CHEMICAL ENGINEERING TRANSACTIONS, Volume 15, 2008
Edited by Renato Del Rosso

Measurement, management and control of odours in wastewater treatment plants by portable GC-MS

Zarra T., Naddeo V., Belgiorno V.
Department of Civil Engineering, University of Salerno
Via Ponte don Melillo, 1, 84084 Fisciano (SA), I

Odour emissions from wastewater treatment plants are considered to be the main cause of disturbance noticed by the exposed population. Odour measurement is carried out using analytical or sensorial methods. Sensorial analysis, being assigned to the "human sensor", is the cause of a considerable uncertainty.
In this study, a novel procedure based on highly innovative on-site analytical tool (portable GC-MS) was used to identify and characterise the odour sources and the volatile substances that cause annoyance in a wastewater treatment plant (WWTP) located in a sensible area, whit the aim to remove the subjective component in the measure of the odours and define the induced impact.
The sources and the main chemical substances responsible for the olfactory annoyances were identified. Results highlight the applicability of highly innovative tool in odour emission measurement, management and control. 44 different substances were detected and approx. half of them were found to be odour relevant components as well as responsible for the typical smell of wastewater treatment plants.

1. Introduction

Odours induced from wastewater treatment plants are considered to be the main cause of disturbance noticed by the exposed population (Stuetz and Frechen, 2001; Bidlingmaier, 1997; Frechen, 1988), and have a relevant impact on tourism economy (Zarra, 2007). Even though a real toxicological-sanitary risk is hardly-ever associated to the odour impact from sources connected to the activities of wastewater management, due to the rarely dangerous nature of the smells as well as the generally very low concentrations, the collective imagination often associates the bad smell to conditions of "non healthy" air. In fact, a valence higher than the one related to more dangerous contaminants, but not directly perceptible from our senses, is often attributed to them (Gostelow et al., 2001; Stuetz and Frechen, 2001, Frechen, 1988; Kehoe et al, 1996). Odour emissions affect quality of life (Brennan, 1993) leading to psychological stress and symptoms such as insomnia, loss of appetite and irrational behaviour (Wilson et al., 1980).
The particular and complex nature of the substances cause of the smell impact, their variability in time and related to the meteo-climatic conditions, and the subjectivity of the smell perception are the elements that delayed their regulation (Gostelow et al., 2001; Bidlingmaier, 1997).

There are few international laws that fix the limits of odour emissions from industrial sources and/or define criteria of quality related to the smell (Both and Koch, 2004). On the other hand, the definition of normative limits on the smell emissions is a problem hardly to solve because of the difficulties related to the subjectivity of the smell perception and the ways for determination of odours in the environment (Zarra et al., 2007). Odours are difficult to measure. A person's response to an odour is highly subjective - different people find different odours offensive, and at different concentrations. There is no universally accepted method for the quantification of odours, and odour measurement has often been regarded as an art as opposed to a science (Koe, 1989; Jiang, 1996).

Nowadays, odour measurement is carried out using two different methods: analytical-instrumental and sensorial. With the sensorial techniques (dynamic olfactometry and/or sociological questionnaires) it is not possible to gather the substances composing the olfactory annoyance as well as their single concentrations. It is therefore not possible to have a measurement of the number of people exposed to the different chemical agents that can cause noxious effects as well as whether they are protracted over time and in what concentrations (Stuetz e Frechen, 2001; Bidlingmaier, 1997; Van Harreveld, 2002). The principal source of uncertainty of the olfactometric method is the biological high variability of the olfactory sensibility. Even when performed according to the EN 13725:2003, the group of panelists does not necessarily represent a statistically representative sample of the exposed population, but only a group of subjects endowed with medium olfactory sensibility. Sensorial analysis, being assigned to the “human sensor”, for its own nature not reproducible, is the cause of a considerable uncertainty, due to the unavoidable human component that interferes in the evaluation (Sneath, 2001; Koster, 1985).

Analytical measurements (GC-MS, colorimetric methods) concern the physical or chemical properties of the odorous compounds, although the most common measurement made by far is odorant concentration. Analytical measurements allow a preliminary screening of the existing substances, but do not allow to get information about the induced annoyance (Dalton, 2002; Davoli, 2004). From a GC-MS analysis it is possible to obtain indications on the numerous substances that constitute principally the odorous mixture. Therefore, it is possible to evaluate if substances indicating an inefficient process are present or not or to evaluate the efficiency of technological systems of odours mitigation as scrubbers or biofilters.

