Nat. Hazards Earth Syst. Sci., 14, 2337–2346, 2014
www.nat-hazards-earth-syst-sci.net/14/2337/2014/
doi:10.5194/nhess-14-2337-2014
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Natural Hazards and Earth System Sciences
Open Access

PM_1 measurements at a site close to an oil/gas pre-treatment plant (Agri Valley – southern Italy): a preliminary study

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Received: 28 February 2014 – Published in Nat. Hazards Earth Syst. Sci. Discuss.: 8 April 2014
Revised: – – Accepted: 30 July 2014 – Published: 3 September 2014

Abstract. A PM_1 (i.e. particulate matter with an aerodynamic diameter less than 1.0 µm) short-term monitoring campaign was carried out in the Agri Valley (southern Italy) in September 2012. This area is of international concern, since it houses one of the largest European on-shore reservoirs and the largest oil/gas pre-treatment plant (i.e. the Centro Olio Val d'Agri – COVA) within an anthropised context. PM_1 measurements were performed in Viggiano, the nearest town to the COVA plant and one of the most populated towns of the Agri Valley. During the study period, the PM_1 daily concentrations ranged from 1.2 to 8.4 µg m^{-3}, with a mean value of 4.6 µg m^{-3}. Regarding the PM_1 chemical composition, it can be observed that S and typical crustal elements were the most abundant constituents of the PM_1 collected. By applying principal component analysis (PCA), it was pointed out that crustal soil, biomass and wood burning, secondary atmospheric reactions involving COVA plant emissions and local soil particles, and traffic were the main sources contributing to the PM_1 measured in the area under study. Moreover, a possible contribution of the long-range transport of African dust was observed.

1 Introduction

Atmospheric aerosols, also referred to as particulate matter (PM), are one of the most challenging environmental issues due to their well-established impact on global climate change, air quality and human health (Pateraki et al., 2014). Atmospheric aerosols affect the natural energy balance of the Earth mainly by reflecting/absorbing solar radiation and by influencing the reflective and absorbing properties of clouds (Boucher et al., 2013; Kaufman and Koren, 2006; Yu et al., 2006). Moreover, they can have an impact on visibility (Deng et al., 2008; Chang et al., 2009), agricultural and natural ecosystems (Grantz et al., 2003), and material and cultural heritages (Ghedini et al., 2011), and can pose a risk to human health because of their adverse effects on both the respiratory and cardiovascular systems (Pope and Dockery, 2006). All these impacts are related both to particle dimension and concentrations and to their chemical composition, which includes trace elements, inorganic ions and carbonaceous species (Almeida et al., 2006). Therefore, a continuous improvement in the knowledge of the PM concentrations as well as their physicochemical properties and origin is required to assess and quantify the above-mentioned impacts better. Up to now, there have been many studies dealing with coarse and fine PM fractions (i.e. PM_{10} and $PM_{2.5}$, aerosol particles with aerodynamic diameters less than 10 and 2.5 µm, respectively), but much less is known and even less has been done about the PM sub-micrometric fraction (referred to as PM_1, aerosol particles with aerodynamic diameters less than 1.0 µm). As a consequence, in recent years, a growing number of studies have focused on the assessment of PM_1 levels and chemical composition, and on the identification of its sources, especially in urban areas (e.g. Garcia et al., 2014; Shi et al., 2014; Titos et al., 2014; Valotto et al., 2014), due to the more adverse effects of PM_1 on human health than PM_{10} and $PM_{2.5}$ (e.g. Wang et al., 2014; Galindo et al., 2013). In fact, these areas exhibit the largest targets of impact and a large concentration of emission sources of anthropogenic type (e.g. industrial activities, road traffic, residential heating) which are expected to produce particles mainly in the sub-micrometric size range containing a broad range of

chemical species, ranging from elemental to organic and inorganic compounds. Among the inorganic compounds, trace metals play a key role. In fact, they have been related to both short- and long-term adverse human health effects such as chronic respiratory diseases, heart disease, lung cancer, and damage to other organs (e.g. Lau et al., 2014; Wild et al., 2009). Moreover, when they are associated with PM, they can be deposited on soils and waters, with potentially adverse consequences for the life system on Earth through their biogeochemical cycling in the atmosphere, hydrosphere and geosphere. Despite this, there is still a relatively limited amount of data on PM_1 concentration and chemical composition available at present (Mirante et al., 2013), and several efforts are required to overcome this gap.

The present study enters this context and shows the preliminary results of a PM_1 sampling campaign carried out in the Agri Valley (southern Italy), an area characterised by the presence of the biggest existing oil/gas pre-treatment plant within an anthropised context. This plant produces the emission of particles mainly in the fine and sub-micrometric size ranges that should represent a real problem, also posing health risks to the population living close to it (Trippetta et al., 2013). The main goal of this study is that, for the first time, PM_1 measurements have been performed at an urban site located in the proximity of such a plant. In fact, although this plant began to work in 2001, only a few studies exist on the air quality in this area (i.e. Trippetta et al., 2013; Pavese et al., 2012).

