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AN INTEGRATED HIGH TEMPORAL RESOLUTION APPROACH TO MONITOR VOCs CONCENTRATIONS AND ODOUR ANNOYANCE NEAR A PETROLEUM PLANT

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Abstract

This study aims to monitor Volatile Organic Compounds (VOCs) and odour annoyance perceived by the exposed population living nearby a petroleum plant through an integrated high temporal resolution methodological approach. The area under investigation is considered one of the most critical industrial areas of the South of Italy (Basilicata) because of presence of the largest Italian petroleum plant, called the "Center Olio Val d'Agri" (COVA). In fact, VOCs and odours emitted from extraction processes, storage tanks and/or gas pipelines may have an adverse impact on health and life quality of population living near the plant. Therefore, in order to assess the potential impact on nearby urban settlements, two monitoring campaigns were carried out. The first campaign was conducted during 2011 and allowed to integrate the information about odours, monitored by means of electronic nose (e-nose), with meteorological data (wind speed and direction) and population complaints reported on questionnaires. In the second one (**from 1st January to 30th July 2017**), the previous approach has been improved with an integrated system consisting of photoionization detector (PID) for VOCs monitoring, a video camera and a telephonic system able to systematize in real time the population complaints. Experimental data obtained revealed that there was correspondence between the VOCs concentration peaks, odour events and population complaints. Moreover, this study highlighted that technologies for high temporal resolution monitoring of both VOCs and odours integrated in a unique system are able to provide real time information about the emissive sources and odor annoyance and to promptly evaluate the impact on the exposed population.

Key words: electronic nose, gas and oil pre-treatment plant, odours, Photo Ionization Detector (PID), Volatile Organic Compounds (VOCs)

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1. Introduction

The increasing interest of scientific community and stakeholders for airborne pollutants monitoring in Val d'Agri (Basilicata, Italy) is due to the presence of the largest Italian gas and oil pre-treatment plant, called the "Centro Olio Val d'Agri" (COVA), nearby the urban settlements. The large-scale plant extracts crude oil from the various wells placed in the surrounding territory and, afterwards, performs the desulphurization process (Calvello et al. 2015; 2017).

Despite exhaustive data on chemical characterization of VOC emission from petrochemical plants and refineries are available in literature, limited information is to date available regarding emissions from industrial plants tailored to extraction and desulphurization processes (Cetin et al., 2003; Faruolo et al., 2014; Kalabokas et al., 2001; Kumar et al., 2017; Lin et al., 2004; Macey et al., 2014; Rodriguez-Espinosa et al., 2017; Tiwari et al., 2010; Wei et al., 2014; Zhang et al., 2017). Several studies highlighted that Volatile Organic Compounds (VOCs) represent

