ULTRA for anions and Dionex CSRS ULTRA II for cations) were utilized in electrochemical suppression mode, operating at 50 mA to convert the eluent solution into weakly conducting water. External standard calibration was carried out using individual anion and cation solutions at a concentration of 1000 mg/L (Inorganic Ventures) was used for determination of water-soluble ions concentrations via High Performance Ion Chromatography [24]. NH_4^+, NO_2^- and NO_3^- are usually the major WSIN species in atmospheric PM. The concentrations of NO_2^- in all samples were below the detection limit so that WSIN, expressed in $nmol_N/m^3$, were evaluated adding only the contribution of ammonium and nitrate.

2.3. Optimization of NPOC parameters

Unlike the TOC method, the analytical procedure for NPOC requires adjusting the sample pretreatment parameters to effectively remove purgeable carbon. Consequently, a multivariate analysis was conducted to investigate the effect of these variables on the NPOC method, accounting for all interactions between parameters. The Design of Experiments (DOE) methodology was employed, specifically utilizing a Central Composite Face-centered (CCF) design including three replicated centre points ($N = 2^k + 2k + nc$, with $k = 3$ and $nc = 3$) [25]. The CCF design was executed using a mixed ambient aerosol extract matrix, obtained by pooling and homogenizing extracts from multiple filters. This approach allowed the derived optimal conditions to account for potential matrix effects while ensuring sufficient sample volume and homogeneity for the entire DOE. The selected variables were sparge gas flow (SPG), sparge time (ST), and acid addition (AA). A total of 17 experiments were conducted in a random order to avoid unwanted systematic effects. The results were analysed using MODDE 12.1 software (Umetrics, Umea, Sweden), and the selected factors were studied at two levels, as reported in Table 1.

Table 2
Experimental domain and response of the Central Composite Face-centred design performed.

Exp No	Run Order	SPG (mL/min)	ST (min)	AA (%)	NPOC/TOC (%)
1	16	50	0.1	0.2	119
2	7	120	0.1	0.2	117
3	10	50	1.9	0.2	104
4	8	120	1.9	0.2	97
5	4	50	0.1	2	122
6	9	120	0.1	2	117
7	6	50	1.9	2	83
8	5	120	1.9	2	77
9	1	50	1	1.1	101
10	13	120	1	1.1	93
11	11	85	0.1	1.1	120
12	17	85	1.9	1.1	80
13	3	85	1	0.2	104
14	12	85	1	2	97
15	14	85	1	1.1	96
16	2	85	1	1.1	98
17	15	85	1	1.1	96

The factor levels were selected based on practical considerations, using the manufacturer's default parameters as a baseline. Specifically, the ranges were set as follows: sparge gas flow (SPG) from 50 to 120 mL/min, sparge time (ST) from 0.1 to 1.9 min, and acid addition (AA) from 0.2 to 2 %. The polynomial equation for 10 factors containing coefficients weighting both linear terms and their interactions is reported in Eq. (1):

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \tag{1}$$

where b_0, b_i, b_{ij}, and b_{ii} represent the coefficient related to the constant, linear, interaction, and quadratic terms, respectively. Using a DOE, the sparging parameters were investigated, evaluating which are potentially significant and their cause-and-effect relationships on the expected experimental outcome fixed as 100 % $WSOC_{NPOC}/WSOC_{TOC}$. A central composite face-centered (CCF) design was employed, with 3 factors sparge gas flow (SPG), sparge time (ST) and acid addition (AA) in the range of 50–120 mL/min, 0.1–1.9 min and 0.2–2 %, respectively.

3. Results and discussion

3.1. Results from MODDE analysis

The multivariate analysis performed by MODDE model allowed us to elucidate (i) the distribution of experimental data, (ii) the significance of factors, and the (iii) model fitting with experimental values, confirmed by the reproducibility and validity of the model.

Table 2 presents the experimental matrix and the corresponding responses (Y, $WSOC_{NPOC}/WSOC_{TOC}$ (%)). The results show that the response ranges from 77 % to 122 %. Furthermore, the central point, performed three times, exhibits good repeatability, as confirmed by the replicate plots in Fig. 2A. This observation, initially derived from the data in Table 2, suggests that the variations observed among individual experiments are primarily attributable to differences in experimental conditions.

Fig. 2B presents the coefficients of Eq. (1). The specific numerical values of these coefficients are reported in Supplementary Table S1. As shown in the figure, a coefficient is considered significant if its confidence interval does not include zero. Based on this criterion, the significant coefficients are those corresponding to SGF, ST, and AA, as well as the interaction term ST × AA. Moreover, the negative values of these coefficients indicate that an increase in these factors leads to a decrease in the response. Residuals N-plot (Fig. 2C) shows that residuals are normally distributed and the points on the probability plot follow close

