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Aerosol advection and sea salt events in Genoa, Italy, during the second half of 2005

Franco Marenco [a,*], Federico Mazzei [a], Paolo Prati [a], Massimiliano Gatti [b]

[a] *Physics Department, University of Genoa and INFN-Genoa, Italy*
[b] *Provincial Administration of Genoa, Office for Environmental Data processing, Italy*

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Abstract

Atmospheric aerosols in the PM_{10} fraction have been simultaneously sampled at three sites in the Genoa urban and suburban area during the second half of 2005, and information on the elemental composition has been gathered through energy dispersive X-ray fluorescence. Thanks to the simultaneous measurements and wind information, a few aerosol transport and transformation processes originated from the nearby sea and in the neighbouring Po Valley have been described. Sea salt concentrations at the three sites were well correlated and often related to Southern sector winds; moreover, by examining the Cl/Na ratio at two sites the time scale for Cl depletion in particulate matter has been estimated as 1–1.5 h for the Genoa atmosphere. During a Northerly gale, excess elemental Si concentrations (peaking more than 4 $\mu g\ m^{-3}$) were found at two sites, and were ascribed to an unknown local source. Finally, during an 11-day long 'heat wave' large concentrations for total PM_{10}, dust and secondary compounds have been found; these large concentrations lead to a number of exceedances of air quality standards, and have been ascribed to advection from the Po Valley.

Keywords: Sea salt; Soil dust; X-ray fluorescence; PM_{10}

1. Introduction

Tropospheric aerosols are a concern for health, with consequences for the respiratory tract (Maynard and Howard, 1999); moreover, they affect ecosystems by reducing photosynthetic activity, and manufactured items by contributing to corrosion (Singh, 1995). Aerosols also represent a climate issue (Houghton et al., 2001; Andreae et al., 2005), because they modify radiative forcing, heat distribution within the atmosphere (and thus atmospheric circulation), and cloud formation (and thus the hydrological cycle; Cruz and Pandis, 1997). For these reasons particulate matter is extensively sampled at urban and industrial areas, in compliance with air quality standards: such a monitoring activity is usually limited to publishing daily concentrations, with no distinction according to composition, origin, and meteorology. However, these pieces of information are essential if one wishes to recognize the natural and anthropogenic components, identify transport from different source regions, or understand the chemical processes occurring on aerosol particles.

* Corresponding author. Tel.: +39 091 7824133.

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In this paper, results of PM_{10} sampling and elemental analysis at three sites in the Genoa urban and suburban area during the second part of year 2005 are discussed, together with meteorological patterns. Genoa is the most populated coastal city in Northwestern Italy (population: 650,000), and it is the chief seaport of the peninsula and one of the largest in the Mediterranean. Its industrial harbour has an extensive area and is located in the town centre, near residential neighbourhoods. The harbour has been rebuilt and greatly modernized after World War II, and the city has become a commercial and industrial centre. Manufacturing industries in town and the surrounding region include: iron and steel, chemicals, petroleum, airplanes, ships, locomotives, motor vehicles, and textiles. A variety of local aerosol emission sources are thus present: traffic, industries, ships, etc.

The city is influenced by a Mediterranean climate and is situated in complex terrain, with the Appenine Mountains near the shoreline reaching 1000 m-amsl altitude. Beside sources within the urban area, aerosol advection must be taken into account. Transport can originate at long distance, and for instance it is known that the Sahara desert has a non-negligible influence on aerosol concentration in the Mediterranean basin Schwikowski et al., 1995; Rodrıguez et al., 2001) and in Northern Italy (Braga Marcazzan et al., 1993; Van Dingenen et al., 2005; Marenco et al., 2006). But transport can also have a regional dimension; Genoa neighbouring source region candidates are the industrialized/polluted Po Valley and the sea.

This research is part of a large project carried out by the University and the Provincial Administration of Genoa

