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**AIR QUALITY IMPACT OF VOCs EMISSION FROM THE HAZARDOUS WASTE
LANDFILLS LOCATED IN GIUGLIANO (NA)**

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Abstract: In a small area of Giugliano municipality, northwest of Naples, are gathered ten landfills where industrial and toxic wastes were illegally dumped together with urban ones during the 1990s and the early 2000s, under the documented control of Camorra (the Neapolitan mafia organization). Those landfills are presently considered one of the major hazards for human health and environment in the area. During 2015 and 2016, field campaigns were performed with sampling techniques suitable to quantify emissions from landfills characterized by different management conditions (e.g. conveyed/non-conveyed biogas emissions). A large variety of VOC species including toxic or carcinogenic compounds such as aromatic hydrocarbons (BTEX: benzene, toluene, ethylbenzene and xylene isomers) non-halogenated (styrene, methyl ethyl ketone or MEK, tetrahydrofuran) and halogenated compounds (trichloroethylene, tetrachloroethylene) and terpenes (such as limonene, p-cymene and pinene), which are responsible for the undesirable odor, were detected and compared with emissions from the controlled urban waste landfill of Malagrotta (Rome), highlighting peculiar differences that could be attributed to the nature of illegally dumped waste. Emission rates for the monitored VOCs were attributed to each landfill using continuous methane measurements to define the daily biogas emission cycle. A Lagrangian particle dispersion model was applied to estimate yearly average and peak atmospheric concentrations of toxic, odorous and ozone precursor substances over the surrounding territory. Local meteorology was reconstructed by high resolution simulations of the WRF meteorological model. VOC concentrations were compared with inhalation unit risks and odor thresholds to establish their relevance for health hazard and annoyance of the resident population. The toxic compounds concentrations complied with all the considered threshold values, allowing to exclude the risk of acute or chronic diseases to the local population. For a complete environmental analysis, the landfills contribution should be added to the other environmental pressures acting over the □terra dei fuochi□area.

Key words: Landfills emissions, VOC, hazardous compounds, urban waste, pollutant dispersion.

INTRODUCTION

Gases and vapors generated by biological decomposition of urban waste in landfills are usually composed by the 60% of methane, 40% of carbon dioxide and 1% of VOCs (US EPA, 1991). If directly released into the atmosphere this biogas can significantly impact the air quality (Butt et al., 2008). For this reason, the EU issued Directive 1999/31/CE defining the procedures to control biogas emissions in urban waste landfills and minimize their impact on the human health and the environment. Biogas emitted from the various uptake pipes must be conveyed to a purification unit, where the condensable components are removed by a chiller and a filter, to permit the safe use of gas for electricity generation. Monitoring should also be performed to ensure that no fugitive emission occurs from the pipelines or from fractures in the sealing system of compacted waste, because some biogas components, such as VOCs, can be potentially toxic to man. Benzene and other aromatic compounds are formed from waste biological decomposition, together with alkenes, carbonyl compounds, alcohols, furans, chlorinated compounds, cyclic alkenes and sulfur containing VOCs. The prolonged exposure to high levels of VOCs present in the biogas produced

by urban waste landfills can cause annoyance but also problems to the human health (Vrijheid, 2000). Biogas emission can increase the levels of carcinogenic benzene and of other aromatics such as toluene, xylenes and styrene that can affect the human health. Chlorinated VOCs such as trichloroethene and tetrachloroethene (PCE) are also of concern because of their potential carcinogenicity. Biogas emission from landfills are of particular concern in Campania, where hazardous waste of various types was illegally dumped together with urban waste since the early 1980's. About 2500 contaminated sites have been identified (Balestri, 2010), most of them located near the urban area of Naples, where the highest population density of Southern Europe is reached. Police investigations established that the most intense and prolonged dumping of toxic waste occurred in the landfills located within Giugliano municipality. They were closed and seized a decade ago by a court injunction. Severe episodes of soil and water contamination were reported together with arsons causing release of contaminants in the atmosphere (Balestri, 2010). While the long-term health effects of water and soil contamination are under investigation (Mazza et al., 2015), nothing was known about the composition of the biogas released in the atmosphere, and its possible impact on human health. The concern about exposure to biogas is growing due to the increasing fugitive emissions caused by the impairment of the biogas management system, by the formation of large fractures in the waste sealing and by damages caused by recent arson episodes. To assess the potential risk represented by atmospheric emissions from Giugliano landfills, the biogas composition was determined and its impact on air quality and health was evaluated applying air quality modelling.

