
Volume 101, issue 19, October 2010
ISSN 0960-8524
ELSEVIER
BIORESOURCE TECHNOLOGY
• biomass • bioenergy • biowastes • conversion technologies •
• biotransformations • food • agriculture •
• production technologies •
Editor-in-Chief: S.C. Ricke
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Available online at www.sciencedirect.com
ScienceDirect

Bioresource Technology 101 (2010) 7330–7337

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Potential odour emission measurement in organic fraction of municipal solid waste during anaerobic digestion: Relationship with process and biological stability parameters

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ARTICLE INFO

Article history:
Received 11 December 2009
Received in revised form 26 April 2010
Accepted 27 April 2010
Available online 23 May 2010

Keywords:
Anaerobic digestion
Biological stability
Electronic nose
GC–MS
Odours

ABSTRACT

The aim of the present study is to investigate the correlation between microbial activity, i.e., biological stability measured by aerobic (OD_{20} test) and anaerobic tests (ABP test), and odour emissions of organic fraction of municipal solid waste during anaerobic digestion in a full-scale treatment plant considering the three stages of the process (input, digested and post-digested waste).

The results obtained indicated that the stabilization of the treated material reduces the odour impact measured by the olfactometric approach. Successive application of gas chromatography mass spectrometry (GC–MS) and electronic nose (EN) allowed the characterization of the different groups of volatile organic compounds (VOCs) responsible of odour impacts determining, also, their concentration. Principal component and partial least squares analyses applied to the EN and GC–MS data sets gave good regression for the OD_{20} vs the EN and OD_{20} vs the GC–MS data. Therefore, OD_{20} reduction could be used as an odour depletion indicator.

1. Introduction

Anaerobic digestion (AD) has been used for over 100 years to stabilize materials such as wastewater sludge, municipal solid waste, and other industrial refuses (Ferrer et al., 2008). In recent years, anaerobic digestion has emerged as one of the technologies of high interest because of its potential usefulness as a low-environmental impact alternative to fossil fuel energy. Anaerobic digestion provides clean fuel from renewable feedstocks (Fredriksson et al., 2006). Anaerobic digestion is a biological process in which biodegradable matter (present in the organic fraction of municipal solid waste – OFMSW, energy crops, and agro-industrial wastes) is degraded or decomposed by the activity of specific microorganisms in the absence of oxygen, producing biogas (mainly methane and carbon dioxide) that can be used for electricity generation (Lissens et al., 2001).

The establishment of an anaerobic metabolism during the AD process produces a set of compounds that could have environmental impacts mainly associated with their odourous potential (Smet et al., 1999) or with their contribution to greenhouse gases emissions (Barlaz, 2006; Moller et al., 2009). Volatile organic compounds (VOC) constitute the main group of odourants emitted in these types of treatment processes. Ketones, alkanes, alkenes, alcohols, acids, terpenes (pinene, cymene and limonene) and organic sulphur compounds are among the VOCs commonly reported (Smet et al., 1999; Staley et al., 2006). In addition, other odourous compounds such as hydrogen sulphide and ammonia have also been related with anaerobically digested wastes (Rosenfeld and Suffet, 2004).

However, even if odour emissions from anaerobic environments are reported in literature, most of the references on VOCs emissions are related to landfills or laboratory scale reactors, and only few of them correspond to full-scale treatment facilities. Data on VOCs emissions from aerobic treatment processes at industrial scale are easier to found (Eitzer, 1995; Komilis et al., 2004; Tsai et al., 2008). Fricke et al. (2005) compared different aspects of aerobic and anaerobic procedures for municipal solid waste treatment including exhaust emissions. These investigators highlighted the scarcity of data on emissions relating anaerobic treatments followed by aerobic processes.

In addition to the production of biogas, the AD also resulted in the production of a residual organic matrix; i.e., digestate (Tani et al., 2006; Zhang et al., 2007) that can be used in agriculture as a nutrient fertilizer and/or an organic amendment (Tambone et al., 2009). The use of digestate in agriculture, especially in open

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doi:10.1016/j.biortech.2010.04.098

fields, needs to meet agronomic standards, but above all it needs to consider the concerns of the population regarding the health problems and annoyance it may cause, particularly because of the odour emission (Edelmann et al., 2005).

Anaerobic digestion leads to stabilization of organic matter (OM) as a consequence of OM degradation (Pognani et al., 2009; Tambone et al., 2009). Biological stability indicates the extent to which readily biodegradable organic matter has decomposed. Therefore, high biological stability after the anaerobic process indicates lower microbial activity in the residual waste than in the starting biomass, as substrate is no longer available. Therefore, high biological stability implies a strong reduction in odour production, as odours are produced by the microbial activity (D'Imporzano et al., 2008). In this way AD is also defined as a biological process able to reduce the environmental impacts of residual waste when it is used in open fields. To our knowledge, few data exist on the effect of AD on the reduction of OFMSW odour impact, particularly to odours associated to the agricultural use of digestate. Therefore, there is a need for scientific data reporting the real odourous impact of the application of digestate in the agriculture. It is also interesting to know how the biological stabilization occurring during the AD process can reduce this impact.

The main objective of the present study is to evaluate the correlation between biological stability parameters and the potential odourous impacts of the OFMSW treated in a full-scale anaerobic digestion plant during different process phases: starting (non-digestion), digestion, and post-digestion. Biological stability parameters are determined by both aerobic (oxygen demand, OD_{20}) and anaerobic (anaerobic biogasification potential, ABP) measurements. In addition, odourous emissions were measured using three different methodologies: olfactometry, an electronic nose (EN), and gas chromatography mass spectrometry (GC–MS) (VOC determination) to get more in-depth information about the nature of odours compounds.