2 Materials and methodologies

2.1 Study area

The Agri Valley is characterised by a large environmental complexity, with naturalistic aspects coexisting along with anthropogenic activities that have potentially high environmental impacts. In fact, on the one hand, the Agri Valley is a farming and breeding area, rich in woods and characterised by a considerable biodiversity that is partly included in the protected area of the Appennino Lucano, Val d'Agri, Lagonegrese National Park. On the other hand, this area houses one of the largest European on-shore reservoirs that, since its discovery in the first half of the past century, has produced a significant and steady increase in the anthropogenic activities linked to the extraction of hydrocarbons (crude oil and gas). At present, there are 25 active productive wells (UNMIG, 2013) located in the upper part of the Agri Valley which are directly connected to an oil/gas pre-treatment plant identified as the Centro Olio Val d'Agri (COVA). In this plant, oil stabilisation and gas conditioning are performed before piping the crude oil to the refinery located in Taranto (Puglia region – southern Italy) through a 136 km long oil pipeline, and introducing the gas into the Italian gas distribution network (Snam Rete Gas S.p.A.). The COVA plant is the largest existing oil/gas pre-treatment plant located in an anthropised area (the nominal treatment capacity of the entire plant is 16 500 $m^3\,g^{-1}$ of crude oil and 3 100 000 S $m^3\,g^{-1}$ of associated gas), and the anthropogenic activity with the highest release of atmospheric pollutant emissions in the Agri Valley (Trippetta et al., 2013). In fact, the pre-treatment processes occurring in the COVA plant imply continuous gaseous and particulate atmospheric emissions from several thermo destroyers and a system of torches where control flames burn continuously. Therefore, it could give rise to a wide range of environmental and especially human health impacts, due to its presence in an area where several small towns (from 1700 to 5400 inhabitants) are settled.

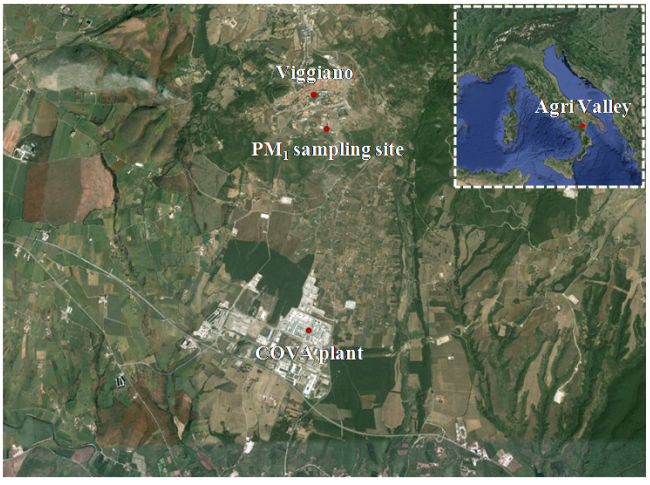

Figure 1. Location of the PM_1 sampling site. The image also reports the location of the Centro Olio Val d'Agri (COVA) plant and the urban area of Viggiano. Aerial photography courtesy of Google Earth (http://earth.google.com/).

2.2 PM_1 measurements

PM_1 measurements were performed in the suburb of Viggiano (40°20′8.59″ N, 15°54′7.43″ E, about 840 m above sea level – a.s.l.) from 1 to 30 September 2012. This site was chosen since Viggiano is the town nearest to the COVA plant, at about 2.4 km away from it (Fig. 1), and is one of the most populated towns of the Agri Valley (about 3100 inhabitants). The PM_1 samples were collected using a low-volume (16.7 L min^{-1} flow rate) gravimetric sampler (TCR Tecora) equipped with a PM_1 cut-off inlet and polycarbonate filters (Ø= 47 mm). The sampling time was 24 h (starting from 12 p.m. LT), and each filter was humidity conditioned in a filter-conditioning cabinet (approximately $T = 20 \pm 2$ °C and RH = 50 ± 5 %) before and after sampling for 48 h. The PM_1 mass was determined with a gravimetric method using an analytical microbalance with a sensitivity of ±1 µg.

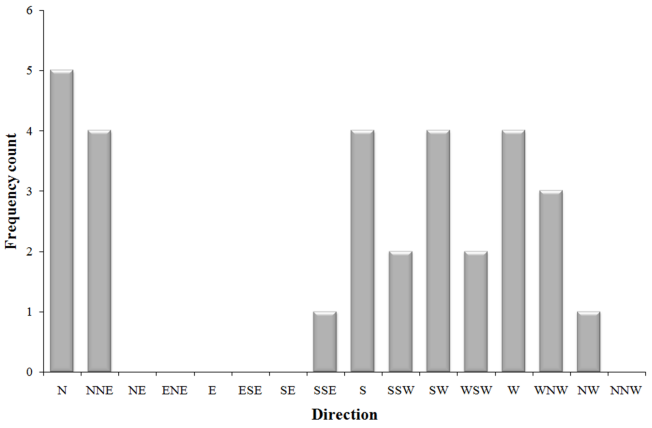

Figure 2. Frequency count of the local wind direction.

