Spatial and seasonal variability of carbonaceous aerosol across Italy

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1. Introduction

The carbonaceous fraction is an important component of the fine atmospheric particulate matter (PM) which accounts for 20–45% of $PM_{2.5}$ and somewhat less (20–35%) of PM_{10} on an annual basis (Putaud et al., 2010; Yttri et al., 2007). Carbonaceous aerosol is composed by OC and a refractory light-absorbing component generally referred to as soot (Baumgardner et al., 2012; Bond and Bergstrom, 2006). Soot is generated by incomplete combustion of organic material from traffic, residential heating, industrial activities and energy production using heavy oil, coal or biofuels. Depending on its empirical determination, soot is reported as elemental carbon (EC) or equivalent black carbon (EBC). EC is quantified by thermal–optical methods, while EBC is derived from optical measurements. In the atmosphere, soot is always associated with other substances from combustion sources, including OC. The sum of OC and EC is known as total carbon (TC). Soot has a primary origin, while OC can be both primarily emitted but also formed in the atmosphere through condensation to the aerosol phase of low vapour pressure compounds emitted as primary pollutants or formed in the atmosphere (Gentner et al., 2012; Robinson et al., 2007). As a result of this, the ratio of particulate OC to EC differs widely, both in space and seasonally, being influenced by primary emission sources, different OC and EC removal rates by deposition, OC phase partitioning, and secondary organic aerosol (SOA) formation and/or reactivity.

The occurrence in the atmosphere of both OC and EC is relevant from both climatic and human health standpoints, which explains the increasing scientific interest in monitoring these chemical species (Bond et al., 2013; Janssen et al., 2011). Although EC represents generally a minor component in terms of mass of the atmospheric fine aerosol, it is the major absorber of visible light, and a driver of global warming, whereas most OC can contribute to warming or scattering depending on functional group composition and mixing with soot particles (Bond and Bergstrom, 2006).

In recent years, a number of epidemiological studies have highlighted the link between short-term and long-term exposure to PM and a broad range of human health impacts, including respiratory and cardiovascular effects as well as premature deaths (WHO, 2012). EC has been suggested as a better proxy for harmful PM from combustion sources, especially from diesel exhaust, than undifferentiated PM (Janssen et al., 2011), although the harmful components might also be other species associated to EC particles (Mills et al., 2011).

A growing consensus is such emerging towards the formulation of an EC-$PM_{2.5}$ standard, including this species in the list of monitored/regulated pollutants, as an important tool for evaluating traffic pollution impacts in urban areas (Grahame and Schlesinger, 2010; Reche et al., 2011).

The present paper aims at providing a large-scale investigation of the average concentrations of OC, EC and TC over the Italian peninsula and at exploring their spatial and seasonal variability under the influence of several controlling factors, i.e. type and strength of the sources and meteorological conditions.

The Italian territory, excluding the islands, is topographically and climatically subdivided into two regions: Continental Italy and Peninsular Italy (Fig. 1).

Continental Italy, in the north, includes the broad, triangle-shaped North Italian Plain (Po Valley) and the high mountain chain of the Alps, and is characterized by a climate similar to continental Europe, with cold winters, distinct differences between seasons, low wind speed and frequent stable atmospheric conditions, especially during winter. The Po Valley, due to the high density of anthropogenic sources, and the orographic and meteorological characteristics particularly unfavourable for pollutants dispersion, is known as a hot spot in Europe in relation to air quality (Carbone et al., 2010; Ferrero et al., 2011).

Peninsular Italy, encompassing all the Italian peninsula south of the junction of the Ligurian Alps with the Apennines, generally fits the Mediterranean climate profile, with higher wind speed and stable atmospheric conditions during summertime.

In spite of the increasing number of OC and EC measurements carried out in Italy in recent years, their spatial distribution is still rather inhomogeneous, with some areas, especially in Central and Southern Italy, still lacking data, and the Po Valley quite extensively monitored. Though a larger number of measurements of the aerosol carbonaceous component were available, the choice in this study has been restricted to data obtained by the thermal–optical method, which provides comparable data. This study represents the first analysis of carbonaceous aerosol data across the Italian territory as a whole.

2. Sampling and analysis

2.1. Sampling

The present database of OC, EC and TC measurements includes data collected during the years 2005–2012 at 37 sites spread along the Italian peninsula (Fig. 1). Only one measurement campaign (MI Mes) dates back to the years 2002–2003. The monitoring stations include industrial, traffic, urban, semi-rural, rural and remote locations, classified on the basis of their distance from pollution sources according to criteria proposed by the European Environment Agency (Larssen and Helmis, 1999). At 32 sites the $PM_{2.5}$ fraction was analysed, in some cases simultaneously to PM_{10} data, while at 5 sites, only PM_{10} data were available. PM mass concentration was measured gravimetrically at all sites, with the exception of RM Ada, MLB and FE Cas where beta attenuation online monitors were employed. Table 1 summarizes the complete list of

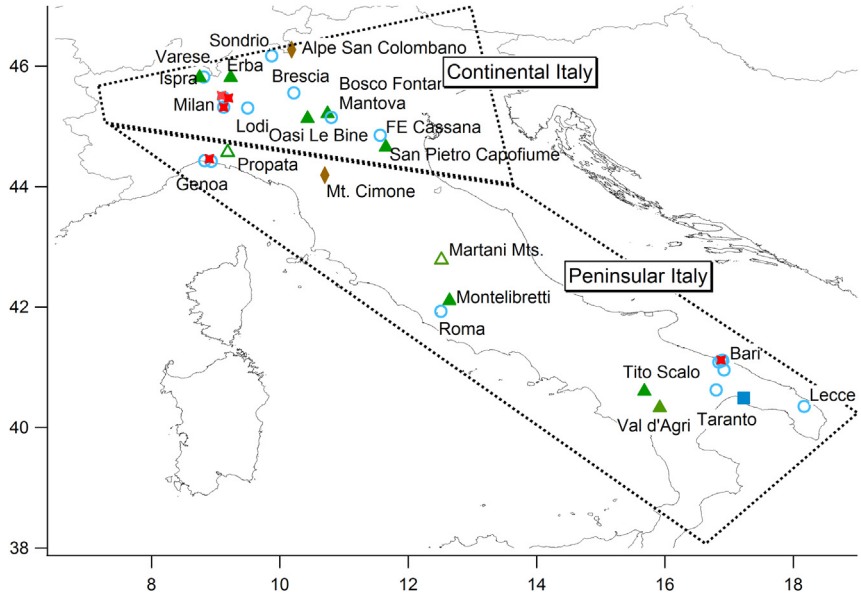

Fig. 1. Map of the monitoring sites over Italy. Diamonds stand for high altitude remote sites (2), empty triangles for medium elevation rural sites, filled triangles for rural background sites (10), empty circles for urban background sites (19), squares for industrial sites (1) and crosses for road traffic sites (5). The geographical separation between continental and peninsular Italy is shown.

monitoring stations, along with sampling periods, type of site, available measurements and indication of the analytical methodology.

