

Odour Emissions Characterization from Wastewater Treatment Plants by Different Measurement Methods

Tiziano Zarra ^{*a}, Martin Reiser ^b, Vincenzo Naddeo ^a, Vincenzo Belgiorno ^a,
 Martin Kranert ^b

^a Department of Civil Engineering, University of Salerno, Via Giovanni Paolo II, 132, 84084 Fisciano (SA), Italy (I)

^b Department of Civil Engineering, Stuttgart University, Bandtåle 1,2, 70569 Stuttgart, Germany (D)
 tzarra@unisa.it

During last decades several techniques were proposed for the measurement of odours in environmental field but until now no one was applied and diffused between worldwide countries. These due to the presence of a large number of variables correlated to fast and continuous variability of odours, their low concentration in environment, the meteorological conditions, the difficulty to sampling a representative volume of air.

In Europe the dynamic olfactometry method was standardized in 2003 by EN 13725 and was proposed for the measurement of odour emissions. At same time several Countries have specific guidelines that norm in different way the assessment of odours.

The scope of this study is to compare and evaluate the principal odour measurement methods (GC-MS, dynamic olfactometry, and electronic nose), nowadays applied in technical practices and reported in current scientific literature, used to identify and characterize the odour emissions from a wastewater treatment plant, with the aim of analysing the weaknesses and strengths of the different techniques. The study of the correlation between odour concentrations measured by different methods was also presented. The evaluation and analyses of the different odour measurement techniques have been carried out at the ISWA Institute of the Department of Civil Engineering, Stuttgart University. The investigated samples, collected at the different odour sources at wastewater treatment plant (WWTP) LFKW located at Stuttgart University Campus (Northern Germany), are analysed by dynamic olfactometry, electronic nose (eNose) and gas chromatography and mass spectrometry (GC-MS).

The results obtained highlight the various data on the odour concentrations between different measurement methods at each sampling source of WWTP. Odour indexes were proposed to compare and evaluate the different sensorial and analytical techniques.

1. Introduction

Odours emitted by wastewater treatment plants (WWTPs) are one of the major concern for local authorities in relation of the nuisance generate in the neighbourhoods (Belgiorno et al., 2012). Responses to odours are highly variable and can result in a wide variety of effects (Zarra et al., 2008) and in addition there is no universally accepted method for the characterization of odours and assessment of their impacts (Naddeo et al., 2012). Currently, the techniques available for odour characterization are classified into three categories (analytical, sensorial and mixed) and each one present different advantages and limits (Belgiorno et al., 2012; Köster, 1986; Jiang, 1996; Gostelow et al., 2001).

Analytical methods are able to identify and quantify the chemical compounds present in the malodorous emissions. These techniques have the advantage of objectivity, repeatability and accuracy (Zarra et al., 2009); while the identification and quantification of specific odours does not directly indicate the potential odour nuisance, this information is useful for identifying and tracking odour sources (Zarra et al., 2009). Main analytical techniques used to identify and quantify the chemicals present in gaseous emissions

include: GC-MS, colorimetric method, catalytic, infrared and electrochemical sensors, differential optical absorption spectroscopy and fluorescence spectrometry (Belgiorno et al., 2013; Gostelow et al., 2001; Zarra et al., 2009). GC-MS is the most powerful analytical tool for the quantification and identification of volatile organic compounds (VOCs) and volatile sulphur compounds (VSCs) (Zarra et al., 2008; Zarra et al., 2009); the main limit of this technique relies on the complexity of odour composed by mixtures of many volatile chemicals, often at concentration lower than the instrumental detection limit (Brattoli et al., 2011).

Sensorial techniques, such as dynamic olfactometry, use the human nose as a sensor and therefore was able to characterize odours nuisance by referring directly on their effects on a panel of qualified examiners. In addition to olfactory properties there are several factors that may influence odour perception, however this category measure the real odour perception but is not applicable to measure continuously odours in the Environment (Köster, 1986; Jiang, 1996; Gostelow et al., 2001; Zarra et al., 2009).