VOC COMPOSITION OF THE BIOGAS

Biogas was collected from the uptake pipes of each landfill and from soil fractures in the sealing system, from which it was freely escaping into the atmosphere. A total of 67 gas pipes and 7 soil fractures were investigated. Since the biogas composition strongly depends upon the type of waste and the time it underwent biological degradation, we compared VOCs relative content in the Giugliano landfills with that detected in correctly managed landfills containing urban waste of similar aging and composition, to highlight possible differences. Malagrotta, located in the SW outskirts of Rome, was the largest landfill in Europe until it was closed down in 2013. Its activity started in the same years as the Giugliano landfills, and it progressively expanded into several pits. The biogas was sampled in the late 1990's from the main ducts at the inlet of the filtration unit of two aged pits, where biogas production was already declining. The sampling and analytical procedures used were the same in all cases, as the biogas was accumulated first in adsorption traps that were later analyzed by GC-MS for the VOC content (Ciccioli et al. 2002). The limited distance between Giugliano and Malagrotta (about 180 km) guarantees their exposure to similar climatic conditions. More than 160 compounds were identified and quantified in the biogas of the various landfills. To simplify the analysis of the differences among the landfills emissions, VOCs were grouped according to the following chemical classes: arenes, alkenes, alkanes, carbonyls, alcohols, heterocyclic, chlorinated and other compounds. The group of arenes included all aromatic compounds from benzene up to tetraalkyl benzenes and benzene containing unsaturated groups.

Table 1. Mean percent composition of the organic classes of VOCs detected in the biogas of the Giugliano Landfills (Naples) compared to Malagrotta landfill (Rome). b. d. l. =below detection limit.

Geographic area	Giugliano							Roma
	Masseria del Pozzo	Ampliamento Masseria	Ampliamento Schiavi	Novambiente	Resit 1b	Resit 2b	Resit X	Malagrotta
Landfill surface (m ²)	125,153	63,581	83,027	50,135	5,041	7,915	7,408	2,400,000
Biogas VOC composition (%)								
ARENES	66.49	67.42	66.78	37.21	78.13	34.21	45.67	37.92
ALKENES	13.59	13.39	14.47	5.38	1.92	1.63	15.83	19.50
ALKANES	13.52	9.30	14.13	56.34	19.78	63.96	37.67	21.73
CARBONYLS	3.58	7.85	2.41	0.27	0.01	0.02	0.54	16.42
ALCOHOLS	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	1.24
HETEROCYCLICS	0.92	1.47	0.51	0.52	b.d.l.	0.03	b.d.l.	0.49
CHLORINATED	1.90	0.56	1.64	0.05	0.19	0.06	0.09	2.66
OTHERS	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.03