The list of sites includes:

- Two high altitude remote sites, Mt. Cimone (CMN), the highest peak of the Northern Italian Apennines and Alpe San Colombano (ASC) in the Lombardy Alps, both representative of the free troposphere, especially during winter.
- Ten rural and semi-rural sites, including two medium-elevation mountain stations and eight ground-level stations;
- One industrial site in Southern Italy;
- Nineteen urban background sites, including eight locations in the Lombardy region, one in the Emilia Romagna region, two within the city of Genoa, one within the city of Rome, and seven in the Southern Italy Apulia region;
- Five road traffic sites.

At all these sites the sampling for OC and EC analysis has been performed on quartz microfiber filters by low or high volume samplers equipped with size selective inlets. In all cases the temporal resolution was 24 h. Evaluations of positive or negative sampling artifacts on OC concentrations can not be done at all sites, so they are not taken into account in the present study.

2.2. EC and OC thermal analysis

At 35 out of the 37 sampling sites, OC and EC were measured on PMx quartz filters by thermal–optical method (TOT) (Birch and Cary, 1996) using Sunset Laboratory OC/EC analysers. TC corresponds to the sum of OC and EC. Three thermal programs have been used at the different sites, which mainly differ for the maximum temperature of the inert phase. While at most sites the high temperature protocols NIOSH 5040 and NIOSH-like were applied, at five locations the low temperature program EUSAAR-2 was used. Since such differences might significantly alter the measured amounts of OC and EC (Chow et al., 2004), the measurements performed by the EUSAAR-2 program have been normalized using a conversion factor derived from the simultaneous measurement of 46 samples collected at MI Pas by both the NIOSH-like and EUSAAR-2 thermal programs. In this way, a more robust analysis of the spatial variability of OC and EC was obtained. For further details see Supplementary material.

2.3. EBC optical measurements

EBC was measured at 3 out of the 37 sampling sites (for CMN both optical and TOT measurements are available). Determination of the EBC mass concentration by absorption measurements implies a series of assumptions, including that (i) absorption is due only to carbonaceous species, (ii) OC does not contribute to absorption, and (iii) the relationship between EBC and light absorption is constant and well-known (Gilardoni et al., 2011b). Assumptions i and ii are verified measuring optical properties at wavelength longer than 500 nm, where the absorption of OC and aerosol mineral components is negligible compared to that of soot. Assumption iii is based on the knowledge of a mass-specific absorption cross section for the conversion of light absorption coefficient σ_{ap} into EBC mass, and is discussed in the Supplementary material.

At the two rural sites in Southern Italy, TITO and GRU, a 7-wavelength MAGEE Scientific Aethalometer Model AE31 has been used for the continuous measurement of EBC on $PM_{2.5}$, with a temporal resolution of five minutes (Pavese et al., 2012). EBC was estimated from the attenuation at 880 nm.

At Mt. Cimone (CMN) a Multi Angle Absorption Photometer (MAAP 5012, Thermo Scientific) continuously provides EBC data since 2005 on $PM_{2.5}$ with a temporal resolution of one minute (Marinoni et al., 2008). EBC is estimated from the absorption at 637 nm (Mueller et al., 2011).

3. Results and discussion

The sampling sites considered in this work have a high heterogeneity in the temporal data coverage, from sites where OC and EC are routinely measured to sites where only a few weeks of data

Table 1
–Sampling and EC, EBC, OC analytic information and number of available measurements for $PM_{2.5}$ and PM_{10} at the 37 sites of the database. Sources of data are reported in the last column.

Site	Code	Long.	Lat.	Alt.	Type of site	Study period	Method	Thermal protocol	PM_{10}#	$PM_{2.5}$#	Reference
Alpe San Colombano	ASC	10.19	46.27	2225	High alt. – rem.	Feb05–Jan08	TOT	NIOSH 5040	98	175	(Perrone et al., 2012)
						Jul12–Sep12	TOT	EUSAAR-2	44		
Monte Cimone	CMN	10.70	44.19	2165	High alt. – rem.	2005–2012	MAAP			1′ time resol.	(Cristofanelli et al., 2013)
						Jul07–Aug07	TOT	NIOSH 5040		**31**	
Monti Martani	MAR	12.52	42.78	1100	Rural bkg/medium elev.	Mar09–Dic09	TOT	NIOSH 5040	23	23	(Moroni et al., 2012)
Propata (GE)	PRO	9.19	44.57	970	Rural bkg/medium elev.	Jul–Nov10 + Jan –Jul12	TOT	EUSAAR-2		101	(Massabo et al., 2013)
Bosco Fontana	BF	10.74	45.21	25	Rural	Feb05–Jun07	TOT	NIOSH 5040	59	25	Parfil Project[a]
Oasi Le Bine	OLB	10.43	45.13	0	Rural	May07–Mar08	TOT	NIOSH 5040	43	26	(Perrone et al., 2012)
Ispra	IPR	8.75	45.81	209	Semi-rural	Jan–Dec08	TOT	EUSAAR-2		358	(Gruening et al., 2009)
San Pietro Capofiume	SPC	11.65	44.65	0	Rural	May–Jul07	TOT	NIOSH 5040		64	
Erba	ERB	9.23	45.81	375	Rural	Mar06	TOT	NIOSH 5040		31	Parfil Project[a]
Val d'Agri	GRU	15.92	40.33	582	Semi-rural	Jan11–Apr11	aethal.			5′ time resol.	(Pavese et al., 2012)
Potenza Tito Scalo	TITO	15.72	40.60	750	Semi-rural	May08–Mar10	aethal.			5′ time resol.	(Pavese et al., 2012)
Roma Montelibretti	MLB	12.64	42.11	232	Semi-rural	2005–2010	TOT	NIOSHlike	2133		Medparticles Project[b]
Taranto via Orsini	TA Ors	17.23	40.49	5	Industrial	Oct05–Feb06	TOT	NIOSH 5040		30	(Amodio et al., 2010)
Ferrara Cassana	FE Cas	11.56	44.85	11	Urban-industrial	Jan11–Jun12	TOT	NIOSHlike	122	122	(Perrino et al., 2014)
Sondrio	SON	9.87	46.17	307	Urban bkg	Apr05–Sep07	TOT	NIOSH 5040	66		Parfil Project[a]
Varese	VA	8.81	45.82	379	Urban bkg	Feb05–Jun07	TOT	NIOSH 5040	78	29	Parfil Project[a]
Brescia	BS	10.22	45.56	149	Urban bkg	Feb05–Jun07	TOT	NIOSH 5040	70	40	Parfil Project[a]
Como Cantù	CAN	9.12	45.47	322	Urban bkg	Feb05–Jun07	TOT	NIOSH 5040	108	87	Parfil Project[a]
Mantova	MN	10.80	45.15	19	Urban bkg	Feb05–Jun07	TOT	NIOSH 5040	42	20	Parfil Project[a]
Milano Lodi	LOD	9.50	45.30	87	Urban bkg	Feb05–Jun07	TOT	NIOSH 5040	72	41	Parfil Project[a]
Milano via Messina	MI Mes	9.12	45.32	122	Urban bkg	Aug02–Dec03	TOT	NIOSH 5040		118	(Lonati et al., 2007)
Milano via Pascal	MI Pas	9.12	45.32	125	Urban bkg	Feb05–Jun07	TOT	NIOSH 5040	115	83	Parfil Project[a]
						Mar12–Dec12	TOT	NIOSHlike	254		Parfil Project[a]
Genova Multedo	GE MUL	8.83	44.43	0	Urban bkg-harbour	May11–Oct11	TOT	EUSAAR-2		69	(Bove et al., 2014)
Genova Corso Firenze	GE FI	8.93	44.42	0	Urban bkg	Feb11–Oct11	TOT	EUSAAR-2		94	(Bove et al., 2014)
Roma Villa Ada	RM Ada	12.51	41.93	50	Urban bkg	2005–2007	TOT	NIOSHlike	1048		Medparticles Project[b]
Bari Pane e Pomodoro	BA PP	16.89	41.12	0	Urban bkg	Mar07–Jul07	TOT	NIOSH 5040	22	39	(Amodio et al., 2010)
Bari San Nicola	BA SN	16.84	41.08	5	Urban bkg	Mar07–Jul07	TOT	NIOSH 5040	19	39	(Amodio et al., 2010)
Bari Casamassima	BA CM	16.92	40.96	223	Urban bkg	Mar07–Jul07	TOT	NIOSH 5040	14	28	(Amodio et al., 2010)
Bari Japigia	BA JA	16.90	41.11	5	Urban bkg	Oct05–Feb06	TOT	NIOSH 5040		32	(Amodio et al., 2010)
Bari Università	BA Uni	16.88	41.11	0	Urban bkg	Oct08	TOT	NIOSH 5040	16	16	(Amodio et al., 2010)
Taranto via Dante	TA DA	16.80	40.63	5	Urban bkg	Oct05	TOT	NIOSH 5040		30	(Amodio et al., 2010)
Lecce	LE1	18.17	40.35	50	Urban bkg	Mar07–Dic07	TOT	NIOSH 5040		25	(Perrone et al., 2011)
	LE2	18.17	40.35		Urban bkg	Apr11–Jul11	TOT	NIOSH 5040	6	6[c]	
Milano Pero	MI Pero	9.09	45.51	144	Traffic, suburban	May06	TOT	NIOSH 5040	7		
Genova Bolzaneto	GE BZ	8.90	44.46	0	Traffic	May11–Oct11	TOT	EUSAAR-2		61	(Bove et al., 2014)
Milano via Senato	MI Sen	9.20	45.47	122	Traffic	Nov12	TOT	NIOSHlike	14		
Bari Corso Cavour	BA CV	16.87	41.12	5	Traffic	Oct05–Feb06	TOT	NIOSH 5040		34	(Amodio et al., 2010)
Milano Torre Sarca	MI Sar	9.12	45.32	125	Traffic	Jul05–Mar08	TOT	NIOSH 5040		146	(Perrone et al., 2012)