2. Methods

2.1. Waste sample collection

A full-scale anaerobic digestion plant located in Northern Italy was monitored during this study. In this plant, 1 MW of electrical power is produced by digesting in four anaerobic continuously stirred thermophilic reactors (CSTR) and in an identical anaerobic post-digester (Pognani et al., 2009), the organic fraction of municipal solid waste (OFMSW). OFMSW came from door to door source separation collection. Waste was composed of 90% (on wet weight basis, w.w.b.) of kitchen wastes and of 5–10% (w.w.b.) of plastic bags.

Anaerobic digestion operated under wet condition and the average total solid contents measured in the digester resulted of 4.65 ± 0.88% w.w. (Table 1).

The plant treats around 30,000 Mg of waste per year. The first stage of the treatment process consists of crushing and squeezing the organic wastes separating plastic bag from the waste. The resulting slurry is then fed to anaerobic digesters at a rate of 0.22 Mg every 15 min. The digesters work under thermophilic conditions (at 55 °C) with a hydraulic retention time (HRT) of 40 days, followed by post-digestion where the material remains for about 10 days.

During the monitoring period (September–December 2008), three sampling campaigns were undertaken (on 15/09/08, 07/10/08 and 11/11/08, indicated as replicates 1, 2 and 3, respectively), each collecting samples from the feed-in (ingestates) (ND) (HRT = 0 days), output from the thermophilic anaerobic reactors (D) (HRT = 40 days), and output from the post-digester (PD) (HRT = 50 days).

Non-digested (ND) and digested samples (D and PD) were directly taken from the roof of the mix tank and fermenters. For each sample composite slurry of about 5 l was obtained by using a 500 ml jar with telescopic bar, used as sampler. Composite samples were stored in a 5 l glass container avoiding headspace presence. Samples were stored in glass containers hermetically closed avoiding any contact with air and any molecules volatilization. Then samples were brought to the laboratory and worked within 2 h.

2.2. Chemical characterization of waste samples

Representative samples were used to carry out all the analytical tests. Total solids (TS), volatile solids (VS), and total organic carbon (TOC) were determined according to standard procedures (APHA, 1998). Ammonia and total N-Kjeldahl (TKN) were analysed on fresh samples according to the analytical method established for wastewater sludge (IRSA CNR, 1994). pH and volatile fatty acids (VFA) were determined according to standard procedures (US Department of Agriculture and US Composting Council, 2002). All analyses were performed in triplicate.

2.3. Anaerobic biogasification potential (ABP)

The estimation of ABP was performed according to Schievano et al. (2008) using 0.62 g of dried matter sample, 37.5 ml of inoculum, and 22 ml of deionized water in 100-ml serum bottles. A control blank was prepared with 60 ml of inoculum. The biogas production was determined and expressed as Nl kg^{-1} TS. All batches were sealed with Teflon hermetic caps, flushed with an N_2 atmosphere, and incubated at 37 ± 1 °C, until no further biogas production was detected (normally around 60 days). Assay bottles were periodically analysed for both quantitative and qualitative determination of biogas production. Quantitative biogas production was estimated by withdrawing extra-pressure gas with a 60-ml syringe. Biogas production of blank control batches was subtracted from biogas production of every sample. Qualitative characterization of biogas was performed by a gas chromatograph (Carlo Erba Megaseries 5300, capillary column 25 m × 0.32 mm diameter and flame ionization detector [FID]) to determine CH_4:CO_2 ratio in the biogas. The carrier gas was nitrogen at 20 kPa pressure and temperatures of injector and FID were 130 and 150 °C, respectively. Comparison of obtained peak areas was carried out with a standard gas mixture of 300:700 ml l^{-1} (v/v) CH_4:CO_2. All the tests were performed in triplicate.

2.4. Oxygen demand (OD_{20})

Oxygen demand test was performed in relation to the method described in Lasaridi and Stentiford (1998), and modified by Adani et al. (2003). To perform the test, 0.4 g of dried matter sample were set in a flask with 500 ml of deionized water, 12 ml of phosphate buffer solution (KH_2PO_4, K_2HPO_4, $Na_2HPO_4 \cdot \cdot 7H_2O$), and 5 ml of nutritive solution ($CaCl_2$, $FeCl_3$, and $MgSO_4$) prepared according to the standard BOD test procedures (APHA, 1998). The oxygen uptake potential is the result of the oxygen demand accrued in a 20-h test (OD_{20}, mg O_2 g TS^{-1}), calculated using the following equation:

$$OD_{20} = \frac{V}{m * TS * 100} * \int_{t=0}^{t=20} |S|_t * dt$$

where m is the mass of the sample (g, wet weight), V the sample volume, TS the total solid content of the sample in % over wet weight, and $|S|_t$ the rate of oxygen consumption at time t (mg O_2 L^{-1} h^{-1}). All the tests were performed in triplicate.

Table 1
Chemical characteristics of the samples analysed (ND: non-digested, D: digested and PD: post-digested).

