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On Line Monitoring of Odour Nuisance at a Sanitary Landfill for Non-Hazardous Waste

Federico Cangialosi*, Gianluca Intini, Dario Colucci

T&A - Tecnologia e Ambiente Srl, spin-off of the Technical University of Bari, via Tanzi 39/E, 70121 Bari, Italy
federico.cangialosi@icloud.com

A field study was carried out to assess the possibility of monitoring online malodours from a sanitary landfill for non-hazardous waste. To that aim, the performance of a multisensory electronic nose and a H_2S continuous analyser used in situ was evaluated to identify odorous compounds in ambient air emitted from the landfill as perceived at the nearest municipal receptor (the city of Statte, Southern Italy) and compared with the results obtained in laboratory by dynamic olfactometry. Alert situations were conventionally established when two consecutive H_2S concentration measurements at 5 min intervals exceeded 20 ppb or when odour emissions measured by the e-nose exceeded 500 OU/m^3 for more than 5 min. The study comprised two main activities: 1) training the e-nose to recognize the odorous compounds emitted from the landfill; 2) evaluating the efficiency of the H_2S continuous analyser to provide useful information related to biogas emission. Activity 1 demonstrated the e-nose effectiveness for on-line monitoring, quantifying and identifying the odours produced by the landfill. Data processing showed that CDA was the most suitable algorithm to achieve best odours' pattern recognition. Activity 2 showed that H_2S measurements, depending on site-specific factors identified by Kolmogorov-Smirnov test, were poorly correlated with odour concentration in ambient air measured by dynamic olfactometry, as dynamic olfactometry takes into account the effect of other emitted compounds or the masking/enhancing effect of other compounds over H_2S. Accordingly, further site-specific investigation is deemed necessary in order to achieve full on-line control of air quality and to adopt proper management measures at sanitary landfills and other odour emitting sources.

1. Introduction

Unpleasant odour emission is often a major cause of citizens' complaints about local environmental quality. Many economic activities and land uses (e.g., waste composting or landfilling, wastewater treatment plants, intensive live stock breeding etc.) emit a level of odour that may potentially compromise neighbour hoods' life quality and, in crowded areas, often causes legal suits toward existing plants or prevents the authorization of new ones. VOCs emitted from industrial sources and characterized by unpleasant odour include mercaptanes, sulphides (disulphides), amines, carboxylic acids, aldehydes, ketones, aliphatic and aromatic hydrocarbons, etc. In addition to regulatory limits to odour emission in developed countries (in Italy, the national law delegates to the regions the definition of the limits of odour emission through the environmental authorizations and some regional regulations), this situation calls for proper techniques and procedures for online malodours' measurement around sanitary landfills and other plants. Three techniques for odour nuisance characterization and quantification are already available: Analytical: chemical analyses; Sensorial: dynamic olfactomerty; Senso-instrumental: electronic nose. Their results, however, are often neither comparable nor useful for continuous online monitoring (Gostelow et al. 2001; Capelli et al., 2008; Giuliani et al. 2012; Gębicki et al. 2017; Zarra et al. 2017; Szulczyński et al. 2018).The analytical approach based on chemical analyses by gas chromatography coupled with mass spectrometry (GC–MS) allows to determine quali-quantitatively the occurrence of odorous substances of known odour threshold level in a complex mixture, but with out correlation with the overall effective odour due to masking and/or synergic effects in the mixture (Stuetz et al. 1999; Davoli et al. 2003). Similarly, in-situ H_2S measurement by a gold-film analyser, considered a valuable odour assessment tool, seldom provides relationship among other odorous chemicals present and their cumulative overall odour threshold (Bull et al. 2014; Fasolino et al. 2016).The sensorial approach (*dynamic* *olfactometry*, EN 13725, 2004),based on the statistical evaluation of the sensorial reaction of a panel of qualified examiners to the progressive dilution of an odorous mixture, is probably the most affordable techniques, yielding the odour concentration (C_{od} in ou_E/m^3 units) response to be compared with the limits in force; however, it cannot provide in-situ/real-time or online measurements. The senso-instrumental approach (*electronic nose*) is the only technique that allows continuous monitoring of odours in-situ (Giuliani et al. 2012; Naddeo et al. 2016).The e-nose instrument depends on a suitable array of non-specific gas chemical sensors combined with a chemometric processing tool. The classification of the odours is obtained by comparing e-nose signals with a database of patterns acquired previously in the training phase, particularly important and delicate, consisting in the analysis of different gas samples of known olfactory quality diluted at different C_{od} values. The training phase allows the instrument to recognize qualitatively the odours emitted by the given sources (a sanitary landfill in our case) by attributing them to a specific olfactory class in that source into a spatial domain(waste acceptance, landfill gas extraction wells, leachate collection tanks etc.) and, quantitatively, by estimating the C_{od} of the analysed air (Capelli et al., 2008). Different statistical models are available to that aim (PCA, CDA, KNN, PLS, SVM) (Zarra et al. 2017; Blanco-Rodrìguez et al. 2018; Moufidet al. 2017).The goal of this study was to evaluate the ability of a multi-sensor commercial e-nose to measure and recognize on line the odours emitted from the sanitary landfill in different operative situations, using different statistical models and H_2S measurements in situ as well as dynamic olfactometry as benchmark.

