



Comparing the Performance of Teflon and Quartz Membrane Filters Collecting Atmospheric PM: Influence of Atmospheric Water

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ABSTRACT

Mass concentration and chemical composition of PM₁₀ and PM_{2.5} was measured during eight one-month winter and summer field studies carried out in the Po Valley (Northern Italy). PM was daily collected on Teflon (T) and on quartz (Q) filters set side-by-side. During the summer periods the differences between the mass concentrations measured on the two filters (T-Q) were within the range of experimental error, while statistically significant positive differences were detected during the winter periods. The sum of the chemical analyses (elements, ions, elemental and organic carbon) allowed the achievement of satisfactory mass closure during the summer periods, while unaccounted masses of the order of 10–20% of the PM mass measured on Teflon were detected during the winter periods. Unaccounted mass and T-Q differences increased during periods of high atmospheric stability, when the ammonium nitrate concentration also increased rapidly. Unaccounted masses and T-Q differences can be attributed to PM-bound and PM-adsorbed water.

Keywords: Aerosol sampling; Filters; Chemical characterisation; Mass closure; Water content.

INTRODUCTION

Sampling of atmospheric particulate matter (PM) can be carried out by filtering air through a variety of collecting media. The European legislation indicates that quartz fiber filters must be used for the determination of PM₁₀, according to the European Standard method EN 12341 (1998), while filters made of glass fiber, quartz, PTFE or PTFE-bonded glass fiber can be used for the determination of PM_{2.5}, according to EN 14907 (2005). This wider choice is due to the requirement to determine not only the mass concentration but also some of the chemical components of PM_{2.5} (at least ionic species, elemental carbon and organic carbon).

In the scientific community, glass or quartz fiber filters are generally preferred for PM mass determination with the beta attenuation method, while Teflon filters are preferred for gravimetric determinations because of their higher insensitivity to relative humidity during the weighing procedure (Brown *et al.*, 2006). When sampling is aimed to chemical characterization, instead, the choice of the filter material depends on the type of analyses to be carried out on the collected dust: no single filter medium is appropriate for all chemical analyses and sampling on multiple substrates

can be necessary when a complete chemical characterization is desired. In general, Teflon membranes show better performances when ions and elements have to be determined, because of their lower blank levels (Chow and Watson, 1998). Instead, the determination of elemental and organic carbon (EC/OC), which has to be carried out at high temperatures, can only be performed on quartz fiber filters. Additional criteria range from practical issues, such as cost or availability, to physical and chemical features, such as mechanical stability, flow resistance, loading capacity, static charge effects, chemical stability, blank levels.

Also in air quality networks, which are usually aimed to the determination of both mass concentration and chemical composition of PM, the choice of the sampling media depends on the subsequent analytical phase. In Europe, the EMEP monitoring network recommends the use of quartz filters for EC/OC determination, Teflon filters for mineral dust and teflon or quartz for heavy metals (EMEP, 2002). In the USA, the PM_{2.5} Federal Reference Method recommends the use of Teflon membrane filters (<http://www.epa.gov/ttnamti1/pmfrm.html>), while the IMPROVE network (Interagency Monitoring of Protected Visual Environments) uses Teflon filters for the determination of PM mass and elements and quartz for the determination of EC/OC (<http://vista.cira.colostate.edu/improve/>). In Canada, the Canadian Air and Precipitation Monitoring Network (CAPMoN) recommends the use of Teflon filters for gravimetric mass determination and subsequent XRF analysis of elements (<http://www.ec.gc.ca/rs-mn/default.asp?lang=>

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These different perspectives reflect in different results in PM determination. It is well known that sampling of atmospheric particles undergoes several artefacts including adsorption of organic vapour, evolution of ammonium salts and retention of water vapour. A number of scientific studies describe the different performance of quartz, cellulose acetate-nitrate, nylon and Teflon filters in retaining organics and in releasing ammonium chloride and nitrate (Schaap *et al.*, 2004; Subramanian *et al.*, 2004; Wittmaack and Keck, 2004; Vecchi *et al.*, 2009). In the case of organics, these studies show that the positive artefact (adsorption of gas-phase organics) prevails on the negative one (release of particulate-phase organics from the sample) and that Teflon filters adsorb little or no gas-phase OC while quartz filters suffer from a relevant adsorption. In the case of ammonium salts, their volatilisation generally dominates on adsorption and the artefact is much higher on Teflon than on quartz filters. Accordingly, the use of quartz filters, which show a higher retention of organics and lower release of ammonium salts, would result in higher PM mass concentration with respect to Teflon membranes.

The performance of Teflon and quartz filters have been compared in many laboratory and field studies aimed to describe and quantify the artefacts (Vecchi *et al.*, 2009 and reference therein). However, there has been relatively little reporting of long time-series of side-by-side determinations of PM mass on quartz and Teflon filters in real atmospheres (Schaap *et al.*, 2004; Vecchi *et al.*, 2009).

In addition, several studies have focused on attempting the mass closure, that is the coincidence between the sum of the chemical determinations and the gravimetric PM mass. In these investigations, parallel samplings were carried out on Teflon and on quartz filters, ions and elements were detected on Teflon, elemental and organic carbon were detected on quartz, the sum of the chemical determinations was compared with the mass amount determined on Teflon (Harrison *et al.*, 2003; Martuzevicius *et al.*, 2004; Tanner *et al.*, 2004; Sillanpaa *et al.*, 2006). When a gap was detected in the mass closure, generally a positive discrepancy (gravimetric-measured mass exceeding the sum of the chemical components), it was attributed to analytical uncertainty, presence of aerosol water, volatilization of organics and nitrates, uncertainty in the assumptions used to estimate chemical species not directly measured, or a combination of (Rees *et al.*, 2004 and cited therein; Terzi *et al.*, 2010). To our knowledge, in these studies the sum of the analytical determinations was not compared with the PM gravimetric mass on quartz.