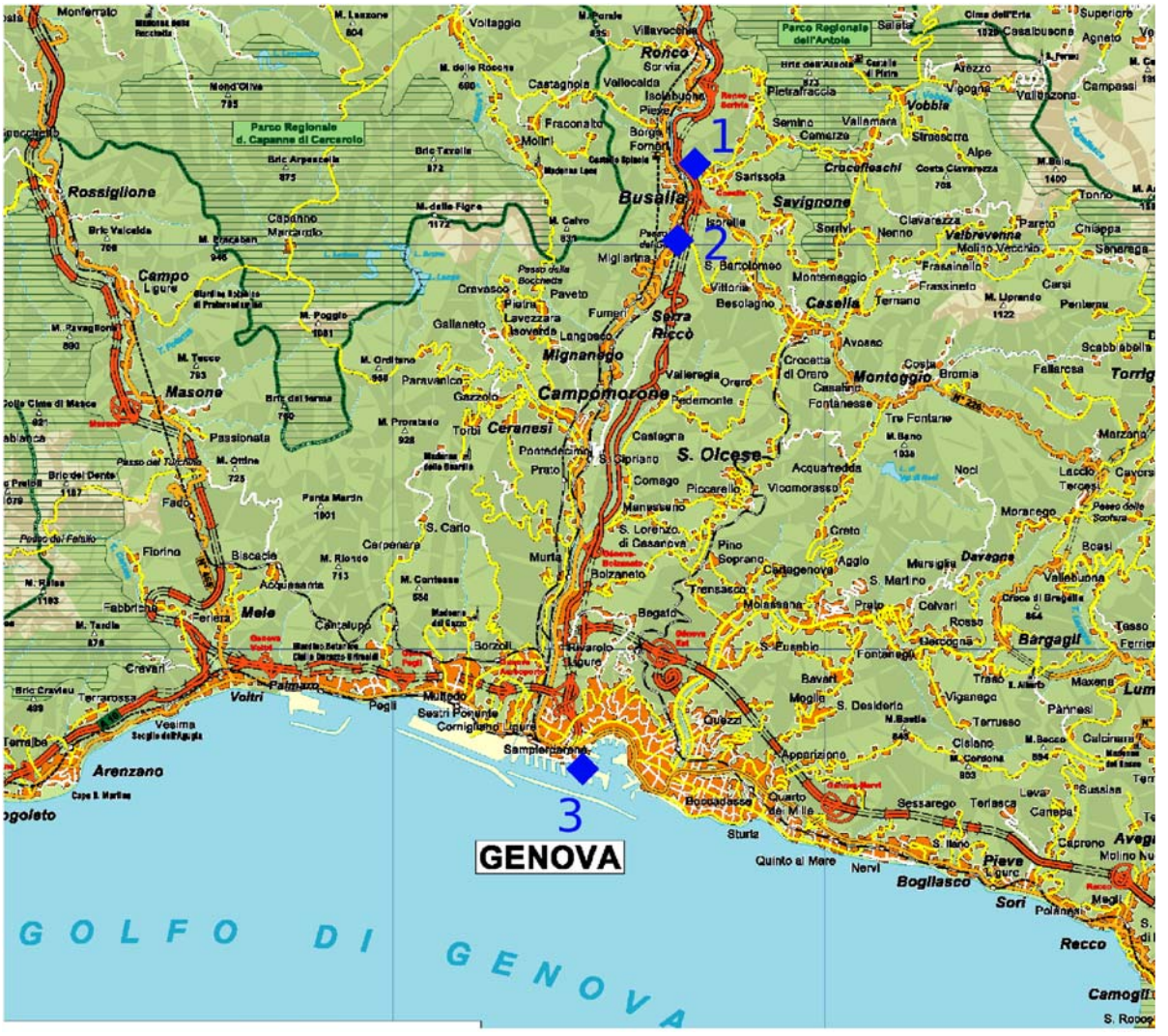

Fig. 1. Map displaying the position of sampling sites (#1 = Busalla; #2 = Passo dei Giovi; #3 = Lanterna).

since April 2003, aimed at characterizing the aerosols in the urban and suburban area by means of elemental analysis (Mazzei and Prati, 2005). A general characterization and source apportionment for the Genoa area is provided in Mazzei (2007); Mazzei et al. (submitted for publication); in this article, instead, we describe a particular experiment, derived from having simultaneous sampling at different sites and from ancillary meteorological information.

Sampling occurred at the following sites during the second half of 2005: Busalla (#1), Passo dei Giovi (#2) and Lanterna (#3); see Fig. 1. Passo dei Giovi (44°33′N, 8°57′E) is located at an altitude of 470 m-amsl, on the ridge of the Appenines, at the separation between the Polcevera Valley (to the South) and the Scrivia Valley (to the North). The Polcevera Valley extends 17 km South to the harbour and contains most industries in town, whereas the Scrivia Valley extends 65 km North where it flows into the Po Valley. Environmental parameters at Passo dei Giovi are considered representative of the rural background near the city. The Busalla site (44°34′N, 8°57′E) has suburban features, is 110 m lower than Passo dei Giovi, and is located on the Northern side of the Appenines, whereas the Lanterna sampler (44°24′N, 8°54′E) has been located South, on the sea front at the end of the Polcevera Valley, within the harbour, and at the foot of the city's major lighthouse (altitude 40 m; under both urban–industrial and maritime influence). The latter two sites are placed near specific anthropogenic sources: an oil refinery 500 m West of site #1, an express highway ~50 m Southwest of site #1, a power plant 150 m South of site #3, with its open-air coal storage, and the city's industrial harbour surrounding site #3. The sampling locations are oriented on a North–South axis, as are the Polcevera and Scrivia valleys: site #2 is 2 km South of site #1, and site #3 is 17 km South of site #2.

2. Sampling and analysis

Particulate matter has been collected on polytetrafluoroethylene filters during 2005, using sequential samplers equipped with PM_{10} sampling heads. The sampler used in Busalla (suburban site) is a Partisol 2025, designed according to US-EPA regulations and set to maintain a flow rate of 1 $m^3\ h^{-1}$ (actual flow rate). The samplers used at Passo dei Giovi (rural site) and Lanterna (harbour site) are of the TCR-Tecora Skypost series, designed according to CEN regulations and set to maintain the flow rate at 2.3 $m^3\ h^{-1}$ (actual flow rate). Equivalence within 10% of the two types of sampler has been previously established (Chiari et al., 2005). The sampling duration was 24 h, with filter changes occurring at midnight local time. Sampling at the Lanterna started on 20 July (Julian Day, JD, 201); sampling at Busalla started on 23 September (JD 266); and sampling at Passo dei Giovi started on 28 September (JD 271). All samplings ended on 19 December (JD 353), with the exception of the Busalla sampling which lasted one more day. Finally, 79 samples were retained in Busalla, 56 were retained at Passo dei Giovi, and 100 samples were retained at the Lanterna. Simultaneous sampling at the three sites occurred on 39 days.