2. Materials and methods

The study concerned a sanitary landfill for non-hazardous waste distant 3 km from Statte, South Italy (Figure1a). The sanitary landfill, active since 2004, occupies a former limestone quarry, with 213.000 m^2 surface and 37 m average depth below ground level for an overall capacity of 6.2 M m^3 of waste.

Figure 1a: territorial framework (by Google)

Figure 1b: sanitary landfill and monitoring points

Emission of malodorous gas was monitored in situ (Figure 1b) by anH_2S continuous analyser(Jerome® J605 by Arizona Instr., AZ) and by a commercial multisensor e-nose equipped with 32 sensors (MSEM32® by Sensigent, Cal.). In order to achieve full control of odour monitoring, the procedure was integrated by an automaticmanagement system (OdorSens®) and automatic air samplers (OdorPrep® by Labservice Analytica). When alert situation was exceeded, the air samplers purged automatically 8 L samples of biogas to be sent for analysis at the dynamic olfactometry laboratory according to the standard method EN 13725:2004. Alert situation was conventionally established (with the Local Environmental Protection Agency),when 2 consecutive measurements at 5 min(specific frequency of the instrument) intervals by the H_2S analyser exceeded 20 ppb, or when overall odour emission measured by the e-nose exceeded 500 OU/m^3 for more than 5 min (specific frequency of the instrument of 10 sec).The equipment was placed at ground level, on the North boundary of the landfill, facing Statte3 km and 0.8 km to the first urban receptor. The study comprised 2 activities: 1) training the e-nose and 2)evaluating H_2S continuous analysis efficiency to provide informations related to the landfill odour emissions, as compared with dynamic olfactometry results.

2.1 Activity 1

A 4-months training of the MSEM32 e-nose was first carried out (March-June 2017) following the procedure suggested by Capelli et al. (2008) and by Giuliani et al. (2012). To that aim 16 biogas samples, contained in 8L Nalophan bags, were taken in duplicate with a system composed by a land box and a 10L/minpump,13 at landfill surface (diffuse emission) by ambient air direct sampling and 3 directly into the gas extraction wells, and analysed by dynamic olfactometry for calibration purposes. Then in July 2017 the e-nose was placed at the North boundary of the sanitary landfill, the closest position (approx. 1 km) to the most sensible receptor in the area (Statte suburbs). A database was implemented in order to build a proper reference space (*Canonical Space*) wherein homogeneous classes of odours can be detected and recognised. Three classes of odours stemming from the landfill were then sampled from: a) waste resulting from mechanical treatment of non-hazardous wastes with high or low organic content (14 samples); b) sludge from the municipal WWTP (6 samples); c) H_2S (6 samples). The Chemometric Data Analysis software (CDA v.11.2 by Sensigent 2017) was employed for the preliminary checking of the response by the 32 sensors of the e-nose, at the sample analyses. After discarding the false responses, the train and the validation set were defined, and a*Principal Component Analysis* (PCA) was applied. A sensitivity analysis was performed to assess the importance for pattern recognition, scale factor (Mean Center and Autoscaling) and the *Importance Index Weighting* (IIW) of the 3 algorithms tested: CDA (*Canonical Discriminant Analysis*), linear, unsupervised, KNN (*K-Nearest Neighbor*) and SVM (*Support Vector Machine*), both nonlinear, supervised. IIW is a proprietary algorithm implemented in CDAnalysis for setting individual effectiveness of the 32 sensors. Data files generated by MSEM32 program can be imported into CDAnalysis and processed in off-line mode. By experimenting with different pre-processing options and pattern classification algorithms, the configuration that works the best for a particular sensing application of the MSEM32 e-nosewas determined.

