

Improving recognition of odors in a waste management plant by using electronic noses with different technologies, gas chromatography–mass spectrometry/olfactometry and dynamic olfactometry

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ABSTRACT

Odor emissions from waste management plants have long been an environmental and economic issue, but only recently regional authorities in Italy are regulating this sector by imposing control and mitigation of the phenomenon. Electronic noses, initially developed as cheap, easy tools to detect volatiles, may have the required time-resolved coverage of the odor emission phenomenon in a cheap and feasible way with respect to chemical analysis of air. One crucial issue to resolve is to evaluate the discriminant capacity of a sensor array in-field and under working conditions. In this paper the authors have studied the responses of electronic noses of different technologies to odors emitted from a waste management plant, by integrating results obtained with dynamic olfactometry and gas chromatography–mass spectrometry/olfactometry, in the aim to implement a monitoring system and improve cleaner production technologies. Three most impacting odor sources in the waste management plant were detected: biogas, a by-product of mechanical treatment of municipal solid wastes, with low organic fraction and a sludge pressed and dehydrated from treatment of urban wastewater. The most odor impacting source was the sludge and the major responsible of the odor impacts were aromatics (in particular 1,3,5-trimethyl benzene), aliphatic hydrocarbons, terpenes and sulphur volatiles (methyl disulphide, carbon disulphide, dimethyltrisulphide). Ten Metal Oxide Semiconductors and 32 polymer/black carbon (Nano Composite Array) sensors in two electronic noses, were tested for discrimination source capabilities. Results of linear discriminant analysis and cross validation give 86.7% successful recognition for Metal Oxide Semiconductors, 53.3% for Nano Composite Array and 93.3% for a selection of sensors belonging to both technologies chosen according to the selectivity towards the odor active molecules. The containment of odors could also be achieved by spraying a specific product and monitoring the process using selected sensors of the arrays. The results of the in-field work demonstrate strengths and weaknesses of different construction technologies in the e-noses arrays, to characterize and monitor in-site and in real time odor emissions from waste management plants.

1. Introduction

The problem of olfactory nuisances felt by the inhabitants surrounding waste management plants, due to the emissions of odor active molecules, is becoming an important environmental and economic issue. Several approaches have been proposed to mitigate

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the environmental burdens of both landfills and waste composting plants: collecting of waste management gases with combined heat and electricity production in centralized plants with GHG emission savings (Niskanen et al., 2013; Wanichpongpan and Gheewala, 2007; Rubio-Romero et al., 2013), mining of existing landfills for material and energy recovery (Kaartinen et al., 2013; Jones et al., 2013) but the emissions of odor active molecules remains an unresolved issue. Gaseous emissions in composting plants are typically composed of nitrogen and sulphur-based VOCs, methane and hydrogen (Shen et al., 2012; D'Imporzano et al., 2008). Among odorous substances identified in gas extraction wells of a sludge management site were methyl mercaptan, valeric and iso-valeric acid, carbon disulphide, acetone, 3-pentanone, methanol, trimethylamine, hydrogen sulphide, n-butylaldehyde, acetic acid, DMS, DMDS, limonene and alpha-pinene (Fang et al., 2012; Van Durme et al., 1992). Quantitative calculations showed that composting of MSWs generates ammonia emissions between 18 and 1150 g NH₃/t of waste (Clemens and Cuhls, 2003) whereas sewage sludge composting facilities generates peaks of the ammonia concentration up to 700 mg NH₃/m³ (Haug, 1993). A plant managing source-separated organic fraction of MSWs showed emission factors for ammonia and VOCs of 3.9 kg/t of wastes and 0.206 kg/t respectively (Cadena et al., 2009). Among abatement strategies that could mitigate odor emissions, extremely important, in connection with the social acceptance and environmental sustainability of waste management facilities, are biocovers that optimize the development and activity of ubiquitous microorganisms that can oxidize VOCs and sulphur compounds (Iranpour et al., 2005). The potential of odor abatement of biocovers is high, with reported removal efficiencies of 70–100% (Hurst et al., 2005; Capanema et al., 2014). Other strategies of odor abatement in waste management plants consist in the addition of bulking agents as rice straw and dry cornstalks (Shao et al., 2014; Zhang et al., 2013). Moreover trickle-bed bioreactors showed pollutants removal above 80% for VOCs (acetone, styrene, benzene, vinyl acetate, p-xylene) and sulphur compounds (H₂S, DMS, DMDS) in the reduction of VOCs and odors in indoor environments (Kasperczyk and Urbaniec, 2015; Kasperczyk et al., 2014). The regional odor concentration limit for industrial activities is equal to 300 OU/m³ for fugitive sources and 2000 OU/m³ for stationary sources (Apulia region, 2015). The Regional Agency for Environmental Protection (ARPA Puglia) has released a specific guideline that considers the possibility of implementing both a predictive approach to evaluate the odor impact on the receptors through dispersion models (ARPA Puglia, 2015) and to monitor in real-time osmogenic emissions with a system that must be correlated with dynamic olfactometry and can be composed of conventional analyzers (for example H₂S analyzers) and electronic noses. Following these guidelines the approach used in this work is aimed at the integration of some specific analytical and sensoristic tools: dynamic olfactometry, chemical characterization of odors (by means of GC-O/MS) and real-time and in-field monitoring of gas sources, by means of electronic noses. A critical review of the existing literature revealed that dynamic olfactometry do not allow the discrimination of the specific substances responsible of the odor but GC-O/MS, recently introduced in the osmogenic emission detection, has partly resolved the problem (Brattoli et al., 2013). For odor quality assessment, humans still are the most efficient instruments for sensorial evaluation, and the European normative CEN EN 13725/2003 (CEN, 2003) establishes the procedures for the selection of panelists of olfactory perception, on the basis of a standard odor perception threshold: 123 mg/m³ of n-butanol in synthetic air. This concentration defines the European Odorimetric Unit (OU) per cubic meter (OU/m³). Costly and time consuming chemical analysis of air, can provide the reconstruction of odorimetric units (OU) by

