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Gas chromatography–mass spectrometry as a tool for estimating odour concentrations of biofilter effluents at aerobic composting and rendering plants

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Abstract

The relationship between chemical concentrations (gas chromatography–mass spectrometry analysis) and odour concentrations (olfactometry) was studied for biofilter emissions from four aerobic vegetable, fruit and garden waste (VFG) composting plants and one animal rendering plant. For the VFG composting plants, the study revealed a good linear relationship of the odour concentration with the total volatile organic compounds (VOC) concentration ($R^2=0.97$, $n=16$) as well as with the concentration of esters and ketones ($R^2=0.9$, $n=19$). For biofilter emissions of the animal rendering plant, the total VOC concentration was a poor estimator for odour concentration. However, for this type of odour, concentrations of organic sulphur containing compounds correlated well with odour concentrations ($R^2=0.94$, $n=8$). The results of the study also showed that the relationship between chemical and odour concentrations is specific for each type of odour and cannot be generalized.

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1. Introduction

Odour pollution is of growing concern in industrial and agricultural areas. Minimising odour nuisance can be achieved through converting plants to a closed design, by changing process parameters and by applying end-of-pipe techniques. The efficiency of odour reduction measures can be evalu-

ated by odour measuring techniques based on either chemical analysis using a variety of instruments or on sensory analysis using the human nose as a detector. Gas chromatography (GC) in connection with various detectors and gas chromatography–mass spectrometry (GC–MS) has been applied to identify the chemical composition of odorous samples [1,2]. Relating results of chemical analysis to sensorial parameters such as odour concentration, intensity or hedonic value remains a challenge.

Olfactometry is the most common method for measuring odour concentrations. Mixtures with different odour concentrations are presented to a panel of assessors using an olfactometer, in which odorous air is stepwise diluted with reference air (according

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to CEN terminology [3]). The standardization of this method is nowadays intensively examined and well founded. Formerly, odour concentration measurements were performed using different methods and national standards, e.g. in Sweden, Denmark, the UK, Germany, the Netherlands and France [4]. To improve and validate such standards, interlaboratory comparisons were conducted in Germany and the Netherlands. In the next step, a working group with experts from ten countries, was formed in the framework of the Committee Européen de Normalisation (CEN) to draft a European olfactometry standard (prEN 13725). To validate the CEN draft standard, a large-scale international comparison using *n*-butanol was conducted in 1996, which showed that the quality objectives were attainable in practice [5].

Although olfactometry provides the best method currently available for odour concentration measurements [6], the method is time consuming, labour intensive, expensive and is subjected to error [7–9]. To overcome these problems, attempts to correlate the concentration of volatile compounds with odour concentration have been reported recently. Noble et al. [10] found a close correlation between the sum of concentrations of hydrogen sulphide and dimethyl sulphide (DMS) and the odour concentration of mushroom composting emissions ($n=44$, $R^2=0.899$). Emissions from livestock wastes like pig slurry contain mostly sulphides, ammonia, volatile fatty acids, phenols and indoles [11]. In the study of Hobbs et al. [12], the residual mean square revealed that hydrogen sulphide and 4-methyl phenol head-space concentrations accounted for the majority of the variance of the relationship with the odour concentration. Little or no contribution to the model was found for acetic acid or ammonia respectively. A previous study of Hobbs et al. [13] indicated that assessment of odour concentrations from livestock waste can be done by measuring the total air concentration of nonmethane VOC, ammonia and hydrogen sulphide. The nonmethane VOC concentration was measured by means of a photo-ionisation detector (10.2 eV). For sewage treatment works, hydrogen sulphide seemed not to be a good marker compound for measuring odour concentrations [14]. On the other hand, Gostelow and Parsons [15] suggest that H_2S is an acceptable indicator for odour

for processes where H_2S is the dominant odorant like sludge treatment.

The potential for using GC–MS as an alternative for olfactometry has not yet been evaluated for VFG composting and animal rendering plant emissions. Several studies have investigated the chemical composition of emissions from both activities [1,2,16–21]. Fewer studies report sensory results at VFG composting sites [22,23] and animal rendering plants [17,24]. The aim of the presented work was to study the relationship between the odour concentration of biofilter effluents at composting and rendering plants measured by olfactometry and the chemical concentration determined by GC–MS analysis. As sulphur compounds are known to contribute considerably to odour nuisance [18,25], special attention was paid to these components.

2. Experimental

2.1. Methodology for sampling area sources

On both composting and rendering plants, different diffusive and non-diffusive odour sources can be identified. However, in this article only the biofilter emissions will be considered because they mainly determine the odorous impact on the neighbourhood.

Biofilters, if not covered and provided with a chimney, are non-point sources with an outward air flow of 50 to 200 $m^3 m^{-2} h^{-1}$. To take samples, the biofilter surface was covered with a polyethylene foil (8 m^2). Three of the four sides were fixed into the biofilter material enabling the emissions to flow out through the one open side. Through a PTFE tube sampling was done for chemical and olfactometric analysis. All gaseous samples were taken and analysed in duplicate.

2.2. GC–MS analysis

2.2.1. Sampling procedure for VOC

Samples were preconcentrated by sorption onto Tenax TA. Homemade glass sampling tubes contained 750 mg Tenax TA (60–80 mesh) (Supelco). Prior to use, tubes were conditioned during 2 h at 220 °C under a helium flow (20 $ml min^{-1}$). Air was sampled with a membrane pump while the air

sampling flow-rate was adjusted using a rotameter. The air sampling flow-rate was set at 0.1–0.5 l min⁻¹ and the sampling volume was 5–10 l. The air stream was passed through an ice water condenser prior to adsorption.

2.2.2. Instrumentation for VOC analysis

Analysis of VOC consisted of different steps: thermal desorption (220 °C), cold trapping (liquid nitrogen) and GC–MS. A 60 m 100% dimethyl polysiloxane column (film thickness 1.5 µm, internal diameter 0.53 mm, JandW Scientific) was temperature programmed from 25 to 100 °C at 2 °C min⁻¹ and from 100 °C to 220 °C at 4 °C min⁻¹. The Varian 2700 GC instrument was provided with a splitter that diverted part of the column eluate to a flame ionisation detector (quantification) and part to a Finnigan MAT 112S mass spectrometer (identification). The main reason for using a splitting system is that the TIC measurement was largely affected by presence of water vapour. A detailed description of the instrumentation and the method can be found elsewhere [2]. Quantification was based on total peak area as calculated from the FID signal, with a Nelson Analytical Chromatography Software system. Calibration was performed by analysing a set of liquid standards of representative analytes for each chemical class of VOC at three different concentrations. Standards were prepared in dichloromethane or isooctane. All analytes were of the highest purity which is commercially available. The mean of the three runs was used for determination of mean response factors per chemical class, expressed in ng AU⁻¹ whereby AU represents the peak area units. The response factor of benzene for example was 0.00071 ng AU⁻¹ with a standard deviation of 4%. The scan range of the mass spectrometer was 40–250 m e⁻¹ with a scan speed of 2.1 s scan⁻¹. Compounds were identified from their mass spectra by comparison with library NIST spectra, on the basis of fragmentation patterns and by comparison with published or determined Kovats retention index data.