We report in this paper the results of a 4-year seasonal study carried out in the Po valley (Northern Italy) by using two co-located sampling instruments simultaneously running quartz and Teflon filters. During the winter the sampling site was characterised by very unfavourable stability conditions, high humidity and high ammonium nitrate concentration. Differences in the PM mass concentration recorded on the two filtering media and comparison of the two series of mass concentration data with the sum of the analytical determinations are reported and discussed.

EXPERIMENTAL

The area of the study was Cassana (coordinates: 44°51'4"N; 11°32'56"E, 10 m above sea level), a hamlet about 6 km from the centre of Ferrara, a medium-size city in the Po Valley (Northern Italy). During the winter, all the Po Valley is characterised by long periods of strong atmospheric stability, which causes ageing of the air mass, worsening of the air quality and relevant increase in the concentration of secondary pollutants. The area of Cassana is influenced by several PM sources, among which the nearby urban area of Ferrara, the highway A13 and a wide industrial area including, among others, a power plant, a urban waste incinerator and many small and medium enterprises.

The study consisted in eight 30-day Special Observation Periods (SOPs) conducted during January and June in the period 2008–2011. During the first six SOPs (January and June 2008–2010) PM₁₀ and PM_{2.5} mass concentrations were measured by two co-located dual channel instruments: the first one was a dual channel beta attenuation automatic monitor (SWAM 5a Dual Channel Monitor – FAI Instruments, Fonte Nuova, Rome – IT) equipped with quartz fibre filters, the second one was a dual channel sampler (HYDRA Dual Sampler, FAI Instruments, Fonte Nuova, Rome – IT) equipped with Teflon filters that were subsequently analysed by gravimetry. During the last two SOPs (January and June 2011) the HYDRA sampler was substituted with a second SWAM 5a Dual Channel Monitor, also equipped with Teflon filters. The two channels of each instrument were devoted to determining PM₁₀ and PM_{2.5}.

Both SWAM 5a Monitor and HYDRA have been certified by TUV as reference samplers. SWAM 5a Dual Channel has also been certified as beta monitor by both TUV and CERT; it complies with EU equivalence criteria for PM measurements against the reference methods (both EN 12341 and EN 14907). The results of the equivalence tests carried out by TUV were the following: 0.11 µg/m³ deviation and 1.34 µg/m³ uncertainty at the limit value (50 µg/m³) for PM₁₀, -0.87 µg/m³ deviation and 1.23 µg/m³ uncertainty at the limit value (30 µg/m³) for PM_{2.5} (TUV Report, 2010). In addition, during the SOPs we periodically checked PM determinations by the beta attenuation method against the gravimetric procedure and the differences were confirmed to be below 2 µg/m³. Differently from the beta monitors used in some studies reported in the scientific literature, that were found to underestimate PM mass (Takahashi *et al.*, 2008), the SWAM 5a Dual Channel Monitor is not heated. This feature avoids the evaporation of volatile aerosol content, which is the most relevant drawback of heated automatic instruments.

Chemical characterisation of the collected dust was carried out according to the method reported in Perrino *et al.* (2009). Briefly, elements were determined on Teflon filters by X-ray fluorescence (X-Lab2000, Spectro Analytical Instruments, Kleve-D); then the filters were water-extracted and analysed for their ionic content by ion chromatography (ICS1000, Dionex Co., CA-U.S.A.); elemental and organic carbon were detected on quartz filters by thermo-optical analysis (OCEC Carbon Aerosol Analyser, Sunset Laboratory, OR-

USA; NIOSH-QUARTZ temperature protocol). This overall analytical procedure allows the determination of each individual component typically accounting for more than 1% of the mass amount of PM₁₀ and PM_{2.5}. For obtaining the mass closure, as reported in Perrino *et al.* (2010), the contribution of elements was calculated by applying the correction for oxygen in metal oxides (Chan *et al.*, 1997; Marcazzan *et al.*, 2001), carbonate was calculated from calcium and magnesium, organic carbon was multiplied by 1.8 to take into account non-C atoms (Turpin and Lim, 2001).

RESULTS AND DISCUSSION

Teflon-Quartz Difference

PM mass concentrations measured on Teflon filters and on quartz filters during the eight SOPs are compared in Fig. 1. The two data sets are very well correlated, with a Pearson's coefficient of 0.966 for PM₁₀ and 0.963 for PM_{2.5}. However, the slopes and intercepts are 0.82 and 3.68 for PM₁₀ and 0.85 and 1.30 for PM_{2.5}, a first indication that the mass concentrations measured on Teflon filters exceed the concentrations measured on quartz. The scatter plots are shown in the upper panels of Fig. 2 (N = 203 for PM₁₀; N = 198 for PM_{2.5}).