[a] PARFIL Project http://ita.arpalombardia.it/ITA/qaria/pdf/Parfil/UO3/UO3_RelFinale_PARFIL.pdf.
[b] MEDPARTICLES Project http://95.110.213.190/medparticles/index.php?lang=en.
[c] Data at LE2 are referred to the PM_1 fraction of aerosol.

are available. For this reason data have been averaged on a seasonal basis, considering the April–September warm period as "summer" and the October–March cold period as "winter".

3.1. Concentration levels of OC and EC/EBC

The average seasonal concentrations of OC and EC for the 32 sites with measurements on $PM_{2.5}$ are plotted in Fig. 2. In order to evaluate the spatial variability, data were subdivided into two large geographical sectors roughly corresponding to Continental Italy (Po Valley and Alps), and Peninsular Italy (south of the Apennines, excluding the islands) (Fig. 1).

The OC concentrations range from 1.2 μg m^{-3} to 15.2 μg m^{-3}, increasing by an order of magnitude from remote to road-traffic influenced sites. The EC concentrations exhibit a larger variability, ranging from 0.1 μg m^{-3} to 5.6 μg m^{-3}, and increasing more than 50 times from remote to traffic sites. The higher spatial variability of EC compared to that of OC reflects the strong influence of primary emissions from local traffic or residential heating, contrary to OC, which is emitted by a much larger number of source types and also produced by secondary formation processes.

The highest concentrations of EC and OC are in all cases observed during the cold period (October–March) and at near source (industrial and traffic) sites. On the contrary, the two high altitude remote sites (ASC and CMN) and the medium elevation site MAR (1100 m asl) exhibit the lowest concentrations in the cold period, when they are decoupled from the Planetary Boundary Layer (PBL), where emission sources are located, hence

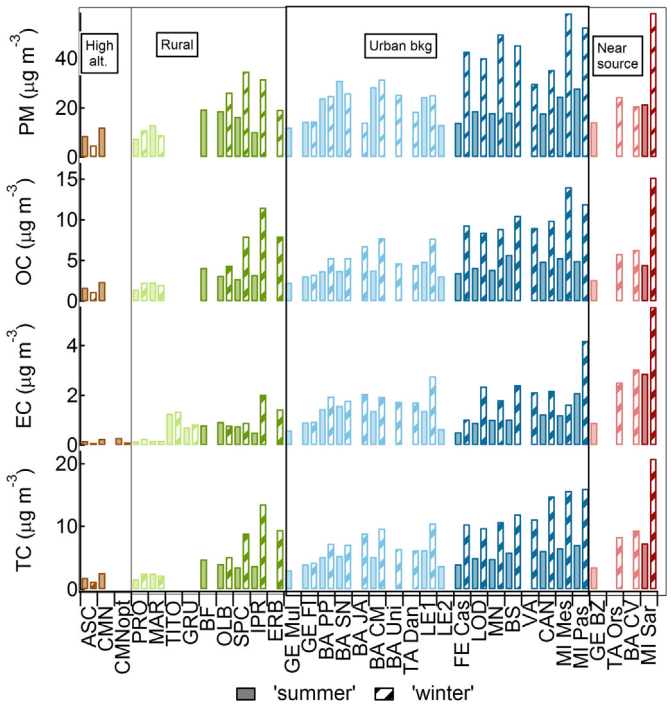

Fig. 2. Summer and winter average concentrations for OC, EC, TC and PM at the 32 sites with measurements on $PM_{2.5}$. Dashed bars are for wintertime while solid bars for summertime. For each category of sites pale colours indicate Peninsular Italy locations while dark colours indicate Po Valley sites. LE2 data are relative to PM_1 instead of $PM_{2.5}$. Data from Ge Mul, GE FI, GE BZ, PRO and IPR, obtained by the EUSAAR-2 protocol are shown after conversion to the NIOSH-like protocol. For CMN optical measurements are also plotted. The site LE2 corresponds to LE1 but measurements are on PM_1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

representative of the free troposphere. At PRO, at 970 m asl in the Ligurian Apennines, concentrations are instead slightly higher during the winter, as at other rural sites.

