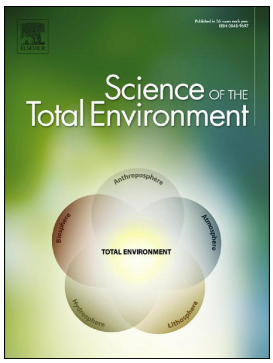
Journal Pre-proof



A multi-analytical approach to study the chemical composition of total suspended particulate matter (TSP) to assess the impact on urban monumental heritage in Florence

Paola Fermo, Valeria Comite, Chiara Ciantelli, Alessandro Sardella, Alessandra Bonazza

PII: S0048-9697(20)33575-0

DOI: https://doi.org/10.1016/j.scitotenv.2020.140055

Reference: STOTEN 140055

To appear in: *Science of the Total Environment*

Received date: 17 April 2020

Revised date: 29 May 2020

Accepted date: 5 June 2020

Please cite this article as: P. Fermo, V. Comite, C. Ciantelli, et al., A multi-analytical approach to study the chemical composition of total suspended particulate matter (TSP) to assess the impact on urban monumental heritage in Florence, *Science of the Total Environment* (2020), https://doi.org/10.1016/j.scitotenv.2020.140055

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 Published by Elsevier.

Journal Pre-proof

A multi-analytical approach to study the chemical composition of total suspended particulate matter (TSP) to assess the impact on urban monumental heritage in Florence

Paola Fermo[1*], Valeria Comite[1], Chiara Ciantelli[2], Alessandro Sardella[3], Alessandra Bonazza[3]

[1]Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133

*corresponding author: paola.fermo@unimi.it

[2]ENEA C. R., Brasimone, 40032, Camugnano, Bologna

[3]Institute of Atmospheric Sciences and Climate, National Research Council of Italy, Via Gobetti 101, 40129, Bologna

Journal Pre-proof

ABSTRACT

In the present paper total suspended particulate matter (TSP) was collected at the S. Marco Museum in Florence during seasonal monitoring campaigns carried out in 2013 and 2014. The analyses focused on the determination of TSP chemical composition: main ions, organic carbon (OC), elemental carbon (EC), water soluble organic compounds (WSOC) and levoglucosan, which is considered the specific marker for wood burning. The analysis of TSP composition in Florence historical center is of interest to assess what the damage caused to the surfaces of the urban monumental heritage could be. TSP higher value has been registered during December 2013 (58,6 $\mu g/m^3$ ± 7,3 $\mu g/m^3$) while the lower value has been registered in July 2013 (28,5 $\mu g/m^3$ ± 2,2 $\mu g/m^3$). OC and EC were also higher in winter with respect to summer. Sulphate is characterized by quite constant values during all the examined periods while ammonium and nitrate were higher in winter. The seasonal contribution of different sources such as combustion processes (from traffic and wood burning) and soil dust resuspension has been evidenced. In particular during winter a high concentration of levoglucosan, the specific marker for wood combustion, has been determined. Finally, all the data obtained were correlated with those previously determined in another study

carried out in 2003 at the Baptistery of San Giovanni in Florence in order to evaluate any possible change in the atmospheric pollution composition.

Keywords: TSP, ions, organic carbon, elemental carbon, levoglucosan, monumental heritage

1. INTRODUCTION

Atmospheric pollutants, in addition to the negative effects on human health, are also responsible for the degradation of building materials in archaeological sites and monumental complexes located in urban environment (Brimblecombe, 1992, et al., 2005; Camuffo, et al., 1983; Sabbioni, et al., 1995; Saiz-Jimenez, 2003) and in particular in city centres where traffic is recognised to be the major cause of pollution. The use of fuels such as fossil fuels, coal and wood have caused a significant worsening of air quality, implying an increasing rate of damage of architectural surfaces directly exposed to local combustion sources (Brimblecombe, 2003; Bonazza et al., 2005, 2007; Comite et al., 2012, 2018, 2019; La Russa et al., 2018; Lamhasni et al., 2019; Ortega et al., 2019; Vidorni et al., 2019; Garcìa-Florentino et al., 2020).

The conservation of cultural heritage and its protection against possible damage caused by air pollution has become consequently the focus of many scientific studies during the last decades (Barca et al., 2010, 2014; Belfiore et al., 2013; Gulotta at al., 2013; La Russa et al., 2013, 2017; Fermo et al., 2015; Comite et al., 2017, 2020; Ruffolo et al., 2015). Nevertheless, most of the campaigns aimed to study multi-pollutants have been carried out mainly to assess air quality because of the negative effects of atmospheric pollution on human health and less attention has been paid to the effects on materials.

In addition, the chemical characterization of particulate matter (PM) has been widely addressed in numerous studies aimed at the identification of its mobile and stationary sources of emission through the application of multi analytical approaches and of statistical methodologies (Atzei et al., 2014; Daellenbach et al., 2016, 2017; Bozzetti et al. 2017; Bove et al., 2016).

PM is responsible of different effects on heritage building surfaces. Since it contains acidic species and carbonaceous particles (Comite et al., 2018) that can act as catalyst in the formation of nitric and sulphuric acid (Vidal et al., 2019), it could be corrosive especially in environments with high relative humidity and temperature. Furthermore, PM is the main cause of soiling because of the presence of carbonaceous particles (organic carbon, OC, and elemental carbon, EC, also known as black carbon), which are responsible for stone darkening. This phenomenon is more pronounced in porous stones where particle penetration is favored. In fact, stones characterized by higher porosity and surface roughness exhibits the highest darkening rate (Comite et al., 2017).

Numerous studies have contributed to deep knowledge of environmental pollution effects such as soiling on building materials. The methods employed generally consist of exposure in outdoor environments of standard samples, for example surface surrogates (Fermo et al., 2018) or marble mock-up samples (Fermo et al., 2018; Vidorni et al. 2019) at specific interval time, in order to determine areas at risk (Vidal et al., 2019) and to acquire data that could be useful for mathematical modeling (Saba et al., 2018) or for assessing pollutants sources using multivariate analysis (Ozga et al., 2014). Alternatively, particulate matter monitoring campaigns with active sampling systems could be performed (Ghedini et al, 2011). Even if all these studies mentioned above have focused on the chemical characterization of urban aerosol aiming at the protection of outdoor monumental heritage against atmospheric pollution impact, the importance of atmospheric particulate matter monitoring in urban centres where most of the historical monuments are located, needs to be deepened and emphasized. Within a previous study carried out by some authors of the present work, atmospheric pollution in the city centre of Florence in the proximity of the Florence Baptistery was collected and characterized (Ghedini et al., 2011).

In the present study total suspended particulate matter (TSP) was collected at the S. Marco Museum in Florence during seasonal environmental monitoring campaigns carried out in 2013 and 2014. The analyses conducted by applying different methodologies and focused on the determination of the TSP constituents (ions, levoglucosan, carbonaceous fraction and water soluble organic compounds)

that are responsible in causing damage, including soiling, on architectural surfaces. Finally, all the data obtained were correlated with those previously determined in 2003 for the Baptistery of San Giovanni in Florence in order to evaluate any possible change in PM sources contribution and so in the atmospheric pollution of the city, to which monuments are subjected.

2. MATERIALS AND METHODS

2.1 Site of investigation

Florence is the most populous city in Tuscany region, it has a humid subtropical climate, with hot summers with moderate or light rainfall and cool, damp winters and summer temperatures higher than along the coasts. The city is a major production and commercial centre in Italy. Traffic is one of the main factors affecting air quality in the city centre.

The site selected in this study is a religious complex of Florence called San Marco. It includes a church and a cloister, now a famous museum (Museum of San Marco). The basilica is one of the old town's churches, which dominates the homonymous square and it serves as a landmark for the surrounding urban area. The site is surrounded by roads with high vehicular traffic. The complex is located where a monastery once stood in the 12th century. In 1437 Cosimo il Vecchio de' Medici decided to rebuild the entire complex, the work was entrusted to Michelozzo, and the decoration of the walls was carried out by Fra Angelico, and his assistants. Since so important masters worked in this complex, this attests to its high artistic value.

2.2 Sampling

Atmospheric particulate matter, and in particular total suspended particulate matter (TSP), i.e. the fraction including particles with aerodynamic diameters up to 100 □m, was collected during a total number of 5 seasonal sampling campaigns conducted in 2013 (during July and December) and in 2014 (during April, July and October). Environmental monitoring was carried out on the loggia of the Museum of San Marco using simultaneously two sampling lines of particular matter (each of

them including two sampling heads), placed at a distance of 40 cm from each other (figure 1), one positioned pointing towards the interior of the loggia (innermost) and the other outermost directly exposed to the busy street Via Giorgio La Pira (in figure 1 the position of the sampling heads are indicated), in order to evaluate the possible differences between a direct expose to traffic and a more protected situation. Each line included two sampling heads since they worked in sequence one after the other to avoid changing the filter every day. The sampling was conducted at around a height of 8 m above street level, employing two TCR TECORA instruments and using quartz fiber filters previously treated at high temperatures (700 ° C) for about an hour and then placed in dryers before being weighed. This process allowed the elimination of possible organic substances present on the filters. Weighing of white filters and filters after sampling were carried out using a microbalance with precision of ± 1 μg. The sampling air flow rate was 40 L min -1 for the duration of 60 minutes every 90 minutes. The active sampling was 16 over 24 hours for each sampled filter, to obtain a sufficient amount of particulate deposited on the filters.

2.3 Analytical techniques

TSP samples collected underwent analyses as follows:

-The determination of organic carbon (OC) and elemental carbon (EC), has been carried out on quartz fiber filters using a TOT (Thermal-Optical Transmittance) Sunset instrument following the methodology conventionally used for their determination in the aerosol particulate matter (Fermo et al. 2006a; Piazzalunga et al., 2013).

-Main ions analysis (Na^+, K^+, Ca^{2+}, Mg^{2+}, NH^{4+}, NO_2^-, NO_3^-, SO_4^{2-}, Cl^-, $HCOO^-$, CH_3COO^-, $CH_3SO_3^-$, $C_2O_4^{2-}$) was performed by IC analysis using a ICS-1000 HPLC system equipped with a conductivity detector (Piazzalunga er al., 2013). Levoglucosan was determined using the same instrument equipped with an amperometric detector by following an analytical procedure reported elsewhere (Piazzalunga et al., 2013).