Mixed techniques use sensorial/analytic approach and propose new instrument that are able to simulate human sense (electronic nose - eNose). eNose has the potentiality to combine "the odour perception" and the continuous "field monitoring". The instrument, based on non-specific gas chemical sensor arrays combined with a chemometric processing tool, provides a suitable technique for in site monitoring of odours (Nicolas et al., 2004; Capelli et al., 2008; Giuliani et al., 2012).

The electronic nose has probably the best potentialities to answer to the expectations of the various actors of the environmental issues in relation with the odours annoyance (Nicolas et al., 2004). eNoses has long been used for a number of different applications from food to cosmetic industries to quality control. However, a number of limitations in environmental field are associated with the properties of chemical sensors, the signal processing performances and the real operating conditions of the environmental field (Nicolas et al., 2004; Capelli et al., 2008; Giuliani et al., 2012).

However continuous odour measurement is necessary to monitor odour emission from wastewater treatments plants as well as to identify strategies to control the impacts of odour emissions on local communities.

The work presents a comparison of performance of three different odour measurement methods (GC-MS, dynamic olfactometry, and eNose) to characterize odour emission from Wastewater Treatment Plant. The study of a correlation between odour concentrations measured by different methods was also presented.

2. Material and methods

2.1 Sampling Program

Research studies were carried out at LFKW wastewater treatment plant (WWTP), localized at the Institute of Sanitary Engineering Water Quality and Solid Waste Management (ISWA) of the Stuttgart University (Baden Wuerttemberg Region, South-western Germany).

The plant treat wastewater from the University Campus and BÜsnau village (Table 1) by a conventional active sludge scheme (Zarra et al., 2008).

Table 1. Design and operational characteristics of the LFKW WWTP.

Parameter	Value
Flow rate	2000 m ³ /d
Average Biogas production	47000 m ³ /year
Grit material production	18 t/year
Sand production	8 t/year
Dried sludges production	2150 t/year
BOD ₅	290 mg/L
COD	500 mg/L

Air emissions was sampled in accordance with EN 13725:2003 by vacuum pump device in 14L of Nalophan bags (films thickness 20µm) at four different sampling points: two in wastewater treatment line (P1, Grit; P2, Aeration) and two in sludge treatment line (P3, Thickener; P4, Centrifuge).

At each investigated treatment unit were collected two samples a week for two consecutive months. A total of 64 bags were sampled during the investigation period at the WWTP. Collected samples were characterized and analysed by sensorial, analytical and mixed methods within 14 hours of sampling to ensure the reliability of the measurements (Zarra et al 2012).

2.2 Analytical measurement

Analytical measurement was carried out by GC-MS (Agilent Technologies Inc., 6890 and 5973 model) equipped with a flame-ionisation detector (FID). The taken samples were adsorbed on a thermo desorption

tubes filled with Tenax TA resin. For gas sampling a gas sampler (Gerstel) was used and a gas volume of 2000 ml was drawn through each tube with a constant flow of 200 ml*min⁻¹. The tube was inserted into the thermo desorption unit of the GC-MS, where it was heated to desorb the compounds on the resin bed into a cooled injection system with an included programmed temperature vaporizer. For thermal desorption the following temperature program was used: starting from 30°C, it ramped at an interval of 30°C min⁻¹ up to 150°C, held for 2 min, then ramped at 60°C min⁻¹ up to 260°C, holding there for 6 min; the helium flow rate was 50 ml min⁻¹. The PTV injector was cooled and held at -100°C for the total desorption time and then ramped at 12°C s⁻¹ in splitless mode to 280°C and held for 3 min. The desorption was done in splitless desorption mode to transfer all compounds to the GC-MS system.

2.3 Sensorial measurement

Sensorial analysis were conducted by dynamic olfactometry of all sampled bags at the Olfactometric Laboratory of the ISWA Institute of the University of Stuttgart.

Olfactometric analyses were carried out according to EN 13725:2003 using an olfactometer model TO8 (ECOMA, GmbH), based on the "yes/no" method. All the measurements were analysed within 14 h after sampling, according to Zarra et al. (2012) studies, relying on a panel composed of 4 trained persons.

