CHEMICAL CHARACTERIZATION OF EMISSIONS FROM A MUNICIPAL SOLID WASTE TREATMENT PLANT.

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Abstract

Gaseous emissions are an important problem in municipal solid waste (MSW) treatment plants. The sources points of emissions considered in the present work are: fresh compost, mature compost, landfill leaks and leachate ponds. Hydrogen sulphide, ammonia and volatile organic compounds (VOCs) were analysed in the emissions from these sources. Hydrogen sulphide and ammonia were important contributors to the total emission volume. Landfill leaks are significant source points of emissions of H₂S; the average concentration of H₂S in biogas from the landfill leaks is around 1700 ppmv. The fresh composting site was also an important contributor of H₂S to the total emission volume; its concentration varied between 3.2-1.7 ppmv and a decrease with time was observed. The mature composting site showed a reduction of H₂S concentration (< 0.1 ppmv). Leachate pond showed a low concentration of H₂S (in order of ppbv). Regarding NH₃, composting sites and landfill leaks are notable source points of emissions (composting sites varied around 30-600 ppmv; biogas from landfill leaks varied from 160 to 640 ppmv). Regarding VOCs, the main compounds were: limonene, *p*-cymene, pinene, cyclohexane, reaching concentrations around 0.2-4.3 ppmv.

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H₂S/NH₃, limonene/*p*-cymene, limonene/cyclohexane ratios can be useful for analysing and identifying the emission sources.

Highlights

- Chemical characterization of emissions of an MSW treatment plant.
- The main VOCs emitted from the sources studied are: limonene, *p*-cymene and pinene.
- Determination of ratios of compounds from the different emission sources.

Keywords:

Municipal solid waste (MSW); landfill; composting; leachate; chemical emissions; volatile organic compounds (VOCs).

1. Introduction

A typical municipal solid waste treatment plant consists of various different sites, including: a landfill site, leachate pond, tipping floor (area to discharge and classify fresh MSW), and sites for anaerobic digestion of MSW and the composting process. These can be sources of odours.

Odours from municipal solid waste (MSW) treatment plants consist of a complex mixture of organic compounds, hydrogen sulphide (H₂S) and ammonia (NH₃). These odours can be an important problem for MSW plant operators and also a source of annoyance to nearby urban populations.

The chemical characterization of the emissions from an MSW treatment plant has proven to be helpful in order to determine which compound or group of compounds are characteristic in each of the point sources of the treatment plant. This characterization is

fundamental to improve the waste treatment system in order to reduce the odorous emissions (Gallego et al., 2012).

Landfill sites are one of the most important sources of gaseous emissions. Landfill emissions contain mainly methane (CH_4) and carbon dioxide (CO_2), from 45 to 55% and 30 to 40%, respectively (Jönsson et al., 2007), both of which are considered to be greenhouse gases contributing to global climate change. Landfill gas may also contain nitrogen (N_2), oxygen (O_2), hydrogen sulphide (H_2S) and ammonia (NH_3) – H_2S and various different organic compounds being the main contributors to the odour.

Among the organic compounds it is possible to find: saturated and unsaturated hydrocarbons, acidic hydrocarbons and organic alcohols, aromatic hydrocarbons, halogenated compounds, sulphur compounds such as carbon disulphide and mercaptans, and other compounds such as siloxanes (Keller, 1988). Although VOC emissions are less than 1% of total gaseous emissions, they are considered to be among the most hazardous air pollutants (Allen et al., 1997). Some of them are known to be toxic or carcinogenic, such as benzene, toluene, ethylbenzene, and m,p,o-xylene (xylenes) (commonly called BTEX). Therefore, control of BTEX concentrations in the vicinity of landfills is really important. In fact, several studies found BTEX in landfills and in the surrounding areas, although these emissions do not pose a health risk, owing to their low concentrations as a result of air dilution (Dincer et al., 2006; Durmusoglu et al., 2010; Kim et al., 2008; Zou et al., 2003). In terms of odours, some VOCs have been identified as responsible for the odour, such as sulphur compounds, alkyl benzenes, limonene, and certain esters (Young and Parker, 1983). In addition, VOCs are known precursors of photochemical smog formation (USEPA, 2004).

