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Abstract: The carbonaceous component of atmospheric aerosols was characterized in Emilia-Romagna region (Northern Italy) in two fall/winter monitoring campaigns conducted through the years 2011-2012 and 2012-2013, in the framework of the Supersito project. Nearly 650 PM2.5 samples were collected at three monitoring stations describing urban background (main city Bologna, MS, Parma and Rimini) and one rural background site (San Pietro, SP). OC and EC values were measured by the thermal-optical transmittance method (TOT). Low flow-rate sampling strategy (24 m3 air volume per day) was used to reduce loading of light absorbing material on the filter surface in order to ensure the correct OC/EC discrimination.

The TC values measured in winter 2011-2012 ranged from 9.8 μgm-3 at San Pietro to 12.0 μgm-3 at Parma, consisting of OC from 8.6 μgm-3 at SP to 9.9 μgm-3 at MS and EC from 1.3 μgm-3 at SP to 2.5 μgm-3 at Rimini.

In winter 2012-2013, lower values were in general found with TC values ranging from 7.8 to 9.1μg m−3 consisting of OC from 5.1 to 7.0 μg m−3 and EC from 1.5 to 2.2 μg m−3.

Such differences can be likely explained by differences in meteorological conditions. In particular, lower temperature in fall/winter 2011/2012 (mean temperature ≈ 2 °C in comparison with ≈ 7 °C in winter 2012/2013) may be the reason of higher pollutant emissions related to domestic heating and lower mixing height (≈ 200 m in 2011/2012 in comparison with ≈ 3800 m in winter 2012/2013) may promote contaminant accumulation.

Both the urban and the rural background sites showed similar OC and EC levels, revealing an homogeneous spatial distribution of the carbonaceous component throughout the region that is consistent with atmospheric homogeneity typical of Po Plain.

In this study, all the sites are characterized by OC/EC ratios ranging from 3 to 9, that are within the 3 to 10 range found at most urban background sites in the Po Valley during fall/winter.

These results are consistent with the large contribution of emission from the wood burning for residential heathig during the cold period. This hypothesis can be likely supported by high levels of polycyclic aromatic hydrocarbons (PAHs) related to combustion and of levoglucosan, as unambiguous

tracer for biomass burning emission, in particulr at MS and SP sites in 2011-2012 winter (Burning PAH $\simeq 4$ ng m^{-3} and levoglucosan $\simeq 1000$ ng m^{-3}).

Cover Letter

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To the Editor of
Atmospheric Research

Dear Editor

with the present letter we intend to submit our manuscript to publication on your journal Atmospheric Research:

Characteristics of carbonaceous aerosols in Emilia-Romagna(Northen Italy) based on two fall/winter field campaigns

V. Costa, D. Bacco, S. Castellazzi, Isabella Ricciardelli, R. Vecchietti, Claudia Zigola, M.C. Pietrogrande.

This paper investigates the carbonaceous component of atmospheric aerosols in Emilia-Romagna region (Northern Italy) in two fall/winter monitoring campaigns in the years 2011-2012 and 2012-2013. Concentrations of Organic and Elemental carbon were measured by the thermal-optical transmittance method.

The obtained results are likely explained by differences in meteorological conditions and contribution of emission sourses, in particular from the wood burning for residential heathig, supported by charatcerization of other chemical markers, such as polycyclic aromatic hydrocarbons and levoglucosan.

In the framework of the Supersito project, designed by Emilia-Romagna Region Agency for Prevention and Environment, this paper integrates the results recently published on other your journals, i.e., Atmospheric Environment 2014, 86, 164-175 and 2014, 97, 215-225.

For this reason we strongly hope that our paper can be taken into consideration for publication on your journal

Sincerely yours,

Prof. M. Chiara Pietrogrande Ferrara, May, 27, 2015

Highlights

- OC/EC measurements at 4 sampling sites in Po Valley (Italy).
- Nearly 650 daily $PM_{2.5}$ samples analyzed in 2 fall/winter campaigns.
- Large contribution of emission from the wood burning for residential heathing.
- Differences between two campaigns related to the meteorological conditions.
- Homogeneous spatial distribution throughout the region.

Characteristics of carbonaceous aerosols in Emilia-Romagna(Northen Italy) based on two fall/winter field campaigns

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Abstract

The carbonaceous component of atmospheric aerosols was characterized in Emilia-Romagna region (Northern Italy) in two fall/winter monitoring campaigns conducted through the years 2011-2012 and 2012-2013, in the framework of the Supersito project. Nearly 650 $PM_{2.5}$ samples were collected at three monitoring stations describing urban background (main city Bologna, MS, Parma and Rimini) and one rural background site (San Pietro, SP). OC and EC values were measured by the thermal-optical transmittance method (TOT). Low flow-rate sampling strategy (24 m^3 air volume per day) was used to reduce loading of light absorbing material on the filter surface in order to ensure the correct OC/EC discrimination.

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In winter 2012-2013, lower values were in general found with TC values ranging from 7.8 to 9.1 $\mu g\ m^{-3}$ consisting of OC from 5.1 to 7.0 $\mu g\ m^{-3}$ and EC from 1.5 to 2.2 $\mu g\ m^{-3}$.

Such differences can be likely explained by differences in meteorological conditions. In particular, lower temperature in fall/winter 2011/2012 (mean temperature ≈ 2 °C in comparison with ≈ 7 °C in winter 2012/2013) may be the reason of higher pollutant emissions related to domestic heating and lower mixing height (≈ 200 m in 2011/2012 in comparison with ≈ 3800 m in winter 2012/2013) may promote contaminant accumulation.

Both the urban and the rural background sites showed similar OC and EC levels, revealing an homogeneous spatial distribution of the carbonaceous component throughout the region that is consistent with atmospheric homogeneity typical of Po Plain.

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These results are consistent with the large contribution of emission from the wood burning for residential heathig during the cold period. This hypothesis can be likely supported by high levels of polycyclic aromatic hydrocarbons (PAHs) related to combustion and of levoglucosan, as unambiguous tracer for biomass burning emission, in particulr at MS and SP sites in 2011-2012 winter (Burning PAH $\simeq$4 ng m^{-3} and levoglucosan $\simeq$1000 ng m^{-3}).

Key words: Organic/Elemental carbon, Po Valley, Thermal-optical method, Wood burning, Residential heating.

Introduction

Carbonaceous aerosol is an ubiquitous and important component of the fine atmospheric particulate matter (PM) which accounts for 20-45% of $PM_{2.5}$ at European rural and urban background sites (Yttri et al, 2007; Putaud et al, 2010; Perrone et al, 2012; Jedynska et al, 2014; Sandrini et al, 2014). In recent years there is increasing evidence of its role in global climate change and radiative budget, involvement in heterogeneous reactions, and possible content of mutagenic and carcinogenic components (Reche et al, 2011; Bond et al, 2013; Perrone et al, 2013). In this context, among the thousands of organic components present in the atmospheric aerosol, elemental (EC) and organic carbon (OC) are usually quantified as more generic indicators of air quality to identify pollution sources and assess their environmental impact (Sillanpää et al, 2005; Andreae and Gelencsér, 2006; Wallén et al, 2010; Cheng et al, 2011; Pio et al, 2011; Jedynska et al, 2014; Zhao et al, 2014). EC is the inert matter with graphitic-like structure released from incomplete combustion of fossil fuels in transportation, heating, and power generation, and of wood and biomass in residential heating and agriculture activities. OC in contrast is an aggregate of organic compounds, such as aliphatic and aromatic hydrocarbons, that are either directly released in the atmosphere by primary sources or secondarily formed in the atmosphere from anthropogenic or biogenic precursors.

For this reason, the characterization of the carbonaceous aerosol was included in the Supersito project for a chemical and physical characterization of atmospheric aerosol in Emilia-Romagna (Northen Italy) (ARPA-EMR, 2012). This region is located at the Eastern side of the Po Valley, the most industrialized and trafficked area in Italy, which is recognized as one of the most air polluted situations in Europe, in particular during the cold seasons, when enhanced anthropogenic emissions from residential heating combined with stagnant atmospheric conditions result into the pollutant accumulation near the source locations (Carbone et al, 2010; Bernardoni et al, 2011; Belis et al, 2011; Bigi et al, 2012; Perrone et al, 2012; Piazzalunga et al, 2013a; Pietrogrande et al, 2013; Perrino et al, 2014; Decesari et al, 2014; Pietrogrande et al, 2014a).

This study concerns nearly 650 $PM_{2.5}$ samples collected in two monitoring campaigns during fall/winter periods in 2011-2012 and 2012- 2013 at four urban and rural locations in the region.