The scope of this study was to identify and characterise the volatile substances that cause annoyance and the main odours sources in a large wastewater treatment plant using a novel procedure based on highly innovative on-site analytical tool, with the scope to remove the subjective component in the measure of the odours.

2. Materials and methods

2.1 Wastewater treatment plant

The identification of the main sources and chemical substances which were responsible of the olfactory annoyances was carried out in full-scale wastewater treatment plant (WWTP) located in the Campania Region, Salerno (SA, Italy) (Figure 1).

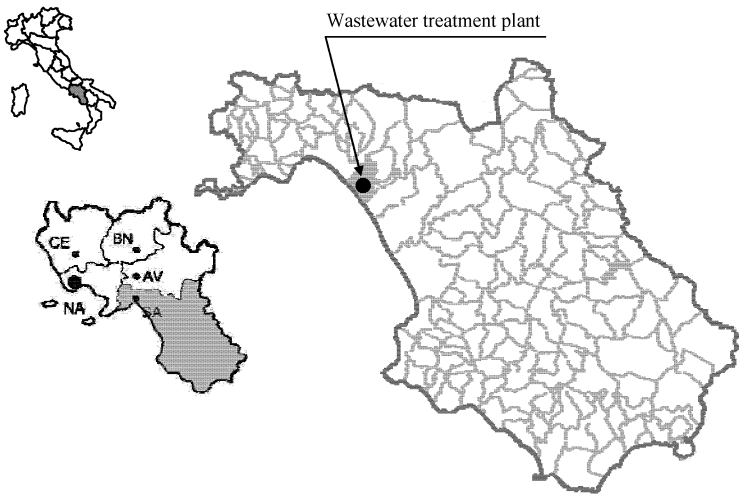

Figure 1. *Localization of the WWTP in the Campania Region, Salerno, Italy.*

The treatment plant have a conventional activated sludge layout showed in Figure 2, and currently treat both domestic and industrial discharges.

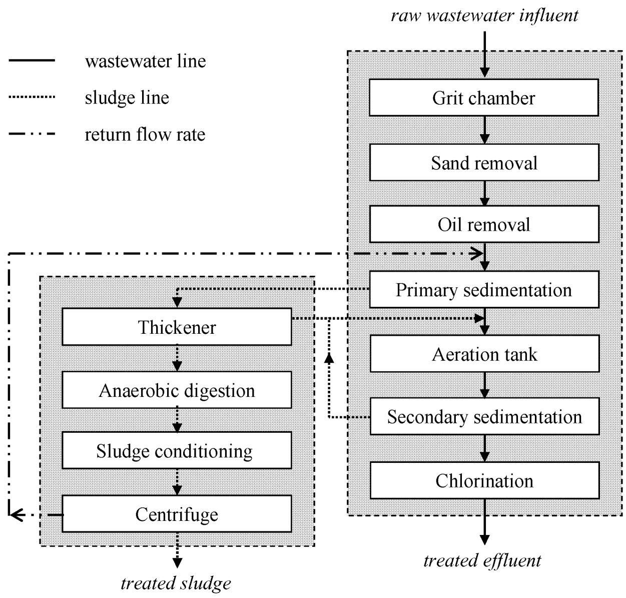

Figure 2. *Flow chart of the WWTP.*

A brief characterization of the investigated WWTP is showed in Table 1.
Odour emissions from wastewater treatment plant are essentially caused by the degradation of organic matter by microorganisms under anaerobic conditions. The development of anaerobic conditions in sewage is often referred to as 'septicity' (Gostelow and Parsons, 2000).

Table 1. Design and operational characteristics of the WWTP.

Parameter	Value
Population equivalent (PE)*	70 000
Hydraulic load *	280 l/ab d
Organic load*	80 g BOD_5/ab d
Daily mean flow rate **	106 000 m^3/d
BOD_5 **	350 mg/L
COD **	780 mg/L
TSS **	580 mg/L
Daily exstraction of primary sludge **	680 m^3/d
Daily exstraction of secondary sludge**	2100 m^3/d
Daily sludge disposal**	44 m^3/d

* design data; ** mean operation data

In wastewater treatment plants, different diffusive and non-diffusive odour sources can be identified (Zarra, 2007). Odours arise from several points at wastewater treatment facilities. One possibility is that odorous compounds are already present in the incoming waste water and are released to the air during treatment activities. Another possibility is the formation of odorous compounds (Stuetz et al., 1998).