A previous study carried out by Davoli et al. (2003) reports that *p*-cymene is a characteristic compound of emissions from landfill. In a more recent work, this result

was also confirmed in the digested waste from an anaerobic digestion (Orzi et al., 2010).

There are progressively more MSW treatment plants that collect and even use landfill gas for electricity production in gas engines, but not all the gas can be collected by these extraction systems, and leakage can still pose a problem. Even with well designed covers, few landfills are thought to recover more than 60% of the available gas, and the losses to the atmosphere through the surface are one of the most important causes (Johannessen, 1999). Therefore, strict control and maintenance of landfills is essential if gas leaks are to be prevented. For this purpose, recent studies suggest landfill biocovers as an effective solution for odour reduction (Capanema et al., 2014; He et al., 2011; Lakhout et al., 2014).

As regards composting, it is known that ammonia is one of the main components of the emissions that result from this practice, especially when the nitrogen content of the composting wastes is high. Ammonia emissions from composting depend on the following parameters: the C/N ratio of the waste, composting temperature and pH. A pH greater than 8 promotes the transformation of NH_4^+ to NH_3 , and ammonia emissions rise with temperature (Beck-Friis et al., 2001; Pagans et al., 2006a).

Hydrogen sulphide, methyl mercaptan, dimethyl sulphide, carbon disulphide and dimethyl disulphide are volatile sulphur compounds produced by composting. These compounds are generated as a result of incomplete or insufficient aeration during this process (Zhang et al., 2013).

After testing the emissions at various stages of the composting process, many studies have concluded that most VOCs are emitted during the early stages of the process (Eitzer, 1995; Gallego et al., 2012; Komilis et al., 2004; Pagans et al., 2006b; Scaglia et al., 2011).

Eitzer (1995) performed a survey of emissions of volatile organic compounds from MSW composting facilities. This survey classified different locations on the facility into: tipping floor, shredder, fresh from newly formed active compost, mid-aged from one-fifth to four-fifths of the way through the active composting region, old if it was at the end of the active composting region, curing if it was still on site but out of the active composting area. The highest concentrations were found in samples taken from the tipping floors, near the shredders, and in the freshest active composting regions, while more mature compost samples exhibited lower concentrations.

Another composting study was carried out in the laboratory by Komilis et al. (2004), but in this case on three organic components of MSW (food wastes, yard wastes and mixed paper wastes) and mixtures of these. This study concluded that all VOCs were emitted early during the composting process and that their production rates decreased with time at thermophilic temperatures. Mixed paper primarily produced alkylated benzenes, alcohols and alkanes. Yard wastes primarily produced terpenes, alkylated benzenes, ketones and alkanes, while food wastes primarily produced sulphides, acids and alcohols.

Yet another composting study was performed in the laboratory by Pagans et al. (2006b). They studied the composting of different organic wastes including, among others, the organic fraction of municipal solid wastes. They concluded that the highest concentrations of VOCs in the exhaust gases of composting processes were detected during the first 48 hrs. of operation. Another conclusion was that the emission of VOCs during composting is not generally related to the biological activity of the process, and that the maximum emission concentration of VOCs did not coincide with the maximum temperature achieved during composting.

Scaglia et al. (2011) studied VOCs emissions from a mechanical-biological treatment (MBT). The MBT process is similar to the composting process; MBT consists in an aerobic process, in which the forced aeration in the waste produces a reduction of the waste reactivity when the MSW is landfilled (Lornage et al., 2007; Scaglia and Adani, 2008; Siddiqui et al., 2013). Their main conclusions were: (i) that odours and VOCs emitted are correlated with the biological stability of the waste, (ii) Nitride and sulphide compounds were the major contributors to the odour emission, (iii) although a great number of groups of compounds were degraded during the biological process, there were other groups of compounds, i.e. aromatic, furans and halogenated compounds which persisted.

Davoli et al. (2003) carried out a characterization of organics from different sources of a treatment plant, and their main conclusions were that fresh wastes are characterized in particular by limonene, while biogas and leachate are characterized by *p*-cymene. Two other terpenes also showed up in the leachate: eucalyptol and camphor.