2.3. Olfactometric measurements

2.3.1. Sampling method

Odour samples were collected in 60-l nalophane

bags by placing the bag in a container and connecting it to the sampling point with a sampling line (PTFE). By evacuating the container, sample air was drawn into the bag over a period of at least 20 min.

2.3.2. Olfactometric measurements

Odour concentrations were determined by a forced choice dynamic dilution olfactometer (Olfaktomat-n, Project Research Amsterdam BV), operated in accordance with the CEN recommendations [3]. Samples were presented to a panel of selected and screened human assessors in a range from 2⁴ to 2¹⁶ dilutions-to-threshold. The olfactometer had two sniffing ports with reference air presented through one port and diluted odorous air through the other, assigned at random. For each presentation, all assessors had to indicate which port emitted the sample and the certainty of the choice (guessing, inkling or certain). Responses were only regarded as being correct if the assessor indicated the correct port and was certain of his choice. In addition, each assessor had to respond correctly to the final two (highest) concentrations presented. As a result, the certainty threshold was measured. Van Harreveld and Heeres [26] concluded from their experiments that the variability in measuring results could be considerably reduced using a “certainty” criterion instead of a “detection” criterion. At the certainty threshold, the odour concentration is one European Odour Unit per cubic metre (ou_E m⁻³) by definition. The odour concentration of the analysed sample is the geometric mean of the odour concentrations determined by the different assessors and is expressed as a multiple (equal to the dilution factor) of 1 ou_E m⁻³ at standard conditions for olfactometry. Assessors were selected on basis of sensitivity to *n*-butanol. In CEN [3] the threshold for the reference compound *n*-butanol is set at 40 ppbv.

2.4. Statistical analysis

The statistical evaluation of data was performed using the SPSS software package version 10. A linear model was built between the dependent variable (odour concentration) and independent variables. In SPSS, there is a choice of three methods for building up the model. The stepwise regression procedure is probably the most widely used [27].

Essentially, this method develops a sequence of regression models, starting with the model with one independent variable. At each step an independent variable is added or deleted. The criterion for adding or deleting an independent variable can be stated equivalently in terms of *t*-statistics or *F*-statistics. In the forward selection procedure stepwise regression is simplified by omitting the test that evaluates whether a variable once entered into the model should be removed or not. A third method of model building is the backward elimination. This procedure is the opposite of forward selection. It begins with the model containing all potential independent variables and identifies the one with the smallest *F*-(or *t*-)value. If this value is smaller than a predetermined limit, the independent variable is not restrained. The model with the remaining independent variables is then fitted, and the next candidate for dropping is identified. This process continues until no further independent variable can be eliminated. The above procedures can lead to different models. As a consequence the results are not always unambiguous. However, for all the statistical analysis that were done in this research (both for the composting plants and the rendering plant) the same result was found with each of the three procedures.

2.5. Description of plants

2.5.1. Composting plants

In Flanders, there are six aerobic composting plants for selectively collected VFG waste. These plants have in total an annual capacity of 300 000 tons of VFG-waste [28]. On all plants, the composting process takes place in closed buildings. Under these conditions, odours emitted by the process can be collected and treated. All these aerobic composting facilities use biofilters to reduce the odour and VOC emissions.

On four different full-scale composting plants, air samples from the effluent of the biofilters were taken during the period February–June 2001. Samples were transferred to the laboratory where GC–MS analysis and olfactometry was done within 24 h.

2.5.2. Rendering plant

Due to the nature of the material processed, animal rendering activities result in the emission of

volatiles and disgusting odours, causing nuisance in the factory's neighbourhood [29]. Several technologies as thermal or catalytic combustion, stage scrubbers and biofilters may be used for the elimination of volatiles from waste gases. In this study, only the results of the effluent from the biofilters from one rendering plant are used.

3. Results and discussion

3.1. Analytical strategy

3.1.1. Sampling and thermal desorption performance

Selection of compounds for concentration determination, was based on breakthrough volumes taken from literature [30]. The temperature of effluents from biofilters was about 10 °C during sampling by the use of the ice cooler. Desorption of compounds was performed at 220 °C. For safe sampling (safe sampling volume is defined as $0.5 \times \text{breakthrough volume}$ [30]), breakthrough volumes larger than 30 l g⁻¹ adsorbing at 10 °C were necessary in the present sampling conditions [30]. Ethanol, *n*-pentane, 2-propanol, methyl acetate and acetone have breakthrough volumes smaller than 30 l g⁻¹ at 10 °C and were for this reason not included in the dataset used for statistical calculations.

To get efficient desorption, breakthrough volumes smaller than 30 ml g⁻¹ at 220 °C are needed. All VOC identified have breakthrough volumes smaller than 30 ml g⁻¹ at 220 °C [30], so desorption can be considered to be quantitative and no compounds has to be excluded for this reason.

3.1.2. Separation

Chromatograms of air samples from a composting plant typically contain a larger number of VOC than the chromatograms of the animal rendering plant (Fig. 1). Generally, more than 90% of the total detected mass in the chromatograms could be identified.