OC and EC concentrations in Ispra (IPR) are higher compared to other rural and semi-rural sites, especially during the winter. A recent comparison with other European rural and remote sites showed that the site of Ispra can be categorized as a typical background site in an environment generally strongly affected by anthropogenic emissions (Henne et al., 2010). In the presence of a very high regional background, this explains the similarities of Ispra carbonaceous aerosol concentrations with other urban sites in the Po Valley.

At the urban background sites in the Po Valley, EC concentrations are similar to the urban background sites in Peninsular Italy, while OC concentrations are higher, particularly in the city of Milan and during winter. Winter OC and EC concentrations in Genoa (GE FI), instead, are significantly lower than at all the remaining sites, likely due to the particular wintertime wind regime of this coastal site, which favours the dispersion of pollutants (Vecchi et al., 2008). In addition, a particular feature of OC and EC concentrations in Genoa is the absence of seasonality, contrary to all the other locations. This finding could in part depend on the increased shipping emissions from the harbour area, very intense during summertime, but also on the lower thermal evolution of the PBL during the warm period under the influence of sea-breeze. Though influenced by the presence of a harbour, Genoa OC and EC concentrations are lower than those measured at other urban sites.

Annual mean OC and EC concentrations were calculated for the sites with complete data coverage; at the other sites, annual means were estimated by averaging data from summer and winter campaigns, when available (Table 2). Locations with only partial data coverage did not allow us to extrapolate an annual mean.

3.2. Seasonal trends of OC and EC/EBC

A distinct seasonality of OC and EC was in general seen for the different types of sites examined, though the trends were different at urban, rural and semi-rural locations on the one side, and at the remote high altitude sites on the other.

Fig. 3 represents the seasonal trends observed at selected stations characterized by a complete or semi-complete annual data coverage: one remote (CMN), one semi-rural (IPR) and two urban background sites in Milan (MI Mes) and Rome (RM Ada). Data at RM Ada correspond to PM_{10} samples.

At the urban and the rural sites, the seasonal behaviour is similar for OC and EC. The concentrations exhibit a summer minimum and a winter maximum. This trend is related to the PBL dynamics, characterized by a seasonal cycle with maxima during the summer (due to the enhanced thermal convection), and minima during winter (due to the occurrence of stable atmospheric conditions). In addition, during winter, the increased strength of some sources (mainly residential heating) causes higher concentrations.

It should also be noted that in the Po Valley, in the absence of strong wind throughout the year, the dispersion of primary emissions is largely dependent on vertical mixing. During winter, the maximum PBL height can be as low as 450 m (Bigi et al., 2012) favouring ageing of the air masses with a relevant increase in the concentration of secondary pollutants (Perrino et al., 2014; Vecchi et al., 2009). Instead, during summer, the PBL height increases due to the strong thermal convective activity, and mixing layer height normally reaches 1500–2000 m (Di Giuseppe et al., 2012). A typical ratio of the summer to winter maximum PBL height is of the order of 2.2 (Carbone et al., 2010).

At coastal sites, the advection of cooler air from the sea (sea-breeze) during summer may significantly affect the PBL growth (Martano, 2002) producing a shallow PBL which increases from the shoreline moving inland. De Tomasi and Perrone (2006) observed in the case of Lecce and Brindisi, in the Apulian region, lower PBL heights during summer months, and the same behaviour can

Table 2
Annual average concentrations of OC, EC and TC on $PM_{2.5}$. The sites are grouped according to the type and geographic region. Data from GE FI, PRO and IPR sites obtained by the EUSAAR-2 protocol, are shown after conversion to the NIOSH-like protocol.

	Site	OC ($\mu g\ m^{-3}$)	EC ($\mu g\ m^{-3}$)	TC ($\mu g\ m^{-3}$)
North Italy high altitude	ASC	1.6	0.15	1.8
	CMNopt		0.18	
Peninsular Italy rural	PRO	1.8	0.19	2.0
	TITO		1.3	
Po Valley rural	OLB	3.3	0.9	4.2
	SPC	3.1	0.78	3.8
	IPR	7.4	1.3	8.7
Peninsular Italy urban background	GE FI	2.4	1.2	3.6
	BA PP	4.5	1.7	6.2
	BA SN	4.4	1.7	6.1
	BA CM	5.8	1.7	7.4
Po Valley urban background	FE Cas	6.4	0.78	7.1
	LOD	6.3	1.7	7.9
	MN	5.4	1.3	6.6
	BS	8.8	1.7	9.9
	CAN	7.0	1.6	8.7
	MI Mes	9.3	1.4	10.7
	MI Pas	8.7	3.2	11.8
Po Valley near-source	MI Sar	9.4	4.5	13.9

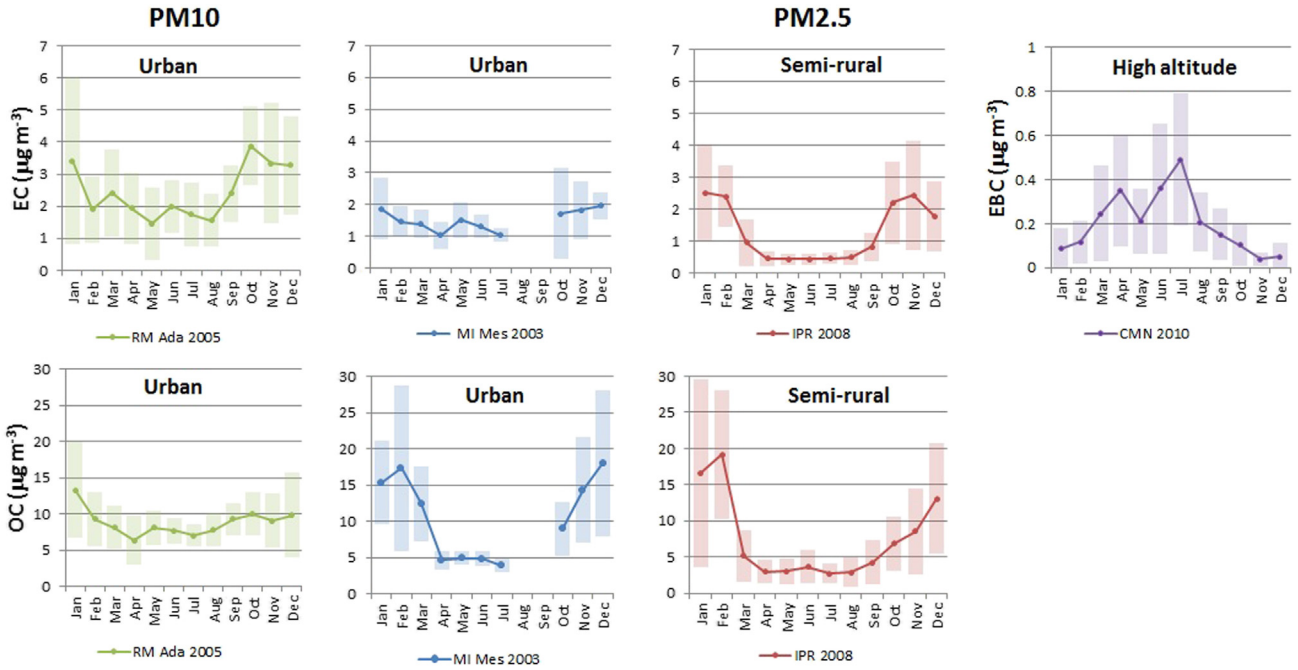

Fig. 3. Monthly mean concentrations of OC and EC at selected sites. The vertical bars indicate one standard deviation. Mi Mes, IPR and CMN data are on $PM_{2.5}$, RM Ada on PM_{10}. For CMN optical EBC data are shown.