2.2 Activity 2

During the second activity the H_2S continuous analysis efficiency to recognize malodorous compounds emitted from the landfill was compared with the results of dynamic olfactometry. The Kolmogorov-Smirnov non-parametric test was adopted using the 2-factors procedure with the equipment operating in different situations: 1)winds upstream the landfill area (S-SE and calms); *2)*waste landfilling activity in or out of service.Finally, the correlation among the results from H_2S analyzer, e-nose and dynamic olfactometry was checked. Activity 2 lasted 4 months more (September-December 2017).

3. Result and discussion

3.1 Activity 1

The individual response of the 32 sensors of the MSEM32 e-nose, evaluated through the corresponding IIW, is reported in Table 1 and shown in Figure2 by reference to 2 classes of odour: municipal WWTP sludge and landfill well biogas. The results allowed to appreciate sensors S2, S4, S5÷S15 and S32 (0.76 ≥IIW ≥ 7.13) performing satisfactorily well toward those classes of odours, while sensors S1 and S3, in spite of their high IIW value, appeared insensitive to the odorous chemicals present into those classes. Sensors S16÷-S31 (not shown in Figure2), have a low IIW value.

Table 1: IIW (Importance Index Weighting) of the 32 sensors (S_i) of MSEM32 e-nose for this work. For the IIW value of sensors S16÷S31, in table is reported only the range of variation.

S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}	S_{11}	S_{12}	S_{13}	S_{14}	S_{15}	S_{16}-S_{31}	S_{32}
2.94	1.11	3.00	1.11	2.33	2.28	1.02	2.06	1.91	0.96	0.76	1.68	1.51	0.83	7.13	0.13÷0.71	1.11

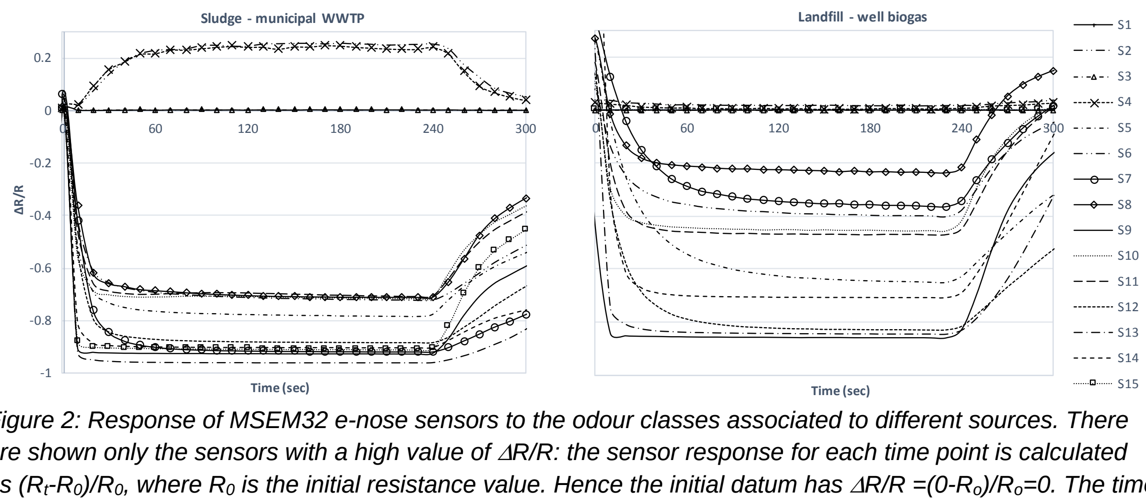

Figure 2: Response of MSEM32 e-nose sensors to the odour classes associated to different sources. There are shown only the sensors with a high value of ΔR/R: the sensor response for each time point is calculated as $(R_t-R_0)/R_0$, where R_0 is the initial resistance value. Hence the initial datum has $\Delta R/R = (0-R_o)/R_o=0$. The time 0 sec corresponds to the start of the odour sampling by the e-nose.

For each simulation, a cross validation test of the results allowed to assess the pertinent *Canonical Space*, wherein the odours are point-confined. The cross validation test, in turn, permitted to evaluate the efficiency of the 3 algorithms tested (CDA, SVM and KNN) to recognize odour classes by means of the probability (C_{prob}), the confidence (C_{conf}) and the distance of each point from its virtual odour class of pertinence. As shown in

Table 2, the best algorithm for pattern recognition in the conditions investigated resulted to be CDA; a similar performance occurred with SVM algorithm but it required more complex mathematical calculations, while the best result with KNN was below 75% (the same of Gębicki et al. 2017, ks=3).As shown in Figure 3, in the best configuration (CDA, MC, all sensors), the *Canonical Space*, where the different classes of odour utilized for training the e-nose are clearly distinct, is 3D with 3 useful principal components: PC1 = 62.53%; PC2 = 36,83%; PC3 = 0,64%.