The general separation of VOC was good enough to allow quantification. From all analysis performed, problems with co-eluting peaks (e.g. 3-methylbutanol and dimethyl sulphide) were encountered in five

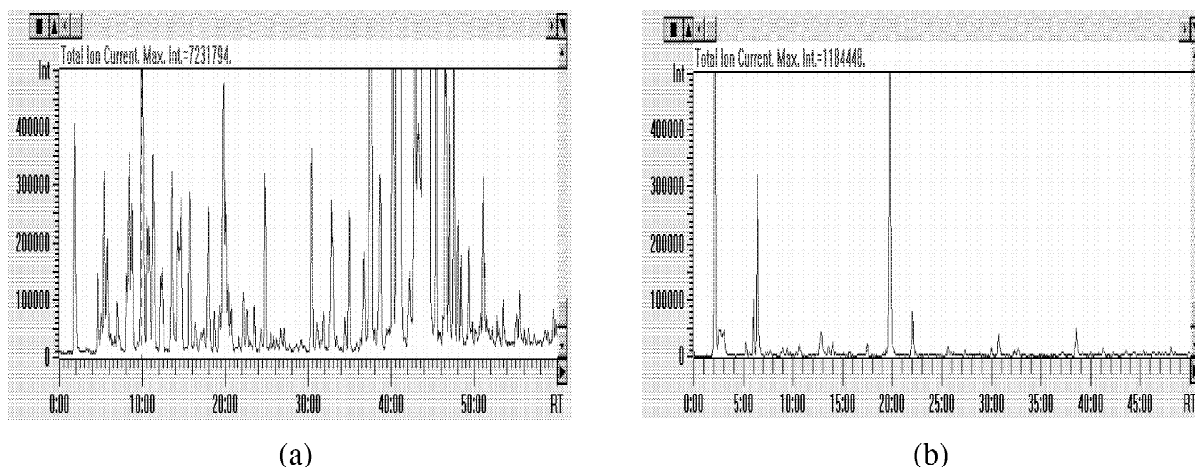


Fig. 1. Chromatogram of the analyses of an air sample from (a) a VFG composting plant (sample 1) and (b) a rendering plant (sample 8) whereby in X- and Y-axis the retention time of compounds (minutes) and number of counts, respectively are represented.

cases only. For co-eluting peaks integration was performed manually.

3.1.3. Quantification

The detection limit of the method, was calculated as the signal-to-noise ratio of 3, expressed in ng l^{-1} . The detection limits (LOD) varied from 0.2 to 5.4 ng l^{-1} . For the hydrocarbons, the LOD were the lowest, e.g. 0.4 ng l^{-1} for dodecane. The highest LOD were found for the aldehydes (e.g. 5.4 ng l^{-1} for 3-methylbutanal).

Problems with off-scale peaks were encountered for limonene in composting samples only. Because limonene contributed significantly to the terpene fraction, concentration data were calculated and included as such in the data base.

3.2. Composting plants

3.2.1. Odour and chemical concentrations

The results of the olfactometric and GC–MS measurements are given in Table 1. Total VOC concentrations vary between 0.09 and 23.6 mg m^{-3} with a mean value of 7.6 mg m^{-3} and a mean relative standard deviation of 12% ($n=19$). Olfactometric concentrations of the biofilter effluent vary between 390 and $13\,050 \text{ ou}_E \text{ m}^{-3}$ with a mean value of $4570 \text{ ou}_E \text{ m}^{-3}$ and a mean relative standard deviation of 20%.

The odorous emissions from composting plants are complex mixtures (Table 2). In this study 89 different chemical compounds were identified in biofilter effluent from VFG composting emissions. The most important groups are terpenes (65% of the total VOC concentration) followed by ketones (8%), hydrocarbons (8%), alcohols (7%), esters (5%), aldehydes (3%) and sulphur compounds (3%). Terpenes occur widely in vegetation and are a major contributor to the fragrance of plants [31]. Limonene and α -pinene are often released from the wood chips used as a bulking agent [32] and plant materials that are present in the biowaste. Terpenes were found to be released from biowaste material during the initial stages of the composting process [2]. According to Homans and Fisher [20] mainly anaerobic conditions in composting piles due to incomplete or insufficient aeration produce sulphur compounds of intensive smell, while incomplete aerobic degradation processes result in the emission of alcohols, ketones, esters and organic acids. Alcohols, carbonyl compounds, esters and ethers are mainly emitted during the initial composting stage, while the volatile organic sulphur compounds are mainly emitted during the thermophilic stage [2].

Before starting the regression analysis, a correlation matrix was calculated for the different variables used for building the regression model (Table 3). In this table, Pearson correlation coefficients are given

Table 1

Consistent dataset of the GC–MS analysis (concentrations in $\mu\text{g m}^{-3}$) and olfactometry (odour concentration in $\text{ou}_\text{E m}^{-3}$) on the effluent of biofilters at VFG composting plants

No.	Sampling date	Plant	Odour ^a	VOC ^a	Hydro-carbons	Alcohols	Aldehydes	Esters	Ketones	Terpenes	S-comp	Cl-comp	Ethers	Furans
1	08/03/01	A	7960±1034	13240±280	50	2420	730	1350	1250	7270	40	nd	30	90
2	15/03/01	A	9120±7048	16030±3147	30	3390	890	1790	1360	8500	nd	nd	nd	70
3	26/03/01	A	3870±331	8170±2845	40	1020	1470	380	840	4280	0	nd	10	110
4	03/04/01	A	11690±1816	12920±4506	50	1290	1310	2620	1150	6360	nd	nd	10	120
5	10/04/01	A	9560±1241	18040±1372	50	2610	1540	3270	1850	8300	120	nd	30	270
6	08/05/01	A	13050±7628	23580±2173	60	4150	3460	2930	2820	9990	100	nd	30	20
7	22/02/01	B	3910±345	4220±250	90	nd	nd	10	nd	4000	80	nd	30	nd
8	06/03/01	B	1740±336	4210±192	200	nd	nd	nd	40	3850	100	nd	20	nd
9	26/03/01	B	10260±3514	9740±1962	60	440	170	550	2160	6120	240	nd	nd	nd
10	03/04/01	B	5010±443	14630 ^b	150	100	130	50	1690	12350	90	40	40	nd
11	16/05/01	B	810±344	340±13	140	nd	0	nd	nd	170	0	30	10	nd
12	14/06/01	B	1020±0	1900±88	80	10	nd	nd	30	1740	20	nd	10	nd
13	22/02/01	C	960±429	3670±492	40	nd	nd	nd	530	2990	100	nd	10	nd
14	15/03/01	C	560±60	1690±187	120	nd	nd	nd	nd	1390	160	10	10	nd
15	10/04/01	C	2130±0	4790±51	190	nd	nd	nd	30	4210	290	nd	50	20
16	26/04/01	C	1180±141	2500±144	80	nd	nd	nd	nd	2170	220	nd	20	nd
17	16/05/01	C	1800±0	3470±154	560	0	nd	nd	10	2260	190	30	270	80
18	14/06/01	C	1740±111	2260±571	130	nd	nd	nd	nd	2030	40	0	20	30
19	06/03/01	D	390±0	90±9	60	nd	nd	nd	nd	20	10	0	0	nd

^a Duplicates.

^b For this case no duplicate for GC–MS analysis was carried out; nd=below detection limit of GC–MS system.

as a measure of linearity between two mutual variables. From Table 3, it becomes clear that there are significant correlations ($\alpha=0.05$) between odour

concentrations on one hand and concentrations of total VOC, aldehydes, terpenes, ethers, alcohols, esters and ketones on the other hand.