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the main pollutants emitted from oil wells (Chen et al., 2016; Wei et al., 2014; Zhang et al., 2017). Main activities of petroleum plant affecting atmospheric VOCs airborne concentration are products handling, discharge and filling of tanks and the treatment of industrial waste water. Specific classes of chemicals have been detected and related to potential sources: a) aromatic hydrocarbons such as benzene, toluene, ethylbenzene and xylenes (BTEX); b) aliphatic alkanes, linear and branched, such as propane, butane, n-pentane, n-hexane, n-heptane, isobutane, isopentane; c) linear alkenes such as propene, 1-butene, 1-pentene and other branched alkenes (Calvello et al., 2017; EPA, 1995; Ryerson et al., 2003; Vega et al., 2011). Aromatic hydrocarbons emissions have been related to industrial waste water treatment whereas alkanes and alkenes emission to tank leaks. Moreover, it was observed that blow down system significantly contributes to CO₂, CO, NO_x and SO_x airborne concentrations as well as to VOCs concentrations (Nwakire, 2015). Fugitive emissions of hydrocarbons from storage tanks, gas pipelines and exhausted areas are also of concern. VOCs monitoring in industrial areas characterized by the presence of a petroleum plant is of great concern due to potential impacts on human health. In fact, several studies highlighted that VOC inhalation exposure could affect human health and in particular it could affect airway mucous membranes, provide feeling of sickness or dizziness and cause asthma, leukemia or brain cancer (Chen et al., 2017; Liu et al., 2008; Ye et al., 2017). Therefore, in order to evaluate the impact of emissions from petroleum plant in Val d'Agri on the surrounding territory, some actions have been made over the last years by the regional authorities. A network of five stations for air quality monitoring has been developed and installed by the Agency for Environmental Protection and Prevention of the Basilicata Region (ARPAB). This network provides concentrations 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. hydrogen sulfide, methane, non-methane hydrocarbons, total hydrocarbons, toluene, ethylbenzene and isomers of xylene) (Calvello et al., 2017). Anyway, although the implementation of the regional monitoring network provides useful information, higher spatial and temporal resolution approach is needed to accurately identify short term pollution events and to evaluate their potential impact on the nearest area around the petroleum plant (Di Gilio, 2015). In fact, in high complexity industrial areas as the investigated one, fugitive emissions due to leaks from the tanks and/or the extraction process and to system over-charging cannot be neglected especially in the case the surrounding territory is populated (Amodio et al., 2013; Amodio et al., 2014; Dambruoso et al., 2014; Di Gilio et al., 2017). In addition, another key problem affecting the quality of life of the exposed population in Val d'Agri is the odour annoyance due to extraction and desulphurization processes. In fact, people that live around petroleum plant frequently complaint odour annoyance. Moreover, it is often difficult to identify the emission sources that determines odour annoyance events, because odour events last often short time. Therefore, this study aims to assess the potential impact of industrial emissions from petroleum plant on urban settlements in Val d'Agri monitoring VOCs and Odours with high spatial and temporal resolution.

2. Material and methods

In the first campaign VOCs and odour monitoring activity started on 1st October 2011 and was carried out for three months placing one electronic nose in a strategic position, downwind with respect to the industrial petroleum plant in the investigated area (Fig. 1).



Fig. 1. Industrial area in Val d'Agri and gas-oil pretreatment plant COVA (red rectangle). Geographical position of Val d'Agri in the South of Italy (in the upper corner)

The position of the device was accurately chosen after a preliminary evaluation of the most predominant wind direction during the previous months. Research activity was mainly addressed to detect odour events produced by the industrial plant with a high temporal resolution and to relate the collected information with the perception of odour annoyance by the exposed population. Odour monitoring was carried out by using an electronic nose (PEN3, Aisense Analytics GmbH, Schwerin, Germany) placed near the petroleum plant at about 2.5 meters above the ground level. The electronic nose is a compact and lightweight portable olfactory system consisting of a gas sampling unit and a sensor array (Capelli et al., 2014). The sensor array is composed of ten thermo-regulated metal oxide thick film sensors (MOS) that are sensitive to several classes of chemical compounds (Table 1). The selectivity of the sensors is influenced by the dopant materials, the working temperature (in the range of 200°C-500°C) and the sensor geometry. When VOCs are adsorbed onto the MOS, there is an oxygen exchange resulting in a decrease in electrical conductivity, detectable by a transducer element (electrode) attached to each sensor. Through a pattern recognition software (Win Muster v. 1.6.2), the PEN3 allows visualization and analysis of the data collected in real time (1 second resolution). Anyway, for the study purpose the data were averaged on 1-minute base.

Table 1. Chemical compounds classes detectable by each MOS

<i>Sensor</i>	<i>Chemical compounds class</i>
1	Aromatic
2	Broadrange
3	Aromatic
4	Hydrogen
5	Aromatic - aliphatic
6	Broad methane
7	Sulphur-organic
8	Broad-alcohol
9	Sulphur-chlor
10	Methane-aliphatic

