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An integrated approach for the evaluation of technological hazard impacts on air quality: the case of the Val d'Agri oil/gas plant

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Abstract

The Val d'Agri area (southern Italy) hosts the biggest on-shore European reservoir and the largest oil/gas pre-treatment plant, named Centro Olio Val d'Agri (COVA), located in a rural/anthropized context. Several hazards are associated to this plant. These are mainly represented by possible impacts of the COVA atmospheric emissions on the local air quality and human health. This work uses a novel approach based on the integration of air quality measurements from the regional monitoring network, additional experimental measurements (i.e., sub-micrometric particulate matter – PM_1 and Black Carbon – BC) and advanced statistical analyses to provide a preliminary evaluation of the Val d'Agri air quality state and give some indications of specific areas potentially affected by COVA hazards. Results show that the COVA plant emissions exert an impact especially on the air quality of the area closest to it. In this area several pollutants specifically related to the COVA combustion processes (i.e., nitrogen oxides, benzene and toluene) show the highest concentration values and significant correlations. The proposed approach represents a first step in the assessment of the risks associated to oil/gas exploration and pre-treatment activities and a starting point for the development of effective and exportable air quality monitoring strategies.

1 Introduction

The Val d'Agri area (Basilicata region – southern Italy) is characterized by the peculiar coexistence of naturalistic features (woods and natural parks), large biodiversity, agricultural activities (cultivated and grazing areas), several small towns on one side, and anthropogenic activities with potential environmental and health impacts on the other. In fact, the Val d'Agri area houses the biggest on-shore European reservoir (crude oil and gas) and the largest existing oil/gas pre-treatment plant (identified as Centro Olio Val d'Agri – COVA) in an anthropized context. In this plant, the fluid extracted from the currently productive 25 wells is transported and separated into three phases: crude oil, natural gas and water. Then, the crude oil is stabilized and conveyed to the Taranto refinery (Puglia Region – southern Italy) through a 136 km long oil-pipeline. Instead, the natural gas is treated and delivered to the Italian gas distribution network (Snam Rete Gas S.p.A.). The COVA has a nominal treatment capacity of 16 500 $m^3 day^{-1}$ of crude oil and 3.1 million $S m^3 day^{-1}$ of associated gas and represents one of the main source of atmospheric pollution of the entire area. In fact, the combustion processes occurring in the COVA plant during normal operating conditions originate both gaseous and particulate emissions exerting possible impacts on the local air quality and also posing health risks to the population living close to this plant (Trippetta et al., 2013). Moreover, the activation of emergency operating procedures deriving from plant malfunctions and anomalies represents a further risk for the environment and human health due to additional and possibly enhanced emissions of atmospheric pollutants. Finally, the COVA plant is also classified as subject to considerable industry injury risk associated to accidental release of crude oil or methane, propane and other toxic products or to fire-raising from methane and crude oil (COVA plant External Emergency Plan, that can be consulted in Italian at http://www.osservatoriovaldagri.it/).

All this implies the need of an efficient monitoring of the air quality state in this area that should be carried out through the use of advanced and integrated observing strategies able to characterize and possibly quantify the environmental and human health impacts of such activity. In order to realize an effective near-real time monitoring of environmental hazards associated to the COVA emissions, an advanced network of five stations devoted to the air quality state control has been placed in the Val d'Agri area. This network is operated by the Agenzia Regionale per la Protezione dell'Ambiente (ARPA) of the Basilicata Region (ARPA Basilicata hereafter) and provides near-real time concentration measurements both of regulated pollutants (i.e., sulfur dioxide, carbon monoxide, nitrogen dioxide, nitrogen oxides, ozone, particulate matter, and benzene) and of several pollutants specifically related to oil/gas extraction and treatment activities (i.e., nitrogen monoxide, hydrogen sulfide, methane, non-methane-hydrocarbons, total hydrocarbons, toluene, ethylbenzene, and isomers of xylene). At our knowledge, this is the first air quality network which provides continuous concentration measurements of so many pollutants in a such small area also if it is compared for example with the very efficient observing network operating near the five refineries in the San Francisco Bay Area described in a recent comprehensive report by Fujita and Campbell (2013). More common observing strategies are mainly devoted to study Volatile Organic Compounds (VOCs) and sulfur dioxide near refineries (Baltrënas et al., 2011; Lin et al., 2008) or near industrial parks including petrochemical industries (Liu et al., 2008; Hsieh et al., 2006). Nevertheless, more efforts should be done. In fact, previous studies carried out in the Val d'Agri area suggested the need of the integration of the existing observations with experimental measurements of sub-micrometric aerosol particles (i.e., PM_1, aerosol particles with aerodynamic diameter less 1.0 µm) and Black Carbon (BC hereafter) due to their possible association with combustion processes such as those occurring in the COVA plant (Trippetta et al., 2013; Pavese et al., 2012). The importance of the measurement of PM_1 and BC is especially related to their adverse effects on environment and human health (e.g., Mohiuddin et al., 2014; Anenberg et al., 2011). Moreover, BC also contributes significantly to the global warming (Bond et al., 2013). Despite this, there is still a relatively limited amount of data for the sub-micrometer atmospheric particle fraction available at present (Mirante et al., 2013) and only recently national and local networks for carbonaceous fraction monitoring have been growing in many countries all over the world often employing aethalometers thanks to their good time-resolution, portability and low costs (see for example the US EPA network in Solomon et al., 2008, the UK Black carbon Network in Butterfield et al., 2010, and the Swiss National Air Pollution Monitoring Network – NABEL in EMPA, 2010).

The present study enters this context and its main goal is to provide a preliminary evaluation of the air quality state of the Val d'Agri area and to give some indications of specific areas potentially affected by hazards deriving from the COVA plant using a novel approach based on the integration of routine air quality measurements, additional experimental measurements and advanced statistical analyses.

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To this aim, as a preliminary phase, daily concentrations of the main pollutants measured at the five monitoring stations located in the Val d'Agri area in the period 1 September–31 October 2013 were considered and analyzed along with simultaneous concentration measurements of PM_1 and BC obtained at two of the five sampling sites and involving additional experimental facilities by the Istituto di Metodologie per l'Analisi Ambientale (IMAA) of the National Research Council of Italy (CNR). In particular, the temporal and spatial variability of the pollutant concentration measurements and the relative correlations were investigated using multivariate statistical techniques which also provided a preliminary indication about the source types contributing to their presence in the local atmosphere.

The possibility to integrate measurements from the existing monitoring network with further key parameters as PM_1 and BC and with an in-depth cluster and spatial variance analyses represents a powerful approach to study the COVA influence on the Val d'Agri environment. This will give useful indications to the stakeholders in order to develop better emission control strategies and to reach a sustainable equilibrium between the environmental impact of energy supply by oil/gas resources and the strong agricultural vocation of the area and to improve the standard livings for the Val d'Agri population.

