

Article

Source Apportionment of PM_{2.5} and of its Oxidative Potential in an Industrial Suburban Site in South Italy

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Abstract: Some studies suggested a role of the atmospheric particulate matter (PM) and of its oxidative potential (OP) in determining adverse health effects. Several works have focused on characterisation of source contributions to PM OP, mainly using three approaches: correlation between OP and chemical markers of specific sources; use of OP as input variable in source apportionment with receptor models; and multi-linear regression (MLR) between OP and source contributions to PM obtained from receptor models. Up to now, comparison of results obtained with different approaches on the same dataset is scarce. This work aims to perform a OP study of PM_{2.5} collected in an industrial site, located near a biogas production and combustion plant (in southern Italy), comparing different approaches to investigate the contributions of the different sources to OP. The PM_{2.5} samples were analysed for determining ions, metals, carbonaceous components, and OP activity with the DTT (dithiotreitol) assay. Results showed that OP normalised in volume (DTT_V) is correlated with carbonaceous components and some ions (NO₃[−], and Ca²⁺) indicating that PM of combustion, secondary, and crustal origin could contribute to the OP activity. The source apportionment, done with the Environmental Protection Agency (EPA)—Positive Matrix Factorization (PMF5.0) model, identified six sources: secondary sulphate; biomass burning; industrial emissions; crustal; vehicle traffic and secondary nitrate; and sea spray. A MLR analysis between the source's daily contributions and the daily DTT_V values showed a reasonable agreement of the two approaches (PMF and MLR), identifying the biomass burning and the vehicle traffic and secondary nitrate as the main sources contributing to DTT_V activity.

Keywords: biogas plant; PM oxidative potential; source apportionment; positive matrix factorization; multi-linear regression

1. Introduction

Several studies worldwide have identified particulate matter (PM), and especially its fine fraction, as a critical parameter responsible for adverse health effects [1–3]. Although the toxic effects of PM have been correlated with some chemical and physical properties, the toxicity mechanisms are not yet fully known. Some studies [1,4,5] suggested that several adverse health effects could be due to the

oxidative potential (OP) of particulate matter, which leads to high concentrations of reactive oxygen species (ROS), chemical species capable of causing damage at the cellular level. Particularly, these ROS trigger an oxidative stress response involving several proinflammatory cascades that ultimately result in pathology [6,7]. For this reason, in the international scientific community, the OP of atmospheric particulate has started to be considered as a general indicator of risks for human health due to atmospheric particulate matter [8]. Thus, several studies were focused to develop/apply biological and chemical assays to quantify the oxidative potential of atmospheric aerosol and cellular oxidative stress response [9] leading to a variety of cellular [10,11] and acellular methods to evaluate OP ([12] and references therein). Acellular assays are faster and less resource-demanding compared to cellular assays, allowing the collection of reasonably large data sets in different locations that could be used in statistical analyses [12]. One common acellular test is the dithiothreitol (DTT) assay, which analyses the rate of DTT depletion catalysed by chemical species present in the PM [13]. Particularly, DTT is a surrogate for the cellular oxidant, such as nicotinamide adenine dinucleotide (NADH) or nicotinamide adenine dinucleotide phosphate (NADPH), which reduces oxygen to the superoxide anion (O_2^-). Overall, the rate of O_2^- generation catalysed by PM is measured evaluating the rate at which DTT is consumed, depending on the concentration of redox-active species in PM.

This study is focused on the water soluble DTT activity of fine aerosol ($PM_{2.5}$). The properties of water soluble urban aerosol are relevant for epidemiologists and policy makers [14–17]. Moreover, some researches established that the water-soluble DTT activity is linked to adverse health impacts of PM [18–21]. The water soluble OP is thought to involve compounds that, because of their solubility, can be readily absorbed and transported by the body and involved in acute oxidative stress episodes, such as those associated with respiratory and cardiovascular ailments [8].

Summarising the results from studies focused on the correlation of OP and chemical composition of PM, it is possible to conclude that components having a strong redox activity are: metals such as Fe, Cu, Mn, and V [22–24], water-soluble organic carbon (WSOC) [16,25–28], elemental carbon (EC) [13,25,29], organic carbon (OC) [25,30,31], and polycyclic aromatic hydrocarbons (PAHs) [13,32,33]. Instead, several other components, including secondary inorganic ions that may contribute significantly to PM mass concentrations, do not have strong correlation with OP [34].

During recent years, several studies [12,34–38] investigated the contribution of atmospheric sources of PM to OP suggesting that this could provide useful information to effectively reduce emissions from sources that release PM with greater potential toxicity. The main approaches used in the literature to estimate source contributions to OP are essentially three. The first is linear or multi-linear (MLR) regression between OP and concentrations of the different chemical species looking at tracers of specific sources [27,39–42]. This is essentially a qualitative approach that could give information regarding the sources influencing OP. The second is the quantitative analysis performed applying MLR to the outputs of receptor models regressing contributions of PM sources against measured OP values. Receptor models used are principal component analysis (PCA) [21,43,44], chemical mass balance (CMB) [8,33,34,43,45], and positive matrix factorization (PMF) [35,46,47]. In the third approach, the measured OP values are included as input in the PMF receptor model [36]. In some cases, results coming from application of different receptor models are compared [34,36,43], however, up to now no comparison has been done among results obtained by application of MLR and the use of OP values as input for the PMF model.

This work aims to perform a study of OP of the water-soluble fraction of $PM_{2.5}$ collected at an industrial site located near a biogas plant in the background area of Sarno territory (Campania region, South of Italy) and to estimate the contribution of $PM_{2.5}$ sources to the measured oxidative potential. Contributions to OP obtained with MLR applied to the outputs (contributions to $PM_{2.5}$) of EPA-Positive Matrix Factorization (PMF5) receptor model will be compared to the contributions obtained directly using OP as input in the PMF5 run.