dividing the concentration of a specific compound by its odor threshold limit, indicating how many times the threshold limit has been exceeded but generally do not establishes the relationship between the concentration and its associated OU (Gallego et al., 2012; Capelli et al., 2008). Nowadays GC-O/MS represents the most popular integration of both chemical characterization and odor measurement techniques, being employed in the performance evaluations of odor abatement (Munoz et al., 2010). Electronic noses, initially developed as instruments capable to mimic the human olfactory system with quicker responses with respect to chemical analysis, are limited by their lack of specificity (as they detect both odorous and odorless volatile compounds), lack of efficiency at remotely located sites and remain promising instruments to monitor the transient odor level near the source, or to serve as inputs to mathematical dispersion models that can predict odor concentrations at remote locations (Romain et al., 2008; Nagle et al., 2003). In literature, array of sensors have been used to differentiate and quantify the main gases emitted from MSWs or to respond to sewage odors over a wide range of odor concentrations (Delgado-Rodríguez et al., 2012; Stuetz et al., 1999) and also in a combination with GC-MS and dynamic olfactometry demonstrating that the three different odor characterization techniques do not necessarily correlate, due to synergistic and masking effects of VOCs in determining odor perception (Capelli et al., 2008). In this paper the authors have studied the use of electronic noses whose arrays were made with different technologies (MOSs and the emerging polymer/black carbon NCA) to monitor odors emitted from a waste management plant, by integrating responses obtained with dynamic olfactometry and GC-O/MS, in the aim to implement a monitoring system and improve cleaner production technologies. Some preliminary results have been recently reported in a conference proceeding (Giungato et al., 2015). The results of this approach can be useful to provide to waste management plant managers, a decision support system and to engineers, a guideline to the sustainable design of waste management plant monitoring systems.

2. Materials and methods

2.1. Site description

The waste management plant is located in the city of Statte, province of Taranto in the Apulia region, in the south-eastern part of Italy. The waste management plant is owned by Italcave SpA and receives non-hazardous industrial wastes, generating biogas which feeds a power generator. Nowadays, in the so called "Lotto 1", the ground level has been reached and the field is producing biogas for electricity purposes whereas in "Lotto 2" (in black), the active batch, wastes are landfilled until the ground level has been reached, then the field is ready for biogas collection and energy production (Fig. 1, left).

2.2. Sampling

Three sources of odors were studied: biogas from the "lotto 1", a MSW having LoW code 191212 (a by-product of mechanical treatment of MSWs, with low organic content) and a sludge with LoW code 190805 (sludge pressed and dehydrated from treatment of urban wastewater) both managed in "lotto 2". In Tables 1–3 are reported some chemical relevant data of the three sources under investigation. Wastes mixed with inert stone materials were covered with a static extractor (Fig. 1, right) and air flowing in the hood, sampled with a depression pump (lung technique) and conveyed inside an 8 L Nalophan bag, at ambient temperature. Samples of mixed air-biogas in "lotto 1" were collected by means of a depression pump (lung technique) placed 1 m apart from the



Fig. 1. Left: Italcave waste management plant “Lotto 1” where are located the biogas collection wells and “Lotto 2” the active batch in which are located the wastes under work, the city of Statte (Taranto province) and surroundings (source: SIT Puglia, <http://www.sit.puglia.it/>). Right: static extractor in the “lotto 2” waste management plant field.

opened valve of a collection well and conveyed inside an 8 L Nalophan bag, at ambient temperature.

In the lung technique the tedlar bag is inserted into a rigid structure in which is operated a small depression by a pump that it expels the air toward the outside and inflates the bag by expansion. With this apparatus sampled air is introduced at atmospheric pressure in the bag without passing through the pump in order to avoid accidental entrainment of oil and interferences.

Table 1
Chemical composition of biogas from the collection network.

Substance	Concentration
Methane	59% v/v
CO ₂	26% v/v
Oxygen	4% v/v
H ₂	<1%
H ₂ S	14 ppm
Ammonia	1.3 ppm
Aromatic solvents	<0.1 mg/m ³

Courtesy of Italcave SpA.

Table 2
Composition of sludge from urban wastewater treatment plant, L₀W code 190805.