-Finally WSOC (water-soluble organic compounds) analysis was performed using a TOC-VCPH Shimadzu instrument in accordance with a methodology already described (Fermo et al., 2015).

2. 4 Quality Assurance/Quality Control

All the analytical methodologies applied have been submitted to a procedure of QA/QC.

As regards the cabonaceous fraction analysis, LOD is 1 μg/cm^2 in the worst case (Piazzalunga et al. 2013) which corresponds to a LOD of 0.5 μg/m^3 (in case of a sampling rate of 1m^3/h) and of 0.2 μg/m^3 (in case of a sampling rate of 2.3 m^3/h). Since in the present work the sampling rate is 40 L/min, i. e. 2,4 m^3/h, LOD is slightly higher than 0.2 μg/m^3. Uncertainty is lower than 5%.

As regards ions analysis, in a previous work (Fermo et al., 2006b) the procedure for recovery evaluation of all the ionic species has been optimized. Estimate of the technique uncertainties and LOD were carried out as described in detail in Fermo et al., 2006b and in Piazzalunga et al, 2013. In particular uncertainty varies between 0.8% (for sulphate) and 4.8% (for levoglucosan). LODs determined for quartz fiber filters (Piazzalunga et al. 2013) vary between 1.5 ng/m^3 (for Mg^{2+}) and 89.3 ng/m^3 (for Na^+) for a sampling rate of 2.3 m^3/h.

The uncertainty of the WSOC method was estimated to be 15% while LOD was 0.1 μg/m^3.

3. RESULTS

Comparing the two TSP concentration trends, internal and external (named inner and out in the following figures), we can observe that the internal ones are slightly lower only in December 2013 and in July 2014 while for the remaining sampling period the trends are quite similar (figure 2).

Considering average TSP concentrations (see figure 3) the higher value has been registered during December 2013 (58,6 μg/m^3 ± 7,3 μg/m^3) while the lower value has been registered in July 2013 (28,5 μg/m^3 ± 2,2 μg/m^3). In general the values measured for the more inner samples are slightly lower or comparable with those detected for the outermost ones indicating that the inner position is affected by almost the same particulate matter impact in terms of mass per volume.

From the point of view of the carbonaceous fraction, both OC and EC concentrations (figure 4a and 4b) presented considerably higher values during winter 2013 showing as maximum values 21,4 $\mu g/m^3$ ± 3,6 $\mu g/m^3$ and 5,2 $\mu g/m^3$ ± 0,9 $\mu g/m^3$, respectively (registered in the outermost position) while in summer OC and EC higher values were 6,97 $\mu g/m^3$ ± 0,65 $\mu g/m^3$ and 1,58 $\mu g/m^3$ ± 0,24 µg/m3 at the inner position in July 2013. The lower OC and EC values have been obtained in July 2014.

In figure 5 main ions concentrations are reported taking into account all the samples inner and out (having available for the ions a lower number of data and since there are no significant differences between inner and out samples, it was decided in this case to calculate an overall average value). Among cations (figure 5a) calcium is present in the higher concentration. Sodium is the second one in order of importance and shows a quite fair agreement with chloride in 2014 (figure 5b) suggesting a probable marine origin for these ions. Ammonium shows the higher value during wintertime and a concentration trend that is in accordance with nitrate. Sulphate is characterized by quite constant values during all the examined periods (figure 5b). Together with main ions also short chain organic acids have been quantified (figure 5c).

Oxalate shows a constant concentration for all the analysed periods. Oxalate has been also associated to biomass burning source (Saarikoski et al. 2007) but its constant contribution indicates the presence of multiples sources. Formic acid is higher during July 2013 while during April 2014 and July 2014 a higher contribution due to methane sulphonic acid has been observed. This specie is considered as a marker for marine aerosol transportation (La Russa et al., 2017).

Levoglucosan, the specific marker for biomass combustion (Piazzalunga et al., 2011a, Piazzalunga et al., 2013, Vassura et al., 2014, Pietrogrande et al., 2017, Massimi et al., 2020) has been also quantified. The higher concentration has been registered during winter (table 1) and the value is in good accordance with what registered in the cold season for other cities affected by wood combustion source (Piazzalunga et al., 2011a) indicating the importance of biomass burning also in Florence.

WSOC (water soluble organic compounds) were also determined (Table 2). These compounds represent an important fraction of OC. Higher concentrations were reached during wintertime while the percentage contribution with respect to OC is quite constant during the different seasons.

In tables 3 and 4 the correlation matrices calculated for the two period, winter (December 2013) and summer (July 2013-July 2014) are reported. The most significative coefficients, highlighted in bold characters, have allowed to make some hypotheses on the chemical species present in the two seasons. The presence of ammonium nitrate is confirmed during winter (with a coefficient of about 0,7). A very good correlation between Cl^- and Na^+ during both seasons indicates the presence of NaCl. Chloride is also well correlated with magnesium, especially in summer. A certain correlation exists between SO_4^{2-} and NH_4^+ in summer (indicating the presence of ammonium sulphate) while in winter these two species are anticorrelated.

Considering the mass balance reported in figure 6, OC concentration has been converted into OM (organic matter) using a conversion factor of 1,6 in accordance with what reported in the literature (Vecchi et al., 2009a). It should be emphasized that the fraction indicated as unknown in figure 6 mainly contains the contribution of soil dust that was not directly quantified in this work. Ions fraction includes all determined cations and anions.

4. DISCUSSION

As regard TSP average concentrations (figure 3) it can be observed that, as expected, during wintertime higher values have been measured. It is interesting to observe the difference between July 2013 and July 2014 probably due to a higher contribution of resuspended dust during summer 2014 as it is also confirmed by the higher unknown fraction for this period (figure 6). If we compare meteorological parameters (available at: https://www.ilmeteo.it/portale/archivio-meteo/Firenze) in July 2013 and in July 2014, the wind speed is almost the same, i.e. on average about 22 Km/h and 20 Km/h in 2013 and 2014, respectively). However, July 2014 was characterized by more frequent wind gusts up to 56 Km/h, just on July 8th, when a maximum in TSP concentration has been also

observed (figure 2). Some wind gusts have been also registered in April 2014 just during the days during which TSP was sampled. This phenomenon is probably responsible of dust transportation which brings to the observed increase of this contribution (reported in figure 6 as unknown since silicates which are the main constituent of this contribution have not been quantified in this work) on TSP mass as observed in April 2014 and July 2014 (figure 6). During summer elements associated to the crustal component such as calcium, magnesium and sodium are very well correlated among them (table 4).

In general, the values measured for the more inner samples are slightly lower or comparable with those detected for the outermost ones. Furthermore, the values of TSP measured during our campaign are in accordance with the results found in the work of Ghedini et al., (2011) also carried out in Florence city center. It is interesting to note that even in that case higher TSP, concentrations attributed to a marked drought that favoured dust suspension (with a contribution of about 40%), have been registered during summer. Our values in the last 3 cases are higher than 50% (figure 6), indicating a significant contribution due to resuspension or dust transportation. In fact it is known that earth crust contribution is heavily influenced by climatic conditions and has a seasonal pattern with higher values in the hot seasons (Diapouli et al., 2017). Furthermore, as stated before, April and July 2014 were characterized by intense wind gusts that could be responsible for dust transportation.

TSP concentrations determined in the present study are also in accordance with the concentrations determined by Perrone et al., (2016) for TSP samples collected in Milan which, from the point of view of PM source contribution, is not so different from Florence (Vecchi et al., 2008).

While in our study we measured OC values of 21.4 and 5.2 µg /m^3 in winter and summer respectively, in Perrone et al., (2016) OC is around 26 and 9 µg /m^3 for the same two seasons. EC in our study is 6.97 and 1.58 µg /m^3 in winter and summer respectively while in Perrone et al., (2016) it is around 6 µg /m^3 in winter and 2 µg /m^3 in summer. It is worth to notice that the values in

Perrone et al., (2016) have been obtained for a traffic site indicating that also for San Marco site this source considerably contributes to PM emission.

OC is both of primary and secondary origin (Vecchi et al., 2009a; Sandrini et al., 2014) and is emitted by multiple sources (Bozzetti et al., 2016, Bozzetti et al., 2017, Daellenbach et al., 2017) including industrial emission and combustion processes while EC is of primary origin and is emitted by wood burning and fossil fuel (Massabò et al., 2015). Considering OC/EC ratios, it can be observed that, with the exception of October 2014, they are higher than 3 indicating for OC a prevailing contribution of secondary sources (Sandrini et al., 2014, Salma et al., 2020). In fact, the highest OC/EC ratios are often linked to atmospheric conditions under which the SOA (secondary organic aerosol) formation is large. The higher OC, and consequently OM value, has been registered during winter and is due to the contribution of sources such as combustion processes including traffic and wood burning as attested by the high levoglucosan concentration registered in December (Table 1). In this case it is worth to notice the high correlation in winter between levoglucosan and OC (0,90 in table 3) and levoglucosan and EC (0,88 table 3). In the same season levoglucosan correlates also with potassium (0,83 table 3) which is considered a marker for wood burning. Furthermore, in wintertime condensation processes due to lower temperatures are also present. An unexpectedly high OM value was also found during July 2013 but this could also be due to the contribution of biogenic aerosols (Bozzetti et al., 2016).

WSOC represent on average 43% of total carbon (OC + EC) with a maximum value of 68% during wintertime. These values are considerably higher than what normally observed for PM10 fraction where this ratio is about 25% (Piazzalunga et al., 2011b). In accordance with the literature, biomass burning is also an important source of WSOC (Urban et al., 2012; Salma et al. 2020; Massimi et al. 2020) that together with levoglucosan and potassium are considered good markers for this source.

In a previous study carried out on powder deposits collected on surfaces of a high porous carbonate stone (Pietra d'Angera) of a famous historical building in Milan (Fermo et al., 2015), WSOC fraction represented less than 10 % of total carbon. The lower value present in the powder deposits

probably was due to the fact that in this specific case most of the water soluble organic substances migrated into the stone causing a worsening of the conservation conditions. Therefore, the presence of a such high concentration of WSOC must cause concern because this particulate, depositing on the surfaces, could represent a serious threat.