Samples have been analyzed gravimetrically with an analytical balance (sensitivity 1 μg), after being conditioned for 48 h at 20±1 °C and 50±5% relative humidity, and electrostatic effects were avoided using a de-ionising gun. The weighing procedure included several reproducibility tests and controls with certified weights, resulting in a typical standard error of±3–5 μg, with a PM deposit on each filter in the range 300–2000 μg. All concentrations given in this paper, gravimetric and elemental, refer to actual air volumes.

Information on the elemental composition has been gathered through the use of energy dispersive X-ray fluorescence, ED-XRF (Van Grieken and Markowicz, 1993). Elemental concentrations have been determined using an ED2000 spectrometer by Oxford Instruments, following a methodology already adopted in previous works (Marcazzan et al., 2001; Ariola et al., 2006). The following elements have been identified: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Sr, Pb. Detection limits (3-σ) were 2–100 ng cm^{-2} on the filter deposit (depending on element); in terms of airborne concentration, 1–50 ng m^{-3} for sampling with Partisol, and 0.4–20 ng m^{-3} for sampling with TCR-Tecora.

3. Winds

The Polcevera and the Scrivia valleys being oriented North–South, at the sampling sites winds oriented along this axis can be expected. In the data analysis wind speed and direction at Fontanafresca have been used: this measurement station is owned by Agenzia Regionale per la Protezione dell'Ambiente Ligure, Centro MeteoIdrologico della Regione Liguria (ARPAL-CMIRL). The wind station is placed at 743 m-amsl on the Appenines near the city, and for wind it is considered representative of the urban and suburban area. A preliminary analysis of the wind data at this and other nearby stations showed that flow is guided by the terrain, and highlighted two major wind regimes. Prevalent winds are from the Northern sector (NW/N/NE), and the second-most important sector

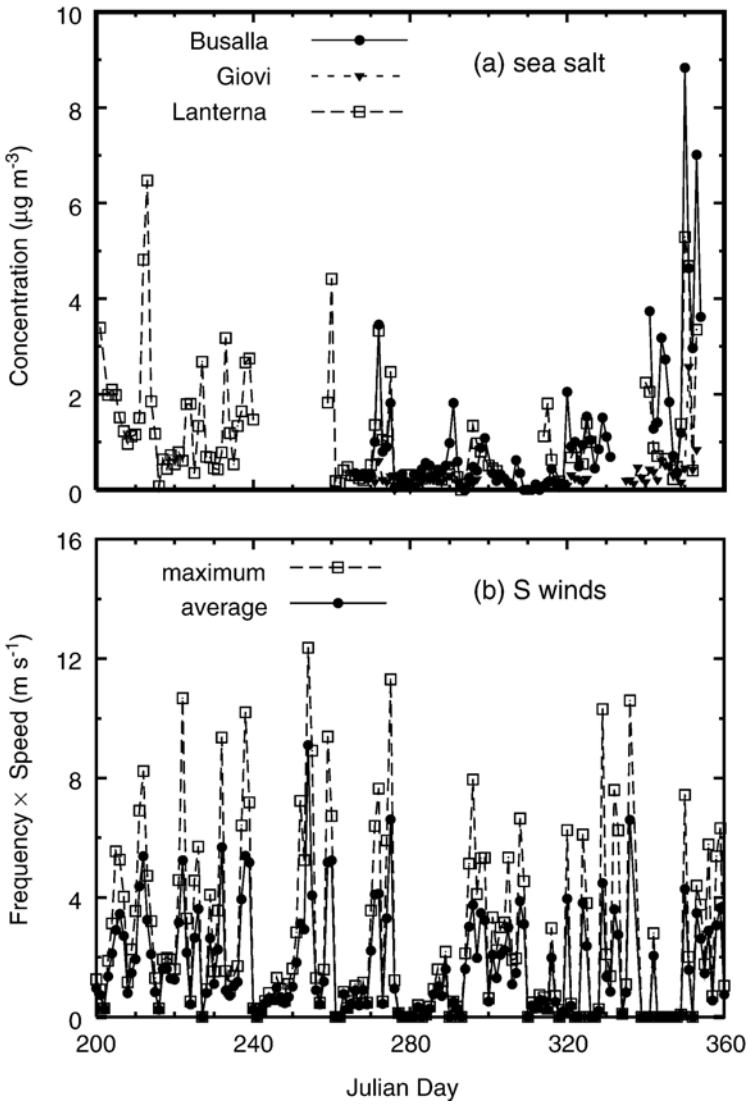

Fig. 2. (a) Concentration of sea salt at Busalla (full circles, solid line), Passo dei Giovi (full triangles, dotted line) and Lanterna (open squares, broken line). (b) Southern sector winds: maximum speed × frequency (open squares, broken line); average speed × frequency (full circles, solid line); wind information is provided by courtesy of ARPAL-CMIRL.

is the Southern one (SW/S/SE), whereas Eastern and Western winds are almost non-existent.