Table 2

Organic volatiles identified in the biofilter effluent from VFG composting plants

Hydrocarbons	Cyclohexane	2-Methylpropanoate	Terpenes	Thujone	Furans	Alcohols
Pentene	Tri-Methylbenzene	3-Methylbutanoate	α -Thujene	3-Thujanone	2-Methylfuran	Ethanol
Hexene	Di-methylethylbenzene	Propylpropionate	α -Phellandrene		3-Methylfuran	2-Propanol
Cyclohexene	Methylpropylbenzene	Propylbutyrate	α,β -Pinene		2-Ethylfuran	1-Propanol
Pentadiene	Ethylidimethylbenzene	Propylhexanoate	Camfene	Ethers		2-Butanol
Pentane	Ethylmethylbenzene	3-Methylbutylacetate	Sabinene	2-Methyl-1,3-dioxane	Ketones	Isobutanol
Hexane	Ethylmethylcyclohexane	Methylhexanoate	β -Myrcene	4-Methyl-1,3-dioxane	Acetone	<i>n</i> -Butanol
Heptane	3,5-Dimethylheptene	Ethylhexanoate	<i>p</i> -Cymene	1,3-Dioxolane	Butanone	2-Pentanol
Octane		Methylpentanoate	δ -3-Carene	2,4-Dimethyl-1,3-dioxane	2-Pentanone	Cyclopentanol
Nonane	Esters	Ethylpentanoate	Limonene	Ethylamylether	3-Pentanone	3-Methylbutanol
Benzene	Ethylheptanoate	Ethylhexanoate	γ -Terpinene		2-Hexanone	2-Methylbutanol
Toluene	Methylbutyrate	Ethylheptanoate	Terpinolene		2-Heptanone	<i>n</i> -Pentanol
Ethylbenzene	Ethylbutyrate	Ethylctoanoate	Camphor	S-compounds		3-Methylpentanol
<i>o,m,p</i> -Xylene	Methylacetate		Sylvestrene	Dimethylsulphide	Aldehydes	<i>n</i> -Hexanol
Styrene	Ethylacetate		Isolongifolene	Ethanthiol	Isobutyraldehyde	
2-Methylpentane	Methylpropionate	Cl-compounds	β -Gurjunene	Dimethyl disulphide	3-Methylbutanal	
3-Methylpentane	Propylacetate	1,3-Dichlorobenzene	4-Terpineol	Methylpropyl disulphide	2-Methylbutanal	
Methylcyclopentane	<i>n</i> -Butylacetate	Dichloromethane	Thujopsene	Carbon disulphide	<i>n</i> -Hexanal	

Table 3
Pearson correlation coefficients between the different variables for the results of the VFG composting plants

	VOC	Odour	Aldehydes	Terpenes	S-comp	Cl-comp	Furans	Ethers	Hydro-carbons	Alcohols	Esters	Ketones
VOC	1	0.907**	0.823**	0.921**	-0.091	-0.071	-0.080	0.520*	-0.293	0.879**	0.855**	0.923**
Odour		1	0.763**	0.782**	-0.083	-0.216	-0.138	0.498*	-0.341	0.813**	0.873**	0.895**
Aldehydes			1	0.584**	-0.207	-0.248	-0.089	0.478*	-0.313	0.861**	0.834**	0.752**
Terpenes				1	-0.007	0.109	-0.076	0.358	-0.222	0.666*	0.630**	0.851**
S-comp					1	-0.007	0.333	-0.162	0.372	-0.243	-0.196	-0.015
Cl-comp						1	0.469*	-0.149	0.572*	-0.282	-0.285	-0.048
Furans							1	0.144	0.924**	-0.117	0.120	-0.164
Ethers								1	-0.078	0.524*	0.723**	0.737
Hydrocarbons									1	-0.359	-0.349	-0.354
Alcohols										1	0.876**	0.764**
Esters											1	0.747**
Ketones												1

* Correlation is significant at the 0.05 level; ** correlation is significant at the 0.01 level.

3.2.2. Relation odour concentration—total VOC concentration

Using SPSS, multiple regression was made between odour concentrations and total VOC concentrations. The variable “plant” was also included as a numerical variable. The following regression equation was found:

$$OC = 239 + 0.56C_{VOC} \quad (R^2 = 0.82, n = 19) \quad (1)$$

where OC is odour concentration ($\text{ou}_E \text{ m}^{-3}$); and C_{VOC} the total VOC concentration ($\mu\text{g m}^{-3}$).

The variable “plant” did not appear in the equation, indicating that results did not allow discriminating emissions from the different VFG composting plants. The intercept of Eq. (1) was not significantly different from 0 (t -test, $\alpha=0.05$). Therefore, in the next step regression through the origin was done. The following equation was found:

$$OC = 0.58C_{VOC} \quad (R^2 = 0.82, n = 19) \quad (2)$$

where $0.4 < b_{VOC} < 0.7$ (95% confidence interval) and b_{VOC} is the regression coefficient of C_{VOC} .

The residuals were considered for examining non-linearity of regression function, non-constancy of error variance, presence of outliers, non-independence of error terms, non-normality of error terms and omission of important predictor variables [27]. There were no departures with the exception of presence of outliers. Measurements 4, 9 and 10 were detected as outliers and were omitted from the

dataset. Regression on the reduced dataset resulted in:

$$OC = 0.55C_{VOC} \quad (R^2 = 0.97, n = 16) \quad (3)$$

where $0.52 < b_{VOC} < 0.59$ (95% confidence interval).

Omitting the outliers did not change the regression coefficient significantly (from 0.58 to 0.55). The ratio between the upper and lower limit of the 95% confidence interval on the slope was reduced from 1.7 to 1.1.

For the odour concentrations, the observed and the predicted values, calculated along the above model, together with their 95% estimation intervals are given in Fig. 2. There is a good agreement between the fitted OC and the observed OC. The absolute value of the difference between the predicted and the observed OC relative to the observed OC varies between 1 and 111% with an average of 35.3% and a median value of 28.7%. The largest deviations occur for odour concentrations lower than $1000 \text{ ou}_E \text{ m}^{-3}$. If those values are omitted from the data set the average of the difference becomes 21.9% and the median value 16.1% ($n=15$).