2. Experimental

2.1. Measurement Site Description and Sampling Campaign

The area investigated is located in the municipality of the town of Sarno (in Campania, southern Italy), about 1.5 km from the industrial area and 4–5 km from the town (Figure 1). The measurement site (coordinates 40°50′14″ N–14°34′49″ E) is located about 1.5 km from the access to the Caserta-Salerno motorway (A30) and at 100 m from the delimitation of a biogas production (from agricultural wastes) and combustion plant (electrical power of 999 kWe, thermal power of 1069 kWt). The plant covers an area of 12500 m², and the cogeneration engine has a continuous operation of 24 h/day and discharges the flue gases through a chimney 10 m tall having an internal diameter of 27 cm.

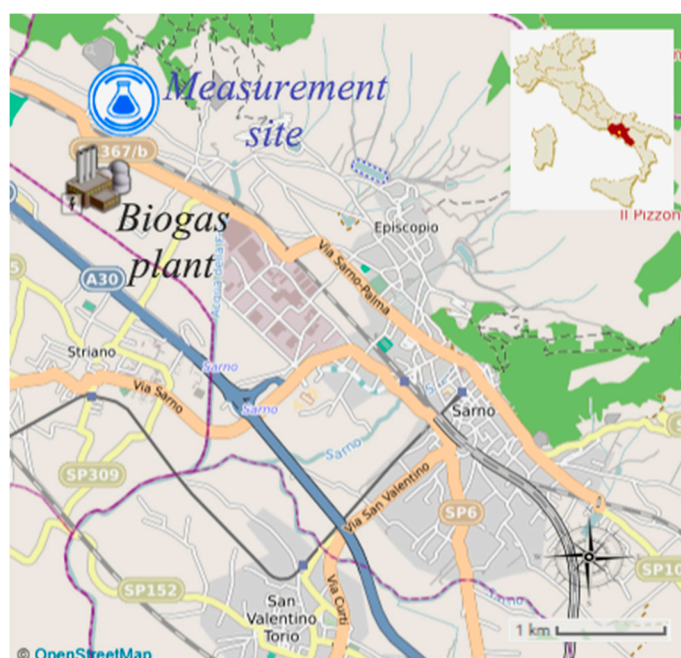


Figure 1. Map of the municipality of Sarno and indications of the location of the measurement site.

The measurement campaign was performed between 30/01/2018 and 28/03/2018, using a low-volume (2.3 m³/h) sequential PM_{2.5} sampler (Zambelli Explorer Plus) equipped with quartz fibre filters (Whatmann, diameter 47 mm). The filters were heated, before use, for 2 h at 700 °C in order to reduce carbon contamination [48]. After sampling they were storage refrigerated (at 4 °C) until the laboratory analysis.

2.2. Gravimetric and Chemical Analysis

The concentration of PM_{2.5} on the sampled filters was evaluated with the gravimetric method using an analytical microbalance (Sartorius Cubis, ± 1 µg). The uncertainty in the evaluation of daily PM_{2.5} concentrations was variable between 1 and 1.6 µg/m³ with an average value of about 10% [49]. The daily PM_{2.5} samples were chemically analysed in order to evaluate the concentrations of elemental carbon (EC), organic carbon (OC), of the main water-soluble ions, and of the main metals.

The EC and OC analyses were done with a Sunset carbon analyser (Sunset Laboratory Inc., OR, USA) operating with the EUSAAR2 protocol (thermo-optical method) [50] on single punch (1 cm²) obtained from 1/4 of filter. The analyser was calibrated using standard sucrose solution (2.198 g/l of carbon in water, CPAchem Ltd., Stara Zagora, Bulgaria). Concentrations obtained from collected samples were corrected by subtracting the average levels measured in blank filters. The average uncertainty of the determination of OC was estimated at 5% while that for EC was 10% [51].

A quarter of filter was used to extract the water-soluble fraction of aerosol (30 min in an ultrasonic bath). Aliquots of the extracts were used for the determination of the major ions using two DIONEX ICS_2000 chromatographs: one dedicated to the analysis of cations and one to that of anions. Anions were separated using an IonPac AS11 2 mm \times 250 mm column with KOH as an eluent in gradient mode. Cations were separated using an IonPac CS16 3 mm \times 250 mm column using an MSA solution as eluent in gradient mode. The average concentrations obtained in collected samples were corrected using measurements done on blank filters.

Another aliquot of each extract was used for the analysis of the oxidative potential of the PM by using the dithiotreitol (DTT) assay [13,52]. The extracts were buffered with 0.5 mL of phosphate buffer 0.5 M at pH = 7.4 for the assay. Reagents used were: DTT 10 mM prepared in 0.5 M phosphate buffer stored at 0 °C, 10% trichloroacetic acid (TCA) prepared in MilliQ, tris(hydroxymethyl)aminomethane (TRIS) 0.4 M buffer at pH 8.9 in ethylenediaminetetraacetic acid (EDTA) 20 mM, 5,5'-dithiobis (2-nitrobenzoic acid) (DTNB) 10 mM in 0.5 M phosphate buffer. The reaction was carried out in vials (obsured) in a bath at 37 °C. Aliquots were taken from the vials at regular intervals of 5 min and the absorbance was measured, after stopping the reaction, using a TIDAS E UV-vis spectrophotometer (J&M Analytik AG, Essingen, Germany). The consumption of DTT over time was determined through a linear fitting of the absorbance versus time. The depletion rate of DTT, opportunely corrected using results obtained in field blanks, was used to determine OP value as DTT-activity normalized in terms of sampled air volume (DTT_V) or in terms of mass of collected aerosols (DTT_M).