Coming to main ions concentrations, high NO_3^- value registered during winter is due to both the contribution of anthropogenic sources such as traffic and also to a minor volatility of ammonium nitrate during the cold season (Vecchi et al., 2009b). In fact, in winter NO3- is highly correlated with both OC and EC (0,90 and 0,88 in table 3). High NO_3^- concentrations have been also linked to Saharan dust events (Moroni et al., 2015). As it can be observed in table 3 and 4, the correlation between nitrate, alkaline and alkaline earth metals (elements linked to dust resuspension) definitely improves in summer suggesting a common source, such as the dust resuspension, for these elements. Nitrate concentrations determined in our study are lower than what found for TSP samples collected in Milan and reported in Perrone et al., (2016) even if the seasonal trend is confirmed.

Sulphates are of secondary origin coming from SO_2 oxidation, being SO_2 produced by combustion processes such as industrial activities (Ielpo et al. 2019). For example, 'oil combustion/secondary sulphates' factor (Bernardoni et al., 2011) was characterised by high S with contribution of secondary sulphate in all the seasons, as we have also observed in our work. Often sulphate is linked to long-range transport episodes from, for example, Eastern Europe countries where fuels with a high sulphur content and heating oil, also containing sulphur, are still employed to a large extend during winter. The highest values registered in July 2013 and July 2014 are due a more intense photochemical activity during the hot season (figure 5b). In this way the measurement of high winter and summer sulphates concentration can be explained.

In Florence (Vecchi et al., 2008) S together with K have been considered marker for traffic source and in particular diesel emissions. In another work potassium has been associated with non-exhaust traffic emission and in particular road/tyres source (Wahlin et al. 2006). Anyway, accordingly to

these studies, potassium can be associated to traffic emissions.

Potassium together with levoglucosan, is also a marker for wood burning and its maximum concentration registered during December 2013 (figure 5a), together with the high correlation between potassium and levoglucosan (table 3), again confirms the importance of the source wood combustion.

From the literature it is well known that sea salt is mostly related to the coarse mode and exhibits significant seasonal variability as well. Even if sea-salt concentrations are highest in costal sites where they can reach a contribution higher then 10 % (Diapouli et al., 2017), nevertheless the contribution of this source for inland cities such as Florence is not negligible representing more than 1% of PM10 (Diapouli et al., 2017). In the present study Cl^- accounts for more than 4 % during July 2014.

Among organic acid oxalate shows, similarly to sulphate, a quite constant concentration during all seasons that can be explained taking into account its different numerous possible origins. Oxalate can be emitted by different sources and is both of primary and secondary origin (Zhou et al., 2015). Direct emissions from biogenic sources and biomass burning (Saarikoski et al. 2007) are deemed major primary sources of this specie; motor exhaust was also retained a possible source even if the direct emission from vehicles has been recently challenged. Secondary formation starting form biogenic compounds or because of photochemical processes, are other possibilities (Zhou et al., 2015).

As regards methane sulphonic acid, considered as marker of marine aerosol transportation, it shows some correlation with chloride during summer while in winter these two species are anti-correlated.

As already pointed out in this paragraph, the results obtained in the present work can be compared to what obtained in a previous study (Ghedini et al., 2011) carried out during 2003 in a sampling site located in Florence city centre (Baptistery of San Giovanni) not so far from San Marco Museum (figure 7).

Journal Pre-proof

As regard the TSP concentration a decrease with respect to 2003 has occurred mainly in summer (figure 8) probably also thanks to some PM emission reduction policies. It is important pointing out that in 2009 there was the pedestrianization of the square of the Cathedral and the Baptistery and, as a consequence, traffic moved from this area to San Marco square that is not so distant. In spite of this TSP values are lower than what measured during 2003. As regard TC, during winter (figure 8) the value is quite similar to that one registered in 2003 confirming the presence of sources responsible for the emission of organic carbon such as traffic, because of the pedestrianization of the Cathedral area, and wood burning. A decreasing of TC has been on the contrary observed during summer in accordance with what observed for TSP. It is also worth to notice that the values determined in Florence in 2003 were high if compared to those determined in the same period in Paris near the Church of Sant'Eustache (8.8 μg /m^3) and in Milan near the Cathedral (9.34 μg /m^3) where the samplings were carried out in pedestrian areas (Cachier et al., 2004).

Average SO_4^{2-} concentration in 2003 was about 5μg/m^3 and 6 μg/m^3 respectively in summer and in winter (Ghedini et al., 2011) while in 2013 SO_4^{2-} concentration at San Marco Museum has decreased to 1,58 μg /m^3 and 1,34 μg/m^3 for the same seasons 10 years after. The lower values measured during 2013-2014 campaigns with respect to 2003 are probably due to the decrease in SO_2 emissions thanks to the progressive replacement of diesel heating systems and the use of fuels with a lower sulphur content.

NO_3^- concentration in 2003 was about 3μg/m^3 and 5 μg/m^3 respectively in summer and in winter (Ghedini et al., 2011) while in 2013 at San Marco Museum was 0,6 μg/m^3 and 4,5 μg/m^3. The fact that nitrate concentration has remained almost unchanged in wintertime indicates that the contribution of traffic source to PM emissions is still important.

The observed differences, even if referred to just two years, could suggest an evolution in the composition of the atmospheric particulate matter with respect to 2003.

This figure is rather worrying as regards possible damage that could be caused to the surfaces. In fact, organic carbon together with elemental carbon is involved in the process of black crust

formation on historical surface monuments (Comite et al., 2018; 2020). Likewise, an increase in the concentration of nitrates is also worrying because it is associated with an increase in the acidity of the particulates that, depositing on the surfaces of historical monuments, can induce degradation phenomenon (Vidal et al., 2019).

5. CONCLUSIONS

Total suspended particulate matter (TSP) was collected in Florence city center at S. Marco Museum during seasonal campaigns carried out in 2013 and 2014. Some seasonal differences have been highlighted with a major contribution of organic matter (OM) during wintertime. The main sources responsible of the higher winter value are combustion processes such as fossil fuel combustion from traffic and wood burning. Indeed, during winter higher levoglucosan (the specific marker for wood burning) and potassium concentrations have been evidenced. OC/EC ratios are in general higher than 3 indicating for OC a prevailing contribution of secondary sources. Sulphate contribution is quite constant during the whole year while nitrate is higher during winter attesting the importance of traffic source (as confirmed by the very good correlation between nitrate and OC and nitrate and EC), even if during the cold season lower pollutants dispersion takes place because of the lower atmospheric mixing layer height, bringing also to higher nitrate concentration. All these pollutants have an important role in causing damage (soiling and degradation phenomenon in general) to the urban monumental heritage.

Finally, the data obtained were compared with those previously determined in 2003 for the Baptistery of San Giovanni in order to evaluate any possible change in the atmospheric pollution composition. In particular a clear decrease in sulphate concentration has been observed probably due to the decrease in SO_2 emissions thanks to the progressive replacement of diesel heating systems and the use of low sulphur fuels.

Acknowledgements

Authors are grateful to the Director and staff of the Museum of San Marco in Florence for their for their helpfulness and cooperation in allowing ISAC team to perform the environmental sampling campaigns in 2013 and 2014.

Reference

Atzei, D., Fantauzzi, M., Rossi, A., Fermo, P., Piazzalunga, A., Valli, G., Vecchi, R. 2014. Surface chemical characterization of PM 10 samples by XPS. Appl. Surf. Sci. 307, 120-128. DOI: 10.1016/j.apsusc.2014.03.178.

Barca, D., Belfiore, C.M., Crisci, G.M., La Russa,M.F., Pezzino, A., Ruffolo, S.A., 2010. Application of laser ablation ICP-MS and traditional techniques to the study of black crusts on building stones: a new methodological approach. Environ. Sci. Pollut. Res. 17, 1433–1447. DOI: 10.1007/s11356-010-0329-8

Barca, D., Comite, V., Belfiore, C.M., Bonazza, A., La Russa, M.F., Ruffolo, S.A., Crisci, G.M., Pezzino, A., Sabbioni, C., 2014. Impact of air pollution in deterioration of carbonate building materials in Italian urban environments. Appl. Geochem. 48, 122–131. DOI: 10.1016/j.apgeochem.2014.07.002

Belfiore, C.M., Barca, D., Bonazza, A., Comite, V., La Russa, M.F., Pezzino, A., Ruffolo, S.A., Sabbioni, C., 2013. Application of spectrometric analysis to the identification of pollution sources causing cultural heritage damage. Environ. Sci. Pollut. Res. 20, 8848–8859. DOI: 10.1007/s11356-013-1810-y.

Journal Pre-proof

Bernardoni, V., Vecchi, R., Valli, G., Piazzalunga, A., Fermo, P. 2011. PM10 source apportionment in Milan (Italy) using time-resolved data. Sci. Total. Environ. 409 (22), 4788-4795. DOI: 10.1016/j.scitotenv.2011.07.048.

Bonazza, A., Sabbioni, C., Ghedini, N., 2005. Quantitative data on carbon fractions in interpretation of black crusts and soiling on European built heritage. Atmos. Environ. 39, 2607-2618. DOI: 10.1016/j.atmosenv.2005.01.040.

Bonazza, A., Brimblecombe, P., Grossi, C., M., Sabbioni, C., 2007. Carbon in black crusts from the Tower of London. Environ. Sci. Technol. 41, 4199-4204. DOI: 10.1021/es062417w.

Bove, M.C., Brotto, P., Calzolai, G., Cassola, F., Cavalli, F., Fermo, P., Hjorth, J., Massabò, D., Nava, S., Piazzalunga, A., Schembari, C., Prati, P., 2016. PM10 source apportionment applying PMF and chemical tracer analysis to ship-borne measurements in the Western Mediterranean. Atmos. Environ. 125, 140-151. DOI: 10.1016/j.atmosenv.2015.11.009.