Substance	Concentration (mg/kg)
Carcinogenic chlorinated aliphatics	<1.0
PAHs	<0.1
Light hydrocarbons (C < 12)	6.62
Heavy hydrocarbons	4910
POPs	<0.1

Courtesy of Italcave SpA.

2.3. Dynamic olfactometry and GC-O/MS analysis

Samples were brought to the panel within 12 h and olfactometric odor concentrations, were determined according to the CEN EN 13725/2003 (CEN, 2003) with an ECOMA (ECOMA GmbH, Honigsee, Germany) olfactometer equipped with four sniffing ports and setup to carry out dilutions ranging from 2² to 2¹⁶ with a constant factor equal to 2. Four panelists were asked to sniff at a single port and to communicate if an odor was detected or not (yes/no method). Chemical analyses of air in the sampled bags, were carried out using a thermal desorber (Markes International Ltd, Unity 2™) connected to a gas chromatograph (Agilent 7890) equipped with an olfactometric detection port (Gerstel) and a mass spectrometer (Agilent 5975) according to the method described by Brattoli (Brattoli et al., 2014).

2.4. Electronic nose analysis

Electronic noses used were purchased from two primary firms of the sector and named Nose_1, having an array of 10 MOS sensors (Table 4), and Nose_2 composed of 32 polymer/black carbon NCA sensors (Table 5, Fig. 2). Five replicates of the sampled bags were

Table 3
Composition of by-products of MSW, L₀W code 191212.

Substance	Concentration (mg/kg)
Carcinogenic chlorinated aliphatics	<1.0
PAHs	<0.1
Light hydrocarbons (C < 12)	<1.0
Heavy hydrocarbons	1168
POPs	<0.1

Courtesy of Italcave SpA.

Table 4
Classes of VOCs detected, as reported by the producer, in the Nose 1 electronic nose.

Sensor	Classes of VOCs detected
A	Wide range of compounds, especially nitrogen containing
B	Sulphur–chlorine compounds
C	Sulphur compounds
D	Short chain hydrocarbons
E	Short chain aliphatic compounds
F	Alcohols
G	Mainly hydrogen
H	Aromatic compounds
I	Aromatic compounds
J	Aromatic and aliphatic compounds

Table 5
Settings for sampling of the bags by the electronic noses used in this work.

	Nose_1	Nose_2
Sampling flux rate	400 mL/min	120 mL/min
Sampling time	40 s	20 s
Sampled quantity	Integral of G/G_0	$(R - R_0)/R_0$
Washing flux	600 mL/min	180 mL/min
Washing time	120 s	30 s

sniffed in a randomized way. The signal of the sensors was the integral of the electrical conductivity G/G_0 (in the case of Nose_1) and the relative variation of resistance $(R - R_0)/R_0$ (in the case of Nose_2) during the acquisition time. The integrated datasets obtained has been explored by PCA and LDA, using R software package (version 3.1.2–2014; The R Foundation for Statistical Computing[®]) and dev-tools, ggbiplot and MASS libraries (Penza et al., 2015; Giungato et al., 2015).

2.5. In-field abatement of odors

In-field abatement of odors has been carried out by atomization of a commercially known product sold for abatement purposes (Table 6) which is composed of a surfactant, dipropylene glycol and a not specified fragrance mixture which is dissolved in water by means of the glycol. Sampling followed the time sequence of Table 7, the sludge obtained from wastewater treatment was sampled at a distance of 1 m downwind, by the lung technique, into bags of nalophan of 8 L capacity. During sampling it was recorded wind prevailing direction (North for 92% of the sampling time) and average speed throughout the experiment of 1.2 m/s. The atomizer used, placed on a small truck, was the “Citizen Compact 90” (Typhoon srl, Cassana – Ferrara – Italy), composed of an 84 HP water-cooled 4-cylinder turbo-engine for pumping, placed at 12 m

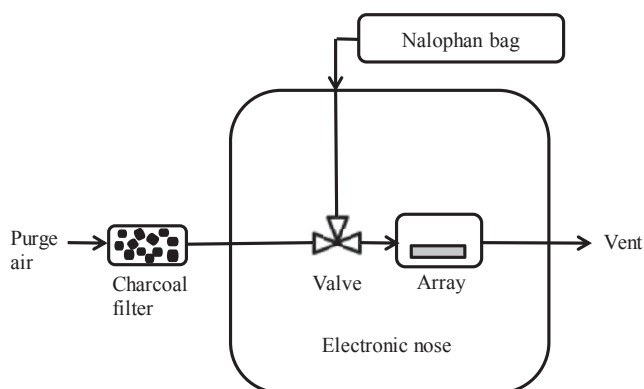


Fig. 2. Scheme of the sampling from a Nalophan bag.

Table 6
Main properties of the product for odor abatement used in this work.

Producer	Labiotech, Povoletto (UD) – Italy
Name	OWD
Description	Formulation based on natural fragrances
Composition	Sodium Lauryl sulphate, CAS 151-21-3; mixture dipropylene glycol, CAS 25265-71-8; fragrance mixture (undefined) water
Use	Diluted in water 0.1–2%

distance from the sampling point, set with atomization flux of 25 L/min directed towards the sampling point, at a concentration of 0.3% by volume in water of the abatement product (Fig. 3). Nalophan bags collected were analyzed by dynamic olfactometry within 24 h and 4 replicates of each bag, were sniffed with the Nose_1 electronic nose in a randomized way.