In this work the thermal-optical transmittance method (TOT) was used, as one of the most widely recognized methods for measuring OC and EC in atmospheric particulates (Yang and Yu, 2002; Chow et al, 2004; Bae et al, 2004; Han et al, 2007; Boparai et al, 2008; Cheng et al, 2011; Piazzalunga et al, 2011; Chow et al, et al, 2011; Cheng et al, 2012; Bautista et al, 2015). Up to date however, there is no standard protocol of analysis and the definition of OC and EC is operative and therefore depending on the technique used. In this work, the EUSAAR2 protocol (European Supersites for Atmospheric Aerosol Research) was employed as recently suggested for samples collected at European regional sites (Cavalli et al, 2010; CEN, 2011; Piazzalunga et al, 2013a).

The most suitable sampling protocol was selected to provide reliable results as applied to aerosol samples collected in a heavily polluted area, as Emilia-Romagna region in winter, that are characterized by high loading of carbonaceus material on the filters.

Further information on the concentration of polycyclic aromatic hydrocarbons and levoglucosan, as markers related to biomass burning, were evaluated in order to give insigth into the potential contribution of wood combustion to influence the thermal behaviour of the carbonaceous species.

2 Materials and Methods

2.1 Aerosol sampling

The duration of the two monitoring campaigns was from 15th November 2011 to 29th March 2012 and from 1st October 2012 to 31st March 2013. Samples were collected at four monitoring stations of Emilia-Romagna ARPA agency (Region Agency for Prevention and Environment), describing different emission situations in the region, i.e., three urban background sites, a main site in Bologna, (MS), two satellite sites in Parma and Rimini, and one rural background site (San Pietro Capofiume). The urban sites are located in different parts of the Emilia-Romagna region, characterized by significant agricultural and industrial activities and the presence of main arterial roads. MS is located in the city of Bologna − which is the most populous city in the region (over

380000 inhabitants), Parma − with about 190000 inhabitants, is situated half-way between Milan to Bologna − and Rimini, with about 150000 inhabitants, is located on the coast of the Adriatic Sea, and therefore visited by many tourists during holidays and week-ends. The rural background station of San Pietro Capofiume, SP, is located on a flat, homogeneous terrain of harvested fields, 40 km north-east from Bologna: it represents the typical low land agricultural areas with sparse towns and villages.

In the framework of the Supersito project, the $PM_{2.5}$ samples were collected on quartz fiber filters (PALL Tissu Quartz 2500 QAO-UP 2500 filters, 47 *mm* of diameter) with automatic outdoor stations at MS, SP, Rimini and Parma sites. A low volume sampler (Skypost PM, TCR TECORA Instruments, Corsico, Milan, Italy) operated at the standard flow rate of 38.3 $Lmin^{-1}$ to collect an air volume of 55 m^3 per day. In addition, the sampler has been properly modified to reduce air flow rate to 16.7 $Lmin^{-1}$ and collect an air volume of 24 m^3 per day. Instrument details and validation of the modified procedure are reported in Supplementary Material.

In the framework of the ARPA-ER air quality monitoring, PM samples are routinely collected in urban areas, including Bologna, Rimini, and Parma, and the rural background San Pietro, using low volume sequential samplers (Swam 5C, FAI Instruments, Roma) to monitor PM_{10} and/or $PM_{2.5}$ concentration on daily basis and measure concentrations of some PAHs in PM_{10} on monthly basis.

After sampling, filter equilibration and weighing was performed following the procedure outlined in the European Standard EN 12341 (CEN, 1998). The quartz fiber filters were heated for 3 h at 800 °C in air before use, to reduce their carbon blank . Thus, the background concentration in the quartz fiber filter and matrix, which could influence the analysis, was minimized.

2.2 Thermal-optical transmission analysis

The samples were analyzed in the ARPA laboratory using a Sunset Laboratory Thermal/Optical Carbonaceous Aerosol Analyzer (Laboratory Inc). The carbon analyzer was routinely checked for leaks and operated using Ultra-High Purity (Grade 6.0) Helium gas. The instrument was calibrated prior to use with injections of sucrose standard solution (concentration of 10 gL^{-1} corresponding to 42 μgcm^{-2} of organic carbon on the filter surface).

According to the used thermal protocol EUSAAR2 (Cavalli et al., 2010), the carbonaceous material (OC) is initially thermally desorbed in an inert atmosphere (99.999% pure He) at relatively low temperature in four steps (200 °C for 120 s; 300 °C for 150 s; 450 °C for 180 s; 650 °C for 180 s). Then desorption is performed to evolve the EC component at higher temperature in four steps (500 °C for 120 s; 550 °C for 120 s; 700 °C for 70 s; 850 °C for 80 s) in an oxidizing atmosphere (2% oxygen/98% helium final mixture in the sample oven). During this stage, organic compounds are vaporized and catalytically oxidized to carbon dioxide but also a percentage of native elemental carbon may be pyrolytically converted into elemental carbon (Pyrolytic Carbon, PC) and therefore interfere in the determination of EC. In order to correct this potential bias, the laser beam transmission through the sample is monitored during the analysis and the point at which the laser transmission returns to the original pre-pyrolysis value is used to define the split between organic and elemental carbon (split point). A premature evolution of light-absorbing carbon containing EC before the EC/OC split will lead to underestimate the EC amount (Chow et al, 2004; Subramanian et al, 2006; Yang and Yu, 2002; Boparai et al, 2008).

2.3 Elemental analysis

Elemental analysis was performed in the laboratory of the University of Ferrara, Department of Chemistry and Pharmaceutical Sciences, using a Thermo Scientific 2000 CHNSO Analyzer equipped with a thermal conductivity detector (TCD). For each measurement a material amount ranging from 2 to 5 mg was analyzed obtained by cutting proper portions of the PM filters. After introduction in the tin capsule, the sample was weighed and put into the combustion reactor using an autosampler.

3 Results and discussion

3.1. Quality assurance of the Thermal Optical Transmittance method

In this work the analytical performance of a thermo-optical-transmission analyzer was assessed for precision, linearity and limits of quantification in order to find out the proper protocol providing a reliable OC/EC quantification in PM samples.

The procedure assured good precision and sensitivity: relative standard deviation RSD% were 5.2%, 6.5% and 3.9% for OC, EC and TC values, respectively, and limits of quantification were 3 $\mu g cm^{-2}$ for OC − corresponding to 0.7 $\mu g m^{-3}$ and 1.6 $\mu g m^{-3}$, collecting 55 m^3 and 24 m^3 air volume, respectively) − and 0.4 $\mu g cm^{-2}$ − corresponding to 0.1 $\mu g m^{-3}$ (55 m^3) and 0.2 $\mu g m^{-3}$ (24 m^3).

In addition, the reliability of the Total Carbon measurements was validated by intercomparison with data obtained by the elemental CHNSO Analyzer, as a different independent instrument which guarantees routine and high capacity analyses (Fellner et al, 2011; Zhao et al, 2011). In general a close agreement was obtained between the values obtained with the two techniques, characterized by a mean percentage difference ≈ 6% (Table 1), that is a meaningful evidence of the reliability of the used TOT procedure to obtain accurate TC determinations. The detailed investigation is reported in the Supplementary material.

3.2. Quantification of OC and EC carbonaceous fractions

In the early part of the first monitoring campaign from 15th November 2011 to 13th February 2012 an air volume of 55 m^3 was collected at the four sampling sites and analyzed for EC, OC and TC (computed as the sum EC+OC). The measured EC values were plotted as a function of TC concentrations to highlight the influence of the filter loading on the TOT measurement (Figs. 1a,b full symbols). A linear increase of TC with EC is expected, indicating a constant contribution of EC to TC, as mainly generated by incomplete combustion of organic material from traffic, residential heating, industrial activities and energy production (Bae et al, 2004; Piazzalunga et al, 2011; Cheng et al, 2012; Jedynska et al, 2014). Such a linearity was found for most of the data measured at Rimini and Parma (Figure 1a, full triangles and diamonds, full line: $R^2 \geq 0.75$). On the contrary, for the values obtained at MS and SP sites (Fig. 1b, full circles and squares) the relationship is linear only up to TC values ≈ 8 μgm^{-3} (solid line: $R^2 \geq 0.8$) and beyond this limit EC seems to reach a maximum constant level close to 1.5 μgm^{-3} for most of the samples. It is noteworthy that such an air concentration corresponds to an EC loading on the filter surface of 15 μgcm^{-2}, under the sampling protocol used, i.e., 55m^3 of air collected on a filter surface of 7.07 cm^2. This concentration is considered as the upper limit to ensure that the laser in the TOT instrumentation operated in optimal conditions to obtain reliable EC concentrations (Shauer et al.2003; Chow et al, 2004; Subramanian et al., 2006; Wallen, et al., 2010; Cheng et al., 2011; Piazzalunga et al., 2011; Baumgardner et al., 2012; Cheng et al., 2012; Piazzalunga et al., 2013a). Subramanian evidenced that loadings of light absorbing material (or soot) on the filter higher than 15 μgcm^{-2} makes the sample too dark to allow to the laser to correctly monitor any variation of the transmission through the filter. This prevents the correct assessment of the split-point for correction of pyrolytic carbon.

