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Sources and chemical characterization of aerosol particles in Agri Valley (Southern Italy): development of environmental indicators

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Abstract

Atmospheric aerosols are one of the most challenging environmental issues mainly due to their adverse effects on air quality and human health (Pateraki et al., 2014). In the framework of INDICARE (Indexing of regional environmental criticalities) project an integrated approach including chemical, geochemical, and mineralogical composition of atmospheric aerosol particles was used to developed environmental indicators to assess the possible natural and/or anthropogenic contributions to the finer atmospheric aerosol particles PM_1 (aerosol particles with aerodynamic diameter less than 1 μm), relating to both local and long-range transport emissions. Measurements were performed in Agri Valley (Basilicata Region – Southern Italy). This is an area of international concern since it houses one of the largest European on-shore reservoirs and the biggest oil/gas pre-treatment plant (i.e., Centro Olio Val d'Agri – COVA) within a natural (Appennino Lucano – Val d'Agri – Lagonegrese National Park) and anthropized context, of about 50,000 inhabitants. Daily PM_1 mass concentrations, 16 trace elements (i.e., Al, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, S, Ti and Zn), geochemical and mineralogical composition of individual aerosol particles were performed. The Principal Component Analysis (PCA) was used to identify the main PM_1 sources. The Hybrid Single Particle Lagrangian Integrated Trajectory model (HYSPLIT) of the National Oceanic and Atmospheric Administration (NOAA) (https://www.ready.noaa.gov/HYSPLIT.php) was used to assess the origin and the path of the incoming air masses over the study area. Special event (i.e., Saharan dust event, gas flaring, shutdown COVA activities) occurred during the study period were considered. Environmental indicators based on the concentration ratios between the trace elements measured in PM_1 were identified. The Ti/Fe ratio was a good indicator of natural contribution to the measured PM_1, whereas (Ni+Pb)/(Cd+Cr) ratio was a good indicator of the anthropogenic

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contribution to the measured PM_1 represented by traffic and industrial activities mainly related to the extraction of hydrocarbons and their pre-treatment in the COVA plant.

Keywords: PM_1; Chemical Analysis; Morphological analysis; Environmental Indicators; SEM/EDX

1. Introduction

Atmospheric particulate matters (PM) are composed by solid and liquid particles suspended in the atmosphere (aerosol). Particles can be produced and released into the atmosphere through both natural (e.g, soil erosion, marine spray, volcanic eruptions) and/or anthropogenic sources (e.g., traffic, energy production plants, home heating, industrial processes) (Jandacka et al., 2019; Cáceres et al., 2019; Almeida et al., 2006; Mazzera et al., 2001). The particles size ranges from a few nanometers up to values of tens of micrometers. PM_1 (i.e., aerosol particles with aerodynamic diameter less 1.0 μm) is a major concern due to its adverse effects on the environment, air quality and human health (Caggiano et al., 2019; Pateraki et al., 2014; Fuzzi et al., 2015). In particular, the health effects induced by atmospheric particulate matter observed through epidemiological and toxicological studies using reference cell models, have shown a strong correlation between an increase in the PM levels and an increase in both acute and chronic pulmonary and cardiovascular diseases and mortality (Samoli et al., 2016; Karottki et al., 2014; Samet et al., 2000). Despite having negative effects on human health and the environment (Wang et al., 2014; Galindo et al., 2013), PM_1, unlike the coarse (PM_{10}) and fine ($PM_{2.5}$) fractions, which have been the subject of numerous scientific studies, is still little studied today. In particular, the knowledge on detailed fine atmospheric aerosol composition and the identification of its possible sources represent an important issue. In this context the present study focuses on PM_1 size fraction (also known as ultrafine fraction) whose chemical composition, given its peculiar and prevalent anthropic origin, is characterized by the presence of numerous trace elements of significant health interest (i.e,. As, Cd, Cr, Hg, Ni, Pb). The compositional features are fundamental in understanding the mechanisms of aerosol formation and transformation and in the distinction between natural and anthropogenic origin of the particulate. The present work was performed in the framework of the INDICARE (Indexing of regional environmental criticalities) project. The identification of the main PM_1 source profiles and the development of environmental indicators were performed by integrating chemical data, statistical analysis, back-trajectories analysis, morphological and mineralogical observations. The study was conducted in Val d'Agri (Basilicata, Southern Italy). This valley is surrounded by mountains, the prevailing land uses are agriculture, pasture, and woodland. At same time, the Agri Valley homes the biggest European on-shore reservoirs and one of the largest oil/gas pre-treatment plants within an anthropized area. In this plant, called ENI Centro Olio Val d'Agri (COVA), the crude oil extracted is processed (i.e., oil stabilization by gas desulfurization, H_2S conversion into liquid S, and gas dehydration) implying continuous gaseous and particulate emissions in atmosphere. The COVA covers an area of 180.000 m^2 and produces 104.000 barrels of oil per day (the nominal treatment capacity of the entire plant is 16.000 m^3g^{-1} of crude oil and 4.666.000 Sm^3g^{-1} of associated gas) (ENI Local Report, 2014). PM_1 daily samples were collected and their chemical, geological and mineralogical compositions were assessed.