2.2 Odour monitoring

Samples of odour emissions were taken at seven different points of the plant during the period May–July 2007. Weather condition (air-wind intensity and direction, temperature, humidity, pressure) were continuously detected in order to both take into consideration the effects of atmospheric dispersion of the substances emitted and perform the GC-MS measurement in optimal condition (under wind, wind speed from 1 to 3 m/s, temperature under 30°C). Table 2 shows the position of the sampling points and the measurement program carried out over the testing period. A total of 21 analyses were carried out.

Table 2. Sampling points and measurements program at WWTP.

ID	No. of analysis	Location	Treatment
P1	5	Raw wastewater influent	Influent
P2	5	Grit chamber	Wastewater
P3	5	Primary sedimentation	
P4	5	Aeration tank	
P5	5	Thickener	Sludge
P6	5	Centrifuge	
P7	5	Sludge disposal	

2.3 Analytical methods

Sampling and identification of the volatile compounds were carried out with a portable GC-MS Hapsite (Inficon, NY, USA). This instrument, certified by the EPA, is designed to carry out a quali-quantitative analysis of a series of compounds listed by the 1990 Clean Air Act (HAP, Hazardous Air Pollutants) directly on-site. The qualitative analysis was used to identify the nature of the volatile substances. Under these conditions, the instrument was set to the molecular weight range between 30-300, with a

temperature program set at 40-100°C with thermal heating gradients of the gas-chromatographic column of 18°C/min and from 110-180°C with thermal gradients of 10°C/min. The sampling time of 10 seconds (Loopfill) was set and a Tenax concentrator was used. The total analysis time was 16,3 minutes.The concentration of the compounds detected was carried out through semi-quantitative analyses using a direct ratio with internal standards commercialized by Inficon (NY, USA).
Measurement of the meteorological parameters (wind velocity, temperature and relative humidity) was carried out using a Kestrel® 4000 Pocket Wind Meter (Nielsen-Kellerman, PA, USA) anemometer and an analogical compass to define wind direction.

2. Results and discussion

Table 3 shows the volatile compounds detected at the WWTP of Salerno and the maximum concentration (MC) of the quantified substances.

Table 3. *The odour emission characterization in WWTP.*

Class	Substances	MC *(mg/m³)*	Class	Substances	MC *(mg/m³)*
Sulphurous	Dimethyl disulphide	0,3562	Alcohols	2-Butoxy-ethanol	0,1098
	Dimethyl trisulphide	0,0541		2-ethenyloxy-ethanol	0,0589
	Sulphur dioxide	0,8512		2-Ethyl-1-ethanol	0,4591
Ketones	Acetone	0,3692	Volatile fat acid	Acetic Acid	0,2154
	2-Butanone	3,9572		Butanoic Acid	0,0315
	Acetophenone	0,7201		Propanoic Acid	0,0216
Aldehydes	Benzaldehyde	0,0421	Hydro-carbons	Texane	ND
	Decanal	0,0351		Undecane	0,0254
	Trimethyl-benzaldehyde	ND		Dimethyl-undecane	ND
	Nonanal	0,0419		Dodecane	0,0802
Aromatics	Ethyl-benzene	0,0105		Tetradecane	ND
	1-Ethyl-2-methylbenzene	ND		Methyl-cyclohexane	ND
	Dimethyl-benzene	0,0196		Tridecane	ND
	1,3,5 Trimethylbenzene	ND		Octane	0,0131
				Nonane	0,0107
	p-Xilene	0,0501		Decane	ND
	1,2,4 Trimetilbenzene	ND	Nitrogenous	Indole	ND
				Scatole	0,0621
	Benzene	0,0395		Dimethylamine	0,2436
	Toluene	0,0812		Methylamine	0,0513
Terpenes	Limonene	0,1657		Ammonia	0,0198
	D-Limonene	0,0421	Others	Tetra-chloroethylene	ND
	α-Pinene	0,0354		Octamethyl-cyclotetrasiloxane	ND

MC: maximum concentration; ND: not determined

The results shows 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.
In fact, of around 44 different substances detected in the mixture by the portable GC-MS, approx. half of them were found to be odour relevant components as well as responsible for the typical smell of wastewater treatment plants.
Dimethyl disulphide was the volatile substance with the lowest Odour Threshold and most detected in the plant. The highest detected concentration (0,3562 mg/m^3) of this substance was found at the sludge thickening unit.
Figure 3 shows the detected sources of odorous substances emissions at large wastewater treatment plants and their ranking for potential impact.