Sample	Sampling data	Process time (days)	pH	TS (%WW)	VS (%TS)	TOC (%TS)	TKN (%TS)	NH_3 (mg l^{-1})	VFA (mg l^{-1})
ND1	15/09/08	0	4.41	15.25[a] ± 0.35[b]	87.49 ± 0.13	45.02 ± 0.84	3.26 ± 0.30	1038 ± 112	21,566 ± 708
ND2	07/10/08	0	4.56	22.05 ± 0.02	89.90 ± 0.14	46.56 ± 0.37	2.61 ± 0.16	1227 ± 21	26,188 ± 9330
ND3	11/11/08	0	3.84	14.29 ± 0.13	86.16 ± 0.20	49.11 ± 0.89	3.40 ± 0.05	834 ± 38	27,220 ± 1881
Mean ND				17.20 ± 3.81[bc]	87.85 ± 1.69[b]	46.90 ± 1.93[b]	3.09 ± 0.41[a]	1033 ± 183[a]	24,135 ± 3024[b]
D1	15/09/08	40	8.20	3.83 ± 0.19	67.61 ± 1.00	39.25 ± 1.09	13.35 ± 0.15	3458 ± 473	7539 ± 148
D2	07/10/08	40	8.22	4.42 ± 0.39	67.11 ± 1.00	37.09 ± 0.84	10.90 ± 0.09	2913 ± 64	6579 ± 598
D3	11/11/08	40	8.13	5.69 ± 0.29	72.02 ± 0.01	42.34 ± 0.71	9.00 ± 0.08	3139 ± 48	10,180 ± 573
Mean D				4.65 ± 0.88[a]	68.91 ± 4.05[a]	39.56 ± 2.46[a]	11.08 ± 1.95[b]	3170 ± 325[b]	8100 ± 1709[a]
PD1	15/09/08	50	8.35	3.77 ± 0.42	64.84 ± 0.13	36.23 ± 0.88	13.07 ± 0.32	3622 ± 38	1021 ± 322
PD2	07/10/08	50	8.28	6.49 ± 0.58	58.06 ± 0.49	35.24 ± 0.89	6.45 ± 0.57	3128 ± 3	1839 ± 166
PD3	11/11/08	50	8.20	4.30 ± 0.01	64.45 ± 0.11	38.35 ± 1.20	11.83 ± 0.06	3266 ± 9	9498 ± 779
Mean PD				4.85 ± 0.60[a]	62.45 ± 3.41[a]	36.61 ± 1.61[a]	10.45 ± 3.16[b]	3339 ± 229[b]	4832 ± 4519[a]

[a] All data reported in Table 1, except pH, are average of three replicates.
[b] The value after symbol (±) is the standard deviation.
[c] Value in the same column followed by the same letter are not statistically different (Tukey test, $P < 0.05$).

2.5. Odour sample collection

From each waste sample the gaseous samples for odour detection were collected using a flux chamber system based on the APAT method (APAT, 2003) (Fig. S1) (see Supplementary material). In brief, four litres of waste sample were put in a tray container and covered with a Plexiglas chamber (38.8 × 50.5 × 40 cm) having a surface of 0.196 m^2. The chamber was then continuously flushed for 10 min with air (airflow rate of 0.35 m^3 h^{-1}). Output gas from the chamber was then taken from the outlet port and stored in Nalophan bags. Bags of different volumes, i.e., 20 l, 2 l, and 3 l, were filled and used for olfactometric, electronic nose, and GC–MS analyses, respectively.

2.6. Olfactometry

Olfactometric analyses were carried out in conformity with the standardized EN method n. 13725 (CEN, 2003). An Olfaktomat-N 6 (six stations) olfactometer (PRA-Odournet B.V., Amsterdam, NL) based on the forced choice method was used as a dilution device. Six panellists were employed during test.

The measuring range of the olfactometer starts from a maximum dilution factor of 33,000 with a dilution step factor of 2. The results of the olfactometry were expressed as odour concentration value (OU_E Nm^{-3}). On the other hand, the odour emission rate (OE) was calculated by using the following equation:

$$OE = CQ/S$$

in which OE is the odour emission rate (OU_E Nm^{-2} h^{-1}), C is the odour concentration (OU_E Nm^{-3}), Q is the incoming air rate to the flux chamber (0.35 m^3 h^{-1}), and S the surface covered by the chamber (0.196 m^2).

2.7. Electronic nose

Air samples were analysed using a PEN2 electronic nose (Airsense Analytics, Schwerin, Germany) equipped with 10 thermo-regulated (150–500 °C) sensors (S1–S10) made of metal oxide semiconductors (MOS). Each sensor is sensitive to a group of class compounds; i.e., S1: aromatic compounds; S2: polar compounds and nitrogen oxides; S3: aromatic compounds, ketones, and aldehydes; S4: H_2; S5: low polarity aromatic and alkane compounds; S6: methane compounds; S7: sulphur compounds and terpenes; S8: alcohols, ketones, and partially aromatic compounds; S9: sulphur-containing and aromatic compounds; and S10: methane at high concentration. The measurement modalities adopted were as reported by D'Imporzano et al. (2008), except that the Nalophan bags were connected directly to the EN through a probe. The following work parameters were used: (i) 300 s for the clean cycle, (ii) 100 s for the measurement cycle, and (iii) three cycles for each bag. Only the last 20 s of the measurement cycles, when the response of the sensors was stabilized, were chosen to create the sensor patterns. A total of 21 measures were obtained for each cycle.

The large amount of data obtained by the EN required the information obtained to be reduced to a limited number of new variables able to describe the totality of the variability (generally two-dimensional variables).

As a consequence, the odour results were elaborated by multivariate analysis. In this work, principal component analysis (PCA) was used to compare odours qualitatively. The multivariate analyses were carried out by an *ad hoc* software (SCAN, Minitab Inc., State College, PA).