probably be extrapolated for the Bari site, which is located on the Adriatic coast of Apulia only 100 km north of Brindisi. No information exist on the PBL seasonal variations in Genoa, another coastal site facing the Northern Tyrrenian sea, but relatively small differences have been observed between summer and winter in Barcelona, which faces the same Mediterranean coast (Sicard et al., 2011).

These differences in the seasonal evolution of the mixed layer height are reflected in differences of the winter to summer ratios of the OC and EC concentrations, which range from values very close to 1 in Genoa to maxima of 4 in the semi-rural site of Ispra (IPR). In general, all the urban background sites in Peninsular Italy exhibit winter to summer ratios ranging from 1 to 1.5 for EC and from 1 to 2 for OC, while in the Po Valley winter to summer ratios range from 1.8 to 2.7 for both EC and OC, with a maximum of 3.4 for OC at the road traffic site MI Sar.

In any case, the marked winter increase of OC and EC concentrations observed in the Po Valley compared to Peninsular Italy, can be related to the vertical thermal structure of the PBL and to likely higher emissions from residential heating, due to the lower winter temperatures in this part of Italy. Such lower temperatures, in addition, promote the increased condensation of fresh traffic exhaust emissions and, in general, semi-volatile species, which can explain the higher winter/summer ratio of OC with respect to EC.

A completely opposite seasonal trend is observed at the remote high altitude station of CMN, where EBC is continuously monitored by the optical method (no measurements of OC are available). In this case, higher EBC concentrations are typical of the summer period, while wintertime concentrations are extremely low. This behaviour is due to the seasonality of the vertical mixing, characterized by enhanced vertical transport of polluted air masses by upslope winds during the warm season, with mainly free tropospheric conditions characterizing the site during winter (Cristofanelli et al., 2013).

3.3. Spatial variability of carbonaceous aerosol concentration across Italy

The levels of OC and EC concentrations in $PM_{2.5}$, summarized in Fig. 2, reveal that the spatial distribution of these chemical species is highly inhomogeneous throughout the country, but is strongly dependent both on the intensity of emissions and on the dynamic properties of the PBL which determine dilution or accumulation. This is evidenced by the strong variability of OC and especially EC concentrations moving from remote to near-source sites, including in this category industrial and road traffic-influenced locations. As already mentioned, this spatial variability is more marked for EC than for OC due to the primary only nature of EC emissions.

The differences in OC concentrations between rural and urban background sites in the Po Valley (with the exception of the metropolitan area of Milan) are rather weak, especially during the summer, when photochemical activity is high, and the formation of SOA plays a relevant role. Rural sites are strongly influenced by urban areas, so that the contribution of very localised sources is less discernible. Only the sites located in the urban area of Milan markedly differ from the regional background, as a result of the higher impact from traffic within the city and industrial activities in the surrounding. During winter, the increased contribution of primary emissions results in more marked differences between rural and urban sites, excluding Ispra, for both OC and EC concentrations and, again, the Milan sites exhibit higher concentrations compared to other Po Valley cities.

Beside the spatial variability among different categories of sites related to the distance from emission sources, data have also been analysed to evaluate the spatial variability at the national scale, taking into account, the separation between Continental (Po Valley) and Peninsular Italy. In this case, a difference in EC and OC concentration levels based not only on the source strength, but also on different dispersion properties of the boundary layer was expected.

For this purpose, the seasonal OC and EC summer and winter mean concentrations at urban background sites in the different regions (urban area of Milan, Po Valley and Peninsular Italy) were analysed with an unpaired Student's *T*-test. The results are summarised in Table 3, where the probability values (*p*-value) are reported. We considered $p < 0.05$ as the threshold for statistically significant differences between the groups. The value of the ratio between the means of the compared groups is added, as an indication of the amplitude of the differences.

OC concentrations at the urban background sites in the Po Valley are statistically higher during the winter, and to a less significant level, even during summer (Table 3 lower panel), compared to Peninsular sites. This marked winter difference is likely due to the lower temperatures of Northern Italy which favour the partitioning of the organic compounds to the condensed phase, and to the lower PBL height which induces the accumulation of gaseous precursors which promote SOA formation. During summer, with a stronger photochemical activity countrywide, the higher OC concentrations are likely due to the occurrence of high pressure systems favouring aerosol ageing in the Po Valley, with respect to the windier conditions at the coastal peninsular sites, favouring pollutants dispersion.

During winter, OC concentrations in Milan are statistically higher than in the other Po Valley sites (Table 3, top panel), possibly due to the rapid oxidation of low-volatility gas species, as observed also in laboratory experiments (Robinson et al., 2007) or, given the cold season, their direct condensation near the source promoted by the low temperatures.

EC concentrations are not statistically different between Po Valley and Peninsular Italy, but when comparing Southern Italy (Apulian) to Po Valley urban sites, EC is statistically higher at Apulian sites (not shown). The reason for this can be ascribed to the different circulating vehicle fleet in these two parts of Italy. In 2012 diesel vehicles were 50% of the total in Apulia vs. 42% in Emilia Romagna and Lombardy taken together (the two regions enclosing all the Po Valley sites). In addition the Euro4 and Euro5 vehicles were 35% of the total in Apulia and 53% in Emilia Romagna/Lombardy as passenger cars, and 18% and 33% as light and heavy duty vehicles in the two regions, respectively (ACI, 2012).

OC and EC PM_{10} concentrations in Rome (6.8 ± 2.5 and 1.7 ± 0.8 μg m^{-3} during summer and 10.2 ± 4.9 and 2.8 ± 1.6 μg m^{-3} during winter for OC and EC respectively) appear similar to the average of those measured at the Po Valley urban background sites (6.3 ± 1.1 and 1.4 ± 0.5 μg m^{-3} during summer and 13.7 ± 2.3 and 3.1 ± 1.1 during winter for OC and EC respectively), while OC and EC PM_{10} concentrations at the rural background MLB station in the area of Rome (5.6 ± 1.7 and 1.0 ± 0.4 μg m^{-3} during summer and 9.3 ± 4.5 and 1.4 ± 0.8 μg m^{-3} during winter) are similar to those measured at the Po Valley rural background site BF (5.9 ± 1.7 and 0.88 ± 0.42 μg m^{-3} during summer and 12.1 ± 3.5 and 1.5 ± 0.4 μg m^{-3} during winter for OC and EC respectively), where measurements on PM_{10} are available. Only during winter, the higher OC concentrations in the Po Valley compared to the Rome area, are again most probably explained by the colder temperatures of Northern Italy compared to Central Italy. Moreover, biomass burning for residential heating probably represents a more relevant contribution in the Po Valley, where it is estimated to be the main primary source of OC, together with traffic, during cold months at both urban and rural sites (Perrone et al., 2012).