Wind speed and direction at Fontanafresca, v and θ respectively, were available every 10 min, and for a simplification the database has been reduced to a measurement every hour by rejecting the remaining data. During the period under study (JD 200–360) 3791 valid wind data were available, with an average speed of 4.4 m s^{-1} (standard deviation: 3.4 m s^{-1}) and a maximum speed of 24 m s^{-1}. Calm winds (v<1.6 m s^{-1}) were observed 17% of the time, and were not further considered; Eastern and Western winds (frequency 5.6%) were also discarded. The remaining winds (2929 hourly data points) were divided with nearly equal probability into Northern sector and Southern sector winds. Southern sector winds were light or gentle in 81% of the cases ($1.6 \le v < 5.5$ m s^{-1}), and moderate to strong in the remaining cases ($5.5 \le v < 13.9$ m s^{-1}), with an average speed of 2.9 m s^{-1} and a maximum speed of 13 m s^{-1}. Northern sector winds were light or gentle in 46% of the cases, moderate to strong in 48% of the cases, and gale ($v \ge 13.9$ m s^{-1}) in 6% of the cases: Their average speed was 3.8 m s^{-1} and their maximum speed was 24 m s^{-1}. To summarize the wind information, the daily average and daily maximum speeds in each of the Northern and Southern sectors have been computed and

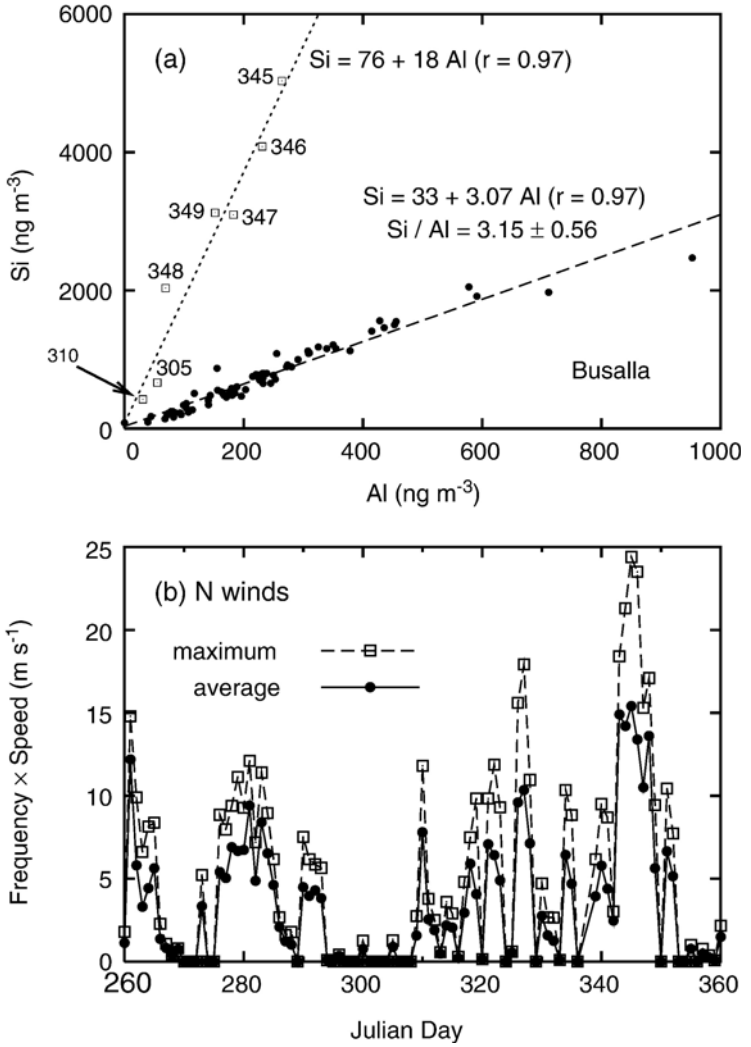

Fig. 3. (a) Si and Al concentrations in the PM_{10} samples collected at Busalla. Correlation lines, obtained by linear regression, are also shown, and were computed by subdividing the data points into two groups: The main group (full circles), shows a Si/Al slope close to 3, and the additional group (open squares) exhibits a slope around 18. The number near each open square indicates the JD of the measurement. (b) Northern sector winds: maximum speed × frequency (open squares, broken line); average speed × frequency (full circles, solid line); wind information is provided by courtesy of ARPAL-CMIRL.

weighed with wind frequency in the same sector. The result, expressed as frequency × speed, is displayed in Figs. 2b and 3b, and represents the relative importance of Northerly and Southerly flows on each given day.

4. Results

4.1. General features

Table 1 reports the average measured concentration for each element, as well as its standard deviation. PM_{10} averages display a slightly decreasing behaviour going from inland to the coast; such behaviour is confirmed when one examines the 39 days for which simultaneous sampling occurred. At all sites, the most abundant element among those detected by ED-XRF is S (a tracer for secondary aerosols). Its concentration is similar at the three sites not only as far as magnitude is concerned, but also in the daily variations: This fact proves for this type of aerosol the existence of a relatively homogeneous regional background. No significant correlation between S and wind speed or direction has been found.