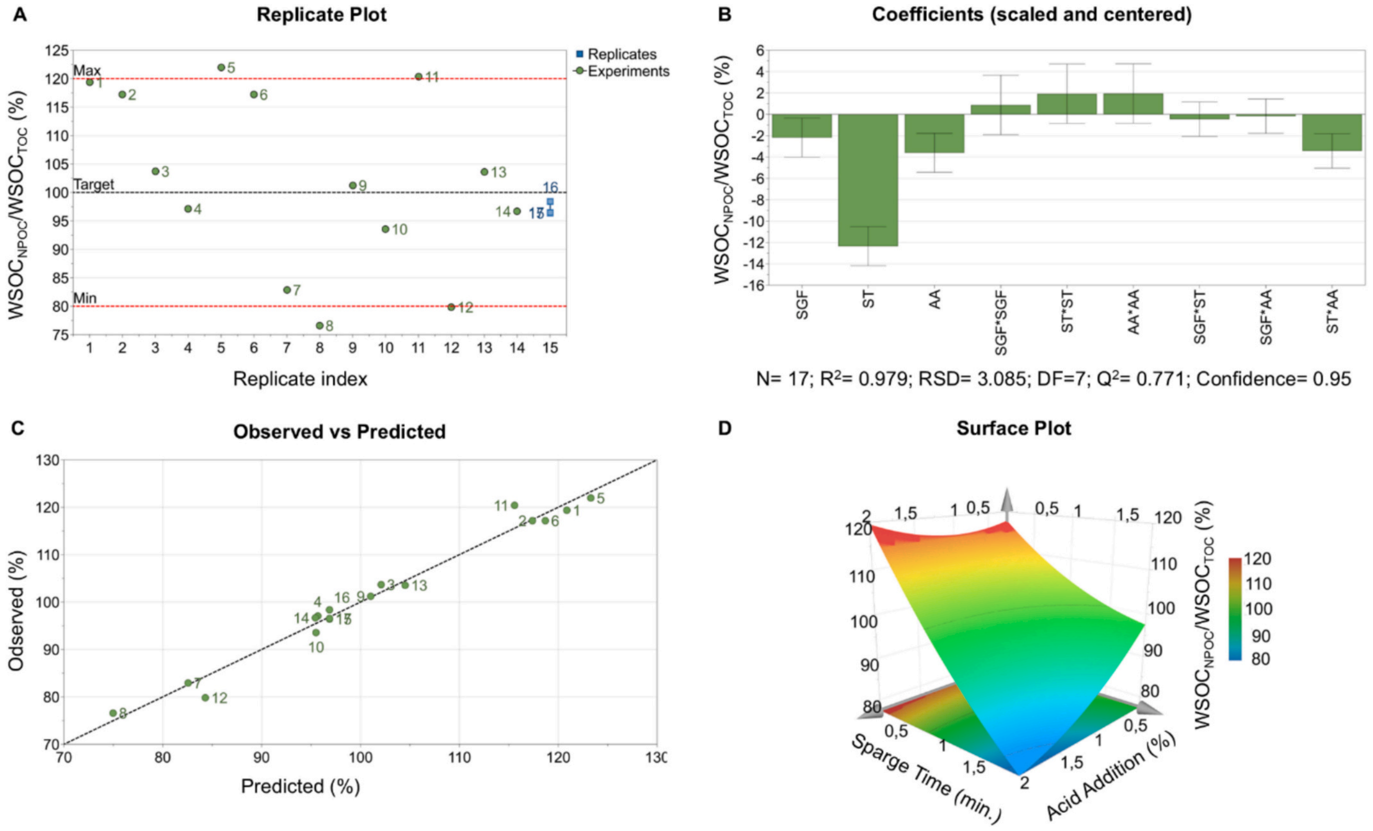

Fig. 2. Replicate plot (A), Coefficient plot (B), Residuals N-plot (C) and Surface Plot AA vs ST (D).