Table 3
Results of the *T*-test applied to the OC and EC average concentrations at urban background sites separated in the three areas Milan, Po Valley and Peninsular Italy. The values in bold are statistically significant ($p < 0.05$).

		MI vs. Po Valley	
		Summer	Winter
EC	*p*	0.0679	0.2455
	Ratio	1.7	1.5
OC	*p*	0.3170	**0.0027**
	Ratio	1.2	**1.4**
TC	*p*	0.0537	**0.0174**
	Ratio	1.3	**1.4**
		Po Valley vs. Peninsular	
		Summer	Winter
EC	*p*	0.3933	0.6633
	Ratio	0.8	1.1
OC	*p*	0.0979	**0.0002**
	Ratio	1.3	**1.6**
TC	*p*	0.4113	**0.0029**
	Ratio	1.1	**1.5**

3.4. OC/EC concentration ratios

$PM_{2.5}$ data have been analysed for the OC/EC ratio, a parameter that can discriminate between different sources of PM. The separation between summer and winter season has been maintained, in order to check for a possible OC/EC seasonality as a function of sources and processes. In general, the OC/EC ratio during summer is mainly affected by the increased production of secondary OC through photochemical activity, and by the increased emission of biogenic precursors of SOA. During winter, the ratio is influenced by primary emissions such as fossil fuels burning, characterized by an OC/EC ratio frequently lower than 1 (Handler et al., 2008), and residential wood burning, which is expected to release more organics. As a consequence, the ratio is typically higher at the rural sites in winter, where residential wood burning is more relevant compared to traffic source (Castro et al., 1999). Depending on the area under investigation, OC/EC varies from high values (up to 15) in the cleanest remote locations where EC is very low, to small values in polluted environments, where the primary sources of both OC and EC are prevailing.

Fig. 4 shows the OC/EC ratios in $PM_{2.5}$ at 30 sites, grouped as high altitude, medium altitude, rural, urban background and near-source (industrial and road traffic affected) sites. Urban background and near-source sites are separated for Peninsular Italy and the Po Valley.

High altitude sites are characterized by the highest OC/EC ratio, ranging from 11 to 15. At such locations EC sources are limited and most of the organic aerosol is aged, hence enriched in secondary OC, leading to these high OC/EC ratios. MAR, although a medium elevation site, exhibits a ratio similar to the high altitude sites.

The ground-level rural sites, all located in the Po Valley, are characterized by OC/EC ratios ranging from 3 to 9, similar to what observed at K-Puszta (Pio et al., 2007) and at other rural sites in Europe (Castro et al., 1999; Pio et al., 2011). At these sites the enrichment in OC in winter can be attributed to wood burning for residential heating (Gelencser et al., 2007; Gilardoni et al., 2011a; Piazzalunga et al., 2011). At OLB, for instance, the biomass burning contribution during the cold period (fall–winter) was estimated very relevant by a recent chemical mass balance (CMB) study (Perrone et al., 2012). During summer, OC/EC values from 4 to 7 suggest a higher contribution of secondary OC, in agreement with literature data that report ratios larger than 2–2.5 for SOA enriched environments (Strader et al., 1999). As mentioned in Section 3.1, during winter anthropogenic emissions strongly influence the IPR site leading to an OC/EC ratio similar to those observed in urban Po Valley areas.

For urban sites in Europe where vehicular emissions are the dominant source of OC, minimum OC/EC ratio as low as 0.7 (Pio et al., 2011) have been reported, in agreement with a low

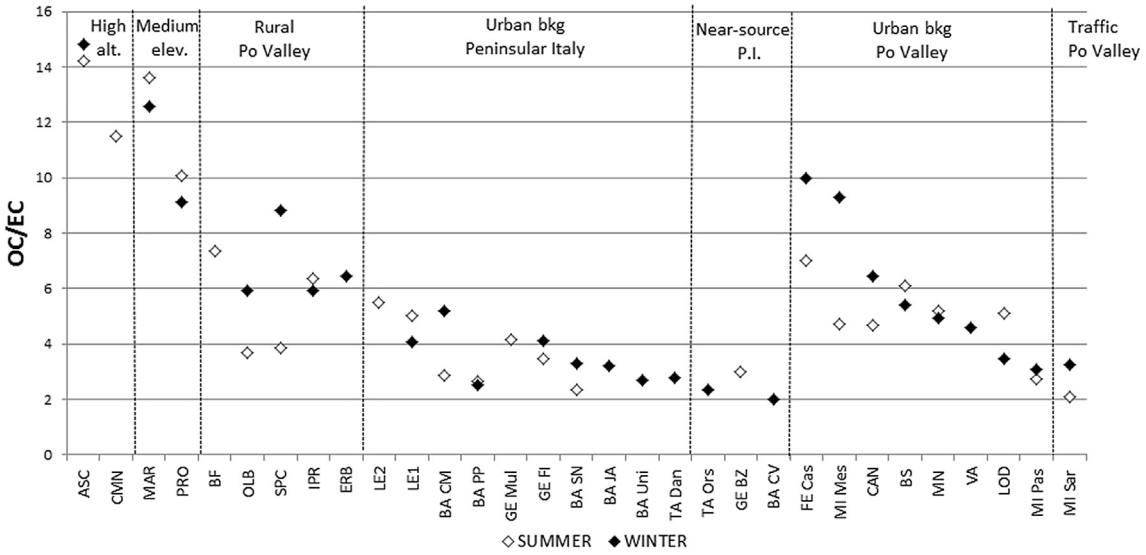

Fig. 4. Seasonal OC/EC ratio on $PM_{2.5}$ at the 30 sites with TOT measurements on $PM_{2.5}$, separated according to the type and to the geographic region. Data from Ge Mul, GE FI, GE BZ, PRO and IPR, obtained by the EUSAAR-2 protocol, are shown after conversion to the NIOSH-like protocol. Near-source sites in Peninsular Italy (P.I.) comprise the industrial site TA Ors and the traffic sites GE BZ and BA CV. LE1 and LE2 represent the same site but LE2 data are relative to PM_1 instead of $PM_{2.5}$.

contribution of secondary OC. The lowest OC/EC ratios of our dataset are observed at traffic sites, with a minimum of 2.1 at MI Sar. At this site, the slightly higher ratio in winter (>3) can be attributed to the contribution of biomass burning (Perrone et al., 2012).