2. Sampling and methods

PM_1 measurements were performed at Viggiano (40°20′ N, 15°54′ E, 975 m a.s.l) (Fig.1). This site was chosen because closest to the COVA plant, about 2.4 km away from it, and because is one of the most populated towns of the Val d'Agri.

Fig. 1. Location of the COVA plant and of the measurement site. Satellite maps courtesy of Google Earth (http://earth.google.com)

Daily PM_1 mass concentrations and 16 trace elements (i.e., Al, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, S, Ti and Zn) PM_1-related were assessed from June 2014 to March 2015. PM_1 aerosol particles were collected using a low volume gravimetric sampler. The trace element concentrations were measured by means of an Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Varian – Vista MPX) or an Atomic Absorption Spectrometry Furnace Graphite (GFAAS). Morphological and chemical analyses were performed on individual particles with great accuracy by means of a Field Emission Scanning Electron Microscope (FESEM, Zeiss Supra 40) coupled with Energy Dispersive X-ray analyses (EDX – Oxford x-act Silicon Drift Detector SDD) with Inca Energy 350 analysis software. Collected samples were carbon-coated and the presence of carbon and oxygen in the polycarbonate filters did not allow to consider elements with atomic number Z</= 8.

The Hybrid Single Particle Lagrangian Integrated Trajectory model (HYSPLIT) of the National Oceanic and Atmospheric Administration (NOAA) (https://www.ready.noaa.gov/HYSPLIT.php) was used to assess the origin and the path of the incoming air masses over the study area.In particular, 120-h back trajectories arriving at 500 m above ground level (a.g.l.) were calculated four times per day (ie.,00:00, 06:00, 12:00, and 18:00) and were identify as "*Marine*" which include long-lasting air masses (more than 3 days) before approaching the studied site, "*Saharian*" that takes into account air masses starting from the Saharan desert and "*NW and NE Continental"* that consist of air masses originating in the North-East or North-West Europe and passing through the European Countriesand generally arriving on our site without crossing the sea.

3. PM_1 measurements and source profiles identification

The PM_1 daily concentrations measured in Agri Valley from June 2014 to March 2015 range from 3 to 16 µg m^{-3} with a mean and a median value of 6 and 5 µg m^{-3}, respectively.

The observed values are generally higher than those measured at a background site, comparable or lower than those found in the urban area but lower than other industrial area (Mbengue et al., 2017; Alastuey et al., 2006; Squizzato et al., 2016; Caggiano et al., 2001).

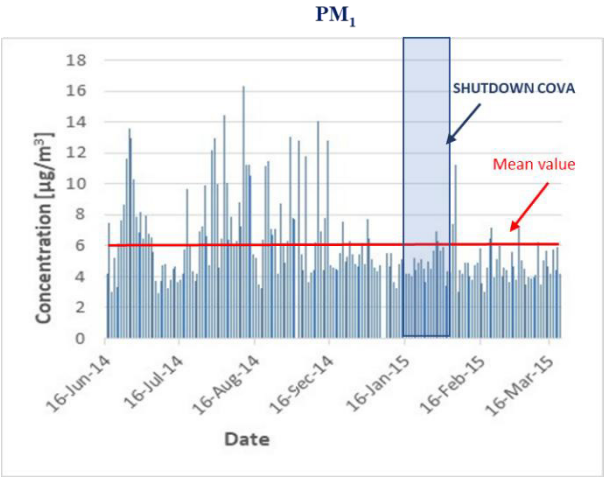


Fig. 2. PM_1 daily concentration recorded in Viggiano from June 2014 to March 2015

As regards the 16 trace elements (i.e., Al, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, S, Ti, Zn) analyzed, we can observe that S, Ca, Na, Mg and K showed the higher average concentrations with values > 100 ng m^{-3}. Fe, Al, Li and Cr showed a moderate abundance with concentrations ranging from 20 to 100 ng m^{-3}. Zn, Ti, Ni, Cu, Mn and Pb showed mean concentrations < 20 ng m^{-3}. Finally, Cd was the only trace element with concentration below 1 ng m^{-3}, see Fig. 3.

