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Chemical identification and quantification of volatile organic compounds emitted by sewage sludge

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Highlights

- 380 VOCs have been detected and quantified in sewage sludge.
- Total VOC emissions increase as the dry and organic matter contents increase.
- Anaerobic digestion and dewatering reduce the sulphuric compound emissions.
- Aromatic compounds and skatole are highly emitted from the undigested sludge.
- OVOCs are dominant in SS 60%.

Abstract

The recycling of organic waste products (e.g. sewage sludge, SS) is currently being promoted as a substitute for mineral fertilizers for agricultural lands. The spreading of SS allows the recycling of the nutrients and organic matter it contains. SS contains various pollutants such as volatile organic compounds (VOCs) that adversely affect the ecosystem and human health through ozone production and serve as critical precursors of atmospheric secondary organic aerosols. There are very few studies quantifying the gaseous compounds emitted from SS, and those studies primarily address their odorant properties for identifying suitable odour abatement techniques. There is an urgent need for more comprehensive quantitative information on VOCs emitted from SS as aerosol precursors. In this context, an experimental study was performed on SS samples taken from a wastewater treatment plant located in France. Undigested SS (UDSS), digested SS (DSS) and SS with 30% and 60% dryness were collected from different stages of treatment sequence and analyzed using atmospheric simulation chambers coupled to proton-transfer-reaction quadrupole ion-guide time-of-flight mass spectrometer. Our study revealed that SS samples emitted a large spectrum of VOCs. 380 compounds were detected, quantified and classified into different chemical groups. The VOC emissions increased with the increase in the dryness of the sample; the highest being in SS 60%, followed by SS 30%, UDSS and DSS. OVOCs were dominant in SS 60%. The statistical analysis showed that the anaerobic digestion and the dewatering to 60% of dryness decreased the emissions of sulphuric compounds. Aromatic compounds and indoles (e.g. skatole) were emitted significantly from the UDSS. Some of these VOCs can serve as precursor gases for atmospheric aerosol formation. The experimental dataset obtained in this study provides an accurate inventory reference for the VOC emissions from SS samples and shows the impacts of the treatment on emission characteristics of VOCs.

Keywords: volatile organic compounds, mass spectrometry, SS, anaerobic digestion and dewatering, aerosol precursors

1. Introduction

Sewage sludge (SS) refers to the residual, solid, semisolid or liquid material that is generated at wastewater treatment plants (WWTPs) as treatment by-products of wastewaters released from various sources (e.g. homes, industries, medical facilities, street runoff, etc.) (Christodoulou & Stamatelatou, 2016; Harrison et al., 2006). SS is composed of organic and inorganic materials, heavy metals and other hazardous materials. Therefore, it is extremely important to properly process SS in order to minimize its environmental repercussions (Iticescu et al., 2018). Nowadays, SS treatment has become a practical issue due to the massive increase of population in urban areas and to the constant changes in living standards.

In Europe, investments in municipal wastewater treatment have been very important in the last decade, but this increasing number in WWTPs arises secondary environmental concerns due to the accumulation of sludge resulting from wastewater treatment processes. Accordingly, SS should be treated as secondary raw material and used as a valuable source of nutrients and organic matter. SS treatment in WWTPs usually includes thickening, digestion and dewatering, which separate the solid and liquid components of the sludge to be easily handled for final disposal (Hall, 1995; Iticescu et al., 2018; Jamil Khan et al., 2006). The main disposal routes of SS are landfilling, recycling as building materials, elimination through thermal processing or use in agriculture. The most feasible ways to reduce the sludge quantities is their recycling and use them as fertilizer (Iticescu et al., 2018). Moreover, the use of SS on land, compared to incineration or sanitary landfill, has lower costs. The agricultural reuse of SS should be prioritized as recommended by the European Commission in the Circular Economy Action Plan (Collivignarelli et al., 2019). This use of SS has been preferred in France where nearly 60% of SS is applied to soil as organic fertilizer providing nutrients for crops, soil buffer and soil amendment (Milieu et al., 2010). However, SS should be treated prior its agricultural application such as by anaerobic digestion, composting or chemical treatment (Christodoulou & Stamatelatou, 2016; Collivignarelli et al., 2019). The composition of anaerobically digested sludge increases its potential as soil amendment and/or fertilizer. For this reason, in Europe, particularly in the Mediterranean region where the high summer temperatures combined with the intensive cultivation practices promote a constant decrease in the soil organic matter, 40% of SS is used as a soil organic amendment due to its high nitrogen, phosphorous and organic matter content (Lamastra et al., 2018). The use of SS in agriculture has been disciplined as each European member state has issued a national legislation based on the European directive 86/278/EEC (Collivignarelli et al., 2019; Di Capua et al., 2020). The characteristics of SS play a significant role when considering the ultimate land application. There are different methods for SS application on soils depending on the total solid content of SS. For instance, liquid or low-solid sludge can be generally injected into the soil to provide better aesthetics. On the contrary, dewatered or semisolid sludge can be spread on the surface and subsequently plowed into the soil (Iticescu et al., 2018). Moreover, the spreading occurs at different climatic condition (e.g. temperature and humidity) and on different types of soils (e.g. soil pH, texture and carbon content)(Colón et al., 2014).

While the use of SS to bring nutrients and organic matter could be beneficial for the soil, it also represents a risk due to the content of contaminants like heavy metals, organic compounds and pathogens. Moreover, SS emits large amounts of hydrogen sulphide (H_2S), ammonia (NH_3) and volatile organic compounds (VOCs) into the atmosphere that are generally associated with odorous nuisance and health risks (Mustafa et al., 2017; Nie et al., 2019). VOCs and semi- VOCs contained in SS may have a harmful impact on the natural environment and human health (Kotowska et al., 2012). These compounds reach WWTPs from households and industrial plants. Some of those compounds undergo biodegradation during the process of wastewater treatment; others remain in the SS in an unchanged form. A large number of VOCs are formed during the decomposition of various organic compounds as well as during metabolic activity of the bacteria that decompose the sludge organic matter in the processes performed at WWTPs and appear as intermediates metabolites (Gomez-Rico et al., 2008). Due to their volatile character, some of these compounds escape to the atmosphere during the SS treatment processes (Kotowska et al., 2012).

In the literature on the subject, only a small number of research papers have been devoted to characterizing the VOCs from SS (Abis et al., 2018, Kotowska et al., 2012; Rincón et al., 2019). Generally, most of the studies related to VOCs emitted from SS are focused on SS composting (Shen et al., 2012; Zhang et al., 2013; Zhu et al., 2016a) or at the level of WWTPs (Nie et al., 2019; Widiana et al., 2019). The main organic compounds reported in these studies were volatile sulphur compounds, volatile fatty acids, alcohols, aldehydes, ketones, alkanes, alkenes, terpenes and aromatics (Byliński et al., 2019; Fisher et al., 2017; Harrison et al., 2006; Rincón et al., 2019). There are very few studies quantifying the gaseous compounds emitted from SS, and those studies primarily address their odorant properties for identifying suitable odour abatement techniques (Byliński et al., 2019; Mustafa et al., 2017; Nie et al., 2018; Rincón et al., 2019). VOCs such as trimethylamine, acetic acid, limonene and ethylbenzene were identified at high levels in anaerobically stabilized sludge (Fisher et al., 2017). Oxygenated VOCs (OVOCs) shows the highest concentration levels and acetone is the major species at SS composting plant (Byliński et al., 2019). Rincón et al., (2019) found that the most emitted chemical families from SS are nitrogenated compounds, terpenes and sulphide compounds. These

VOCs are precursors of secondary organic aerosols (SOA) and tropospheric ozone (O_3), resulting in environmental issues of air quality and climate (Atkinson, 2000).

Lelieveld et al., (2015), using an atmospheric chemistry model to investigate the link between premature mortality and emission source categories in urban and rural environments showed that agriculture has an impact on particulate matter, and in many European countries, its contribution to PM2.5 is 40% or higher. In these modeled agricultural emissions, the authors only consider the NH_3 emissions that form inorganic PM2.5. However, SOA formation from precursor VOCs emitted by agriculture was not estimated. This makes a part of the gap between the modeled and measured aerosols. The authors explained this by the underestimated agricultural sources (Lelieveld et al., 2015). To date, there is only one estimation of SOA formation from precursor gases emitted from the agricultural sector (Ciuraru et al., 2021). This recent study performed on undigested SS showed atmospheric particle formation from oxidized organic molecules and sulphur dioxide (SO_2), which are both emitted by SS (Ciuraru et al., 2021). These SOA are readily formed from ozonolysis of skatole emitted by the SS. The authors suggest that this additional VOC source (e.g. skatole) may have a significant influence on atmospheric particle formation during the spreading periods as a high nucleation rate can locally and briefly induce the formation of a significant annual source of particles. They also suggested that skatole emissions can change the chemistry and oxidative capacity of the atmosphere via their contribution to local concentrations (Ciuraru et al., 2021).

There is an urgent need for more comprehensive quantitative information on VOCs emitted by SS as aerosol precursors and their comparability at different treatment stages. This comparability would help to identify the impact of sludge treatment at WWTPs on VOC emissions and thus reducing the environmental risk of land applied sludge. The present study extensively characterized the VOC emissions upon thickening, anaerobic digestion and dewatering of SS and compared them with undigested samples. The results of this study provide an accurate inventory reference for the VOC emissions from SS samples and specific tracers for each type of treatment.

2. Materials and methods

2.1. Sample description

The SS samples were taken from a wastewater treatment plant in France at the end of the following treatment stages: thickening (undigested SS – UDSS), anaerobic digestion (digested SS – DSS) and dewatering (SS with 30% and 60% of dryness - SS 30% and SS 60%, respectively). The first step, thickening, was performed by simple decantation or flotation, or by dewatering and centrifugation, which allowed reaching a dryness of 1 to 10%. In the second step, anaerobic digestion, a biological process of sludge stabilization, the organic matter was transformed into water, CO_2 and CH_4 by anaerobic microorganisms. The last step was the dewatering by thermal drying to reach up the 30% and 60% of dryness. The main physicochemical properties of the bulk SS samples used in this study are listed in **Table S1**.The samples were stored at 4 ^{0}C before the experiments. For the experiments, we used 500 g of the solid samples (SS 30% and SS 60%), 500 mL of DSS and 1 L of UDSS.

2.2. Chamber experiments

Experiments were performed in poly(methyl methacrylate) chambers with Teflon walls in a temperature-controlled room (**Figure 1**). In this work, two chambers were used : a 0.03 m^3 (0.2 m height, 0.27 m width, 0.55 m length) and a 0.18 m^3 (0.57 m height, 0.57 m width, 0.57 m length) (Ciuraru et al., 2021). The SS was uniformly spread on a stainless steel plate with an area of 0.14 m^2 and 0.32 m^2 for the 0.03 m^3 and 0.18 m^3 chambers, respectively. The thickness of the spreaded sample was around 0.5 cm. Three replicates were performed for each sample under the same experimental conditions. During the experiments, the chamber was purged with purified dry air at a flow rate of 6 L min^{-1} and 8.6 L min^{-1} for the 0.03 m^3 and 0.18 m^3 chambers, respectively. The cycle of the dry air or its residence time in the 0.03 m^3 and 0.18 m^3 chambers was 5 min and ~20 min, respectively. The VOCs were analyzed online using a proton transfer reaction mass spectrometer. In addition, the amount of SO_2, CO_2 and H_2O emitted from the sample was continuously monitoring (Ciuraru et al., 2021). Ammonia was measured only for one experiment due to the availability of the equipment. Blank tests (i.e., without sample) were performed for both chambers.