Moreover, information regarding the odour annoyance perceived by the population living nearby the petroleum plant were collected through the compilation of suitable questionnaires. People were asked to provide detailed information on each perceived odour event in terms of occurrence date, duration and intensity of annoyance, the latter specified on the basis of an odour intensity scale from level 1 (perceivable odour) to level 3 (very strong odour) passing through level 2 (strong odour). The odour intensity scale was associated to a chromatic scale: level 1 was associated to green colour, level 2 to yellow colour and level 3 to red colour. The information collected by questionnaires were integrated with meteorological data in order to have a more accurate interpretation of experimental results. On the basis of obtained results showing the correspondence between the odour events registered and the population complaints, and in order to have a comprehensive overview about the potential fugitive emission sources impacting on the territory, a second monitoring campaign from 1st January to 30th July 2017 was planned improving the methodological approach and coupling odour monitoring with VOCs measurements. The variation of the TVOCs concentration over the time was monitored by means of a high-time resolution photo-ionization detector (Corvus, Ion Science Ltd, UK), placed at about 2.5 meters above the ground level. The instrument was factory calibrated against Isobutylene, thus Total VOCs concentration was reported as ppm equivalent of this gas. The integrated system consisting of one electronic nose and one photoionization detector was installed in the area, downwind with respect the industrial plant. Both the sensors were remotely controlled through GSM-wireless network. In addition, meteorological sensors for temperature, relative humidity, wind speed and direction monitoring as well as a video camera were placed close to the integrated system in order to collect data that could be considered representative of the monitoring site (Fig. 2).



(a)



(b)

Fig. 2. PID (Corvus), Electronic nose (PEN3) (a) and meteorological sensors (b)

During the second campaign, conducted during 6 months from January to June 2017, instead of questionnaires, the odour impact assessment was carried out through a telephonic system called OdorLab (LabService Analytica srl) able to systematize population complaints. Each citizen (called receptor) was georeferenced on the territory map and, using a telephone switchboard, communicated the odour perception and its intensity choosing among 3 levels of intensity, visualized with different colors. The odour intensity scale and the chromatic association was the same used in the first campaign. The phone calls were promptly recorded and displayed on a real time map on a website, accessible from stakeholders.

3. Result and discussions

The analysis of high temporal resolution data from the 10 MOS of the electronic nose, during the first monitoring campaign, revealed that a significant response was particularly obtained for sensors n.7 and n. 9 (Table 1), sensitive to sulphur-organic compounds and sulphur-chlorinated compounds respectively (recognised as target pollutants emitted by the investigated source). For this reason, attention was mainly paid on the signal-time profiles of the aforementioned sensors. Data treatment and analysis consisted in integration of the electronic nose data with wind direction data as well as number and intensity of complaints from population derived from questionnaires. More specifically, the correlation between monitored data and wind direction coming from the source to the receptor (electronic nose downwind with respect the industrial plant) was considered. As representative output from the first monitoring campaign, data collected from 11 October to 21 October are reported in Fig. 3. When most significant odour annoyance events occurred and peak signals of MOS 7 and 8 were registered from both sensors, correspondence was observed with the wind

direction that promoted the transport of the emitted pollutants from the industrial source to the receptor. Moreover, the correspondence was also observed with the odour perception from the exposed population and the complaints noted, day by day, on the questionnaires.

Similarly to the results obtained from the first campaign, during the second one peak events of sulphurate and chlorinated compounds were registered by sensor 7 and 9 in correspondence of wind blowing from petroleum plant to receptor site. In addition sensors number 2 and 5 showed peaks in simultaneously to high concentrations of Total VOCs and population calls registered by OdorLab (three calls with level 3 of intensity). These results suggested the coherence of resulted obtained by different technologies and devices and the importance of the integration of obtained information to identify the emission sources. In fact, peaks registered by sensor 2 and 5 suggest that the emissive finger print of the investigated source probably changed and became more complex over the time due to potentially increased fugitive emissions (e.g. tanks leaks) resulting in higher concentrations of VOCs, more specifically aromatic and aliphatic hydrocarbons. In Fig. 4 is reported for example one day when 5 events were registered and perceived by the exposed population.

Finally, the most significant odour events perceived by the population were also confirmed by images registered by the video camera showing the flame of gas flaring (Fig. 5). Therefore, as shown in Fig. 4, the methodological approach developed in the present study revealed to be a useful tool to both identify short term events and validate in real time warnings from the population living in the area around the petroleum plant. In fact, a conventional approach based on experimental mean data (averaged on longer time frame) doesn't allow to collect useful information to recognize the short term odor emissions determining annoyance events.