To determine the PM_1 chemical composition, the filters were acidic digested following the chemical protocol described in Caggiano et al. (2001). The total concentrations of Al, Be, Ca, Cr, Fe, K, Li, Mg, Mn, Na, P, Ti, S and Zn were measured by inductively coupled plasma optical emission spectrometry (ICP-OES). Cd, Cu and Pb were measured by means of graphite furnace atomic absorption spectrometry (GFAAS). The blank (reagent+beaker+blank filter) contribution was evaluated, and the resulting values were subtracted from the ICP-OES and GFAAS measurements of real samples. For all elements, blanks were found to be less than 10 % of the measured values. The method detection limit (MDL) was used to determine the lowest concentration level that could be detected, statistically different from a blank. Ten blanks were prepared and analysed, and MDLs were determined by adding 3 standard deviations of the blank readings to the average blank values (Yatkin and Bayram, 2007). Moreover, the validity of the whole analytical procedure was checked using the National Institute of Standards and Technology (NIST) standard reference material Urban Particulate Matter, SRM 1648. The results show that the MDL and recovery percentage ranged from 0.00013 to 0.79 ppm and from 63 to 135 %, respectively.

2.3 Meteorology

Measurements of meteorological parameters (atmospheric pressure, temperature, global radiation, relative humidity, rainfall, and local wind speed and direction) were provided by the "Protezione Civile Gruppo Lucano", which has a meteorological station operating in the same place where PM_1 measurements were collected. By analysing the daily mean values of the main meteorological parameters, it can be observed that the pressure ranged from 1005 to 1022 hPa, with a mean value of 1016 hPa. The daily mean temperature ranged from 13 °C to 26 °C, with a mean value of 19 °C. The relative humidity ranged from 26 to 86 %, with the 90th percentile higher than 76 %, while precipitation was registered on nine days, with values ranging from 0.3 to 17.3 mm. Finally, as for the wind, its speed ranged from 0.7 m s^{-1} to 3.8 m s^{-1}, with a mean value of 1.7 m s^{-1}, and all the values, except for one of them, were included in the second and third classes of the Beaufort scale. Regarding the local wind direction, its frequency count is reported in Fig. 2.

Table 1. Explorative statistical parameters of PM_1 and trace element daily concentrations registered at the Viggiano site in September 2012. The number of observations is 30. Legend: *m* denotes mean value, SD denotes standard deviation, Md denotes median value, Min denotes minimum value, and Max denotes maximum value. The PM_1 and trace element daily concentrations are expressed in μg m^{-3} and ng m^{-3}, respectively.

	m	SD	Md	Min	Max
PM_1	4.6	1.7	4.4	1.2	8.4
Al	156.1	177.2	79.0	26.7	730.9
Be	1.2	0.1	1.2	1.1	1.4
Ca	1500.5	1097.8	1145.0	331.4	5408.7
Cd	0.6	0.2	0.5	0.3	1.2
Cr	38.1	3.6	38.3	26.5	46.0
Cu	16.9	38.6	8.6	0.4	204.7
Fe	277.8	294.2	182.6	108.1	1531.3
K	105.8	87.5	73.2	33.1	347.7
Li	33.0	7.3	34.4	11.0	46.1
Mg	264.2	101.4	235.1	107.1	598.0
Mn	4.0	3.0	3.0	1.4	16.2
Na	239.8	99.1	219.5	115.1	590.3
P	38.3	19.7	35.7	6.1	79.8
Pb	5.3	3.2	4.7	1.2	15.0
S	3523.2	6161.8	1545.6	642.8	25 888.3
Ti	15.1	16.7	8.5	3.6	67.4
Zn	97.7	150.8	25.0	4.3	638.6

3 Results and discussion

3.1 Explorative statistical analysis

Table 1 reports a summary of the explorative statistical analysis carried out on PM_1 and trace element daily concentrations measured at the Viggiano site in September 2012. As Table 1 shows, the PM_1 daily concentrations range from 1.2 to 8.4 μg m^{-3}, with a mean value of 4.6 μg m^{-3}, and are characterised by a nearly normal distribution (Fig. 3). By comparing the mean value of the PM_1 daily concentrations registered in Viggiano with those reported in other studies, it can be observed that it is generally lower than those found at other sites (Cusack et al., 2013; Onat et al., 2013; Perrone et al., 2014; Theodosi et al., 2011; Caggiano et al., 2010; Pérez et al., 2008a, b; Marenco et al., 2006; Gomišček et al., 2004) and, in particular, it is lower than the PM_1 concentration mean value (11.0 ± 5.1 μg m^{-3}) measured close to the COVA plant from July to November 2011 (Trippetta et al., 2013). Regarding the latter, this could be due to the combination of