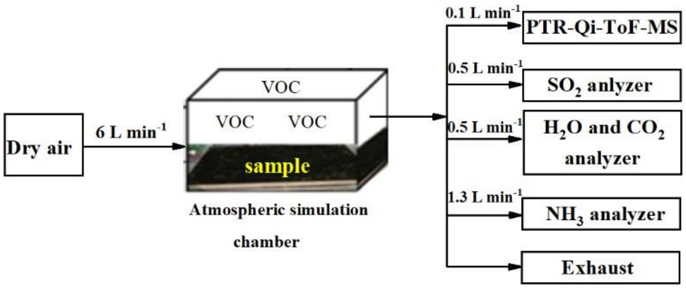

Figure 1: Schematic representation of the experimental setup. The flow rate toward each instrument is given.

2.3. PTR-Qi-ToF-MS measurements

The emitted VOCs were measured in real-time using online proton transfer reaction quadrupole-ion-guide time-of-flight mass spectrometry (PTR-Qi-ToF-MS, Ionicon Analytic GmbH). The PTR-Qi-ToF-MS instrument has been described in detail elsewhere (Abis et al., 2018; Sulzer et al., 2014). In this work, the PTR-Qi-ToF-MS was operated under the same standard conditions used by Ciuraru et al., (2021). The measurement period was set to 1s, which means that each mass spectrum of range *m/z* 10-510 was recorded every second. Raw PTR-Qi-ToF-MS data were recorded by TofDaq software (TofWerk AG, Switzerland). PTR-Qi-ToF mass spectra were processed using the PTR viewer 3.2.12 (Ionicon analytik GmbH) and the mMass software (Strohalm et al., 2010). Mass calibration was performed following the procedure described in the supplementary material, section 1.1. In PTR-Qi-ToF-MS, single charge ions are detected (M^+) and all the detected ions are protonated $(MH)^+$ due to the proton transfer reaction occurring in the drift tube.

The signal of a particular ion was monitored until it reached a steady state (usually after 3 cycles of dry air in the chamber), then 120 mass spectra were extracted from the region where the signal was stable (see, e.g., Figure S1). The same procedure was applied for the three replicates. To identify the emitted VOCs, a peak table was created for each sample using the mMass software (Strohalm et al., 2010) by selecting the peaks with a signal-to-noise ratio > 3.0 (S/N > 3.0) from the three averaged spectra. The mass range chosen for analysis was between *m/z* 31 and 400. Signals identified as instrumental background or related to water clusters such as *m/z* 37.03, *m/z* 38.03, *m/z* 39.03 and *m/z* 55.03 were excluded from the data analysis. The PTR viewer 3.2.12 software (Ionicon analytik GmbH) was subsequently used to identify the chemical molecular formula corresponding to each protonated molecular ion in the peak lists. Following this step, the averaged mass spectra were used to calculate the average mass concentration and emission flux of the emitted compounds (details in supplementary material, section 1.2).

2.4. Double bond equivalent method

The Double bond equivalent (DBE) method was used for the possible molecular structure assignments of $C_cH_hN_nO_oS_s$. DBE value was calculated for each molecule with chemical formula C_xH_y as follows:

$$DBE = c - h/2 + n/2 + 1 \qquad \textbf{(1)}$$

where c, h and n are the numbers of carbon, hydrogen and nitrogen atoms inside the molecule. DBE is independent of the number of oxygen and sulphur atoms in the molecules (Sabbah et al., 2021). It represents the level of unsaturation of the molecules that determines the total number of rings and double or triple bonds (π-bonds) involving carbon atoms (because each ring or double bond results in a loss of two hydrogen atoms) (Dobbins et al., 1998). The sub-classification of hydrocarbons with corresponding DBE value is illustrated in **Figure S4**.

2.5. Statistical analysis

Statistical analysis of the emitted VOCs was performed to identify the chemical compounds that characterize the differences between the samples and mark each treatment step. In this work, principal component analysis (PCA), a powerful statistical tool for classifying samples and revealing trends and patterns in databases, was performed with a matrix containing the integrated peak areas (variables) against the mass spectra (observations). The volcano plot was performed for identifying the chemical compounds that contribute to the diversity between two samples. Python and R software (R Studio version 4.0.3) were used to perform PCA and volcano plot, respectively. For more details on statistical analysis, see the supplementary material, section 1.3.

3. Results

3.1. Distribution of VOCs in the samples

An example of a PTR-Qi-ToF average mass spectrum for each sample is given in **Figure S3**. The molecular formula assignment of detected peaks (S/N > 3.0) was selected based on the following criteria: (i) the exact *m/z* value (ii) the theoretical isotopic distribution of the associated molecular formula (iii) the coherence of atoms contained in the compound, with respect to chemical rules such as valence of atoms, etc., and (iv) mass uncertainty of assignment (in ppm). Following this procedure, the vast majority of the detected peaks were assigned to a suitable molecular formula and only a few were unassigned (**Table 1**). The list of assigned and unassigned peaks for each sample is provided in the associated data file. PTR-Qi-ToF-MS does not allow unambiguous recognition of the compounds, such as isomers. However, for the assignments under discussion, we tentatively identified the structural formula based on the literature (Byliński et al., 2019; Fisher et al., 2017; Harrison et al., 2006; Kotowska & Isidorov, 2012; Mustafa et al., 2017; Nie et al., 2018; Rincón et al., 2019). The average mass uncertainty of the assignments was less than 20 ppm (**Table 1**). The assigned peaks corresponded to either a VOC or its ^{13}C-containing isotopic peak. The total number of assigned VOCs in UDSS, DSS, SS 30% and SS 60% were 233, 193, 192 and 186, respectively and used for further data interpretation.

Table 1: PTR-Qi-ToF-MS results for SS samples analysis. The numbers in bold correspond to the total number of assigned VOCs in each sample.

Sample name	# of detected peaks	# of assigned peaks	# of unassigned peaks	# of peaks corresponding to VOCs	# of peaks corresponding to ^{13}C isotopes	Average mass uncertainty (ppm)
UDSS	305	285	20	**233**	52	~17
DSS	287	259	28	**193**	66	~15
SS 30%	331	286	45	**192**	94	~11
SS 60%	303	275	28	**186**	89	~10

Abbreviations: UDSS- Undigested SS; DSS-Digested SS; SS 30%-SS with 30% dryness; SS 60%-SS with 60% dryness.

In this work, 380 compounds were detected and quantified in all SS samples using PTR-Qi-ToF-MS, with 81 compounds commonly found in all samples. Among SS samples, UDSS was the largest emitter (233 VOC) with 93 compounds specific for this sample. The number of compounds emitted exclusively from DSS, SS 30% and SS 60% was 30, 22 and 32, respectively (**Figure 2**). These compounds may hence be specific tracers for each type of SS emissions (listed in **Table S2**).

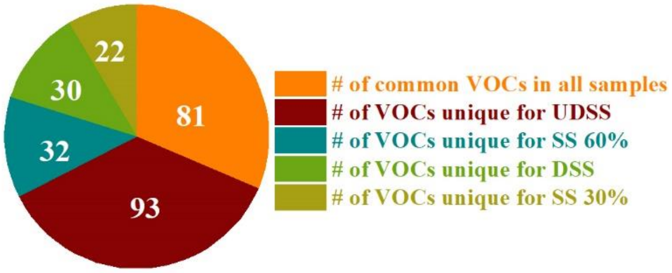

Figure 2: Distribution of assigned VOCs by their number (#) among SS samples. Abbreviations: UDSS-Undigested SS; DSS-Digested SS; SS 30% -SS 30% with dryness; and SS 60% -SS with 60% dryness.

The assigned VOCs were classified into the following chemical groups: Hydrocarbons (*HC*), Oxygenated compounds (*O-compounds*), Sulphuric compounds (*S-compounds*), Nitrogenated compounds (*N-compounds*) and Other compounds (*Others*: chemical compounds containing more than one heteroatom in their molecular formula "e.g. C_3H_7NO, $C_3H_7NO_2$, C_5H_6OS, $C_9H_{17}NS$, C_5H_7NOS, etc"). The number of compounds assigned to each chemical group is shown in **Figure 3**. The speciation of VOCs varied among the analyzed samples. For instance, the DSS showed more HC and fewer O-compounds and N-compounds compared to UDSS. The dewatering step increased the number of HC; about half of the assigned molecular formulas in SS 30% and SS 60% being HC.

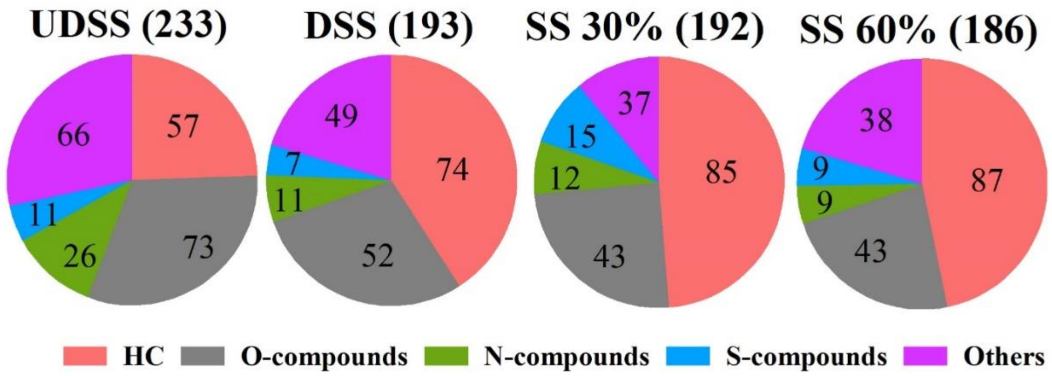

Figure 3: The number of compounds assigned for each chemical group in each sample. The total number of assigned VOCs is given in parentheses. Abbreviations: UDSS-Undigested SS; DSS-Digested SS; SS 30%-SS with 30% dryness; and SS 60%-SS with 60% dryness.

3.2. Classification of HC by the DBE method

DBE analysis was performed on the HC emitted from all samples in this work. The obtained DBE values ranged from 1 to 8 with six sub-classes of HC: aliphatic (linear alkenes or alkynes), alicyclic (cycloalkanes, cycloalkenes, or cycloalkynes), aromatic (benzene and its derivatives), terpenes and polycyclic aromatic hydrocarbons (PAHs). In this work, 95 compounds were assigned as HC in all samples. The DBE value of each HC was calculated (listed in **Table S3**). The DBE versus the C number of all assigned HC is illustrated in **Figure 4**. DBE value increased with the decreasing number of H atoms in the molecular formula (from C_nH_{2n} to C_nH_{2n-12}). A homologous series of compounds with different degrees of alkylation (substitution of peripheral H by CH_3 groups leading to no change in the DBE) had constant DBE value but different C numbers. For each series, the proposed general molecular formula and the corresponding DBE value is indicated in **Figure 4**. The emitted HC were either cyclic, include π-bonds or both (see **Figure S4**). Several aliphatic and alicyclic compounds with $1 \leq \text{DBE} \leq 3$ were found. Such compounds might be alkenes, alkynes, dienes, cycloalkanes, cycloalkenes, cycloalkynes or polyenes. Peaks at m/z 69.06, 137.13 and 205.19 were assigned to $C_5H_8H^+$, $C_{10}H_{16}H^+$ and $C_{15}H_{24}H^+$, respectively and identified as terpenes (situated on the dashed line in **Figure 4**). In this study, 47 compounds of the emitted HC were aromatic with $4 \leq \text{DBE} \leq 8$.