This hypothesis can be confirmed by investigating the optical data reported in Figure 2, which shows the dependence of the initial laser attenuation of the sample, T_0, as a function of filter loading, that would be described by the Lambert-Beer expression (Eq. 1):

$$\ln T_0 = k\, C_{EC} \qquad (1)$$

where C_{EC} is the concentration of carbon evolved in the oxidation step (expressed as EC mass per unit filter area, μgcm^{-2}) and k is the net attenuation coefficient of EC.

For the filters collected at Rimini and Parma most of the experimental EC loadings are lower than the limit of 15μgcm^{-2} (Figure 2, full triangles and diamonds) and the laser attenuation increases more or less linearly with EC loading (solid grey line: $R^2 \approx 0.8$). From the linear regression (Eq.1) the specific attenuation coefficient can be estimated obtaining a value close to 0.2 $cm^2\mu g^{-1}$ consistent with those reported for the EC (Subramanian et al., 2006).

However, nearly 10% of the samples collected at MS and SP sites (Figure 2a, full circles and squares) show high EC filter loadings in the 15-22 μgcm^{-2} range. Generally, for such heavily loaded filters the “shadowing” effect was found, that means that carbon yields lower attenuation than for more lightly loaded filters (Weingartner et al, 2003; Chow et al, 2004; Subramanian et al, 2006; Cheng et al., 2012). Therefore, these data were excluded from the database. Nearly 90% of the data show an acceptable linear relationship (solid black line: $R^2 = 0.8$) from which a specific attenuation coefficient ≈ 0.15 $cm^2\mu g^{-1}$ was computed, which indicates that a weak shadowing effect is still present in the samples (Subramanian et al, 2006). These drawbacks have been previously found for highly loaded PM samples collected in heavily polluted areas, such as in air monitoring campaigns in Po Plain during wintertime (Piazzalunga et al, 2011; Piazzalunga et al, 2013a).

To limit loading of carbonaceous aerosol and avoid data rejection, a lower air volume of 24 m^3 per day was collected by operating with a reduced air flow rate of 1 m^3h^{-1} using a modified configuration of the sampler. The chosen sampling method assured a comprehensive sampling throughout the day with good reliability of the modified instrument configuration (see Supplementary Material). Using this procedure, 140 $PM_{2.5}$ samples were collected in the final part of the first monitoring campaign from 14th February to 29th March 2012 at the four sampling sites and analyzed for EC, OC and TC.

Plotting the measured EC valued as a function of TC (Fig. 1a,b, grey symbols) all the obtained values show a linear relationship, also including the data of MS and SP sites (grey lines: $R^2 \approx 0.75$). In fact, the sampling protocol (24m^3 of air collected on a filter surface of 13 cm^2) limits the EC loading on the filters so that all the experimental data are below the limit of 15 μgcm^{-2} (that correspond to ≈ 8 μgm^{-3} in the air). As a consequence, the optimal optical behavior is guaranteed for the all the data (Figure 2, empty symbols), also including MS and SP samples (empty circles and squares in the figure): laser attenuation increases linearly with EC loading (dashed line: $R^2 = 0.82$) yielding a consistent estimate of the specific attenuation coefficient, 0.19 $cm^2\mu g^{-1}$ (Subramanian et al, 2006; Wallen et al, 2010).

The OC, EC and TC values measured at each site during the winter 2011-2012 are reported in Table 2 (mean and standard deviation values in 1st-3rd lines). In general, similar values were measured at the four sites with TC mean values ranging from 9.8 μgm^{-3} at San Pietro to 12.0 μgm^{-3} at Parma, consisting of OC from 8.6 μgm^{-3} at SP to 9.9 μgm^{-3} at MS. Larger differences were found for EC values, that are lower (1.3 - 1.4 μgm^{-3}) at MS and SP sites in comparison with those at Rimini and Parma (2.5 and 2.1 μgm^{-3}, respectively).

The 24 m^3 air volume sampling protocol was used in the second campaign in winter 2012-2013. A total of 300 $PM_{2.5}$ filters were collected from 1st October 2012 to 31th March 2013 at the four sampling sites and analyzed for EC, OC and TC (mean and standard deviation values for each site reported in Table 3, 1st-3rd lines). All the data measured at the four sites show the expected linear relationship between EC and TC values (dashed lines: $R^2 \geq 0.8$, Fig. 1a,b, empty symbols).

In general, the obtained values are lower in comparison with those of fall/winter 2011-2012, with TC values ranging from 7.8 μgm^{-3} at San Pietro to 9.1 μgm^{-3} at Main Site, consisting of OC from 5.1 μgm^{-3} at Parma to 7.0 μgm^{-3} at Rimini. In this campaign EC values show higher homogeneity than in the first one, ranging from 1.5 μgm^{-3} at SP to 2.2 μgm^{-3} at MS.

3.3. Variation of OC and EC concentrations

At our knowledge, these data are the first extensive results concerning different sites of Emilia-Romagna region, while several studies have been carried out in Lombardia, that is the Western region of the Po Plain, as densely populated as Emilia-Romagna (Gilardoni et al, 2011; Bigi et al, 2012; Perrone et al, 2012; Piazzalunga et al, 2013b; Perrino et al, 2014).

The results of this study are similar to others reported in the cold period (October-March) for semi-rural sites in Po Valley and lower than those reported at the city site of Milan strongly impacted by anthropogenic emission sources (Belis et al., 2011; Perrone et al., 2012; Piazzalunga et al., 2013a), as recently reviewed by Sandrini (Sandrini et al, 2014). In particular, our data are very close to those occurred between 2010 and 2012 during a field study carried out in the area of Ferrara, in the Eastern part of the Emilia-Romagna, i. e., OC ≈ 9 μgm^{-3} and EC ≈ 1 μgm^{-3} (Perrino et al, 2014). The measured values are in good agreement with the atmospheric EC/OC concentrations found in southern European areas in cold period (Sillanpaa et al, 2005; Yttri et al., 2007; Jedynska et al, 2014), in particular with the average concentrations of OC close to 6 μgm^{-3} and EC above 2 μgm^{-3} found in Rome and Athens.

In this study both the urban and the rural background sites showed similar levels of OC and EC concentrations in $PM_{2.5}$, summarized in Tables 2 and 3, revealing that the contribution of very localized sources is weakly discernible, making the spatial distribution of the carbonaceous component rather homogeneous throughout the region. This indicates that also the rural site SP is strongly influenced by the emissions from urban areas. Such an atmospheric homogeneity is typical of Po Plain, as likely due to similar meteorological conditions, such as temperature and low dispersion properties of the boundary layer, which determine similar accumulation of pollutants and atmospheric reactions of gaseous precursors which promote SOA formation (Carbone et al., 2010;

Giraldoni et al., 2011; Perrone et al., 2013; Paglione et al., 2014; Sandrini et al, 2014; Decesari et al, 2014).

The higher OC and EC levels in 2011/2012 campaign in comparison with those in 2012/2013 can be likely explained by differences in meteorological conditions. In fact, during the colder winter 2011/2012 (mean temperature ≈ 2°C with maximum of 5°C in November 2011) higher pollutant emissions related to domestic heating may be expected in comparison with winter 2011/2012 (mean temperature 7°C≈ with maximum of 12°C in November 2012). In addition, more stagnant atmospheric situation in winter 2011/2012 (mixing height ≈ 200 m in comparison with ≈ 3800 m in winter 2012/2013) promotes contaminant accumulation (Pietrogrande et al., 2014a, 2014b).

3.4. OC/EC concentration ratios

The ratio between OC and EC values was computed as an useful parameter to discriminate between different sources and processes contributing to carbonaceous PM, being influenced by primary emission sources and secondary organic aerosol formation. For references, the OC/EC ratios of 6.0–20 are used for emissions from biomass burning and 1.0–4.2 for vehicular emissions. In addition, ratios larger than 2-2.5 were found for secondary OC enriched aerosols (Pio et al., 2011; Jedynska et al., 2014; Sandrini et al., 2014).

Figure 3 shows the OC/EC ratios at all sites in the two monitoring campaigns (full and empty symbols: 2011/2012 and 2012/2013 campaigns, respectively), from which the mean and standard deviation values were computed for each site (Tables 2 and 3, 4th line, for 2011/2012 and 2012/2013 campaigns, respectively).