2 Materials and methodologies

2.1 The ARPA Basilicata air quality monitoring network

The Val d'Agri air quality monitoring network consists of five monitoring stations, named Viggiano Zona Industriale (VZI), Viggiano 1 (V1), Masseria De Blasiis (MDB), Grumento Nova (GN) and Costa Molina Sud 1 (CMS). The monitoring stations are located at a distance ranging between about 500 m and about 4800 m from the COVA plant and are representative of the air quality of an area of about 100 km^2 around this plant (Fig. 1).

All the stations provide continuous and near real time measurements of the concentrations of sulfur dioxide (SO_2), carbon monoxide (CO), nitrogen monoxide and dioxide (NO and NO_2, respectively), nitrogen oxides (NO_x, that is the sum of NO and NO_2), ozone (O_3), hydrogen sulfide (H_2S), methane (CH_4), Non-Methane-HydroCarbons (NMHC), Total Hydro-Carbons (THC, i.e. the sum of CH_4 and NMHC), benzene (C_6H_6), toluene, ethylbenzene, and isomers of xylene. Moreover, V1, MDB, GN and CMS also provide continuous and near real time measurements of the concentrations of particulate matter with aerodynamic diameter less than 10 µm and 2.5 µm (PM_{10} and $PM_{2.5}$, respectively). Regarding VZI, it is equipped for the measurement of the PM_{10} concentrations only. These measurements are provided with a time lag of several months due to the instrumentation used (i.e., a gravimetric sampler). A summary of the methods used for the measurements of the concentrations of each pollutant is reported in Table 1.

All the air quality monitoring stations also provide measurements of the main meteorological parameters: air temperature (T), atmospheric pressure (P), relative humidity (RH), wind speed (ws) and direction (wd), global radiation (GR) and rainfall (rf).

2.2 Experimental PM_1 and BC measurements

PM_1 measurements were performed in Viggiano at about 170 m (SW direction) away from V1-ARPA Basilicata monitoring station (Fig. 1). This site was chosen since Viggiano is the nearest town to the COVA plant, at about 2400 m away from it, and one of the most populated town of the Val d'Agri area (about 3100 inhabitants). 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 12.00 p.m.), 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.

Regarding BC measurements, they were performed close to the COVA plant by placing a dedicated instrument at VZI – ARPA Basilicata monitoring station. This location was chosen for its closeness to the COVA where continuous combustion processes were thought to impact on BC content. A Rack-Mount 7-wavelenghts Magee Scientific Aethalometer AE31 (370, 470, 520, 590, 660, 880, 950 nm) was used to estimate BC mass concentrations and to detect the presence of its organic fraction through the UV-absorbing Particulate Matter (UVPM) quantity. The aethalometer measures light attenuation due to the presence of absorbing carbonaceous aerosol deposits on a quarz fiber filter (Hansen, 2005). Corresponding absorption coefficients are obtained at the 7 wavelengths and converted to mass concentrations with, in particular, measurements at 880 nm wavelength used to obtain BC content assuming a mass-specific absorption cross section of 16.6 $m^2 g^{-1}$ (Nair et al., 2012; Reche et al., 2011). If the organic component is present in carbonaceous aerosols, an enhanced absorption at the UV wavelengths is recorded, leading to a qualitatively detection of this component through measurements at 370 nm (Esposito et al., 2012). For the data considered in this work the instrument was equipped with a cut size-selective cyclone to intake particles with aerodynamic diameters less than 2.5 µm at a flow-rate of 4 $L\,min^{-1}$ and a time-resolution of 5 min.

2.3 Meteorology and air masses history

A summary of the main meteorological parameters averaged over the period 1 September–31 October 2013 is reported in Table 2 for the five monitoring stations.

Poor variations were observed for all parameters showing a quite homogeneous meteorological situation all over the study area. Looking at the prevailing wind directions, westerly winds were more frequent for all the sites except for VZI monitoring station where a south-eastern component was present. During the study period the area was affected by frequent anti-cyclonic systems as verified by the map of the 850 hPa geopotential heights obtained from the NOAA-NCEP/NCAR (National Oceanic and Atmospheric Administration – National Centers for Environmental Prediction/National center for Atmospheric Research) global reanalysis database (http://www.esrl.noaa.gov/psd/data/gridded/data.ncep.reanalysis.derived.html, Kalnay et al., 1996) (Fig. 2).

The same database was used to initialize HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory, Draxler and Rolph, 2003) model cluster analysis of backward trajectories in order to assess the main air masses transport patterns interesting the study area from 1 September to 31 October. In particular, five-day backward trajectories arriving at 500 m above ground level (a.g.l.) were computed 4 times daily and further put together in different clusters according to similar transport patterns. A map with the mean trajectory for each representative cluster and the corresponding percentage of occurrence is shown in Fig. 3. As Fig. 3 shows, 48 % of the total backward trajectories travelled very low before reaching the study area and among these, 45 % were of local origin remaining over the Tirrenian Sea. This could have favoured the accumulation of pollutants in the lowest atmospheric layers during the study period.

3 Results and discussion

3.1 Explorative statistical analysis

Table 3 reports a summary of the explorative statistical analysis carried out on the pollutant mean daily concentrations measured in the area under study from 1 September to 31 October 2013. Concentration measurements of ethylbenzene and isomers of xylene were not considered in this study due to the presence of several data missing. As Table 3 shows, significantly higher values of NO, NO_2, NO_x, C_6H_6 and toluene daily concentrations were registered at VZI monitoring station with respect to the other four stations. These compounds mainly originate from anthropogenic sources also including the COVA plant. In fact, NO_x and VOCs represent some of the main gaseous emissions of this plant (ENI, 2012). Therefore, the higher concentration values recorded at VZI monitoring station should be also related to a COVA contribution to their presence in the local atmosphere. Furthermore, CH_4 daily concentrations showed higher values at

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MDB monitoring station probably due to its proximity to several farms devoted to the dairy cow breeding. In fact, the livestock sector is one of the largest contributors to greenhouse gases emissions, mostly as CH_4 emissions, globally (Van Middelaar et al., 2014; Liang et al., 2013). Finally, higher H_2S concentration values were registered at CMS station.

Figure 4 reports the temporal pattern of the PM_1 daily concentrations. As Fig. 4 shows, the PM_1 daily concentrations ranged from 1.1 to 7.4 $\mu g\,m^{-3}$ with a mean value of 2.7 $\mu g\,m^{-3}$. Due to the lack of PM_1 measurements performed in the area under study during the considered period, these values were compared with the unique PM_1 concentration measurements presently existing for this area and reported in a previous study (Trippetta et al., 2013). Results show that the PM_1 daily concentrations registered during the period under consideration were lower than the PM_1 concentration mean value ($11.0 \pm 5.1\,\mu g\,m^{-3}$) measured close to the COVA plant from July to November 2011.