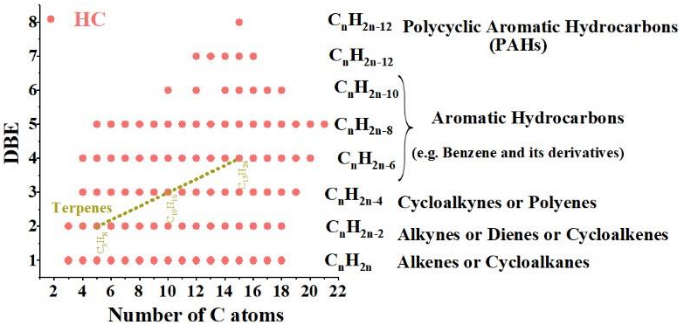

Figure 4: DBE vs. the number of carbon (C) atoms plot for the HC emitted from all SS samples. The proposed molecular formula of the compounds having the same DBE and differing by one carbon number is shown to the right with the possible sub-class(s) name. Compounds identified as terpenes are highlighted by a dashed line on the diagram.

Figure 5 (a) shows the bar graph representation of the HC sub-classes identified using DBE analysis. The total emission fluxes of HC sub-classes are displayed. Aromatic compounds dominated the emissions among the HC from UDSS (31.96 ± 0.55 µg m^{-2} min^{-1}). The emission of aromatic compounds was as follows: UDSS > SS 60% > SS 30% > DSS. Compounds with DBE = 2 were emitted dominantly from SS 60% (76.58 ± 10.77 µg m^{-2} min^{-1}). SS 30% was characterized by the high emissions of HC with DBE = 3 (49.68 ± 11.59 µg m^{-2} min^{-1}). Terpenes showed the highest emissions from SS 60% (24.37 ± 3.74 µg m^{-2} min^{-1}). Their emission flux was about the half in SS 30% (12.73 ± 3.17 µg m^{-2} min^{-1}) and lower in DSS and UDSS (2.53 ± 1.34 and 0.55

± 0.04 µg m^{-2} min^{-1}, respectively). In **Figure 5 (b)**, the total emission flux of VOCs as a function of the dry matter content of the sample is represented, the former decreased as the dry matter of SS sample decreased.

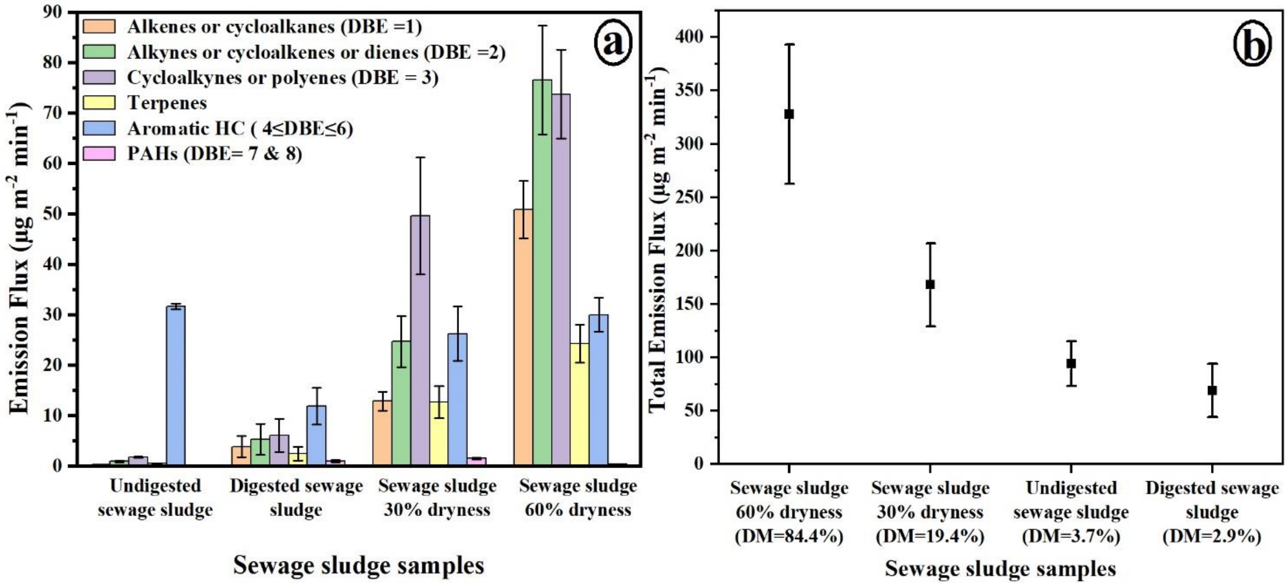

Figure 5: (a) Classification of HC detected in each SS sample by using the DBE method. The total emission flux of HC sub-classes in each sample is illustrated. The error bars shown in the figure represent the standard deviation of the average emission flux obtained from the three replicates of each sample. (b) Total emission flux of HC emitted from each SS versus the dry matter of the sample.

3.3. Emission characteristics of VOCs

The mass concentration and emission flux of assigned and unassigned peaks (unknown compounds) are given in the associated data file. The mass concentration of the assigned VOC was estimated based on their mixing ratio and considering the molecular weight of the compound. The total mass concentration of each chemical group was calculated by summing the concentrations of the individual compounds in each chemical group. The chemical groups contributed to a different extent to the total concentration of VOCs as shown in **Figure 6**. HC was the maximum concentrated chemical group in all samples. The second most abundant group in SS 60% and DSS was O-compounds (1425 ± 739 and 511 ± 171 µg m^{-3}, respectively). In contrast, in UDSS and SS 30%, S-compounds represented the second most abundant group (1038 ± 448 and 372 ± 131 µg m^{-3}, respectively). The concentration of other compounds containing more than one heteroatom in their molecular formulas was the lowest in all samples (less than 300 µg m^{-3}) and their contribution to total concentration was less than 20%.

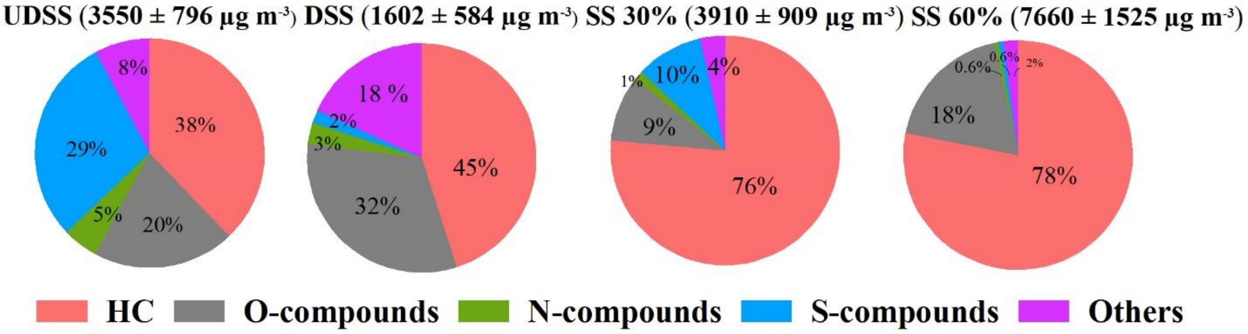

Figure 6: Percentage contribution of each chemical group to the total mass concentration of assigned VOCs. The total concentration of VOCs obtained in each sample is given in parenthesis. Abbreviations: UDSS-Undigested SS; DSS-Digested SS; SS 30%-SS with 30% dryness; and SS 60%-SS with 60% dryness.

Table 2 shows the emission fluxes of VOCs and the total emission flux of each chemical group. The highest VOC emission fluxes were observed in the SS 60% (328 ± 65 µg m^{-2} min^{-1}), followed by the SS 30%, UDSS and DSS samples with 168 ± 39, 94 ± 21 and 69 ± 25 µg m^{-2} min^{-1}, respectively. Compounds having the highest emission flux in all samples were HC. The emission flux of O-compounds was as follows: SS 60% > SS 30% > DSS > UDSS. The compounds designated as others were highly emitted from DSS (12 ± 3 µg m^{-2} min^{-1}), compared to the other samples.

Table 2: Total emission flux of each chemical group found in SS samples. The standard deviation of the average emission flux obtained from the three replicates of each sample is displayed.

Sample name	Total emission flux (µg m^{-2} min^{-1})	Total emission flux of each chemical group (µg m^{-2} min^{-1})				
		HC	O-compounds	N-compounds	S-compounds	Other compounds
UDSS	94 ± 21	36 ± 1	19 ± 6	4.77 ± 1.47	28 ± 12	7.37 ± 0.59
DSS	69 ± 25	31 ± 14	22 ± 7	2.08 ± 0.62	1.2 ± 0.3	12.48 ± 3.04
SS 30%	168 ± 39	128 ± 27	16 ± 5	2.12 ± 0.35	16 ± 6	6.01 ± 0.65
SS 60%	328 ± 65	256 ± 32	61 ± 32	1.87 ± 0.39	2.0 ± 0.2	7.06 ± 0.77

Abbreviations: UDSS-Undigested SS; DSS-Digested SS; SS 30%-SS with 30% dryness; and SS 60%-SS with 60% dryness.

The emission flux of each sulphuric and nitrogenated compound is illustrated in **Figure 7**. Comparable emission fluxes of N-compounds were found in DSS, SS 30% and SS 60% while they showed the highest in UDSS (4.77 ± 1.47 µg m^{-2} min^{-1}). This was explained by a high contribution of an ion corresponding to *m/z* 132.08 and assigned as $C_9H_9NH^+$, with emission flux 2 ± 1 µg m^{-2} min^{-1}. The highest emission fluxes of S-compounds were observed in UDSS (28 ± 12 µg m^{-2} min^{-1}); this was attributed to strong emissions of CH_4SH^+, $C_2H_6SH^+$ and $C_2H_6S_2H^+$.

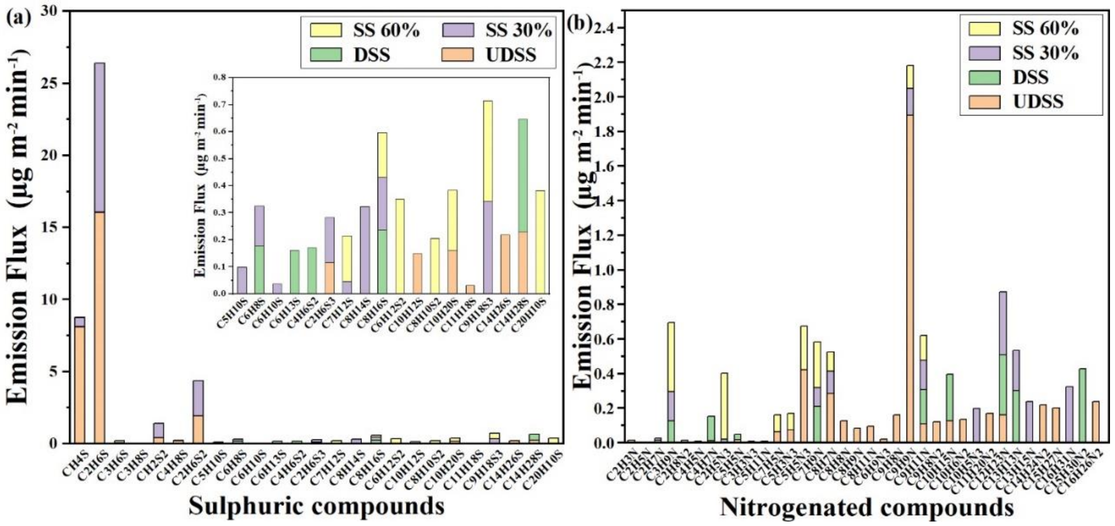

Figure 7: (a) Emission fluxes of sulphuric compounds emitted from SS samples. The enlarged section to the right shows sulphuric compounds with fluxes less than 1 µg m^{-2} min^{-1}. (b) Emission fluxes of nitrogenated compounds emitted from SS samples. Abbreviations: UDSS-Undigested SS; DSS-Digested SS; SS 30%-SS with 30% dryness; SS 60%-SS with 60% dryness.