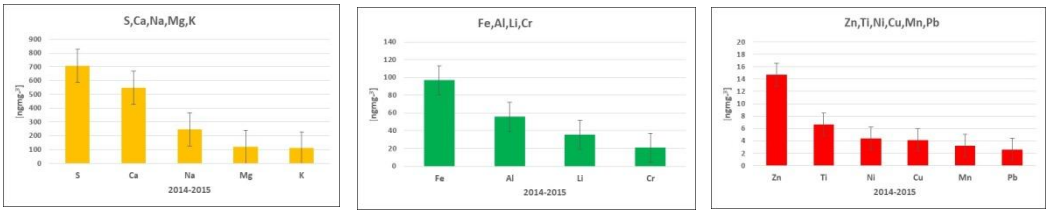


Fig. 3. Trace elements average concentrations

To identify the possible anthropogenic and natural sources profiles of the trace elements, Principal Component Analysis (PCA) was performed. The PCA is a multivariate statistical technique widely applied to study the correlation structure among the different

atmospheric pollutants and identify the likely sources (Okubo et al., 2013; Yatkin & Bayram, 2007). Results show that the first component (PC_1), includes K, Li and Mg that are elements mainly related to biomass burning sources such as cooking fires, post-harvest crop residue burning. The dominant trace elements, Al, Fe, Mg and Ti, present in the second component (PC_2) are generally related to natural sources such as soil dust particles and natural sources from long-range transport such as Saharan dust. Finally, we found tree anthropogenic components (PC_3, PC_4, and PC_5) including Ca, Na, S, PM, Cd, Cr, Zn, Cu, Ni and Pb that are elements typical of anthropogenic sources such as industrial and traffic sources. Because the COVA is the major industrial plant present in the study area, we can conclude that the third component is mainly correlated to COVA activities. These results agree with the local anthropogenic sources and with industrial emissions located in the sampling site.

Table 1. Loading of each species to the five component PCA results. Loadings with values higher than 0.5 are reported in bold. PC = varimax loadings, P% = percentage of explained variance; CP% = cumulative percentage of explained variance

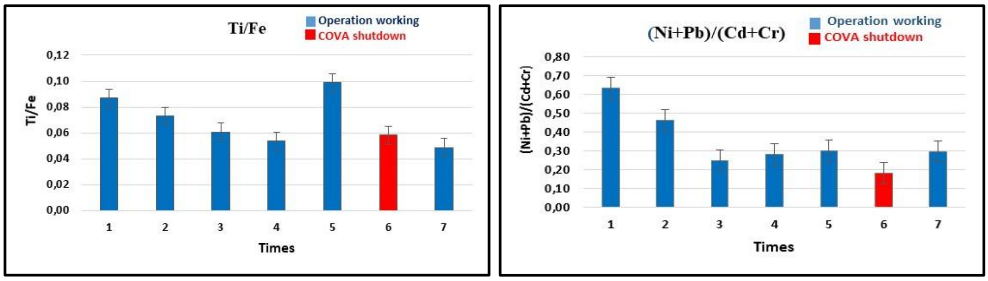
	PC_1	PC_2	PC_3	PC_4	PC_5
Al	**0,69**	0,11	0,22	0,08	-0,16
Cd	0,09	-0,03	-0,07	**0,78**	0,08
Ca	0,36	0,30	**0,50**	-0,20	0,15
Cr	0,36	-0,31	0,07	**0,54**	0,19
Cu	-0,06	0,10	0,06	0,28	**0,59**
Fe	**0,76**	-0,15	0,08	0,05	0,02
K	0,20	**0,81**	0,13	-0,09	0,26
Li	-0,05	**0,81**	-0,10	-0,03	-0,16
Mg	0,13	**0,85**	0,08	-0,01	-0,03
Mn	**0,69**	0,10	0,03	0,24	0,30
Na	-0,16	0,33	0,36	**0,57**	-0,10
Ni	0,36	0,12	**0,58**	-0,01	-0,24
Pb	-0,08	0,37	0,37	0,18	-0,26
S	0,21	0,00	**0,73**	0,21	-0,32
Ti	**0,69**	0,34	-0,09	-0,09	0,22
Zn	0,20	-0,12	-0,14	-0,06	**0,69**
PM	0,47	0,01	**0,66**	-0,10	-0,17
P%	20	15	11	8	7
CP%	20	35	46	54	61