Daily values of BC and UVPM content are reported in Fig. 5. BC daily concentrations were found in the range from 288 $ng\,m^{-3}$ to 1125 $ng\,m^{-3}$ with a mean value of 551 $ng\,m^{-3}$. Also in the case of BC, a comparison was possible with the unique dataset of BC concentration measurements available for the area described in Pavese et al. (2012). In that case, a slightly lower monthly mean value of 494 $ng\,m^{-3}$ was obtained in February 2011, while higher mean monthly values of 822 $ng\,m^{-3}$, 735 $ng\,m^{-3}$ and 858 $ng\,m^{-3}$ were found in January, March and April 2011, respectively.

For UVPM, estimated values were included in the range from 2 $ng\,m^{-3}$ to 267 $ng\,m^{-3}$ with a mean value of 84 $ng\,m^{-3}$ implying a constant presence of the organic component of carbonaceous particles during the sampling period.

3.2 Cluster analysis

In order to study the correlation structure between the pollutant concentration data registered in each site and obtain a preliminary indication about the source types contributing to their presence in the local atmosphere, Cluster Analysis (CA) was used. In particular, a clustering algorithm of hierarchical type was applied to the Pearson correlation (ρ) matrix and the furthest neighbour method was chosen as criterion for forming clusters (Legendre and Legendre, 1985).

For this analysis, THC was considered as the sum of CH_4 and NMHC and NO_x as the sum of NO and NO_2 in order to avoid redundant information.

By applying the CA to the pollutant concentration data recorded at VZI monitoring site, three clusters and three isolated variables were found (Fig. 6a). In particular, the first cluster is composed of C_6H_6 and toluene, the second includes SO_2 and NO_x, the third consists of BC, UVPM and THC. CO, H_2S, and O_3 represent the isolated variables. By analysing each identified cluster, it can be observed that C_6H_6 and toluene, which belong to the aromatic VOCs group, show a good correlation ($\rho = 0.86$). This could suggest a common source of these two compounds in the considered area. Major sources of ambient VOCs, especially of benzene, toluene, ethylbenzene, and isomers of xylene (BTEX), include vehicular emissions, automobile service stations and industrial emissions (Caselli et al., 2010). In particular, the vehicular emissions come from different contributions: exhaust emissions (cold and hot), evaporative emissions, and emissions from brake and tyre wear. Among the BTEX industrial emissions, those related to the petroleum production processes represent an important source of these compounds (Godoi et al., 2013). Therefore, the presence of C_6H_6 and toluene in the local atmosphere of the Viggiano industrial area could be due to the contribution both of traffic and COVA emissions. Focusing on the second cluster, SO_2 and NO_x show a significant correlation ($\rho = 0.69$). These two gaseous compounds represent the main gases emitted by the COVA thermodestroyers (ENI, 2012). Therefore, the significant SO_2 and NO_x correlation could suggest the influence of the COVA emissions on the local air quality. Regarding the third cluster, a good correlation is found between BC and UVPM ($\rho = 0.53$) and between these two parameters and THC ($\rho = 0.45$). The formation of this cluster can be explained by incomplete combustion processes as a common source of all the three parameters and highlights the strong interaction between the particle phase represented by BC and the organic molecular species contained in UVPM. These molecules, quantitatively determined by THC concentration measurements, are verified to have a high probability to be adsorbed on BC particles surfaces (Kim et al., 2009). From concentration values in Table 3, it can be easily verified that more than 90 % of THC is constituted by methane so that a good correlation between BC, UVPM and CH_4 can be inferred from cluster analysis. Since the presence of methane in the local atmosphere of the area covered by VZI monitoring station is very likely related to the COVA combustion processes rather than traffic, the same prevailing source can be attributed to BC and UVPM emission at the sampling site under consideration.

By considering V1 monitoring site, the application of the CA to the pollutant daily concentration data pointed out three clusters and four isolated variables (Fig. 6b). Since the PM_1 monitoring site is very close to V1 monitoring station, it can be assumed that these two sites are representative of the same area implying that PM_1 measurements can be considered along with those performed at V1 monitoring station in CA. As Fig. 6b shows, the first cluster includes PM_{10} and $PM_{2.5}$, the second is composed of NO_x, C_6H_6 and toluene and the third consists of CO and THC. H_2S, O_3, PM_1, and SO_2 represent the isolated variables. Focusing on each single cluster, it can be observed that PM_{10} and $PM_{2.5}$ show the highest value of the correlation coefficient ($\rho = 0.93$). This indicates that they could share some sources and/or emission processes (Parmar et al., 2001). Due to the large number of sources emitting particulate matter in the considered area, the lack of the PM_{10} and $PM_{2.5}$ chemical characterisation, and the absence of significant correlations between $PM_{10}/PM_{2.5}$ and other pollutants, their main origin was not identified. Regarding the second cluster, NO_x and C_6H_6 are significantly correlated with each other ($\rho = 0.74$) and with toluene ($\rho = 0.65$). Moreover, focusing on the third cluster, it can be observed that CO and THC are characterised by a correlation coefficient of 0.54. All these compounds, although they are included into two separate clusters, could be originated from common sources. In fact, CO, NO_x, VOCs and hydrocarbons as NMHC are the main emissions of petrol and diesel-engine motor vehicles. Moreover CO, NO_x, VOCs and hydrocarbons, in this case as CH_4, are

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included among the main gaseous emissions of the COVA plant (ENI, 2012). If one considers that V1 monitoring station is located at about 5 m far from the main road connecting the industrial area with the town of Viggiano and at about 2300 m from the COVA plant, this cluster could reveal the influence of both traffic- and COVA plant-related emissions on the local atmosphere.

When applying the CA to the pollutant daily concentrations measured at MDB monitoring site, two clusters and four isolated variables are found (Fig. 6c). In particular, the first cluster is composed of PM_{10}, $PM_{2.5}$ and CO, the second includes C_6H_6, toluene and NO_x. H_2S, O_3, SO_2, and THC represent the isolated variables. By considering the correlation coefficients, it can be observed that PM_{10} and $PM_{2.5}$ are significantly correlated with each other ($\rho = 0.94$) and with CO ($\rho = 0.60$). A significant correlation between CO and PM measurements was found in areas affected by emissions coming from residential wood combustion (e.g., Bignal et al., 2008) and agricultural burning smoke (Gonçalves et al., 2011) and/or in sites exposed to traffic emissions (Perez et al., 2004). All these types of emissions characterise the area where MDB monitoring station is located. In fact, MDB is placed in a rural area where open burning of grass and forest is a common practice used for clearing field waste in farming and ranching. Moreover, MDB is about 1400 m far from a high-speed motorway (i.e., SS 598) characterised by a moderate volume of traffic consisting in cars and heavy vehicles. The proximity of the MDB monitoring station to the SS 598 could also justify the second cluster identified where C_6H_6 and toluene are significantly correlated with each other ($\rho = 0.86$) and with NO_x ($\rho = 0.60$). In fact, benzene and toluene are considered to be emitted from vehicle-related activity including vehicular exhaust and gasoline evaporation (Seco et al., 2013; Wang et al., 2012) while NO_x are significantly related to heavy-duty vehicle emissions (e.g., Fu et al., 2013).