3. Results and discussion

Dehydrated sludge showed higher odor impacts (Table 8) probably due to sulphur containing volatiles in particular MDS, carbon disulphide, DMDS whereas, in the case of the by-products of mechanical treated MSWs, were aromatic, aliphatic hydrocarbons and terpenes (in particular 1,3,5-trimethyl benzene, see Tables 9 and 10).

Five replicates of the sampled bags, the biogas source, the sample with LoW code 190805 (by products of mechanical treated MSW) and the sample with LoW code 190805 (dehydrated sludge) were sniffed with both electronic noses and PCA score plots and loadings were represented in Figs. 4 and 5. Sensors of the Nose_1 whose loadings pointed towards the PCA score plots of the sensors signals, when the biogas bag was sniffed (each plot represents one replicate) were: C, D, E, F and G. This result is in agreement to the presence of methane in the biogas whereas H, I, J PCA loadings points towards sludge and MSW scores, according to the presence of 1,3,5-trimethylbenzene odorant having an “urban waste” descriptor (see also Table 9). PCA loadings of the sensors of the Nose_2 (Fig. 5) all point towards PCA score plots of the sensors signals when the biogas bag was sniffed. Recognition capabilities of the electronic noses were different for the Nose_1 with respect to the Nose_2 and the sum of both arrays do not improve the results (Table 11). Best results were achieved by selecting specific sensors of both technologies following the selectivity towards the characteristic chemicals emitted from the sources as H, G, D, C, belonging to Nose_1 and S1, S2, belonging to the Nose_2 and the recognition capabilities of the model raised to 93.3% (Giungato et al., 2015).

Before atomization sludge presents a very high odor load of 4597 OU/m³ (Fig. 6) that is lowered by the atomization to 861 OU/m³, after spraying, there is an increase in the concentration of odor to 1933 OU/m³, when the process finished. This suggests that the atomization phase should last as long as the source is exposed to air before being covered by the inert material. A good correlation exists, between odor concentration and A sensor signal of the

Table 7
Sequence of operations in the abatement experiment.

Before	2.5 min with a lung pump a nalophan bag is loaded 1 m from the waste, downwind;
Atomization	Atomizer operated upwind and the mixed product is released on the waste for 30 s;
During	2.5 min with a lung pump at 1 m from the waste, downwind;
After	Waiting for 10 min then sampling for 2.5 min using a lung pump, 1 m from the waste, downwind;



Fig. 3. Atomizer used in the abatement experiment (left), with details of the nozzle (right).

Table 8

Odor concentration, odor flux rate and specific odor flux rate of landfilled wastes, used in this work.

Sample	LoW code	Odor concentration (OU/m ³)	Specific odor flux rate (20 °C) OU/(s m ²)	Odor flux rate (20 °C) OU/s
By-products of mechanical treated MSWs	191212	912	14	7000
Dehydrated sludge	190805	375,585	5700	400,000

electronic nose Nose_1 during abatement (Fig. 7) with $R^2 = 0.97$. In this case the not-specific sensor has a higher correlation with the concentration of odor and could be useful to set an alert limit beyond which abatement systems should be activated, in a hypothetical management system of the plant.

4. Conclusions

Although odor emissions from waste management plants have since long been an environmental and economic problem connected to waste management, only recently regional authorities in Italy are regulating this sector by imposing controls and mitigation of the phenomenon and sanctioning who provokes discomfort in

the population living in the surrounds. Electronic noses, initially developed as cheap, easy tools to detect VOCs, are recently being tested to detect odors as may have the required time-resolved coverage of the odor emission phenomenon. One crucial issue in order to implement an odor monitoring system by means of electronic noses is to evaluate the discriminant capacity of a sensor array in-field and under working conditions. For this reason the paper presents for the first time a comparison between two different array technologies in the construction of electronic noses: one is mature and advanced (based on metal oxide semi-conductors) and the other one is emerging (based on polymer/black carbon – Nano Composite Array). Among wastes examined in this work, dehydrated sludge from wastewater treatment plants was the most impacting source of odorous VOCs, due basically to sulphur containing volatiles, in particular MDS, carbon disulphide, DMDS. The second source, the by-product of mechanical treated MSWs with low organic content, showed the emission of aromatics (in particular 1,3,5-trimethyl benzene), aliphatic hydrocarbons and terpenes. Two commercial e-noses, named Nose_1 and Nose_2 with different array technologies (MOSs and polymer/black carbon NCA respectively), have been tested for both real-time and in-field detection of odors in the waste management plant and to monitor the abatement process. LDA and CV statistics revealed that Nose_1 is able to discriminate successfully 86.7% of samples, the Nose_2

Table 9

Substances identified by GC-O/MS and odor descriptor in the sample with LoW code 190805 (by-products of mechanical treated MSW).