2.4 eNose measurement

Odour measurements were performed with the multisensor array system seedOA (Sanitary Environmental Electronic Device for Odour Application) according to procedure proposed by Giuliani et al (2013). The seedOA consists in a set of 12 metal oxides non-specific gas sensors (MOS), 2 specific gas sensors and 2 internal conditions sensors (humidity and temperature), placed on two different levels of a innovative measurement chamber (CODE[®]) (Viccione et al. 2012) patented by the SEED research group of the University of Salerno. All the used sensors (TGS, Figaro, F) were chosen according to their suitability for sanitary environmental engineering applications. Working flow rate was settled equal to 300 ml/min. A specific software controls the hardware and allows the acquisition of the sensor signals.

To train the seedOA and create the qualitative and quantitative model, were collected from each of the investigated sources, before starting the monitoring program, five samples. Each sample was diluted according to the ratio 1:2, 1:10, 1:25 and analyzed by both seedOA and dynamic olfactometry. All the acquired data are then processed by the Linear Discriminant Analysis (LDA) and the Partial Least Squares regression (PLS) statistical mathematical method to define the quantitative model.

2.5 Comparison of odour emissions detected by different methods

In order to compare and assess the odour emissions detected by different measurement methods were calculated several odour index according to Zarra et al (2009). This approach allows to determinate an odour index for each measurement methods that give an dimensionless and comparable value of the odour perception. Calculated indexes are following: Analytical Odour Index (AOI), Sensorial Odour Indexes (SOI and SOIen).

Analytical Odour Index (AOI) was determinable at i-th sampling point (P_i) by the following expression:

$$AOI_i = \sum_{y=1}^n \left(\frac{C_y}{OT_y} \right)$$

where: n is the number of relevant volatile compounds at P_i; C_y is the concentration of y-th volatile substances detected by GC-MS analysis at P_i; OT_y is the Odour Threshold of the y-th volatile substances detected. The OT_y values used for the determination of AOI are the lowest values proposed by Ruth (1986) to take into account people with more sensitive olfaction; this approach gives greatest values of AOI for the same measured concentrations.

Sensorial Odour Index (SOI) was determinable at i-th sampling point (P_i) by the following ratio: U_i/U_s. Where U_i is the concentration of odour emission at i-th sampling point (P_i) detected by dynamic olfactometry and expressed in terms of OU/m³; while U_s is the Odour concentration at the threshold value (1 OU/m³). Similarly SOIen was the Sensorial Odour Index, where the Odour concentrations (U_i) was detected by eNose.

3. Results and discussions

3.1 Odour emissions characterization by analytical methods

Analytical analyses show (Table 2) the presence of a wide variety of organic sulphides and organic nitrogen-based compounds along with some oxygenated organic compounds and organic acids, mercaptans (R-SH) and amines at all sampling point. Several substances were detected in Odour emissions; the highest number of different substances was detected at aeration treatment unit (P2).

Table 2. LFKW Odour emission characterization by GC-MS (C_{max} maximum concentration detected)