3.4. Comparison between the samples

Table 3 summarizes the main characteristics of each SS sample. To better uncover the similarities and differences between samples, PCA was performed based on the samples' mass spectra. The first three principal components, PC1, PC2 and PC3, comprised 71.30%, 17.17% and 9%, respectively of data variation. Together they accounted for 97% of the total variance and were enough to discriminate between the samples. Thus, PC1, PC2 and PC3 were considered for data interpretation.

Table 3: Characteristics of the analyzed SS samples. The total number of VOCs, total mass concentration, total emission flux as well as the percentage of dry matter in each sample are displayed. The uncertainty in the calculation is given next to each value.

Sample name	Number of assigned VOCs	Total mass concentration of assigned VOCs ($\mu g\ m^{-3}$)	Total emission flux of assigned VOCs ($\mu g\ m^{-2}\ min^{-1}$)	Dry matter (%)
UDSS	233	3550 ± 796	94 ± 21	3.7
DSS	193	1602 ± 584	69 ± 25	2.9
SS 30%	192	3910 ± 909	168 ± 39	19.4
SS 60%	186	7660 ± 1525	328 ± 65	84.4

Abbreviations: UDSS-Undigested SS; DSS-Digested SS; SS 30%-SS with 30% dryness; SS 60%-SS with 60% dryness.

Figure 8 shows that positive PC2 separated DSS from the other samples. The corresponding loading plot suggested that DSS was highly influenced by N&O-compounds and oxygenated VOC (OVOC) emissions. The negative value of PC2 separated UDSS from the other samples. The loading plot (Figure S5) showed that UDSS was characterized by S-compounds. Thiazole compounds such as $C_3H_3NSH^+$, $C_5H_7NSH^+$, $C_6H_7NSH^+$, $C_{10}H_7NSH^+$ and $C_8H_7NS_2H^+$ showed high contribution in UDSS. Dewatered samples (SS 30% and SS 60%) were separated from UDSS and DSS by PC1. Based on the loading plots (Figure S5), SS 60% and SS 30% were associated with HC, O-compounds and S-compounds. PC3 (~9%) allowed for better discrimination between SS 60% and SS 30% than PC1 and PC2. From PC3 loading plot, SS 60% received a high contribution from OVOCs while SS 30% was dominated by S-compounds.

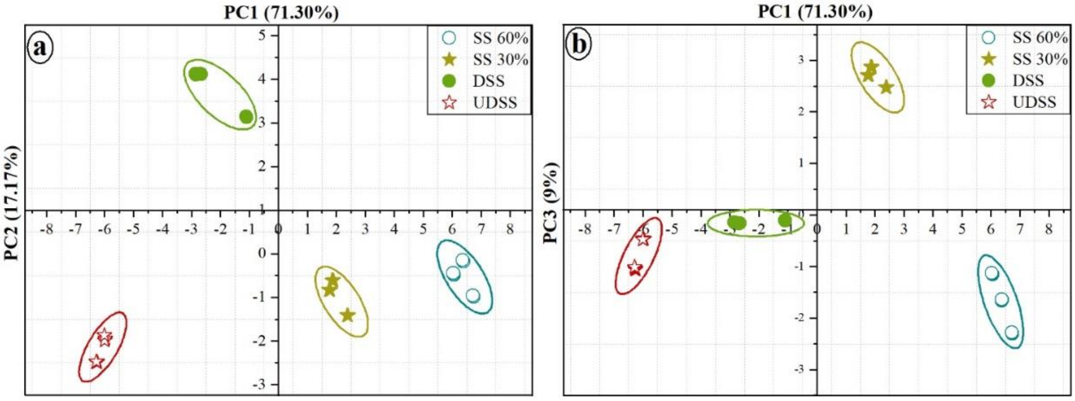

Figure 8: Score plots of (a) PC2 vs. PC1 and (b) PC3 vs. PC1 for SS samples. The percentage contribution of each PC to total variance is given in parenthesis. The ellipses highlight data points coming from the same sample and are added for visual purposes only. Abbreviations: UDSS-Undigested SS; DSS-Digested SS, SS 30%-SS with 30% dryness; and SS 60%-SS with 60% dryness.

In order to determine how the treatment stage affects the profile of VOC emissions, the samples collected at consecutive treatment steps were compared: DSS versus UDSS to identify the impact of anaerobic digestion and SS 30% and SS 60% versus DSS to uncover the impact of the dewatering step. The results are illustrated in **Figure 9**. The assignments of detected ions having high statistical significance and fold change > +1 (red circles) or < -1 (green circles) are provided in Table S4. UDSS was characterized by S-compounds while DSS was associated with OVOCs (**Figure 9, a**). This supported the PCA results. In addition, three compounds showed high significance and fold change in UDSS compared with DSS: $C_7H_8H^+$, $C_9H_9NH^+$ and $C_7H_8OH^+$. The comparison between dewatered sludge and DSS is illustrated in **Figure 9 (b and c)**. SS 30% was dominated by S-compounds and HC compared with DSS while SS 60% was influenced by O-compounds and HC. The dewatered samples were also compared to determine the impact of dry matter on VOC emissions (**Figure 9, d**). The results illustrated that SS 30% was characterized by high S-compound emissions while SS 60% was influenced by OVOCs.

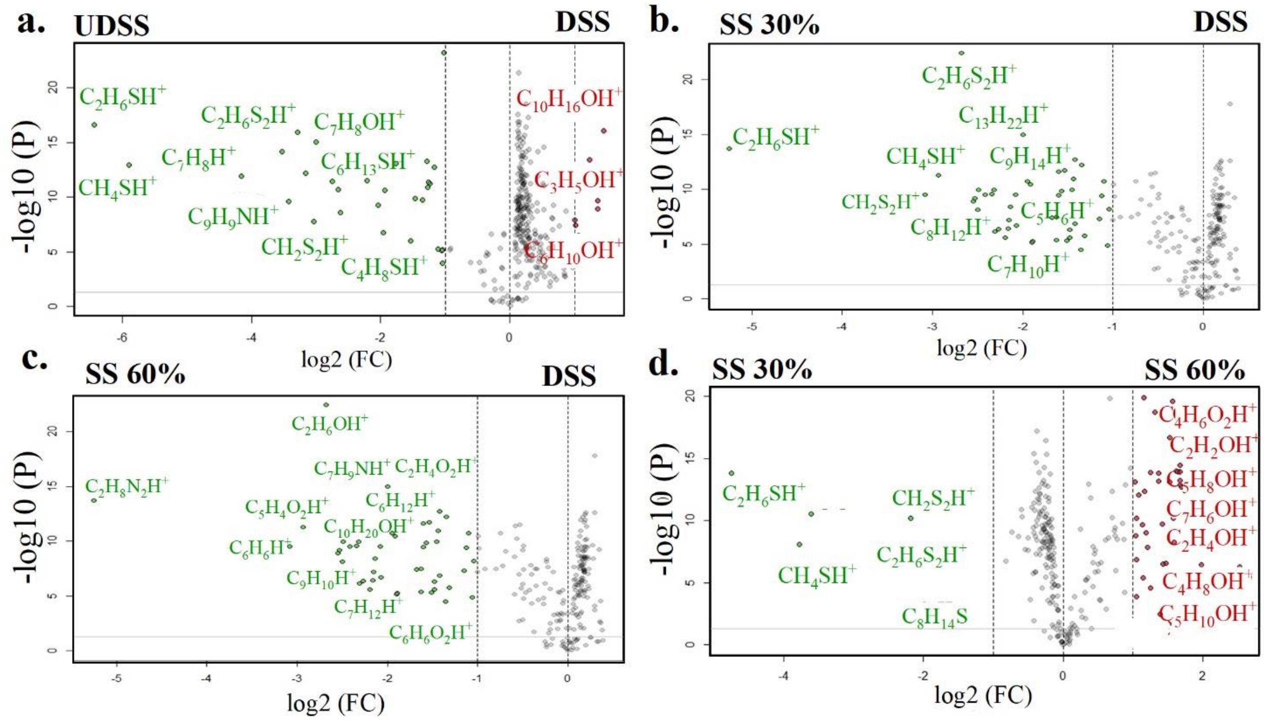

Figure 9: Volcano plots showing the «differential expression» of detected chemical compounds in (a) UDSS and DSS (b) SS 30% and DSS (c) SS 60% and DSS and (d) SS 30% and SS 60%. Grey points correspond to chemical species that have either a low statistical significance or fold change, and thus do not contribute to the separation between the two samples. The chemical assignments of protonated ions ($VOCH^+$) are shown. Red circles represent the significant mass peaks with fold change > +1 and green circles represent the significant peaks with fold change < -1. Abbreviations: UDSS-Undigested SS; DSS-Digested SS; SS 30%-SS with 30% dryness; and SS 60%-SS with 60% dryness.

4. Discussion

The assigned VOCs were classified into five major chemical groups (1) HC, (2) S-compounds, (3) O-compounds, (4) N-compounds and (5) other compounds. In the following sections, the results of this study were discussed by the chemical group and based on comparison with the literature of the subject.

4.1. Hydrocarbons

Compounds assigned as HC had the highest emission fluxes in all samples. PTR-Qi-ToF-MS helps to determine the molecular formula of a compound but not its chemical structure. Such identification is possible by combining complementary analytical techniques, such as gas chromatography with mass spectrometry (GC-MS) (Ni et al., 2012). In this work, the DBE method was applied to classify the assigned HC into smaller sub-classes of compounds with the same DBE value but different degree of alkylation. To our knowledge, DBE analysis was performed here for the first time on PTR-Qi-ToF-MS data. In this study, no linear alkanes with DBE = 0 were found. This could be explained by their lower proton affinity than water and therefore the proton transfer reaction with H_3O^+ is not an effective mechanism for their detection (Amador-Muñoz et al., 2016). However, this does not exclude their emissions from samples as several linear alkanes were detected in SS using GC-MS (Fisher et al., 2017; Kotowska & Isidorov, 2012; Nie et al., 2018). Mustafa et al., (2017) related the presence of alkanes to the decomposition of organic matter in SS. The SS 60% with the highest dry matter content showed the maximum emission fluxes of HC compared to the other samples.