Table 2: Results of Pattern Recognition Tests (P.R.T.), only the best three results, one by algorithm, are shown compared to the 18 tests performed.

Algorithm type	Scaling Factor	Active Sensors	Landfill-biogas		Municipal-waste		Sludge-WWTP		H_2S		P.R.T.
			C_{conf}	C_{prob}	C_{conf}	C_{prob}	C_{conf}	C_{prob}	C_{conf}	C_{prob}	
CDA	MC	S1÷S32	High	99	Medium	75	Medium	84	High	100	100 %
SVM	Auto	IIW > 0.7	Svm	0.97	Svm	0.99	Svm	0.96	Svm	0.98	100 %
KNN	MC	S1÷S32	Hight	100	Low	65	P.R. wrong		Hight	88	75 %

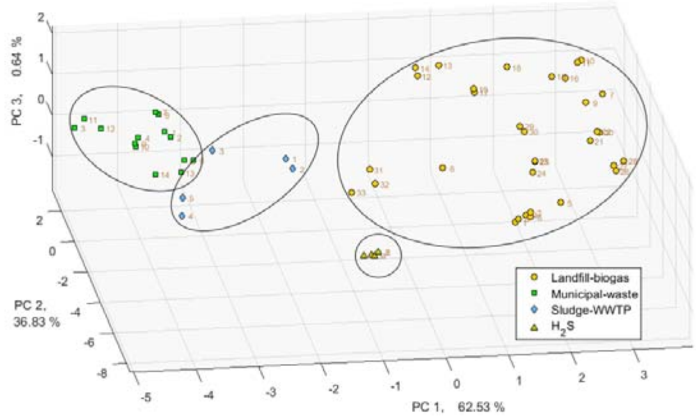

Figure 3: Score plot in Canonical Space with Mean Center

3.2 Activity 2

As shown in Figure4, given the same wind conditions and landfilling activities (Yes/No), no correlation resulted between H_2S measurements with the Jerome J605 continuous analyzer and odour concentrations obtained with MSEM32 e-nose.

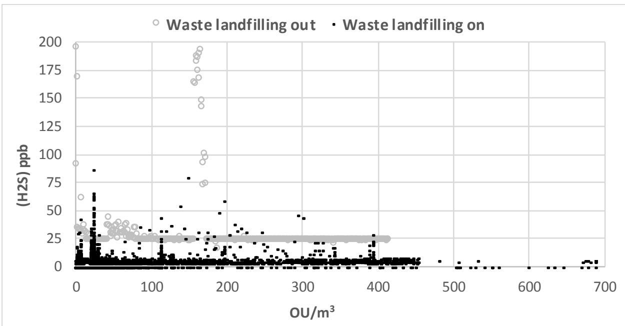

Figure 4: Absence of correlation between H_2Scontinuous measurements bythe Jerome J605 analyzer and OU/m^3 values obtained by MSEM-32 e-nose with appreciable S-SE wind + calms.

The non-parametric Kolmogorov-Smirnov test provided largely different p-values for the continuousH_2S analyzer Jerome J605and the e-nose (2.6E-89 and 4.6E-22 respectively). Wind characteristics (direction and velocity) as well as the waste disposal into the landfill, hence, play a significant role: as expected, odours significantly different quali-quantitatively are emitted if the waste landfilling activity is on (ON) (Figure5a, 6a) or stopped (Figure5b, 6b).

A total of 21 alert situations occurred during Activity 2: in 19% of cases the wind did not blow from the landfill. With S-SE wind (+ calms), 59% of cases occurred with waste landfilling on and 41% during the night.

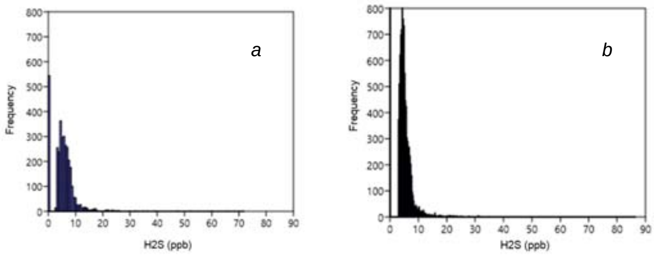

Figure 5: Different probability distributions of H_2S (ppb) measured by Jerome J605 continuous analyzer, in correspondence of SSE wind and calms (a:Waste landfilling on; b: Waste landfilling out).