Fig. 1 shows that Teflon – quartz differences (T-Q) were clearly higher during the winter period, when they varied from –6 to +23 µg/m³ for PM₁₀ (average value: 5 ± 6 µg/m³) and from –7 to +27 µg/m³ for PM_{2.5} (average value: 4 ± 5 µg/m³). Teflon and quartz results during the winter period were compared by using the Student's t test and the differences were found to be significant at 99% confidence level. T-Q values show a reasonably good correlation with the mass concentration, with a Pearson's coefficient of 0.553 for PM₁₀ and 0.402 for PM_{2.5}. The scatter plots of T-Q vs. PM concentration on Teflon during the winter period are shown in the lower panels of Fig. 2 (N = 113 for PM₁₀; N = 114 for PM_{2.5}). During the summer period, instead, the average T-Q values were 0 ± 3 µg/m³ for PM₁₀ and 1 ± 3 µg/m³ for PM_{2.5} and were not correlated with PM mass concentration (R² < 0.1).

During the summer period, when the PM₁₀ concentration rarely exceeded 30 µg/m³, and during the few days of clean air occurring during the winter, T-Q differences can be considered to be within the experimental error. However, it is clear that in the high concentration range (above 50 µg/m³) these differences cannot be attributed to measurement uncertainty. Also, it is surprising that we find positive T-Q differences while most of the known artefact mechanisms, such as the adsorption of organics and the release of ammonium nitrate, would lead to negative T-Q values.

It is worth noting that the T-Q differences were observed, at similar extent and with the same statistical significance, during the 2008–2010 SOPs, when PM on Teflon filters was detected gravimetrically and PM on quartz filters was measured by the beta attenuation method, and during the 2011 SOPs, when all the PM determinations were carried out by the beta attenuation methods. This is a further evidence that beta measurements were equivalent to gravimetric determinations.

Mass Closure on Teflon and on Quartz filters

The analysis of the chemical composition of PM can add relevant information to this discussion. Comparing the gravimetric mass of PM₁₀, as measured on the Teflon filter (PM_{TEF}), to the sum of the chemical determinations (PM_{CHEM}) carried out on Teflon (elements and ions) and on quartz (EC/OC), we obtained a satisfactory mass closure for the summer periods, with unaccounted mass concentrations of the order of 2–3 µg/m³. During the winter, instead, chemical determinations clearly underestimated the gravimetric mass (the differences were significant at 99% confidence level). The average value, standard deviation and 90th percentile of the unaccounted mass concentrations during the eight SOPs are reported in Table 1. The data show that the unaccounted mass was mostly in the fine fraction of PM, and that underestimations of the order of 10 µg/m³ (10–20% of the PM mass concentration) were rather frequent during the winter period. The daily comparison between PM_{TEF} and PM_{CHEM} during the four winter SOPs is reported in Fig. 3.

The results show that PM_{CHEM} was much lower than PM_{TEF} during periods of high concentration, corresponding to periods of high atmospheric stability. Previous studies carried out with the aid of natural radioactivity measurements, which is able to trace the variations in the height of the mixing layer, have shown that PM concentration considerably and sharply increases during periods of intense stability conditions that do not slacken during daytime hours. These periods are also characterised by a relevant increase of secondary species concentration, particularly of ammonium nitrate (Vecchi *et al.*, 2004; Perrino *et al.*, 2008; Ferrero *et al.*, 2009). Table 2 reports the average values of PM_{TEF} and of the unaccounted mass concentration recorded during the four winter SOPs, grouped as a function of ammonium nitrate concentration in PM₁₀. Ammonium nitrate contribution to PM sharply increases with increasing PM concentration and the unaccounted mass also increases with increasing ammonium nitrate concentration. In the very high concentration range, when PM₁₀ exceeds 100 µg/m³, ammonium nitrate may constitute up to 30–35% of the total PM_{TEF} mass and the unaccounted fraction may reach the remarkable value of 20%.

However, in geographical areas where stability conditions are less critical than in the case of the Po valley, the mass closure is generally satisfactory. By applying the same method to obtain the mass closure to many other field studies carried out in different sites of the Mediterranean area (Perrino *et al.*, paper in preparation), we obtained unaccounted masses below 2–3 µg/m³. Fig. 4 reports the mass closure obtained during three of these field studies, carried out in the urban background station of Rome during October–December 2007, in the urban area of Palermo (Sicily, South-Italy) during March–May 2011 and in Montelibretti (peri-urban area of Rome) during June 2006. Identical calculations were applied to all these studies; the only difference concerned the OC to OM conversion factor, which was set at 1.6 for the urban area of Palermo and to 1.8 for the other two sites (peri-urban or urban background). The two upper graphs in Fig. 4 show the good agreement