2.8. Gas chromatography–mass spectrometry

Volatile organic compounds (VOC) from air samples were analysed by SPME/GC–MS (Davoli et al., 2003). A manual SPME device and divinylbenzene (DVB)/Carboxen/polydimethylsiloxane (PDMS 50–30 μm fiber – Supelco, Bellefonte, PA, USA) were used. The analytes were adsorbed from the air samples by exposing the fiber, preconditioned for 3 h at 250 °C as suggested by the supplier, in Nalophan bags for 30 min at room temperature. A solution of perdeuterated p-xylene in methanol was used as internal standard (IS) for quantitative analysis. VOC analysis was performed using an Agilent 5975C Series GC/MSD. Volatiles were separated using a capillary column for VOC (Meta.VOC, Teknokroma, Sant Cugat del Vallès, Barcelona, Spain) 30 m × 0.32 mm ID, with a film thickness of 3.0 μm. The carrier gas was helium at a flow rate of 1 ml min^{-1}. VOCs were desorbed, exposing the fiber in the GC injection port for 3 min at 250 °C. A 2 mm glass liner was used, and the injection port was in splitless mode. The temperature program was isothermal for 3 min at 35 °C, raised to 200 °C at a rate of 8 °C/min. The transfer line to the mass spectrometer was maintained at 250 °C. The mass spectra were obtained by electronic impact at 70 eV, with a multiplier voltage of 1294 V and collecting data at a m/z range of 33–300. Compounds were tentatively identified by comparing their mass spectra with those contained in the NIST (USA) 98 library. Semi-quantitative analysis for all the identified compounds was performed by direct comparison with the internal standard. Results were expressed as part per billion on a volume basis (ppbv).

GC–MS data were reduced in chemical classes that were then used for the successive principal component analysis (PCA) (Davoli et al., 2003) using an *ad hoc* software (SCAN, Minitab Inc., State College, PA).

2.9. Statistical analyses

All statistical analyses otherwise reported in each specific paragraph were performed with the SPSS statistical software (version 13) (SPSS, Chicago, IL).

Partial least squares (PLS) analysis (Einax et al., 1997) was used for modeling the relationship of odours (OU as $OU_E\ Nm^{-2}\ h^{-1}$) with the EN data (dimensionless arbitrary unit) and GC–MS data (molecular classes expressed as ppbv), and with respirometric data (OD_{20} expressed as mg O_2 g TS^{-1}) using an *ad hoc* software (SCAN, Minitab Inc., State College, PA). Both the goodness of fit, i.e., regression coefficient (R^2), and the goodness of prediction, i.e., cross-validation regression coefficients (R^2_{cv}) (R^2 obtained using values calculated by using the regression model) were reported. The cross-validation regression coefficient was calculated as an error of the prediction by the leave-one-out cross-validation procedure. This procedure allows the selection of more appropriate latent vectors, thus reducing their total number (i.e., the selection of the EN sensor and organic compound classes able to predict olfactometric units).

For the GC–MS data, organic compound classes were used for PLS application, taking into consideration those classes that were effectively represented; i.e., esters, aromatics, alcohols, carbonyl, and terpenes (see subsequent text).

3. Results and discussion

The chemical characteristics of the analysed samples are shown in Table 1. There was a clear difference in the TS, VS, and TOC contents of non-digested and digested materials as a consequence of OM degradation. However, this difference did not exist for samples corresponding to digested and post-digested wastes. Regarding the VFA content, the higher values in the starting samples (ND) were ascribed to the hydrolysis and successive fermentation of organic matter that occurred during waste transportation and storage. During anaerobic digestion and post-digestion, VFA were transformed to CH_4 and CO_2, resulting in digested (D) and post-digested (PD) samples with lower VFA concentration. Total nitrogen (TKN) content was lower in ND samples than in both D and PD materials because of nitrogen concentration as a consequence of volatile solid degradation. Ammonia concentration (NH_3) increased, as well, during the process due to the mineralization of the organic N.

The biological stability of the materials (Table 2), measured as OD_{20} and ABP, increased throughout the treatment process as a consequence of the degradation of organic matter (Schievano et al., 2008; Pognani et al., 2009). This was confirmed by the good linear and positive correlations (Pearson correlation) obtained by processing the mean values of biological stability parameters vs VS and TOC (Tables 1 and 2, i.e., OD_{20} and ABP vs VS and TOC (OD_{20} vs VS: $r = 0.92$, $P < 0.05$; $n = 9$ OD_{20} vs TOC content: $r = 0.91$, $P < 0.05$; $n = 9$; ABP vs VS: $r = 0.88$, $P < 0.05$; $n = 9$; ABP vs TOC content: $r = 0.86$, $P < 0.05$; $n = 9$). The fact that correlation coefficients were higher for OD_{20} than ABP could indicate that biological stability was affected, mostly by the degradation of the more readily degradable organic matter. This is confirmed by the good correlation obtained for OD_{20} and VFA content (OD_{20} vs VFA content: $r = 0.93$, $P < 0.05$; $n = 9$), with OD_{20} being more greatly affected than ABP by the easily degradable organic matter (Schievano et al., 2008).

As the biological stability increased, odour emissions reduced (reported as odour unit per square meter per hour: $OU_E\ Nm^{-2}\ h^{-1}$) (Table 2), although no correlation was found between these parameters, and no statistical significance was observed between average values reported in Table 2. This was due to the high variability of the emitted odours measured in the starting sample, which reflected the variability of the feeding waste that generally occurs in a full-scale plant (Pognani et al., 2009). In particular, when starting sample was characterized by low odour emissions (see Sample ND3) (Table 2) only a slight odour reduction occurred during the process. Nevertheless, when odour impact of the starting sample was high (see Samples ND1 and ND2) (Table 2), a strong reduction occurred in the digested samples.