Substances	C_{max} [$\mu\text{g/L}$]				Substances	C_{max} [$\mu\text{g/L}$]			
	P1	P2	P3	P4		P1	P2	P3	P4
1-4-dichlorobenzene	-	14,08	-	-	dodecane	-	3,82	3,56	-
2-butanone	-	-	-	327,06	ethyl-benzene	-	-	15,45	-
2-butoxy-ethanol	-	-	-	103,08	hexane	-	-	3,90	-
2-ethyl-hexanol	-	28,21	37,07	44,26	hydrogen disulfide	6,54	1,82	3,22	14,02
2-methyl-1-ethyl-benzene	12,57	-	-	-	limonene	10,66	15,11	9,19	111,21
2-methyl-dioxolane	44,70	-	-	-	methyl-cyclohexane	-	5,08	11,60	-
α -pinene	-	11,91	-	15,20	nonanal	10,76	6,54	5,64	23,19
acetic acid	-	56,89	-	103,03	nonane	11,03	4,80	-	-
benzaldehyde	-	9,81	14,47	67,66	octamethyl-cyclotetrasiloxane	-	-	570,07	11,52
benzene	10,15	9,35	21,69	-	octane	12,55	-	-	14,62
butanoic acid	-	22,76	-	-	p-Xylene	23,85	15,93	41,58	14,59
decanal	6,26	7,68	4,82	23,60	propanoic acid	-	11,17	-	-
decane	8,29	-	-	-	sulfur dioxide	-	-	663,49	230,14
dimethyl-benzene	10,00	-	18,73	11,35	tetrachloroethylene	11,80	-	-	-
dimethyl-disulfide	-	-	29,88	252,98	tetradecane	4,09	3,52	3,49	-
dimethyl-trisulfide	-	-	1,13	43,67	toluene	30,75	11,04	514,31	289,94
dimethyl-undecane	-	-	20,28	-	tridecane	-	3,10	3,34	-
dimethylamine	197,34	-	-	-	trimethyl-benzene	11,98	9,53	8,58	7,41
					undecane	5,64	-	2,61	-

Sulfur dioxide was the volatile substance detected with highest concentration in the plant, confirming its key role in odour emission from WWTP (Gostelow et al., 2001; Belgiorno et al., 2012). The monitoring point at sludge treatment line (P4) has reported the heights average concentrations of volatile substances. Toluene, sulfur dioxide, octamethyl-cyclotetrasiloxane and dimethyl-disulfide are the detected substances with highest variability overall the plant. Some volatile compounds as methanethiol are expected in the odour emissions but are not present in Table 2 due to the difficulty of their determination by GC-MS (Brattoli et al. 2011).

3.2 Odour emissions characterization by dynamic olfactometry

In Figure 1 were summarized the results of sensorial characterization of Odour emissions by dynamic olfactometry at the LFKW plant.

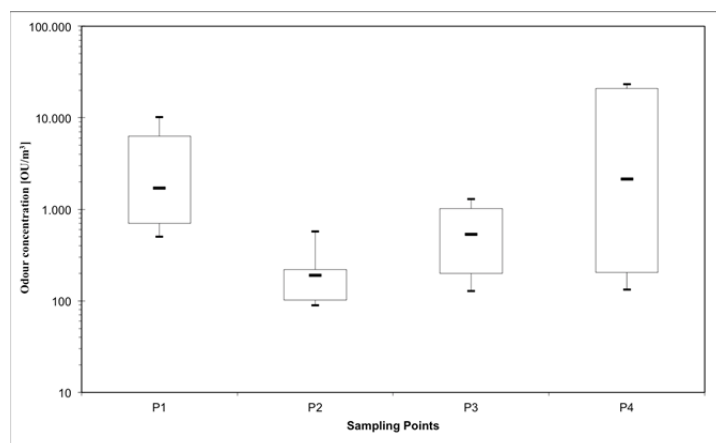


Figure 1. Characterization of Odour emission at LFKW plant by dynamic olfactometry.

3.3 Characterization of Odour emission at LFKW plant by eNose

Results of odour characterization by trained seedOA eNose are represented in Figure 2. Data indicate that the multi sensors array is able to detect the Odours with similar sensitivity of dynamic olfactometry.

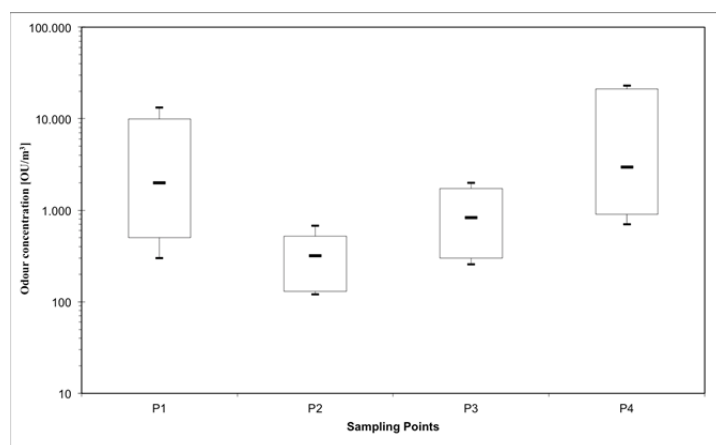


Figure 2. Characterization of Odour emission at LFKW plant by eNose.