4.1.1. Aliphatic and alicyclic compounds

A group of 16 aliphatic compounds (C_3 - C_{18}) with DBE = 1 were either alkenes or cycloalkanes and found in all samples (**Figure 4**). SS 60% showed the highest emission flux (50.93 ± 5.64 µg m^{-2} min^{-1}) compared to 12.93 ± 1.83, 3.95 ± 2.08, 0.35 ± 0.03 µg m^{-2} min^{-1} from SS 30%, DSS and UDSS, respectively. This variation was attributed to a compound detected at *m/z* 57.06 and assigned as $C_4H_8H^+$, comprising 34% of the total aliphatic compound emission flux in SS 60%. Other aliphatic compounds with high emission fluxes in SS 60%

were $C_3H_6H^+$, $C_5H_{10}H^+$ and $C_6H_{12}H^+$. Compounds assigned as $C_8H_{16}H^+$ and $C_9H_{18}H^+$ were identified as ethyl cyclohexane and propyl cyclohexane, respectively, in anaerobically stabilized biosolids subjected to aging by Fisher et al., (2017). These compounds were highly emitted from SS 60% compared to the other samples. Compounds such as $C_{10}H_{20}H^+$, $C_{11}H_{22}H^+$ and $C_{12}H_{24}H^+$ identified as pentyl cyclopentane, pentyl cyclohexane and hexyl cyclohexane, respectively, were found in SS formed during municipal WWTPs (Kotowska & Isidorov, 2012).

Fifteen compounds with DBE = 2 that were alkynes, dienes or cycloalkenes were found in all samples. These compounds showed high emissions from SS 60% (76.58 ± 10.77 $\mu g\ m^{-2}\ min^{-1}$), this was attributed to the high emissions of compounds $C_3H_4H^+$, $C_7H_{12}H^+$, $C_4H_6H^+$, $C_6H_{10}H^+$, $C_8H_{14}H^+$ and $C_9H_{16}H^+$, contributing to 85% of the total emissions of compounds with DBE = 2 from SS 60%. $C_8H_{14}H^+$ and $C_9H_{16}H^+$ were identified as 1-methyl-2-methylenecyclohexane and methyl-(methylethylidene) cyclohexane, respectively (Fisher et al., 2017). 15 compounds having DBE = 3 (cycloalkynes or polyenes) with the highest emissions from SS 60% of 73.81 ± 8.83 $\mu g\ m^{-2}\ min^{-1}$ were also detected. Therefore, SS 60% showed the maximum emission flux of aliphatic or alicyclic compounds compared to the other three samples.

4.1.2. Terpenes

Three ions at *m/z* 69.07, 137.13 and 205.19 assigned as $C_5H_8H^+$, $C_{10}H_{16}H^+$ and $C_{15}H_{24}H^+$, respectively were emitted from all sludge samples. These compounds were identified as terpenes, a class of compounds with the formula $(C_5H_8)_n$, which are typical unsaturated HC and frequently attributed to biogenic origin. SS 60% showed the highest emission flux of terpenes (24.37 ± 3.73 $\mu g\ m^{-2}\ min^{-1}$), **Figure 5**. Terpenes such as isoprene (C_5H_8), monoterpenes ($C_{10}H_{16}$) and sesquiterpenes ($C_{15}H_{24}$) were identified in SS samples (Byliński et al., 2019; Fisher et al., 2017; Nie et al., 2018; Kotowska & Isidorov, 2012). The use of fragrant aromatic detergents and green waste were considered potential sources of terpenes and HC (Mustafa et al., 2017). Several studies showed terpenes and aromatic compounds emission from SS samples and composting processes (Schiavon et al., 2017; Tsai et al., 2008; Zhang et al., 2013; Zhu et al., 2016b). In this work, terpenes contributed slightly to the total mass concentration of VOCs, ranging from 0.58% - 7.42% for different samples. This consisted with the results reported by Rincón et al., (2019), where terpenes emission varied from 0.07% - 21% of the total mass concentration from samples characterized by a reduced content of vegetal materials, such as pig slurry, turkey manure and solid fraction of anaerobically digested pig slurry and SS. High terpenes emission (21-90%) was observed from samples with lignocellulosic content such as biowastes and green wastes (Rincón et al., 2019). The decaying process of vegetable material, bacterial degradation of lignin and cellulose and aerobic degradation of organic matter resulted in high terpenes emission (Eitzer, 1995; Moreno et al., 2014; Schiavon et al., 2017). Their organic matrices were mainly constituted of fruits, vegetables, leaves, brush and food waste (Eitzer, 1995). $C_{10}H_{16}H^+$ was identified as limonene (cyclic monoterpenes) in SS at different processing units of the composting plant (dewatered room, dewatered sludge, blender room, fermentation workshop and product) with measured concentrations of 5.2 ± 0.5, 23.0 ± 4.4, 290.1 ± 109.1, 252.6 ± 120.9, and 27.9 ± 6.2 $\mu g\ m^{-3}$, respectively (Nie et al., 2018). In this work, $C_{10}H_{16}H^+$ was emitted from all SS samples. Concentrations measured at SS 60% and SS 30% gas phase emissions were 28.29 ± 13.09 and 6.83 ± 0.52 $\mu g\ m^{-3}$, respectively. They were relatively higher than the concentrations of dewatered sludge measured by Nie et al., (2018). The composition of composting materials and the deodorants used in the composting plant were considered the main origin of limonene in the composting plant (Nie et al., 2018).

4.1.3. Aromatic compounds

Most of the detected HC (37 compounds) were aromatic with $4 \leq DBE \leq 6$. Those compounds had at least one aromatic ring and suffered from extensive dehydrogenation as revealed by the group of peaks illustrated in **Figure 4**. In contrast to aliphatic and alicyclic compounds, aromatic compounds showed the highest emission flux in UDSS (31.7 ± 0.55 $\mu g\ m^{-2}\ min^{-1}$) followed by SS 60%, SS 30% and DSS. The high emissions of aromatic compounds from UDSS were attributed to a compound $C_7H_8H^+$ (*m/z* 93.07) with a concentration of 981 ± 5 $\mu g\ m^{-3}$. It constituted 82% of the total aromatic compounds emission from UDSS. $C_7H_8H^+$ was identified as toluene in SS (Byliński et al., 2019; Fisher et al., 2017; Harrison et al., 2006; Kotowska & Isidorov, 2012; Nie et al., 2018). Toluene dominated the aromatic compounds emitted from SS analyzed at different processing units of the composting plant (dewatered room, dewatered sludge, blender room, fermentation workshop and product) (Nie et al., 2019). The measured concentrations of toluene were 262 ± 116, 118 ± 12, and 57 ± 15 $\mu g\ m^{-3}$ in the fermentation workshop, dewatered sludge and dewatered room, respectively (Nie et al., 2019). The amount of toluene emitted from UDSS exceeded the values reported by Byliński et al., (2019). The authors showed a fluctuation in toluene mixing ratios between 1 ppb and 27 ppb during the measurement period of samples collected from WWTPs in Poland. Toluene is widely used in domestic and industrial environments and it can be easily biodegraded under aerobic conditions (Wilson et al., 1994). This might explain the high emissions of toluene from UDSS. In addition, the very high concentration of toluene might be associated with a specific industrial discharge to these WWTPs. Moreover, Chiriac et al., (2011) reported that spices and other household products are the main sources of toluene.

Other compounds such as $C_{10}H_{12}H^+$, $C_{10}H_{14}H^+$, $C_{15}H_{22}H^+$, $C_{16}H_{26}H^+$ and $C_{17}H_{28}H^+$ were emitted from all the sludge samples. Such compounds were reported in SS samples (Byliński et al., 2019; Fisher et al., 2017; Kotowska & Isidorov, 2012; Nie et al., 2018; Nie et al., 2019, Rincón et al., 2019). The tentative chemical identification of these compounds based on literature is given in the associated data file. Benzene and its derivatives (e.g. C_8H_{10} and C_9H_{12}), identified in SS using off-line GC-MS measurements (Fisher et al., 2017; Kotowska & Isidorov, 2012), were found in our samples. Toluene, benzene, ethylbenzene and xylene (BTEX) have been widely found in the gas emissions from SS (Wilson et al., 1994; Zhu et al., 2016b). BTEX and $C_9H_{12}H^+$, found in all our samples, were frequently attributed to anthropogenic sources and reported inside farm buildings (Ciganek & Neca, 2008; Kammer et al., 2020). BTEX was produced in large quantities and is extensively employed in a broad spectrum of industrial applications, primarily as solvents, components of gasoline, and in the production of other chemicals. For example, toluene is present in many consumer products, including household aerosols, paints, varnishes, adhesives and glues (Mrowiec et al., 2005). Five PAHs with $7 \leq \text{DBE} \leq 8$ showed the lowest emission fluxes among all HC. Among all PAHs, only $C_{15}H_{18}H^+$ (m/z 199.15) was identified in SS samples as 1,6-dimethyl-4-(1-metyhylethyl) naphthalene (Kotowska & Isidorov, 2012).

4.2. Volatile organic sulphur compounds (VOSCs)

Sulphur in the sludge mainly exists in the form of organic sulphur or sulphur oxides, such as thioamino acids, sulfonic acids and sulphate (Xue et al., 2021). The emission of sulphuric compounds could be associated with the biodegradation of sulphur-containing amino acids such as methionine and cysteine (Higgins et al., 2003; Mackie et al., 1998; Schiavon et al., 2017). This conversion leads to the formation of volatile organic sulphur compounds (VOSCs) and H_2S under anaerobic conditions (Du & Parker, 2012). In this work, twenty-five detected peaks were assigned as VOSCs. UDSS and SS 30% showed higher emission fluxes of VOSCs compared to other samples (**Table 2**).

A compound detected at m/z 63.02 and assigned as $C_2H_6SH^+$ was emitted from all samples except SS 60%. It was the most abundant VOSC in UDSS (604 ± 311 µg m^{-3}) and SS 30% (241 ± 109 µg m^{-3}). CH_4SH^+ was emitted from all samples. It was the second most abundant VOSCs in UDSS (304 ± 112 µg m^{-3}). CH_4SH^+ was identified as methanethiol (or mercaptan) in SS (Byliński et al., 2019; Fisher et al., 2017; Nie et al., 2018). $C_2H_6SH^+$, identified as dimethyl sulphide (DMS), was emitted from UDSS, DSS and SS 30%. $CH_2S_2H^+$ and $C_2H_6S_2H^+$ were emitted from UDSS and SS 30%. $C_2H_6S_2H^+$, identified as dimethyl disulphide (DMDS) in SS (Byliński et al., 2019; Fisher et al., 2017), was measured in this work with an average concentration of 72 ± 18 and 57 ± 12 µg m^{-3} in UDSS and SS 30%, respectively. It was around half the average concentration measured by Nie et al., (2019); 144 ± 37 µg m^{-3}. This difference might be related to the high photochemical reactivity of DMDS, thus it would be expected that most of DMDS could be lost before the sample introduced into the chamber. In addition, DMDS was found to be the dominant pollutant in other studies (Ding et al., 2015; Duan et al., 2014). $C_2H_6S_3H^+$ and $CH_4O_3SH^+$, identified as dimethyl trisulphide (DMTS) and methane sulphonic acid, respectively in SS (Fisher et al., 2017), were emitted from UDSS and SS 30%. Yao et al., (2019) reported the dominance of methanethiol and DMS among the sulphuric compounds in municipal solid waste disposal plants. In the current study, CH_4SH^+ (methanethiol), $C_2H_6SH^+$ (DMS), $CH_2S_2H^+$ and $C_2H_6S_2H^+$ (DMDS) constituted 96% and 91% of total VOSC emission flux in UDSS and SS 30%, respectively. VOSCs (e.g. methanethiol, DMS and DMDS) have been selected as core indicators for odour nuisance in SS (Byliński et al., 2019; Fisher et al., 2017; Nie et al., 2018). This might explain the intense odour of UDSS sample as those compounds were highly emitted from this sample.