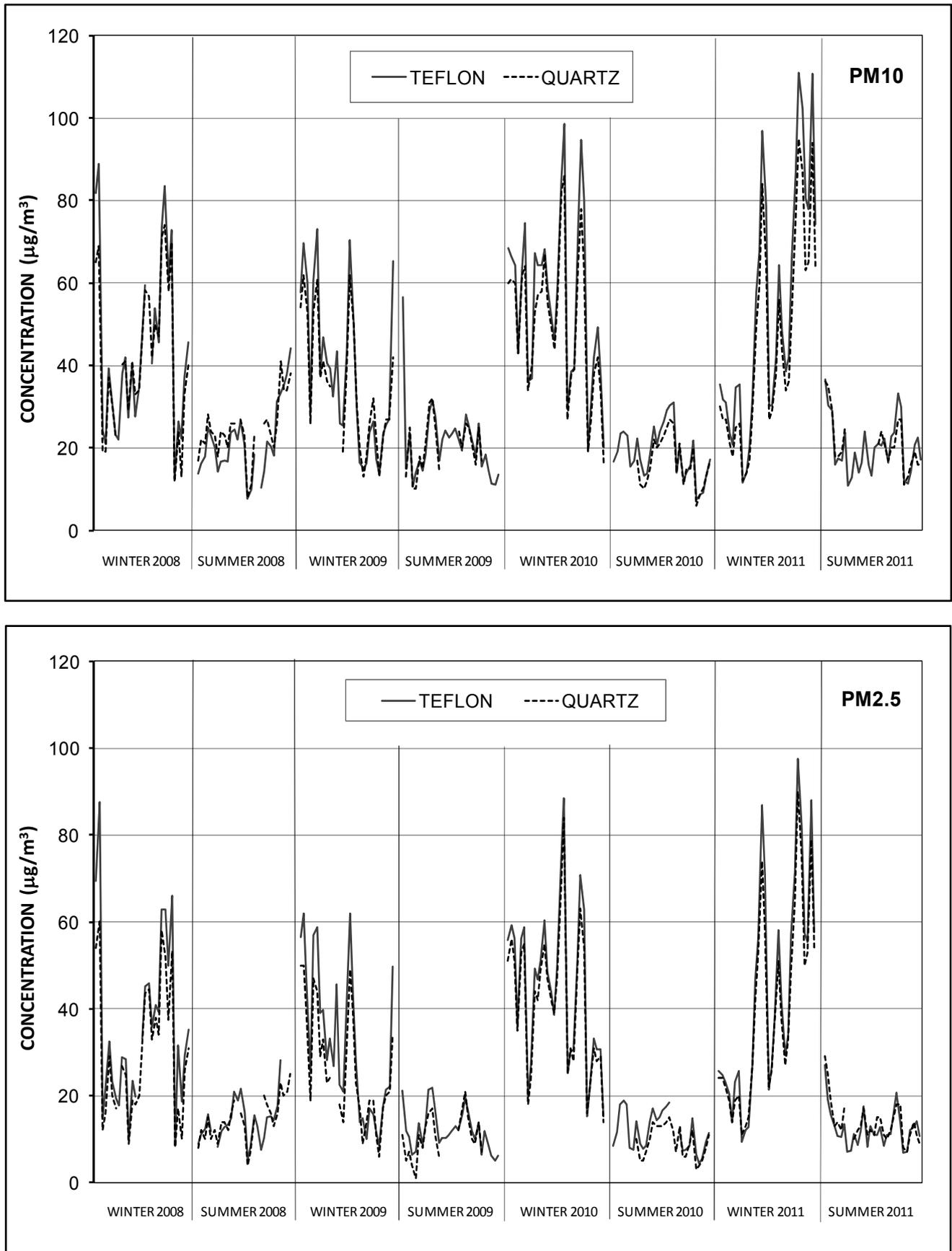


Fig. 1. Comparison of PM_{10} (upper panel) and $\text{PM}_{2.5}$ (lower panel) mass concentrations as determined on quartz and on Teflon filters during eight seasonal field campaigns.