In literature, only few attempts are mentioned to find a relationship between odour concentrations and total VOC concentrations at composting facilities. For VFG waste in particular, no references about such relationship were found. For a composting plant handling biosolids produced by a wastewater treatment plant, Hentz et al. [33] noticed that the odour

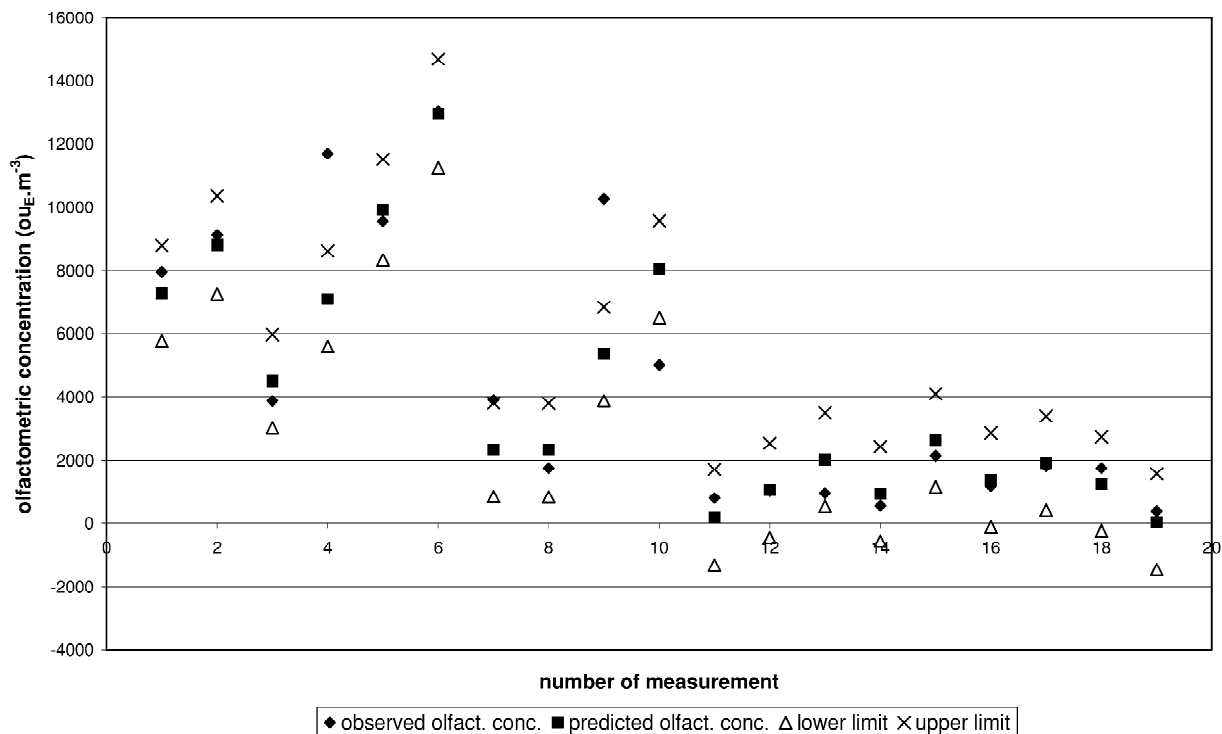


Fig. 2. Observed and predicted odour concentrations with 95% estimation intervals for the biofilter effluent of VFG composting plants, using the relationship between OC and total VOC concentration (Eq. (3)); each point is the average of two sample determinations.

emissions of the composting process followed a similar pattern to VOC emissions. These data were however not quantitatively investigated. Kryzmien et al. [25] studied the relationship between odour and chemical concentrations at a lab-scale composting system processing food residues, yard trimmings, agricultural waste and food waste. The authors compared the profiles of odour concentrations and chemical concentrations of compounds belonging to defined chemical classes over time. The results indicated that there might be a reasonable correlation between the release of VOC and odours but no statistical treatment of the data was presented.

3.2.3. Relation odour concentration—concentration of chemical classes

Next to the relationship of odour concentrations with total VOC concentrations, the relationship with the sum of the concentrations of compounds belonging to defined chemical classes (esters, terpenes, ...) was examined. For this purpose, multiple

regression was executed with the different groups and the variable “plant” as possible estimators. The following equation was found:

$$OC = 1491 + 1.8C_{\text{est}} + 2.6C_{\text{ket}} \quad (R^2 = 0.90; n = 19) \quad (4)$$

where C_{est} is the total concentration of esters ($\mu\text{g m}^{-3}$); and C_{ket} the total concentration of ketones ($\mu\text{g m}^{-3}$).

All the regression coefficients were significantly different from 0. The 95% confidence intervals for the coefficients were calculated on

$$570 < b_0 < 2412$$

$$0.8 < b_{\text{est}} < 2.7$$

$$1.4 < b_{\text{ket}} < 3.8$$

The same residual analysis as described earlier was done but no departures were found. The ob-

served odour concentrations and the values predicted according to Eq. (4) are depicted in Fig. 3. The absolute value of the difference between the predicted and the observed OC relative to the observed OC varies between 7 and 279%. The average is 56.1% and the median value 22.6%. If the results are calculated without the cases with an observed OC lower than $1000 \text{ ou}_E \text{ m}^{-3}$, the average value becomes 22.2% and the median value 18.7%. Although differences are not large, the estimation based on total VOC concentration performs better than the estimation based on concentrations of chemical classes. For odour concentrations larger than $1000 \text{ ou}_E \text{ m}^{-3}$, the predictive power of the models is good especially taking into account the inherent large variability on sensorial properties.

From the different groups of chemicals present, concentrations of esters and ketones seem to be the best estimators for the odour concentration of the effluent from biofilters at VFG composting plants.

The results of the above multiple regression models do not imply that other variables (aldehydes, alcohols, terpenes) do not contribute to the odour concentration. They are not retained as they are too strongly correlated with already withdrawn variables (esters and ketones).