The tendency of odour increment in the final sample (PD) with respect to the digested sample (D) (Table 2), could be ascribed to the lower microbiological activity (see ABP data) for PD with respect sample D, that limited odour stripping from the biomass *via* biogas production, thus resulting in odour concentration in the waste. Nevertheless, differences observed were not statistically different.

Odours are due to the presence of volatile organic compounds in the air. Nevertheless, direct quantification of the VOCs did not allow determination of the odour impact (odour units), and no relationship was found between these two parameters (Table 2). Moreover, the VOC contents appeared very similar, on the average, for all samples considered, although a reduction during the process was observed (Table 2).

Dynamic olfactometry and VOC measurement both represented quantitative measurements of the molecules present in air

Table 2
Biological stability indices and odours emission characteristic of the samples analysed (ND: non-digested, D: digested and PD: post-digested).

Sample	Sampling data	Process time (days)	OD_{20} (mg O_2 g^{-1}TS)	ABP (Nl kg^{-1}TS)	Odour ($OU_E\ Nm^{-2}\ h^{-1}$)	VOC (ppbv)	NH_3 (ppmv)
ND1	15/09/08	0	279.70[a] ± 21.50[b]	546.89[a] ± 2.42	119,446[c]	2,328[c]	0[c]
ND2	07/10/08	0	218.50 ± 18.67	483.12 ± 8.71	76,017	1672	15
ND3	11/11/08	0	293.79 ± 0.18	481.60 ± 1.36	36,243	6005	5
Mean ND			264.00 ± 40.03[bd]	503.87 ± 33.60[b]	77,235 ± 41,614[a]	3335 ± 2335[a]	6.67 ± 7.64[a]
D1	15/09/08	40	116.28 ± 19.55	217.16 ± 0.84	5458	1208	104
D2	07/10/08	40	152.99 ± 11.21	338.00 ± 3.06	17,550	1178	54
D3	11/11/08	40	136.46 ± 0.87	441.05 ± 0.41	29,331	1694	45
Mean D			135.24 ± 18.40[a]	332.07 ± 100.24[ab]	17,446 ± 11,936[a]	1360 ± 290[a]	67.67 ± 31.79[b]
PD1	15/09/08	50	88.93 ± 3.31	101.49 ± 10.1	13,314	1303	30
PD2	07/10/08	50	83.13 ± 3.84	192.87 ± 2.54	40,213	1180	45
PD3	11/11/08	50	112.89 ± 12.36	178.75 ± 0.38	23,087	2784	57
Mean PD			94.98 ± 15.80[a]	157.70 ± 44.25[a]	25,538 ± 13,615[a]	1756 ± 893[a]	44 ± 13.53[ab]

[a] The data are average of three replicates.
[b] The data are a single replicate.
[c] The value after symbol (±) is the standard deviation.
[d] Value in the same column followed by the same letter are not statistically different (Tukey test, $P < 0.05$).

samples, but they were not able to identify the kind of molecules present in the air that were responsible for the odours.

The electronic nose has been used in the past to give a rapid characterization of the organic molecules composing the air and to follow the changes in emitted volatile compounds during the fermentation process (Eklöv et al., 1998). In this work it was used to track the odour fingerprint of both ingestate and digestate. The EN patterns for the samples analysed, presented in Fig. 1, showed a decrease in the EN sensor responses with the process time and with the acquirement of biological stability.

These results point to a possible relationship between the EN response, and OD_{20} and ABP indices. Before the AD process began (ND samples), S1 and S3 (aromatic compounds), S2 (polar compounds and nitrogen oxides), S6 (methane compounds), and S8 (alcohols) had a strong peak. After 40 days of anaerobic digestion (D samples) and after post-digestion (PD samples), the sensor signals listed above weakened, except for S2 (Fig. 1).

Fig. 2 shows the final elaboration of the EN data (Fig. 1) using a PCA bi-plot graph in which two principal components are reported (PC1 = 66% and PC2 = 21%, in which % represents the total variance