In this study, nearly all OC/EC ratios range from 3 to 9, that is the same range found at most urban background sites in the Po Valley during fall/winter (Sandrini et al, 2014). These values are consistent with the general finding that the OC/EC ratio during cold season is mainly affected by the primary emissions due fossil fuels burning, characterized by OC/EC values frequently lower than 1, and residential wood burning, which is expected to release an enriched OC fraction (Piazzalunga et al., 2011; Pio et al., 2011; Sandrini et al., 2014; Jedynska et al., 2014). In addition, also production of secondary OC through photochemical activity has been found significant in the investigated region also in the cold periods leading to thigh OC/EC ratios (Decesari et al., 2014; Paglione et al, 2014; Pietrogrande et al, 2014b).

Similar values ranging from 3 to 9 have been reported for ground-level rural and urban sites located in the Po Valley (Sandrini et al., 2014), consistent to what observed at other rural sites in Europe (Jedynska et al., 2014). However, it must be noted that the values of this study were lower than those (≈ 10) measured during cold season in other sites in the Eastern part of the Po Valley

(Piazzalunga et al., 2011; Perrone et al., 2012; Piazzalunga et al., 2013b) and even at Cassana, located at close distance (ca. 50 km) from it (Perrino et al., 2014).

Higher OC/EC values were measured at MS and SP in comparison with those at Rimini and Parma. In particular, the OC/EC ratios at MS and SP were ≈ 8 and ≈ 6 in the first and second campaigns, respectively, while those at Rimini and Parma were ≈ 5 and ≈ 3.5 in the first and second campaigns, respectively. Such differences may be likely ascribed to the difference in the relative contribution of local emission sources, since MS and SP are strongly influenced by larger anthropogenic emissions from Bologna metropolitan area (Pietrogrande et al, 2014b). In particular, higher OC/EC ratios may suggest increased influence from wood burning for residential heating, which contributes more to OC than EC (Pio et al.,2011; Sandrini et al., 2014).

This is especially true for the values measured during the first campaign, although these values may be overestimated by the negative bias in EC data. Anyway, the obtained results are consistent with similar values observed in urban Po Valley areas in cold season, where wood combustion was estimated to accounts for up to 40-70% of OC in winter (Perrone et al., 2012; Bernardoni et al. 2013; Piazzalunga et al., 2013b; Perrino et al, 2014; Paglione et al., 2014; Sandrini et al, 2014).

3.5. Insights in the aerosol composition of the carbonaceous PM

In order to confirm these data and identify the potential contribution of biomass burning to OC and EC, the concentration of relevant molecular markers related to biomass burning were investigated: in particular, selected polycyclic aromatic hydrocarbons (PAHs) and levoglucosan. Among the PAHs that substantially contribute to the carbonaceous PM fraction, 8 PAHs largely released into the atmosphere by biomass combustion processes were studied, i.e., pyrene, fluoranthene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene and benzo[a]py-rene (BaP). The study concerns the total PAH contribution (total PAH burning, obtained by summing the measured concentrations) and the separated contributions of B(a)P, as an indicator for toxic PAHs, and of Benzo(b)+(j)fuorantenes (BbjF), as the most abundant PAHs. The average values for each sampling campaign were computed from the monthly concentrations (Tables 2 and 3, 5th-7th lines). In general, the total PAH levels range from 2.4 to 4.5 ngm^{-3} and the concentration of B(a)P and BbjF are in 0.4-0.6 ngm^{-3}and 0.7 – 1.1 ngm^{-3} ranges, respectively.

Such a contribution is exceptionally higher for the samples collected at MS and SP sites in 2011-2012 winter, when the total burning PAHs increase up to 7.7 ngm^{-3}, BbjF up to 1.9 ngm^{-3} and B(a)P slightly exceeds the limit value of 1 ngm^{-3} imposed by EUD (European Union Directive, 2005) (Table 2, 5th-7th lines).

This finding is consistent with other studies which demonstrated that domestic burning of wood materials - logs, briquettes, chips and pellet - for home heating is a diffuse regional source in Northern Italy that accounts for a significant quote of PAHs to carbonaceous aerosol, in particular in the coldest months (December-February) (Belis et al, 2011; Piazzalunga et al, 2013b; Perrone et al, 2013; Gianelle et al, 2013; Paglio et al, 2014; Pietrogrande et al, 2014c).

This conclusion can be confirmed from the abundance of levoglucosan, as unambiguous tracer for biomass burning emission, measured in atmospheric $PM_{2.5}$ at Main Site and San Pietro sites in two intensive experimental campaigns conducted in the framework of the Supersito project, from 16th November to 7th December 2011 and from 23rd October to 11th November 2012. Extremely high levels were found in fall 2011 ($\approx$ 1000 ngm^{-3}, Table 2, 8th line) indicating strong impact of wood burning, while the contribution was moderate in early fall 2012 ($\approx$ 250ngm^{-3}, Table 3, 8th line) (Pietrogrande et al., 2014b).

The strongest impact of wood burning emission in 2011-2012 at MS and SP sites in comparison with the other sites may be a possible explanation of the distinct thermal-optical behavior of the filters collected there (Figs. 1b and 2a). In fact, several studies report that emission from wood combustion contains a high fraction of light-absorbing charring which strongly affects the optical properties of the carbonaceous material typically decreasing the filter transmittance (Yang and Yu, 2002; Shauer et al.2003; Subramanian et al, 2006; Han et al, 2007; Chow et al, 2011; Cheng et al, 2011; Piazzalunga et al, 2011; Frey et al, 2014).

In addition, it has been reported that large amount of charring would cause the premature evolution of EC yielding underestimated EC results, with the negative bias increasing with the amount of charring, presumably through new charring formation and/or the existing charring pyrolyzing into more light-absorbing species (Piazzalunga et al, 2011; Cheng et al, 2012).

4 Conclusions

The large dataset measured in this study provides insight into characteristics and origins of carbonaceous aerosol in Emilia Romagna region giving information comparable with those found at other semi-rural sites in Po Valley.

In conclusion, substantial homogeneity was found in the spatial pattern of EC and OC at the four sampling sites indicating a common background level in Po Valley in cold seasons, due to strength of anthropogenic emission sources and the stagnant atmospheric conditions. Comparison with PAH and levoglucosan levels indicated that in fall/winter air quality is strongly impacted by emissions from wood burning for domestic heating.

At the state of the art, additional information on the chemical composition based on a wider range of source markers may give deeper insight into the contribution of the different emission sources as well as into the occurrence of photochemical oxidative reactions in the atmosphere. The on-going studies will clarify this point.

The accurate discrimination between OC and EC during the thermal evolution cycle in TOT analysis is the still an unsolved problem, since it strongly depends on the characteristics of the collected aerosol, mainly sample loading and chemical composition. For these reasons, further studies are needed to investigate the charring behavior of heavy loaded PM filters, in particular for samples strongly impacted by biomass smoke, i.e., the influences of wood type and burning condition on optical and thermal properties of ambient aerosols.

5 Acknowledgements

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References

Andreae, M., Gelencsér, A., 2006. Black carbon or brown carbon? the nature of light-absorbing carbonaceous aerosols. Atmos. Chem. Phys. 6, 3131–3148.

ARPA-EMR, 2012. Web page: supersito http://www.supersito-er.it.

Bae, M., Schauer, J., DeMinter, J., Turner, J., Smith, D., Cary, R., 2004. Validation of a semi-continuous instrument for elemental carbon and organic carbon using a thermal-optical method. Atmos. Environ. 38, 2885–2893.

Baumgardner, D., Popovicheva, O., Allan, J., Bernardoni, V., Cao, J., Cavalli, F., Cozic, J., Diapouli, E., Eleftheriadis, K., Genberg, P. 2012. Soot reference materials for instrument calibration and intercomparisons: a workshop summary with recommendations. Atmos. Meas. Tech. 5, 1869–1887.

Bautista, A.T.VII, Pabroa, P.C.B., Santos, F.L., Quirit, L.L., Asis, J.L.B., Dy, M.A.K., Martinez, J.P.G., 2015. Intercomparison between NIOSH, IMPROVE_A, and EUSAAR_2 protocols: Finding an optimal thermal–optical protocol for Philippines OC/EC samples. Atmos. Poll. Res. 6, 334-342.

Belis, C., Cancelinha, J., Duane, M., Forcina, V., Pedroni, V., Passarella, R., Tanet, G., Douglas, K., Piazzalunga, A., Bolzacchini, E., 2011. Sources for PM air pollution in the Po plain, Italy: I. critical comparison of methods for estimating biomass burning contributions to benzo(a)pyrene. Atmos. Environ. 45, 7266–7275.