Substance	Retention time (min)	Odor descriptor	Substance	Retention time (min)	Odor descriptor
Ethanol	4.91		β -Pinene	31.0	
Acetone	5.12		p-Ethyltoluene	31.2	
Methylcyclobutane	5.87		β -Myrcene	32.1	
5-Butanone	6.35		1-, 2-, 3-Trimethylbenzene	32.5	
Ethoxyethene	6.82		Decane	32.9	
Benzene	8.32		3-Carene	33.9	
Methylcyclohexane	11.3		p-Dichlorobenzene	34.1	
Toluene	14.4		o-Cymene	34.8	
Octane	16.5		Limonene	35.4	
Tetrachloroethylene	17.4		m-Propyl-toluene	36.8	
Chlorobenzene	20.3		γ -Terpinen	37.3	
Ethylbenzene	21.5		Acetophenone	37.8	
m/p-Xylene	22.2		Dihydromyrcenol	38.0	
Styrene	23.8		Methyl benzoate	39.3	
o-Xylene	24.2		Fenchone	38.9	
Nonane	24.6		Nonanal	39.6	
m-Ethyltoluene	26.7		Hexadecanal	40.1	
α -Pinene	27.5		Camphor	41.5	
2-Methyl-3-ethylheptane	28.1		1-Propene-1-thiol	41.6	
Camphene	28.6		Naftalene	43.0	
Isocumene	29.2		Undecanal	43.5	
2,3-Dimethyloctane	29.6		4-Phenylcyclohexene	47.3	
1,3,5-Trimethylbenzene	30.9	Urban waste			

Table 10

Substances identified by GC-O/MS and odor descriptor in the sample with LoW code 190805 (sludge from wastewater treatment plant).

Substance	Retention time (min)	Odor descriptor
Ethanol	4.90	
Acetone	5.12	
Carbon disulphide	5.49	Intense garlic
2-Butanol	6.45	Intense garlic
2-Butanone	6.45	Intense garlic
Benzene	8.32	Intense garlic
2-Propanol, 1-methoxy	9.60	Intense garlic
Methylthioacetate	10.1	Intense garlic
Dimethyl sulphide	13.2	Intense garlic
Pyridine	13.4	
Toluene	14.5	
S-Methyl propanethioate	16.6	
2-Methylpyridine	18.6	
Dimethyl disulphide	19.2	
Nonane	24.5	
Propanedioic acid	25.9	
Dimethyltrisulphide	30.5	Intense garlic
1-Heptylamine	33.2	
3,3-Dimethyloctane	34.6	
Limonene	35.4	
Undecane	39.3	
Isomenthol	42.5	
α -Terpineol	43.1	
Dodecane	43.3	

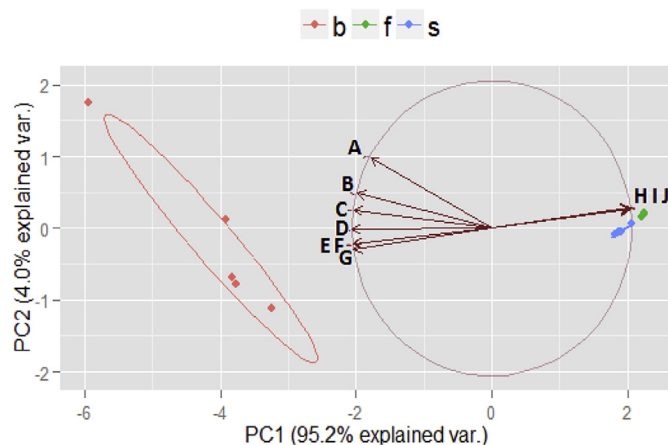


Fig. 4. First two principal components of the three sources in sensor array signals, using Nose_1. Legend: b = biogas; s = by-product of mechanical treated MSW; f = sludge from wastewater treatment plant; sensors: see Table 4. Extrapolated from Giungato et al., 2015.

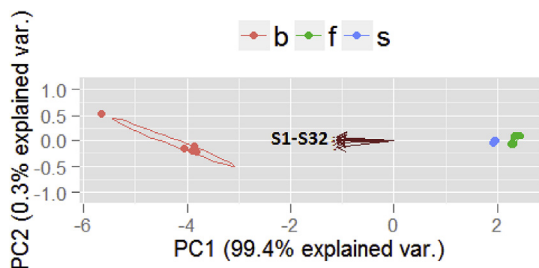


Fig. 5. First two principal components of the three sources in sensor array signals, using Nose_2. Legend: b = biogas; s = by-product of mechanical treated MSW; f = sludge from wastewater treatment plant; sensors: S1–S32 the 32 sensors of the array. Extrapolated from Giungato et al., 2015.

Table 11

LDA recognition by CV ($k = 1$, leave one-out method) of the Nose_1, Nose_2, of an hypothetical array made by integrating Nose_1 and Nose_2 and that relative to a selection of six sensors belonging of both e-noses chosen according to chemical selectivity.

Sensors	LDA recognition (%)
Nose_1	86.7
Nose_2	53.3
Nose_1+ Nose_2	60.0
Selected sensors	93.3

Extrapolated from Giungato et al., 2015.