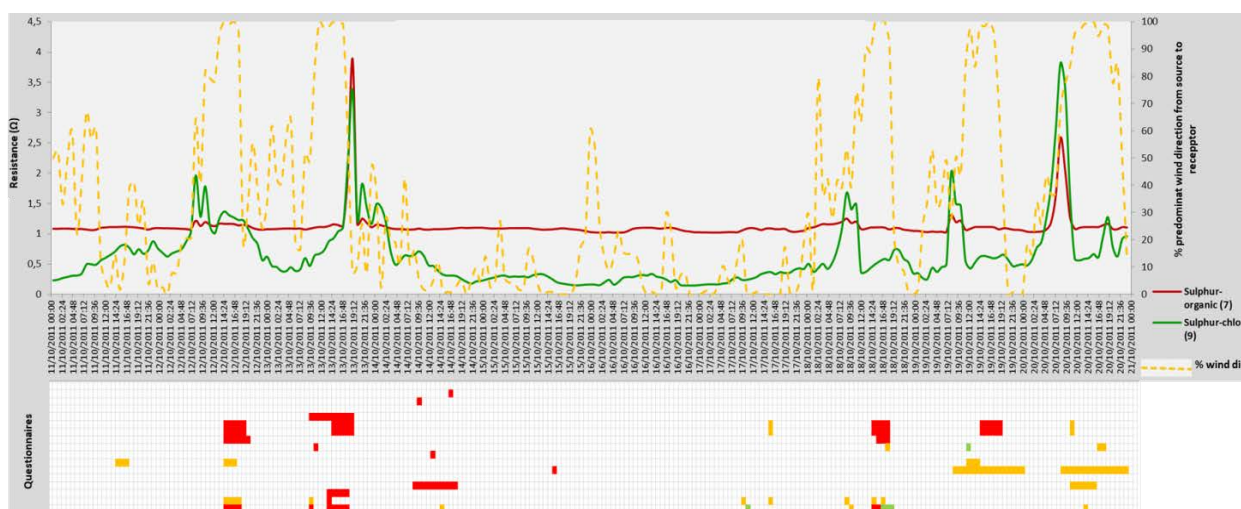


Fig. 3. Electronic nose (PEN 3) data (sensors n.7, 9) integrated with predominant wind direction (%) and information from questionnaires