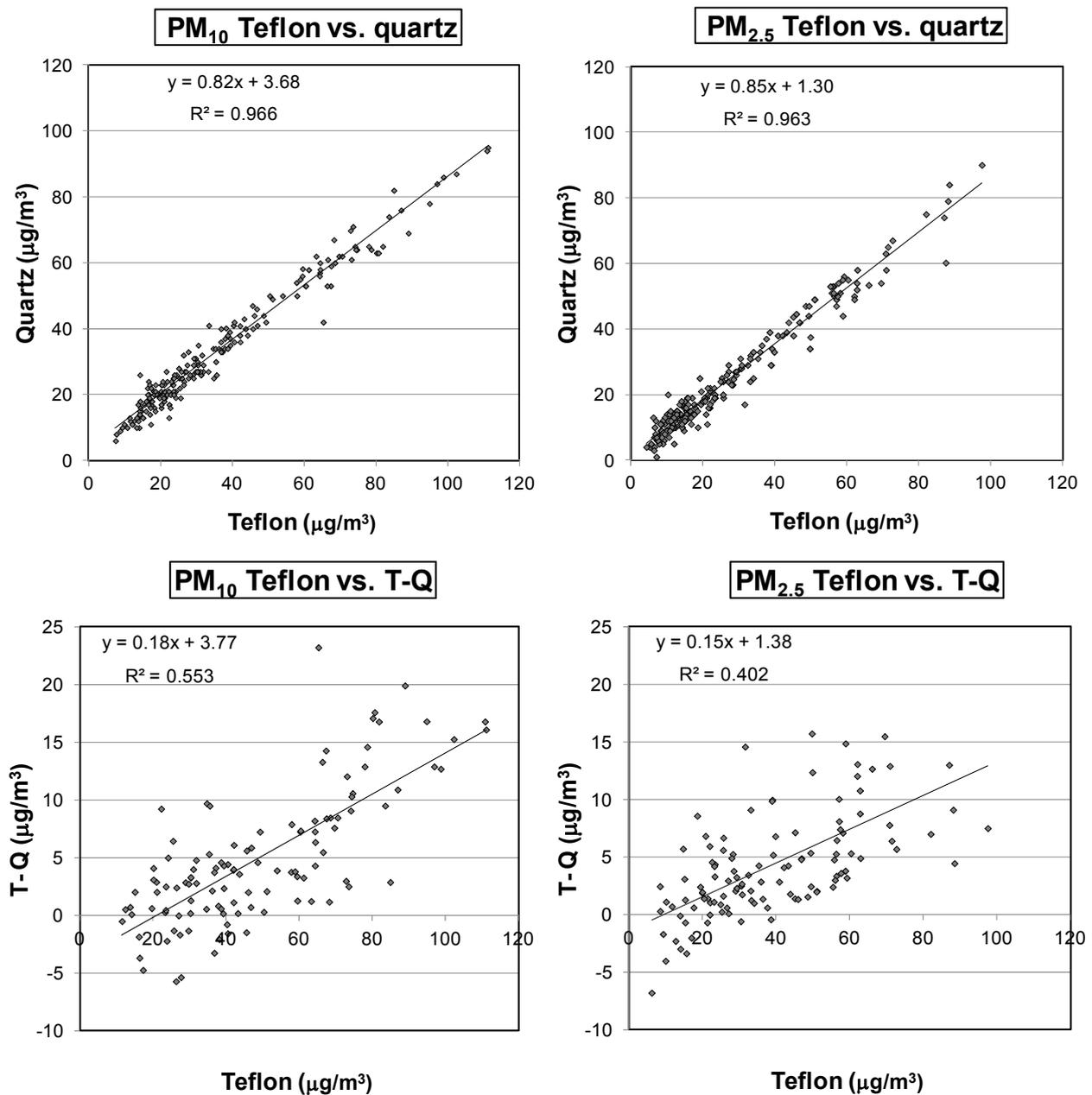


Fig. 2. Scatter plot of PM mass concentration determined on quartz and on Teflon filters for PM₁₀ (left upper panel) and PM_{2.5} (right upper panel) during all SOPs; scatter plot of the T-Q difference against mass concentration determined on Teflon filters for PM₁₀ (lower left panel) and PM_{2.5} (lower right panel) during the winter SOPs only.

Table 1. Difference between the PM mass concentration determined on the Teflon filters and the sum of the chemical determinations (unaccounted mass concentration: PM_{TEF} - PM_{CHEM}).

	PM ₁₀ (μg/m ³)			PM _{2.5} (μg/m ³)		
	AVG	ST. DEV.	90%	AVG	ST. DEV.	90%
WINTER 2008	4.7	5.5	10.3	4.5	6.8	12.0
WINTER 2009	4.8	5.7	10.6	4.7	5.8	11.1
WINTER 2010	4.5	7.0	14.0	3.2	5.2	10.0
WINTER 2011	8.8	7.3	15.9	5.1	6.3	14.3
SUMMER 2008	1.1	2.8	4.5	1.3	2.6	4.0
SUMMER 2009	1.2	1.8	3.5	0.8	1.8	3.2
SUMMER 2010	1.7	2.2	4.8	1.1	2.1	4.3
SUMMER 2011	0.6	2.7	3.2	0.4	2.5	2.8