eNose characterization of Odour emissions present a lowest variability of Odour concentrations respect the characterization of same air samples carried out by dynamic olfactometry (Figure 1). In addition the lowest concentration detected by eNose are generally highest respect the concentrations detected by dynamic olfactometry. Otherwise comparable values were detected for Odour concentration greater than 1000 OU/m³.

3.4 Comparison of Odour emissions detected by different methods

In Figure 3 was plotted the SOIen and AOI in function of the Sensorial Odour Index (SOI) for all analyses carried out at each sampling point.

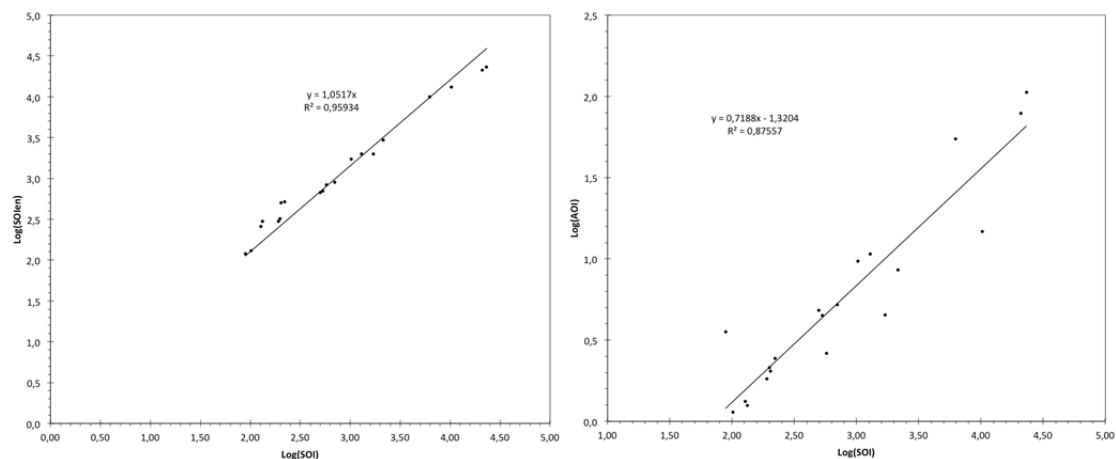


Figure 3. Correlation of Sensorial Odour Index (SOI) vs SOIen (left) and AOI (right)

The distribution of results show a great linear correlation between SOIen and SOI with an $R^2=0,956$, this confirm the ability of used eNose to give a odour characterization comparable to dynamic olfactometry with the potential advantage to carry out a continuous monitoring of emissions. The slope of the trend line is slightly greater than one (1,0517), this confirms that the tested eNose has a tendency to estimate higher concentrations of Odour; this tendency is greater at low concentrations while it becomes negligible for concentrations higher than 1000 OU/m³.

At same way Analytical Odour Index (AOI) have a comparable trend vs Sensorial measurements (SOI) with a $R^2=0,875$ (Figure 3). Trend line is quite less than one because: i) some volatile compounds detected by GC-MS was missing by detection limits of the instrument; ii) odour concentrations measured by

dynamic olfactometry have a lower reliability for concentration under 100 OU/m³ iii) was found a wide range of odour concentration from 100 to 15000 OU/m³, used for the calculation of SOI, respect the range of the ratio Cy/OT_y used for the AOI. For similar reason the trend line does not pass through the origin.