Bozzetti, C., Daellenbach, K.R., Hueglin, C., Fermo, P., Sciare, J., Kasper-Giebl, A., Mazar, Y., Abbaszade, G., El Kazzi, M., Gonzalez, R., Shuster-Meiseles, T., Flasch, M., Wolf, R., Křepelová, A., Canonaco, F., Schnelle-Kreis, J., Slowik, J.G., Zimmermann, R., Rudich, Y., Baltensperger, U., El Haddad, I., Prévôt, A.S.H. 2016. Size-Resolved Identification, Characterization, and Quantification of Primary Biological Organic Aerosol at a European Rural Site. Environ. Sci. Technol. 50 (7), 3425-3434. DOI: 10.1021/acs.est.5b05960.

Bozzetti, C., El Haddad, I., Salameh, D., Daellenbach, K.R., Fermo, P., Gonzalez, R., Minguillón, M.C., Iinuma, Y., Poulain, L., Elser, M., Müller, E., Slowik, J.G., Jaffrezo, J.-L., Baltensperger, U.,

Marchand, N., Prévôt, A.S.H., 2017. Organic aerosol source apportionment by offline-AMS over a full year in Marseille. Atmos. Chem. and Phys.17 (13), 8247-8268. DOI: 10.5194/acp-2017-54.

Brimblecombe, P., 1992. A brief history of grime: accumulation and removal of soot deposits on buildings since the 17th century. in: Webster, R.G.M. (Eds.), Stone Cleaning and the Nature, Soiling and Decay Mechanisms of Stone. Proceedings of the International Conference 1992, pp. 14 (Edinburgh, UK).

Brimblecombe, P., 2003. The Effects of Air Pollution on the Built Environment. Air Pollution Reviews. Imperial College Press, London, UK.

Brimblecombe, P., Grossi, C.M., 2005. Aesthetic thresholds and blackening of stone buildings. Sci. Total Environ. 349, 175–189. DOI: 10.1016/j.scitotenv.2005.01.009.

Camuffo, D., Del Monte, M., Sabbioni, C., 1983. Origin and growth mechanisms of the sulfated crusts on urban limestone. Water Air Soil Pollut. 19, 351–359. DOI: 10.1007/BF00159596.

Cachier, H., Sarda-Estéve, R., Oikonomou, K., Sciare, J., Bonazza, A., Sabbioni, C., Greco, M., Saiz-Jimenez, C., Hermosin, A., Reyes, J. 2004. Aerosol characterisation and sources in different European urban atmospheres: Paris, Seville, Forence and Milan. in: Saiz-Jimenez C. (Eds.). Air Pollution and Cultural Heritage. pp 03-14. DOI: 10.1201/b17004-3.

Comite, V., Barca, D., Belfiore, C.M., Bonazza, A., Crisci, G.M, La Russa, M.F., Pezzino, A., Sabbioni, C. 2012. Potentialities of spectrometric analysis for the evaluation of pollution impact in deteriorating stone heritage materials. Rendiconti online della Soc. Geol. It., 86th Congresso

Journal Pre-proof

Nazionale della Società Geologica Italiana, 18-20 settembre 2012, Arcavacata di Rende, Cosenza, 21 (PART 1), 652-653.

Comite, V., Álvarez de Buergo, M., Barca, D., Belfiore, C.M., Bonazza, A., La Russa, M.F., Pezzino, A., Randazzo, L., Ruffolo, S.A. 2017. Damage monitoring on carbonate stones: Field exposure tests contributing to pollution impact evaluation in two Italian sites. Constr Build Mater. 152, 907-922. DOI: 10.1016/j.conbuildmat.2017.07.048.

Comite, V., Fermo, P. 2018. The effects of air pollution on cultural heritage: the case study of Santa Maria delle Grazie al Naviglio Grande (Milan). EPJ.133 (Issue 12), Article number 556. https://doi.org/10.1140/epjp/i2018-12365-6.

Comite, V., Pozo-Antonio, J.S., Cardell, C., Rivas, T., Randazzo, L., La Russa, M.F., Fermo, P. 2019. Metals distributions within black crusts sampled on the facade of an historical monument: The case study of the Cathedral of Monza (Milan, Italy). 2019 IMEKO TC4 International Conference on Metrology for Archaeology and Cultural Heritage, MetroArchaeo, 73-78.

Comite, V., Pozo-Antonio, J.S., Cardell, C., Rivas, T., Randazzo, L., La Russa, M.F., Fermo, P.2020. Environmental impact assessment on the Monza Mathedral (Italy): a multi-analytical approach. IJCS. 11 (Special Issue 1), 291-304.

Daellenbach, K.R., Bozzetti, C., Křepelová, A., Canonaco, F., Wolf, R., Zotter, P., Fermo, P., Crippa, M., Slowik, J.G., Sosedova, Y., Zhang, Y., Huang, R.-J., Poulain, L., Szidat, S., Baltensperger, U., El Haddad, I., Prévôt, A.S.H., 2016. Characterization and source apportionment of organic aerosol using offline aerosol mass spectrometry. Atmos. Meas. Tech. 9 (1), 23-39. DOI: 10.5194/amtd-8-8599-2015.

Daellenbach, K.R., Stefenelli, G., Bozzetti, C., Vlachou, A., Fermo, P., Gonzalez, R., Piazzalunga, A., Colombi, C., Canonaco, F., Hueglin, C., Kasper-Giebl, A., Jaffrezo, J.-L., Bianchi, F., Slowik, J.G., Baltensperger, U., El-Haddad, I., Prévôt, A.S.H. 2017. Long-term chemical analysis and organic aerosol source apportionment at nine sites in central Europe: Source identification and uncertainty assessment. Atmos. Chem. Phys. 17 (21), 13265-13282. DOI: 10.5194/acp-2017-124.

Diapouli, E., Manousakas, M.I., Vratolis, S., Vasilatou, V., Pateraki, S., Bairachtari, K.A., Querol, X., Amato, F., Alastuey, A., Karanasiou, A.A., Lucarelli, F., Nava, S., Calzolai, G., Gianelle, V.L., Colombi, C., Alves, C., Custódio, D., Pio, C., Spyrou, C., Kallos, G.B., Eleftheriadis, 2017. K. AIRUSE-LIFE +: Estimation of natural source contributions to urban ambient air PM10 and PM2. 5 concentrations in southern Europe - Implications to compliance with limit values. Atmos. Chem. Phys. 17 (5), 3673-3685. DOI: 10.5194/acp-2016-781

Fermo, P., Piazzalunga, A., Vecchi, R., Valli, G., Ceriani, M. 2006a. A TGA/FT-IR study for measuring OC and EC in aerosol samples. Atmos. Chem. Phys. 6, 255–266. DOI: 10.5194/acp-6-255-2006

Fermo, P., Piazzalunga, A., Vecchi, R., Valli, G. 2006b. Set-up of extraction procedures for ions quantification in aerosol samples. Chem Eng Trans 10:203–208

Fermo, P., Turrion, R.G., Rosa, M., Omegna, A. 2015. A new approach to assess the chemical composition of powder deposits damaging the stone surfaces of historical monuments. Environ. Sci. Pollut. Res. 22 (8), 6262-6270. DOI: 10.1007/s11356-014-3855-y

Journal Pre-proof

Fermo, P., Goidanich, S., Comite, V., Toniolo, L., Gulotta, D. 2018. Study and characterization of environmental deposition on marble and surrogate substrates at a monumental heritage site. Geosci. 8 (Issue 9), Article number 349. DOI: 10.3390/geosciences8090349.

García-Florentino, C., Maguregui, M., Ciantelli, C., Sardella, A., Bonazza, A., Queralt, I., Carrero, J.A., Natali, C., Morillas, H., Madariaga, J.M., Arana, G. 2020. Deciphering past and present atmospheric metal pollution of urban environments: The role of black crusts formed on historical constructions. J. Clean. Prod. 243, 118594. DOI: 10.1016/j.jclepro.2019.118594.

Ghedini, N., Ozga, I., Bonazza, A., Dilillo, M., Cachier, H., Sabbioni, C. 2011. Atmospheric aerosol monitoring as a strategy for the preventive conservation of urban monumental heritage: The Florence Baptistery. Atmos. Environ. 45 (33), 5979-5987. DOI: 10.1016/j.atmosenv.2011.08.001.

Gulotta, D., Bertoldi, M., Bortolotto, S., Fermo, P., Piazzalunga, A., Toniolo, L., 2013. The Angera stone: a challenging conservation issue in the polluted environment of Milan (Italy). Environ. Earth Sci. 69, 1085–1094. DOI: 10.1007/s12665-012-2165-2.

Ielpo, P., Mangia, C., Marra, G.P., Comite, V., Rizza, U., Uricchio, V.F., Fermo, P., 2019. Outdoor spatial distribution and indoor levels of NO2 and SO2 in a high environmental risk site of the South Italy. Science of the Total Environment, 648, pp. 787-797.

Lamhasni, T., El-Marjaoui, H., El Bakkali, A., Lyazidi, S.A., Haddad, M., Ben-Ncer, A., Benyaich, F., Bonazza, A., Tahri, M. 2019. Air pollution impact on architectural heritage of Morocco: Combination of synchronous fluorescence and ATR-FTIR spectroscopies for the analyses of black crusts deposits. Chemosphere, 225, 517-523. DOI: 10.1016/j.chemosphere.2019.03.109

La Russa, M.F., Belfiore, C.M., Comite, V., Barca, D., Bonazza, A., Ruffolo, S.A., Crisci, G.M., Pezzino, A., 2013. Geochemical study of black crusts as a diagnostic tool in cultural heritage. Appl. Phys. A Mater. Sci. Process. 113, 1151–1162. DOI: 10.1007/s00339-013-7912-z-.

La Russa, M.F., Fermo, P., Comite, V., Belfiore, C.M., Barca, D., Cerioni, A., De Santis, M., Barbagallo, L.F., Ricca, M., Ruffolo S.A. 2017. The Oceanus statue of the Fontana di Trevi (Rome): The analysis of black crust as a tool to investigate the urban air pollution and its impact on the stone degradation. Sci. Total. Environ. 593-594, 297-309. DOI: 10.1016/j.scitotenv.2017.03.185.