Bernardoni, V., Vecchi, R., Valli, G., Piazzalunga, A., Fermo, P., 2011. PM10 source apportionment in Milan (Italy) using time-resolved data. Sci. Tot. Environ. 409, 4788–4795.

Bigi, A., Ghermandi, G., Harrison, R.M., 2012. Analysis of the air pollution climate at a background site in the Po valley. J. Environ. Monit. 14, 552–563.

Bond, T.C., Doherty, S.J., Fahey, Forster, P., Berntsen, T., DeAngelo, B., Flanner, M., Ghan, S., Kärcher, B., Koch, D., 2013. Bounding the role of black carbon in the climate system: A scientific assessment. J. Geophys. Res. Atmospheres 118, 5380–5552.

Boparai, P., Lee, J., Bond, T. 2008. Revisiting thermal-optical analyses of carbonaceous aerosol using a physical model. Aeros. Sci. Technol. 42, 930–948.

Carbone, C., Decesari, S., Mircea, M., Giulianelli, L., Finessi, E., Rinaldi, M., Fuzzi, S., Marinoni, A., Duchi, R., Perrino, C., 2010. Size-resolved aerosol chemical composition over the Italian peninsula during typical summer and winter conditions. Atmos. Environ. 44, 5269–5278.

Cavalli, F., Viana, M., Yttri, K., Genberg, J., Putaud, J., 2010. Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol. Atmos. Meas. Tech. 3, 79–89.

CEN (1998) Cen 12341: Air quality-determination of the PM10 fraction of suspended particulate matter-reference method and field test procedure to demonstrate reference equivalence of measurement methods. European Committee for Standardization, Brussels, Belgium.

CEN (2011) Cen/tr 16243: Ambient air quality - guide for the measurement of elemental carbon (EC) and organic carbon (OC) deposited on filters. European Committee for Standardization, Brussels, Belgium.

Cheng, Y., He, K., Duan, F., Zheng, M., Du, Z., Ma, Y., Tan, J., 2011. Ambient organic carbon to elemental carbon ratios: Influences of the measurement methods and implications. Atmos. Environ. 45, 2060–2066.

Cheng, Y., Duan, F., He, K., Du, Z., Zheng, M., Ma, Y., 2012. Intercomparison of thermal-optical method with different temperature protocols: Implications from source samples and solvent extraction. Atmos. Environ. 61, 453–462.

Chow, J., Watson, J., Chen, L., Arnott, W., Moosmüller, H., Fung, K., 2004. Equivalence of elemental carbon by thermal/optical reflectance and transmittance with different temperature protocols. Environ. Sci. Technol. 38, 4414–4422.

Chow. J., Watson, J., Robles, J., Wang, X., Chen, L., Trimble, D., Kohl, S., Tropp, R., Fung, K., 2011. Quality assurance and quality control for thermal/optical analysis of aerosol samples for organic and elemental carbon. Anal. Bioanal. Chem. 401, 3141–3152.

Decesari, S., Allan, J., Plass-Duelmer, C., Williams, B.J., Paglione, M., Facchini, M.C., O'Dowd C., Harrison, R.M., Gietl, J.K., Coe, H., Giulianelli, L., Gobbi, G.P., Lanconelli, C., Carbone, C., Worsnop, D., Lambe, A.T., Ahern, A.T., Moretti, F., Tagliavini, E., Elste, T., Gilge, S., Zhang, Y., Dall'Osto, M., 2014. Measurements of the aerosol chemical composition and mixing state in the Po Valley using multiple spectroscopic techniques. Atmos. Chem. Phys. 14, 12109–12132.

EUD (European Union Directive), 2005. Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air. Off. J. L 23 (26/01), 0003e0016.

Fellner, J., Aschenbrenner, P., Cencic, O., Rechberger, H., 2011. Determination of the biogenic and fossil organic matter content of refuse-derived fuels based on elementary analyses. Fuel 90, 3164–3171.

Frey, A.K., Saarnio, K., Lamberg, H., Mylla□ri, F., Karjalainen, P., Teinila□, K., Carbone, S., Tissari, J., Niemela□, V., Ha□yrinen, A., Rautiainen, J., Kyto□ma□ki, J., Artaxo, P., Virkkula, A., Pirjola, L., Ro□nkko□, T., Keskinen, J., Jokiniemi, J., Hillamo, R., 2014. Optical and Chemical Characterization of Aerosols Emitted from Coal, Heavy and Light Fuel Oil, and Small-Scale Wood Combustion. Environ. Sci. Technol. 48, 827−836.

Gianelle, V., Colombi, C., Caserini, S., Ozgen, S., Galante, S., Marongiu, A., Lanzani, G., 2013. Benzo(a)pyrene air concentrations and emission inventory in Lombardy region, Italy. Atmos. Poll. Res. 4, 257-266.

Gilardoni, S., Vignati, E., Cavalli, F., Putaud, J., Larsen, B., Karl, M., Stenström, K., Genberg, J., Henne, S., Dentener, F., 2011. Better constraints on sources of carbonaceous aerosols using a combined ^{14}C–macro tracer analysis in a european rural background site. Atmos. Chem. Phys. 11. 5685–5700.

Jedynska, A., Hoek, G., Eeftens, M., Cyrys, J., Keuken, M., Ampe, C., Beelen, R., Cesaroni, G., Forastiere, F., Cirach, M., 2014. Spatial variations of PAH, hopanes/steranes and EC/OC concentrations within and between European study areas. Atmos. Environ. 87, 239–248.

Han, Y., Cao, J., Chow, J.C., Watson, J.G., An, Z., Jin, Z., Fung, K., Liu, S., 2007. Evaluation of the thermal/optical reflectance method for discrimination between char- and soot-EC. Chemosphere 69, 569–574.

Paglione, M., Saarikoski, Carbone, S., Hillamo, R., Facchini, M.C., Finessi, E., Giulianelli, L., Carbone, C., Fuzzi, S., Moretti, F., Tagliavini, E., Swietlicki, E., Eriksson Stenström, K., Prévôt, A.S.H., Massoli, P., Canaragatna, M., Worsnop, D., Decesari, S., 2014. Primary and secondary biomass burning aerosols determined by proton nuclear magnetic resonance (1H-NMR) spectroscopy during the 2008 EUCAARI campaign in the Po Valley (Italy) Atmos. Chem. Phys. 14, 5089–5110.

Perrino, C., Catrambone, M., Dalla Torre, S., Rantica, E., Sargolini, T., Canepari, S., 2014. Seasonal variations in the chemical composition of particulate matter: a case study in the Po valley. Part I: macro-components and mass closure. Environ. Sci. Poll. Res. 21, 3999–4009.

Perrone, M., Larsen, B., Ferrero, L., Sangiorgi, G., De Gennaro, G., Udisti, R., Zangrando, R., Gambaro, A., Bolzacchini, E., 2012. Sources of high PM2.5 concentrations in Milan, northern Italy: molecular marker data and CMB modelling. Sci. Tot. Environ. 414, 343–355.

Perrone, M., Gualtieri, M., Consonni, V., Ferrero, L., Sangiorgi, G., Longhin, E., Ballabio, D., Bolzacchini, E., Camatini, M., 2013. Particle size, chemical composition, seasons of the year and urban, rural or remote site origins as determinants of biological effects of particulate matter on pulmonary cells. Environ. Poll. 176, 215–227.

Piazzalunga, A., Bernardoni, V., Fermo, P., Valli, G., Vecchi, R., 2011. Technical note: On the effect of water-soluble compounds removal on EC quantification by TOT analysis in urban aerosol samples. Atmos. Chem. Phys. 11, 10193–10203.

Piazzalunga, A., Bernardoni, V., Fermo, P., Vecchi, R., 2013a. Optimization 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.

Piazzalunga, A., Anzano, M., Collina, E., Lasagni, M., Lollobrigida, F., Pannocchia, A., Fermo, P., Pitea, D., 2013b. Contribution of wood combustion to PAH and PCDD/F concentrations in two urban sites in northern Italy. J. Aerosol Sci. 56, 30–40.

Pietrogrande, M.C., Bacco, D., Rossi, M., 2013. Chemical characterization of polar organic markers in aerosols in a local area around Bologna, Italy. Atmos. Environ. 75, 279–286.

Pietrogrande, M.C., Bacco, D., Visentin, M., Ferrari, S., Casali, P., 2014a. Polar organic marker compounds in atmospheric aerosol in the Po valley during the Supersito campaigns-Part 2: Seasonal variations of sugars. Atmos. Environ. 97, 215–225.