The analysis of metal content was carried out by mineralization of $\frac{1}{4}$ of each filter and successive analysis using an ICP-QMS (inductively coupled plasma-quadrupole mass spectrometry, ICP-QMS 7500I, Agilent Technologies, Santa Clara, CA, USA). Mineralization was done with a microwave (Ethos1-Milestone) and a mixture of ultrapure acids: 6mL of HNO₃, 3 mL of H₂O₂, and 1mL of HF (Romil® UPA). The temperature program for microwave filter mineralization consists of a ramp during which the solutions are brought from room temperature to 190 °C in 25 min, and an isothermal during which the temperature of 190 °C is maintained for 15 min. The solutions obtained from microwave mineralization were then diluted to 50 mL with fully deionized ultrapure water (18 M Ω cm⁻¹ resistivity) produced using the Purelab Ultra system (Elga, High Wycombe, UK). The ICP-MS was calibrated using the multi-elemental standard solution IMS-102 (10 μ g/L, Ultrascentific, Santa Clara, CA, USA). The calibration curves had R² = 0.999 for arsenic and R² = 1 for all other elements. A standard reference material was used at known concentrations (NIST 1648a) to evaluate recoveries that ranged between 90% and 100%. The concentration of the elements was obtained subtracting that found in blanks. Concentrations lower or comparable with blanks or lower than the method detection limit (MDL) were replaced with MDL/2.

2.3. Source Apportionment Approach

The PM_{2.5} chemical composition was used for source apportionment based on the positive matrix factorization (EPA-PMF5.0) receptor model that uses the Multilinear Engine (ME-2). This is widely used in scientific literature to evaluate the contribution of specific sources to atmospheric aerosol [53–55]. Concentrations and uncertainties from the chemical analysis were used directly as input to PMF. The input variables were classified using the signal-to-noise (S/N) criteria and also considering the percentage of data above the detection limit as a complementary criterion [56–58]. The species OC, EC, NH₄⁺, K⁺, DMA (dimethylamine), Mg²⁺, Ca²⁺, Cl⁻, NO₃⁻, Mn, and Ni were classified as strong variables; the species Na⁺, SO₄²⁻, Oxa, Al, Cr, Fe, Co, Zn, Pb, and Tl were classified as weak variables and, consequently, the model uses these variables with tripled uncertainties. The PM_{2.5} was categorized as “total variable”. The final dimension of the input matrix was [48 \times 22] and it respects the limits defined by Henry et al. [59], where the minimum required number of samples in order to obtain a statistically stable factor analysis is:

$$N > 30 + 0.5 \times (S + 3) \quad (1)$$

where S is the number of species considered.

Two PMF5 runs were done, the first without using DTT_V in the input dataset (this run is referred throughout the paper as “without DTT_V ”) and the second including DTT_V (in $\text{nmol}/\text{min}\cdot\text{m}^3$) and its uncertainty among the model input variables (this run is referred throughout the paper as “with DTT_V ”). In both cases, the uncertainties on the factor profiles and on source contributions were obtained using the bootstrap method [60].

After the PMF study, a MLR analysis was also performed. The multi-linear regression analysis has been performed between the daily contributions of the sources identified by the PMF (using the dataset without DTT_V) and the daily measured DTT_V values (as the dependent variable), in order to have an independent estimate of the source contributions to OP. The MLR has been performed using the XLSTAT tool and imposing the intercept equal to zero.

3. Results and Discussion

3.1. $PM_{2.5}$ and Chemical Species

The median and average concentrations of $PM_{2.5}$ and of the different chemical species are reported in Table 1 together with their standard deviations and inter-quartile ranges (IQR between 25th and 75th percentiles).

Table 1. Average and median concentrations of particulate matter ($PM_{2.5}$) and chemical species detected together with inter-quartile ranges and standard deviations.

Species	Average St. Dev. ($\mu\text{g}/\text{m}^3$)	Median Range 25–75th ($\mu\text{g}/\text{m}^3$)	Species	Average St. Dev. (ng/m^3)	Median Range 25–75th (ng/m^3)
$PM_{2.5}$	16.26 9.53	1.14 9.69–19.43	Al	1036.9 838.6	727.15 412.82–1289.01
OC	4.79 3.74	3.60 2.69–5.70	Cr	3.37 4.63	1.83 0.80–3.20
EC	0.70 0.51	0.53 0.39–0.84	Mn	4.33 3.83	3.02 0.80–3.20
Na^+	0.28 0.32	0.14 0.06–0.39	Fe	324.0 759.1	113.74 55.45–235.85
NH_4^+	0.29 0.38	0.10 0.01–0.48	Co	0.17 0.16	0.09 0.07–0.29
K^+	0.23 0.20	0.19 0.12–0.29	Ni	19.57 21.57	15.90 13.42–20.56
DMA	0.003 0.007	0.001 0.0005–0.002	Zn	26.0 25.6	18.02 9.76–33.97
Mg^{2+}	0.07 0.02	0.07 0.05–0.08	Pb	4.59 3.72	3.48 1.88–6.63
Ca^{2+}	0.57 0.20	0.57 0.46–0.69	Tl	0.05 0.07	0.02 0.01–0.07
NO_3^-	1.56 1.22	1.14 0.79–1.91	Cl^-	560.0 420.0	410.0 270.0–640.0
SO_4^{2-}	1.48 0.95	1.17 0.69–2.13	Oxa	64.9 62.2	53.7 0.05–101.7

The average concentration of $PM_{2.5}$ was $16.3 \mu\text{g}/\text{m}^3$ and the chemical species analysed explain, on average, 75.0% of $PM_{2.5}$ mass. The carbonaceous material (OC + EC) represents 33.8% (29.5% OC and 4.3% EC); water-soluble ions represent 32.4%, and analysed metals about 8.8%.