When the importance of functional groups in odour emissions from composting plants is considered, sulphur compounds (e.g. methyl mercaptanes and methyl sulphides) are often mentioned as one of the most important ones. In literature indications about the relationship of odours with sulphur compounds are given for different types of composting but not for VFG composting. In mushroom composting emissions, Noble et al. [10] found a very close correlation ($R^2=0.90$, $P<0.001$) between the OC and the combined H_2S and DMS concentration. Van Durme et al. [32] reported DMS, DMDS (dimethyl disulfide), limonene and α -pinene to be the main odorants present at a composting facility for waste-

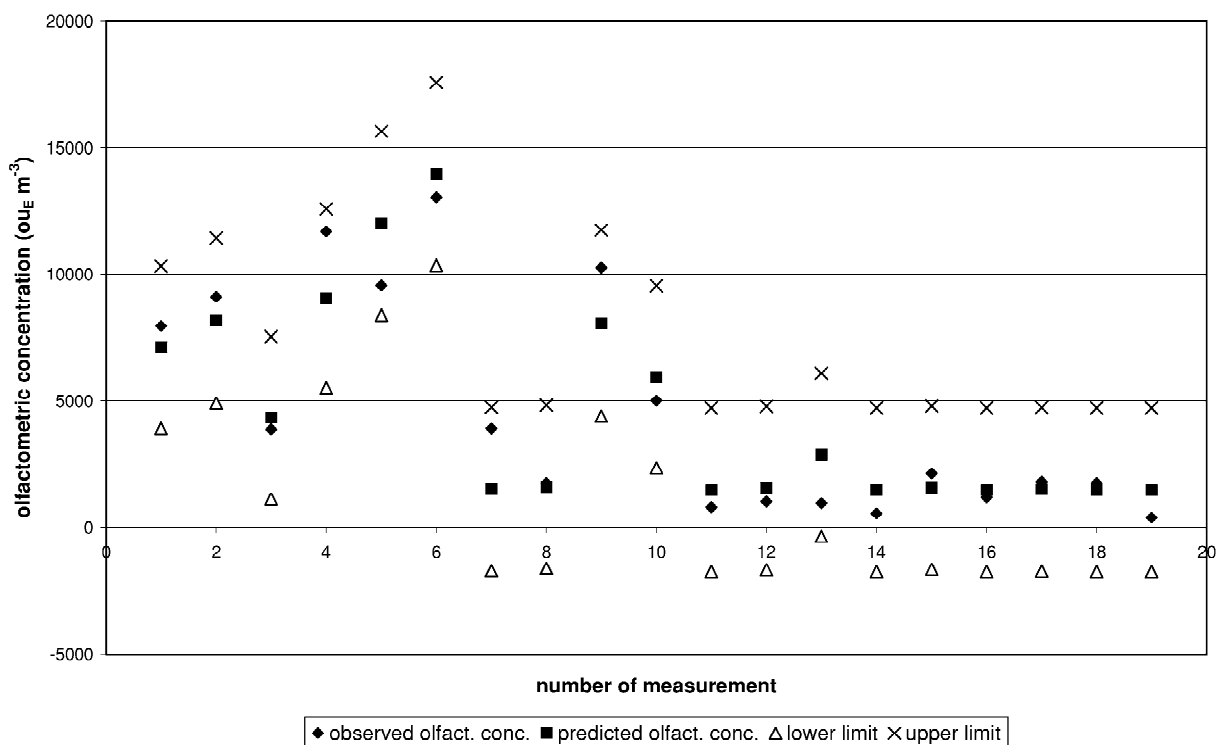


Fig. 3. Observed and predicted odour concentrations with 95% estimation intervals for the biofilter effluent of VFG composting plants, using the relationship between OC and concentrations of esters and ketones (Eq. (4)); each point is the average of two sample determinations.

water sludge. In an aerated static pile sludge system Hentz et al. [33] reported a good linear correlation between the odour concentration and the concentration of DMDS. Most researchers involved in compost odour control, focus their attention on controlling the organic sulphur compounds [34]. However, this study indicates that for the effluent of biofilters at VFG composting plants the S-compounds are not a predictor for the odour concentration.

3.2.4. Evaluation of both relationships

The number of cases to be collected for an exploratory observational regression study depends on the size of the pool of potentially useful explanatory variables. More cases are required when the pool is large than when it is small. A general rule of thumb states that there should be at least six to 10 cases for every variable in the pool [27]. In this study, 10 variables were retained as possible explanatory variables for the model and according to the above rule of thumb 60 measurements should have been done. Instead, only 19 measurements were done what is theoretically not enough. Nevertheless, a good model was obtained with the concentration of esters and ketones. The model with total VOC concentration as only predictor (Eq. (3)) is preferred because of two reasons. First the correlation coefficient R^2 was higher ($R^2=0.97$ compared to 0.90 for the model with esters and ketones). Secondly, with one predictor fewer measurements are necessary to have a reliable model. For reasons of validation, it

would be useful to enlarge the dataset by additional measurements.

3.3. Animal rendering

The results of the olfactometric measurements and GC–MS analysis, are given in Table 4. In Table 5 all VOC identified in one or more samples of the biofilter effluent are listed. Total VOC concentrations vary between 0.03 and 0.71 mg m⁻³ with a mean value of 0.29 mg m⁻³, being a factor 23 lower than the mean biofilter effluent concentration at the VFG composting plants. The mean relative standard deviation of the GC–MS measurements is 26% ($n=9$). As far as the chemical concentrations are concerned, the most important groups are the sulphur containing compounds (44% of the total VOC concentration) followed by the hydrocarbons (28%), chlorinated compounds (15%), ketones (16%) aldehydes (7%) and alcohols (2%). In the emissions of biofilters at the animal rendering plant, no terpenes nor esters are detected which is a second difference with the emissions at VFG composting plants.

The odour concentration varies between 1740 and 83540 ou_E m⁻³ with a mean value of 21220 ou_E m⁻³ and a mean relative standard deviation of 27%.

First, a correlation matrix was calculated for all possible predictors (Table 6). Based on the Pearson correlation coefficients, there was a significant correlation ($\alpha=0.05$) between the odour concentration and the concentration of organic S-compounds, aldehydes and the total VOC concentration.

Table 4

Consistent dataset for the GC–MS analysis (concentrations in $\mu\text{g m}^{-3}$) and olfactometry (odour concentration in ou_E m⁻³) on air samples from an animal rendering plant

No.	Odour ^a	VOC ^a	Hydro-carbons	Ketones	Aldehydes	S-comp	Cl-comp	Ethers	Furans
1	13590±2431	280±141	150	nd	10	120	nd	nd	nd
2	16560±7473	370±148	100	0	40	200	30	nd	nd
3	3330±967	30 ^b	10	0	nd	10	nd	nd	nd
4	3780 ^b	120 ^b	30	0	20	10	50	10	nd
5	1740 ^b	240 ^b	20	0	nd	10	190	10	10
6	17070±2508	360±71	100	nd	60	190	0	10	nd
7	47420±6908	500±65	60	nd	0	440	nd	0	nd
8	83540±9833	710±58	50	0	140	510	nd	nd	0
9	3920±2148	30 ^b	20	0	0	10	0	0	0

^a Duplicates.

^b For these samples no olfactometry and/or GC–MS duplicate was done; nd=below detection limit of GC–MS system.