53.3% of the samples under the experimental conditions used in this work. PCA confirm those results as the higher collinearity of the sensors PCA loadings in the Nose_2, revealed the higher sensitivity in response versus biogas odor active molecules. The sum of both arrays does not improve the results as the recognition capabilities lower to 60.0%. Best results were achieved by choosing specific sensors of both technologies, following the criterion of the selectivity towards the characteristic chemicals emitted from the sources. The selected sensors were: H, G, D, C, belonging to Nose_1 and S1, S2, belonging to the Nose_2. The recognition capabilities of the model in which only six sensors were used in order to discriminate

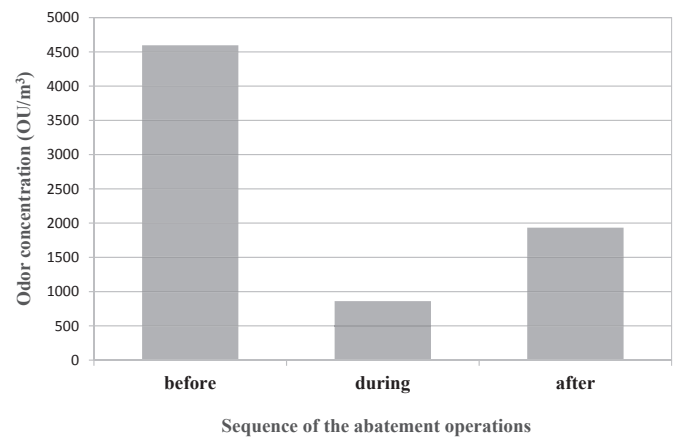


Fig. 6. Odor concentration in ambient air at 1 m distance downwind from a sludge from wastewater treatment plant (LoW code 190805), before, during and after atomization of the abatement product (see Table 7).

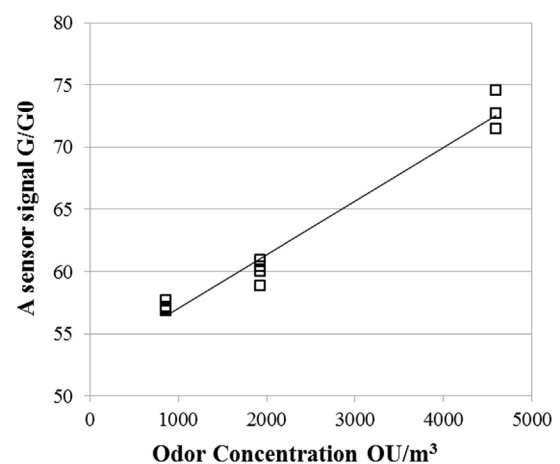


Fig. 7. Correlation between odor concentration and signal of the sensor A ($R^2 = 0.97$) before, during and after atomization of the abatement product (see Table 7).

sample of wastes or odor sources (as biogas), in this case, rose to 93.3%. The statistical analysis revealed that arrays of selected low-cost commercially available gas sensors may be very useful in odor recognition and subsequently for implementing an odor control management system, provided the number of sensors is reduced, by selecting those belonging to both the technologies having specific responses towards the classes of molecules of interest. Also the abatement process, by atomization of a specific commercial product, could be monitored using e-noses, provided a selection of specific sensors in the array was made. Before the abatement experiment in fact, sludge presents a very high odor load (4597 OU/m³) that is lowered during the atomization to 861 OU/m³. After the atomization there is an increase in the concentration of odor to 1933 OU/m³. This suggests that the atomization phase should last as long as the source is exposed to air before being covered by the inert material. A good correlation exists, between odor concentration and the signal of the "A" sensor of the electronic nose Nose_1 during abatement ($R^2 = 0.97$) making feasible the possibility of calibrating the sensor signals to set an alert limit beyond which abatement systems should be activated. The setup of an odor monitoring system should be based on electronic noses whose sensors should be chosen according to the chemicals being responsible of odor discomfort. This selection could be made both by testing on the field a series of commercial arrays and by using statistical techniques, integrated with chemical analysis of sampled air, to select those sensors useful to detect malodors in the specific application. In this way the results from our study could be used to reduce odor problems from waste management plant and future developments of this work may be the integration of sensor signals with atmospheric dispersion models, in order to have the evaluation of the odor impact of the waste management plant operations on receptors living in the surrounds and to predict the "wind days", in which some operations should be avoided.