Pietrogrande, M.C., Bacco, D., Visentin, M., Ferrari, S., Poluzzi, V., 2014b. Polar organic marker compounds in atmospheric aerosol in the Po valley during the Supersito campaigns-Part 1: Low molecular weight carboxylic acids in cold seasons. Atmos. Environ. 86, 164–175.

Pietrogrande, M.C., Perrone, M.G., Sangiorgi, G., Ferrero, L., Bolzacchini, E., 2014c. Data handling of GC/MS signals for characterization of PAH sources in northern Italy aerosols. Talanta 120, 283–288.

Pio, C., Cerqueira, M., Harrison, R.M., Nunes, T., Mirante, F., Alves, C., Oliveira, C., Sanchez de la Campa, A., Artíñano, B., Matos M., 2011. OC/EC ratio observations in Europe: Re-thinking the approach for apportionment between primary and secondary organic carbon. Atmos. Environ. 45, 6121-6132.

Putaud, J.P., Van Dingenen, R., Alastuey, A., Bauer, H., Birmili, W., Cyrys, J., Flentje, H., Fuzzi, S., Gehrig, R., Hansson, H.C., 2010. A European aerosol phenomenology–3: Physical and chemical characteristics of particulate matter from 60 rural, urban, and kerbside sites across Europe. Atmos. Environ. 44, 1308–1320.

Reche, C., Querol, X., Alastuey, A., Viana, M., Pey, J., Moreno, T., Rodríguez, S., González, Y., Fernández-Camacho, R., Rosa, J., 2011. New considerations for PM, black carbon and particle number concentration for air quality monitoring across different European cities. Atmos. Chem. Phys. 11, 6207–6227.

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, A., 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.

Schauer, J.J, Mader, B.T., Deminter, J.T., Heidemann, G., Bae, M.S., Seinfeld, J.H., Flagan, R.C., Cary, R.A., Amith, D., Huebert, B.J., Bertram, T., Howell, S., Kline, J.T., Quinn, P., Bates, T., Turpin, B., Lim, H.J., Yu, J.Z., Yang, H., Keywood, M.D., 2003. ACE-Asia Intercomparison of a Thermal-Optical Method for the Determination of Particle-Phase Organic and Elemental Carbon Environ. Sci. Technol. 37, 993-1000.

Sillanpää, M., Frey, A., Hillamo, R., Pennanen, A., Salonen, R., 2005. Organic, elemental and inorganic carbon in particulate matter of six urban environments in Europe. Atmos. Chem. Phys. 5, 2869–2879.

Subramanian, R., Khlystov, A., Robinson, A., 2006. Effect of peak inert-mode temperature on elemental carbon measured using thermal-optical analysis. Aerosol Sci. Technol. 40, 763–780.

Wallén, A., Lidén, G., Hansson, H.C., 2010. Measured elemental carbon by thermo-optical transmittance analysis in water-soluble extracts from diesel exhaust, woodsmoke, and ambient particulate samples. J. Occup. Environ. Hygiene 7, 35–45.

Weingartner, E., Saathoff, H., Schnaiter, M., Streit, N., Bitnar, B., Baltensperger, U., 2003. Absorption of Light by Soot Particles: Determination of the Absorption Coefficient by Means of Aethalometers. J. Aerosol Sci. 34, 1445–1463.

Yang, H., Yu, J.Z., 2002. Uncertainties in charring correction in the analysis of elemental and organic carbon in atmospheric particles by thermal/optical methods. Environ. Sci. Technol. 36, 5199–5204.

Yttri, K., Aas, W., Bjerke, A., Cape, J., Cavalli, F., Ceburnis, D., Dye, C., Emblico, L., Facchini, M.C., Forster, C., Hanssen, J.E., Hansson, H.C., Jennings, S.G., Maenhaut, W., Putaud, J.P., Tørseth, K., 2007. Elemental and organic carbon in PM10: a one year measurement campaign within the European monitoring and evaluation programme EMEP. Atmos. Chem. Phys. 7, 5711–5725.

Zhao, J., Peng, P., Song, J., Ma, S., Sheng, G., Fu J., 2011. Characterization of macromolecular organic matter in atmospheric dust from Guangzhou, China. Atmos. Environ. 45, 5612-5620.

Figure captions

Figure 1: Scatter plots of EC versus TC concentrations measured on $PM_{2.5}$ filters showing influence of the filter loading on the TOT measurement.

full symbols: November 2011- February 2012 data (55 m^3 day^{-1} air sampling protocol);

full grey symbols: February-March 2012 data (24 m^3 day^{-1} air sampling protocol);

empty symbols: October 2012- March 2013 data (24 m^3 day^{-1} air sampling protocol).

1a: $PM_{2.5}$ filters collected at Parma (triangles) and Rimini (diamonds):

solid black line: overall linear regression of November 2011-February 2012 data (regression equation in inset);

solid grey line: overall linear regression of February-March 2012 data (regression equation in inset);

dashed line: overall linear regression of 2012-2013 data (regression equation in inset).

1b: $PM_{2.5}$ filters collected at Main Site (circles) and San Pietro (squares):

solid black line: linear regression of November 2011- February 2012 data with TC values ≤ 8 μgm^{-3} (regression equation in inset);

solid grey line: overall linear regression of February-March 2012 data (regression equation in inset);

dashed line: average linear regression of 2012-2013 data (regression equation in inset).

Figure 2: Scatter plots of laser attenuation as a function of EC filter loadings (μgcm^{-2}) for 2011-2012 samples.

Symbols: circles: Main Site; squares: San Pietro; triangles: Parma; diamonds: Rimini.

Colours: full symbols: November 2011- February 2012 data (55 m^3 day^{-1} air sampling protocol);

empty symbols: February-March 2012 data (24 m^3 day^{-1} air sampling protocol).

solid black line: MS and SP sites: linear regression of November 2011- February 2012 data with EC values $\leq$ 15μgcm^{-2} (regression equation in inset);

solid grey line: Parma and Rimini sites: overall linear regression of November 2011- February 2012 data (regression equation in inset);

dashed line: overall linear regression of February-March 2012 data (regression equation in inset).

Figure 3: Scatter plots of OC/EC ratios versus EC concentrations measured at all sites in the two monitoring campaigns.

Symbols: circles: Main Site; squares: San Pietro; triangles: Parma; diamonds: Rimini.

Colours: full symbols: November 2011- March 2012 data; empty symbols: October 2012- March 2013 data.

Table 1: Comparison between Total carbon values measured with OCEC Sunset Analyzer (Sunset) and Elemental Analyzer (CHNSO). The percentage difference (diff%) was computed as $(CHNSO - Sunset)/CHNSO * 100$.

$PM_{2.5}$ sample	Sunset	CHNSO	diff%
nr.	$\mu g\, cm^{-2}$	$\mu g\, cm^{-2}$	%
1	17.67	18.97	7
2	16.71	17.57	5
3	17.44	18.06	3
4	8.65	10.37	17
5	13.10	14.52	10
6	11.11	12.01	7
7	20.86	20.99	1
8	27.10	33.22	18
9	21.91	20.93	-5
10	27.72	25.31	-10
11	29.40	27.23	-8
12	17.81	18.31	3
13	19.53	21.33	8
14	19.93	19.18	-4
15	23.86	24.10	1
16	28.23	27.85	-1

Table 2: Concentration values measured during the first monitoring campaign in fall/winter 2011-2012 at the four sampling sites. The average values and standard deviations of measured data were computed for the whole campaign.