Focusing on GN monitoring site, CA results pointed out two clusters and three isolated variables (Fig. 5d). In particular, the first cluster is composed of PM_{10} and $PM_{2.5}$, the second includes C_6H_6, toluene, NO_x, and THC. H_2S, O_3, and SO_2 represent the isolated variables. In particular, PM_{10} and $PM_{2.5}$ show the highest value of the correla-

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tion coefficient ($\rho = 0.91$) meaning that they are characterised by a similar behaviour. However no suggestion about their origin, and as a consequence no indication about the sources affecting the local air quality, is provided by CA in this case. Focusing on the second cluster, it can be observed that C_6H_6 and toluene are significantly correlated with each other ($\rho = 0.81$) and with NO_x ($\rho = 0.74$). Then, this group correlates with THC ($\rho = 0.53$). As found for V1 monitoring station, these correlations highlight the traffic- and COVA plant-related contributions that can be justified if it is considered that GN monitoring station is located in the suburbs of Grumento town where a contribution deriving from traffic is expected and it is at about 2800 m far from the COVA plant.

When applying the CA to the pollutant daily concentrations measured at CMS monitoring site, three clusters and three isolated variables are found (Fig. 6e). In particular, the first cluster is composed of PM_{10} and $PM_{2.5}$, the second includes C_6H_6, THC and toluene, the third is represented by CO and H_2S. NO_x, SO_2, and O_3 represent the isolated variables. By considering the correlation coefficients between the variables included in each cluster, it can be observed that PM_{10} and $PM_{2.5}$ show the highest value of the correlation coefficient ($\rho = 0.97$) but CA does not provide any suggestion about their origin also this case. Regarding the second cluster, C_6H_6 and THC are significantly correlated with each other ($\rho = 0.75$) and with toluene ($\rho = 0.48$). As found for V1 and GN monitoring stations, these correlations could be attributed to COVA plant-related contributions. Finally, focusing on the third cluster, it can be observed that CO and H_2S are correlated with each other ($\rho = 0.48$). This cluster very likely reveals the impact of the COVA emission in the local air quality probably deriving from the incomplete combustion of the natural gas in the system of torches of the plant.

3.3 Data spatial variance

In order to better assess the pollutant concentration spatial variability, a coefficient of divergence (COD) and the Pearson correlation coefficients (ρ) were calculated between the pollutant concentrations measured at the five air quality stations.

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Regarding the COD, it was calculated for each parameter and for each couple of stations to obtain an estimate of the dataset uniformity degree following Eq. (1)

$$\mathrm{COD}_{j,k} = \sqrt{\frac{1}{p}\sum_{i=1}^{p}[(x_{ij}-x_{ik})/(x_{ij}+x_{ik})]^2} \quad (1)$$

where x represents the daily concentrations and the i, j and k indexes refer respectively to the sampling day and to the two sampling stations (Wongphatarakul et al., 1998). The CODs can vary from zero (maximum degree of homogeneity) to one (minimum degree of homogeneity) for the considered pollutant concentrations measured at each pair of sampling sites.

COD and ρ values are reported in Tables 4 and 5, respectively.

A substantial homogeneity was observed for CH_4 and O_3 when they were compared to the other pollutants. In fact, they show low values of CODs and relatively high ρ values very likely due to their longer residence times in the atmosphere with respect to the other pollutants. This peculiar feature allowed a more uniform distribution of them over the entire area which was also favoured by frequent high pressure conditions characterising the considered period (see Fig. 2).

Focusing on the comparison between the CH_4 and O_3 concentrations measured at the five air quality stations, the higher COD and the lower ρ values found when the coupling with the MDB station was considered, confirm the peculiarity of this site for CH_4 production, as already reported in Sect. 3.1. Then, looking at the O_3 ρ values, the highest values were found when VZI and MDB stations were excluded from the coupling implying that these two stations are different from the others for what concerns ozone. This is in accordance with the lower mean values of O_3 found at VZI and MDB stations (see Table 3) where at the same time high concentration values of both NO_x and NMHC, the two well known main ozone precursors, are found. This confirms the larger probability to detect ozone enhancement in sites far from where it is formed through secondary processes (Li et al., 2013).

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Regarding PM_{10} and $PM_{2.5}$, a comparison was possible except for VZI station where no measurements were available for these two parameters. For the remaining stations, very low CODs and very high ρ values were obtained highlighting a spread and homogeneous diffusion of such pollutants over the study area. This could be due to common sources of these two parameters and their uniform presence in the local atmosphere could be also associated to the prevalence of high pressure systems over the area during the study period.

For benzene, toluene and nitrogen compounds, higher values of COD and correspondingly lower ρ values were found when the coupling with VZI station was considered. This can be attributed to an additional source of such compounds other than traffic present at VZI and related to the COVA emissions as previously assessed by the cluster analysis. Looking in particular at NO_x, benzene and toluene, good values of ρ and low values of COD were found when the other four stations were considered suggesting a common source of traffic in agreement with cluster analysis results.

Regarding SO_2, COD values did not show any particular trend while the lowest ρ values were found when MDB station was considered. In the case of H_2S, lowest ρ values were found for VZI coupling suggesting the presence of a source of this pollutant at the sampling site located close to the COVA plant. At the same time, the highest CODs correspond to the coupling with MDB station where particularly low mean values of this parameter were registered as reported in Table 3 probably due to the upwind position of this station with respect to the COVA (see Fig. 1 and Table 2 where prevailing wind direction are mentioned).

As to CO, a lack of homogeneity was present for all the stations. This, in agreement with what found by cluster analysis, reflects the presence of several different sources of CO in the area including COVA emissions, traffic and combustion processes related to agricultural activities.

Finally, when NMHC are considered, a lack of homogeneity was present for all the stations probably due to their short time of residence in the atmosphere.