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References

- Apulia region, 2015. Modifications to the Apulia region law published on January 22, 1999, n. 7, as modified and integrated by the regional law published on June 14, 2007, n. 17. Law n. 23, Apulia bulletin n. 56/2015 (in Italian). beta.regione.puglia.it/documents/10192/4725366/N56+suppl_22_04_15.pdf/610c4295-7ab0-4990-8f67-9fdd2ab100bc?version=1.0 (accessed 04.22.15).
- ARPA Puglia, 2015. Guidelines for issuing opinions concerning the atmospheric emissions produced by wastewater treatment plants. http://www.arpa.puglia.it/cjjournal/view_article_content?groupid=13879&articleId=3598710&version=1.0&resultGroupId=13879 (accessed 04/22/2015).
- Brattoli, M., Cisternino, E., Dambruoso, P.R., de Gennaro, G., Giungato, P., Mazzone, A., Palmisani, J., Tutino, M., 2013. Gas chromatography analysis with olfactometric detection (GC-O) as a useful methodology for chemical characterization of odorous compounds. *Sensors* 13, 16759–16800. <http://dx.doi.org/10.3390/s131216759>.
- Brattoli, M., Cisternino, E., de Gennaro, G., Giungato, P., Mazzone, A., Palmisani, J., Tutino, M., 2014. Gas chromatography analysis with olfactometric detection (GC-O): an innovative approach for chemical characterization of odor active volatile organic compounds (VOCs) emitted from a consumer product. *Chem. Eng. Trans.* 40, 121–126. <http://dx.doi.org/10.3303/CET1440021>.
- Cadena, E., Colón, J., Sánchez, A., Font, X., Artola, A., 2009. A methodology to determine gaseous emissions in a composting plant. *Waste Manag.* 29, 2799–2807. <http://dx.doi.org/10.1016/j.wasman.2009.07.005>.
- Capanema, M.A., Cabana, H., Cabral, A.R., 2014. Reduction of odors in pilot-scale landfill biocovers. *Waste Manag.* 34, 770–779. <http://dx.doi.org/10.1016/j.wasman.2014.01.016>.
- Capelli, L., Sironi, S., Del Rosso, R., Centola, P., Il Grande, M., 2008. A comparative and critical evaluation of odor assessment methods on a landfill site. *Atmos. Environ.* 42, 7050–7058. <http://dx.doi.org/10.1016/j.atmosenv.2008.06.009>.
- CEN, 2003. Air Quality. Determination of Odor Concentration by Dynamic Olfactometry. EN 13725:2003. European Committee for Standardization (CEN).
- Clemens, J., Cuhls, C., 2003. Greenhouse gas emissions from mechanical and biological waste treatment of municipal waste. *Environ. Technol.* 24, 745–754. <http://dx.doi.org/10.1080/09593330309385611>.
- D'Imporzano, G., Crivelli, F., Adani, F., 2008. Biological compost stability influences odor molecules production measured by electronic nose during food-waste high-rate composting. *Sci. Total Environ.* 402, 278–284. <http://dx.doi.org/10.1016/j.scitotenv.2008.04.053>.
- Delgado-Rodríguez, M., Ruiz-Montoya, M., Giraldez, I., López, R., Madejón, E., Díaz, M.J., 2012. Use of electronic nose and GC-MS in detection and monitoring some VOC. *Atmos. Environ.* 51, 278–285. <http://dx.doi.org/10.1016/j.atmosenv.2012.01.006>.
- Fang, J.-J., Yang, N., Cen, D.-Y., Shao, L.-M., He, P.-J., 2012. Odor compounds from different sources of landfill: characterization and source identification. *Waste Manag.* 32, 1401–1410. <http://dx.doi.org/10.1016/j.wasman.2012.02.013>.
- Gallego, E., Roca, F.J., Perales, J.F., Sánchez, G., Esplugas, P., 2012. Characterization and determination of the odorous charge in the indoor air of a waste treatment facility through the evaluation of volatile organic compounds (VOCs) using TD-GC/MS. *Waste Manag.* 32, 2469–2481. <http://dx.doi.org/10.1016/j.wasman.2012.07.010>.
- Giungato, P., Barbieri, P., Lasigna, F., Ventrella, G., Briguglio, S.C., Demarinis Loiotile, A., Tamborra, E., de Gennaro, G., 2015. Integration of different electronic nose technologies in recognition of odor sources in a solid waste composting plant. In: Fassò, A., Pollice, A. (Eds.), *Proceedings of the GRASPA2015 Conference, Bari, 15–16 June, 2015. Special Issue of GRASPA Working Papers. ISSN: 2037-7738.*
- Haug, R.T., 1993. *The Practical Handbook of Compost Engineering.* Lewis Publishers, Boca Raton.
- Hurst, C., Longhurst, P., Pollard, S., Smith, R., Jefferson, B., Gronow, J., 2005. Assessment of municipal waste compost as a daily cover material for odor control at landfill sites. *Environ. Pollut.* 135 (1), 171–177.
- Iranpour, R., Cox, H.H.J., Deshusses, M.A., Schroeder, E.D., 2005. Literature review of air pollution control biofilters and biotrickling filters for odor and volatile organic compound removal. *Environ. Prog.* 24 (3), 254–267. <http://dx.doi.org/10.1002/ep.10077>.
- Jones, P.T., Geysen, D., Tielemans, Y., Van Passel, S., Pontikes, Y., Blanpain, B., Quaghebeur, M., Hoekstra, N., 2013. Enhanced landfill mining in view of multiple resource recovery: a critical review. *J. Clean. Prod.* 55, 45–55. <http://dx.doi.org/10.1016/j.jclepro.2012.05.021>.
- Kaartinen, T., Sormunen, K., Rintala, J., 2013. Case study on sampling, processing and characterization of landfilled municipal solid waste in the view of landfill mining. *J. Clean. Prod.* 55, 56–66. <http://dx.doi.org/10.1016/j.jclepro.2013.02.036>.
- Kasperczyk, D., Urbaniec, K., 2015. Application of a compact trickle-bed bioreactor to the biodegradation of pollutants from the ventilation air in a copper-ore mine. *J. Clean. Prod.* 87, 971–976. <http://dx.doi.org/10.1016/j.jclepro.2014.09.009>.
- Kasperczyk, D., Urbaniec, K., Barbusinski, K., 2014. Removal of pollutants from the air in a copper-ore mine using a compact trickle-bed bioreactor. *Chem. Eng. Trans.* 39, 1309–1314. <http://dx.doi.org/10.3303/CET1439219>.
- Munoz, R., Sivret, E.C., Parcsi, G., Lebrero, R., Wangb, X., Suffet, I.H. (Mel), Stuetz, R.M., 2010. Monitoring techniques for odor abatement assessment. *Water Res.* 44, 5129–5149. <http://dx.doi.org/10.1016/j.watres.2010.06.013>.
- Nagle, H.T., Gutierrez-Osuna, R., Kermani, B.G., Schiffman, S.S., 2003. Environmental monitoring. In: Pearce, T.C., Schiffman, S.S., Nagle, H.T., Gardner, J.W. (Eds.), *Handbook of Machine Olfaction-Electronic Nose Technology.* Wiley-VCH, Weinheim, pp. 419–444.
- Niskanen, A., Värri, H., Havukainen, J., Uusitalo, V., Horttanainen, M., 2013. Enhancing landfill gas recovery. *J. Clean. Prod.* 55, 67–71. <http://dx.doi.org/10.1016/j.jclepro.2012.05.042>.
- Penza, M., Suriano, D., Cassano, G., Pfister, V., Amodio, M., Trizio, L., Brattoli, M., De Gennaro, G., 2015. A case-study of microsensors for landfill air-pollution monitoring applications. *Urban Clim.* 14 (3), 351–369. <http://dx.doi.org/10.1016/j.uclim.2014.09.002>.
- Romain, A.-C., Delva, J., Nicolas, J., 2008. Complementary approaches to measure environmental odors emitted by landfills areas. *Sensors Actuators B* 131, 18–23. <http://dx.doi.org/10.1016/j.snb.2007.12.005>.
- Rubio-Romero, J.C., Arjona-Jiménez, R., López-Arquillos, A., 2013. Profitability analysis of biogas recovery in municipal solid waste landfills. *J. Clean. Prod.* 55, 84–91. <http://dx.doi.org/10.1016/j.jclepro.2012.12.024>.
- Shao, L.-M., Zhang, C.-Y., Wua, D., Lü, F., Li, T.-S., He, P.-J., 2014. Effects of bulking agent addition on odorous compounds emissions during composting of OFMSW. *Waste Manag.* 34, 1381–1390. <http://dx.doi.org/10.1016/j.wasman.2014.04.016>.
- Shen, Y., Chen, T.-B., Gao, D., Zheng, G., Liu, H., Yang, Q., 2012. Online monitoring of volatile organic compound production and emission during sewage sludge composting. *Bioresour. Technol.* 123, 463–470. <http://dx.doi.org/10.1016/j.biortech.2012.05.006>.