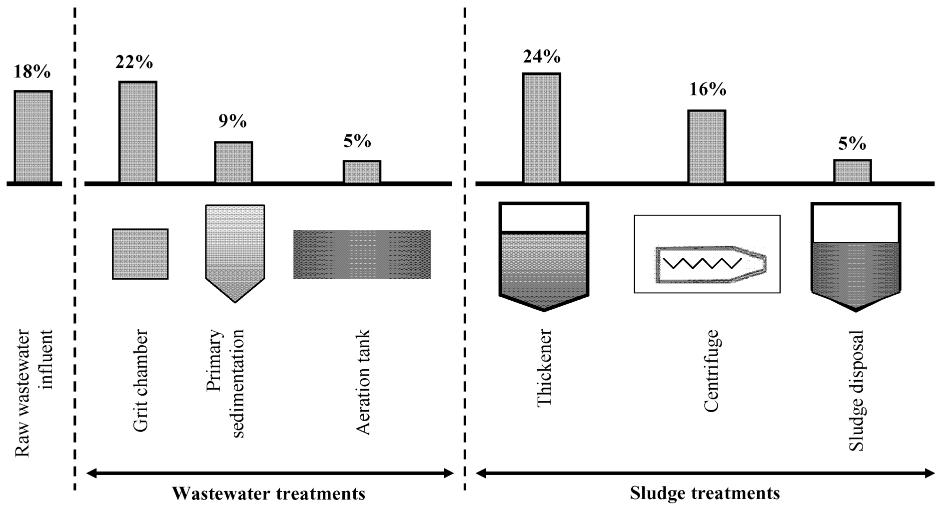

Figure 3. *Percentage distribution of the potential odour impact at WWTP.*

The results shows that the major contribution to potential odour impact are originated from sludge handling activities and followed by grit removal unit and raw wastewater influent respectively.
Figure 4 shows the percentage composition of the odour emissions for each source treatment unit monitored; in this figure, hydrocarbon and aromatic compounds are not included in the percentage calculations.

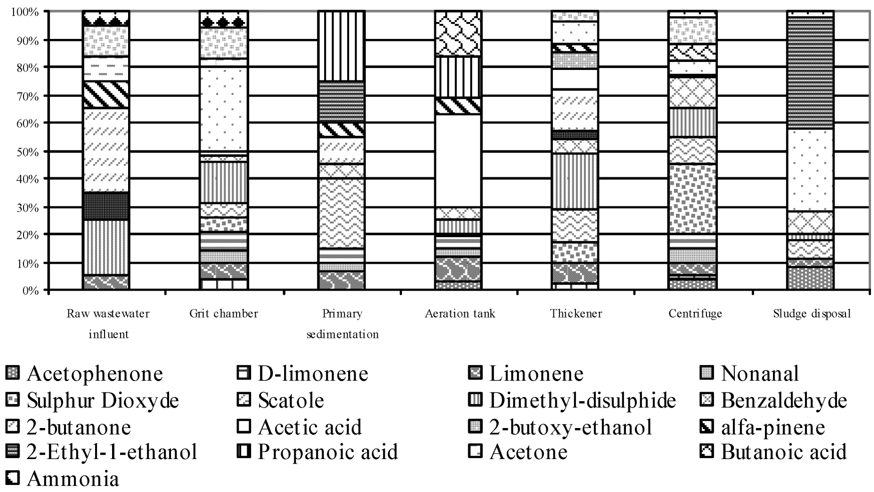

Figure 4. *Percentage composition of odour emissions for each monitored source treatment unit at the WWTP.*