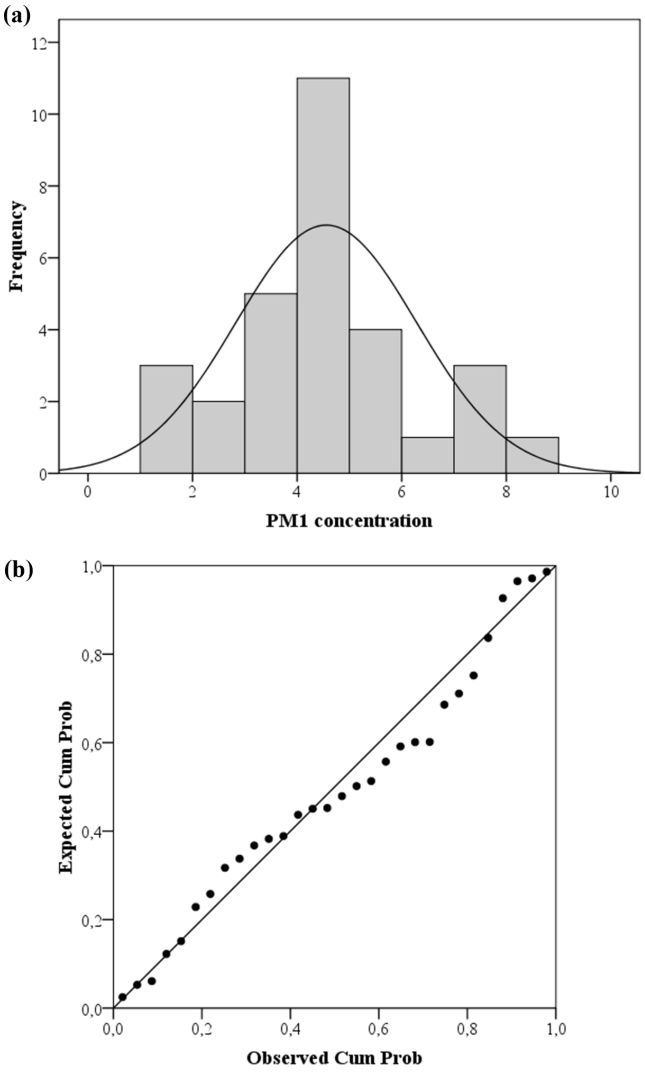

Figure 3. (a) Frequency and **(b)** normal P–P plot of the PM_1 daily concentration data recorded in Viggiano in September 2012. The black line represents the normal fit.

two factors: the geographical position of Viggiano with respect to the COVA plant, and the wind features of the area. In fact, Viggiano is about 2400 m from the COVA plant, and the difference in height between the two locations is about 200 m. Moreover, the area under study is generally characterised by wind speed values that could favour the dispersion of atmospheric pollutants, consequently reducing their concentrations in the local ambient air.

By considering the PM_1 chemical composition, Table 1 provides a summary of the explorative statistical analysis performed on trace element concentration data. As Table 1 shows, S, followed by typical crustal elements, are the most abundant constituents of the PM_1 collected in the study area. Regarding the frequency distribution, the results of the Shapiro–Wilk normality test ($p < 0.05$) point out that Be, Cr, Li and P are the only elements that approach a normal distribution. In fact, they are the only elements characterised by skewness values close to zero (values not shown). All the other elements are positively skewed towards the lower concentrations, as confirmed by the median concentrations lower than the corresponding mean concentrations.

3.2 Source identification

3.2.1 Enrichment factor technique

The crustal enrichment factor (EF) technique was applied to the PM_1 chemical data to obtain preliminary information about elements originating both from natural processes and from human activities (Mbengue et al., 2014; Hassan et al., 2013; Yongming et al., 2006). The enrichment factor for a generic X element with respect to a reference crustal Y element is defined as $EFX = (X/Y)$ air/(X/Y) crust, where EFX is the enrichment factor of the X element, (X/Y) air is the concentration ratio of X to Y in the aerosol sample, and (X/Y) crust is the average concentration ratio of X to Y in the crust (Fang et al., 2006; Quiterio et al., 2004; Chao and Wong, 2002). In this study, the Earth crust chemical composition was provided by Taylor and McLennan (1985), and Al was used as a reference element, assuming that its anthropogenic sources are negligible (Chithra and Shiva Nagendra, 2013). According to Song et al. (2012), the elements were classified into three types by the EFs as follows: crustal elements (EFs < 10), mixed elements ($10 \leq$ EFs ≤ 100) and elements of anthropogenic origin (EFs > 100).

Figure 4 shows the EF mean values of the different trace elements. As Fig. 4 shows, EF values lower than 10 were found for Ti, Mn, Fe, and K. This suggests that their main sources are of a crustal type (e.g. soil and re-suspended dust) and that anthropogenic activities give a negligible contribution to their atmospheric levels. Na, Mg, Ca and P EF mean values of 10, 12, 32 and 39, respectively, suggest that these elements are partly derived from anthropogenic sources and human activities. Finally, Cd, S, Li, Zn, Be, Pb, Cr and Cu are characterised by EF mean values higher than 100, indicating that these elements are of an almost total anthropic origin.