La Russa, M.F., Comite, V., Aly, N., Barca, D, Fermo, P., Rovella, N., Antonelli, F., Tesser, E., Aquino, M., Ruffolo, S.A. 2018. Black crusts on Venetian built heritage, investigation on the impact of pollution sources on their composition, E.P.J. 133, (Issue 9), Article number 370. DOI: 10.1140/epjp/i2018-12230-8

Massabò, D., Caponi, L., Bernardoni, V., Bove, M.C., Brotto, P., Calzolai, G., Cassola, F., Chiari, M., Fedi, M.E., Fermo, P., Giannoni, M., Lucarelli, F., Nava, S., Piazzalunga, A., Valli, G., Vecchi, R., Prati, P. 2015. Multi-wavelength optical determination of black and brown carbon in atmospheric aerosols. Atmos. Environ. 108, 1-12. DOI: 10.1016/j.atmosenv.2015.02.058.

Massimi, L., Simonetti, G., Buiarelli, F., Di Filippo, P., Pomata, D., Riccardi, C., Ristorini, M., Astolfi, M.L., Canepari, S. Spatial distribution of levoglucosan and alternative biomass burning tracers in atmospheric aerosols, in an urban and industrial hot-spot of Central Italy. Atmospheric Research, 239, art. no. 104904, DOI: 10.1016/j.atmosres.2020.104904

Journal Pre-proof

Moroni, B., Castellini, S., Crocchianti, S., Piazzalunga, A., Fermo, P., Scardazza, F., Cappelletti, D. 2015. Ground-based measurements of long-range transported aerosol at the rural regional background site of Monte Martano (Central Italy). Atmos. Res.155, 26-36. DOI: 10.1016/j.atmosres.2014.11.021.

Ortega-Morales, O., Montero-Muñoz, J.L., Baptista Neto, J.A., Beech, I.B., Sunner, J., Gaylarde, C. 2019. Deterioration and microbial colonization of cultural heritage stone buildings in polluted and unpolluted tropical and subtropical climates: A meta-analysis. Int. Biodeter. Biodegr. 143, art. no. 104734. DOI: 10.1016/j.ibiod.2019.104734.

Ozga, I., Ghedini, N., Giosuè, C., Sabbioni, C., Tittarelli, F., Bonazza, A. 2014. Assessment of air pollutant sources in the deposit on monuments by multivariate analysis. Sci Total Enviro. 490, 776-784. DOI: 10.1016/j.scitotenv.2014.05.084.

Perrone, M.G., Zhou, J., Malandrino, M., Sangiorgi, G., Rizzi, C., Ferrero, L., Dommen, J., Bolzacchini, E. 2016. PM chemical composition and oxidative potential of the soluble fraction of particles at two sites in the urban area of Milan, Northern Italy. Atmos. Environ. 128, 104-113. DOI: 10.1016/j.atmosenv.2015.12.040.

Piazzalunga, A., Belis, C., Bernardoni, V., Cazzuli, O., Fermo, P., Valli, G., Vecchi, R. 2011a. Estimates of wood burning contribution to PM by the macro-tracer method using tailored emission factors. Atmos. Environ. 45(37), 6642-6649 DOI: 10.1016/j.atmosenv.2011.09.008.

Piazzalunga, A., Bernardoni, V., Fermo, P., Valli, G., Vecchi, R. 2011b. Technical Note: On the effect of water-soluble compounds removal on EC quantification by TOT analysis in urban aerosol samples. Atmos. Chem. Phys. 11 (19), 10193-10203. DOI: 10.5194/acp-11-10193-2011.

Piazzalunga, A.; Bernardoni, V.; Fermo, P.; Vecchi, R. 2013. 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, 1123–1132. DOI: 10.1007/s00216-012-6433-5.

Pietrogrande, C., Barbaro, E., Bove, M.C., Clauser, G., Colombi, C., Corbella, L., Cuccia, E., Dalla Torre, S., Decesari, S., Fermo, P., Gambaro, A., Gianelle, V., Ielpo, P., Larcher, R., Lazzeri, P., Massabò, D., Melchionna, G., Nardin, T., Paglione, M., Perrino, C., Prati, P., Visentin, M., Zanca, N., Zangrando, R. 2017. Results of an interlaboratory comparison of analytical methods for quantification of anhydrosugars and biosugars in atmospheric aerosol. 184, 269-277. https://doi.org/10.1016/j.chemosphere.2017.05.131.

Ruffolo, S.A., Comite, V., La Russa, M.F., Belfiore, C.M., Barca, D., Bonazza, A., Crisci, G.M., Pezzino, A., Sabbioni, C., 2015. Analysis of black crusts from the Seville Cathedral: a challenge to deepen understanding the relationship among microstructure, microchemical features and pollution sources. Sci. Total Environ. 502, 157–166. DOI: 10.1016/j.scitotenv.2014.09.02.

Saarikoski, S., Sillanpää, M., Sofiev, M., Timonen, H., Saarnio, K., Teinilä, K., Karppinen, A., Kukkonen, J., Hillamo, R., 2007. Chemical composition of aerosols during a major biomass burning episode over northern Europe in spring 2006: Experimental and modelling assessmentS. Atmospheric Environment, 41 (17), pp. 3577-3589. DOI: 10.1016/j.atmosenv.2006.12.053

Saba, M., Quiñones-Bolaños, E.E., Barbosa López, A.L. 2018. A review of the mathematical models used for simulation of calcareous stone deterioration in historical buildings. Atmos. Environ. 180, 156-166. DOI: 10.1016/j.atmosenv.2018.02.043.

Sabbioni, C., 1995. Contribution of atmospheric deposition to the formation of damage layers. Sci. Total Environ. 167, 49–56. DOI: 10.1016/0048-9697(95)04568-L.

Saiz-Jimenez, C., 2003. Air pollution and Cultural Heritage. Proceedings of the International Workshop on Air Pollution and Cultural Heritage, Seville, Spain.

Salma, I., Vasanits-Zsigrai, A., Machon, A., Varga, T., Major, I., Gergely, V., Molnár, M., 2020. Fossil fuel combustion, biomass burning and biogenic sources of fine carbonaceous aerosol in the Carpathian Basin, Atmospheric Chemistry and Physics, 20 (7), pp. 4295-4312. DOI: 10.5194/acp-20-4295-2020

Sandrini, S., Fuzzi, S., Piazzalunga, A., Prati, P., Bonasoni, P., Cavalli, F., Bove, M.C., Calvello, M., Cappelletti, D., Colombi, C., Contini, D., de Gennaro, G., Di Gilio, A., Fermo, P., Ferrero, L., Gianelle, V., Giugliano, M., Ielpo, P., Lonati, G., Marinoni, A., Massabò, D., Molteni, U., Moroni, B., Pavese, G., Perrino, C., Perrone, M.G., Perrone, M.R., Putaud, J.-P., Sargolini, T., Vecchi, R., Gilardoni, S. 2014. Spatial and seasonal variability of carbonaceous aerosol across Italy. Atmos. Environ. 99, 587-598. DOI: 10.1016/j.atmosenv.2014.10.032

Urban, R.C., Lima-Souza, M., Caetano-Silva, L., Queiroz, M.E.C., Nogueira, R.F.P., Allen, A.G., Cardoso, A.A., Held, G., Campos, M.L.A.M. Use of levoglucosan, potassium, and water-soluble organic carbon to characterize the origins of biomass-burning aerosols 2012 Atmospheric Environment, 61, pp. 562-569. DOI: 10.1016/j.atmosenv.2012.07.082

Vassura, I., Venturini, E., Marchetti, S., Piazzalunga, A., Bernardi, E., Fermo, P., Passarini, F. 2014. Markers and influence of open biomass burning on atmospheric particulate size and composition during a major bonfire event. Atmos. Environ. 82, 218-225. DOI: 10.1016/j.atmosenv.2013.10.037.

Vecchi, R., Chiari, M., D'Alessandro, A., Fermo, P., Lucarelli, F., Mazzei, F., Nava, S., Piazzalunga, A., Prati, P., Silvani, F., Valli, G. 2008. A mass closure and PMF source apportionment study on the sub-micron sized aerosol fraction at urban sites in Italy. Atmos. Environ. 42 (9), 2240-2253. DOI: 10.1016/j.atmosenv.2007.11.039

Vecchi, R., Bernardoni, V., Fermo, P., Lucarelli, F., Mazzei, F., Nava, S., Prati, P., Piazzalunga, A., Valli, G. 2009a. 4-hours resolution data to study PM10 in a "hot spot" area in Europe. Environ. Monit. Assess. 154 (1-4), 283-300. DOI: 10.1016/j.scitotenv.2011.07.048

Vecchi, R., Valli, G., Fermo, P., D'Alessandro, A., Piazzalunga, A., Bernardoni, V. 2009b. Organic and inorganic sampling artefacts assessment. Atmos. Environ. 43 (10), 1713-1720. https://doi.org/10.1016/j.atmosenv.2008.12.016.

Vidal, F., Vicente, R., Mendes Silva, J. 2019. Review of environmental and air pollution impacts on built heritage: 10 questions on corrosion and soiling effects for urban intervention. J. Cult. Herit. 37, 273-295. DOI: 10.1016/j.culher.2018.11.006.

Vidorni, G., Sardella, A., De Nuntiis, P., Volpi, F., Dinoi, A., Contini, D., Comite, V., Vaccaro, C., Fermo, P., Bonazza, A. 2019. Air pollution impact on carbonate building stones in Italian urban sites, E.P.J. 134 (9), art. no. 439. DOI: 10.1140/epjp/i2019-12943-0.

Wåhlin, P., Berkowicz, R., Palmgren, F. 2006. Characterisation of traffic-generated particulate matter in Copenhagen. Atmospheric Environment, 40 (12), pp. 2151-2159. DOI: 10.1016/j.atmosenv.2005.11.049

Journal Pre-proof

Table 1 Levoglucosan concentrations in TSP samples collected inner and out (see figure 1) on the loggia of San Marco during 2013-2014.

	Levoglucosan (ng/m^3)				
	JULY 2013	**DECEMBER 2013**	**APRIL 2014**	**JULY 2014**	**OCTOBER 2014**
OUT	50	1080	40	15	20
dev.st OUT	10	170	4	4	2
INNER	80	860	60	30	20
dev.st INNER	30	180	20	10	10

Journal Pre-proof

Table 2 WSOC concentrations in TSP samples collected inner and out (see figure 1) on the loggia of San Marco during 2013-2014.