The group of alkanes included all linear, branched and cyclic components. Alkenes included monoterpenes. In addition to linear aldehydes and ketones, other cyclic carbonyl compounds were included in this class. Furans and thiophene were classified as heterocyclic compounds. The class of chlorinated compounds included not only all saturated and unsaturated chlorine containing volatiles, but also aromatic compounds, such as chlorobenzenes. All components with different structures and functional groups were classified as other compounds. Table 1 summarizes the average VOC composition in biogas by classes. The Giugliano landfills are grouped as a function of the companies that were managing them. The biogas composition of Masseria del Pozzo, Ampliamento Masseria and Ampliamento Schiavi, managed by the same company, and that of Resit 1b, was characterized by an elevated relative content of arenes, 2-3 times higher than that measured at Malagrotta. Increased levels of arenes was mirrored by a decrease in the relative content of all other VOC classes. The dominant component in the biogas of Novambiente and Resit 2b were alkanes, 2-3 times higher than the fraction measured in Malagrotta biogas. The increase was concurrent with a drop in the relative content of alkenes and carbonyl compounds. A high relative content of alkanes indicates an advanced stage of biochemical waste degradation. Intermediate features were showed by Resit X landfill. The large dominance of the arenes fraction in some of the Giugliano landfills could have implied a high content of toxic components such as benzene and styrene. The detailed analysis of VOC species showed an average relative content of benzene in the biogas of the Giugliano landfills comparable to that present in Malagrotta. The relative contents of styrene were, instead, one order of magnitude lower than that of Malagrotta. The high arenes content was mostly due to xylenes and p-cymene. This last compound originates from the microbial transformation of some monoterpenes, particularly limonene, and it can be taken as an indicator of the prolonged anaerobic waste degradation. The abundance of p-cymene, together with the lower content of limonene in the biogas of the Giugliano landfills, suggests a more advanced aging process of waste in Giugliano compared to Malagrotta. Among the chlorinated components, di-, tri- and tetrachlorethenes were detected only in the biogas of Masseria del Pozzo, Ampliamento Masseria and Amplimento Schiavi, with the lower homolog as the dominant component, while in the biogas of Malagrotta 1,1-dichloroethene was always a minor component and tri- and tetrachloroethenes, together with 1,2-dichloroethene, were the dominant ones. We can suppose that 1,1-dichloroethene of industrial origin was dumped in the Giugliano landfills, together with other industrial solvents. This might also explain the high relative contents of m- and p-xylenes found in the biogas of the same landfills and the presence of MEK among carbonyls. Mixtures of xylenes (xylols) are in fact common components of ink, paint, rubber, and adhesives. MEK is a common solvent in industrial processes involving gums, resins, cellulose production, synthetic rubber industry, production of paraffin wax, and in household products such as lacquer and varnishes, paint remover, and glues. Considering the composition of the heterocyclic compounds in the biogas, the relative contents of 2-methylfuran and 2,5-dimethyl furan in the Giugliano landfills (Masseria del Pozzo, Ampliamento Masseria and Ampliamento Schiavi) were equal/higher than those detected in Malagrotta and much higher than tetrahydrofuran, which was, instead, one of the dominant component in Malagrotta. Although the origin of 2-methylfuran from decomposition of fibers and sugars in urban wastes cannot be excluded, the lack of this component in the more aged wastes of Resit 1b, Resit 2b and Novambiente, where alkanes were the dominant components, suggests that 2-methylfuran might have been another solvent illegally dumped in the Giugliano landfills. 2-Methylfuran is widely used in pharmaceutical industry for the manufacturing of many common drugs, but also for making pesticides, flavors or fragrances.

ATMOSPHERIC DISPERSION AND POTENTIAL IMPACT ON HUMAN HEALTH OF VOCS

The air quality impact and possible related hazards for human health due to the Giugliano landfill VOCs emission were evaluated through the application of the Lagrangian dispersion model SPRAY (Anfossi et al., 2010). A computational domain of 12x12 km² with a horizontal grid spacing of 100 m was defined to include the nearest inhabited areas and to obtain a space resolution sufficient to describe the concentration near the landfills, where maximum values are expected for non-buoyant surface level emissions. Local meteorology was reconstructed by means of the WRF meteorological model (<http://www.wrf-model.org/>). Nested grids were employed to reach a horizontal grid spacing of 1 km over the target area. WRF results were verified to reproduce meteorological observations from Naples and Grazzanise airports, and from a sonic anemometer located at the southern edge of the Masseria del Pozzo landfill. Model simulations covered a year-long period (01/11/2015 - 31/10/2016) allowing to estimate average and maximum pollutants concentrations. The compounds to be simulated have been chosen considering their relative