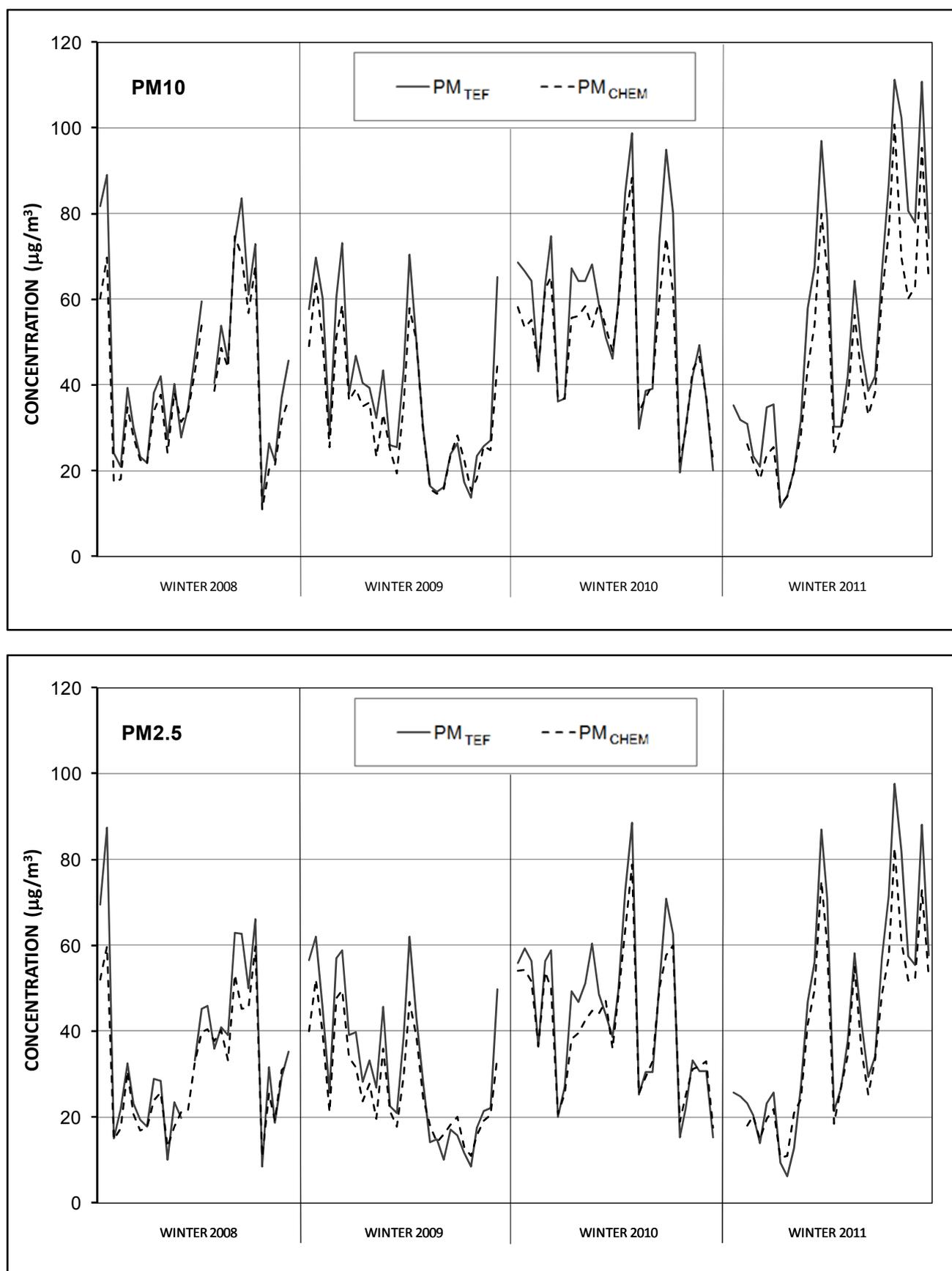
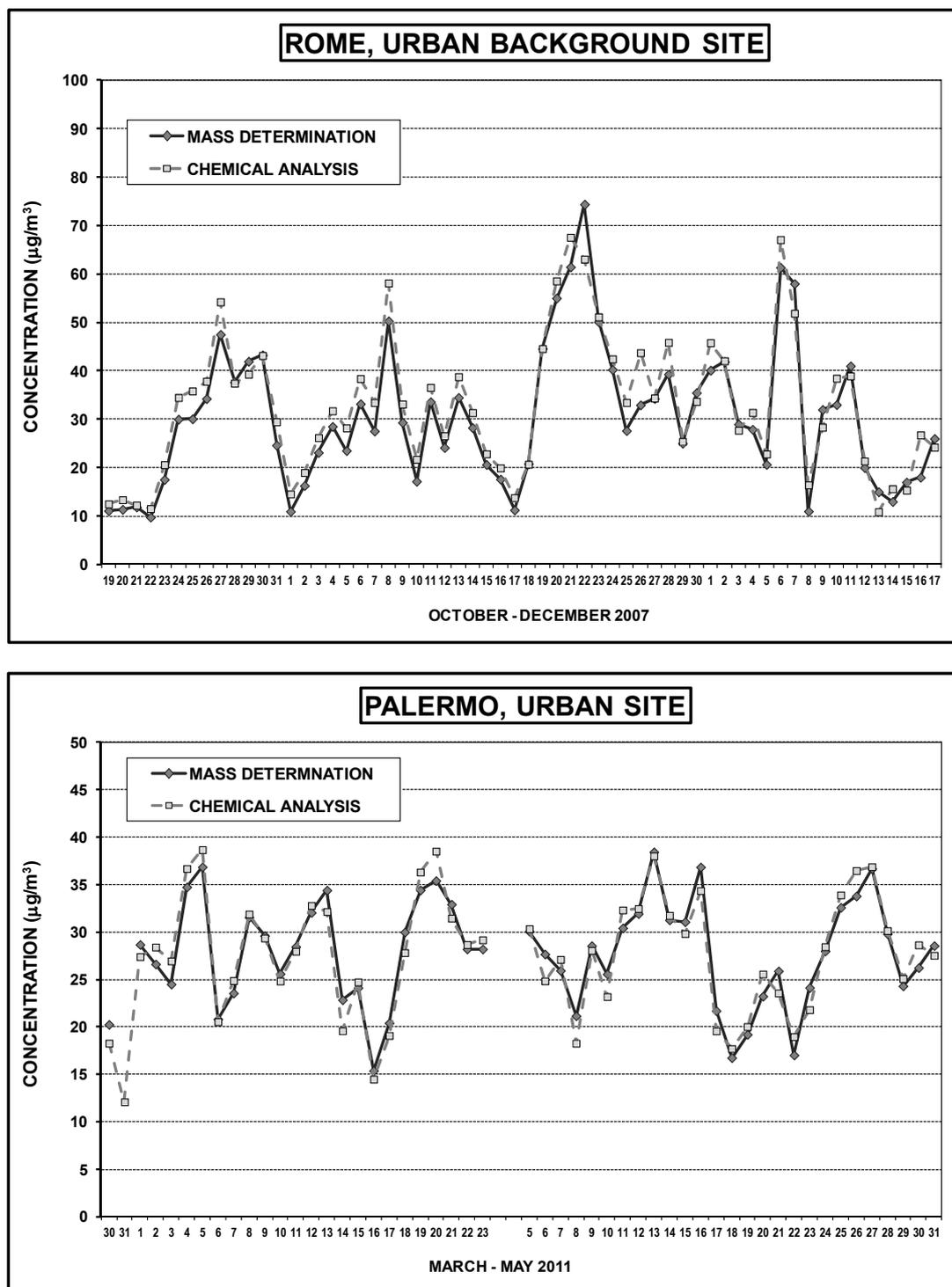


Fig. 3. Comparison of PM_{10} (upper panel) and $\text{PM}_{2.5}$ (lower panel) mass concentrations determined on Teflon filters (PM_{TEF}) and calculated as the sum of the analytical determinations (PM_{CHEM}) during the four winter SOPs.

Table 2. Ammonium nitrate and unaccounted mass concentration ($PM_{TEF} - PM_{CHEM}$) in PM_{10} during the four winter SOPs.

N of samples	NH_4NO_3 ($\mu g/m^3$)	PM_{TEF} ($\mu g/m^3$)	NH_4NO_3/PM_{TEF} (%)	UNACCOUNTED MASS ($\mu g/m^3$)
27	0–5	22	13	1
45	5–10	43	17	4
13	10–15	65	20	6
17	15–20	75	24	10
8	> 20	90	30	11

**Fig. 4.** Comparison of the mass concentrations determined on Teflon filters and calculated as the sum of the analytical determinations during three studies carried out in different areas of Italy.