- Stuetz, R.M., Fenner, R.A., Engin, G., 1999. Assessment of odors from sewage treatment works by an electronic nose, H₂S analysis, and olfactometry. *Water Res.* 33, 453–461.
- Van Durme, G.P., McNamara, B.F., McGinley, C.M., 1992. Bench-scale removal of odor and volatile organic compounds at a composting facility. *Water Environ. Res.* 64, 19–27.
- Wanichpongpan, W., Gheewala, S.H., 2007. Life cycle assessment as a decision support tool for landfill gas to energy projects. *J. Clean. Prod.* 15 (18), 1819–1826. <http://dx.doi.org/10.1016/j.jclepro.2006.06.008>.
- Zhang, H., Schuchardt, F., Li, G., Yang, J., Yang, Q., 2013. Emission of volatile sulfur compounds during composting of municipal solid waste (MSW). *Waste Manag.* 33, 957–963. <http://dx.doi.org/10.1016/j.wasman.2012.11.008>.

Glossary

Notation list

CV: cross validation
DMDS: dimethyl disulphide

DMS: dimethyl sulphide
G: electrical conductivity [Siemens]
GC–MS: gas chromatography–mass spectrometry
GC–O/MS: gas chromatography–mass spectrometry/olfactometry
GHG: greenhouse gas
LCA: life cycle assessment
LDA: linear discriminant analysis
LoW: list of wastes according to the Commission Decision 2000/532/EC, amended by Commission Decision 2014/955/EU
MOS: metal oxide semiconductor
MSW: municipal solid waste
NCA: nano composite array
OU: odorimetric unit
OU/(s m²): specific odor flux rate
OU/m³: odorimetric units per cubic meter
OU/s: odor flux rate
PAHs: polycyclic aromatic hydrocarbons
PCA: principal component analysis
PTFE: poly tetra fluoro ethylene
R: resistance [Ohm]
VOC: volatile organic compound