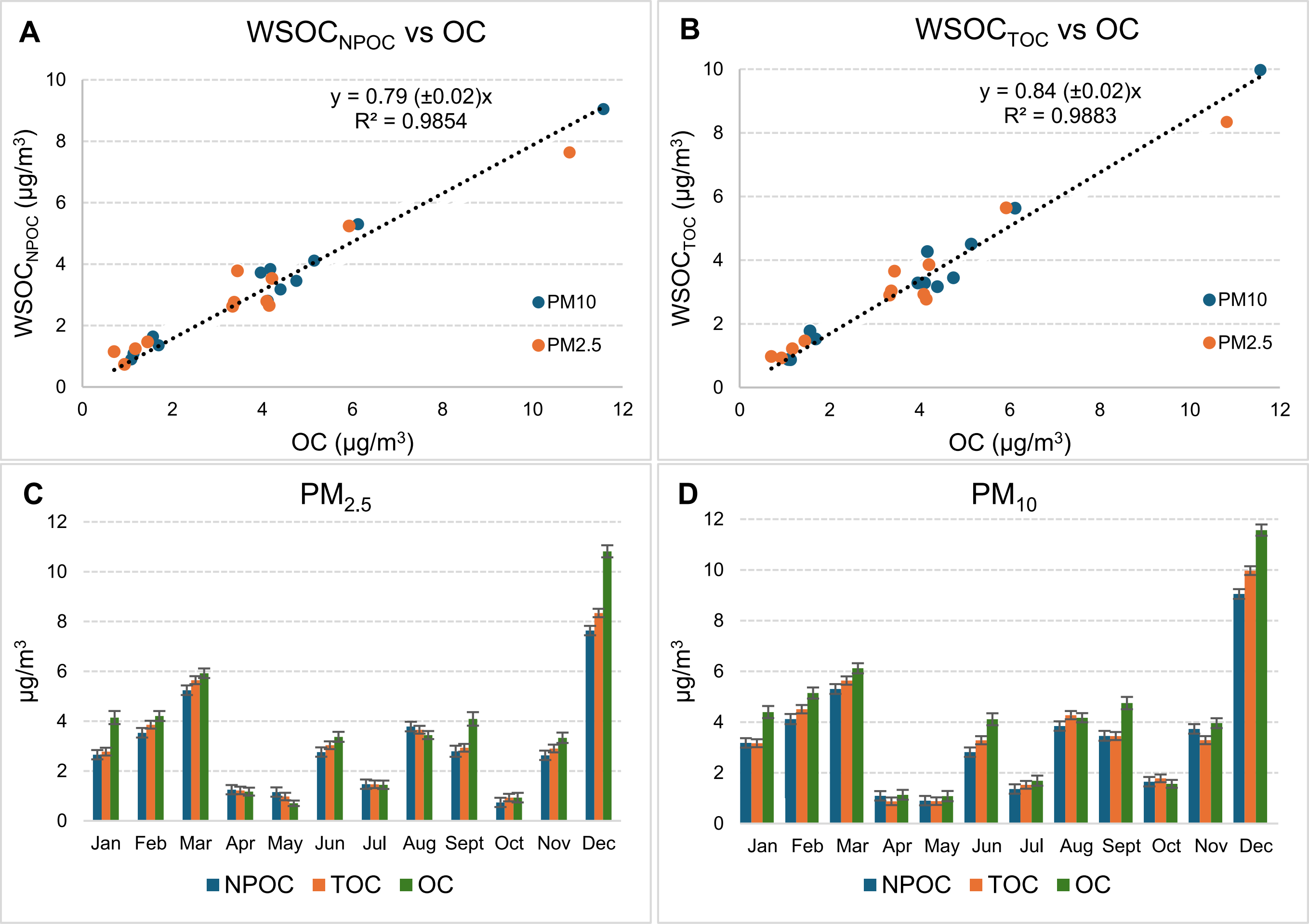

Fig. 3. Correlation between $WSOC_{NPOC}$ and OC (A) and between $WSOC_{TOC}$ and OC (B); average concentrations (±standard deviation, $n = 3$) of $WSOC_{NPOC}$, $WSOC_{TOC}$, and OC in $PM_{2.5}$ (C) and PM_{10} (D). Error bars represent the standard deviation of the triplicate analyses.

to a straight line. Fig. 2D presents the surface plot of acid addition and sparge time, obtained by setting the sparge gas flow to 85 mL/min. The slope of the surface confirms the dependence of the response on these two factors. The Maximize tool in MODDE was set in Target mode at 100, corresponding to the condition where $WSOC_{NPOC}$ equals $WSOC_{TOC}$. Based on this optimization, the tool identified the optimal operating conditions as a sparge time of 44 s, a sparge gas flow of 101 mL/min, and an acid addition of 1.4 %.

3.2. *$PM_{2.5}$ and PM_{10} daily samples*

Fig. 3 presents an analysis of the relationship between water-soluble organic carbon (WSOC) and organic carbon (OC) in particulate matter, as well as the seasonal variations in different carbonaceous fractions for $PM_{2.5}$ and PM_{10}.

Fig. 3A and B show scatter plots of WSOC vs. OC for non-purgeable organic carbon (NPOC) and total organic carbon (TOC), respectively for both $PM_{2.5}$ (orange) and PM_{10} (blue). The high coefficient of determination (R^2) values in both panels indicate a strong correlation, suggesting that a significant fraction of OC is water-soluble. The regression analysis was performed by combining both PM_{10} and $PM_{2.5}$ datasets, with the intercept constrained to zero. The slopes obtained (0.73 for $WSOC_{NPOC}$ and 0.81 for $WSOC_{TOC}$) indicate a very good agreement between OC and WSOC, with slightly lower values derived from the NPOC method compared to the TOC approach. This comparison highlights that both analytical procedures provide consistent estimates of the WSOC fraction of OC, confirming that about 70–80 % of OC is water soluble. A comparison between $WSOC_{NPOC}$ and $WSOC_{TOC}$ for daily samples analysed using the same extracts was reported in Fig. S2, revealing a very good agreement between the two measurement techniques. The data show a near 1:1 relationship, with a regression slope of 0.93 ± 0.01 and a coefficient of determination (R^2) of 0.9968. This indicates that $WSOC_{NPOC}$ reproduces $WSOC_{TOC}$ values with high accuracy, albeit with a slight systematic underestimation. Importantly, this high degree of correlation holds consistently for both PM_{10} and $PM_{2.5}$, confirming the robustness and reliability of the NPOC approach in quantifying water-soluble organic carbon. A statistical comparison of the analytical sensitivity was performed using the Limits of Detection (LODs) calculated as 3σ of the blank measurements. An F-test performed on the variance of the blank measurements showed no statistically significant difference between the TOC and NPOC analytical precision ($P = 0.19$), indicating that the analytical sensitivity of the two protocols is equivalent. Furthermore, the average WSOC concentrations obtained with the two methods are nearly identical both for $PM_{2.5}$ ($WSOC_{NPOC} = 3.1 \pm 0.6$ $\mu g/m^3$ and $WSOC_{TOC} = 3.0 \pm 0.6$ $\mu g/m^3$) and for PM_{10} ($WSOC_{NPOC} = 3.4 \pm 0.6$ $\mu g/m^3$ and $WSOC_{TOC} = 3.5 \pm 0.7$ $\mu g/m^3$). Overall the combined average across all fractions further confirms the excellent agreement between the two methods: $WSOC_{TOC} = (3.3 \pm 0.5)$ $\mu g/m^3$ and $WSOC_{NPOC} = (3.2 \pm 0.4)$ $\mu g/m^3$. The comparison was also extended to the monthly samples analysed from different extracts, as reported in Fig. S3. Although the monthly samples showed a larger scatter compared to Fig. S2, indicating additional uncertainty associated with the use of different parts of the filters and separate extractions, the agreement between the two methods remains good.