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4 Conclusions

Daily pollutant concentrations available in the Val d'Agri area for the period 1 September–31 October 2013 were considered and analyzed along with simultaneous concentration measurements of PM_1 and BC obtained involving additional experimental facilities. In particular, the temporal and spatial variability of the pollutant concentration measurements and the intra- and inter-site correlations were investigated using multivariate statistical techniques. Preliminary indications about the source types contributing to the presence of pollutants in the local atmosphere and some indications about specific areas potentially affected by hazards deriving from the COVA plant have been also provided. Results show that the COVA plant emissions exert an impact on the air quality over the entire area. These impacts have been mainly revealed in the area closest to the COVA plant represented by VZI station. Moreover, the area where CMS monitoring station is located seems also to be significantly affected by the COVA plant-related emissions. Focusing on VZI station, it can be observed that several pollutants specifically related to the combustion processes occurring in this plant (i.e., NO_x, benzene and toluene) show the highest concentration values and significant correlations. In particular, the significant correlation found between BC and UVPM content and THC (mainly constituted by CH_4) could indicate the COVA incomplete combustion processes as a source of carbonaceous compounds in this area and highlights the role of BC as a vehicle for organic compounds in the environment. Regarding CMS station, the impact of the COVA emissions in the local air quality is probably deriving from the incomplete combustion of the natural gas in the system of torches of the plant. Traffic represents an additional and important source of atmospheric pollutants over the entire area. Moreover, the contribution of emission deriving from dairy cow breeding and agricultural-related activities has been found in the area where MDB monitoring station is located. This is in fair agreement with the prevailing rural features of this area. Results also show that PM_1 is not correlated with any pollutant suggesting the need of further investigation on this parameters so as to define its main origin. Regarding the

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inter-site variability of the pollutant concentrations, a substantial homogeneity was observed for CH_4, O_3, PM_{10} and $PM_{2.5}$ when they were compared to the other pollutants. This is probably due to peculiar features of these pollutants (referring to CH_4 and O_3), probable common sources (referring to PM_{10} and $PM_{2.5}$) and the prevalence of high pressure systems over the area during the study period (for all of them). Focusing on the single air quality station, COD and ρ values confirm the presence of an additional CH_4 source in the area where MDB station is located. Moreover, a difference among VZI and MDB stations and the remaining stations is observed if O_3 is considered. Finally, a confirmation of remarkable differences between VZI station and the others has been found when concentration values of NO_x, benzene, toluene and H_2S are considered.

In conclusion, the present study preliminarily highlights that a novel approach based on the integration of routine air quality measurements, innovative experimental measurements and advanced statistical analyses is suitable to give a realistic picture of the emission features of the area and to distinguish areas mainly affected by the COVA plant emissions. This methodology represents an attempt to build an integrated observing strategy applicable to other similar industrial sites.

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Table 1. Summary of the methods used for the measurements of the concentrations of each pollutant.

Parameter	Measurement principle
SO_2	UV fluorescence
NO	Chemiluminescence
NO_2	Chemiluminescence
NO_x	Chemiluminescence
$PM_{2.5}$	Beta attenuation[1]
PM_{10}	Beta attenuation[1]/gravimetric[2]
O_3	UV absorption
CO	Non dispersive IR detection (NDIR)
C_6H_6	Gas chromatography with Photo Ionization Detector (GC-PID)
H_2S	UV fluorescence
CH_4	Photo Ionization Detection (PID)
NMHC	Photo Ionization Detection (PID)
THC	Photo Ionization Detection (PID)
Toluene	Gas chromatography with Photo Ionization Detector (GC-PID)
Ethylbenzene	Gas chromatography with Photo Ionization Detector (GC-PID)
Isomers of xylene	Gas chromatography with Photo Ionization Detector (GC-PID)

[1] V1, GN, MDB and CMS monitoring stations.
[2] VZI monitoring station.

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Table 2. Mean ± standard deviation (m ± sd) of the main meteorological parameters measured at the five air quality monitoring stations from 1 September to 31 October 2013. Regarding the wind direction (wd), the prevailing directions evaluated for the entire period of observation are reported.

Monitoring station	T (°C)	RH (%)	P (hPa)	ws ($m\,s^{-1}$)	Prevailing wd	GR ($W\,m^{-2}$)	rf (mm)
VZI	17 ± 3	74 ± 9	946 ± 4	1.2 ± 0.5	SE/SW	174 ± 59	1.8 ± 3.9
V1	17 ± 2	66 ± 11	933 ± 4	3.4 ± 1.6	SW/NW	159 ± 55	1.4 ± 4.3
MDB	16 ± 3	75 ± 8	948 ± 4	3.1 ± 1.6	NW	149 ± 47	1.1 ± 3.5
GN	17 ± 3	64 ± 11	932 ± 4	2.4 ± 1.3	SW	106 ± 42	0.1 ± 0.6
CMS	18 ± 3	73 ± 11	939 ± 4	3.7 ± 1.7	NW	167 ± 58	1.3 ± 3.8

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Table 3. Statistical parameters of the atmospheric pollutant daily concentrations measured at the five air quality monitoring stations from 1 September to 31 October 2013. Mean ± standard deviation (m ± sd) and the range of variability (min–max) are reported for each pollutant. Legend: n.a. = not available.