4. Development of environmental indicators

4.1 Crustal and Anthropic ratios

During the study period a partial shutdown of the COVA plant occurred (from 26 January to 16 February 2015). The production activities were reduced and/or suspended to carry out maintenance operations and the plant was progressively stopped following different phases (ENI, Local Report 2014). Moreover, gas flaring, fire and Saharan dust

event occurred in the area under study. The whole dataset (184 days) was divided into 7-intervals to compare the operation working period of the plant (162 days) with the shutdown one of the COVA (22 days). PCA results and a one-way ANOVA test ($p < 0.05$) were considered. The main fingerprints both anthropic activities and crustal origin were identified.



a) b)

Fig. 4. Crustal indicator (a) and Anthropic indicator (b) calculated during operation working and COVA shutdown. Each time interval includes 26, 27, 27, 27, 28, 22 and 29, respectively daily measurements

As regard the Crustal Indicator the results clearly show that the Ti/Fe ratio ranging between 0.05 and 0.10 showing similar values during the study period mainly related to the crustal orography and the geological features of the area. Regarding the anthropic indicator, we found that during the period of operation working of the COVA (blue) the ratio (Ni+Pb)/(Cd+Cr) ratio shows values higher than ones observed during the shutdown COVA plant (red), see Fig.4. This result is clearly linked to the shutdown of COVA plant that is the main industrial activity present in the study area.

4.2 Single particle analysis

Single particle analysis was performed by FESEM/EDX during four occurrences such as Saharan dust, gas flaring, COVA shutdown and fire events. Approximately 300 particles were analyzed for each sample using 15.000X magnifications, an acceleration voltage from 10 to 15 kV and apertures of 20 µm and 60 µm. Particles were divided into different classes based on the morphology and chemical composition and then gathered into the following seven different groups: Crustal particles, Cl-rich particles, S-rich particles, Mixed particles, Soot agglomerate, Metal particles and Particles with low atomic number elements (Z</= 8) or with only Na or K (Fig.5).

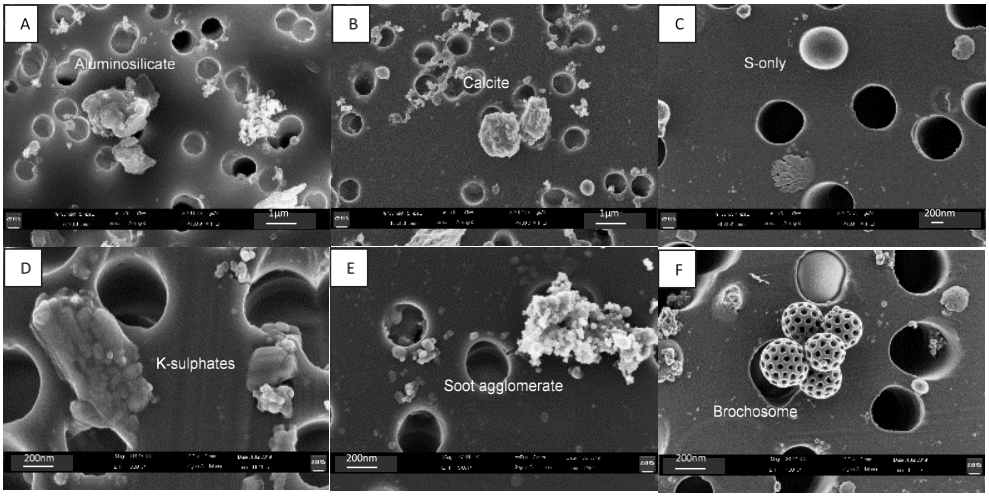


Fig. 5. FESEM images of crustal particles (a, b); S-rich particles (c, d); soot agglomerate (e); and particles with low atomic number elements (Z</= 8) or with only Na or K (f)