Table 5
Organic volatiles identified in the biofilter effluent from an animal rendering plant

Hydrocarbons		S-compounds	Furans
Pentane	Toluene	Dimethyl sulphide	Furan
Hexane	Ethylbenzene	Dimethyl disulphide	2-Methylfuran
Heptane	<i>o,m,p</i> -Xylene	Dimethyl trisulphide	
Octane	Methylethylcyclohexane	Carbon disulphide	Ketones
Nonane			Acetone
Decane		Halogenated VOC	Butanone
Undecane	Aldehydes	1-Chlorobutane	
Dodecane	3-Methylbutanal	Tetrachloroethylene	Alcohols
Tridecane	2-Methylbutanal	Dichloromethane	Ethanol
2-Methylpentane	<i>n</i> -Hexanal		
3-Methylpentane	Isobutyraldehyde	Ethers	
Benzene	Benzaldehyde	2-Methyl-1,3-dioxolane	

3.3.1. Relation odour concentration—total VOC concentration

By performing regression on the dataset, the following relationship was found between the odour concentration and the total VOC concentration

$$OC = -11285 + 110.5C_{VOC} \quad (R^2 = 0.79, n = 9) \quad (5)$$

From a one-sample *t*-test ($\alpha = 0.05$) it was concluded that the intercept was not significantly different from zero. Regression through the origin resulted in the following equation

$$OC = 85.1C_{VOC} \quad (R^2 = 0.83, n = 9) \quad (6)$$

with

$$56.2 < b_{VOC} < 114.1 \quad (95\% \text{ confidence interval})$$

The aptness of the above model was checked by

residual analysis and no departures were found. The observed and predicted odour concentrations for this model are given in Fig. 4. The absolute value of the difference between predicted and observed OC relative to observed OC ranges between 10 and 1074% with a mean value of 175.9% (median 76.0%). The values are much larger than the corresponding values calculated for the VFG composting plants. Also the 95% estimation intervals in Fig. 4 are larger in comparison with those calculated for the composting sector. Therefore it was concluded that total VOC concentration cannot be used as an estimator of the odour concentration of the rendering plant biofilter emissions.

3.3.2. Relation odour concentration—concentration of chemical classes

A multiple regression was made between the odour concentration as dependent variable and the

Table 6
Pearson correlation matrix between the different variables for the results of the animal rendering plant

	Odour	VOC	Aldehydes	S-comp.	Cl-comp.	Furans	Ketones	Ethers
Odour	1	0.904**	0.781*	0.954**	-0.345	0.073	0.268	-0.224
VOC		1	0.752*	0.941**	-0.144	0.183	0.304	-0.070
Aldehydes			1	0.676*	-0.253	0.108	0.490	-0.106
S-comp.				1	-0.377	-0.033	0.157	-0.156
Cl-comp.					1	0.862**	0.387	0.338
Furans						1	0.477	0.093
Ketones							1	-0.200
Ethers								1

* Correlation is significant at the 0.05 level; ** correlation is significant at the 0.01 level.

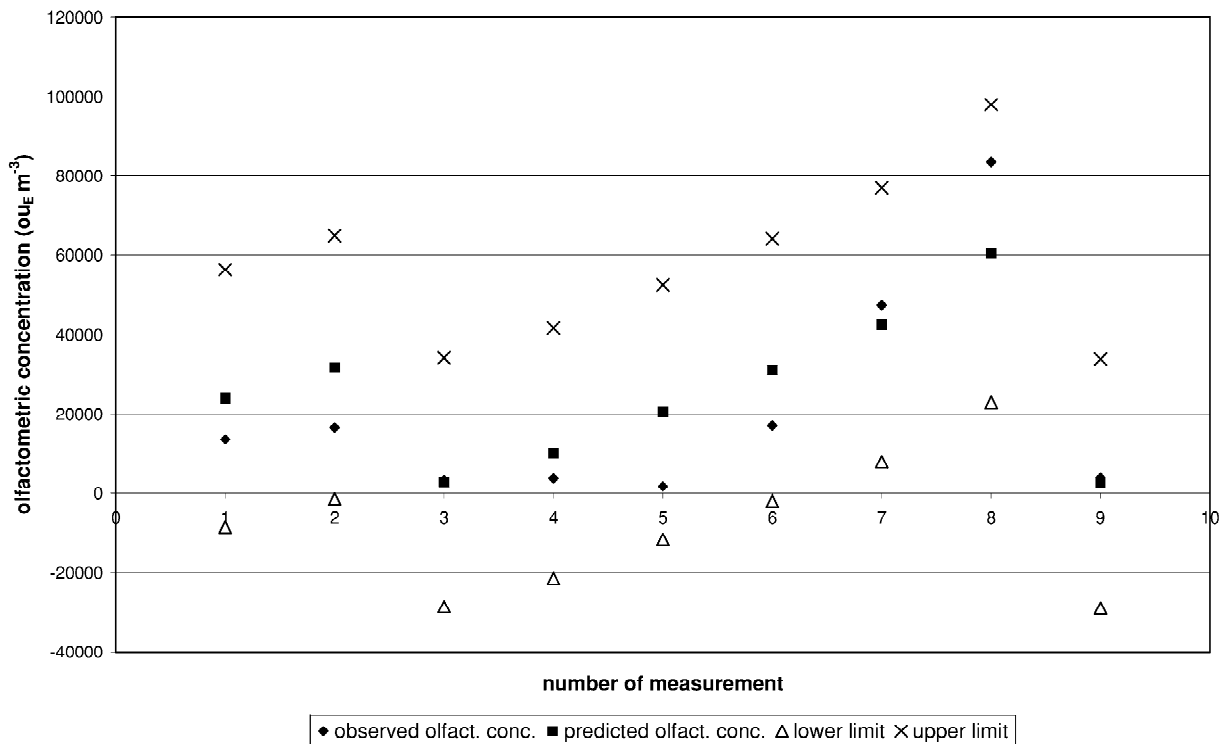


Fig. 4. Observed and predicted odour concentrations with 95% estimation intervals for the biofilter effluent of the animal rendering plant, using the linear correlation between OC and total VOC (Eq. (6)); each point is the average of two sample determinations.

different chemical classes as independent variables. The following regression model was found

$$OC = -1526 + 135.8C_{S\text{-comp}} \quad (R^2 = 0.90, n = 9) \quad (7)$$

The *t*-test on the regression coefficients proved that the intercept was not significantly different from zero. Consequently, in the next step the regression line was forced through the origin

$$OC = 131.6C_{S\text{-comp}} \quad (R^2 = 0.94, n = 9) \quad (8)$$

with

$$105.9 < b_{VOC} < 157.4 \quad (95\% \text{ confidence interval})$$

The aptness of the model was checked but no departures were found. The observed and the predicted values for the odour concentration with Eq.