An analysis of the Pearson correlation coefficients among the different chemical species could give information regarding possible aerosol sources. In order to investigate the secondary inorganic aerosol in $PM_{2.5}$, the correlation between the species NH_4^+ , NO_3^- , and SO_4^{2-} has been studied. However, the concentration of ammonium is not sufficient to fully neutralise nitrate and sulphate, calcium nitrate and/or sulphate are likely present. Calcium sulphate can be partly due to the advection of Saharan dust, observed in some specific days, which can lead to an increase of this compound in $PM_{2.5}$ [55]. In Figure 2a the correlation between the sum of NH_4^+ and Ca^{2+} concentrations and the sum of NO_3^- and SO_4^{2-} concentrations in $PM_{2.5}$ was reported. The two time series are well correlated (Pearson 0.97, $p < 0.05$) and Figure 2a shows that that secondary inorganic aerosol contributes significantly to the $PM_{2.5}$ concentrations especially in days with high aerosol loads.

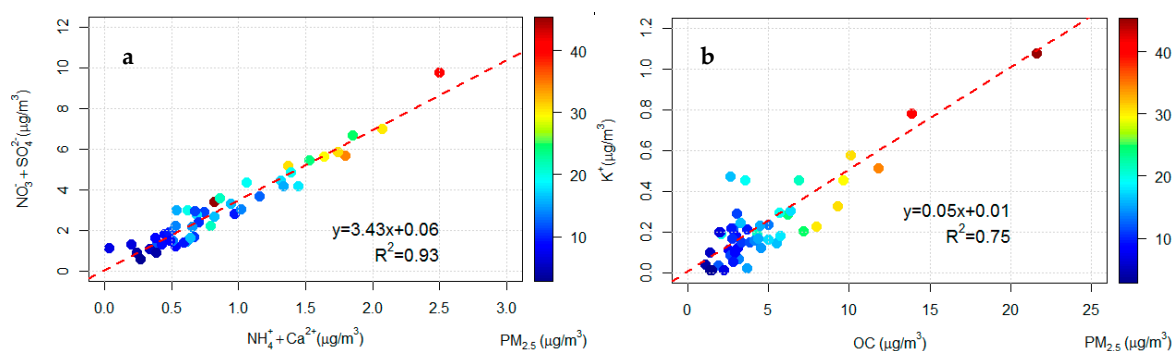


Figure 2. (a) Comparison of the daily sum of the NH_4^+ and Ca^{2+} concentrations and the sum of NO_3^- and SO_4^{2-} in $PM_{2.5}$. (b) Comparison daily concentrations of OC and K^+ in $PM_{2.5}$.

Figure 2b shows the correlation of the time series of organic carbon (OC) and of K^+ concentrations. K^+ is a good tracer of biomass burning emissions [57,61,62]. Considering the good correlation between this two species (Pearson 0.87, $p < 0.05$), especially at high loads of $PM_{2.5}$, it is possible to assume, in the study area, the presence of biomass burning sources contributing to the $PM_{2.5}$ and a large fraction of OC could be attributed to biomass burning. This hypothesis is confirmed by the high correlation between OC and EC concentrations ($R^2 = 0.97$, $p < 0.05$) and the high values for OC/EC (7.1, standard deviation 1.5). Values between 5 and 12 are typically observed for biomass combustion but lower values are expected for traffic emissions [63].

A good correlation was observed between the concentrations of Na^+ and Cl^- (Pearson 0.91, $p < 0.05$) and between Na^+ and Mg^{2+} (Pearson 0.71, $p < 0.05$) which indicates the presence of a contribution of marine aerosol in $PM_{2.5}$, in agreement with the proximity of the measurement site to the coast (about 15 km) and with the fact that, during the sampling periods, different events of Saharan dust transport were observed, using the back-trajectories of air masses evaluated with Hysplit (<http://arl.noaa.gov/ready/>) and the simulations of the Dust REgional Atmospheric Model (BSC-DREAM8b, <https://ess.bsc.es/bsc-dust-daily-forecast>) (not reported here), which are generally associated with transport of marine aerosol in Southern Italy [64].

A correlation was observed between the crustal elements Mn with Fe (Pearson 0.70, $p < 0.05$), and Al (Pearson 0.65, $p < 0.05$), suggesting the presence of a crustal contribution that, although usually more relevant in PM_{10} , can also contribute to $PM_{2.5}$ [57,65].

A correlation between Ni and Cr was observed (Pearson 0.79, $p < 0.05$), indicating a probable common source of anthropic origin (potentially of industrial origin).

3.2. Oxidative Potential and Correlation with Chemical Composition

In Table 2 the DTT_V ($nmol/min \cdot m^3$) and DTT_M ($pmol/min \cdot \mu g$) levels detected at Sarno are shown, together with other values obtained from other studies focused on the $PM_{2.5}$ fraction. The average level for DTT_V is comparable or slightly lower than the levels observed in other northern Italian cities and that those observed in $PM_{2.5}$ at the Environmental-Climate Observatory of Lecce. It is also shown

that the average obtained value for DTT_V and DTT_M is in average lower or comparable to the ranges of the OP detected for $PM_{2.5}$ collected in different sites of Europe and America.

Table 2. Comparison between dithiothreitol (DTT_V) and DTT_M measured in $PM_{2.5}$ collected in this work and in other sites of Italy, Europe, and USA.