Busalla (suburban site) and the Lanterna (harbour site) display rather similar features also for the other elemental concentrations: At these sites the constituents of mineral dust (Al, Si and Ca) are relatively abundant, and the same can be said for the elements in sea salt (Na and Cl) and for Mg (which may be ascribed to both). A noticeable feature

Table 1
Summary of elemental and gravimetric concentrations in PM_{10} (ng m^{-3}) for Busalla, Passo dei Giovi, and Lanterna (ordered from North to South) during the sampling period: average±standard deviation

Element	Busalla (suburban)	Giovi (rural)	Lanterna (harbour)
Na	530±700 (69)	170±200 (53)	500±460 (99)
Mg	180±120 (67)	43±29 (41)	146±78 (100)
Al	230±160 (78)	49±47 (56)	230±160 (100)
Si	920±860 (79)	160±150 (56)	680±430 (100)
P	48±25 (79)	12.4±7.0 (55)	24±14 (100)
S	1700±790 (79)	1120±740 (56)	1630±850 (100)
Cl	390±540 (69)	67±77 (45)	490±620 (97)
K	350±180 (79)	190±120 (56)	240±130 (100)
Ca	370±240 (79)	40±30 (55)	1200±1200 (100)
Ti	16.9±9.3 (72)	4.5±2.5 (38)	28±17 (100)
V	6.9±3.4 (39)	3.6±2.4 (39)	24±17 (100)
Cr	4.3±1.4 (42)	9±14 (44)	11±30 (97)
Mn	9.2±4.5 (78)	3.7±2.4 (54)	17±30 (100)
Fe	430±250 (79)	127±85 (56)	590±380 (100)
Ni	7.9±8.4 (78)	8.8±7.7 (56)	10.6±8.1 (99)
Cu	12.1±6.3 (79)	4.3±5.5 (56)	14±11 (100)
Zn	46±22 (79)	22±13 (56)	61±99 (100)
Se	1.6±0.4 (33)	0.9±0.5 (33)	1.8±1.0 (35)
Br	5.4±2.6 (77)	3.5±1.8 (54)	5.1±2.6 (97)
Sr	3.0±1.2 (57)	0.9±0.3 (23)	8.7±9.3 (96)
Pb	18±11 (79)	11.8±9.7 (56)	10.5±8.8 (100)
PM_{10}	35,000±14,000 (79)	31,000±16,000 (56)	27,000±12,000 (100)

The number of valid samples for which there is a detectable quantity of the given element (i.e. above the minimum detection limit) is given in parentheses for each element and site.

is the large concentration of Ca at the Lanterna, which makes it the second-most abundant element at this site, overtaking Si. Large Ca/Al ratios in coarse fractions have been observed in the past in the whole urban area (Mazzei and Prati, 2005), as well as in other urban areas such as Firenze and Napoli (D'Alessandro et al., 2003). Also abundant are other elements which can be ascribed to both natural and anthropogenic sources, such as K and Fe.

In comparison, Passo dei Giovi (rural site) exhibits peculiar features: The PM_{10} concentration remains in the same range, but elemental concentrations are drastically reduced (with the exception of S). K is the second-most abundant element, keeping a concentration smaller but comparable to the other two sites, whereas elements characterizing mineral dust and sea salt are reduced to one third or less. Adding up the detected elements for this site yields only 7% of the gravimetric concentration, whereas this percentage is larger at the other sites (15% to 21%): This probably expresses the circumstance that the compounds of the unmeasured elements (C and N compounds) play a decisive role.

4.2. Sea salt

Sea salt concentration has been computed as 1.46[Na]+[Cl] as in a previous paper (Marenco et al., 2006). Campaign averages are 1.0 μg m^{-3} at Busalla (suburban site), 0.3 μg m^{-3} at Passo dei Giovi (rural site), and 1.2 μg m^{-3} at the Lanterna (harbour site), and the temporal evolution is shown in Fig. 2a. A good correlation exists between Busalla and the Lanterna for the common part of the dataset (correlation coefficient 0.86); the correlation between Busalla and Passo dei Giovi is also good, although weaker (correlation coefficient 0.75). Among the features common to the three sites, note the peak on JD 350–351 (only JD 351 at Passo dei Giovi), characterized by large concentrations: 8.8 μg m^{-3} at Busalla, 5.3 μg m^{-3} at the Lanterna, and 2.6 μg m^{-3} at Passo dei Giovi.

Sea salt concentrations can be related to the nearby sea if marked by simultaneous Southern sector winds (Fig. 2b): see e.g. the double peak on JD 272 and 275 at the three sampling sites, and the corresponding double peak in wind speed; several other coincidences are found in Fig. 2. In this regard, there is the remarkable fact that several sea salt peaks are in fact correlated with strong Southerly winds occurring on the day before. Moreover, two sea salt peaks observed at the two sites more distant from the sea but not at the Lanterna (JD 291 and 344) fall in periods of Northerly winds, which excludes for them the hypothesis of nearby production (long-range transport is probably responsible).

Having at the Lanterna a sampling site near the sea shore, it is possible to investigate the Cl/Na ratio: For fresh sea salt a value near 1.8 is expected, as deduced from the tabulated composition of sea water given in Lide (1992). This ratio is expected to be reduced as the salt ages, since Cl is volatilized in the atmosphere by reacting with acidic species (Pakkanen, 1996; ten Brink, 1998; Lee et al., 1999). In the dataset, large Cl/Na ratios (>1.3) are observed on 7 days presenting a peak of marine aerosols; and for three of these cases the ratio is very close to the expected (1.7–1.8). This circumstance seems to suggest that nearby production may be the dominant sea salt source.