3. Conclusions

Odours induced by wastewater treatment plant are considered to be the main cause of annoyance noticed by the exposed population.
The evaluation and characterization of the odours emissions have been applied to the case study of a large WWTP located in the Campania Region, Salerno (SA, Italy). 44 different substances are detected in the treatment phases. Approx. half of them were found to be odour relevant components as well as responsible for the typical smell of wastewater treatment plants. The major contribution to odour impact are originated from sludge handling activities (45%) and followed by grit removal unit (22%) and raw wastewater influent (18%) respectively.
Dimethyl disulphide is identified as key compound connected to the specific treatment process. It was the volatile substance most detected in the plant, with a average concentration of 0,2861 mg/m^3; the highest concentration (0,3562 mg/m3) of these substance was detected at the sludge thickening unit.
The results show a new way that scientific research could be carried out in order to both identify and characterize odours impact as well as control the efficiency of plants directly on-site.
Results obtained by portable GC-MS analysis indicated the potential role of the technique in the study of environmental engineering plants, while highlighting the need for a more comprehensive analysis suite.

4. References

Bidlingmaier W., 1997, Odour emissions from compost plants – Dimensioning values for enclosed and open plants. Rhombos-Verlag, Berlin.

Both R., and Koch E., 2004, Odour regulation in Germany; an improved system including odour intensity, hedonic tone and odour annoyance. In Environment Odour Management Odour Emission, Odour Nuisance, Olfactometry, Electronic sensors, Odour Abatement. Odour Conference. VDI-Berichte 1850, Cologne.

Brennan B., 1993, Odour nuisance. Water and Waste Treatment, 36, 30-33.

Dalton P., 2002, Olfaction in Yantis. Handbook of Experimental Psycology, Edizioni S. Stevens.

Davoli E., 2004, I recenti sviluppi nella caratterizzazione dell'inquinamento olfattivo. Tutto sugli odori, Rapporti GSISR.

EN 13725, 2003, Air quality—determination of odour concentration by dynamic olfactometry, Comitè Europè en de Normalisation, Brussels, pp. 1–70.

Frechen F. B., 1988, Odour emissions and odour control at wastewater treatment plants in West Germany. Water Science and Technology, 20, 261-266.

Gostelow P., and Parsons S. A., 2000, Sewage treatment works odour measurement. Water Sci. Technol. 41 (6), 33±40.

Gostelow P., Parsons S.A., and Stuetz R.M. ,2001, Odour measurements for sewage treatment works. Water Research, Vol. 35, Nr.3, 579-597.

Jiang J. K., 1996, Concentration measurement by dynamic olfactometer. Water Environ. Technol. 8, 55±58.

Kehoe J., Harcus J., Smith M., and Warren M., 1996, Acquisition, review and correlation of odour literature for the air & waste management association. EE-6 odour committee, University of Windsor.

Koe L. C. C., 1989, Sewage odors quantification. In Encyclopedia of Environmental Control Technology, Wastewater Treatment Technology, Vol. 3, cd P. N. Cheremisinoff, pp. 423±446. Gulf Publishing Company, Houston.

Koster E. P., 1985, Limitations Imposed on Olfactometry Measurement by the Human Factor, Elsevier Applied Science Publisher.

Sneath R.W., 2001, Olfactometry and the CEN Standard EN13725, In: Odours in Wastewater Treatment: Measurement, Modelling and Control. Eds Stuetz R. and Frechen B.F., IWA Publishing.

Stuetz R. M., Engin G., and Fenner R. A., 1998, Sewage odour measurements using a sensory panel and an electronic nose. Water Sci. Technol. 38, 331±335.

Stuetz R., Frechen F.B., 2001, Odours in wastewater treatment: measurement, modelling and control. IWA Publishing, ISBN 1 900222 46 9.

Van Harreveld A. P., 2002, Scent-Smell-Stink-Stech: How to Draw the Nuisance Line?, Proceedings of Enviro Odour Conference.

Wilson G.E., Huang Y.C., and Schroepfer W., 1980, Atmospheric sublayer transport and odor control. J. Environ. Eng. Div., Proc. Am. Soc. Civil Eng., 106, 389-401.

Zarra T, Naddeo V., and Belgiorno V., 2007, Portable gas chromatography-mass spectrometry as a tool for estimating the odour emissions of composting plants in air pollution management. Proceeding of 10th international conference on environmental science and technology, 5th- 7th september 2007 -Coss, Greece.

Zarra T., 2007, Procedures for detection and modelling of odours impact from sanitary environmental engineering plants. PhD Thesis, University of Salerno, Salerno, Italy.