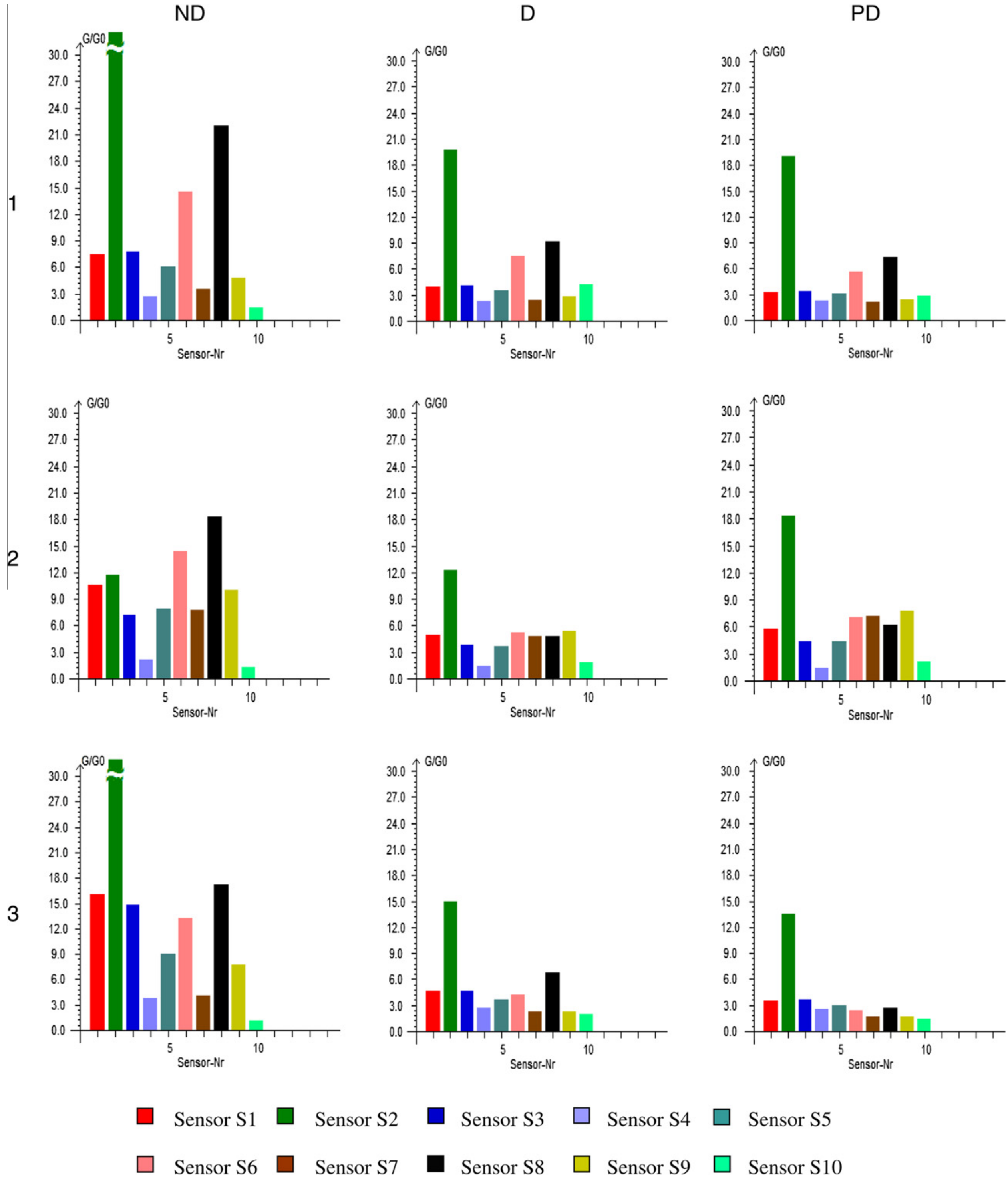

Fig. 1. EN signal registered in samples of indigestate (ND), digestate (D), and post-digestate (PD) coming from the three sampling campaigns (Sampling data, 1: 15/09/08, 2: 07/10/08 and 3: 11/11/08). (*x*-axis represents sensor number and *y*-axis relative sensor signal).

explained). PC1 and PC2, which together accounted for 87% of the total variance, indicated that the odour fingerprints were similar when the biological stabilities of the samples were similar. This was confirmed by the good regression found in the PLS analysis of OD_{20} vs the EN ($R^2 = 0.99$; $R^2_{cv} = 0.98$, $P < 0.01$, sensors selected: S1–S7).

From these data, it can be concluded that the odour reduction due to the acquirement of biological stability was accompanied by a change in the organic molecules composing the air in the wastes studied.

This fact is confirmed by the data in Fig. 3, which shows the VOC fingerprints analysed by GC–MS as compound classes (Table 3) and elaborated on a bi-dimensional PCA plot; i.e., samples having similar biological stability showed similar VOC patterns. Again, good regression was found in the PLS analysis of OD_{20} vs the GC–MS data ($R^2 = 0.95$; $R^2_{cv} = 0.78$, $P < 0.01$, organic compounds selected: ester, aromatics, and alcohols). The statistical data showed that the GC–MS data were less predictive than the EN data in describing OD_{20}.

To get more in-depth knowledge of the organic molecules comprising waste-air, single molecules were elaborated from the GC–MS spectra and quantified.

The VOCs present in the air of the ingestate consisted mostly (average of 3 measures) of terpenes (61%), alcohols (18%), and esters (9%) (Table 3). The changes that occurred during anaerobic digestion led to digested samples characterized by still-high presence of terpenes (51% and 58% for D and PD samples, respectively), strong reduction of both alcohols and esters, and high presence of carbonyl compounds (40% and 34% for D and PD samples, respectively).

Fresh wastes (ND) were particularly characterized by the presence of the terpenes, limonene (Table 4) and beta-pinene, both widespread in fruits, vegetables, and pine species (Staley et al., 2006), and thus compose the VOCs of the OFMSW (Smet et al.,

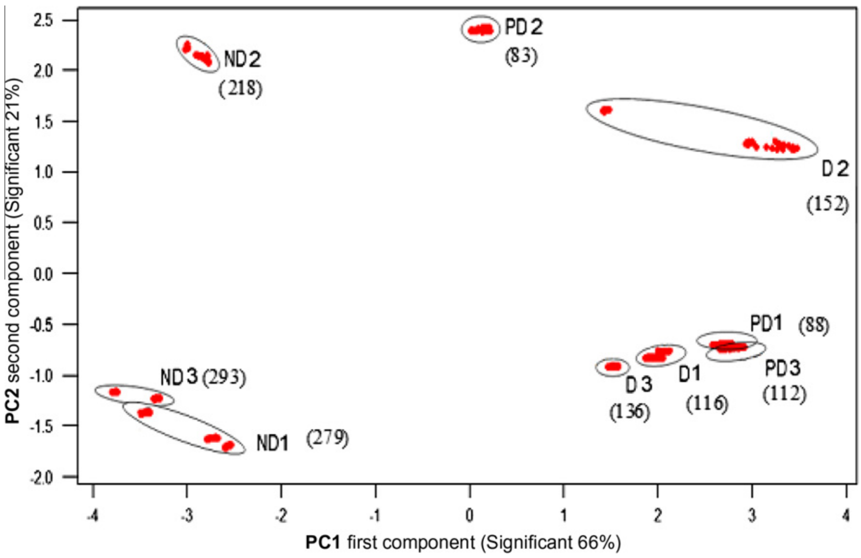

Fig. 2. PCA plot of odours measured by Electronic nose (*x*, in parenthesis are reported respirometric data (OD20 as mg O_2 g^{-1} TS) (Sampling data, 1: 15/09/08, 2: 07/10/08 and 3: 11/11/08).