The present work tries to identify the main components in emissions from an MSW treatment plant, considering: biogas leaks from the landfill site, emissions from the leachate pond and the composting site. With this objective, emissions from different sites within the MSW treatment plant were characterized. Based on the concentration of hydrogen sulphide, ammonia and some volatile organic compounds, series of ratios were proposed to characterize each emission. This in return can help to determine the main source of emission within the MSW treatment plant.

2. Materials and methods

2.1. Description of the studied fractions and the experiments.

On the MSW treatment plant considered in this study, an anaerobic digester treats the fraction of municipal solid waste consisting of particles smaller than 40 mm in size; the products of this anaerobic digestion are biogas and digestate, which make up the solid effluent. There is another site on the MSW treatment plant where the composting is done. The composting is carried out with an initial mixture composed of: the digestate and the fraction of municipal solid waste with particle size between 40 and 80 mm. At the end of the composting process the compost is refined. Finally, the fraction of waste that cannot be recycled is disposed of in the landfill site. The biogas emitted by the landfill is extracted and utilized in gas engines to generate electrical power. In addition, the leachate produced by various processes and the landfill site is collected in a pond.

It was proposed that samples be collected from the following waste products:

- A fresh compost fraction: this comprises the fraction of municipal solid waste with particle size less than 80 mm and the digestate.
- Rejected compost fraction: fraction rejected after the composting process. This fraction contains organic matter as well as plastic, glass and other non-fermentable materials.
- Leachate pond.
- Biogas leaks from the landfill area.

Except for landfill leaks, the rest of samples were sampled in a big tank where they were introduced. The dimensions of these tanks were 1m x 1m x 1m and they were filled halfway to the top. Carrying out the experiments in tanks has the advantage of removing possible external interferences, such as, for instance, from road traffic. Although, it is essential in these experiments that the diffusion of the compounds given

off be allowed. Therefore, on top of the tank there was a short cylindrical tube, 19 cm in diameter and 19 cm in length, which allowed diffusion and also avoided water saturation (Figure 1). This is the critical point in this experiment, the aperture of the tank must not be too big to avoid external interferences, but neither too tight because the water saturation could cause problems during sampling.

Figure 1

2.2. Sampling and analysis

2.2.1. Point sources studied in the tank experiments (leachate pond, fresh and rejected compost)

The period of time for the tank experiments was 4 days. The sampling by accumulation of volatile organic compounds (VOCs) was carried out using Radiello[®] diffusive samplers. The sampling of H₂S and NH₃ was done with Ogawa passive samplers when their concentrations were not too high (in the order of ppb). In other cases, 10 measurements were carried out in each experiment with an MX6 iBrid portable multi-gas detector (total acquisition time in each experiment: around 5 minutes).

Passive samplers were chosen for their simplicity, speed of analysis, low cost and weight of passive sampling, and were positioned in the upper part of the tank.

- Ammonia:

To analyse for ammonia in the leachate tank, two Ogawa passive samplers were used. These samplers were used to collect ammonia in the environment (Roadman et al., 2003). The samplers, small cylinders 10 mm high and of 20 mm internal diameter are closed at one end by a polyethylene cap, which has a fibreglass filter fitted inside it. At the other end, there is a cast iron mesh and a Teflon membrane. The fibreglass filters

were impregnated with a citric acid solution. The method of analysis is based on the reaction between the ammonia ion with phenol and sodium hypochlorite, which is intensified by sodium nitroprusside, and the colour produced can be detected by a spectrophotometer (Roadman et al., 2003).

To the sampling of NH_3 in the tanks containing fresh and rejected composting fractions, a MX6 iBrid portable multi-gas detector was used and periodic readings were taken. Ogawa passive samplers were not suited for composting fractions, because NH_3 emissions were in the range of ppm.