4.3. Oxygenated volatile organic compounds (OVOCs)

In this work, 104 VOCs were assigned as OVOCs. Their highest emission flux was observed in SS 60%, followed by DSS, UDSS and SS 30% (**Table 2**). Among OVOCs, 59% of compounds contained one O atom, 30% contained two O atoms and 6% and 5% included three and four O atoms, respectively. This indicated that the emitted OVOCs were not highly oxidized. Accordingly, OVOCs were classified into different groups based on the number of O atoms in the molecular formula. The first group of compounds having the molecular formula $C_nH_{2n}O$ and characterized by CH_2 repetitive unit was tentatively identified as carbonyl compounds (i.e. aldehydes or ketones). The second group included compounds with molecular formula $C_nH_{2n-2}O$ and was either unsaturated or cyclic carbonyl compounds. The last group of compounds ($C_nH_{2n}O_2$) was either carboxylic acids or esters.

A compound detected at *m/z* 45.03 and assigned as $C_2H_4OH^+$ was emitted from all samples with high emissions from SS 60% (14.87 ± 8.35 µg m^{-2} min^{-1}). This compound was identified in stabilized dewatered sludge and anaerobically stabilized biosolids as acetaldehyde (Byliński et al., 2019; Fisher et al., 2017). Two compounds at *m/z* 33.03 and *m/z* 47.05 were assigned as CH_4OH^+ and $C_2H_6OH^+$, respectively. CH_4OH^+ was emitted from all samples except SS 30%. It showed a relatively high emission flux from SS 60% (7.42 ± 4.19 µg m^{-2} min^{-1}) compared with DSS and SS 60%. $C_2H_6OH^+$ was only emitted from DSS and SS 60%. CH_4OH^+ and $C_2H_6OH^+$ were identified in SS as methanol and ethanol, respectively (Byliński et al., 2019; Fisher et al., 2017; Kotowska & Isidorov, 2012). Methanol and ethanol were the end products of various organic metabolic processes (Kotowska & Isidorov, 2012). Methanol was found in green waste as the most relevant alcohol and it was an intermediate product of microbial metabolism of wood and plants (Rincón et al., 2019). $C_3H_6OH^+$ (*m/z* 59.05) was emitted from all samples and identified as acetone. It was reported to be the most abundant OVOC in SS samples (Byliński et al., 2019; Fisher et al., 2017; Kotowska & Isidorov, 2012; Nie et al., 2018). Another compound $C_4H_8OH^+$ (*m/z* 73.06) was emitted from all our samples and identified as 2-butanone (Byliński et al., 2019; Fisher et al., 2017; Harrison et al., 2006; Nie et al., 2018). The concentrations of $C_4H_8OH^+$ in this work were comparable with that measured in SS analyzed at different processing units of the composting plant (< 200 µg m^{-3})(Nie et al., 2019). $C_2H_4O_2H^+$ (*m/z* 61.03) was emitted from all samples and it was identified as acetic acid in SS samples (Byliński et al., 2019; Fisher et al., 2017). Acetic acid was one of the main VOC contributors in composting gas emissions of SS and it could be associated with anoxic conditions and partial anaerobic organic matter degradation (Byliński et al., 2019). The emission of OVOCs is primarily caused by the breakdown of lipids and proteins during composting (Mackie et al., 1998). In addition, the decomposition by-products of easily degradable organic matter in waste were the potential sources of OVOCs (Scaglia et al., 2011). In the current study, the highest OVOC emission fluxes were found in SS 60%, collected at the last step of SS treatment. Our findings agreed with other studies, where the OVOCs dominated the emissions during waste maturation and from sludge obtained at the last steps of treatment (Davoli et al., 2003; Nie et al., 2019).

Three compounds detected at *m/z* 95.05, 123.08 and 109.06 and assigned as $C_6H_6OH^+$, $C_8H_{10}OH^+$ and $C_7H_8OH^+$, respectively were emitted from UDSS. $C_7H_8OH^+$ was identified as 3-methylphenol (Harrison et al., 2006; Kotowska & Isidorov, 2012) or cresol (Mackie et al., 1998). $C_6H_6OH^+$ and $C_8H_{10}OH^+$ were identified as phenol and 2-ethylphenol, respectively (Mackie et al., 1998). Cresol, phenol and 2-ethylphenol were known to be associated with urea and feces as a result of the metabolic degradation of aromatic amino acid tyrosine (Chen et al., 2004; Mackie et al., 1998). Thus, the three compounds were of identical biological origin. This could explain the exclusive emissions of $C_6H_6OH^+$ along with $C_7H_8OH^+$ and $C_8H_{10}OH^+$ from UDSS. Therefore, these compounds could be considered as emission tracers for UDSS.

4.4. Nitrogenated organic compounds

Thirty-six nitrogenated compounds were found in this study (**Figure 7, b**). Among them, only one compound was emitted from all samples ($C_9H_{11}NH^+$, *m/z* 134.10) and 26 compounds were emitted only from UDSS. The maximum emission fluxes of N-compounds was observed in UDSS (4.77 ± 1.47 µg m^{-2} min^{-1}) and the other samples showed almost the same levels (**Table 2**). A compound detected at *m/z* 60.08 and assigned as $C_3H_9NH^+$ was emitted from all samples except UDSS. This compound showed the maximum emission flux in SS 60% at 0.398 ± 0.215 µg m^{-2} min^{-1}. $C_3H_9NH^+$ was identified in SS samples as trimethyl amine (TMA) by TD-GC-MS (Fisher et al., 2017; Kotowska & Isidorov, 2012). Rosenfeld et al., (2001) reported that TMA was produced from the biological degradation of proteins and emitted from land application of dewatered sludge. This consisted with our results as TMA showed higher emissions from SS 60% compared to SS 30% and DSS. The presence of TMA in sludge subjected to dewatering might be due to the degradation of polymers used in this process as suggested by Fisher et al., (2017). In addition, animal excrements such as feces and urine released large amounts of TMA into the atmosphere (Sintermann et al., 2014).

Several N-compounds were tentatively identified as small amines such as $C_2H_5NH^+$, $C_2H_7NH^+$ and $C_3H_9NH^+$. Others were associated with one or more aromatic rings and belong to indoles, pyridine, quinolone, etc (e.g. $C_7H_9NH^+$, $C_9H_{11}NH^+$, $C_5H_5NH^+$ and $C_{13}H_{13}NH^+$). The compounds $C_2H_3NH^+$, $C_5H_5NH^+$ and $C_7H_5NH^+$ were identified in SS as acetonitrile, pyridine and benzonitrile, respectively (Byliński, et al., 2019; Fisher et al., 2017). Two volatile organic aromatic compounds detected at *m/z* 132.08 and 118.06 and assigned as $C_9H_9NH^+$ and $C_8H_7NH^+$, respectively were emitted from all samples except DSS. The highest emission flux of these two compounds was in UDSS. $C_8H_7NH^+$ and $C_9H_9NH^+$ were identified as indole and skatole (3-mehyl indole), respectively (Ciuraru et al., 2021; Gebicki et al., 2016; Mackie et al., 1998; Ni et al., 2012). Indole and skatole were the major end-products of tryptophan metabolism and released onto manure by bacterial degradation (Mackie et al., 1998). They have been selected as major malodorous compounds that contributed to the strong odour nuisance in animal waste facilities and SS treatment plants (Gebicki et al., 2016; Ni et al., 2012).

4.5. Other gas phase emissions

Several compounds containing more than one heteroatom in their molecular formula were found in this work. Among these, significant concentrations of compounds containing both N and O atoms (N&O-compounds) were detected. The emission fluxes of N&O-compounds were the highest in DSS (11.54 ± 2.85 $\mu g\ m^{-2}\ min^{-1}$) followed by SS 60% (5.63 ± 0.68 $\mu g\ m^{-2}\ min^{-1}$), UDSS (5.60 ± 0.4 $\mu g\ m^{-2}\ min^{-1}$) and SS 30% (5.48 ± 0.59 $\mu g\ m^{-2}\ min^{-1}$). $C_6H_{11}NOH^+$ (*m/z* 114.09) was identified as caprolactam which is a cyclic amide of caproic acid (Kotowska & Isidorov, 2012). It was emitted from DSS only with a concentration of 3.71 ± 0.89 $\mu g\ m^{-3}$. $C_{12}H_{15}N_3O_6H^+$ was emitted from all the samples with emission flux $< 0.5\ \mu g\ m^{-2}\ min^{-1}$. It was reported as one of SS's organic chemicals and identified as a fragrance material (Harrison et al., 2006). In addition, the mixing ratio of SO_2 emitted from each sample was measured. The results showed that UDSS was characterized by the highest SO_2 emissions (4.5 ppb), which was almost double that of DSS (2.6 ppb), SS 30% (2.6 ppb) and SS 60% (2.1 ppb). Moreover, in our study, NH_3 emissions were measured only for DSS. The average mixing ratio of ammonia emitted from DSS was 3239 ppm. Lim et al., (2018) reported ammonia as one of the main odour compounds.

4.6. Impact of treatment stage on VOC emissions

Our results showed that the anaerobic digestion decreased the total number of emitted VOCs and dewatering step had little impact. This impact was also observed on the number of the characteristic compounds (**Table S2**), where UDSS showed the maximum number (93) compared with the anaerobically digested and dewatered sludge. Chen et al., (2014) studied the impact of the sludge drying process on odour and VOC emissions. The authors illustrated that the total organic compounds in the sludge were significantly decreased after drying. In this work, the total emission flux of VOCs increased with the increase in the dry matter content. For instance, DSS had the lowest dry matter (2.3%) and showed the lowest emission flux of VOCs. However, after dewatering to reach 60% of dryness, the emission flux of VOCs was the highest. This was interrelated to the highest organic matter content in this sample (60.4%) (**Table 3**). The HC emission flux increased with the increase in the dry matter of the sample (**Figure 5, b**). The emissions of aromatic HC were comparable between UDSS and dewatered sludge while in DSS it was almost one-third lower. This indicated that anaerobic digestion reduced the aromatic compound emissions while dewatering had a lower impact. This reduction could result from their biodegradation during the treatment process.

Anaerobic digestion decreased the VOSC emissions by 96%. The reduction in VOSC emissions could be explained either by their loss during the anaerobic digestion treatment process or their degradation by bacterial action. The emissions of VOSCs from SS 30% increased by 92% then decreased (in SS 60%). Sulphuric compounds might not totally be lost but incorporated in the sludge by bacterial action during anaerobic digestion.