abundance in the biogas together with their toxicity. They include: benzene, toluene, ethylbenzene, p- and o- xylene, styrene, 1,1-dichloro ethylene, tri- and tetrachloro ethylene, 1,2-dichloro benzene and MEK. Due to the features of the chemical species emitted and to their limited atmospheric transport time over the considered area, pollutants were assumed to be non-chemically reactive. The hourly average emission rate for all the VOC species was computed from CH₄ emission rate considering their average concentration ratio within the biogas sampled over each landfill. During the whole period of investigation, biogas sampling was supplemented by continuous methane flux measurements obtained by eddy covariance system located at the southern edge of Masseria del Pozzo landfill. Methane emissions were allocated to the different landfills with the support of airborne measuring campaigns realized with Sky Arrow ERA aircraft, which monitored methane fluxes while flying over the landfills area.

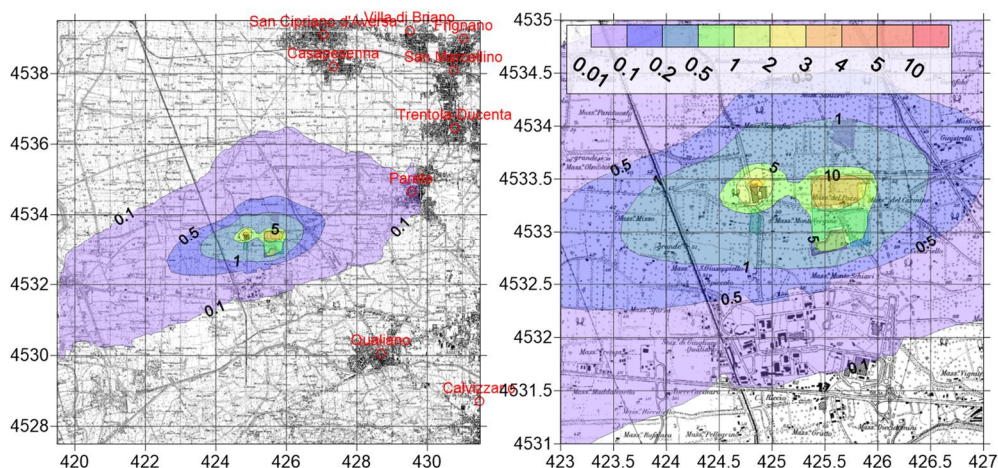


Figure 1. Benzene annual average concentration (ng m^{-3}) over the whole computational domain (left) and zoomed over a $4 \times 4 \text{ km}^2$ area surrounding the landfills (right).

The annual mean concentrations estimated for benzene inside the landfill area were lower than 30 ng m^{-3} (Figure 1) with highest values over and around Resit landfills, where hourly maximum values reached 303 ng m^{-3} . Concentrations decreased significantly in the surrounding areas, where maximum hourly values of $10\text{-}20 \text{ ng m}^{-3}$ were reached in the uninhabited area at the border of the landfills. Predicted concentration values were much lower both of the 5 ng m^{-3} limit for the annual average and of the 360 ng m^{-3} exposure level corresponding to the screening level target risk of one occurrence over a million. Model simulation estimated o-xylene concentrations slightly higher than benzene, while toluene, p-xylene, ethylbenzene and MEK concentrations were about one order of magnitude higher than those of benzene.