	WSOC (μg/m^3)				
	JULY 2013	**DECEMBER 2013**	**APRIL 2014**	**JULY 2014**	**OCTOBER 2014**
OUT	3,2	15,8	**2,6**	**1,7**	2,2
dev.st OUT	0,3	1,9	**0,2**	**0,1**	0,4
INNER	3,6	14,4	3,0	1,9	2,1
dev.st INNER	0,1	2,1	0,4	0,1	0,1

Journal Pre-proof

Table 3 Correlation matrix among the analyzed species during winter (December 2013)

	OC	EC	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	CH_3COO^-	$HCOO^-$	$CH_3SO_3^-$	Cl^-	NO_3^-	SO_4^{2-}	$C_2O_4^{2-}$	Levo
OC	1,00														
EC	0,97	1,00													
Na^+	0,09	0,06	1,00												
NH_4^+	0,37	0,43	0,14	1,00											
K^+	0,67	0,63	0,70	0,41	1,00										
Mg^{2+}	-0,05	-0,17	0,66	-0,32	0,50	1,00									
Ca^{2+}	0,49	0,36	0,40	-0,32	0,58	**0,77**	1,00								
CH_3COO^-	0,62	0,71	-0,07	0,71	0,36	-0,59	-0,31	1,00							
$HCOO^-$	0,54	0,60	-0,08	0,61	0,28	-0,60	-0,35	0,93	1,00						
$CH_3SO_3^-$	0,68	0,75	-0,22	0,58	0,35	-0,41	-0,04	0,75	0,68	1,00					
Cl^-	-0,19	-0,23	**0,89**	-0,16	0,47	0,74	0,35	-0,34	-0,32	-0,42	1,00				
NO_3^-	**0,77**	**0,85**	0,05	**0,70**	0,44	-0,47	-0,07	0,85	0,78	0,74	-0,28	1,00			
SO_4^{2-}	-0,15	-0,26	0,74	-0,29	0,46	**0,96**	0,63	-0,56	-0,57	-0,42	0,87	-0,49	1,00		
$C_2O_4^{2-}$	0,61	0,65	0,23	0,84	0,60	-0,18	-0,07	0,81	0,74	0,73	-0,02	0,74	-0,13	1,00	
Levo	**0,9**	**0,8**	0,3	0,54	**0,8**	0,0	0,4	**0,62**	0,49	0,59	0,0	**0,77**	0,02	**0,69**	1,00

| | | |

Table 4 Correlation matrix among the analyzed species during summer (July 2013-July 2014)

	OC	EC	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	CH_3COO^-	$HCOO^-$	$CH_3SO_3^-$	Cl^-	NO_3^-	SO_4^{2-}	$C_2O_4^{2-}$	Levo
OC	1														
EC	0,85	1,00													
Na^+	0,00	-0,01	1,00												
NH_4^+	0,59	0,27	-0,36	1,00											
K^+	0,32	-0,07	0,32	0,50	1,00										
Mg^{2+}	0,07	0,02	**0,97**	-0,31	0,36	1,00									
Ca^{2+}	0,30	0,24	**0,90**	-0,23	0,37	**0,95**	1,00								
$CH3COO^-$	0,57	0,61	-0,14	0,54	0,09	-0,23	-0,13	1,00							
$HCOO^-$	0,39	0,43	0,06	0,30	0,06	-0,09	-0,03	0,88	1,00						
$CH_3SO_3^-$	-0,51	-0,41	0,49	-0,62	-0,15	0,42	0,31	-0,46	-0,26	1,00					
Cl^-	0,05	0,01	**0,95**	-0,35	0,32	**0,95**	0,94	-0,23	-0,10	**0,51**	1,00				
NO_3^-	0,40	0,34	0,50	-0,02	0,23	0,45	0,58	0,10	0,11	0,34	0,63	1,00			
SO_4^{2-}	0,49	0,19	0,65	0,40	0,76	0,70	0,75	0,16	0,13	-0,04	0,70	0,54	1,00		
$C_2O_4^{2-}$	0,8	0,7	0,3	0,28	0,3	0,4	0,6	0,35	0,28	-0,09	0,3	0,46	0,56	1,00	

	1	3	4		4	0	0				6				
Levo	0,45	0,06	-0,31	0,62	0,66	-0,23	-0,11	0,11	0,04	-0,48	-0,28	-0,11	0,28	0,25	1,00

Journal Pre-proof

Figure captions

Fig.1 Pictures showing the area where the sampling site was located with respect to San Marco square (Florence) and the loggia of San Marco Museum where the two samplers were placed, one towards the street (sampling heads 1 and 2) and the other pointing towards the interior (sampling heads 3 and 4).

Figure 2 Daily atmospheric TSP concentration inner and out (see figure 1) on the loggia of San Marco during 2013- 2014.

Figure 3 Monthly average atmospheric concentrations of total suspended particulate matter collected inner and out (see figure 1) on the loggia of San Marco during 2013- 2014.

Figure 4 Monthly average atmospheric concentrations of a) OC and b) EC in TSP samples collected inner and out (see figure 1) on the loggia of San Marco during 2013-2014.

Figure 5 Monthly average atmospheric concentrations of main cations a), main anions b) and short chains organic acids c) in TSP samples collected inner and out (see figure 1) on the loggia of San Marco during 2013-2014.

Figure 6 Mass balance of the analysed TSP samples during the different seasons.

Figure 7 Location of the two monitoring sites: Florence Baptistery (Ghedini 2011) and San Marco Museum.

Figure 8 Comparison between TSP and TC values obtained in Florence during 2003 (Ghedini et al., 2011)

Journal Pre-proof

and during 2013-2014 (present study).

Journal Pre-proof

Sample CRediT author statement

Paola Fermo: Methodology, conceptualization, validation, formal analysis, investigation, data curation, writing original draft, writing - Review & Editing, project administration; **Valeria Comite**: formal analysi, data curation, writing - review & editing; **Chiara Ciantelli**: Investigation; **Alessandro Sardella**: Investigation, Review and Editing; **Alessandra Bonazza:** Conceptualization, Resources, Review and Editing, Supervision

Journal Pre-proof

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.

Journal Pre-proof

Journal Pre-proof

Highlights:

- Chemical characterization of TSP to study the impact on urban heritage in Florence
- Ions, OC, EC, WSOC and levoglucosan analysis
- Impact of traffic and wood burning during wintertime
- Comparison with data acquired 10 years ago to indicate atmospheric pollution change

Journal Pre-proof

Figure 1

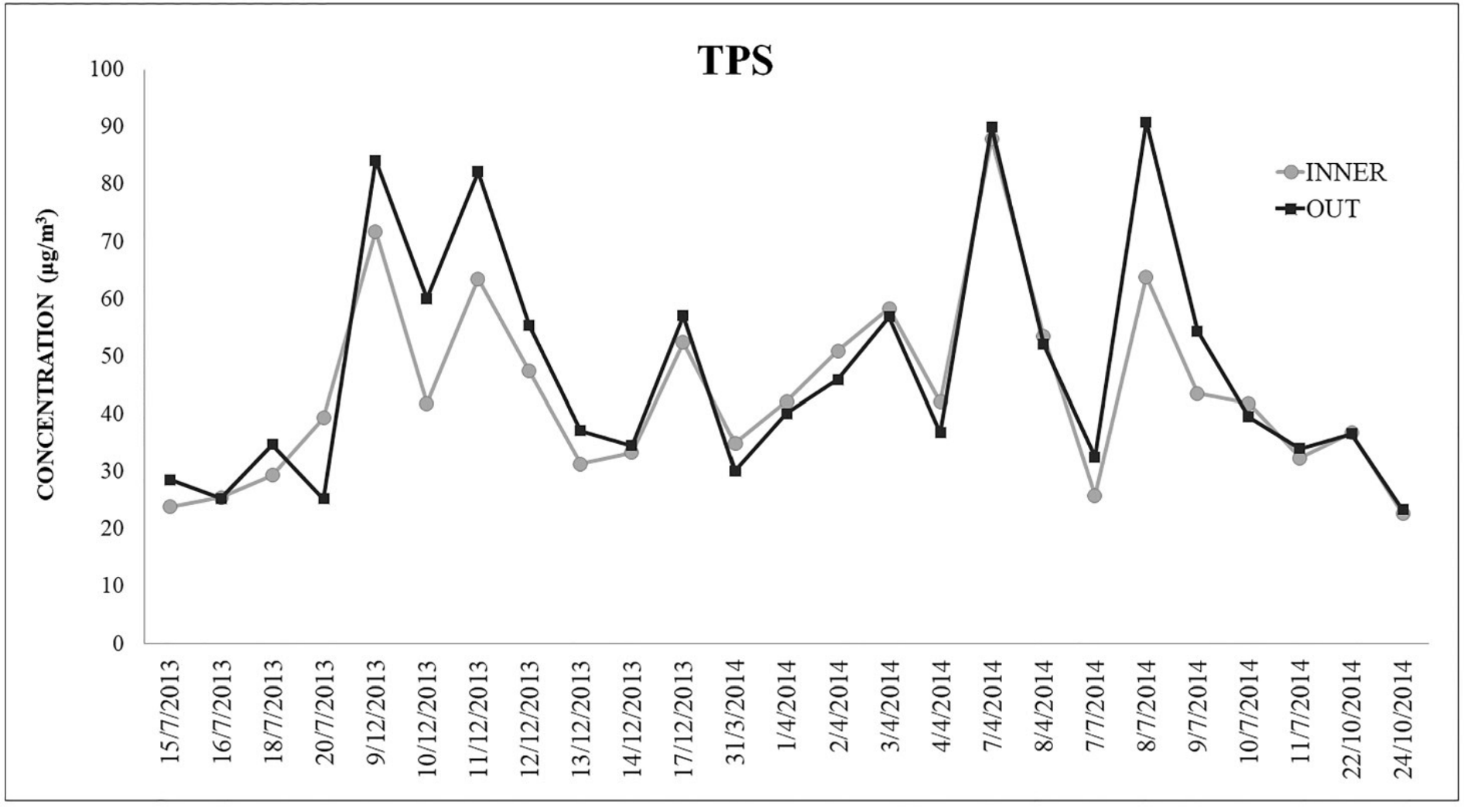

TPS
CONCENTRATION (µg/m³)
100
90
80
70
60
50
40
30
20
10
0
INNER
OUT
15/7/2013
16/7/2013
18/7/2013
20/7/2013
9/12/2013
10/12/2013
11/12/2013
12/12/2013
13/12/2013
14/12/2013
17/12/2013
31/3/2014
1/4/2014
2/4/2014
3/4/2014
4/4/2014
7/4/2014
8/4/2014
7/7/2014
8/7/2014
9/7/2014
10/7/2014
11/7/2014
22/10/2014
24/10/2014