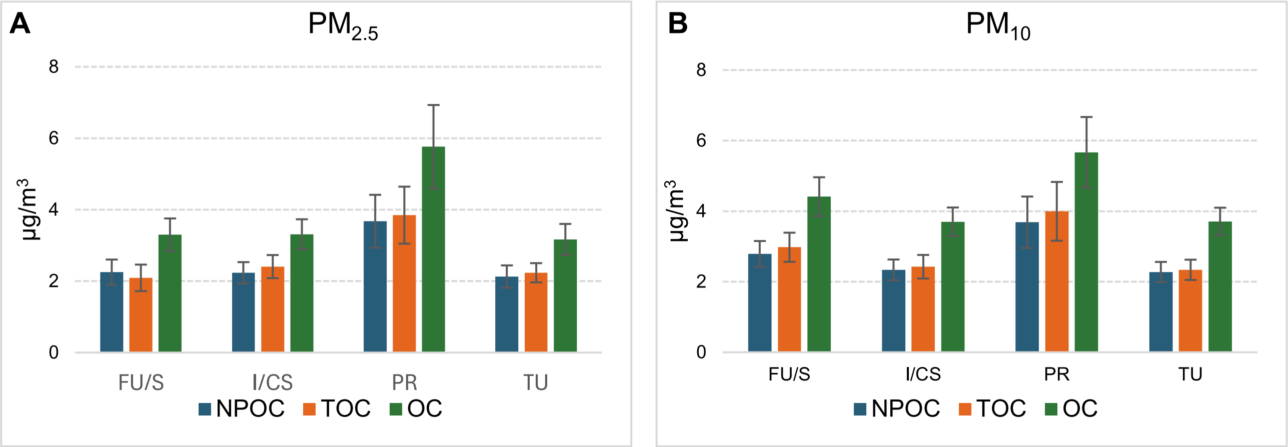

Fig. 4. Average concentrations (±standard errors) of $WSOC_{NPOC}$, $WSOC_{TOC}$, and OC in $PM_{2.5}$ (A) and PM_{10} (B) at different sampling sites: FU/S (urban/suburban background), I/CS (suburban industrial/commercial), PR (province), and TU (urban traffic).

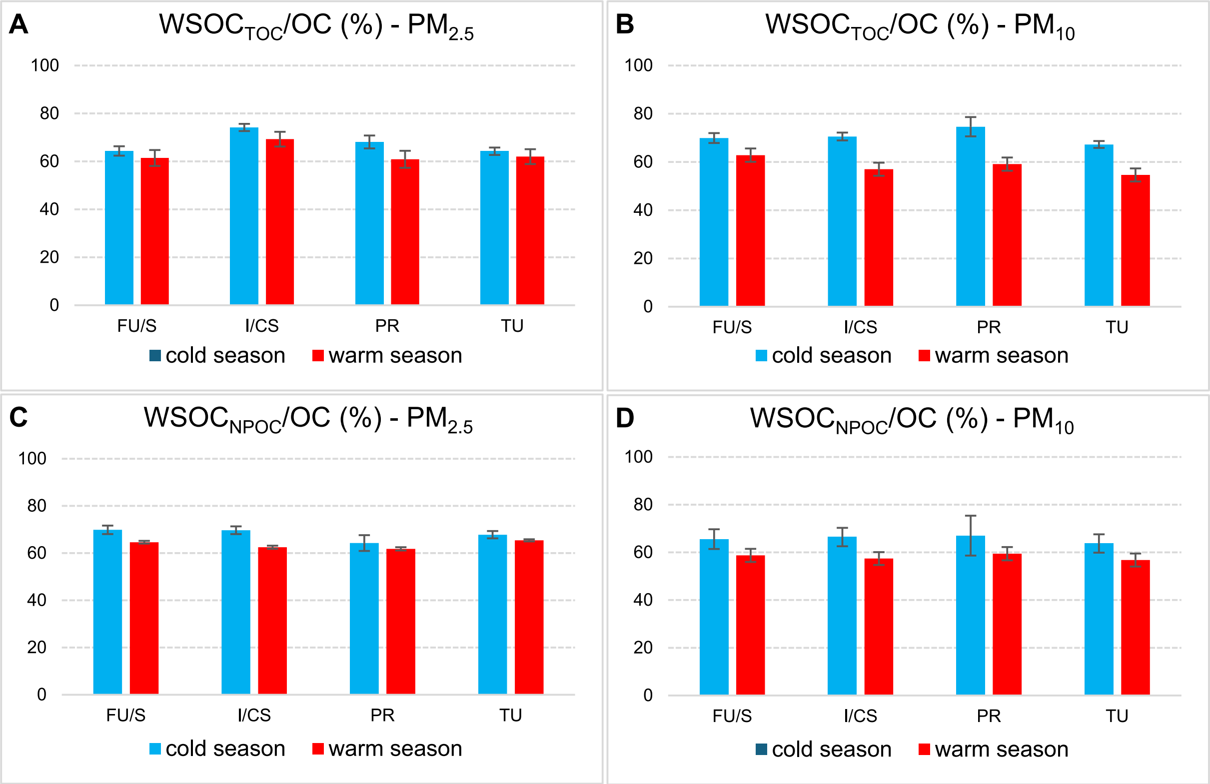

Fig. 5. Seasonal variation of $WSOC_{TOC}$/OC in $PM_{2.5}$ (A) and PM_{10} (B), and $WSOC_{NPOC}$/OC in $PM_{2.5}$ (C) and PM_{10} (D). Error bars represent the standard errors.