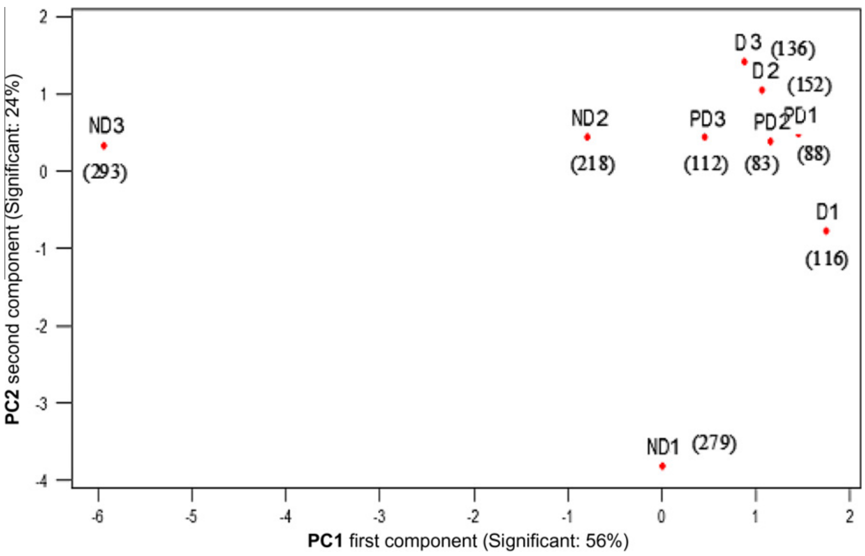

Fig. 3. PCA plot of total VOCs measured by GC–MS analysis (organic compounds classes from Table 3) in parenthesis are reported respirometric data (OD20 as mg O_2 g^{-1} TS) (Sampling data, 1: 15/09/08, 2: 07/10/08 and 3: 11/11/08).

Table 3
Volatile organic compounds (VOCs) emitted (ppbv) from samples studied: non-digested (ND, 0 days of process); digested (D, after 40 days of process) and post-digested (PD, after 50 days of process) wastes. The mean percentage of each type of VOCs over the total VOCs emission is also presented.

Sample (sampling data)	ND				D				PD			
Organic compound classes	1 (15/09/08) ppbv	2 (07/10/08) ppbv	3 (11/11/08) ppbv	Mean %	1 (15/09/08) ppbv	2 (07/10/08) ppbv	3 (11/11/08) ppbv	Mean %	1 (15/09/08) ppbv	2 (07/10/08) ppbv	3 (11/11/08) ppbv	Mean %
Nitrogen compounds	0.00	0.00	3.42	0.03	0.00	7.11	0.66	0.19	0.00	3.19	0.00	0.06
Esters	224.31	310.29	355.26	8.89	0.00	12.73	1.66	0.35	39.55	6.90	60.12	2.02
Aliphatic hydrocarbons	2.07	30.23	20.43	0.53	0.48	13.65	14.02	0.69	14.42	9.44	22.55	0.88
Aromatic hydrocarbons	19.27	39.07	28.49	0.87	22.28	40.03	55.05	2.88	41.77	29.68	20.93	1.75
Alcohols	762.00	412.93	585.00	17.59	81.89	82.64	38.50	4.98	76.26	35.40	0.00	2.12
Ethers	78.70	0.17	0.00	0.79	4.19	6.36	1.72	0.30	1.30	1.72	4.26	0.14
Carbonyl compounds	558.04	171.38	19.03	7.48	685.38	515.01	423.63	39.80	680.96	463.60	671.64	34.47
Terpens	683.47	708.29	4749.90	61.38	413.91	500.50	1150.79	50.61	449.33	630.18	1999.43	58.44
Sulphur compounds	0.00	0.00	79.60	0.79	0.00	0.00	8.08	0.20	0.00	0.00	4.80	0.09
Halogenates	0.08	0.00	0.00	0.00	0.00	0.00	0.33	0.01	0.00	0.00	1.05	0.02
Acids	0.00	0.00	164.75	1.65	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total VOCs	2327.94	1672.35	6005.87	100	1208.12	1178.03	1694.44	100	1303.60	1180.12	2784.77	100

Table 4
Main compounds found in the air samples analysed: non-digested (ND, 0 days of process); digested (D, after 40 days of process) and post-digested (PD, after 50 days of process) wastes.