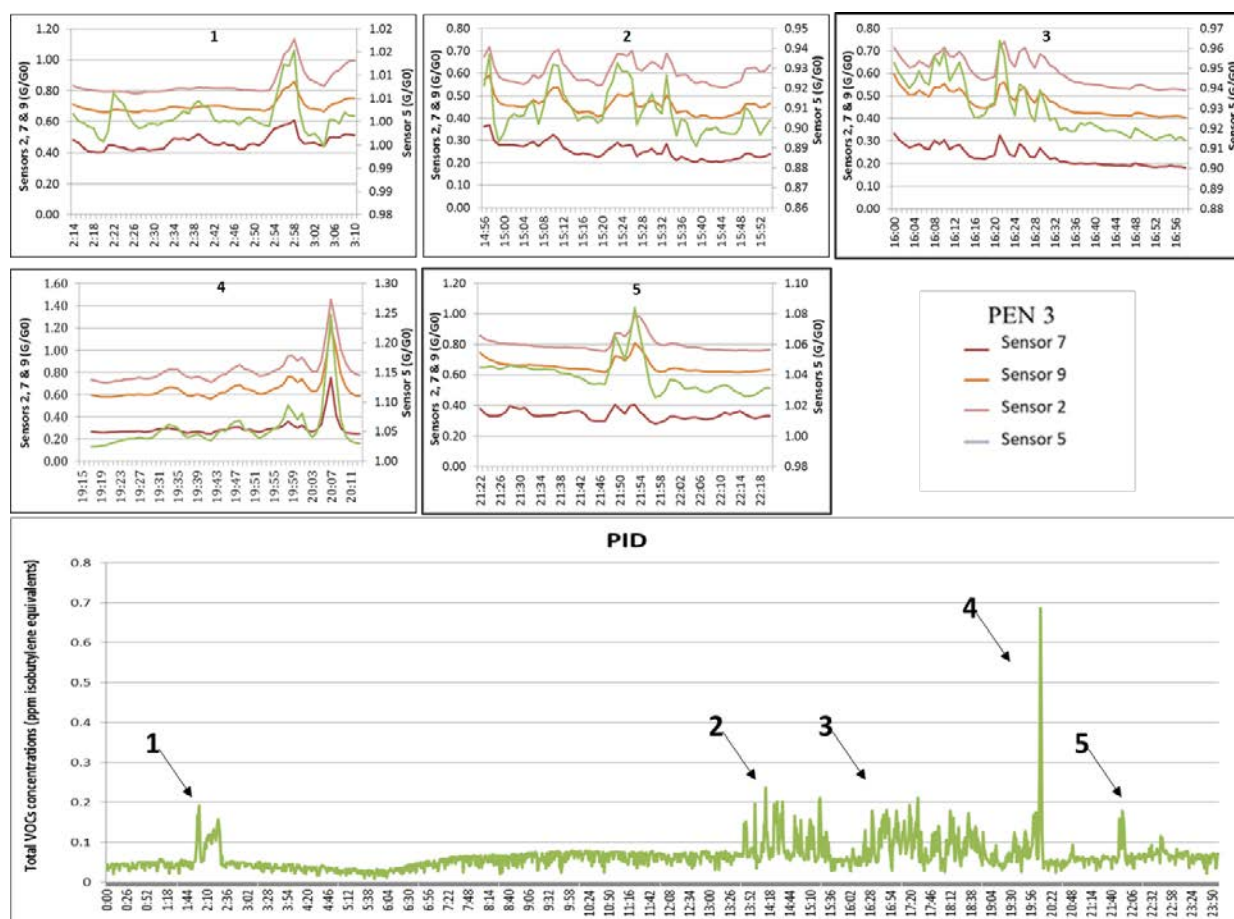


Fig. 4. VOCs Concentration (ppm) monitored by PID (Corvus) and electronic nose (PEN 3) data during 5 VOCs events occurring on one day – second monitoring campaign: 1-is the first event, of high VOCs concentrations, 2-is the second event, 3-the third event, 4-the fourth event and 5-the fifth event

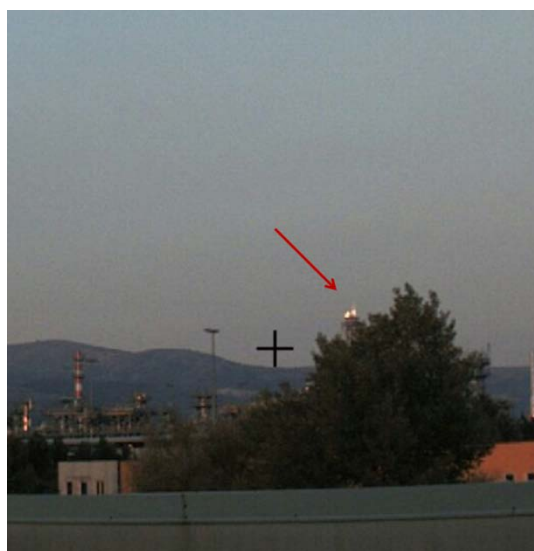


Fig. 5. Flame of gas flaring during the odour event number 4

4. Conclusions

The innovative and integrated approach for VOCs and odour monitoring in a complex industrial area characterized by the presence of the largest Italian gas and oil pre-treatment plant and its proximity to the urban settlements revealed to be a useful tool to collect

real time information about the emission sources and their impacts on the urban settlement. Experimental data obtained showed correspondence between the VOCs concentration peaks, odour events and population complaints. This study highlights that technologies for high temporal resolution monitoring of both VOCs and odours integrated in a unique

system are able to identify short term events and validate in real time warnings from the population that would not have been confirmed through a conventional approach.

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