Figure 2

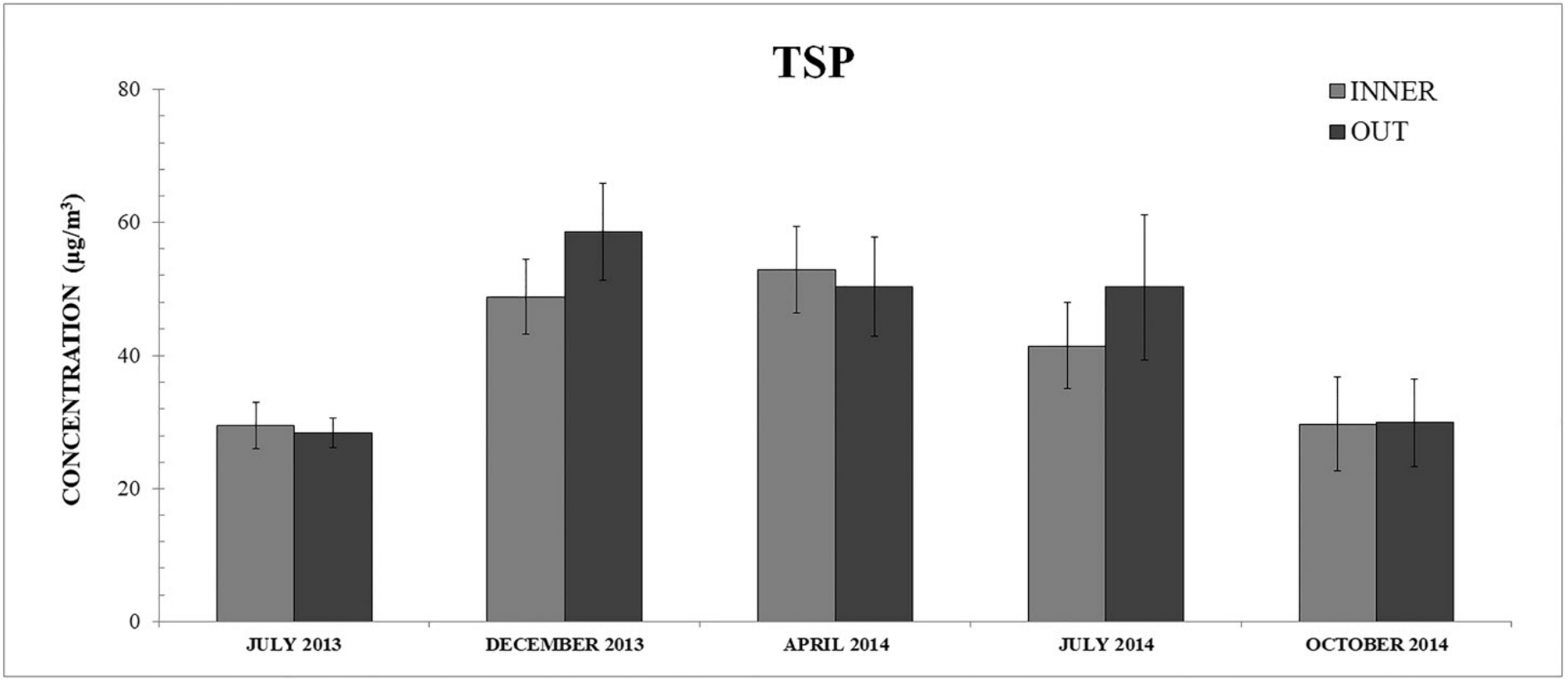
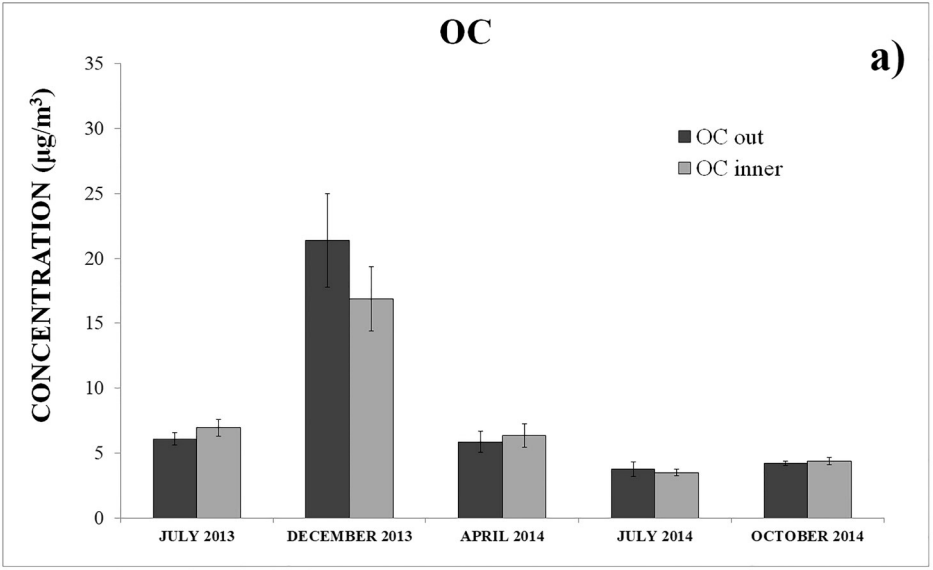

TSP
INNER
OUT
CONCENTRATION (µg/m³)
80
60
40
20
0
JULY 2013
DECEMBER 2013
APRIL 2014
JULY 2014
OCTOBER 2014

Figure 3


OC
a)
CONCENTRATION (µg/m³)
35
30
25
20
15
10
5
0
OC out
OC inner
JULY 2013
DECEMBER 2013
APRIL 2014
JULY 2014
OCTOBER 2014

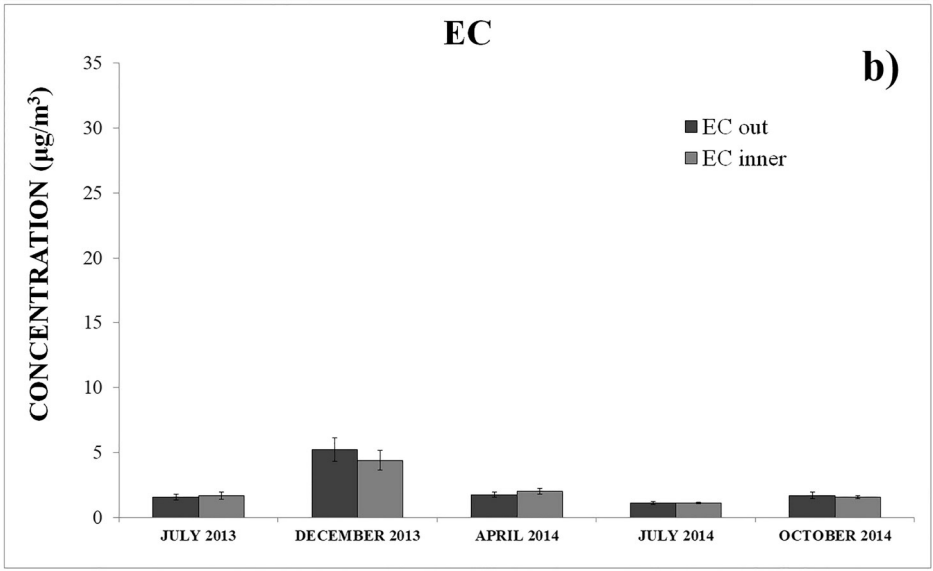
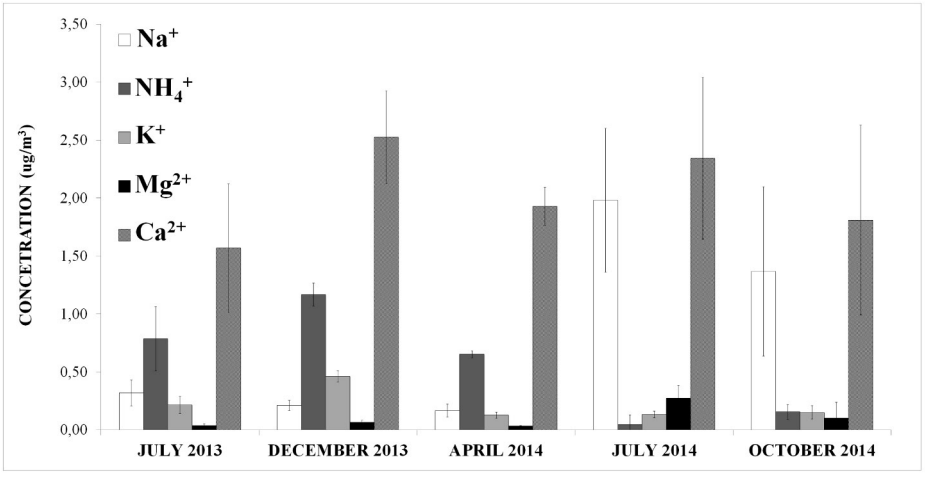
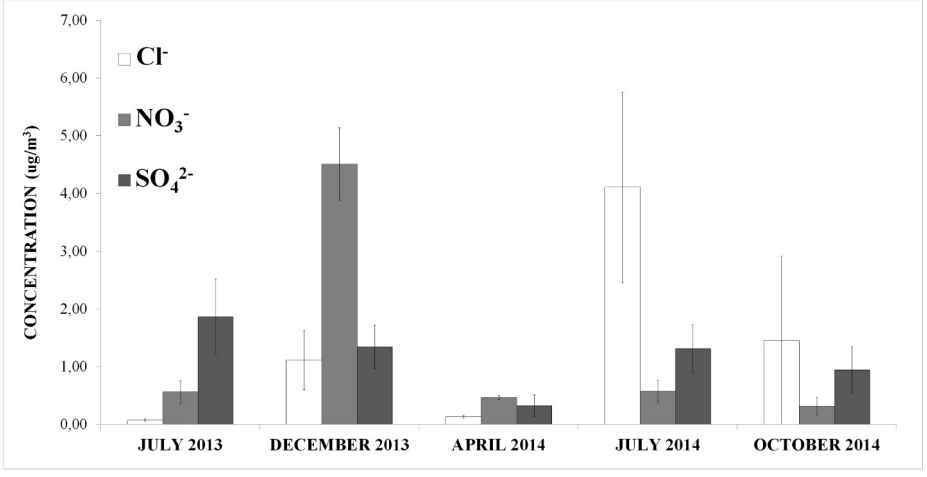