Parameter	m.u.	ARPA Basilicata monitoring stations				
		VZI	V1	MDB	GN	CMS
SO_2	$\mu g\,m^{-3}$	5.61 ± 1.88 (3.31–12.39)	6.74 ± 0.77 (5.34–10.68)	7.56 ± 1.08 (5.07–9.83)	3.69 ± 1.00 (1.91–6.85)	3.41 ± 1.30 (1.31–7.13)
NO	$\mu g\,m^{-3}$	5.05 ± 1.83 (2.34–8.42)	1.03 ± 0.44 (0.12–2.48)	1.31 ± 0.64 (0.38–3.38)	0.98 ± 0.48 (0.18–2.60)	0.73 ± 0.40 (0.16–1.66)
NO_2	$\mu g\,m^{-3}$	12.63 ± 4.30 (6.45–25.26)	4.36 ± 1.96 (1.09–13.32)	4.89 ± 1.34 (2.62–7.95)	3.62 ± 1.54 (0.44–7.03)	3.49 ± 1.30 (0.46–7.25)
NO_x	$\mu g\,m^{-3}$	20.35 ± 6.63 (9.95–37.96)	5.94 ± 2.36 (2.21–17.12)	6.89 ± 1.98 (3.21–11.84)	5.13 ± 2.05 (1.22–9.33)	4.60 ± 1.75 (0.85–9.19)
PM_{10}	$\mu g\,m^{-3}$	n.a.	16.09 ± 6.35 (6.12–36.63)	20.97 ± 7.21 (11.50–39.40)	15.25 ± 5.16 (5.80–25.80)	18.31 ± 5.68 (8.91–36.00)
$PM_{2.5}$	$\mu g\,m^{-3}$	n.a.	8.99 ± 4.03 (3.30–22.20)	11.69 ± 4.59 (3.80–21.90)	8.74 ± 3.73 (2.90–16.40)	8.63 ± 3.94 (2.50–18.80)
O_3	$\mu g\,m^{-3}$	58.68 ± 14.32 (25.96–90.34)	82.73 ± 13.72 (50.28–116.38)	48.76 ± 14.76 (18.24–81.21)	85.32 ± 15.48 (47.07–124.72)	69.99 ± 14.57 (37.57–104.31)
CO	$mg\,m^{-3}$	0.34 ± 0.11 (0.17–0.58)	0.17 ± 0.05 (0.05–0.40)	0.15 ± 0.03 (0.10–0.22)	0.33 ± 0.08 (0.11–0.60)	0.22 ± 0.05 (0.09–0.30)
C_6H_6	$\mu g\,m^{-3}$	0.91 ± 0.16 (0.63–1.44)	0.30 ± 0.11 (0.12–0.52)	0.28 ± 0.11 (0.08–0.60)	0.17 ± 0.10 (0.03–0.49)	0.22 ± 0.07 (0.10–0.39)
Toluene	$\mu g\,m^{-3}$	1.01 ± 0.38 (0.50–2.27)	0.43 ± 0.19 (0.12–0.97)	0.34 ± 0.15 (0.13–0.81)	0.19 ± 0.10 (0.05–0.43)	0.24 ± 0.08 (0.12–0.43)
CH_4	$\mu g\,C\,m^{-3}$	958.03 ± 34.99 (887.0–1038.0)	902.69 ± 16.75 (874.0–946.0)	1114.94 ± 95.97 (972.00–1609.00)	944.44 ± 33.21 (814.00–1005.00)	911.92 ± 26.57 (856.00–978.00)
NMHC	$\mu g\,C\,m^{-3}$	103.26 ± 108.59 (27.75–563.58)	24.08 ± 9.08 (4.04–44.69)	103.02 ± 81.56 (0.89–342.68)	146.05 ± 10.85 (121.75–164.59)	65.08 ± 23.81 (4.87–111.84)
THC	$\mu g\,C\,m^{-3}$	1060.97 ± 90.91 (979.16–1455.15)	926.81 ± 23.03 (881.84–980.90)	1217.50 ± 116.53 (1065.88–1949.11)	1094.41 ± 39.38 (959.69–1169.32)	976.84 ± 21.93 (934.32–1018.41)
H_2S	$\mu g\,m^{-3}$	1.87 ± 0.37 (0.99–2.71)	1.80 ± 0.43 (1.02–2.79)	0.56 ± 0.36 (0.10–2.14)	1.59 ± 0.50 (0.50–3.14)	2.72 ± 0.47 (1.07–3.74)

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Table 4. Coefficients Of Divergence (CODs) calculated for each pollutant and each couple of stations. Legend: n.c. = not calculable.

COD	VZI/V1	VZI/CMS	VZI/GN	VZI/MDB	V1/CMS	V1/GN	V1/MDB	CMS/GN	CMS/MDB	GN/MDB
SO_2	0.17	0.31	0.26	0.24	0.38	0.32	0.11	0.18	0.43	0.37
NO	0.66	0.75	0.68	0.60	0.32	0.30	0.28	0.30	0.38	0.29
NO_2	0.52	0.57	0.56	0.44	0.21	0.23	0.18	0.19	0.19	0.23
NO_x	0.56	0.63	0.60	0.49	0.20	0.19	0.17	0.16	0.22	0.21
PM_{10}	n.c.	n.c.	n.c.	n.c.	0.10	0.08	0.16	0.12	0.10	0.17
$PM_{2.5}$	n.c.	n.c.	n.c.	n.c.	0.16	0.10	0.16	0.12	0.24	0.16
O_3	0.19	0.10	0.20	0.10	0.09	0.03	0.28	0.11	0.19	0.29
CO	0.36	0.27	0.17	0.40	0.21	0.35	0.16	0.25	0.20	0.39
C_6H_6	0.46	0.60	0.67	0.51	0.19	0.36	0.13	0.31	0.18	0.33
Toluene	0.45	0.60	0.67	0.50	0.33	0.43	0.21	0.24	0.22	0.32
CH_4	0.03	0.03	0.02	0.08	0.01	0.03	0.11	0.02	0.10	0.09
NMHC	0.54	0.29	0.44	0.52	0.50	0.73	0.62	0.45	0.50	0.56
THC	0.08	0.06	0.05	0.09	0.03	0.08	0.14	0.06	0.11	0.07
H_2S	0.20	0.23	0.23	0.60	0.24	0.21	0.58	0.32	0.69	0.55

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Table 5. Pearson correlation coefficients (ρ) calculated for each pollutant and each couple of stations. Legend: n.c. = not calculable.

ρ	VZI/V1	VZI/CMS	VZI/GN	VZI/MDB	V1/CMS	V1/GN	V1/MDB	CMS/GN	CMS/MDB	GN/MDB
SO_2	0.31	0.29	0.002	−0.26	0.40	0.50	−0.14	0.4	−0.31	−0.22
NO	0.04	0.37	0.15	0.32	0.37	0.19	0.27	0.55	0.41	0.18
NO_2	−0.44	−0.22	−0.34	−0.20	0.53	0.54	0.49	0.60	0.60	0.71
NO_x	−0.33	−0.02	−0.12	0.03	0.55	0.53	0.43	0.60	0.63	0.55
PM_{10}	n.c.	n.c.	n.c.	n.c.	0.92	0.89	0.87	0.85	0.86	0.89
$PM_{2.5}$	n.c.	n.c.	n.c.	n.c.	0.91	0.91	0.88	0.87	0.87	0.93
O_3	0.90	0.95	0.89	0.93	0.97	0.98	0.84	0.96	0.91	0.85
CO	−0.08	0.12	0.19	0.22	−0.07	0.06	0.02	0.25	0.59	0.31
C_6H_6	0.50	0.55	0.4	0.48	0.7	0.74	0.73	0.64	0.72	0.76
Toluene	−0.16	0.17	−0.15	0.05	0.67	0.72	0.59	0.67	0.65	0.71
CH_4	0.55	0.89	0.63	0.37	0.63	0.49	0.37	0.74	0.37	0.20
NMHC	−0.39	0.48	−0.54	0.25	0.11	0.77	0.22	−0.05	0.54	0.23
THC	−0.38	−0.14	−0.42	−0.09	0.62	0.65	0.53	0.63	0.39	0.34
H_2S	−0.09	−0.19	−0.16	−0.2	0.07	0.12	0.24	0.12	0.09	0.15