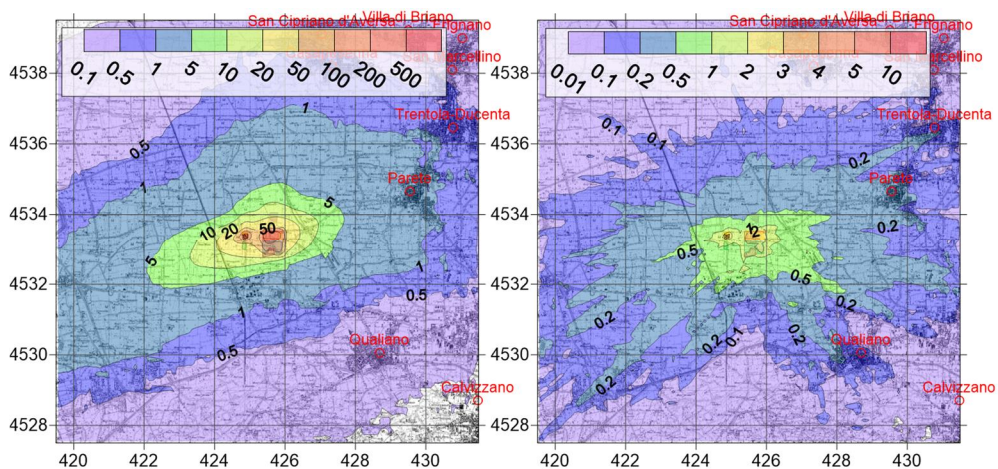


Figure 2. p-Xylene annual average (left) concentration (ng m^{-3}) and hourly maximum (right) concentration ($\mu\text{g m}^{-3}$).

Annual mean concentrations reached values of 100 ng m⁻³ for toluene, ethylbenzene, MEK, and 200 ng m⁻³ for p-xylene nearby the landfills (Figure 2), where the maximum hourly average concentration exceeded 1 µg m⁻³ for toluene, ethylbenzene, MEK, and 2 µg m⁻³ for p-xylene (Figure 2). The nearest residential area (Parete) was influenced by yearly average concentrations of about 1 ng m⁻³ for toluene, ethylbenzene, MEK, and 2 ng m⁻³ for p-xylene. Maximum hourly concentrations reached over the same area were 200 ng m⁻³ for toluene, ethylbenzene, MEK, and 300 ng m⁻³ for p-xylene. All the concentrations were by far lower than the reference thresholds for toxic non-carcinogenic risk and WHO guideline values. Estimated annual average concentrations of ethylbenzene and p-xylene were much lower than values causing a cancer risk of one case over a million to the exposed population. Only the maximum hourly average concentrations reached values of the same order of cancer risk thresholds (~1 µg m⁻³) over the landfills bodies. The highest VOCs concentrations were predicted during wintertime, when atmospheric stability and weak wind hinder the dispersion of pollutants emitted by ground level sources. Concentration values estimated for the other toxic VOCs (styrene, 1,1-dichloro ethylene, tetrachloroethene, trichloroethylene, 1,2-dichlorobenzene) were orders of magnitudes lower than those of benzene and orders of magnitude lower than the threshold values for cancer and non-cancer risks. The modelling results indicated that the potential risk for the population living at the borders of landfill is low, although it cannot be excluded that biogas emission might be a source of annoyance when stable conditions are established over the site.

CONCLUSIONS

The performed monitoring showed that toxic compounds were present in the emission of the Giugliano landfills and some of them could be associated with dumping of toxic waste. The air quality impact assessment, performed by atmospheric dispersion modelling, showed that the emission rates were not sufficient to induce acute or chronic diseases to the local population. Although these landfills are no longer in operation, they must be kept under control to avoid an increase in VOC fugitive emissions due to fracturing of the sealing system, increasing the risks of fires and explosions. VOCs emissions can contribute to ozone and particle formation when mixed with all the other VOC, NO_x and particles emitted from sources active within the Naples-Caserta territory, including ship traffic in the port and gulf of Naples, biomass burning for domestic heating, illegal open burning of wastes and forest fires.

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