3.2.2 Weekday–weekend variations of the PM_1 and trace element concentrations

The comparison between weekday (i.e. from Monday to Friday) and weekend concentrations is a methodology widely used to point out the contribution of local anthropogenic activities that could be characterised by a weekly pattern. Figure 5 reports the mean values of PM_1 and trace element concentrations registered on weekdays and weekends. By calculating the average percentage variation in the PM_1 and trace element concentrations between weekdays and weekends, it can be observed that, except for Zn and Pb, the trace elements that on average show higher concentrations on weekends than on weekdays are either of a prevailing natural origin

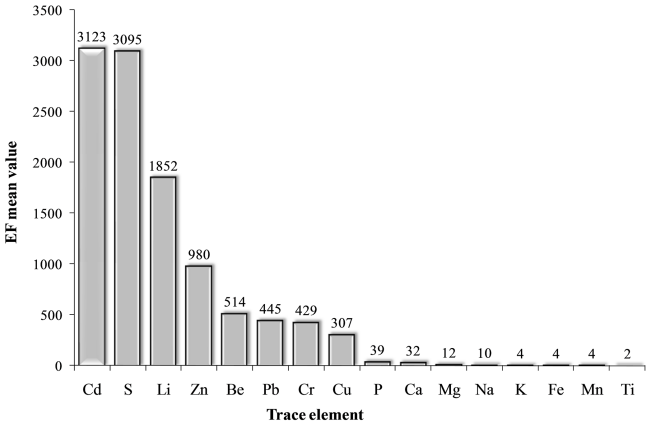

Figure 4. Mean values of the trace element enrichment factor (EF). EF mean values are plotted in decreasing order.

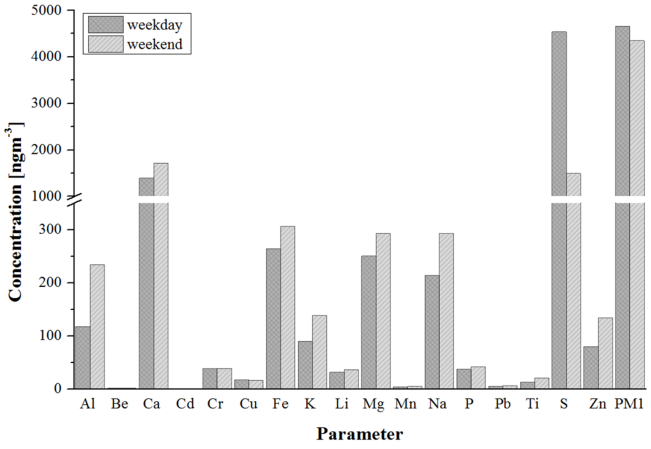

Figure 5. Mean values of the PM_1 and trace element concentrations registered on weekdays (i.e. from Monday to Friday) and weekends.

or are significantly affected by the contribution of natural sources (i.e. Ca and Mg). A possible explanation for the observed increases should be provided by considering the local meteorological features during the two considered periods. In fact, on weekends, the temperatures show slightly higher mean values, while the relative humidity is on average lower. Moreover, only two rainy days out of the nine registered during the entire study period occur on weekends. Finally, no significant variation is observed in wind speed. All this implies that weekends are characterised by slightly dryer and warmer conditions that could facilitate the soil drying and the consequent re-suspension of soil and/or road dusts. The latter could also be supported by the higher concentration values of Zn and Pb that, when they are associated with crustal elements, are typical tracers of road dust contributions. As for S, the variation observed should be related to a change in the emissions of the COVA plant, which is expected to be the main source of sulfur compounds in the study area, with about 0.033 kt of SO_2 per year (the average value referred to the 2009–2011 period) emitted only by its thermodestroyers. These contribute approximately 95 % to the total emissions of SO_2 of the COVA plant under normal operating conditions (ENI, 2012).

3.2.3 Principal component analysis

In order to identify preliminarily the main PM_1 sources, principal component analysis (PCA) was used. PCA is a multivariate statistical technique widely applied to study the correlation structure among the different atmospheric pollutants and to identify the source types that can give rise to their presence in the atmosphere (Okubo et al., 2013; Yatkin and Bayram, 2007; Vallius et al., 2005; Quiterio et al., 2004; Dìaz et al., 2002). In this study, each variable was normalised to unit variance, and all the principal factors with eigenvalues greater than 0.8 were retained. To clarify the meaning of the principal components (PCs), the retained factors were subsequently subjected to the normalised varimax rotation. Chemical species were considered to identify source categories only when factor loadings were greater than or equal to 0.5 (absolute value) (Caggiano et al., 2010; Callén et al., 2009). SPSS© for Windows version 12.0 was used for the multivariate statistical analysis.