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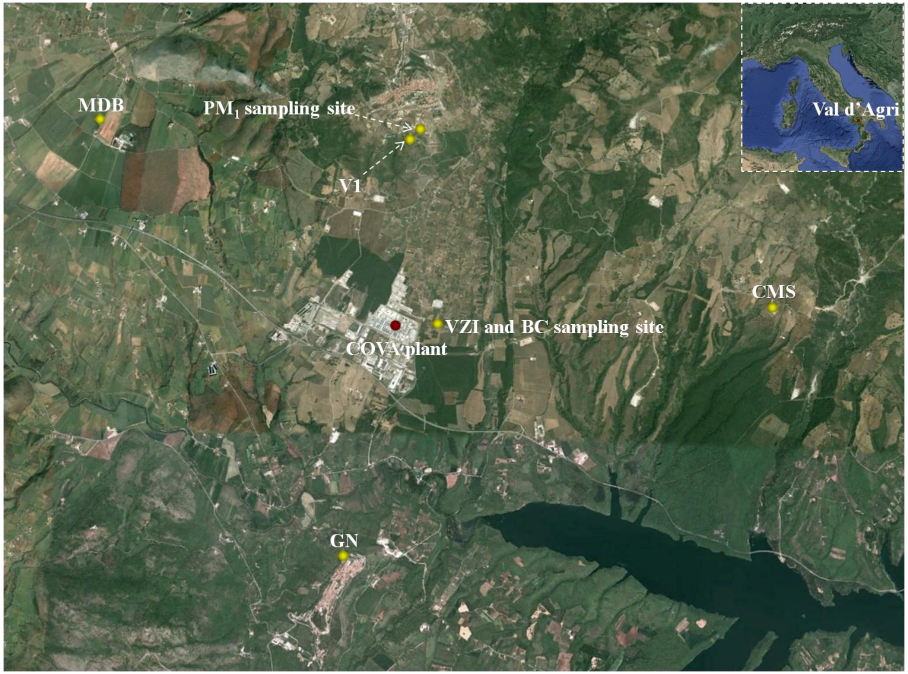

Fig. 1. Location of the five stations of the ARPA Basilicata air quality monitoring network. The image also reports the location of the BC and PM_1 sampling sites and of the Centro Olio Val d'Agri (COVA) plant. Aerial photography to courtesy of Google Earth (http://earth.google.com/). Legend: Viggiano Zona Industriale (VZI), Viggiano 1 (V1), Masseria De Blasiis (MDB), Grumento Nova (GN) and Costa Molina Sud 1 (CMS).

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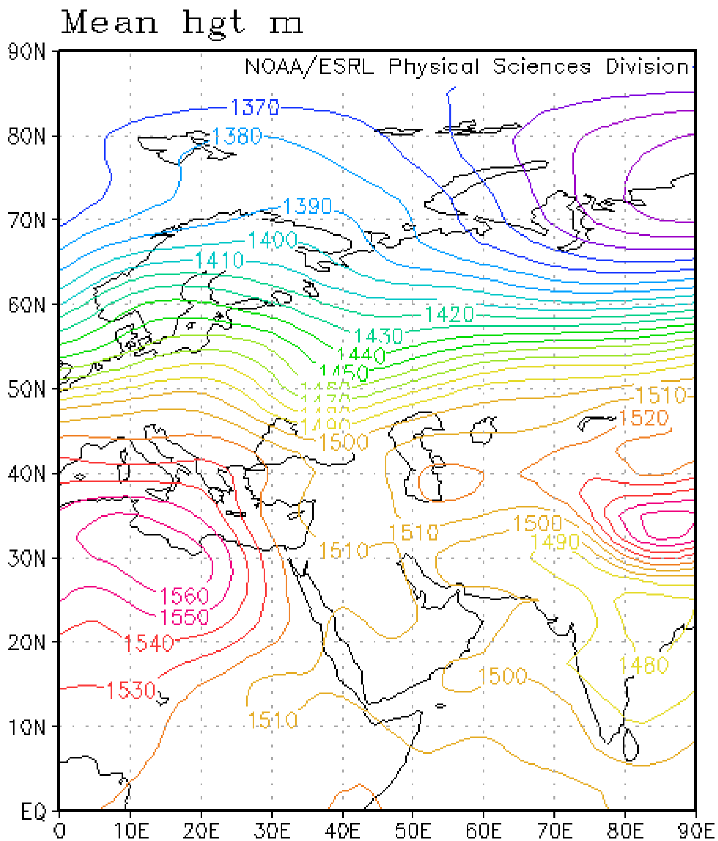

Fig. 2. Map of the 850 hPa geopotential heights averaged for the period 1 September–31 October from NOAA-NCEP/NCAR (National Oceanic and Atmospheric Administration – National Centers for Environmental Prediction/National center for Atmospheric Research) Reanalysis Database.

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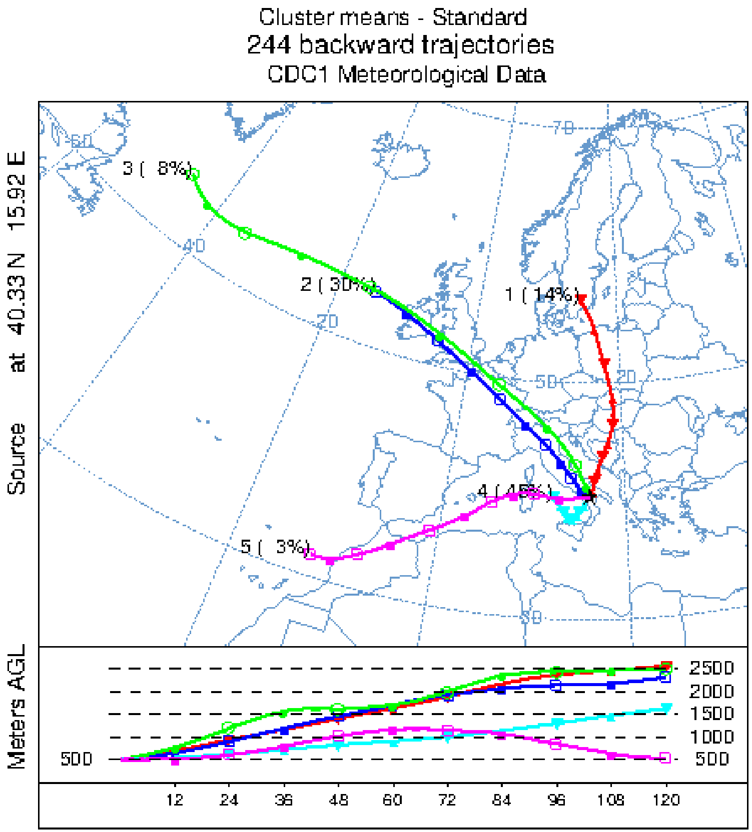

Fig. 3. Maps with average trajectories for each obtained cluster and corresponding percentage of occurrence (given in brackets) for the period 1 September–31 October. The numbers outside the brackets identify each cluster.