Location Site	Site	DTT_V (nmol/min·m ³)	DTT_M (pmol/min·µg)
Sarno, IT current study	Urban background	0.19 (±0.10)	11.67 (±8.43)
Lecce (ECO), IT [30]	Urban background	0.40 (±0.26)	14.5 (±7.6)
Bologna, IT [66]	Urban	Range: 0.3–1.7	-
Athens, GR [21]	Urban background	0.33 (±0.20)	27.9 (±14.4)
Netherlands [67]	Urban background	1.4	Range: 30–80
	Farm	2.7	-
	Traffic	1.7	-
	Traffic	3.3	-
Atlanta, GA [37]	Near road	0.23	24.9
	Urban	0.33	37.6
	Traffic	0.32	33.2
	Rural	0.28	36.1
Los Angeles, CA [41]	Urban	0.62 (±0.21)	7.3 (±1.6)
San Joaquin Valley, CA [23]	Rural	-	23
Fresno, CA [68]	Urban	-	39
Rome [69]	Urban and urban background	0.23 (0.11–0.34)	-

The analysis of correlation between DTT_M and DTT_V with the chemical species (in µg/m³) in $PM_{2.5}$ showed that DTT_M does not have any statistically significant correlation. Instead, DTT_V showed a good correlation with carbonaceous components: OC (Pearson 0.63, $p < 0.05$) and EC (Pearson 0.68, $p < 0.05$), indicating that combustion sources could contribute the measured OP activity. Other correlations are observed with some ions: NO_3^- (Pearson 0.65, $p < 0.05$) and Ca^{2+} (Pearson 0.63, $p < 0.05$), indicating that PM of crustal origin or resuspended dust and of secondary origin could contribute to the OP activity. Lower correlations (Pearson ~0.5, $p < 0.05$) have been observed with NH_4^+ , K^+ , and Pb.

3.3. Source Apportionment Results for $PM_{2.5}$

The PMF5 allowed us to characterise, as best solution, looking at the physical interpretation of results and at the stability running bootstrap, six sources contributing to $PM_{2.5}$. The scaled residuals were symmetrically distributed for almost all variables, meaning that the model was able to reasonably fit each chemical species. The sources found are: secondary sulphate; biomass burning; industrial emissions; crustal; traffic and secondary nitrate; sea spray. The final solution was obtained by applying a constraint (constrained solution) to the base profile, in order to optimize the starting solution (base solution). The constraint was applied to the “vehicular traffic and secondary nitrate” profile, setting the ratio: OC/EC = 2.3, obtained as the average value of the OC/EC ratios calculated on the traffic profiles present in the European database SPECIEUROPE DATABASE 2.0 (<http://source-apportionment.jrc.ec.europa.eu/Specieurope/index.aspx>). The constraint had the objective of improving the separation of the contributions related to the sources “vehicular traffic and secondary nitrate” and “biomass burning” that could present a certain level of collinearity and therefore the use of these constraints helped to separate the two sources [58]. The final dQ variation compared

to the solution base was limited to 0.4%. The bootstrap of the constrained solution (applied with 100 runs with random seed and $R = 0.6$) gave a good mapping of the PMF5 solution with unmapped cases limited to 1% (for industrial source profile). The swap between the profiles was 18% and 10% respectively for “traffic and secondary nitrate” and for “secondary sulphate” source profiles, while were $\leq 2\%$ for the other source profiles. The analysis of G-space plot performed for both the base and the constrained solutions revealed that no edges were evident suggesting that the factors found were linearly independent. Successively, a second PMF run was done including the DTT_V among the input variable.

In Figure 3, the source chemical profiles obtained by input dataset “with DTT_V ” and “without DTT_V ” are compared while in Figure 4 the source contributions are compared. Figures show that the introduction of DTT_V as input variable in PMF produces little changes in the profiles and almost no changes in estimated contribution to $PM_{2.5}$ considering the uncertainties.

Particularly, the contribution of the sources identified by the PMF model using dataset “without DTT_V ”, expressed both in absolute concentrations ($\mu g/m^3$) and relative (% of measured $PM_{2.5}$), showed that the biomass burning contribution is the predominant one, representing about 32.8% ($\pm 1.4\%$) of $PM_{2.5}$, followed by secondary sulphate ($19.7 \pm 2.4\%$) and nitrate and vehicular traffic ($17.0 \pm 3.9\%$). The industrial (primary) contribution represents 5.4% ($\pm 2.3\%$) of $PM_{2.5}$. Finally, the contributions of natural origin vary between 12.9% ($\pm 2.3\%$) for the sea spray (aged) up to 14.7% ($\pm 2.1\%$) for the crustal contribution.