Sample (sampling data)	ND			D			PD		
Organic compounds	1 (15/09/08) ppbv	2 (07/10/08) ppbv	3 (11/11/08) ppbv	1 (15/09/08) ppbv	2 (07/10/08) ppbv	3 (11/11/08) ppbv	1 (15/09/08) ppbv	2 (07/10/08) ppbv	3 (11/11/08) ppbv
Ethanol	281	176	365	–	7	4	–	–	–
2-Butanol	208	105	131	75	63	17	57	24	12
1-Propanol	121	79	36	–	–	–	–	–	–
Ethyl acetate	55	130	158	–	–	–	–	–	–
d-Limonene	450	433	4389	178	323	920	10	26	778
p-Cymene	80	64	–	134	53	59	352	501	1083
Beta-pinene	78	80	26	–	–	–	–	–	–
Camphor	–	–	–	–	28	21	29	37	40
Acetic acid	86	43	–	–	–	–	–	–	–
Propanoic acid	4	85	–	–	–	–	–	–	–
2-Butanone	337	32	12	556	416	311	589	337	558
2 and 3-Pentanone	–	–	–	15	18	12	20	16	12
2-Heptanone	–	–	–	24	24	43	24	32	35

1999). Terpenes have been reported to be stripped during the first stage of aerobic biological processes, thus decreasing its concentration (Pierucci et al., 2005). Since anaerobic conditions are far different from the aerobic setting as no forced aeration is considered, terpenes were more or less conserved, thus also indicating that no significant degradation occurred, except in the sample 3 (Table 3). On the other hand, digested samples showed a high presence of p-cymene (Table 4), probably coming from the microbial transformation of d-limonene (Termonia and Termonia, 1999). p-Cymene has been reported to be a marker of the presence of old refuse kept under anaerobic conditions resulting in biogas production (Davoli et al., 2003).

The high presence of alcohols (ethanol, butanol, and propanol) (Table 4) in the air of fresh material was the consequence of microbial alcohol formation from waste substrate during the period of storage under nearly anaerobic conditions at low pH (Staley et al., 2006).

In the successive stable methanogenic phase, bacteria were able to oxidize the alcohols to ketone *via* the reduction of CO_2 to CH_4 (Widdel, 1986). The high presence of ketones, mainly 2-butanone, in the air of D and PD samples (Table 4) seems to confirm this report.

These results partially contrasted with how found for aerobic environment (composting). For example Eitzer (1995), reported during unsorted MSW-composting, the high presence of terpenes, but, also, the high presence of aromatic hydrocarbons. On the other hand VOCs emitted depended by the matrix composted. Komilis et al. (2004), studying VOCs emitted during composting of different organic matrices, showed for similar organic matrix used in this work, i.e., food waste, a different pattern of emission. Food waste composting emitted, mainly, sulphides, followed by acid/ester, alcohols, terpens but, also, aromatic hydrocarbon. Contrarily, when mixed waste (mix paper) was considered, aromatic of xenobiotic origin were, also, largely emitted.

When anaerobic environment, i.e., landfill, was studied (Eklund et al., 1998), gas composition differed from our study for the presence of the high concentration of aromatic hydrocarbons because of the presence unsorted MSW.

Nevertheless, Komilis et al. (2004) indicated that aromatic hydrocarbons were emitted even if only food waste were composted, suggesting further studied to investigate source of non-biogenic VOCs in MSW.

In this study aromatic hydrocarbon were detected, as well, but at very low concentration (Table 3) if compared with Komilis et al., data (Komilis et al., 2004). Aromatic hydrocarbons detected were, mainly, toluene and various alky-benzene that probably suggested a non-biogenic origin.

In conclusion differences occurred in different studies reported in the literature, depend by the process performed (aerobic vs anaerobic), by the different waste considered (unsorted MSW or food waste from source separated collection), by the different origin of the food waste because of different diet (Italy vs USA), and by the presence/absence of aeration that promoted volatile organic compound stripping from waste.

When each class of molecules (Table 3) in the air waste was considered together with the olfactometric analyses, no significant ($P < 0.05$) correlations were found. Therefore, the organic molecules by themselves were not able to describe the odour emitted by the wastes. Gralapp et al. (2001) suggested that human odourous response (OU measurement) may be based on compounds that are not detected by GC–MS analysis or by the presence of synergic effects between different organic molecules.

Therefore, the synergistic effect and the complexity of the organic compounds in air, more than a single organic or inorganic compound, were responsible for the odour impact. Both the EN and GC–MS data, when successively elaborated by principal component analysis, allowed the description of organic molecules as a whole. Thus, it can be assumed that PCA and GC–MS elaboration allows the study of the complex effects of the organic molecules. In effect, when the sensor data from the EN analysis and the organic compound classes from GC–MS analysis were considered together by PCA analyses, and the results correlated with the odour unit by PLS analysis, good regressions were found for the EN (EN vs OU: $R^2 = 0.99$, $R^2_{cv} = 0.95$; $P < 0.01$, sensors selected: S1–S7) but lower for the GC–MS data (GC–MS vs OU: $R^2 = 80$, $R^2_{cv} = 0.40$; $P < 0.01$, organic compounds selected: esters).

Therefore, the EN and though much less, GC–MS were able to describe the odour impact of the waste by multivariate statistical analysis. Above all, after correct calibration, the EN could replace olfactometry as a tool for odour impact measurement (Defoer et al., 2002). The olfactometry approach, despite being the accepted method for determining odour concentration (CEN, 2003) in air, has as its main drawback the fact that it must be conducted in a controlled laboratory setting and a sufficient number of panelists must be available to conduct the analysis. Moreover, during the olfactometric session, the panelists are required to inhale environmental air samples that might contain hazardous compounds.

4. Conclusion

The acquirement of biological stability due to organic matter degradation reduces much of the odour impact of the OFMSW (digestate). Therefore, the measurement of the biological stability by the determination of the oxygen uptake rate (OD_{20}) could be used as a first indication of the potential odour impact of the digestate such as the good regressions found for OD_{20} vs both EN and GC–MS data confirmed.

Acknowledgements

Mr. G. Bianchi is gratefully acknowledged for his help in GC–MS analysis.

This study was supported by Lombardy Region and ARAL, Italy (National Program for Biofuels – ProBio Biogas).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.biortech.2010.04.098.

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