The impact of dry matter was illustrated upon a comparison between dewatered samples. SS 30% showed higher emissions of VOSCs compared with SS 60%. The emission of sulphuric compounds increased with the increase in the temperature during sludge treatment (Mrowiec et al., 2005). This phenomenon has been also explained by Ding et al., (2015) who studied the effect of thermal drying temperature and processing time on VOC emissions from sludge. This study revealed that higher emissions of pollutants and VOSCs were observed at higher drying temperatures. In addition, the concentration of odours, total VOCs and amines changed with the drying temperature (Ding et al., 2015). A similar aspect was also reported by Deng et al., (2009) where the authors investigated the VOCs released during the sludge drying process under 140 – 170 ºC. Consequently, the higher drying temperature lead to higher emissions of pollutants and odorants. This agreed with our results as SS 30% showed higher VOSC emissions than SS 60%. SS 30% might be subjected to lower drying temperature compared to SS 60%, which resulted in higher emissions of VOSCs from SS 60% during the dewatering step. Both samples emitted lower sulphuric compounds compared with UDSS. This indicated that a big part of soluble fractions of sulphur form was separated from the sludge during dewatering, thus dewatered sludge contained less sulphur than the raw sludge. The high contribution of OVOCs in SS 60% could be explained by more heterogeneous oxidation reactions occurring at the solid sample surface. Thus, the composition of gas-phase emissions from dewatered sludge were affected by the sludge characteristics, moisture content, and drying conditions, such as temperature, time and drying process type. The thermal drying of SS could involve the release of VOCs that were contained in the sludge and evaporated due to thermal effect (Anderson et al., 2002; C. Gross, 1993; Gomez-Rico et al., 2008). Several studies investigated the gas-phase emissions during the thermal drying process (Anderson et al., 2002; Deng et al., 2009; Ding et al., 2015; Gomez-Rico et al., 2008), but to our knowledge, detailed quantitative and qualitative research on the VOC emissions from sludge subjected to dewatering treatment are not investigated yet. Such characteristics may be important for agricultural purposes. The four types of analyzed sludge can be applied in agricultural field, however the way and amounts of applied sludge depends on the soil, crop, local conditions and state regulations.

5. Conclusions and environmental implications

This study gives comprehensive qualitative and quantitative information on VOCs emitted by SS. We showed that SS samples emitted a large spectrum of VOCs. In this work, 380 compounds were detected and quantified, with 81 compounds commonly found in all samples. The assigned VOCs were classified into the following chemical groups: hydrocarbons, oxygenated, sulphuric, nitrogenated and “other” compounds (containing distinct heteroatoms in the molecular formula). Different sub-classes of HC were identified using the DBE method, which is applied for the first time on PTR mass spectra. Some aliphatic and alicyclic compounds, many aromatic HC and terpenes were found. From the DBE analysis, the efficiency of this method to simplify the analysis of a complex mixture through classification was illustrated. HC showed maximum emissions among all VOCs in all samples. OVOCs were dominant in SS 60% while VOSC showed elevated emissions from UDSS.

The total VOC emissions increased with the increase in the dry matter and organic matter contents of SS samples. The anaerobic digestion decreased the VOSC emissions (e.g. CH_4SH^+, $C_2H_6SH^+$ and $C_2H_6S_2H^+$). Similarly, these emissions decreased after dewatering to higher degrees of dryness (e.g. 60%). The results showed that anaerobic digestion and dewatering had positive impacts in decreasing the potential emissions of VOSC and aromatic compounds that can serve as secondary organic aerosol precursors and affect the atmospheric chemistry. For example, terpenes such as limonene were found in this work. Limonene, which has a high level of chemical reactivity (Ni et al., 2015; Nie et al., 2019), contributes to the atmospheric reactivity of VOCs and contributes to ozone and aerosol formation in atmosphere (Ni et al., 2015; Nie et al., 2019). Several sulphuric compounds found in our samples (e.g. DMS, DMDS, methanethiol, etc) can participate in the (photo)chemical reactions in the atmosphere (Shon et al., 2005). The emissions of sulphuric compounds were reduced after the anaerobic digestion and dewatering to higher degrees of dryness (60%). Moreover, amines (TMA), indoles and skatole can be important species for atmospheric chemistry, as they can lead to secondary organic aerosol formation (Ciuraru et al., 2021; Yao et al., 2018; Yu et al., 2012). Recently, skatole emitted from UDSS at emission flux of 50 $\mu g\ m^{-2}\ min^{-1}$ was demonstrated as a key gas-phase precursor for secondary organic aerosol formation in the presence of ozone and SO_2 (Ciuraru et al., 2021). Accordingly, the significant emissions of skatole from UDSS can contribute to particle formation in the presence of photo-oxidants (such as ozone) as this sample also emitted the highest amount of SO_2 compared to the other three samples.

Laboratory measurements using atmospheric simulation chambers can provide information to support field measurements and recommendations for VOC abatement in WWTPs. The results of this work provide an accurate inventory reference for the VOC emissions from SS samples. The comparability of SS emissions at different treatment stages helps identify the impact of sludge treatment at WWTPs on VOC emissions. The environmental risk of land-applied sludge might be reduced upon treatment due to the decrease of individual VOC emissions.

Author contribution statement

K.H. performed chamber experiments, analysed the data and wrote the manuscript. R.C. and C.F. designed the study and performed critical editing and review of the manuscript. F.L. helped for PTR-ToF-MS data analysis and contributed to the manuscript. S.H. provided expertize in organic waste recycling and contributed to the manuscript. D.P. contributed to the manuscript. All authors commented on the manuscript.

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References

Abis, L., Loubet, B., Ciuraru, R., Lafouge, F., Dequiedt, S., Houot, S., Maron, P. A., & Bourgeteau-Sadet, S. (2018). Profiles of volatile organic compound emissions from soils amended with organic waste products. *Science of the Total Environment*, *636*, 1333–1343. https://doi.org/10.1016/j.scitotenv.2018.04.232

Amador-Muñoz, O., Misztal, P. K., Weber, R., Worton, D. R., Zhang, H., Drozd, G., & Goldstein, A. H. (2016). Sensitive detection of n-alkanes using a mixed ionization mode proton-transfer-reaction mass spectrometer. *Atmospheric Measurement Techniques*, *9*(11), 5315–5329. https://doi.org/10.5194/amt-9-5315-2016

Anderson, N. J., Dixon, D. R., Harbour, P. J., & Scales, P. J. (2002). Complete characterisation of thermally treated sludges. *Water Science and Technology*, *46*(10), 51–54. https://doi.org/10.2166/wst.2002.0287

Atkinson, R. (2000). Atmospheric chemistry of VOCs and NOx. *Atmospheric Environment*, *34*(12–14), 2063–2101. https://doi.org/10.1016/S1352-2310(99)00460-4

Byliński, H., Barczak, R. J., Gębicki, J., & Namieśnik, J. (2019). Monitoring of odors emitted from stabilized dewatered sludge subjected to aging using proton transfer reaction–mass spectrometry. *Environmental Science and Pollution Research*, *26*(6), 5500–5513. https://doi.org/10.1007/s11356-018-4041-4

C. Gross, T. S. (1993). Thermal Drying of SS. *Water and Environment Journal*, *7*(3), 255–261. https://doi.org/10.1111/j.1747-6593.1993.tb00843.x

Chen, W.-H., Deng, M.-J., Luo, H., Zhang, J.-Y., Ding, W.-J., Liu, J.-X., & Liu, J.-X. (2014). Characteristics of odors and VOCs from sludge direct drying process. *Huan Jing Ke Xue= Huanjing Kexue*, *35*(8), 2897—2902.

Chiriac, R., De Araujos Morais, J., Carre, J., Bayard, R., Chovelon, J. M., & Gourdon, R. (2011). Study of the VOC emissions from a municipal solid waste storage pilot-scale cell: Comparison with biogases from municipal waste landfill site. *Waste Management*, *31*(11), 2294–2301. https://doi.org/10.1016/j.wasman.2011.06.009

Christodoulou, A., & Stamatelatou, K. (2016). Overview of legislation on SS management in developed countries worldwide. *Water Science and Technology: A Journal of the International Association on Water Pollution Research*, *73*(3), 453–462. https://doi.org/10.2166/wst.2015.521

Ciganek, M., & Neca, J. (2008). Chemical characterization of volatile organic compounds on animal farms. *Veterinarni Medicina*, *53*(12), 641–651. https://doi.org/10.17221/1969-VETMED

Ciuraru, R., Kammer, J., Decuq, C., Vojkovic, M., Haider, K., Carpentier, Y., Lafouge, F., Berger, C., Bourdat-Deschamps, M., Ortega, I. K., Levavasseur, F., Houot, S., Loubet, B., Petitprez, D., & Focsa, C. (2021). New particle formation from agricultural recycling of organic waste products. *Npj Climate and Atmospheric Science*, *4*(1), 5. https://doi.org/10.1038/s41612-021-00160-3

Collivignarelli, M., Abbà, A., Frattarola, A., Carnevale Miino, M., Padovani, S., Katsoyiannis, I., & Torretta, V. (2019). Legislation for the Reuse of Biosolids on Agricultural Land in Europe: Overview. *Sustainability*, *11*(21), 6015. https://doi.org/10.3390/su11216015

Colón, J., Alarcón, M., Healy, M., Namli, A., Ponsá, S., Sanin, F. D., & Taya, C. (2014). Producing sludge for agricultural applications. *Innovative Wastewater Treatment and Resource Recovery Technologies*, 292–314.

Deng, W.-Y., Yan, J.-H., Li, X.-D., Wang, F., Zhu, X.-W., Lu, S.-Y., & Cen, K.-F. (2009). Emission characteristics of volatile compounds during sludges drying process. *Journal of Hazardous Materials*, *162*(1), 186–192. https://doi.org/10.1016/j.jhazmat.2008.05.022

Di Capua, F., Spasiano, D., Giordano, A., Adani, F., Fratino, U., Pirozzi, F., & Esposito, G. (2020). High-solid anaerobic digestion of SS: Challenges and opportunities. *Applied Energy*, *278*, 115608. https://doi.org/10.1016/j.apenergy.2020.115608

Ding, W., Li, L., & Liu, J. (2015). Investigation of the effects of temperature and sludge characteristics on odors and VOC emissions during the drying process of SS. *Water Science and Technology*, *72*(4), 543–552. https://doi.org/10.2166/wst.2015.246

Dobbins, R. A., Fletcher, R. A., & Chang, H.-C. (1998). The evolution of soot precursor particles in a diffusion flame. *Combustion and Flame*, *115*(3), 285–298. https://doi.org/10.1016/S0010-2180(98)00010-8

Du, W., & Parker, W. (2012). Modeling volatile organic sulfur compounds in mesophilic and thermophilic anaerobic digestion of methionine. *Water Research*, *46*(2), 539–546. https://doi.org/10.1016/j.watres.2011.11.043

Duan, Z., Lu, W., Li, D., & Wang, H. (2014). Temporal variation of trace compound emission on the working surface of a landfill in Beijing, China. *Atmospheric Environment*, *88*, 230–238. https://doi.org/10.1016/j.atmosenv.2014.01.051

Eitzer, B. D. (1995). Emissions of Volatile Organic Chemicals from Municipal Solid Waste Composting Facilities. *Environmental Science & Technology*, *29*(4), 896–902. https://doi.org/10.1021/es00004a009

Fisher, R. M., Barczak, R. J., Alvarez Gaitan, J. P., Le-Minh, N., & Stuetz, R. M. (2017). Odorous volatile organic compound (VOC) emissions from ageing anaerobically stabilised biosolids. *Water Science and Technology*, *75*(7), 1617–1624. https://doi.org/10.2166/wst.2017.030

Gebicki, J., Byliński, H., & Namieśnik, J. (2016). Measurement techniques for assessing the olfactory impact of municipal sewage treatment plants. *Environmental Monitoring and Assessment*, *188*(1), 1–15. https://doi.org/10.1007/s10661-015-5024-2

Gomez-Rico, M. F., Fullana, A., & Font, R. (2008). Volatile organic compounds released from thermal drying of SS. *WIT Transactions on Ecology and the Environment*, *111*, 425–433. https://doi.org/10.2495/WP080411

Hall, J. E. (1995). SS Production, Treatment and Disposal in the European Union. *Water and Environment Journal*, *9*(4), 335–343. https://doi.org/10.1111/j.1747-6593.1995.tb00950.x

Harrison, E. Z., Oakes, S. R., Hysell, M., & Hay, A. (2006). Organic chemicals in SSs. *Science of the Total Environment*, *367*(2–3), 481–497. https://doi.org/10.1016/j.scitotenv.2006.04.002

Higgins, M. J., Yarosz, B. D. P., Caldwell, Chen, Y.-C., & Mass, N. A. (2003). Mechanisms of Volatile Sulfur Compound and Odor Production in Digested Biosolids. *Residuals and Biosolids*.