Winter 2011/2012	Main Site		San Pietro		Rimini		Parma	
	μg m^{-3}	SD	μg m^{-3}	SD	μg m^{-3}	SD	μg m^{-3}	SD
OC	9.9	4.1	8.6	4.3	9.5	4.2	9.8	3.7
EC	1.3	6.0	1.4	5.3	2.5	5.6	2.1	5.8
TC	11.9	4.2	9.8	4.3	11.9	3.6	12.0	4.0
OC/EC	6.8	3.0	6.9	3.0	4.7	1.7	4.8	1.5
	ng m^{-3}	SD	ng m^{-3}	SD	ng m^{-3}	SD	ng m^{-3}	SD
Burning PAH	6.1	2.1	7.7	3.0	4.5	0.7	4.2	1.8
BaP	1.1	0.3	1.1	0.4	0.5	0.1	0.6	0.3
BbjFs	1.6	0.5	1.9	0.8	0.8	0.5	1.1	0.7
Levoglucosan*	1042	490	967	386				

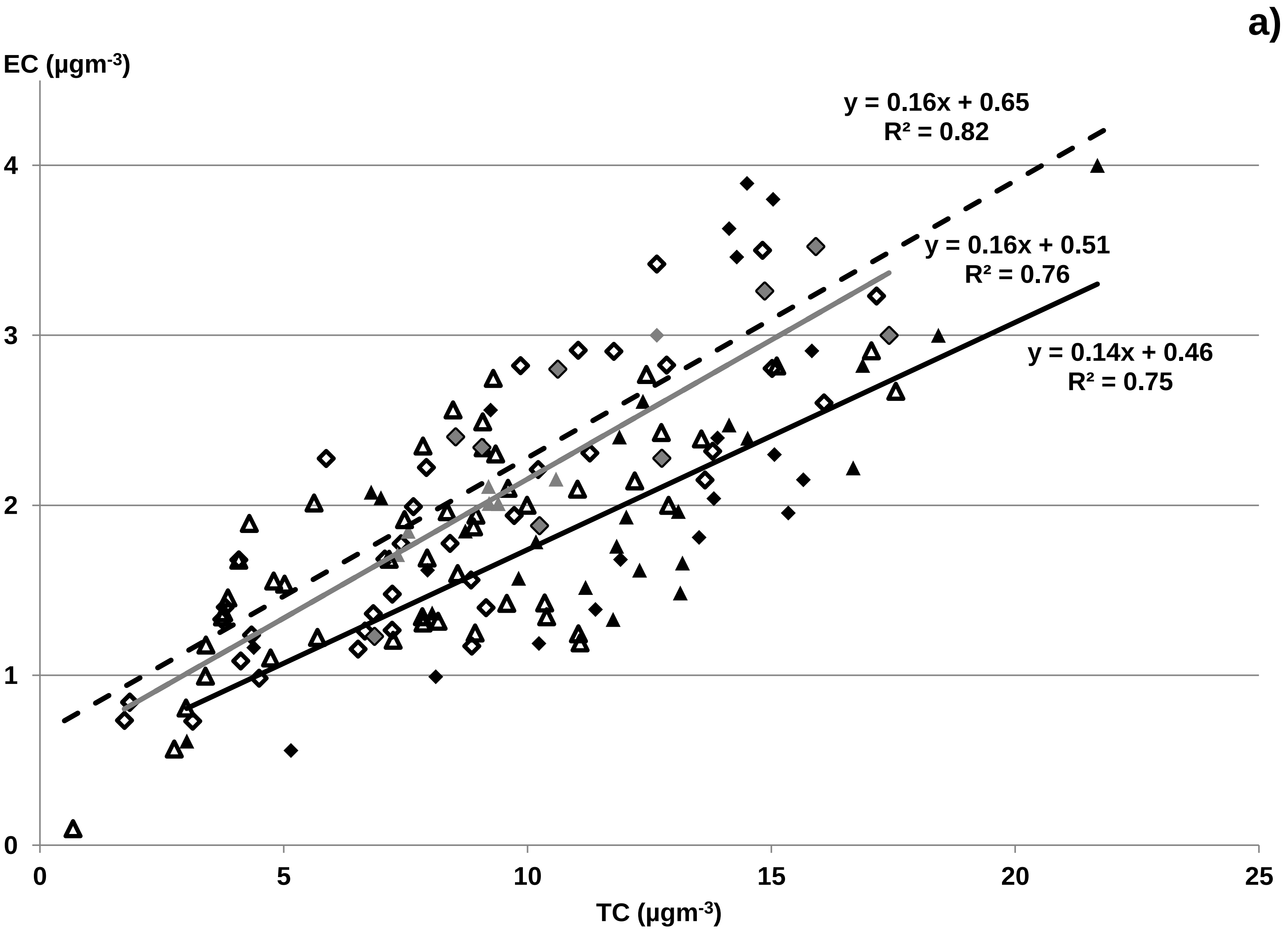
*Measured in the intensive campaign from 16th November to 7th December 2011.

Table 3: Concentration values measured during the second monitoring campaign in fall/winter 2012-2013 at the four sampling sites. The average values and standard deviations of measured data were computed for the whole campaign.

Winter 2012/2013	Main Site		San Pietro		Rimini		Parma	
	μg m^{-3}	SD	μg m^{-3}	SD	μg m^{-3}	SD	μg m^{-3}	SD
OC	6.9	3.7	6.4	3.7	7	3.6	5.1	4
EC	2.2	0.9	1.5	0.7	2.1	0.9	1.7	0.6
TC	9.1	4.2	7.8	4.1	9	4.3	8	3.9
OC/EC	3.3	1.6	4.5	1.5	3.5	1.2	3.7	1.7
	ng m^{-3}	SD	ng m^{-3}	SD	ng m^{-3}	SD	ng m^{-3}	SD
Burning PAH	4.9	2.3	3.6	1.9	3.1	1.9	2.4	1.8
BaP	0.9	0.6	0.4	0.3	0.5	0.3	0.4	0.2
BbjFs	1.4	0.8	0.8	0.4	0.8	0.6	0.7	0.6
Levoglucosan**	289	144	233	115				

*Measured in the intensive campaign from 23rd October to 11th November 2012.

Figure 1


a)
EC (µgm-3)
y = 0.16x + 0.65
R² = 0.82
y = 0.16x + 0.51
R² = 0.76
y = 0.14x + 0.46
R² = 0.75
4
3
2
1
0
0
5
10
15
20
25
TC (µgm-3)

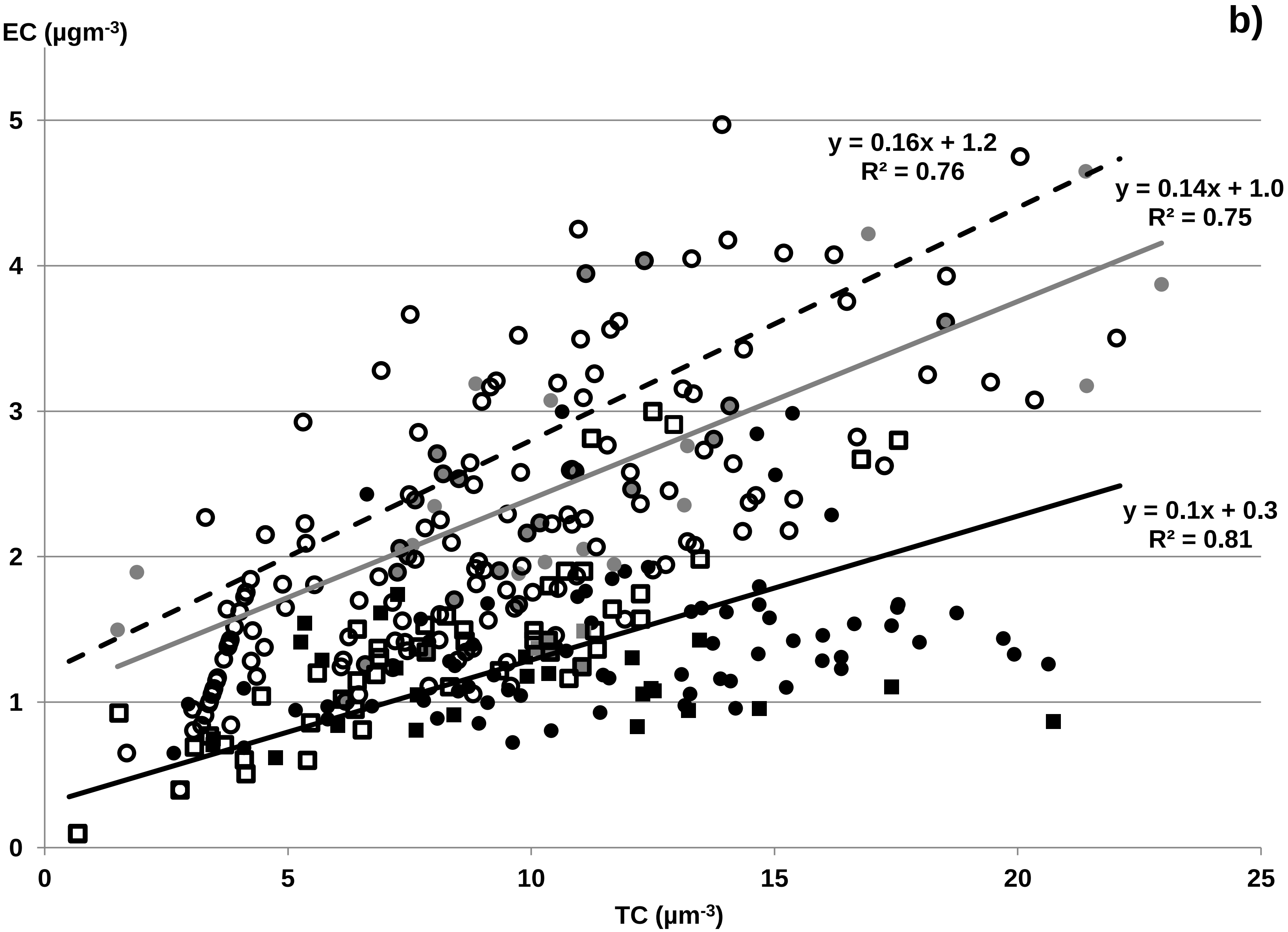

b)
EC (µgm-3)
0
1
2
3
4
5
0
5
10
15
20
25
TC (µm-3)
y = 0.16x + 1.2
R² = 0.76
y = 0.14x + 1.0
R² = 0.75
y = 0.1x + 0.3
R² = 0.81