The temporal trend of daily measurements, aggregated by month, for OC, TOC, and NPOC concentrations in $PM_{2.5}$ (Fig. 3C) and PM_{10} (Fig. 3D) shows some trends: higher concentrations are observed during the cold months (November–March) for both $PM_{2.5}$ and PM_{10}, while the lowest values occur in spring and summer (April–August). The winter peak is particularly pronounced in December, when OC, $WSOC_{TOC}$, and $WSOC_{NPOC}$ concentrations reach their maximum values. This seasonal pattern is likely influenced by increased biomass burning, reduced atmospheric dispersion, and enhanced condensation of semi-volatile organic compounds under lower temperatures as was observed in a previous study in this area (Cesari et al., 2018). The differences between OC, $WSOC_{TOC}$, and $WSOC_{NPOC}$ remain relatively stable throughout the year. WSOC concentrations obtained using the TOC and NPOC protocols exhibit a strong correlation, confirming the trends observed in Fig. 3A and B. The comparison between $PM_{2.5}$ (Fig. 3C) and PM_{10} (Fig. 3D) shows that PM_{10} generally has, as expected, higher total carbon concentrations, especially during the winter peak.

3.3. $PM_{2.5}$ and PM_{10} monthly samples

Fig. 4 illustrates the mean concentrations of $WSOC_{NPOC}$, $WSOC_{TOC}$, and OC measured in both $PM_{2.5}$ (A) and PM_{10} (B) across the different sampling sites, namely the urban/suburban background (FU/S), the suburban industrial/commercial area (I/CS), the provincial area (PR), and the urban traffic site (TU).

Overall, OC concentrations were consistently higher than both $WSOC_{TOC}$ and $WSOC_{NPOC}$ across all sites and size fractions, reflecting the presence of a non-soluble organic carbon fraction. Notably, $WSOC_{TOC}$

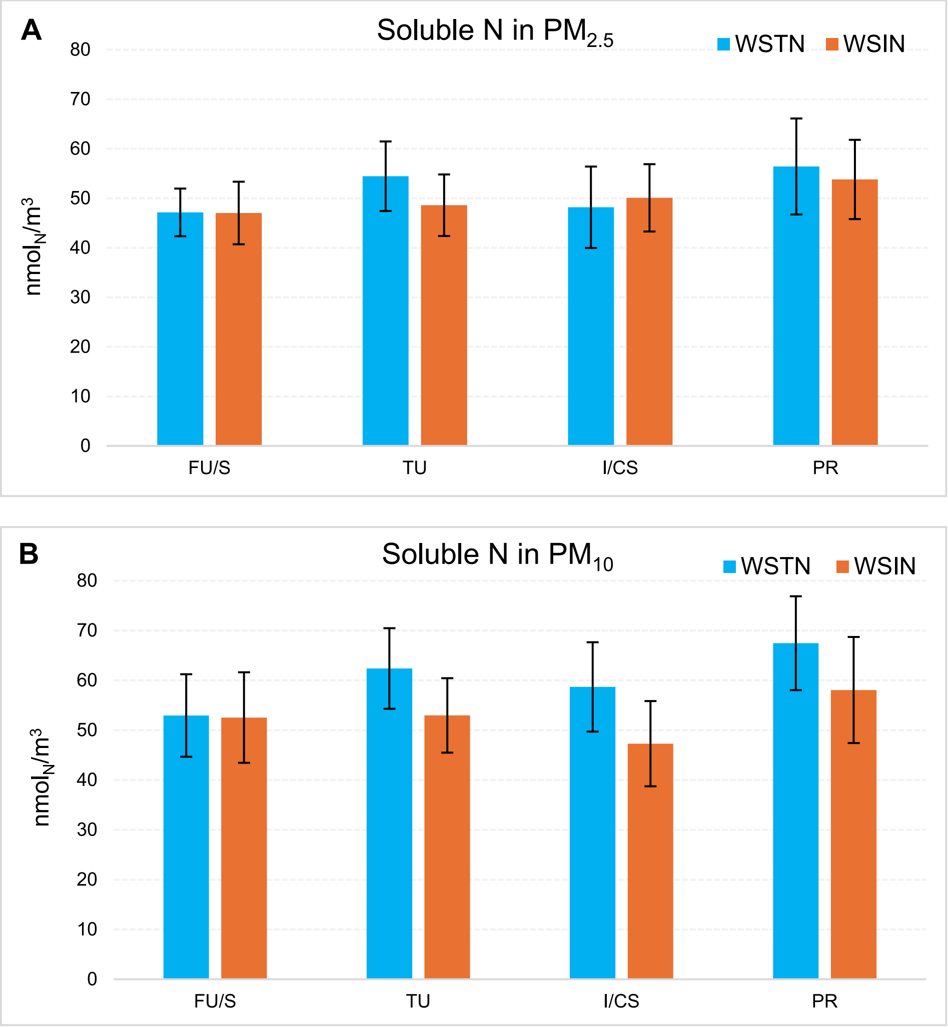

Fig. 6. Comparison of total and inorganic water-soluble nitrogen in $PM_{2.5}$ (A) and PM_{10} (B) monthly samples. Error bars represent the standard errors.

and $WSOC_{NPOC}$ values exhibited a good correlation in both $PM_{2.5}$ and PM_{10} fractions (Fig. S2, supplementary material), and no statistically significant differences were observed between them.

The seasonal variation of the water-soluble organic carbon to total organic carbon ratio (WSOC/OC) for $PM_{2.5}$ and PM_{10} was evaluated across the different sites, based on data obtained using both the TOC and NPOC analytical protocols. The results, presented in Fig. 5, are shown separately for the cold (October to March) and warm (April to September) seasons. Notably, no significant differences were observed between the WSOC/OC ratios derived from the two analytical methods, confirming what was already observed for the daily samples. This suggests that the choice of WSOC measurement protocol does not significantly influence the results, indicating a relatively stable behaviour of the water-soluble organic fraction regardless of the analytical approach.