In Table 2 were reported criteria to define particle groups and classes on basis to elemental composition and morphology of the particles. Damage to some species under electron bombardment were also used to distinguish they (Ebert et al., 2002). Results highlighted that the alumosilicate particles, calcium sulphates and agglomerated soot are the type of particles that best distinguishes the Dust event. This is also characterized by a low presence of S-only particles and relatively by high concentrations of ammonium salts (ammonium nitrates). These results could be due to the sampling period. In fact, during the winter period there is usually an increase in the atmosphere of ammonium nitrate and a decrease in sulphates. The gas flaring event is the richest in of S-only particles. We can observe that the Sulphur does not mark the soot and does not coating on other particles (example crustal particles). The S-only particles have a spherical shape and sometimes surrounded by halos due to deliquescence, i.e. they show a flat circular morphology with branched (dendritic) structures due to supersaturation. Since a certain amount of time is required for the interaction between SO_2/H_2S and particles present in the atmosphere, the high concentration of S-only particles can indicate a very close source in the study area. Because COVA is the main industrial plant in the area, we can consider this found mainly related to the activities COVA and to rare events such as gas flaring (Margiotta et al., 2015).

Table 2. Classification criteria according to elemental composition and morphology of different particle classes and groups and their number percentage for each event

Particle groups	Particle classes	Elemental composition	Morphology	Gas flaring	Fire	Dust	Shutdown COVA
				24/08/2014	30/08/2014	03/12/2014	11/02/2015
Crustal particles	Aluminosilicates	Si-Al ±K±Mg±Na±Ca±Fe±S	Irregular or lamellar	8,6	5,7	37,6	0,7
	Quartz	Si	Irregular	1,7	0,5	1,1	0,4
	Calcite/Dolomite	Ca±Mg	Irregular	0,4	1,0	1,1	0,4
Cl-rich particles		Na-Cl +/- Ca	Deliquescent or cubic	2,6	1,9	0,0	0,4
S-rich particles	Gypsum	Ca-S	Prismatic, columnar aggregates	1,7	4,8	9,6	0,7
	K-sulphates	K-S (+/- Ca+/-Na)	Droplet or irregular with rough surface	7,3	17,2	1,4	8,9
	Na-sulphates	Na-S	Droplet or irregular with rough surface	3,0	2,4	0,7	3,5
	Only S particles	S	Droplet or smooth and irregular	60,3	38,3	1,4	39,7
Mixed particles silicates-sulphates		Complex	Irregular aggregate	1,7	3,8	0,4	2,8
Agglomerated soot	Agglomerated soot	No elementi with Z>8 or only S ± Na ± Ca	Spherical Clusters	0,4	5,3	5,3	1,4
Metal particles	Metal oxides/hydroxides	Fe±Cu±Ti±Mn	spherical or irregular	2,2	1,4	1,1	0,7
Particles with low atomic number elements (Z</= 8) or with only Na or K	Organic particles, ultra-fine soot, ammonium-sodium-potassium nitrates	Elements with Z? 8 ± Na or K	Deliquescent , droplet, complex, chain of nanospherical particles	9,9	17,7	40,4	40,4
Total (%)				100	100	100	100

In the Fire event sample, we found a relatively high content of particles referable to sulphate of K as well as the presence of agglomerated soot and crustal particles affected by S. This result is consistent with the kind of air mass analyzed. It is known that elements such as S and K are fingerprint to biomass burning processes (Pavese et al., 2016). Moreover, the long-range air masses have produced the aging of the soot and crustal particles that are linked to compounds of the S. The sample collected during the "COVA shutdown" (Background) does not show any peculiarity in the concentration and type of particles analyzed for exception a relatively higher content of ammonium salts which could be explained by the seasonality (winter period) of the sampling.

5. Conclusion

In the framework of INDICARE (Indexing of regional environmental criticalities) project, environmental indicators were developed to assess the possible natural and/or anthropogenic contribution to the PM_1 atmospheric aerosol particles. Daily PM_1 mass concentrations, 16 trace elements (i.e., Al, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, S, Ti and Zn), geochemical and mineralogical composition of individual aerosol particles were performed. The Principal Component Analysis (PCA) was used to identify the main PM_1 sources. During the study period a partial shutdown of the COVA plant, gas flaring, fire and Saharan dust event occurred in the area under study. Single particle analysis was performed by FESEM/EDX during these occurrences. Results showed that the Ti/Fe ratio allows to identify the contribution of the crustal sources (e,g., local resuspension, long-range transport, dust) while the (Ni+Pb)/(Cd+Cr) ratio allows to discriminate anthropic sources mainly linked to industrial activities. In conclusion, the integrated chemical data, statistical analysis, back-trajectories analysis, morphological and mineralogical observations allowed to discriminate natural sources from anthropogenic ones and the presence of compound originate from the interaction between particles in the atmosphere.

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