EC
b)
CONCENTRATION (µg/m³)
35
30
25
20
15
10
5
0
EC out
EC inner
JULY 2013
DECEMBER 2013
APRIL 2014
JULY 2014
OCTOBER 2014

Figure 4


3,50
3,00
2,50
2,00
1,50
1,00
0,50
0,00
CONCETRATION (ug/m3)
Na+
NH4+
K+
Mg2+
Ca2+
JULY 2013
DECEMBER 2013
APRIL 2014
JULY 2014
OCTOBER 2014


7,00
6,00
5,00
4,00
3,00
2,00
1,00
0,00
CONCENTRATION (ug/m3)
Cl-
NO3-
SO42-
JULY 2013
DECEMBER 2013
APRIL 2014
JULY 2014
OCTOBER 2014

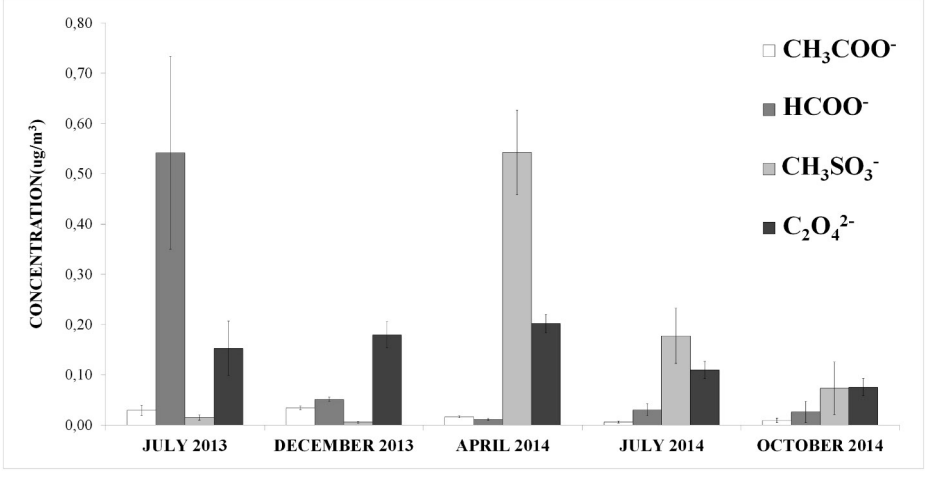
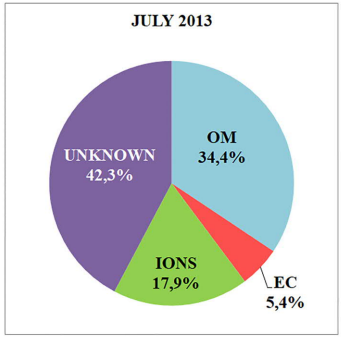
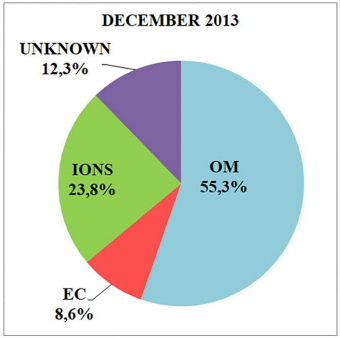
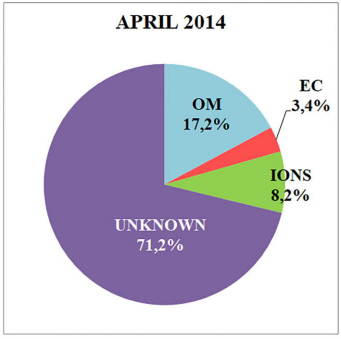
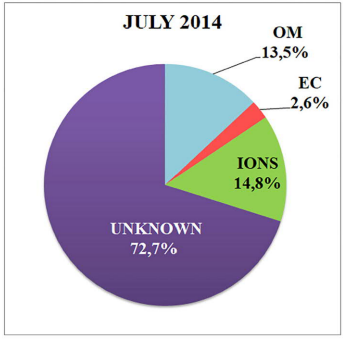

0,80
0,70
0,60
0,50
0,40
0,30
0,20
0,10
0,00
CONCENTRATION(ug/m3)
CH3COO-
HCOO-
CH3SO3-
C2O42-
JULY 2013
DECEMBER 2013
APRIL 2014
JULY 2014
OCTOBER 2014

Figure 5


JULY 2013
OM
34,4%
EC
5,4%
IONS
17,9%
UNKNOWN
42,3%


DECEMBER 2013
UNKNOWN
12,3%
OM
55,3%
EC
8,6%
IONS
23,8%


APRIL 2014
OM
17,2%
EC
3,4%
IONS
8,2%
UNKNOWN
71,2%


JULY 2014
OM
13,5%
EC
2,6%
IONS
14,8%
UNKNOWN
72,7%

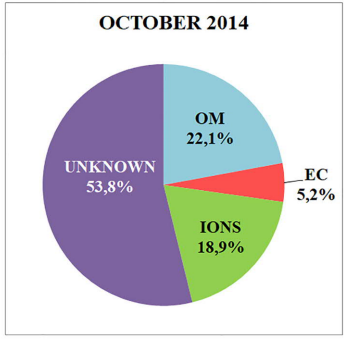

OCTOBER 2014
OM
22,1%
EC
5,2%
IONS
18,9%
UNKNOWN
53,8%

Figure 6

San Marco Museum
Baptistery of San Giovanni
Google Earth
Image Landsat / Copernicus
N
90 m

Figure 7

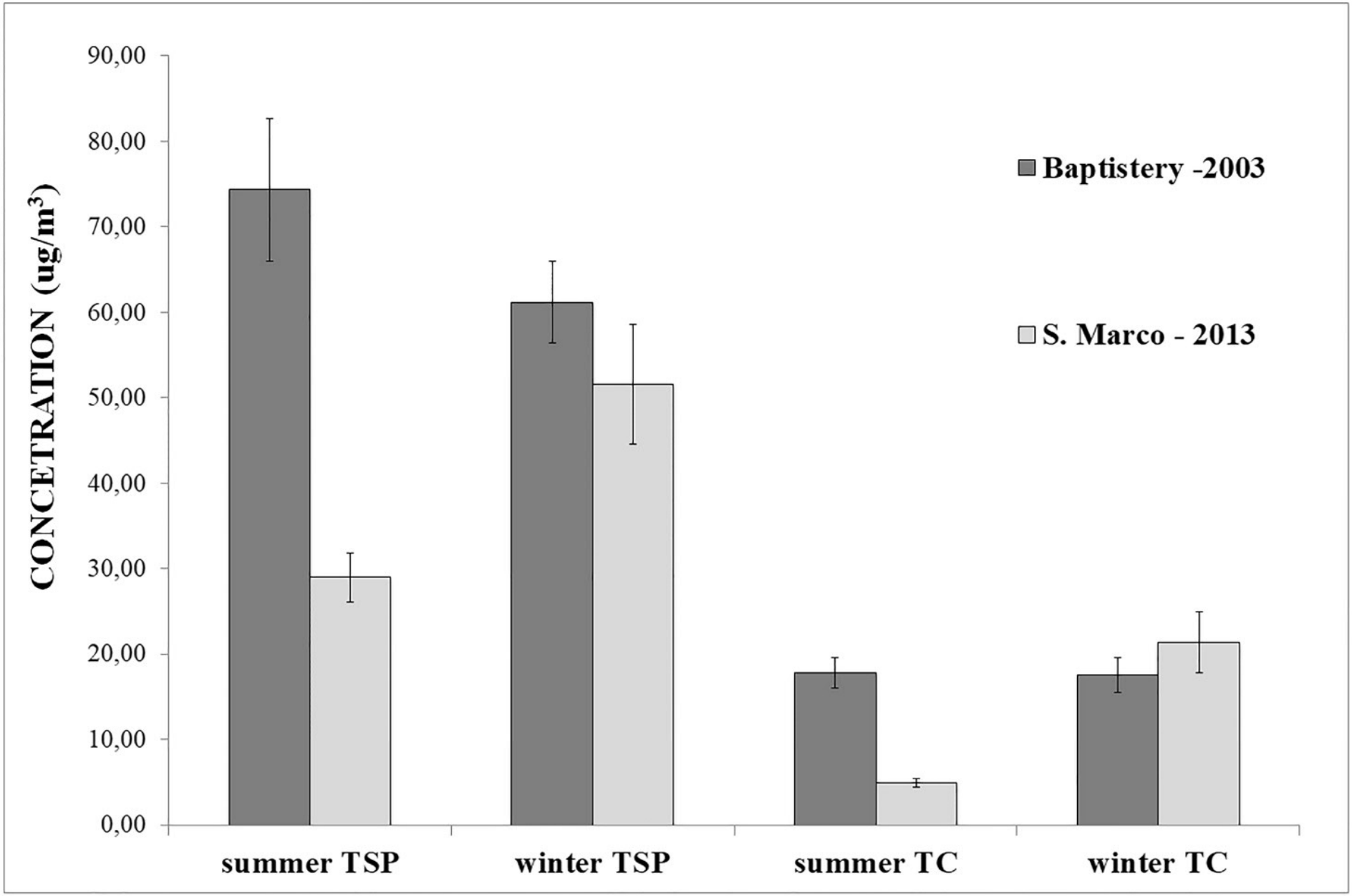

90,00
80,00
70,00
60,00
50,00
40,00
30,00
20,00
10,00
0,00
CONCETRATION (ug/m3)
Baptistery -2003
S. Marco - 2013
summer TSP
winter TSP
summer TC
winter TC

Figure 8