In both seasons, the spatial variability of WSOC/OC is limited for both size fractions, not significant considering the uncertainty. However, it was observed a clear seasonal trend, with higher WSOC/OC values during the cold season across all sites, especially for PM_{10}. This seasonal trend may be attributed to a stronger influence of combustion sources such as biomass burning during the cold season, as well as to meteorological conditions favouring the condensation of organics in PM samples. The average solubility of organic carbon was comparable in $PM_{2.5}$ (66 % ± 2 %) and PM_{10} (63 % ± 3 %), indicating that the fraction of water-soluble organic carbon remains relatively stable regardless of particle size.

On the monthly samples, the NPOC methods was applied in N-mode to quantify the water-soluble total nitrogen (WSTN) content. The TOC method was also applied for quality control; however, previous comparative studies on similar matrices showed no significant statistical difference between WSTN results obtained from the NPOC and TOC approaches. The values derived from the NPOC method are reported throughout this study, enabling the analysis to focus on the partitioning of WSTN into its inorganic (WINS) and organic (WSON) components, particularly since the measurement of soluble nitrogen is available concurrently with the soluble carbon determination. In this analytical configuration, the total nitrogen present in the sample undergoes thermocatalytic oxidation, generating nitrogen monoxide (NO), which is subsequently detected by chemiluminescence. This thermo-oxidative approach allows WSTN to be quantified on the same aqueous extract prepared for WSOC analysis, providing additional information on soluble nitrogen without requiring further sample processing. Fig. 6 shows the comparison between WSTN (measured by the thermos-oxidative method) and WSIN (calculated as the sum of the main aerosol species NH_4^+ and NO_3^- by ion chromatography), reported as the annual means of total soluble nitrogen in $PM_{2.5}$ and PM_{10} monthly samples.

The differences between WSTN and WSIN were not significant compared to uncertainties at all sites and for both size fractions. In addition, at the same site, a higher amount of WSTN (and WSIN) was observed in PM_{10} compared to $PM_{2.5}$. The limited differences between water-soluble nitrogen in the two size fractions are related to the different size distributions of ammonium at this site. Ammonium, primarily existing as ammonium sulphate (NH_4HSO_4/$(NH_4)_2SO_4$) or

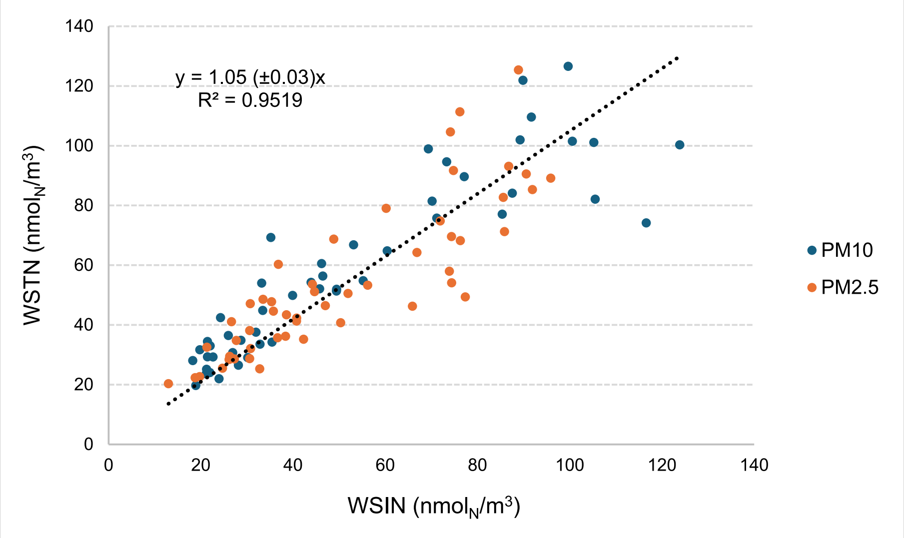

Fig. 7. Correlation between WSTN and WSIN in $PM_{2.5}$ and PM_{10} monthly samples.

partially neutralized ammonium nitrate (NH_4NO_3), is mainly concentrated in the fine ($PM_{2.5}$) fraction. Conversely, nitrate dominates in the coarse fraction ($PM_{10-2.5}$), where it is mainly associated with crustal cations such as calcium (Ca_2^+) and marine sodium (Na^+), forming salts like sodium nitrate ($NaNO_3$) and calcium nitrate ($Ca(NO_3)_2$). This distribution pattern of WSIN is consistent with previous studies conducted at this site [24]. Slightly larger values of WSTN compared to WSIN were observed in PM_{10} that can suggest a small contribution of soluble organic nitrogen in the coarse fraction. In the literature, some studies reported organic nitrogen in the fine fractions as the most susceptible to secondary formation processes in the atmosphere that produce complex compounds containing organic nitrogen [26,27]. Therefore, the mentioned organic nitrogen could be explained by pollution influences from direct sources, i.e. local factors such as anthropogenic pollution sources (vehicular traffic, agricultural activities), and particular atmospheric conditions favouring condensations of organic compounds.

The scatter plot between WSTN and WSIN in monthly aerosol samples is shown in Fig. 7. The data exhibit a strong positive correlation, with a coefficient of determination (R^2) of 0.78, indicating that a substantial portion of the variability in WSTN can be explained by the inorganic nitrogen content. These results support the value of WSTN measurements as a complementary parameter to standard ion chromatography analyses for a more comprehensive assessment of nitrogen in atmospheric aerosols.