(8) are given in Fig. 5. The absolute value of the difference between predicted and observed OC relative to observed OC varies between 9 and 77% with a mean value of 39.5% (median 40.7%). So in contrast with the VFG composting plants, organic S-compounds can be used as an estimator for the odour concentration from rendering plant biofilter emissions. When the concentrations of the S-compounds for the VFG composting plants and the animal rendering plant are compared, about the same range of concentrations for both plants is found (0 to 300 $\mu\text{g m}^{-3}$ for the VFG composting plants; 0 to 520 $\mu\text{g m}^{-3}$ for the animal rendering plant). The relative contributions of the groups however vary between the two types of waste processing sectors. At the rendering plant, the contribution of the S-compounds is 44% of the total VOC-concentration while at the VFG composting plants, they count only for 3% of the total VOC emission. Powers [6] also noted that

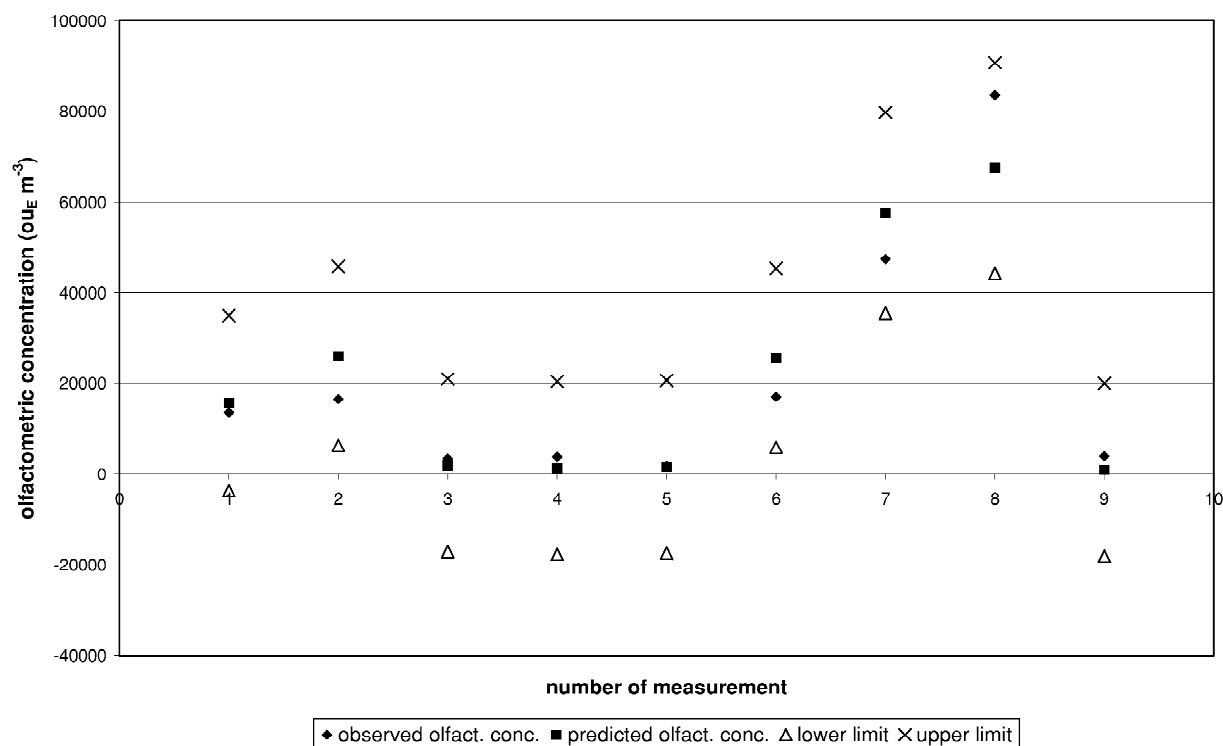


Fig. 5. Observed and predicted odour concentration with 95% estimation intervals for the biofilter effluent of the animal rendering plant, using the relationship between OC and concentration of sulphur compounds (Eq. (8)); each point is the average of two sample determinations.

the relative contribution of the odorants is important in determining the odour. The author examined the difference in odour characteristics of samples collected from swine and dairy facilities. Panellists routinely discriminated between the two types of samples. Yet, the compounds identified using GC–MS, were the same for the two samples, but the relative contributions of the compounds varied between the two species and that seemed to cause a difference in odour.

As the biofilter removal efficiency is dissimilar for the different chemical groups (e.g. the removal efficiency of aldehydes is higher than the removal efficiency of sulphur compounds [35]), the relative contribution of the chemical classes to the composition of the biofilter influent and the effluent is different. This implies that the relationships between the olfactometric measurements and the GC–MS

analysis found in this study are only applicable for the effluent of biofilters and not for the influent. Also Gostelow and Parsons [36] concluded that a different relationship exists between the odour concentration and the H₂S-concentration before and after the odour treatment at a sewage treatment plant.

4. Conclusion

Olfactometry and GC–MS analysis of biofilter effluents were performed at four aerobic VFG composting plants and one animal rendering plant. Relationships between the odour concentration and the results of GC–MS analysis were studied for both types of effluents. For the VFG composting plants, the odour concentration correlated with the total concentration of VOC ($R^2=0.97$, $n=16$) as well as

with the concentration of esters and ketones ($R^2 = 0.9$, $n = 19$). The mean of the absolute values of the difference between the predicted and the observed odour concentration relative to the observed OC was 35.3% (median 28.7%) for the model with the total VOC concentration as independent variable. For the model with the concentrations of esters and ketones as independent variables, this mean difference was 56.1% (median 22.6%). The highest deviations were found for the cases with an odour concentration lower than $1000 \text{ ou}_E \text{ m}^{-3}$. Both relationships are useful at the six aerobic VFG composting plants in Flanders and indicate that odour concentrations of biofilter emissions in this sector can be estimated by GC–MS analysis. Preference is given to the model with one predictor, namely total VOC concentration, as fewer measurements are necessary to obtain a statistically reliable model and a higher correlation coefficient was calculated.

For animal rendering plants, this study reveals that odour evaluation can be done by measuring the concentration of sulphur containing organic compounds ($R^2 = 0.94$, $n = 9$). The relative mean difference between the predicted and the observed odour concentrations was 39.5% (median 40.7%).

From these results it is clear that it is possible to find a relationship between the odour concentration and the GC–MS analysis either with the total VOC concentration or with the concentration of one or more of the chemical classes. For reasons of validation, it would be useful to extend both datasets by additional measurements.

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