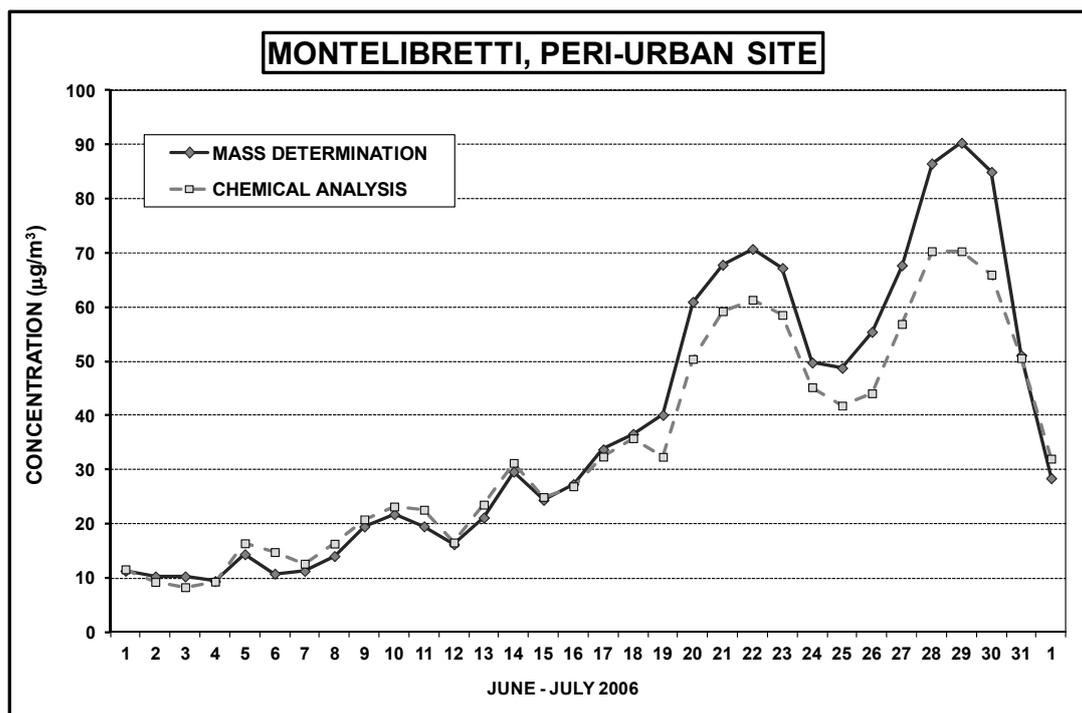


Fig. 4. (continued).

between PM_{TEF} and PM_{CHEM} that is generally observed in the Mediterranean basin, during the whole year. The lower graph shows, instead, the critical situation occurred during the last part of the June 2006 campaign in Montelibretti: again, the underestimation of PM_{CHEM} with respect to PM_{TEF} reached values as high as $20 \mu\text{g}/\text{m}^3$ (more than 20% of the collected mass). This period was characterised by a relevant Saharan dust outbreak, recorded on Central Italy from 20 to 30 June 2006 (Bouchlaghem *et al.*, 2009).

To sum up, from our studies it appears that two situations are critical for obtaining a satisfactory mass closure: long and heavy stability periods (very often occurring in the Po Valley) and desert dust advection. These two situations are characterised by a very different chemical composition of PM: prevalence of secondary species during atmospheric stability, prevalence of soil components during desert dust advection. However, a common feature of these two events is the presence of high concentration of hygroscopic dust components, which seems to suggest a role of PM-bound or PM-adsorbed water.

It is interesting to note that the unaccounted mass fairly reduces when comparing the sum of the analytical determinations with the PM mass determined on quartz, instead of Teflon. Figs. 5(a) and 5(b) show the scatter plots obtained in the two cases during the winter SOPs of the Cassana field study: when attempting the mass closure with the PM mass determined on quartz, the Pearson's coefficient increases from 0.934 to 0.958, the slope increases from 0.82 to 0.99 and the value of the intercept decreases from 4.80 to $1.36 \mu\text{g}/\text{m}^3$. Also, the unaccounted masses on Teflon filters agree well with T-Q (Fig. 5(c)), suggesting that a species that is not measured by our chemical characterisation is responsible for nearly all the difference between PM mass

determinations on Teflon and on quartz.

Estimate of the Water Content

On the basis of the above discussed results, we suggest that the different behaviour of Teflon and quartz filters might be explained by their different response to atmospheric water. The hydrophilic nature of quartz fibre filters and their wettability (Zdziennicka *et al.*, 2009), in fact, facilitates the transfer of water molecules from the dust particles to the membrane, from where they may easily evaporate during the sampling. The hydrophobic nature of Teflon membranes, instead, prevents this transfer and water molecules remain linked to the dust particles until the end of the sampling. Indeed, the clogging of Teflon membranes during fog events is a common experience.

To obtain a first validation of our hypothesis we carried out the thermogravimetric analysis of some Teflon filters collected in Cassana during the winter SOPs. This technique allows a rough quantitative estimate of the water content, which is released in the temperature ranges $80\text{--}180^\circ\text{C}$ and $225\text{--}275^\circ\text{C}$ (Perrino *et al.*, 2012). The analysis showed water contents of the order of 10–20% of the PM mass, consistent with the extent of T-Q differences and with the concentration of the unaccounted masses. These findings suggest the necessity of a reliable analytical technique for the quantitative measurement of PM-bound and PM-adsorbed water on Teflon filters.