Jamil Khan, M., Qasim, M., & Umar, M. (2006). Utilization of SS as organic fertiliser in sustainable agriculture. *Journal of Applied Sciences*, *6*(3), 531–535. https://doi.org/10.3923/jas.2006.531.535

Kammer, J., Décuq, C., Baisnée, D., Ciuraru, R., Lafouge, F., Buysse, P., Bsaibes, S., Henderson, B., Cristescu, S. M., Benabdallah, R., Chandra, V., Durand, B., Fanucci, O., Petit, J. E., Truong, F., Bonnaire, N., Sarda-Estève, R., Gros, V., & Loubet, B. (2020). Characterization of particulate and gaseous pollutants from a French dairy and sheep farm. *Science of the Total Environment*, *712*, 135598. https://doi.org/10.1016/j.scitotenv.2019.135598

Kotowska, U., Żalikowski, M., & Isidorov, V. A. (2012). HS-SPME/GC–MS analysis of volatile and semi-volatile organic compounds emitted from municipal SS. *Environmental Monitoring and Assessment*, *184*(5), 2893–2907. https://doi.org/10.1007/s10661-011-2158-8

Lamastra, L., Suciu, N. A., & Trevisan, M. (2018). SS for sustainable agriculture: Contaminants' contents and potential use as fertilizer. *Chemical and Biological Technologies in Agriculture*, *5*(1), 10. https://doi.org/10.1186/s40538-018-0122-3

Lelieveld, J., Evans, J. S., Fnais, M., Giannadaki, D., & Pozzer, A. (2015a). The contribution of outdoor air pollution sources to premature mortality on a global scale. *Nature*, *525*(7569), 367–371. https://doi.org/10.1038/nature15371

Lim, J.-H., Cha, J.-S., Kong, B.-J., & Baek, S.-H. (2018). Characterization of odorous gases at landfill site and in surrounding areas. *Journal of Environmental Management*, *206*, 291–303. https://doi.org/10.1016/j.jenvman.2017.10.045

Mackie, R. I., Stroot, P. G., & Varel, V. H. (1998). The online version of this article , along with updated information and services , is located on the World Wide Web at: Biochemical Identification and Biological Origin of Key Odor Components in Livestock Waste 1 ABSTRACT : *Journal of Animal Science*, *76*, 1331–1342.

Milieu, L., WRc, & and RPA. (2010). *Environmental economic and social impacts of the use of SS on land.* (Project Interim Reports Final Report; Part III).

Moreno, A. I., Arnáiz, N., Font, R., & Carratalá, A. (2014). Chemical characterization of emissions from a municipal solid waste treatment plant. *Waste Management*, *34*(11), 2393–2399. https://doi.org/10.1016/j.wasman.2014.07.008

Mrowiec, B., Suschka, J., & Keener, T. C. (2005). Formation and Biodegradation of Toluene in the Anaerobic Sludge Digestion Process. *Water Environment Research*, *77*(3), 274–278. https://doi.org/10.2175/106143005X41852

Mustafa, M. F., Liu, Y., Duan, Z., Guo, H., Xu, S., Wang, H., & Lu, W. (2017). Volatile compounds emission and health risk assessment during composting of organic fraction of municipal solid waste. *Journal of Hazardous Materials*, *327*, 35–43. https://doi.org/10.1016/j.jhazmat.2016.11.046

Ni, J. Q., Robarge, W. P., Xiao, C., & Heber, A. J. (2012). Volatile organic compounds at swine facilities: A critical review. *Chemosphere*, *89*(7), 769–788. https://doi.org/10.1016/j.chemosphere.2012.04.061

Ni, Z., Liu, J., Song, M., Wang, X., Ren, L., & Kong, X. (2015). Characterization of odorous charge and photochemical reactivity of VOC emissions from a full-scale food waste treatment plant in China. *Journal of Environmental Sciences*, *29*, 34–44. https://doi.org/10.1016/j.jes.2014.07.031

Nie, E., Zheng, G., Gao, D., Chen, T., Yang, J., Wang, Y., & Wang, X. (2019). Emission characteristics of VOCs and potential ozone formation from a full-scale SS composting plant. *Science of the Total Environment*, *659*, 664–672. https://doi.org/10.1016/j.scitotenv.2018.12.404

Nie, E., Zheng, G., Shao, Z., Yang, J., & Chen, T. (2018). Emission characteristics and health risk assessment of volatile organic compounds produced during municipal solid waste composting. *Waste Management*, *79*. https://doi.org/10.1016/j.wasman.2018.07.024

Rincón, C. A., De Guardia, A., Couvert, A., Le Roux, S., Soutrel, I., Daumoin, M., & Benoist, J. C. (2019). Chemical and odor characterization of gas emissions released during composting of solid wastes and digestates. *Journal of Environmental Management*, *233*(November 2018), 39–53. https://doi.org/10.1016/j.jenvman.2018.12.009

Rosenfeld, P. E., Henry, C. L., Dills, R. L., & Harrison, R. B. (2001). Comparison of odor emissions from three different biosolids applied to forest soil. *Water, Air, and Soil Pollution*, *127*(1–4), 173–191. https://doi.org/10.1023/A:1005286429528

Sabbah, H., Commodo, M., Picca, F., De Falco, G., Minutolo, P., D’Anna, A., & Joblin, C. (2021). Molecular content of nascent soot: Family characterization using two-step laser desorption laser ionization mass spectrometry. *Proceedings of the Combustion Institute*, *38*(1), 1241–1248. https://doi.org/10.1016/j.proci.2020.09.022

Schiavon, M., Martini, L. M., Corrà, C., Scapinello, M., Coller, G., Tosi, P., & Ragazzi, M. (2017). Characterisation of volatile organic compounds (VOCs) released by the composting of different waste matrices. *Environmental Pollution*, *231*, 845–853. https://doi.org/10.1016/j.envpol.2017.08.096

Shen, Y., Chen, T.-B., Gao, D., Zheng, G., Liu, H., & Yang, Q. (2012). Online monitoring of volatile organic compound production and emission during SS composting. *Bioresource Technology*, *123*, 463–470. https://doi.org/10.1016/j.biortech.2012.05.006

Shon, Z., Kim, K., Jeon, E., Kim, M., Kim, Y., & Song, S. (2005). Photochemistry of reduced sulfur compounds in a landfill environment. *Atmospheric Environment*, *39*(26), 4803–4814. https://doi.org/10.1016/j.atmosenv.2005.06.024

Sintermann, J., Schallhart, S., Kajos, M., Jocher, M., Bracher, A., Münger, A., Johnson, D., Neftel, A., & Ruuskanen, T. (2014). Trimethylamine emissions in animal husbandry. *Biogeosciences*, *11*(18), 5073–5085. https://doi.org/10.5194/bg-11-5073-2014

Strohalm, M., Kavan, D., Novák, P., Volný, M., & Havlíček, V. (2010). MMass 3: A cross-platform software environment for precise analysis of mass spectrometric data. *Anal Chem 82*, *11*, 4648–4651. https://doi.org/10.1021/ac100818g

Sulzer, P., Hartungen, E., Hanel, G., Feil, S., Winkler, K., Mutschlechner, P., Haidacher, S., Schottkowsky, R., Gunsch, D., Seehauser, H., Striednig, M., Jürschik, S., Breiev, K., Lanza, M., Herbig, J., Märk, L., Märk, T. D., & Jordan, A. (2014). A Proton Transfer Reaction-Quadrupole interface Time-Of-Flight Mass Spectrometer (PTR-QiTOF): High speed due to extreme sensitivity. *International Journal of Mass Spectrometry*, *368*, 1–5. https://doi.org/10.1016/j.ijms.2014.05.004

Tsai, C.-J., Chen, M.-L., Ye, A.-D., Chou, M.-S., Shen, S.-H., & Mao, I.-F. (2008). The relationship of odor concentration and the critical components emitted from food waste composting plants. *Atmospheric Environment*, *42*(35), 8246–8251. https://doi.org/10.1016/j.atmosenv.2008.07.055

Widiana, D. R., Wang, Y. F., You, S. J., Yang, H. H., Wang, L. C., Tsai, J. H., & Chen, H. M. (2019). Air pollution profiles and health risk assessment of ambient volatile organic compounds above a municipal wastewater treatment plant, Taiwan. *Aerosol and Air Quality Research*, *19*(2), 375–382. https://doi.org/10.4209/aaqr.2018.11.0408

Wilson, S. C., Burnett, V., Waterhouse, K. S., & Jones, K. C. (1994). Volatile Organic Compounds in Digested United Kingdom SSs. *Environmental Science and Technology*, *28*(2), 259–266. https://doi.org/10.1021/es00051a012

Xue, S., Ding, W., Lin Li, Ma, J., Chai, F., & Liu, J. (2021). Emission, dispersion, and potential risk of volatile organic and odorous compounds in the exhaust gas from two sludge thermal drying processes. *Waste Management*, *138*, 116–124. https://doi.org/doi.org/10.1016/j.wasman.2021.11.040

Yao, L., Garmash, O., Bianchi, F., Zheng, J., Yan, C., Kontkanen, J., Junninen, H., Mazon, S. B., Ehn, M., Paasonen, P., Sipilä, M., Wang, M., Wang, X., Xiao, S., Chen, H., Lu, Y., Zhang, B., Wang, D., Fu, Q., Wang, L. (2018). Atmospheric new particle formation from sulfuric acid and amines in a Chinese megacity. *Science*, *361*(6399), 278–281. https://doi.org/10.1126/science.aao4839

Yao, X., Ma, R., Li, H., Wang, C., Zhang, C., Yin, S., Wu, D., He, X., Wang, J., Zhan, L., & He, R. (2019). Assessment of the major odor contributors and health risks of volatile compounds in three disposal technologies for municipal solid waste. *91*, 128–138. https://doi.org/10.1016/j.wasman.2019.05.009

Yu, H., McGraw, R., & Lee, S.-H. (2012). Effects of amines on formation of sub-3 nm particles and their subsequent growth: MULTICOMPONENT NUCLEATION WITH AMINES. *Geophysical Research Letters*, *39*(2), n/a-n/a. https://doi.org/10.1029/2011GL050099

Zhang, H., Schuchardt, F., Li, G., Yang, J., & Yang, Q. (2013). Emission of volatile sulfur compounds during composting of municipal solid waste (MSW). *Waste Management*, *33*(4), 957–963. https://doi.org/10.1016/j.wasman.2012.11.008

Zhu, Y., Zheng, G., Gao, D., Chen, T., & Wu, F. (2016a). Odor composition analysis and odor indicator selection during SS composting. *Journal of the Air & Waste Management Association*, *66*(9), 930–940. https://doi.org/10.1080/10962247.2016.1188865