Simultaneous sea salt events at the Lanterna and Busalla on days in which Southern winds prevail can help giving an evaluation of the time scale over which Cl loss occurs. Such a loss is to be expected because secondary sulfuric and nitric acid are possibly present in the Genoa atmosphere, being thought to originate from combustion and/or industrial processes, and also from biogenic emissions on land and the sea (Singh, 1995). The estimation of the time scale for Cl loss is attempted in Table 2, where an exponential decay law has been assumed:

$$\frac{\mathrm{Cl}}{\mathrm{Na}} = \left(\frac{\mathrm{Cl}}{\mathrm{Na}}\right)_0 e^{-t/\tau} \quad (1)$$

where $(\mathrm{Cl/Na})_0$ is evaluated at the Lanterna, Cl/Na is evaluated at Busalla, t is evaluated from the distance between the sampling sites and the daily average speed of Southern winds, and τ is the lifetime of Cl in the local atmosphere (dependent on the concentration of acidic species).

Note that for the 3 days listed in Table 2 Southern winds are rather persistent, as indicated from their observed daily frequency; moreover wind speed can be considered sufficiently constant (standard deviation: 30–45% of the average). The resulting τ has to be taken as a rough evaluation of the decay constant for Cl with respect to Na in atmospheric sea salt, since daily averages were used and wind speeds were for a nearby but different location. It can be seen that in the Genoa atmosphere the lifetime is of the order of 1–1.5 h: Being so short, it can be concluded that certainly large Cl/Na ratios indicate fresh sea salt, but on the contrary low ratios may indicate marine air masses aged by as little as 1 h. However, care is needed in manipulating Cl/Na ratios as the Na concentration may be underestimated by up to 25–50% due to X-ray self-attenuation within the samples during ED-XRF analysis (D'Alessandro et al., 2003; Lucarelli et al., 2004). In this work we do not correct Na concentrations; however the Cl lifetime reported in Table 2 does not depend on the absolute Na values, if one assumes that the correction is similar at both sites.

Table 2
Simultaneous sea salt events at the Lanterna and Busalla on days in which Southern winds prevail: sea salt concentrations, Cl/Na ratios by weight, Southern wind frequency, average Southern wind speed, time needed at the average Southern wind speed to cover the 19 km separating the two sites, and estimated Cl lifetime calculated assuming an exponential decay

JD	Lanterna		Busalla		Southern wind		Time of flow t (min)	Cl lifetime τ (min)
	μg m^{-3}	Cl/Na	μg m^{-3}	Cl/Na	%	m s^{-1}		
272	3.3	1.0	3.5	0.5	75%	5.5	58	75
275	2.5	1.3	1.8	0.5	96%	6.9	46	49
350	5.3	1.4	8.8	0.6	88%	4.9	65	84

The number of valid samples for which there is a detectable quantity of the given element (i.e. above the minimum detection limit) is given in parentheses for each element and site.

4.3. Excess Si

A feature, considered peculiar, is found by correlating Al and Si concentrations at Busalla (suburban site), both being normally considered tracers for mineral dust (Fig. 3a): Data fall on two distinct regression lines, with no intermediate points. This looks like an indication for the existence of two different sources for the same elemental couple: In the main data stream the Si/Al proportionality coefficient is around 3, whereas for a smaller number of days a coefficient six times larger is observed. As a term of comparison, consider that Si/Al=3.4 is reported in Mason (1966) as the soil dust average; Si/Al≅3 has been generally found in the Genoa area (Mazzei and Prati, 2005; Mazzei, 2007); that a Si/Al ratio between 2 and 2.3 has been found at Cape Verde for Saharan and Sahelian aerosols (Chiapello et al., 1997); that this same ratio on soil samples has been found to range 2.4–4.8 (Krueger et al., 2004); and that at Mt. Cimone, in Northwestern Italy, the average Si/Al ratio was 2.3 for African dust events and 2.7 for other days (Marenco et al., 2006). Therefore it seems appropriate to explain the Si/Al≅3 data stream as a signature of 'common' mineral dust, whereas points aligning on the line with slope 18 should be ascribed to a different and unknown source (which can be natural or anthropogenic). Note that Si exhibits a similar behaviour when plotted with the concentration of other crustal elements (Ca, Ti, Sr); however at the same sampling site such elements are all well correlated with Al and no similar splitting of the regression line can be observed among them.