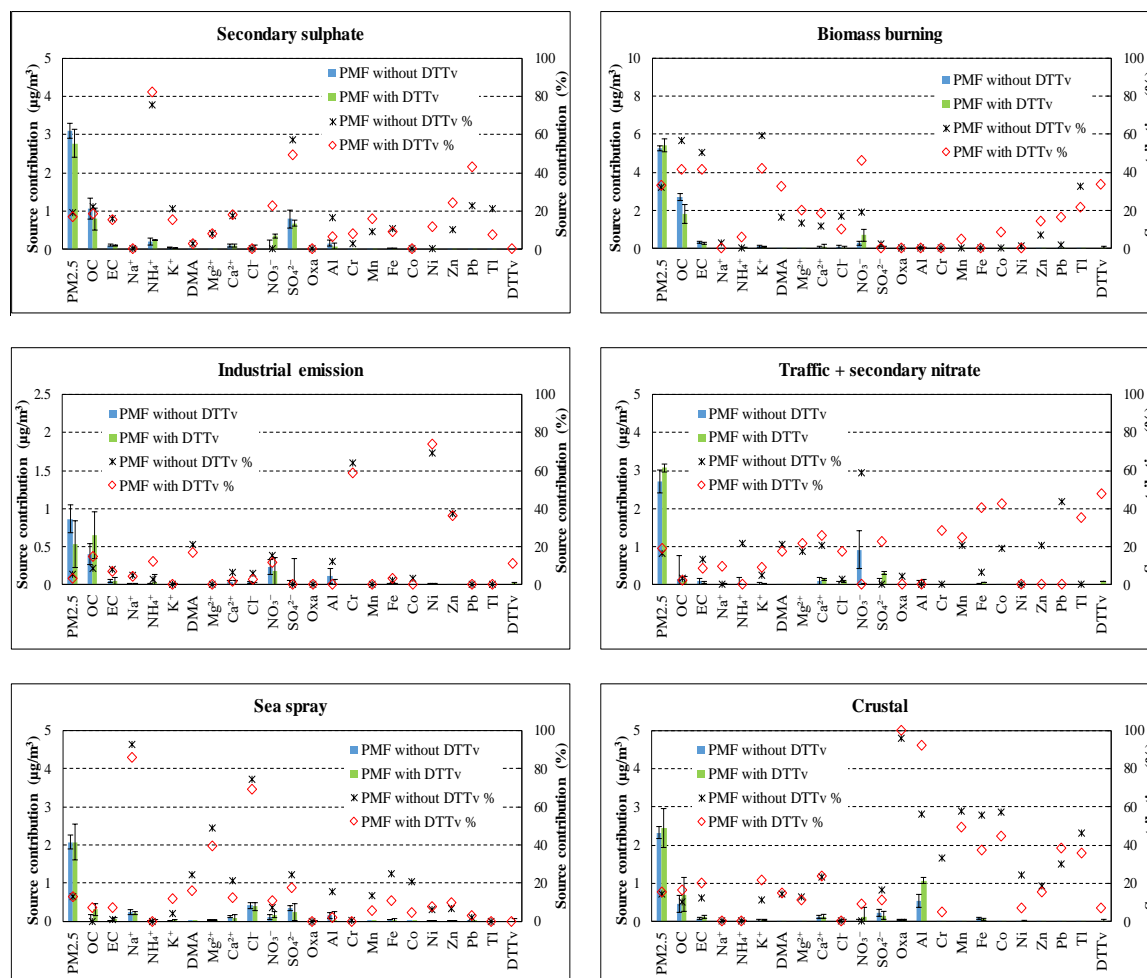


Figure 3. Comparison of source chemical profiles obtained by datasets “with DTT_V ” and “without DTT_V ”.

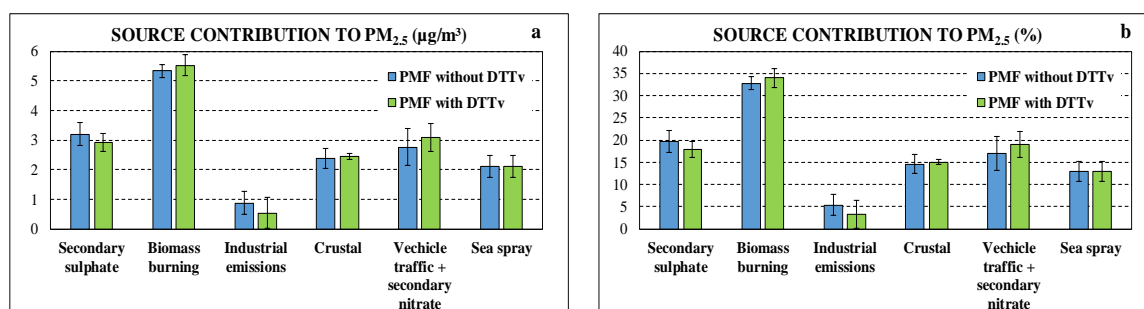


Figure 4. Comparison of source contributions obtained by datasets “with DTT_v” and “without DTT_v” in absolute (a) and relative (b) terms.

3.4. MLR Analysis

In order to estimate the contributions of the PM sources to the OP (in terms of DTT_v) and also to validate our results previously obtained with PMF5, we used a multi-linear regression, assuming that the OP is linearly linked to the PM_{2.5} due to the different sources, according to the formula [35]:

$$DTT_v = m_{PM} \times \beta + \varepsilon \quad (2)$$

where DTT_v is the dependent variable, i.e., a matrix ($n \times 1$) in nmol/min·m³, m_{PM} the ($n \times p$) matrix with the PM contributions attributed to each source by PMF “without DTT_v” in µg/m³, and ε the ($n \times 1$) uncertainty matrix in nmol/min·m³. Finally, n is the number of samples and p the number of sources. The estimator β matrix ($p \times 1$) represents the slopes, expressed in nmol/min·µg.

The results of PMF “without DTT_v”-MLR approach (for simplicity, named MLR in this section) are characterised by an $R^2 = 0.90$ (R^2 correct = 0.88) and a MSE (mean standard error) equal to 0.05. These results, together with the F-test results (at 95% a confidence level) indicated that the model gave a good fit of the variables considered.

In Table 3, the results of MLR analysis, in terms of coefficients of β , standard error, P-values and 95% confidence intervals, are reported. Considering the p -value (with $\alpha = 0.05$) shown for each source investigated, it has been noted that the model gave a good fit for all sources except for secondary sulphate which has a p -value $> \alpha$. This finding is in agreement with other works [8,34], where ammonium sulphate source gave an insignificant contribution to DTT_v. For this reason and according with what has been done in other works [34,43,46], the MLR analysis has been performed again excluding this factor and maintaining only statistically significant sources.

Table 3. Multi-linear regression (MLR) analysis results and parameters indicating the goodness of the fit produced by the model for each source.