By applying the PCA to the concentrations of the trace elements measured in PM_1, six significant components (PCs), explaining 81 % of the data variance, were pointed out (Table 2).

PC_1 explains 22 % of the data variance and is characterised by high loadings (loading absolute value ≥ 0.8) of Mn (0.96) and Fe (0.92), and by moderate loadings ($0.8 <$ loading absolute value ≤ 0.5) of Al (0.75), Na (0.69) and K (0.57). All these elements are abundant in the Earth's crust rocks and soils (Yu et al., 2013; Sudheer and Rengarajan, 2012), and their presence in the local atmosphere could be related to the resuspension from fields or bare soils by local winds and to the long-range transport of dust from the Saharan region, whose occurrence is very frequent in Mediterranean countries during the spring and summer months (e.g. Pey et al., 2013; Caggiano et al., 2011; Mona et al., 2006). The presence of K may also suggest the influence of the biomass and wood burning in this component. In fact, K is the most common inorganic species used to trace this kind of source (Cusack et al., 2013; Kim et al., 2010). Therefore, PC_1 identifies the PM_1 crustal fraction, with a minor contribution of biomass and wood burning. This is consistent with the rural features of the area, where farming is a bedrock of the local economy. Moreover, domestic fires, mainly related to cooking and heating, often occur, and open burning of grass and forest is a common practice used for clearing field waste in farming and ranching.

PC_2, which explains 15 % of the data variance, is characterised by high loadings of Ca (0.81) and S (0.80), and by moderate loadings of Ti (0.77) and Mg (0.65). Sulfate

Table 2. PCA results after the normalised varimax rotation for chemical element concentrations in PM_1. Loadings and percentage of explained variance (P %) are reported. Loadings less than 0.5 are not reported.

PC_1		PC_2		PC_3		PC_4		PC_5		PC_6	
$P\% = 22$		$P\% = 15$		$P\% = 13$		$P\% = 12$		$P\% = 11$		$P\% = 8$	
Al	0.75	Ca	0.81	Zn	0.85	Cd	0.82	Li	0.85	Cu	0.87
Mn	0.96	S	0.80	Be	0.59	Pb	0.64	P	−0.66		
Fe	0.92	Ti	0.77	Na	0.57	Mg	0.56	Cr	0.55		
Na	0.69	Mg	0.65								
K	0.57										

particles recorded in this area are mainly formed by secondary atmospheric reactions of sulfur gaseous compounds emitted from the COVA plant and by particles coming from the local soil (Lettino and Fiore, 2013). Calcium sulfates (mainly formed as gypsum) and magnesium sulfates, as well as mineral particles including Ti in their composition, may also be related to the long-range transport of African dust (Dall'Osto et al., 2010). Therefore, PC_2 identifies secondary atmospheric reactions involving COVA plant emissions and local soil particles, with a possible minor contribution of natural emissions from long-range transport of African dust.

PC_3 explains 13 % of the data variance and is significantly characterised by Zn (0.85), with moderate contributions of Be (0.59) and Na (0.57). Zn is considered a good marker for tyre wear emissions (Salvador et al., 2007) as well as tailpipe emissions, due to its use in motor oil (López et al., 2011). Moreover, Zn and Na have been found in particulate matter released during wood combustion, especially bark combustion (Jöller et al., 2007). Regarding Be, the EF analysis results indicate that its origin is almost totally anthropic, so its presence in this component should be related to contributions of anthropogenic sources identified as fossil fuel combustion and vehicle emissions (Duan et al., 2012). Based on this, PC_3 can be classified as mixed, including contributions coming from traffic and combustion processes (wood and fossil fuels).

PC_4 explains 12 % of the data variance, and is significantly related to Cd (0.82) and, to a lesser extent, to Pb (0.64) and Mg (0.56). Cd is generally related to exhaust emissions from gasoline, lubricating oils and the abrasion of tyres and brake linings. Regarding Pb, although the European Union member countries, including Italy, have phased out leaded gasoline since 1994, banning it in 2002, Pb is still widely used in a number of car components, including lead wheel weights, solder in electronics and lead–acid batteries. The wear of such components may generate particles containing Pb (Song et al., 2012). Finally, Mg, when associated with traffic tracers, is one of the potential markers of resuspended road dust. Based on this, PC_4 can be related to the resuspension of road dusts from paved or non-paved roads (Lim et al., 2010).

PC_5, explaining 11 % of the data variance, is significantly characterised by Li (0.85), with a moderate contribution of Cr (0.55). Li and Cr are found in vehicle exhaust and coal fly ash (Chandra Mouli et al., 2006). Therefore, PC_5 can be classified as mixed, including contributions coming from traffic and coal combustion processes. PC_5 also includes P (−0.66), but the negative sign of the loading might indicate an independent behaviour of P with respect to the other two elements included in this component. This is probably be due to different sources of this element, such as the resuspension of soil particles containing both naturally occurring and fertiliser-derived P, primary biogenic aerosols, and combustion sources (fossil fuel, biomass burning, biofuels) (Lettino and Fiore, 2013; Mahowald et al., 2008).