CONCLUSIONS

Different performances of Teflon and quartz filters have been observed in areas characterised by unfavourable atmospheric conditions (frequent atmospheric stability

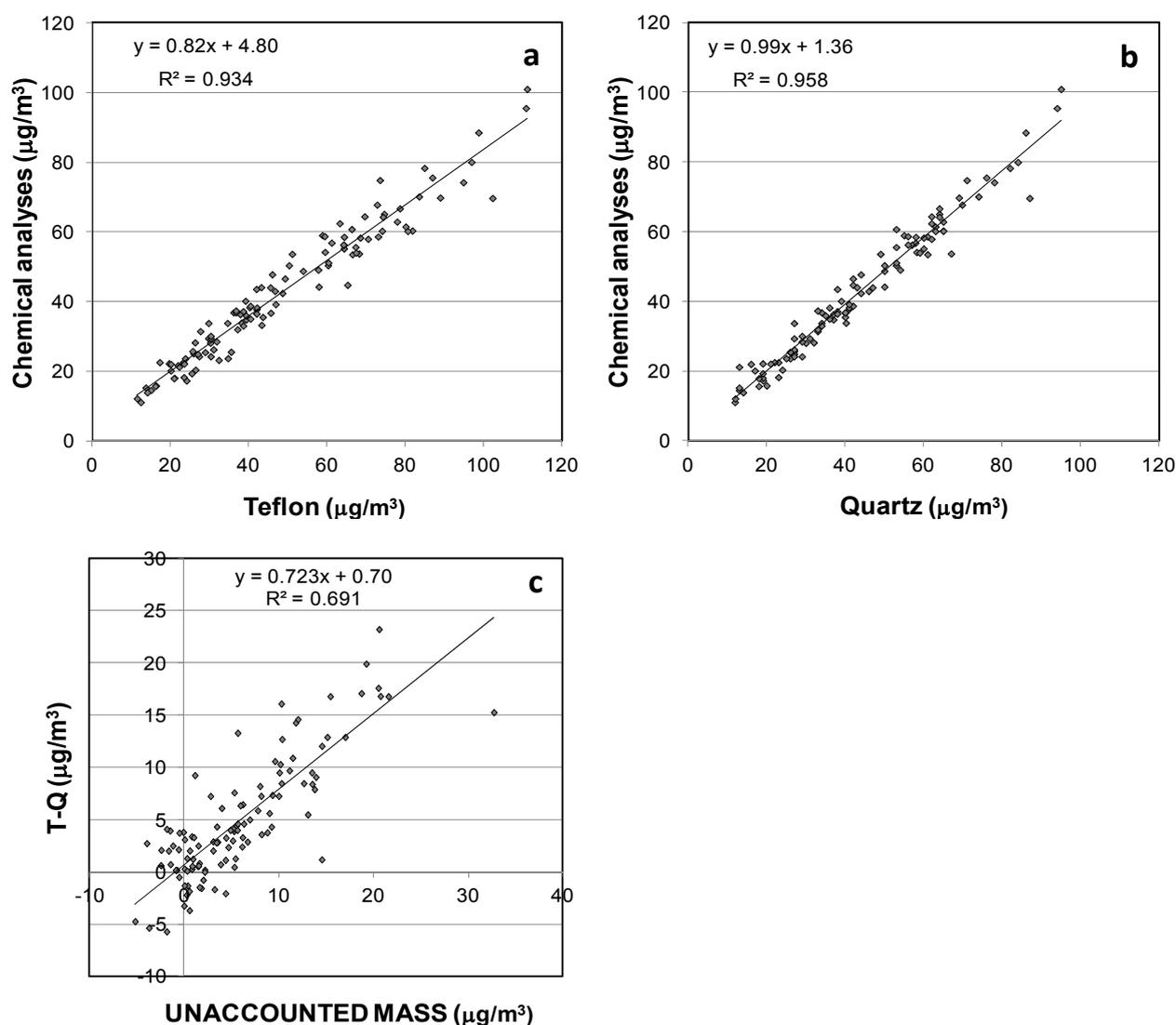


Fig. 5. Scatter plot of the mass concentration reconstructed from the sum of the analytical determinations and measured on Teflon (left panel) or quartz (right panel) filters.

leading to enhanced aging of the air masses), where PM amount determined on Teflon may considerably exceed the amount determined on quartz. This difference is of particular concern when considering the necessity to meet the requirements of EU legislation in terms of PM average concentration and number of exceedances, a goal that is particularly hard in these areas. This different behaviour of Teflon and quartz membranes may cause relevant difficulties also in several other circumstances, for example when comparing the databases produced by networks employing different sampling media, when interpreting the results of field studies carried out by using Teflon or quartz without distinction, when interpreting the results of inter-comparison exercises aimed to evaluate the performance of PM monitors in the case that the reference and the candidate instruments use different membranes, etc..

In the same unfavourable environmental situations, a considerable difference between the mass concentration determined on Teflon filters and the sum of the chemical

determinations of macro-components has also been detected. This finding has led us to hypothesize that PM-bound and PM-adsorbed water may play a role in determining the increase of the PM mass collected on Teflon filters. The hypothesis has been confirmed by some preliminary determinations of the water content of PM carried out by thermogravimetric analysis.

Our results suggest that a routine analytical method for determining the water content of PM is needed, also in the perspective to determine the real exceedances of PM limit values.

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