- Hydrogen sulphide:

To analyse for hydrogen sulphide in the leachate tank, three Ogawa passive samplers were used. In this case, the filters were impregnated with a silver nitrate solution. They were subsequently leached in a basic cyanide solution to liberate the sulphide collected as Ag_2S and/or AgSH on the filter. The H_2S content of the washed solution was analyzed according to the AgNO_3/FMA (Fluorescein Mercury Acetate) fluorimetric method, which is based on the quenching of FMA by the Ag_2S formed from the H_2S (Axelrod et al., 1969; Farwell et al., 1987; Natusch et al., 1972; Shooter et al., 1995). During the analysis, precautions had to be taken to minimize the reaction of the FMA with atmospheric oxygen. Owing to the complexity of the analysis, an extra passive sampler was placed, making a total of three samplers in each tank.

For analyses of fresh and rejected composting fractions, a MX6 iBrid portable multi-gas detector was also used to take periodic readings of the H_2S concentration. Composting fraction emissions also show H_2S concentrations in order of ppm.

- Volatile Organic Compounds (VOCs):

216 Volatile organic compounds (VOCs) were sampled by Radiello[®] diffusive samplers.
217 These samplers consist of a cylindrical adsorbing cartridge placed inside a cylindrical
218 diffusive body. Radial symmetry offers important advantages: better capacity for
219 enrichment of the substrate; and reproducibility and stability with air speed. Bruno et al.
220 (2007) tested Radiello diffusive samplers by using them in the detection of odorous
221 compounds on solid waste treatment plants, and concluded that the diffusive sampling
222 method is highly reproducible.

223 The adsorbing cartridge used in this study was a stainless steel cylinder 5.8 mm in
224 diameter with 100 mesh grid opening, packed with 530 mg activated charcoal of 35-50
225 mesh particle size.

226 Four Radiello[®] diffusive samplers were placed in each of the tanks; two of the samples
227 were extracted with carbon disulphide as suggested in the Radiello manual, and the rest
228 were extracted with hexadecane, to be able to measure the most volatile compounds,
229 including the carbon disulphide. Hexadecane is employed as extraction solvent by U.S.
230 Environmental Protection Agency in Method 3820 (USEPA, 1986). Hexadecane was
231 employed due to its high boiling point, it is a non-polar, long-chain alkane, and it
232 presents low viscosity. For these reasons, it had been established beforehand that
233 extraction with hexadecane is more appropriate for the most volatile organic
234 compounds. In this way, the experiment provided more information about the adsorbed
235 organic compounds.

236 The extracts were analysed by GC/MS (an Agilent 6890N gas chromatograph interfaced
237 to an Agilent 5973N quadrupole mass-selective detector); an Agilent DB-624 capillary
238 column (30m x 0.25mm and a film thickness of 1.4µm) was used; Toluene D-8 and 4-
239 bromofluorobenzene were employed as internal standards. We used the NIST Library to
240 identify possible compounds and obtained a high percentage of coincidence between the

mass spectrum of the detected and the proposed compounds. Where the peaks of several compounds overlapped, identification was based on an analysis of boiling points.

Figure 2 shows the variation of the boiling points obtained from literature for the different compounds proposed using the NIST library vs. the retention times of these compounds in the GC column, in order to test the proposed compounds follow a consistent variation. This column is an intermediate polarity column (Agilent DB-624), so that non-polar and certain polar compounds leave in order of increasing boiling points; the boiling points that came out in this case corresponded to polar compounds, such as 3-hydroxy-2-butanone, 2-methyl-3-buten-2-ol, or 2-butanol. Similar analyses were carried out on the other three samples.

Figure 2

The concentrations of the compounds that were identified can be calculated from the following equation (1):

$$C = \frac{m}{Q \cdot t} \quad (1)$$

where m is the quantity of analyte adsorbed on the cartridge, Q is the sampling rate, and t is the sampling period. The sampling rate (Q) can be calculated from the following equation (2):

$$Q \text{ (cm}^3\text{/s)} = k(\text{cm}) \cdot D_{AB}(\text{cm}^2\text{/s}) \quad (2)$$

where k is the Radiello[®] geometric constant and D_{AB} is the diffusion coefficient of the organic compounds in air. The diffusion coefficients were predicted by the method developed in Fuller et al. (1966).