4. Conclusions

This study provided a comprehensive comparison between two analytical methodologies, Total Organic Carbon (TOC) and Non-Purgeable Organic Carbon (NPOC), for the determination of water-soluble organic carbon (WSOC) in atmospheric particulate matter ($PM_{2.5}$ and PM_{10}), while simultaneously evaluating the total water-soluble nitrogen (WSTN) content. Results demonstrated a strong correlation between WSOC concentrations measured using both protocols, confirming the reliability of the NPOC method with differences that are generally within the estimated uncertainties at all sites analysed. Notably, the NPOC approach requires a smaller sample volume and offers improved sensitivity at low WSOC concentrations, representing a practical advantage in routine monitoring. The similar solubility of organic carbon was comparable in $PM_{2.5}$ and PM_{10} suggesting that solubility of carbon remains quite stable for particles of different sizes. The solubility of organic carbon was comparable, and the ratio WSOC/OC was similar at the different sites analysed. However, it was observed a seasonal variability, with higher WSOC/OC ratios during the cold season, highlighting the influence of emission sources and meteorological conditions on the solubility of organic carbon.

Furthermore, both protocol enables simultaneous quantification of water-soluble nitrogen without additional sample preparation or instrumentation, enhancing analytical efficiency. The measured WSTN was comparable, within the uncertainty with the measurements of inorganic nitrogen via ion chromatography suggesting that the content of organic soluble nitrogen was limited in this dataset. Overall, these findings support the adoption of the NPOC method as a robust and efficient alternative to TOC method for WSOC analysis in atmospheric aerosol studies.

CRediT authorship contribution statement

Antonio Pennetta: Writing – review & editing, Writing – original draft, Methodology, Conceptualization. **Ermelinda Bloise:** Writing – original draft, Investigation. **Daniela Cesari:** Writing – review & editing, Supervision. **Giuseppe Deluca:** Writing – original draft, Investigation, Data curation. **Adelaide Dinoi:** Writing – review & editing, Supervision. **Maria Rachele Guascito:** Writing – review & editing, Supervision. **Eva Merico:** Writing – original draft, Investigation. **Serena Potì:** Writing – original draft, Investigation. **Paola Semeraro:** Investigation, Data curation. **Florin Unga:** Writing – original draft, Investigation. **Daniele Contini:** Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2025.116305.

Data availability

The data that has been used is confidential.

References

[1] T.C. Bond, R.W. Bergstrom, Light absorption by carbonaceous particles: an investigative review, Aerosol Sci. Technol. 40 (2006) 27–67, https://doi.org/10.1080/02786820500421521.

[2] M.G. Lionetto, M.R. Guascito, M.E. Giordano, R. Caricato, A.R. De Bartolomeo, M. P. Romano, M. Conte, A. Dinoi, D. Contini, Oxidative potential, cytotoxicity, and intracellular oxidative stress generating capacity of PM_{10}: a case study in south of Italy, Atmosphere (Basel) 12 (2021), https://doi.org/10.3390/atmos12040464.

[3] H. Moosmüller, W.P. Arnott, C.F. Rogers, Methods for real-time, in situ measurement of aerosol light absorption, J. Air Waste Manage. Assoc. 47 (1997) 157–166, https://doi.org/10.1080/10473289.1997.10464430.

[4] D. Contini, R. Vecchi, M. Viana, Carbonaceous aerosols in the atmosphere, Atmosphere (Basel) 9 (2018), https://doi.org/10.3390/atmos9050181.

[5] A. Piazzalunga, V. Bernardoni, P. Fermo, R. Vecchi, Optimisation of analytical procedures for the quantification of ionic and carbonaceous fractions in the atmospheric aerosol and applications to ambient samples, Anal. Bioanal. Chem. 405 (2013) 1123–1132, https://doi.org/10.1007/s00216-012-6433-5.

[6] D. Contini, D. Cesari, A. Genga, M. Siciliano, P. Ielpo, M.R. Guascito, M. Conte, Source apportionment of size-segregated atmospheric particles based on the major water-soluble components in Lecce (Italy), Sci. Total Environ. 472 (2014) 248–261, https://doi.org/10.1016/j.scitotenv.2013.10.127.

[7] D. Cesari, A. Genga, P. Ielpo, M. Siciliano, G. Mascolo, F.M. Grasso, D. Contini, Source apportionment of $PM_{2.5}$ in the harbour-industrial area of Brindisi (Italy): identification and estimation of the contribution of in-port ship emissions, Sci. Total Environ. 497–498 (2014) 392–400, https://doi.org/10.1016/j.scitotenv.2014.08.007.

[8] J.C. Chow, J.G. Watson, D. Crow, D.H. Lowenthal, T. Merrifield, Comparison of IMPROVE and NIOSH carbon measurements, Aerosol Sci. Technol. 34 (2001) 23–34, https://doi.org/10.1080/02786820119073.

[9] A.P. Sullivan, R.J. Weber, Chemical characterization of the ambient organic aerosol soluble in water: 1. Isolation of hydrophobic and hydrophilic fractions with a XAD-8 resin, J. Geophys. Res. Atmos. 111 (2006), https://doi.org/10.1029/2005JD006485.

[10] A. Asa-Awuku, G.J. Engelhart, B.H. Lee, S.N. Pandis, A. Nenes, Atmospheric Chemistry and Physics Relating CCN Activity, Volatility, and Droplet Growth Kinetics of β-Caryophyllene Secondary Organic Aerosol. www.atmos-chem-phys.net/9/795/2009/, 2009.

[11] S.R. Suda, M.D. Petters, G.K. Yeh, C. Strollo, A. Matsunaga, A. Faulhaber, P. J. Ziemann, A.J. Prenni, C.M. Carrico, R.C. Sullivan, S.M. Kreidenweis, Influence of functional groups on organic aerosol cloud condensation nucleus activity, Environ. Sci. Technol. 48 (2014) 10182–10190, https://doi.org/10.1021/es502147y.