Figure 2

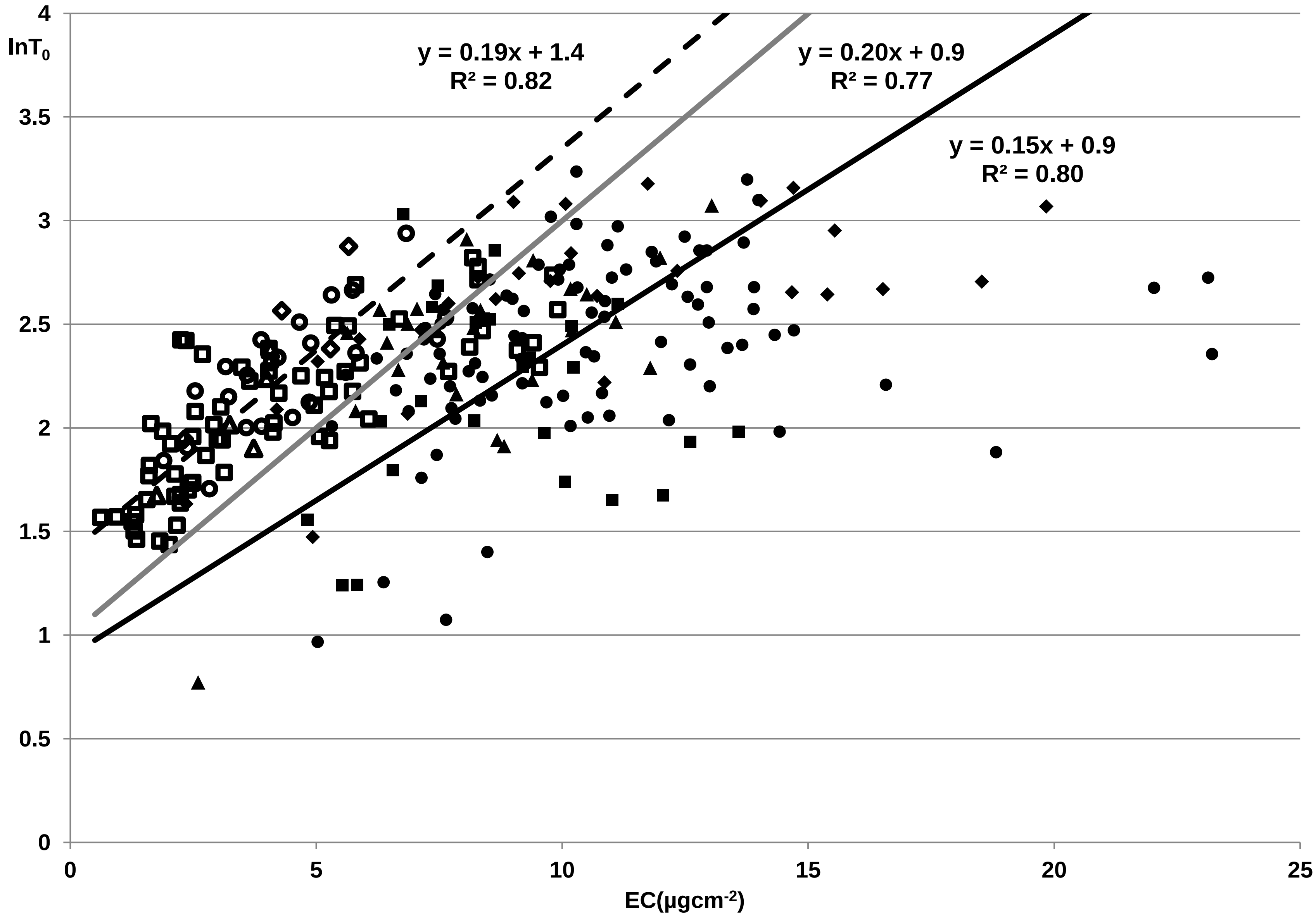
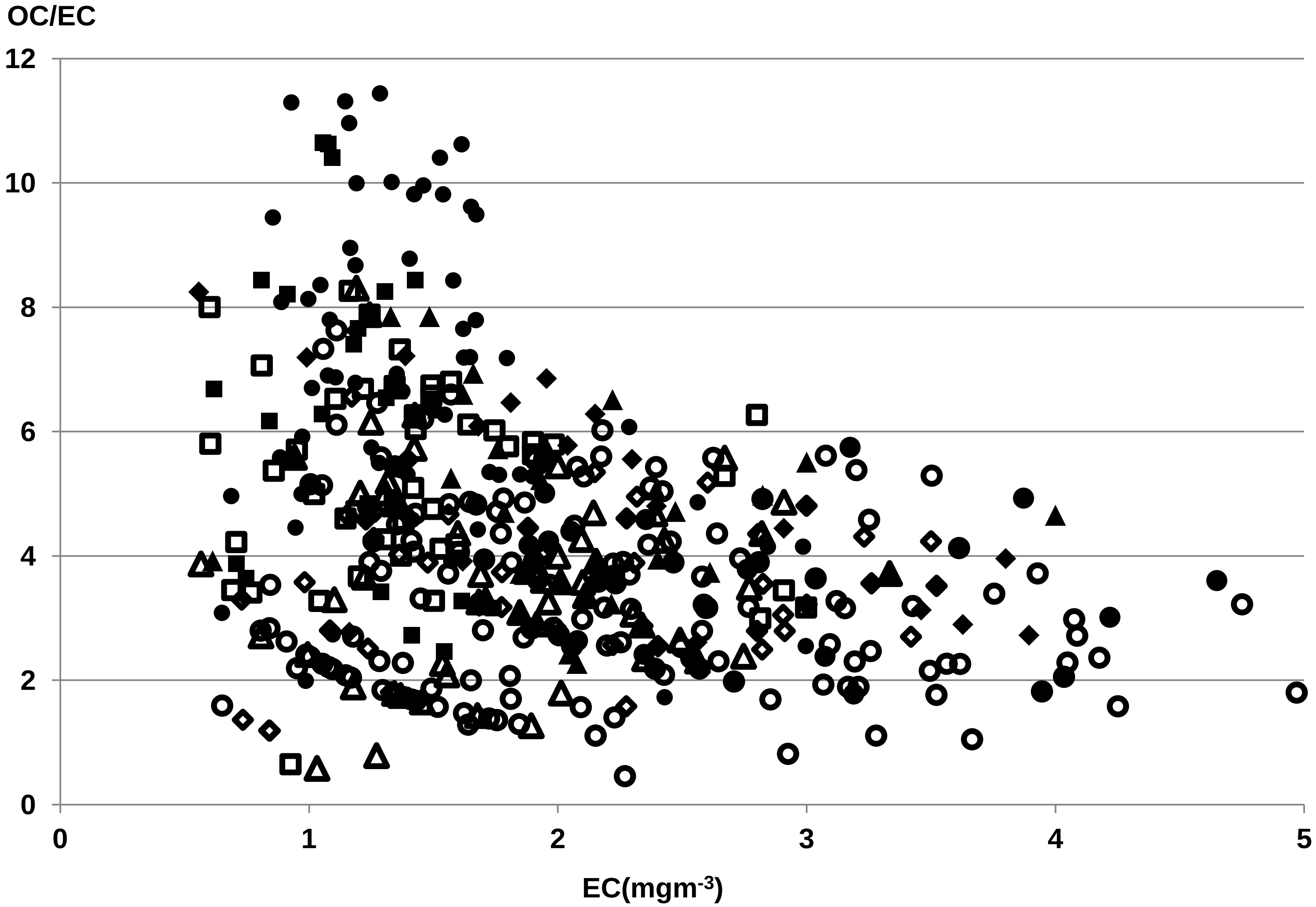

lnT$_0$
4
3.5
3
2.5
2
1.5
1
0.5
0
0
5
10
15
20
25
EC(µgcm^{-2})
y = 0.19x + 1.4
R² = 0.82
y = 0.20x + 0.9
R² = 0.77
y = 0.15x + 0.9
R² = 0.80

Figure 3



Supplementary material