2.2.2. Landfill leaks:

- Ammonia and hydrogen sulphide:

These compounds were analyzed directly at leaks from the landfill site using an MX6 Ibrid portable detector. Several readings were taken to get a representative result. A total of 10 readings were taken from 2 different landfill leaks, and the total acquisition time was around 5 minutes.

- Volatile Organic Compounds (VOCs):

Radiello[®] diffusive samplers were positioned in places close to the landfill leaks for two days, less time than in the other point sources' samplings, because the concentration in landfill leaks was expected to be higher than in the other point sources. There were two Radiello[®] diffusive samplers to each of the two landfill leaks that were sampled. Carbon disulphide and hexadecane were also used to carry out the extractions.

3. Results and discussion

Hydrogen sulphide and ammonia were important contributors to the emissions of a MSW treatment plant. Table 1 shows the average concentrations of H₂S and NH₃ obtained in the experiments carried out in the experimental set-ups (fresh and rejected compost fraction).

Table 1

The sampling with the leachates was also carried out in the tank. Nevertheless, there is no significant level of emissions from the leachates. Their emissions are in the order of ppbv, and therefore the measurements were carried out with Ogawa passive samplers. The concentration of H₂S was 12.4 ± 2.0 ppbv and NH₃ was not detected.

H₂S and NH₃ were analyzed directly at landfill leaks site using an MX6 Ibrid portable detector. The concentration of H₂S was 1665 ± 124 ppmv and the NH₃ concentration was 395 ± 170 ppmv.

Landfill leaks contain the highest concentration of H₂S, which predominates over NH₃. In contrast, the composting processes are characterized by emissions with NH₃ predominating over H₂S, which are lower in the old composting source (rejected compost fraction). The ratio of NH₃/H₂S emissions is higher in the old composting source because the initial mixture that is composted consists of the fraction that is municipal solid waste and the digestate, which constitute the effluent from the anaerobic digestion. Thus, the presence of hydrogen sulphide is to be expected.

Ammonia was not detected in the experimental set-up used to characterise the leachate, probably due to excessive moisture in the atmosphere, especially during the night. Therefore, this excess water in Ogawa passive samplers could have prevented the ammonia from being retained in the filter, because ammonia is very soluble in water. In any case, NH₃ emissions would be small because the leachate has a pH of around 7, and taking into account the ammonium/ammonia equilibrium, NH₄⁺ prevails under acid conditions and remains in the liquid phase. A specific experiment was conducted to determine ammonia emissions from a more alkaline leachate (pH ca. 8), by using the MX6 Ibrid portable detector in a small vessel. The ammonia concentration was one quarter that of hydrogen sulphide (NH₃: 8 ppmv; H₂S: 32 ppmv). Under warm temperature conditions in a recent leachate, the ammonia emitted by this leachate was half that of hydrogen sulphide (NH₃: 6 ppmv; H₂S: 12 ppmv).

VOC concentrations of the samples are shown in Appendix A.

152 volatile organic compounds were identified in the different sources of emissions considered (Table A.1).

Total VOC concentrations in each of the point sources studied are shown in Figure 3.

Figure 3

VOC concentration is the highest in the fresh composting sample. Other studies (Bruno et al., 2007; Eitzer, 1995; Gallego et al., 2012; Scaglia et al., 2011), also showed that the earlier waste treatments were the source points with the highest concentrations of these compounds.

The landfill leaks are also important sources of emissions of VOCs. High concentrations were observed in spite of the fact that landfill leaks were sampled out in the open.

The results show that the main organic compounds emitted by all these sources are limonene, *p*-cymene and pinene, as also observed in similar studies (Davoli et al., 2003; Gallego et al., 2012; Orzi et al., 2010). Other significant compounds that were detected were 2-butanone, dimethyl disulphide, β -phellandrene (noteworthy in fresh composting source), toluene (notable in landfill leaks), 3-carene (significant in fresh composting source and landfill leaks).

Table 2 lists the volumetric percent contribution by groups of compounds and some majority compounds in emissions of VOCs.