Finally, PC_6 explains 8 % of the data variance, and is exclusively related to Cu (0.87). Cu is a good tracer of traffic emissions and is generally associated with brake wear abrasion (López et al., 2011). Wood combustion, waste incineration and oil combustion also contribute to its presence in the atmosphere (Al-Masri et al., 2006). Moreover, Cu is also associated with industrial emissions (Mbengue et al., 2014). Due to the variety of sources that could contribute to the presence of Cu in the atmosphere and the potential presence of all of these sources close to the sampling site, this component is classified as "unidentified".

3.2.4 Trace element concentrations and local wind direction

The consistency of the sources identified by the PCA with the features of the area under study was evaluated by analysing the variability of the trace element mean concentrations as a function of the local wind direction (Fig. 6). It should be noted that, since the winds came mainly from the sectors from SSE to NW, the directional contributions of most of the source factors were dominated by these wind sectors.

As Fig. 6 shows, four groups can be defined as a function of the concentration variability degree with respect to the wind directions:

1. no variability;
2. low variability;
3. moderate variability;

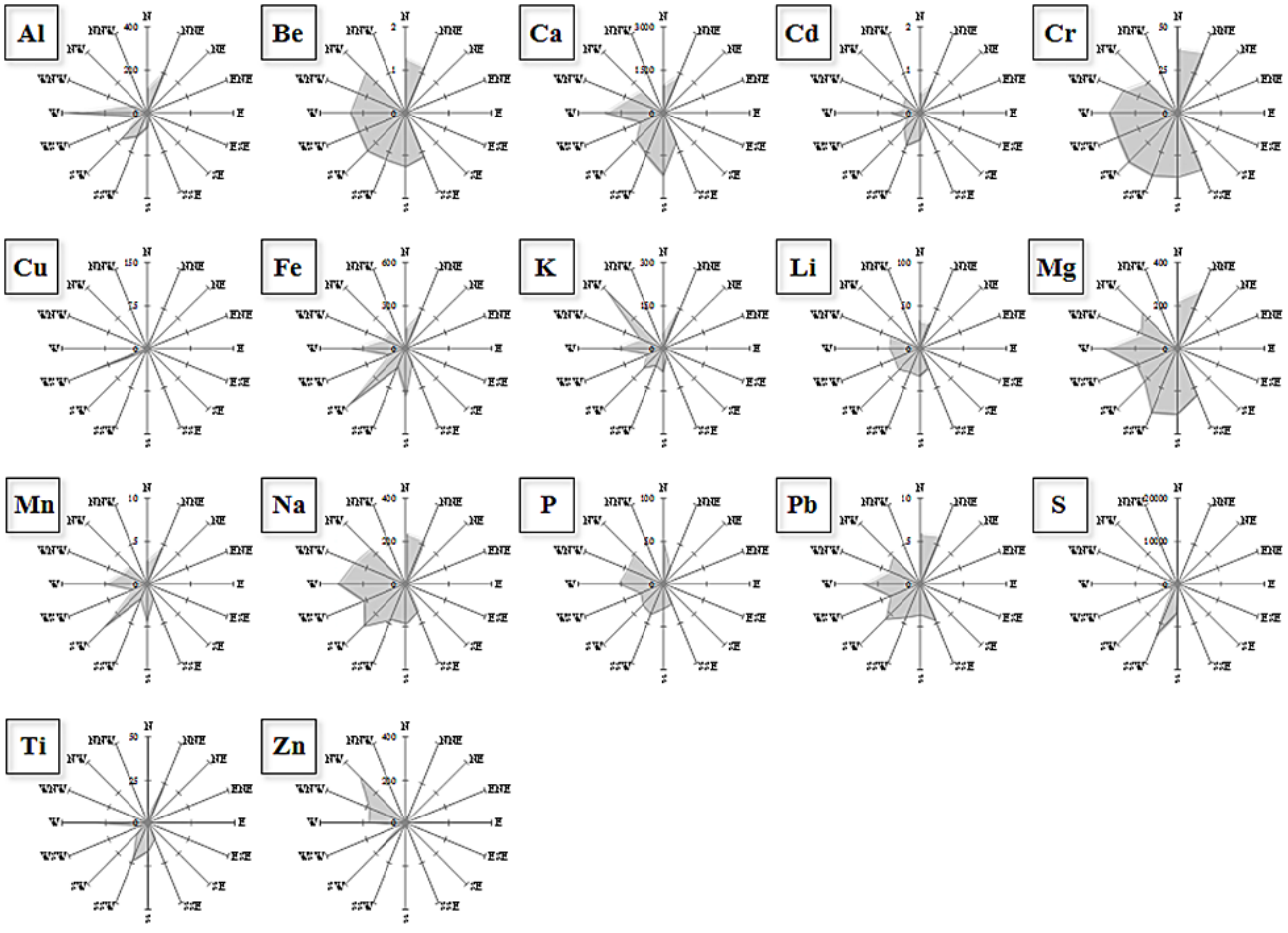

Figure 6. Mean values of the trace element concentrations (ng m^{-3}) as a function of the local wind direction.