A substantial difference emerges from the data of Fig. 4 between the urban background sites in the Po Valley and those in Peninsular Italy. In fact, most Peninsular locations are characterized by consistently low values of the OC/EC ratio, ranging from 2 to 5, with no substantial differences between winter and summer. This suggests similar sources of carbonaceous aerosol throughout the year, characterized by a stable seasonal pattern. The increased OC/EC ratio during winter at CM, a small town in the Province of Bari, suggests an influence of wood burning for domestic heating (Amodio et al., 2010).

At most urban background sites in the Po Valley, quite higher levels of OC/EC occur both during summer (from 5 to 7) and winter (from 3 to 10). Urban background sites in the Po valley show OC/EC ratios similar to the rural sites, due to the regional influence of SOA from both anthropogenic and biogenic sources in summer, and the widespread use of wood burning for residential heating in winter (Larsen et al., 2012). At FE Cas (Perrino et al., 2014) and CAN, a significant contribution of wood burning to winter pollution has been confirmed by measuring levoglucosan, a specific tracer of biomass burning. Also, a study of OC/EC ratio as a function of wind direction at the MI Mes site indicated a strong influence from nearby areas where wood consumption for domestic heating is large (Lonati et al., 2007). According to macro-tracers (EC, OC, and levoglucosan), micro-tracers (arabitol and mannitol), and ^{14}C measurements in Ispra, primary and secondary biomass burning OC contributes to 70% and 15% of total OC during winter and summer, respectively (Gilardoni et al., 2011a). Wood combustion for domestic heating also influences the carbonaceous particles concentration in Milan where, by a macro tracer approach (levoglucosan) (Piazzalunga et al., 2011) the primary contribution to OC was estimated from 21 to 25% during winter in MI Pas, consistent with what obtained by Bernardoni et al. (2013) through ^{14}C analysis. Biomass burning was estimated to account for 56–73% of OC during the cold period also at the traffic site MI Sar (Perrone et al., 2012), in spite of the masking effect of primary emissions from traffic.

On the other hand, condensation of semi-volatile organic species from the gas phase, favoured by the lower temperatures and the frequent episodes of air stagnation, is responsible for higher OC/EC ratio in the Po Valley even during winter, compared to the peninsular sites. In the Po Valley, in fact, SOA from anthropogenic activities represent an important contribution during both winter and summer, accounting for about 30% and 85% of OM respectively (Gilardoni et al., 2011a; Larsen et al., 2012).

Plotting the average OC/EC ratio for each site against the corresponding EC concentrations helps in classifying the different sites according to the sources and processes mostly affecting their OC and EC levels (Pio et al., 2011; Querol et al., 2013). In Fig. 5, data were plotted separating summer and winter data. The remote high altitude sites occupy the uppermost left side of the plot, characterized by the highest levels of the OC/EC ratio due to the very low EC concentrations. On the opposite side of the plot, road-traffic influenced sites are characterized by the lowest levels of the ratio, in this case with the highest EC concentrations, denoting the prevalent primary origin of OC. The remaining sites lie in the middle, above or below the fitting curve, according to the dominance of primary or secondary OC, or to the influence of biomass burning. In particular, the points that deviate most from the curve toward high OC/EC levels represent the sites, both urban and rural, more strongly influenced by wood combustion for domestic heating. On the contrary, most points that fall on the curve or below correspond to sites dominated by primary emissions by traffic, for which the increase of EC from summer to winter occurs at more or less constant OC/EC ratio.

A clear separation exists between urban background sites in the Po Valley and in Peninsular Italy, particularly during winter, when the higher levels of the OC/EC ratio in the Po Valley again denote a significant contribution of primary (from biomass burning) and secondary OC.

3.5. Contribution of carbonaceous matter to $PM_{2.5}$

The lowest $PM_{2.5}$ mass concentration values are observed at the mountain sites (high altitude, ASC and CMN, and medium altitude,

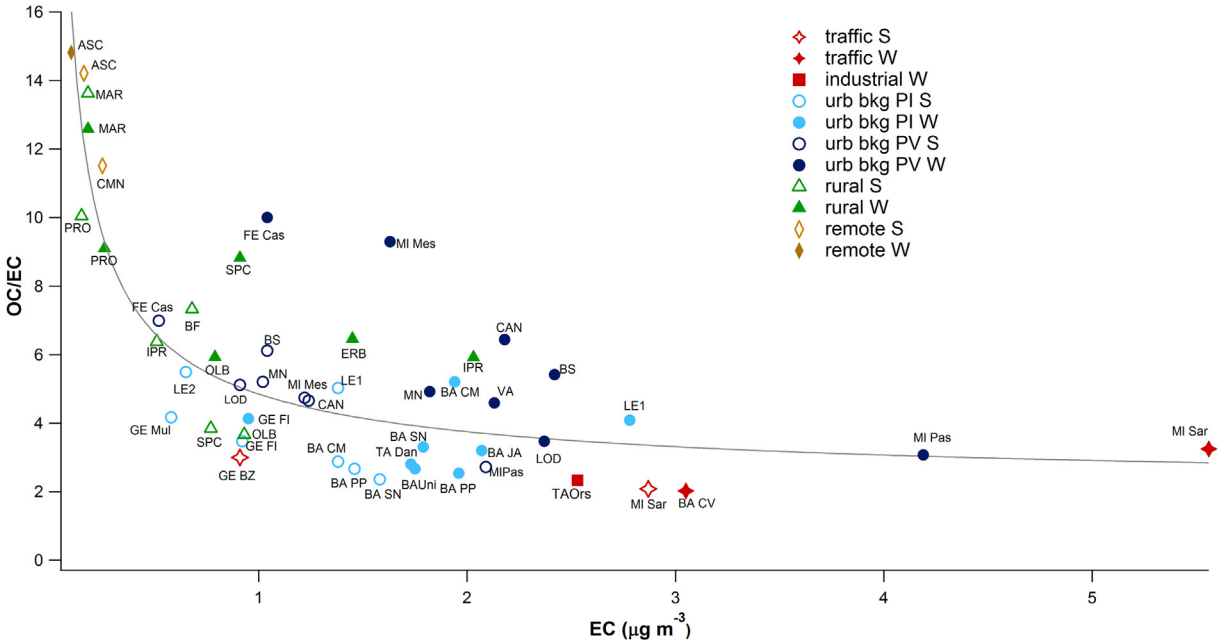

Fig. 5. OC/EC ratios at remote, rural, urban and near-source sites in $PM_{2.5}$, separated for summer (S) and winter (W). PI stands for Peninsular Italy, while PV stands for Po Valley. Data from the urban background sites Ge Mul, GE FI, GE BZ, PRO and IPR, obtained by EUSAAR-2 protocol are shown after conversion to the NIOSH-like protocol.

MAR and PRO), while the highest concentrations occur at the Po Valley sites. Maxima are observed during winter in the city of Milan (58.4 µg m^{-3} at the Milan traffic site, MI Sar), with high values observed throughout the Po Valley, where some monitoring stations exceed the air quality limits (25 µg m^{-3} to be met in 2015; EC, 2008) (Fig. 6). The seasonal $PM_{2.5}$ averages in Fig. 6 point out a more distinctive seasonality throughout the Po Valley if compared to the rest of the monitoring stations, where the PM concentration difference between winter and summer is less pronounced.