Source	B Coefficients	Standard Error	p -value	Lower 95%	Upper 95%
Biomass burning	0.008	0.002	<0.0001	0.005	0.012
Industrial emission	0.037	0.008	<0.0001	0.022	0.053
Crustal	0.017	0.004	<0.0001	0.009	0.025
Traffic and secondary nitrate	0.017	0.003	<0.0001	0.010	0.024
Sea spray	0.010	0.004	0.014	0.002	0.019

In Figure 5 the measured and reconstructed daily DTT_v values obtained with the two approaches (directly by PMF results and using MLR analysis) are compared. The measured and reconstructed data are highly correlated for the PMF “with DTT_v” approach with a slope comparable to one and negligible intercept. The comparison of measured and reconstructed DTT activity using MLR also shows a good correlation but with larger scatter on the data comparable to what has been observed also in other works using MLR approach [8,21,39].

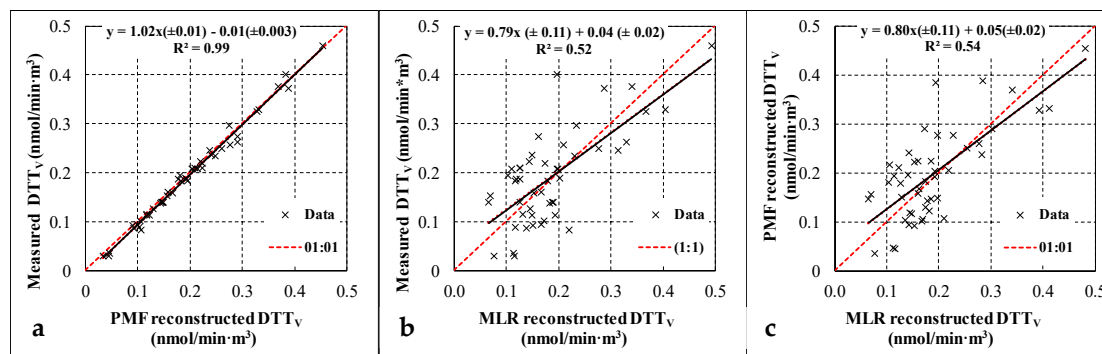


Figure 5. (a) PMF reconstructed vs. measured oxidative potential (OP) of fine aerosol; (b) MLR reconstructed vs. measured OP of fine aerosol; (c) PMF reconstructed OP vs. MLR reconstructed OP.

Figure 6 compares the contributions, in absolute and relative terms, of the different sources to DTT_V obtained with PMF “with DTT_V” and MLR approaches. Both approaches indicate negligible contribution of secondary sulphate to the DTT_V activity. There are some differences among the results of the two approaches, mainly in combustion sources (i.e., biomass burning, industrial, and traffic emissions); however, these differences are comparable to the differences in average source contributions to DTT activity estimated using different receptor models [34,36]. Despite these differences, both approaches give a similar trend with large contributions to DTT_V due to biomass burning as found in other research works [8,34,36,43,46]. The other combustion sources, that are vehicle traffic and secondary nitrate and industrial emission (the latter larger in MLR results), also contributes significantly to the DTT_V activity. In MLR results, crustal source contributes significantly to DTT_V, confirming the correlation observed for DTT_V and Ca²⁺. Contrarily, PMF “with DTT_V” showed limited crustal contributions to DTT_V, in agreement with the results of a MLR study reported in literature [46] and with a previous study which highlighted as the crustal matter is characterized by a lower specific OP [30]. Another difference between PMF “with DTT_V” and MLR results is for marine contribution that is negligible for the former, contrarily to MLR that showed a certain contribution to the DTT_V activity. In general terms, the contributions to DTT_V and PM_{2.5} are not correlated in the same way for all sources: the industrial factor gives the smallest contribution to PM_{2.5} but has a contribution to DTT_V that is greater than that of secondary sulphate, which has a larger contribution to PM_{2.5}.

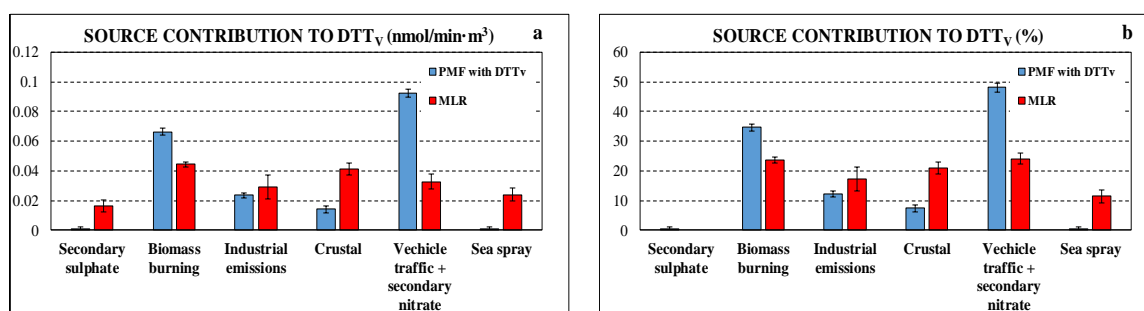


Figure 6. Comparison of source contributions to DTT_V obtained using the two approaches, PMF with DTT_V and MLR in absolute (a) and relative (b) terms.

Figure 7 shows the time series of source contributions to PM_{2.5} (a) and to DTT_V (b) activity using the PMF “with DTT_V” approach. Despite the large daily variability, there is a general considerable contribution coming from combustion sources, i.e., biomass burning and traffic emissions, followed by industrial emission. Further, the DTT_V time series is well correlated with the PM_{2.5} time series showing simultaneous peaks during the measurement period.