4. high variability.

The first group includes Be, Cr and Li. These are the only three elements that do not show any variability as a function of the wind direction indicating sources uniformly distributed over the entire study area, a feature that belongs to the identified sources of these elements in the study area (i.e. vehicle emissions and fossil fuel combustion).

The second group includes Ca, Cd, Mg, Na, P and Pb. All of them do not show a marked increase along a specific direction. The observed low variability is consistent with the multiple sources of these elements identified in the area under study, that is, wood combustion processes and/or soil and road dust resuspension. All of them have in common a certain feature: they are characterised by a good spatial distribution.

The third group includes all the elements of prevailing natural origin (i.e. Al, Fe, K, Mn and Ti). All these elements are characterised by a quite similar variability and show inputs coming from preferential directions. In particular, the major sources of Al, Fe, Mn and Ti are in the SW and W directions, where cultivated and uncultivated soils are located, with contributions from the NNE direction as well. The latter are probably related to resuspension of dust from a soccer field made of bare artificial soil not covered by grass. K is the only element of prevailing natural origin that moves slightly away from this behaviour. In fact, it shows fairly homogeneous contributions from all the directions, except for a concentration peak observed along the NW direction. The uniformity of the contributions could be explained by considering that, in addition to crustal soil, domestic fires and open burning of grass and forest contribute to the presence of this element in the local atmosphere. These sources are widespread over the entire area, and this could justify its behaviour. Instead, the peak observed along the NW direction can be due to a forest fire occurring just along this direction during the study period.

The last group includes Cu, S and Zn. Cu shows a marked peak along the WSW direction and very low contributions from all the other directions, indicating the presence of a specific source of this element that has not been identified yet. Regarding S, it is interesting to note that the highest S concentrations are registered when wind comes from the SSW direction. The COVA plant is located just along this direction

and, considering that sulfur is known to be a typical tracer of refinery operations and residual oil combustion in all PM size ranges (Saffari et al., 2013), this confirms the occurrence of secondary atmospheric reactions of sulfur gaseous compounds emitted by the COVA plant and mineral aerosols. Finally, the major sources of Zn are in the NW direction. Along this direction, the urban centre of Viggiano is located. Viggiano is the closest place to the sampling site where the major contributions from traffic and residential wood burning are expected, and this could explain the observed variability.

4 Conclusions

For the first time, PM_1 measurements have been performed in an urban centre located close to an oil/gas pre-treatment plant. In particular, PM_1 and trace element concentrations were measured in Viggiano (Agri Valley – southern Italy) in September 2012. During the study period, the PM_1 daily mean concentration is $4.6\,\mu g\,m^{-3}$, a result lower than those found at other sites. By considering the PM_1 chemical composition, S, followed by typical crustal elements (i.e. Ca, Fe, Mg, Na, Al, and K), were the most abundant constituents of the inorganic species measured. The investigation of the main PM_1 emission sources performed by the integrated use of complementary tools such as the enrichment factor technique, principal component analysis, and the analysis of the concentration variability as a function of the different days of the week and the wind data, highlights the fact that emissions of crustal type, biomass and wood burning-related emissions, secondary atmospheric reactions involving COVA plant emissions and local soil particles, and both direct and indirect traffic-related emissions, can contribute to the PM_1 measured in the area under study. Moreover, a possible contribution of the long-range transport of African dust is observed. The results obtained give a preliminary but realistic picture of the emission features of the area, where anthropogenic activities both typical of little urban settlements and related to industrial plants where oil/gas processing occurs are placed in a rural context.

Moreover, they also highlight the need for long-term measurements of PM_1 concentrations and chemical composition in the area under study, in order to improve the present knowledge of PM_1, the identification of the PM_1 sources and the quantification of the relative contribution, and to study the long-term trends and seasonality of the PM_1 data.

PM_1 long-term measurements could also be useful for supporting other types of studies (e.g. epidemiological studies), and the government and regulatory bodies in their decision-making processes, like the development of effective emission reduction strategies or the authorisation of this type of plant in anthropised areas. In fact, several oil/gas pre-treatment plants will be built in similar areas (e.g. Centro Olio Tempa Rossa, Corleto Perticara – southern Italy) in the near future.

Acknowledgements. This work was carried out in the framework of the research agreement between Regione Basilicata – Osservatorio Ambientale della Val d'Agri and the Istituto di Metodologie per l'Analisi Ambientale (IMAA) of the National Research Council (CNR). The authors would like to thank Protezione Civile Gruppo Lucano-Viggiano for the logistic support and for providing meteorological data.

Edited by: F. Vallianatos
Reviewed by: two anonymous referees

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