In order to evaluate the contribution of the total carbonaceous matter (TCM) to the mass of PM, OC is commonly converted to organic matter (OM) to account for the non-C atoms included in the OC species. OM is hence inferred from filter OC measurements using an assumed OM/OC ratio, although this is one of the most critical factors of uncertainty in mass closure calculations, depending strongly on the locations, sources, meteorology and primary vs. secondary nature of OC (Day et al., 2009).

In recent years, a series of techniques have been applied to quantify OM/OC, including organic functional group analysis (Gilardoni et al., 2007) and the high resolution time of flight aerosol mass spectrometry (HR-ToF-AMS) measurements, which have the advantage of a direct quantification of this parameter at high-time-resolution (Aiken et al., 2008).

In the present study, the concentrations of OM on filters were obtained multiplying OC by the OM:OC ratios determined by HR-AMS-TOF measurements performed at some of the stations considered in this study. Four different OM/OC ratios have been applied to remote, high altitude, rural, urban and road-traffic influenced sites. A factor 1.9 has been applied at the high altitude sites ASC and CMN. This ratio was derived from AMS data collected during the PEGASOS experimental campaign in summer 2012 at CMN (Rinaldi, personal communication). At the rural sites, the factors 1.7 during winter and 1.8 during summer have been applied, derived by AMS data collected during the Supersito Project campaigns at San Pietro Capofiume (SPC) during spring and winter (Gilardoni et al., 2014; Saarikoski et al., 2012). For the urban sites, a factor of 1.6 was used, derived from AMS measurements performed in Milan during the Supersito campaign in February 2014

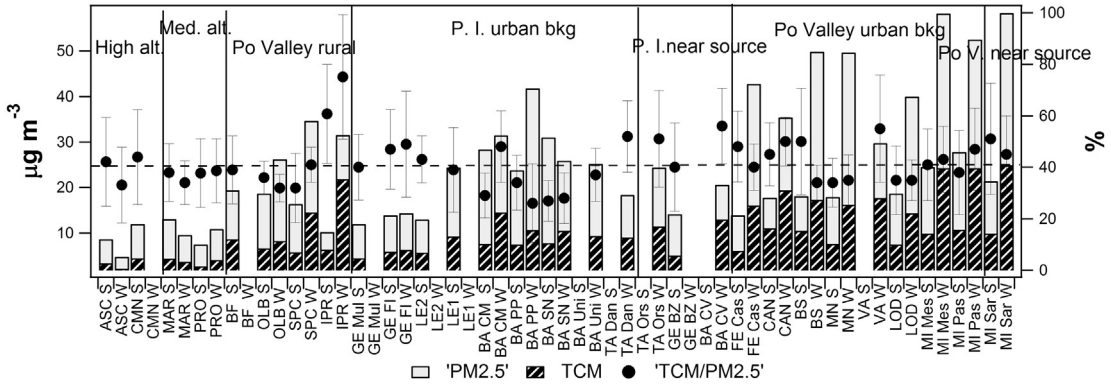

Fig. 6. Summer and winter $PM_{2.5}$ mass concentrations (grey) and superimposed TCM mass (dashed) at the 30 sites with measurements on $PM_{2.5}$. The sites are subdivided on a regional basis in Peninsular Italy (P.I.) and Po Valley and on the distance from emission sources in urban background and near-source (industrial and traffic) sites. The relative contribution of TCM to $PM_{2.5}$ is reported as black dots with bars corresponding toone standard deviation.

(Gilardoni, personal communication). Finally, a factor 1.5 was used for road-traffic sites, which was determined by AMS in the near-roadway environment at Las Vegas (Brown et al., 2013).

A conversion factor of 1.1 was used to convert EC to elemental matter (EM) to take into account the contribution of oxygen to this fraction (Kiss et al., 2002).

On a seasonal basis, the TCM contribution to $PM_{2.5}$ ranged from 26% at the Bari urban background sites to 75% at IPR during winter.

At high altitude, medium altitude and rural background sites, excluding the semi-rural site IPR, TCM contribution ranges from 30 to 40%, with only small differences between summer and winter. At these sites a higher summer TCM/$PM_{2.5}$ contribution may have been expected considering the enhanced emission of VOCs from the vegetation and the increased photochemical activity promoting SOA formation. On average, on annual basis, the contribution of TCM to $PM_{2.5}$ mass was 37 ± 3% at rural sites (excluding IPR due to strong anthropogenic influence during winter), 38 ± 9% at urban background sites in Peninsular Italy, 42 ± 7% at the Po Valley urban background sites, and 47% at traffic sites, in quite good agreement with data from (Putaud et al., 2010), with a significant difference only for the Po Valley rural sites, characterized by substantially higher organic contributions compared to other European rural sites.

4. Conclusions

Aerosol OC and EC data from 37 sites spread throughout the Italian territory have been analysed. The average concentrations of OC and EC increase as a function of distance from the emission sources, from remote, to rural, urban and traffic sites. This spatial difference is less discernible for OC in the Po Valley, during both summer and winter, due to the large influence of regional SOA formation and widespread use of wood burning for residential heating. These results highlight the importance of regional background aerosol and the need of control measures for both primary carbonaceous particles, as well as SOA precursors, at both local and regional scale.

The Italian peninsula is spatially inhomogeneous from the standpoint of aerosol sources, topography, land/sea contrast and meteorology; although OC and EC concentrations exhibit in general maxima in winter and minima in summer, this seasonal variability is characterised by different behaviour in different geographic regions. The effect of the annual evolution of the PBL, for instance, is particularly important in the Po Valley. In this area, the PBL height is higher in summer as a result of intense thermal convection, while it is much reduced during winter due to the cold temperatures. On the contrary, summer maxima and winter minima of OC and EC concentrations at the high altitude remote sites are the result of the increased convective transport by valley breezes during the warm period and the decoupling of the sampling sites from the PBL during the cold season.

The analysis of the OC/EC ratio shows a decreasing trend moving from the remote high altitude sites, characterized by the highest levels, to the traffic sites, where OC/EC reaches the lowest values. In addition, the summer and winter OC/EC ratios evidence a different behaviour between the Po Valley and Peninsular Italy. Higher OC/EC ratios in the Po Valley, both during summer and winter, suggest that the formation of secondary OC and the increased condensation of semi-volatile OC plays a more important role on OC concentrations throughout the year compared to peninsular sites. Also, the increased winter OC/EC ratios indicate that biomass burning, mainly wood combustion for domestic heating, is a widespread source of OC, not only at the rural, but also at the urban sites.

The limited availability of data and the scarcity of continuous monitoring of OC and EC over Peninsular Italy makes it difficult to discuss the effect of meteorology and emission sources of carbonaceous aerosol material in these areas and to extend our analysis to the whole Italian territory. A better spatial and temporal coverage of these measurements is a key for designing effective PM abatement measures and to verify the effects of their implementation.

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Appendix A. Supplementary data

Supplementary data related to this article can be found on line.

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