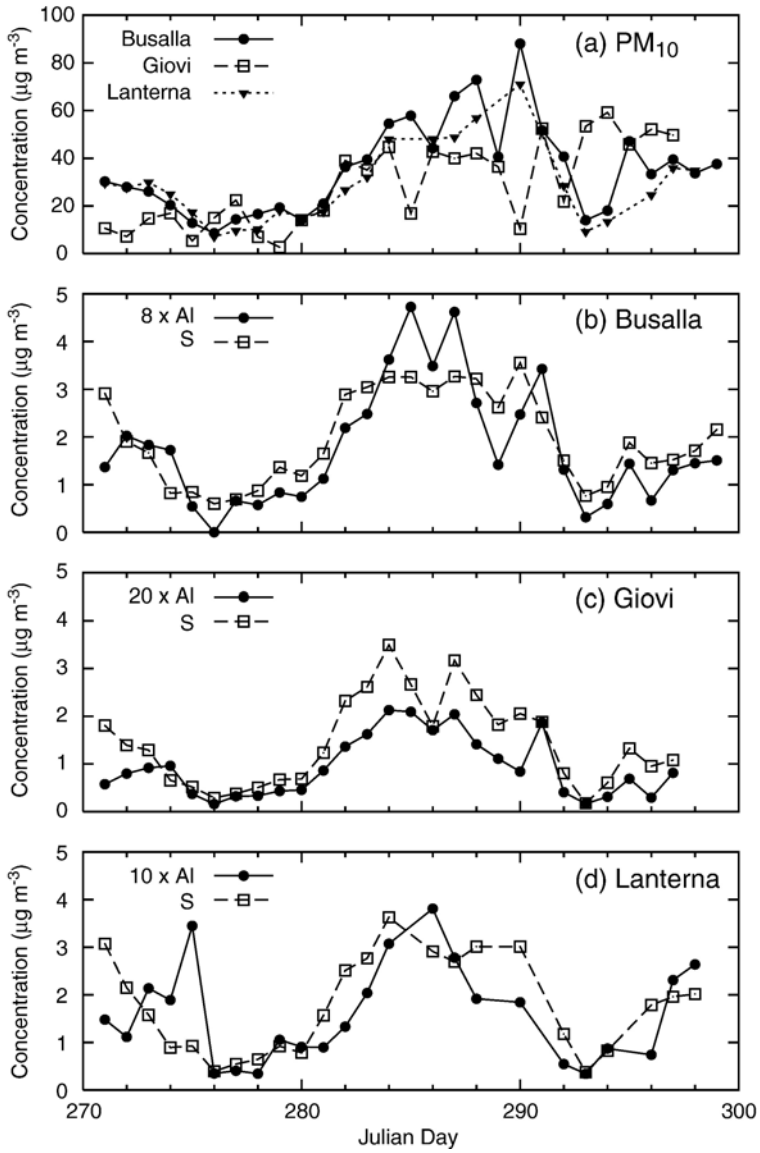

Fig. 4. Concentrations during and around the JD 282–292 episode. In panel (a) the PM_{10} concentration at Busalla (full circles, solid line), Passo dei Giovi (open squares, broken line) and Lanterna (full triangles, dotted line) is shown. In the remaining panels the concentrations of Al (full circles, solid line) and S (open squares, broken line) for (b) Busalla, (c) Passo dei Giovi, and (d) Lanterna. The Al concentration has been multiplied by (a) 8, (b) 20 and (c) 10 for a graphical purpose.

The additional Si source has been named 'excess Si,' and quantified as:

$$[\text{excess Si}] = [\text{Si}] - 3[\text{Al}] \quad (2)$$

Excess Si is unknown in terms of origin and composition, and the chemical form under which it is to be found is also unknown: The above formula only accounts elemental Si and neglects other possible elements bound or correlated to it. If for instance the usual Si oxide is assumed, the result obtained with the above formula would have to be multiplied by 2.14. Fig. 3a suggests the presence of Al associated with excess Si; however, the *de facto* correlation of Al with excess Si might also be explained by peculiar meteorological conditions (see below) which may act on different sources simultaneously: We think that the latter interpretation is more correct, as indeed in Busalla we observe on those days a correlated increase of Al, Ca, Ti, Sr, S, Na, and other elements. Searching in the literature, a possible

origin of the excess Si could be fly ash from industrial or energy production processes (Almeida et al., 2005).

In Fig. 3a it can be seen that excess Si is mostly found during a 5-day episode (JD 345–349), during which the average concentration of excess Si was 2.9 μg m^{-3}, and the peak concentration was 4.2 μg m^{-3}; concentrations are therefore large enough for seriously considering this aerosol type. It is interesting to note that at the rural site Passo dei Giovi the excess elemental Si is also found on 2 days (JD 348–349), simultaneous with the longer Busalla episode, although concentrations are far smaller (peak 0.6 μg m^{-3}). At the Lanterna (harbour site), only the 'common dust' data stream with Si/Al ~3 is observed.

By comparison, during the JD 345–349 episode at Busalla enrichment factors for Si, with respect to Al and Ti taken as reference elements, are 6.1 and 7.2 respectively, whereas for the remaining samples at this site (the additional two excess Si days also excluded) the enrichment factor for Si is 0.9 with respect to both Al and Ti. With Al taken as a reference element, the Si enrichment factor (0.9) is very stable throughout the campaign, showing no difference with the other two sites and displaying the only exception of the excess Si episode days. Other crustal enrichment factors at Busalla with respect to Al do not depend upon dividing the dataset into excess Si and non-excess Si cases: Ca 3.2 (3.1 during the episode); Ti 1.0 (0.9 during the episode); Fe 3.1 (2.3 during the episode). A similar result is obtained when enrichment factors are computed with respect to Ti.