4. Conclusions

Odour emissions and chemical substances responsible of the nuisance were identified at selected treatment sources of the WWTP with both analytical and sensorial analyses. More than 30 different substances are detected and quantified at the plant. Sulfur dioxide and the dimethyl-disulfide are among the detected substances with highest concentration and variability overall the plant. However, they are not able alone to describe the offensive character of Odour emissions.

Odour characterization by dynamic olfactometry gave a good measurement of real perception of Odours at emission points, but this approach was expensive in terms of time, sampling operation and transportations and costs. Characterization by eNose give results in terms of Odour concentrations comparable with dynamic olfactometry, but a major variability was detected at lower concentrations. The main advantage of eNose is the potential ability in applications for continuous and remote monitoring of odour emissions.

Comparison between the concentrations of volatile substances emitted at the WWTP and detected by GC-MS vs the odour concentrations detected by sensorial methods (dynamic olfactometry and eNose) were studied analytically through a definition of specific odour indexes. The observed correlation between analytical odour index (AOI) vs sensorial odour index (SOI) shows that the methods are comparable.

References

- Belgiorno, V., Naddeo, V., Zarra, T., 2012, *Odour Impact Assessment Handbook*, Wiley & Son. London. ISBN: 978-1-119-96928-0
- Brattoli M., de Gennaro G., de Pinto V., Demarinis Loiotile A., Lovascio S. and Penza M., 2011, *Odour Detection Methods: Olfactometry and Chemical Sensors*, *Sensors*, 11, 5290-5322, doi: 10.3390/s110505290.
- Capelli L., Sironi S., Céntola P., Del Rosso R., Il Grande M., 2008. Electronic noses for the continuous monitoring of odours from a wastewater treatment plant at specific receptors: Focus on training methods. *Sensors and Actuators B* 131, 53–62.
- Giuliani, S., Zarra, T., Nicolas, J., Naddeo, V., Belgiorno, V., Romain, A.C., 2012, An alternative approach of the e-nose training phase in odour impact assessment, *Chemical Engineering Transactions*, 30, pp. 139-144.
- Gostelow P., Parsons S.A., Stuetz R.M., 2001. Odour measurements for sewage treatment works. *Water Research* 35, 579–597.
- Jiang J.K., 1996, Concentration measurement by dynamic olfactometer, *Water Environ. Technol.*, 8, 55-58.
- Köster E.P., 1986. Limitations imposed on olfactometric measurements by the human factor, in *Odour Prevention and Control of Organic Sludge and Livestock Farming*. Nielsen V.C., Voorburg J.H. L'Hermite P., Eds., Elsevier Applied Science, London, UK, 86–93.
- Naddeo V., Zarra T., Giuliani S., Belgiorno V., 2012, *Odour Impact Assessment in Industrial Areas*, *Chemical Engineering Transactions*, 30, pp. 85-90
- Nicolas J., Romain A. C., 2004. Establishing the limit of detection and the resolution limits of odourous sources in the environment for an array of metal oxide gas sensors. *Sensors and Actuators B*, 99, 384–392
- Ruth J.H., 1986, *Odour thresholds and irritation levels of several chemicals substances: a review*, *Am Ind Hyg Assoc J.*, 47(3):A142-51.
- Viccone, G., Zarra, T., Giuliani, S., Naddeo, V., Belgiorno, V. 2012, Performance study of e-nose measurement chamber for environmental odour monitoring. *Chemical Engineering Transactions*, 30, pp. 109-114.
- Zarra T., Naddeo V., Belgiorno V., Reiser M. and Kranert M., 2008. Odour monitoring of small wastewater treatment plant located in sensitive environment. *Water Science and Technology*. 58 (1), 89-94.
- Zarra T., Naddeo V., Belgiorno V., Reiser M., Kranert M., 2009. Instrumental characterization of odour: a combination of olfactory and analytical methods. *Water Science and Technology*, 59 (8), 1603-1609.
- Zarra, T., Reiser, M., Naddeo, V., Belgiorno, V., Kranert, M., 2012, A comparative and critical evaluation of different sampling materials in the measurement of odour concentration by dynamic olfactometry, *Chemical Engineering Transactions*, 30, pp. 307-312.