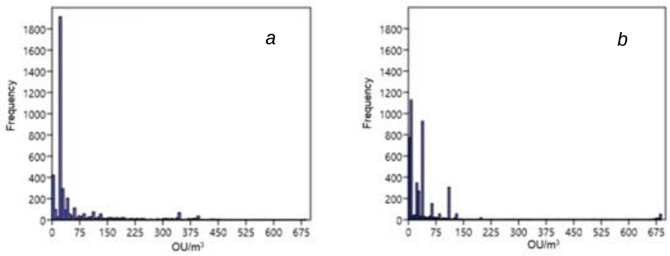

Figure 6: Different probability distributions of OU/m^3 measured by MSEM-32 e-nose, in correspondence of SSE wind and calms (a:Waste landfilling on; b: Waste landfilling out).

As already seen for in Figure4, the data in Figure7 indicate that the dynamic olfactometry measurements do notshow any correlation withH_2S measurements byJerome J605 continuous analyzer during those 21 alert situations, in agreement with Stuetz et al., (1999), Capelli et al., (2008) and Bull et al., (2014).

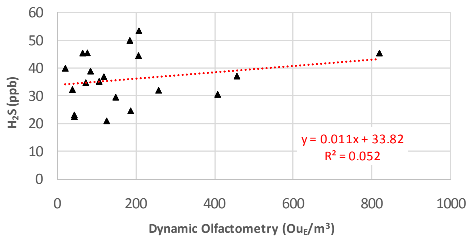

Figure 7: Absence of correlation between H_2Scontinuous measurements by Jerome J605 analyzer and ou_E/m^3 values obtained by dynamic olfactometry

No correlation (R^2=0.0666)was found between values obtained by the MSEM-32 e-nose and by dynamic olfactometry measured in the same 10 min time-window adopted by the Jerome J605 continuous H_2S analyzer. However, with wind from the landfill (S-SE + calms) and at night (landfilling service out), the MSEM-32 e-nose predicted OU/m^3 values with a regression coefficient (R^2 = 0.58, Figure 8b) comparable to the one achieved during its training (R^2=0.60, Figure 8a). In those conditions, odour emissions are due to biogas diffusion from landfill surface and this confirms that e-nose quantitative training was carried out correctly. Wind calms, usually occurring at night-time and early in the morning, favour odour stagnation in the atmosphere.

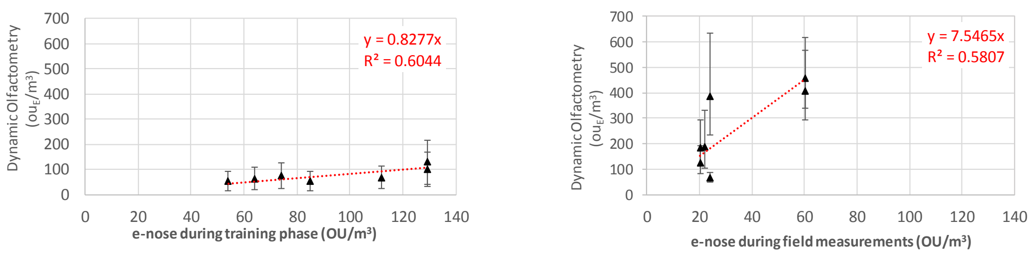

Figure 8. Correlation between OU/m^3 values obtained by the dynamic olfactometry and the e-nose.

Finally, evidences collected during this campaign indicated that other odorous activities carried on in that same area may interference with malodours by the sanitary landfill and, hence, with their appreciation by the e-nose.

4. Conclusions

The results of a field study carried out to assess the possibility of continuous odour monitoring at a malodorous plant by combining chemical analysis (H_2S portable continuous analyser) with sensorial (dynamic olfactometry) and senso-instrumental (electronic nose) techniques were partly satisfying. In the case investigated (a sanitary landfill for non-hazardous waste) major interferences were expected from plant operation regime (day-time *vs.* nigh-time), weather conditions (wind direction, velocity and intensity; humidity; temperature; solar radiation), presence of other malodorous activities in the area, etc. Even in comparable situations (wind calms, no waste landfilling), however, instrumental odour measurements carried out simultaneously by an H_2S continuous analyser (Jerome® J605 by Arizona Instr., AZ) and by a commercial multisensor e-nose (MSEM32® by Sensigent, Cal.) cannot be correlated, while the measurements done with the e-nose proved to correlate with those obtained by dynamic olfactometry. Further site-specific investigation is deemed necessary in order to achieve full on-line control of air quality and to adopt proper management measures at sanitary landfills and other noxious odour emitting sources.

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