We find (Fig. 3b) that the JD 345–349 excess Si episode is quasi-simultaneous with the strongest Northern sector winds in the observation period. On JD 343–348 a low pressure system dominated the Thyrrenian Sea, and Northern sector gale force winds were observed for 6 days, with an average speed of 14 m s^{-1}, and daily maxima ranging 15–24 m s^{-1}; the strongest gusts (24 m s^{-1}) were observed on JD 345–346. Those 6 days included almost 80% of all the observations with wind speed $v \geq 13.9$ m s^{-1} during the observation period (JD 200–360). Our excess Si episode begins and ends 1 day later than this gale, and this coincidence with the strong Northerlies suggests that the phenomenon is somehow correlated with meteorology: It could either be an aerosol which is lifted locally by strong winds, or one that is advected by a source located upwind in the Scrivia Valley. The fact that this aerosol's concentration is already very reduced at Passo dei Giovi (2 km downwind) and unobserved at the Lanterna (19 km downwind) can be considered as a hint that it is a short-lived and a rather local phenomenon; we therefore do not believe that its advection could originate far in the Po Valley and suspect a source closer in the Scrivia Valley.

4.4. October episode

An 11-day period of large PM_{10} concentrations is observed on JD 282–292 (Fig. 4a). At Busalla (suburban site), the average concentration in this period is increased to 54 μg m^{-3}, and on 6 of these 11 days the concentration exceeds 50 μg m^{-3}, a threshold not to be exceeded more than 35 days per year according to present European standards (indicative limit for 2010: 7 days per year). At the Lanterna (harbour site), the average concentration in this period is 45 μg m^{-3} and on 2 days the 50 μg m^{-3} threshold is exceeded. At these two sites, the maximum concentration for the whole campaign is reached on JD 290, with 88 and 71 μg m^{-3}, respectively. At Passo dei Giovi (rural site) an increase of concentration is also observed (average 35 μg m^{-3}, 2 exceedances of the 50 μg m^{-3} threshold), although the PM_{10} concentration tends to display a different temporal behaviour. When the elemental concentrations are examined, the same general behaviour is observed at the three sites for Al (a tracer for mineral dust) and S (a tracer for secondary compounds): see Fig. 4b–d. This large aerosol period is therefore probably related to meteorological causes rather than a temporary increase of source activity: Either pollutant sinks (dispersion and deposition) are inhibited, or advection of aerosol-laden air masses occurs from a more polluted area, or both.

At the beginning of the 11-day period the Eastern European anticyclone rapidly extended to the Thyrrenian Sea; other high pressure systems, located in Northern Europe and Northern Africa, later alternated their influence over Northwestern Italy, which therefore continued to remain in anticyclonic conditions for the whole period. Local meteorological observations displayed large atmospheric pressures and temperatures, and the absence of rainfall. However, in general the anticyclonic conditions did not reduce atmospheric dispersion: Moderate to strong Northerlies were observed (Fig. 3b); it is therefore difficult to associate the aerosol increase only to local production or growth. Most probably, instead, winds have been responsible for the advection of aerosol-laden air masses to the Genoa area from the industrialized Po Valley, located upwind. We conclude that the typical heat wave conditions leading to an increase of pollutant concentration and to the absence of dispersion most probably built a strong aerosol reservoir in the Po Valley (affected by a continental climate); and that this aerosol was transported to the Genoa area by winds. Rainfall on JD 292 can be considered one of the causes of the reduction of atmospheric concentrations at the end of the period.

5. Conclusions

Daily elemental concentrations in PM_{10} at three sampling sites in the urban and suburban area of Genoa have been measured during the second half of 2005. The average PM_{10} concentration that has been found generally decreases going from inland to the coast: This fact could be due to the influence of a generally polluted area in the Po Valley, at North. As usual with this type of measurement, a large variability of all measured concentrations has been observed, and in general the sampled area showed a significant complexity. In particular, we point out to a relatively well-mixed secondary aerosol component, traced by the S concentration. We also underline a large Ca concentration at the Lanterna (harbour site), both in absolute concentration and relative to Al and Si; this suggests a locally different mineral dust component. For Passo dei Giovi (rural site), local peculiarities were found and elemental concentrations have been found very low with respect to the PM_{10} concentration, with the exception of S and K. With great probability, therefore, important aerosol components at this site are represented by compounds not observable with the ED-XRF technique, such as carbonaceous and nitrate aerosols, and further measurements should not omit a simultaneous characterization by chemical methodologies.

Sea salt concentration at the three sites has been found correlated, and episodes with large concentrations (reaching 8.8 $\mu g\ m^{-3}$) were observed; marine aerosol has been mostly related to local production by Southern winds. By comparing the Cl/Na ratio at the Lanterna and at Busalla, the time scale over which Cl loss occurs has been estimated as 1–1.5 h; note that this time is expected to vary, being dependent upon the concentration of acidic species in the atmosphere and other ambient conditions. Two cases influenced by particular meteorological conditions have been studied. Both cases were related to Northern sector winds and lasted several days. In the first case, meteorology was dominated by a low over the Thyrrenian Sea and by gale force winds. Under these conditions an aerosol source enriched in Si with respect to mineral dust appeared in Busalla (suburban site) for 5 days, peaking at more than 4 $\mu g\ m^{-3}$; its signal has been detected for 2 days at Passo dei Giovi as well. In the second case, anticyclonic conditions prevailed, and were accompanied by a general increase of PM_{10} concentrations as well as tracers for mineral dust and secondary compounds. This episode lasted for 11 days and contributed to a significant number of exceedances. A significant part of the aerosols was probably advected to the Genoa area by the Northerly winds, and wet deposition was inhibited by the absence of rainfall.

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