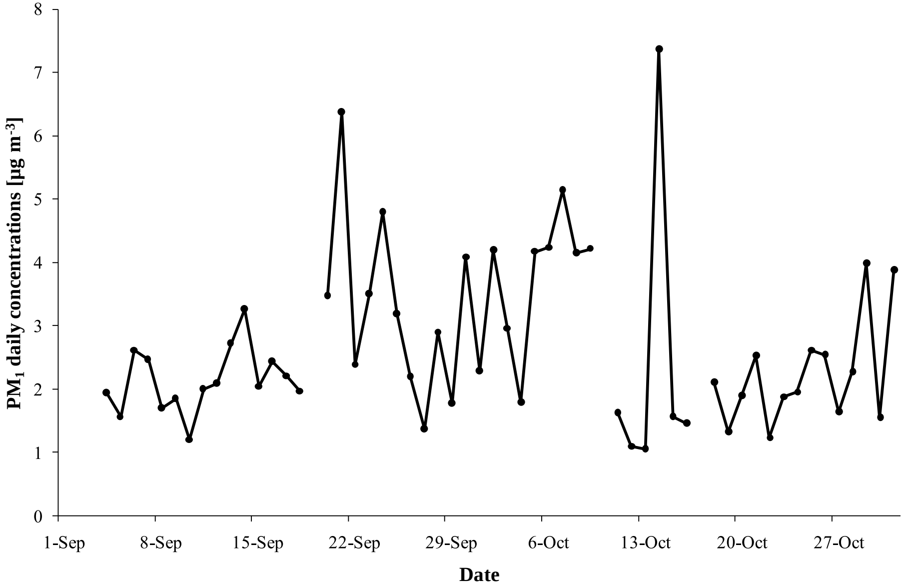

Fig. 4. Temporal pattern of the PM_1 daily concentrations measured at Viggiano town from 1 September to 31 October 2013.

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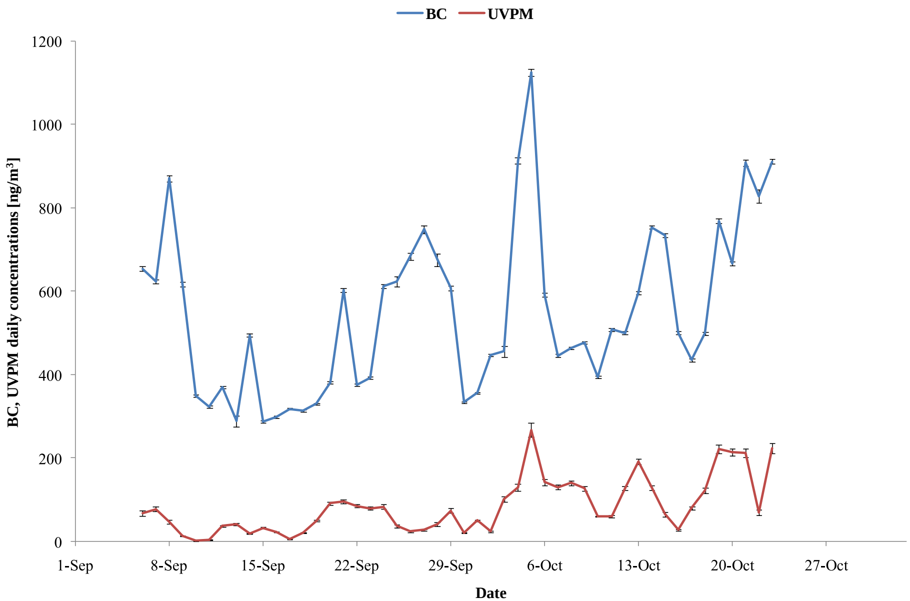

Fig. 5. Temporal patterns of daily values of Black Carbon (BC) and UV-Particulate Matter (UVPM) content obtained at Viggiano Zona Industriale (VZI) station from 6 September to 23 October 2013.

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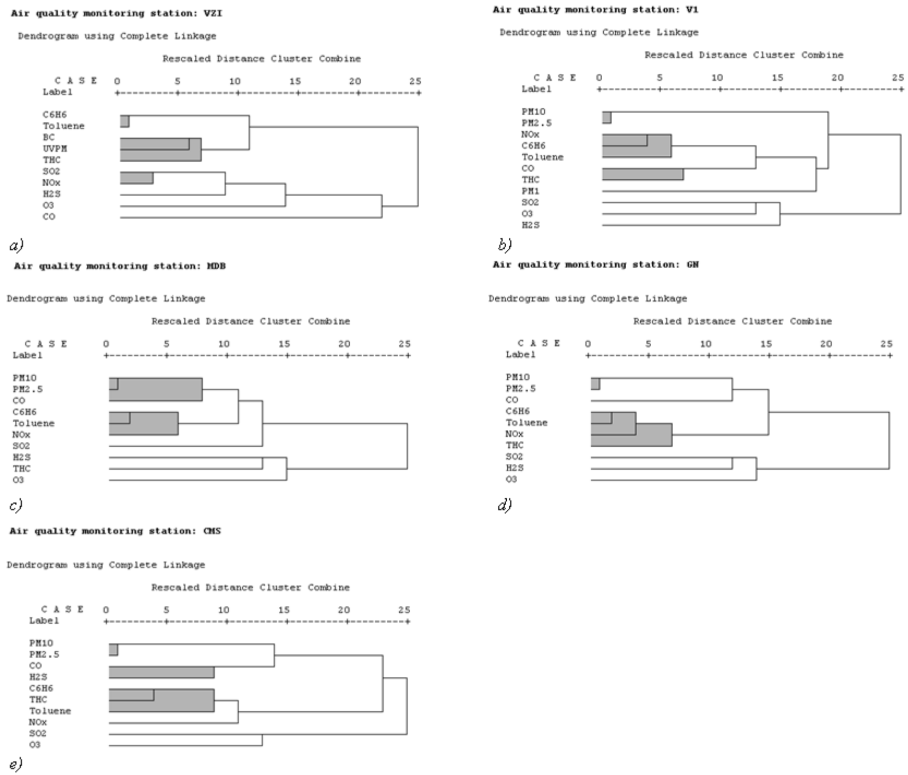

Fig. 6. Dendrograms obtained by applying the furthest neighbour clustering method to the pollutant concentration data recorded at: **(a)** VZI monitoring site, **(b)** V1 monitoring site, **(c)** MDB monitoring site, **(d)** GN monitoring site and **(e)** CMS monitoring site. The clusters are represented in grey.

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