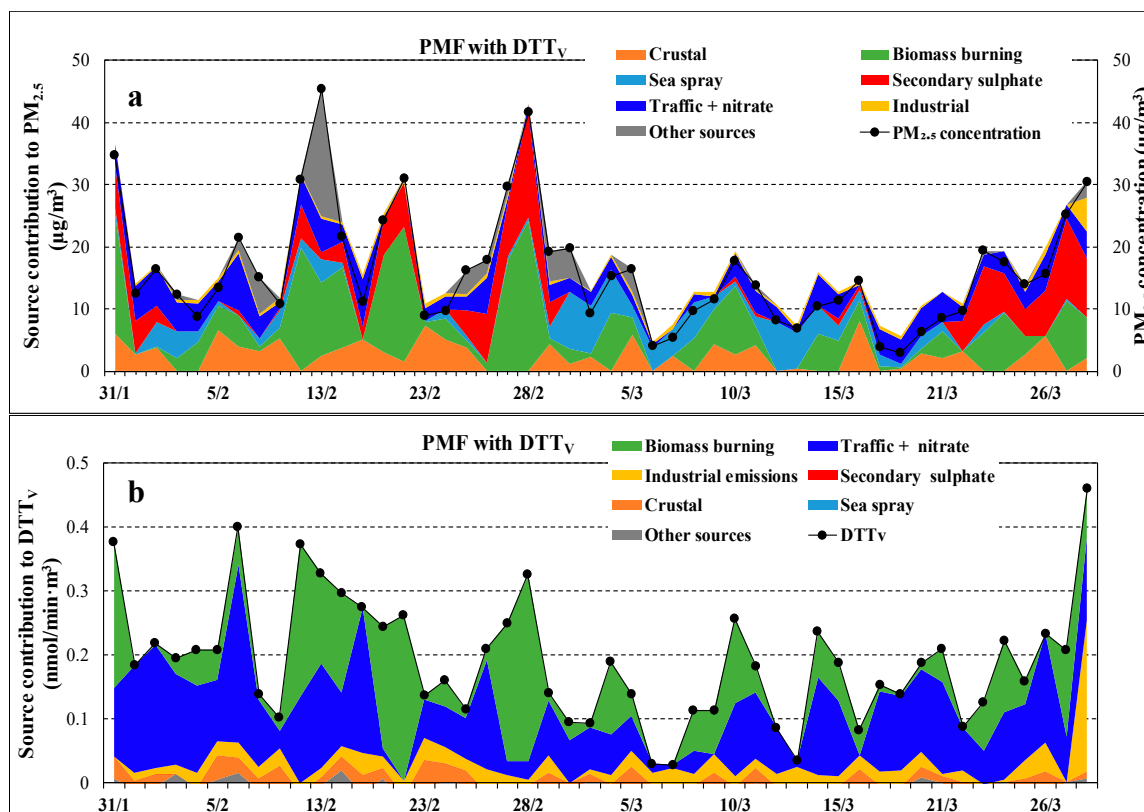


Figure 7. Time series of source contributions to $PM_{2.5}$ (a) and to DTT_V (b) activity obtained by PMF “with DTT_V ” approach. The figure includes measured $PM_{2.5}$ concentrations (black marks).

4. Conclusions

A study of the contribution of $PM_{2.5}$ sources to the OP evaluated using the DTT assay in an industrial site located near a biogas production and combustion plant is reported. Two approaches are used and compared: the first is to include DTT_V in the input of the receptor model EPA PMF5 and the second is to use a multi-linear regression (MLR) for estimating the source contributions to OP. The main conclusions of this study are summarized as follows:

- During the measurement period the average concentration of $PM_{2.5}$ was $16.3 \mu\text{g}/\text{m}^3$. The carbonaceous material represents 33.8%; water-soluble ions represent a total of 32.4%, and the analysed metals represent about 8.8% of $PM_{2.5}$.
- The correlations between some of the chemical species investigated indicate possible contributions to the $PM_{2.5}$ concentrations from biomass burning; marine aerosol; crustal and industrial sources.
- The DTT_V and DTT_M levels detected at Sarno are comparable or slightly lower than the levels observed for $PM_{2.5}$ in other Italian, European, and USA cities.
- The DTT_V showed a good correlation with carbonaceous components as possible origin of the source combustion processes. Other correlations were observed with NO_3^- , Ca^{2+} , and, to a lower extent NH_4^+ , K^+ , and Pb.
- The PMF5 model identified six sources contributing to $PM_{2.5}$: biomass burning, $32.8 \pm 1.4\%$; secondary sulphate, $19.7 \pm 2.4\%$; vehicle traffic and secondary nitrate, $17.0 \pm 3.9\%$; crustal, $14.7 \pm 2.1\%$; sea spray, $12.9 \pm 2.3\%$; and industrial (primary) emissions, $5.4 \pm 2.3\%$. Introducing the DTT_V as input variable does not change significantly these results.
- Contributions of sources to DTT_V were estimated using two independent approaches: a MLR analysis performed between measured DTT_V and output of the PMF; a PMF run including DTT_V in the input variables. The two approaches gave a similar trend with negligible contribution

of sulphate and larger contributions of combustion sources: biomass burning and road traffic. Major differences were observed for crustal and marine sources that are larger using MLR.

- Comparison of daily DTT_V reconstruction with the two approaches shows a better agreement with a lower scattering in the data with the PMF “with DTT_V” approach compared to MLR.
- In general, the contributions to DTT_V and PM_{2.5} are not correlated for all sources: The industrial factor has the smallest contribution to PM_{2.5} but shows a contribution to DTT_V that is greater than that of secondary sulphate which has a larger contribution to PM_{2.5} and a negligible contribution to DTT_V.

These results provide further evidences that combustion sources (biomass burning and traffic emissions) are the major contributors to the OP^{DTT} activity of PM. At the site analysed, the PMF seems to show a good ability, even better than using external MLR approach, in investigating the contribution of the PM sources on the OP activity, despite the differences in the units of measurement of the variables considered (OP activity and chemical species); however, further investigations are needed in different conditions to confirm this result.

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