Table 2

It is apparent from Table 2 that aromatic compounds, and specifically *p*-cymene, can be considered as biogas markers. This result is in agreement with the study carried out by Davoli et al. (2003), who considered *p*-cymene to be a biogas marker. Orzi et al. (2010) also found a high presence of *p*-cymene in digested wastes (from anaerobic digestion).

The contribution of BTEX compounds is also the greatest in the landfill leaks; it is for this reason that strict control and maintenance of landfills are important.

It is also evident that limonene is an important component in emissions from all the sources except for the landfill leaks. Landfill emissions show a decrease of limonene concentration in comparison to fresh waste emissions, whereas *p*-cymene shows a great increase, as other studies also report in anaerobic processes (Davoli et al., 2003; Orzi et al., 2010). A great contribution of terpenes was observed in all source points studied. Many studies also found a high concentration of terpenes in the emissions from MSW facilities. Their emissions are common because they come mainly from fragrances in detergents and household products, or they can also originate from vegetable waste and the degradation of organic matter (Chiriac et al., 2011; Davoli et al., 2003; Eitzer, 1995; Gallego et al., 2012; Scaglia et al., 2011). Furthermore, the most important contribution of pinene occurred in the landfill leaks.

With regard to sulphur compounds, these occur mostly under anaerobic conditions, which correspond to the landfill leaks and the fresh composting fraction (mixture of MSW and digestate derived from anaerobic digestion).

The highest contribution from oxygenated compounds comes from the rejected compost fraction. This is in agreement with Davoli et al. (2003), who found that during waste maturation there is an increase of oxidative level of compounds.

In Table 2, it is also clear that cyclohexane occurs mostly in the leachate pond source; hence cyclohexane could be considered a marker of the leachate pond source for this plant. Cyclohexane is used as a non-polar solvent for the chemical industry and can be added to lacquers, resins, paint, varnish, removers, and fungicides. Cyclohexane is a liquid that does not bind well to soil, that makes its way into the ground can move through the ground and enter groundwater (USEPA, 1994). Gallego et al. (2012) also

found cyclohexane in the emissions from different sources points in an MSW facility, although leachate ponds were not studied in this work.

Table 3 shows the ratios of the most common and important compounds emitted by all the sources on the MSW treatment plant. These ratios can be applied to analyse the concentrations of VOCs, H₂S and NH₃ in the MSW treatment plant surroundings, in order to deduce the most important emission source point. Knowing these ratios enables a rapid identification of the source points responsible for the emissions. Samplings of the surrounding area of the MSW treatment plant would be quicker, because the analyst would search just the characteristic compounds in the chromatogram.

Table 3

Emissions from landfill leaks are associated with high *p*-cymene/limonene, pinene/limonene and H₂S/NH₃ ratios. As regards both composting sources, the contribution of ammonia is greater than that of hydrogen sulphide, but in the early stages of the composting process the difference between NH₃ and H₂S is slightly less marked. Limonene and *p*-cymene were two important compounds with high concentration in some emission source points, and some interesting conclusions can be obtained comparing the values of their emissions. It is notable that the contributions of *p*-cymene and limonene to the emissions are similar in the case of the fresh composting mixture. Whereas for the mature compost (rejected compost fraction), limonene makes a greater contribution to emissions than *p*-cymene. In the leachate pond, cyclohexane is present in a relatively high concentration in this plant, and practically only appears in this source point, but the contribution of limonene is greater than cyclohexane and also greater than *p*-cymene and pinene.

It should also be noted that some of these ratios could vary in different MSW treatment plants, although many studies also showed an important contribution of H₂S, NH₃ (Fang

et al., 2012; Smet et al., 1999), and some characteristic VOCs, such as: *p*-cymene, limonene and pinene (Davoli et al., 2003; Gallego et al., 2012; Orzi et al., 2010; Sadowska-Rociek et al., 2009; Smet et al., 1999) to the emission concentration.

4. Conclusions

The emissions of four samples of an MSW treatment plant, representative of the possible source points of emissions, were studied: fresh compost, mature compost, landfill leaks and leachate pond. The objective of this study was double: the determination of the compounds evolved and the determination of some significant ratios of compounds characteristic of each emission source points.