[12] E. Barbaro, M. Feltracco, D. Cesari, S. Padoan, R. Zangrando, D. Contini, C. Barbante, A. Gambaro, Characterization of the water soluble fraction in ultrafine, fine, and coarse atmospheric aerosol, Sci. Total Environ. 658 (2019) 1423–1439, https://doi.org/10.1016/j.scitotenv.2018.12.298.

[13] Y. Miyazaki, Y. Kondo, M. Shiraiwa, N. Takegawa, T. Miyakawa, S. Han, K. Kita, M. Hu, Z.Q. Deng, Y. Zhao, N. Sugimoto, D.R. Blake, R.J. Weber, Chemical characterization of water-soluble organic carbon aerosols at a rural site in the Pearl River Delta, China, in the summer of 2006, J. Geophys. Res. Atmos. 114 (2009), https://doi.org/10.1029/2009JD011736.

[14] A. Besis, M.P. Romano, E. Serafeim, A. Avgenikou, A. Kouras, M.G. Lionetto, M. R. Guascito, A.R. De Bartolomeo, M.E. Giordano, A. Mangone, D. Contini, C. Samara, Size-resolved redox activity and cytotoxicity of water-soluble urban atmospheric particulate matter: assessing contributions from chemical components, Toxics 11 (2023), https://doi.org/10.3390/toxics11010059.

[15] Y.J. Kim, E.S. Kim, Total organic carbon (TOC) quantification: effect of presence of inorganic carbon (IC) and volatile organic compounds (VOCs), Sci. Total Environ. 993 (2025) 180024, https://doi.org/10.1016/J.SCITOTENV.2025.180024.

[16] A. Dinoi, M. Conte, F.M. Grasso, D. Contini, Long-term characterization of submicron atmospheric particles in an urban background site in southern Italy, Atmosphere (Basel) 11 (2020), https://doi.org/10.3390/atmos11040334.

[17] D. Contini, A. Genga, D. Cesari, M. Siciliano, A. Donateo, M.C. Bove, M.R. Guascito, Characterisation and source apportionment of PM_{10} in an urban background site in Lecce, Atmos. Res. 95 (2010) 40–54, https://doi.org/10.1016/j.atmosres.2009.07.010.

[18] A. Dinoi, D. Cesari, A. Marinoni, P. Bonasoni, A. Riccio, E. Chianese, G. Tirimberio, A. Naccarato, F. Sprovieri, V. Andreoli, S. Moretti, D. Gullì, C.R. Calidonna, I. Ammoscato, D. Contini, Inter-comparison of carbon content in $PM_{2.5}$ and PM_{10} collected at five measurement sites in southern Italy, Atmosphere (Basel) 8 (2017), https://doi.org/10.3390/atmos8120243.

[19] A. Dinoi, A. Donateo, M. Conte, M. Conte, F. Belosi, Comparison of atmospheric particle concentration measurements using different optical detectors: potentiality and limits for air quality applications, Measurement (London) 106 (2017) 274–282, https://doi.org/10.1016/j.measurement.2016.02.019.

[20] M. Conte, E. Merico, D. Cesari, A. Dinoi, F.M. Grasso, A. Donateo, M.R. Guascito, D. Contini, Long-term characterisation of African dust advection in South-Eastern Italy: influence on fine and coarse particle concentrations, size distributions, and carbon content, Atmos. Res. 233 (2020), https://doi.org/10.1016/j.atmosres.2019.104690.

[21] S. Paik, J.H. Vincent, Filter and cassette mass instability in ascertaining the limit of detection of inhalable airborne particulates, Am. Ind. Hyg. Assoc. J. 63 (2002) 698–702, https://doi.org/10.1080/15428110208984757.

[22] F. Cavalli, M. Viana, K.E. Yttri, J. Genberg, J.-P. Putaud, Atmospheric Measurement Techniques toward a Standardised Thermal-Optical Protocol for Measuring Atmospheric Organic and Elemental Carbon: The EUSAAR Protocol, 2010. www.atmos-meas-tech.net/3/79/2010/.

[23] E. Merico, D. Cesari, A. Dinoi, A. Gambaro, E. Barbaro, M.R. Guascito, L. C. Giannossa, A. Mangone, D. Contini, Inter-comparison of carbon content in PM_{10} and $PM_{2.5}$ measured with two thermo-optical protocols on samples collected in a Mediterranean site, Environ. Sci. Pollut. Res. 26 (2019) 29334–29350, https://doi.org/10.1007/s11356-019-06117-7.

[24] D. Cesari, G.E. De Benedetto, P. Bonasoni, M. Busetto, A. Dinoi, E. Merico, D. Chirizzi, P. Cristofanelli, A. Donateo, F.M. Grasso, A. Marinoni, A. Pennetta, D. Contini, Seasonal variability of $PM_{2.5}$ and PM_{10} composition and sources in an urban background site in southern Italy, Sci. Total Environ. 612 (2018) 202–213, https://doi.org/10.1016/j.scitotenv.2017.08.230.

[25] R. Leardi, Experimental design in chemistry: a tutorial, Anal. Chim. Acta 652 (2009) 161–172, https://doi.org/10.1016/j.aca.2009.06.015.

[26] X. Yu, Y.K. Wong, J.Z. Yu, Abundance and sources of organic nitrogen in fine ($PM_{2.5}$) and coarse ($PM_{2.5–10}$) particulate matter in urban Hong Kong, Sci. Total Environ. 901 (2023), https://doi.org/10.1016/j.scitotenv.2023.165880.

[27] C.W. Leung, X. Wang, D. Hu, Characteristics and source apportionment of water-soluble organic nitrogen (WSON) in $PM_{2.5}$ in Hong Kong: with focus on amines, urea, and nitroaromatic compounds, J. Hazard. Mater. 469 (2024), https://doi.org/10.1016/j.jhazmat.2024.133899.