The concentrations of ammonia and hydrogen sulphide were measured by passive samplers or directly by a portable multi-gas detector. In addition, 152 organic compounds were identified and their concentrations measured, detected and characterised by Radiello[®] diffusive samplers.

The most important compounds with relative high concentrations were: hydrogen sulphide, ammonia, limonene, *p*-cymene and pinene. Comparing the source point of fresh compost and mature compost, it was shown that higher concentrations are obtained with the fresh compost.

Landfill leak emissions are characterised by high *p*-cymene/limonene, pinene/limonene and H₂S/NH₃ ratios. However, fresh compost emissions can be characterized by relative low H₂S/NH₃ ratio and *p*-cymene and limonene show a similar contribution. For the leachate pond, the most significant aspect is a relative cyclohexane/limonene ratio. These ratios can be useful for analysing the incidence of each focus on the concentrations detected outside the MSW treatment plant. Although the proposed ratios can be different for other MSW treatment plants, the methodology can be applied.

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Appendix-A. Supplementary data.

Table A.1 shows the data from the concentrations of VOCs in emissions from the different sources in the MSW studied.

Table A.1

FIGURES:

Figure 1: Schematic representation of the experimental tanks.

Figure 2: Boiling points of the compounds emitted from the fresh composting source vs. retention times in the capillary column.

Figure 3: Total VOC concentrations.

TABLES:

Table 1: Average concentration levels of H₂S and NH₃ in emissions..

Compound	Sampling day	Fresh compost fraction ^a (ppmv)	Rejected compost fraction ^a (ppmv)
H ₂ S	1 st day	3.2	< 0.1
	2 nd day	2.6	< 0.1
	4 th day	1.7	< 0.1
NH ₃	1 st day	63	28
	2 nd day	80	50
	4 th day	557	98

The standard deviations are: 0.3 ppmv for H₂S and 3.0 ppmv for NH₃ approximately (bold values) and 2, 4 and 13 ppmv respectively, for NH₃ in fresh compost fraction column.

1 ppmv of H₂S and NH₃ are equivalent to 1518 and 759 µg/Nm³.

^a Experiments carried out in tanks. H₂S and NH₃ measured with MX6 Ibrid portable detector.

Table 2: Volumetric percent contributions of compounds to the total emissions of VOCs.

	Fresh compost fraction	Rejected compost fraction	Leachate pond	Landfill leaks
Aromatics	31.76	6.25	6.91	49.97
<i>p</i> -Cymene	29.89	4.13	0.85	35.80
BTEX	0.87	1.58	3.59	13.40
Terpenes	52.66	68.18	48.97	32.45
Limonene	32.61	58.22	33.60	3.35
Pinene	12.32	6.28	13.38	24.35
Eucalyptol	0.89	0.00	0.31	0.42
Hydrocarbons	2.28	5.16	18.32	13.83
C4-C5 Hydrocarbons	0.10	0.34	0.81	15.46
Sulphur compounds	5.11	0.93	0.37	1.80
Oxygenated compounds	8.00	16.70	11.01	0.78
Alcohols	1.85	5.97	1.80	0.00
Ketones	5.78	9.05	8.13	0.78
Esters	0.40	1.73	0.87	0.00
Nitrogen compounds	0.00	1.11	0.00	0.00
Cyclic compounds	0.19	1.66	14.33	0.96
Cyclohexane	0.01	0.06	14.14	0.00
Halogenated compounds	0.00	0.01	0.09	0.21

Table 3: Volumetric ratios (ppbv compound i/ppbv compound j) of contribution of the main compounds.

Ratios (ppbv compound i/ ppbv compound j)	Fresh compost fraction	Rejected compost fraction	Leachate pond	Landfill leaks
<i>p</i> -cymene/limonene	0.92	0.07	0.03	10.69
pinene/limonene	0.38	0.11	0.07	7.27
pinene/ <i>p</i> -cymene	0.41	1.52	2.76	0.68
cyclohexane/limonene	0.00	0.00	0.42	0.00
cyclohexane/ <i>p</i> -cymene	0.00	0.01	16.66	0.00
H ₂ S/NH ₃	0.05-0.003	< 0.001	2-4	3-9