Chemical and olfactive impacts of organic matters on odor emission patterns from the simulated construction and demolition waste landfills

Kunyu Jiang¹, Zhaowen Cheng², Ziyang Lou¹,²,³,⁴,*, Luochun Wang¹,*, Hailin Lu⁵, Bijun Xu⁶, Ningben Jin⁶

¹ College of Environmental and Chemical Engineering, Shanghai University of Electric Power, Shanghai 200090, China
² School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China
³ Shanghai Engineering Research Center of Solid Waste Treatment and Resource Recovery, Shanghai 200092, China
⁴ Institute for Urban Governance, Shanghai Jiao Tong University, Shanghai 200240, China
⁵ Shanghai Environment Group Co., Ltd, Shanghai 200336, China
⁶ Shanghai Environmental Sanitation Engineering Design Institute Co., Ltd, Shanghai 200001, China

ABSTRACT

The explosive increase of construction and demolition waste (CDW) caused the insufficient source separation and emergency disposal at domestic waste landfills in many developing countries. Some organic fractions were introduced to the CDW landfill process and resulted in serious odor pollution. To comprehensively explore the impacts of organic matters on odor emission patterns, five CDW landfills (OIL), with organic matters/ inert CDW components (O/I) from 5% to 30%, and the control group only with inert components (IL) or organics (OL) were simulated at the laboratory. The chemical and olfactive characters of odors were evaluated using the emission rate of 94 odorants content (ER\text{total}), theory odor concentration (TOC\text{total}), and e-nose concentration (ER\text{ENC}), and their correlations with waste properties were also analyzed. It was found that the main contributors to ER\text{total} (IL: 93.0% NH₃; OIL: 41.6% sulfides, 31.0% NH₃, 25.9% oxygenated compounds) and TOC\text{total} (IL: 64.1% CH₃SH, 28.2% NH₃; OIL: 71.7% CH₃SH, 24.8% H₂S) changed significantly. With the rise of O/I, ER\text{total}, TOC\text{total}, and ER\text{ENC} increased by 10.9, 20.6, and 2.1 times, respectively. And the organics content in CDW should be less than 10% (i.e., DOC<101.3 mg/L). The good regressions between waste properties (DOC, DN, pH) and ER\text{ENC} (r=0.86, 0.86, -0.88, p<0.05), TOC\text{total} (r=0.82, 0.79, -0.82, p<0.05) implied that the carbon sources and acidic substances relating to organics degradation might result in that increase. Besides, the correlation analysis results (ER\text{ENC} vs. TOC\text{total}, r=0.96, p<0.01; vs. ER\text{total}, r=0.86, p<0.05) indicated that e-nose perhaps was a reliable odor continuous monitoring tool for CDW landfills.

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¹ Corresponding authors.
E-mails: louworld12@sjtu.edu.cn (Z. Lou), wangluochun@shiep.edu.cn (L. Wang).

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Introduction

With the acceleration of urbanization and economic growth, the amount of construction and demolition (CDW) waste increased explosively (Yuan and Shen, 2011; Zheng et al., 2017). In many developing countries, some of them went into the domestic waste landfill as an emergency measure due to the restriction of special disposal facilities and funding budget (Asakura, 2015; Inoue, 2005; Lee et al., 2006; Zheng et al., 2017). For instance, around 1.55 billion tons of CDW were produced in China each year, of which about 36.8% was disposed at the landfill together with municipal solid waste (MSW) for saving the cost and land (Aslam et al., 2020; Yuan and Shen, 2011). In addition, although some mechanical separation technologies were enforced, there were still around 2.9%–28.9% of organic matters leaved in the CDW, according to our field investigations (Appendix A Table S1) and literature review (Chung et al., 2019; Lee et al., 2006; Montero et al., 2010; SMBS, 2020). Odor pollution often broke out during the CDW landfill process when some organic matters were leaved or mixed (Allen et al., 1997; Asakura, 2015; Chung et al., 2019; Flynn, 1998; López and Lobo, 2014), such as the issue of Laogang CDW landfill area in February, 2018 (ECC-MEEC, 2019), which seriously influenced the healthy lives of on-site workers and surrounding residents.

CDW mainly consisted of the inert components (e.g., gypsum drywalls, concretes, metals, etc.) and organic fractions (e.g., woods, wallpapers, paints, etc.) (López and Lobo, 2014; Sun et al., 2016; Yang et al., 2006). The sulfate (SO₄²⁻, 8.2–79.9 g/kg) of gypsum drywalls would be reduced into H₂S by the sulfate-reducing bacteria (SRB) under anaerobic conditions (Chung et al., 2019; Eun et al., 2007; Inoue, 2005; Spring et al., 2012). The concentration of H₂S detected in the ambient air and surface soil vapor of CDW landfills reached 4.6–76 μg/m³ and 4.6–18214 μg/m³, respectively (Chung et al., 2019; Lee et al., 2006). The main source of H₂S was inert CDW components, primarily as gypsums, but it was probably affected by the residual organic matters (Asakura, 2015; Xu and Townsend, 2014; Yang et al., 2006). The organic fractions would be biodegraded into short-chain acids and alcohols through anaerobic digestion, which were favorable carbon sources for and acidity regulators for the SRB (Ko et al., 2015; Lou et al., 2015; Orzi et al., 2010). It was reported that the dissolved organic carbon (DOC) of SRB culture medium was in direct proportion to the H₂S content in the range from 10 to 320 mg/L (Sun et al., 2016). But the high level of organic matters would adversely inhibit the growth of SRB due to the toxicity of accumulated products (e.g., acids and H₂S) and the substrate competition of methanogens (Li et al., 2020; O’Flaherty et al., 1998; Omil et al., 1998; Reis et al., 1992). The limitation for organic fractions leaved or mixed in CDW was heatedly discussed. Ono and Tanaka (2003) suggested that the DOC of CDW filtrate should be less than 30 mg/L to avoid the acute poisoning of H₂S (~1518 μg/m³). Asakura (2015) thought that limit could extend to 200 mg/L. But they were carried out by the cultivation of SRB with liquid nutrition medium, which was greatly differed from the practical landfill process (e.g., the microbial biomass, water content, alkalinity, etc.) and probably overstated the generation potential of H₂S (Ko et al., 2015; Long et al., 2017). In Japan, the protective paper sheets of gypsum board, one of typical organic fractions in the CDW, should be removed, and the limitation of ignition loss for CDW residues was 5% (Inoue, 2005). In Europe, the gypsum board was not permitted entering the non-hazardous waste landfill, and the limit of DOC for other inert components was 160 mg/L (EC, 2003). But there was no prohibition on the landfill of gypsum board and lack of the special CDW landfill area in many developing districts, owing to the poor separation technology and waste management system. Therefore, it was essential to comprehensively assess the relationships between organic matters and odor emission patterns based on the practical landfill process with real CDW.

Besides, the organic fractions could be biodegraded into varieties of odorous substances in the anaerobic environment (Ding et al., 2012; Duan et al., 2014; Lou et al., 2015). It was reported that amounts of sulfides (21–886 μg/m³), NH₃ (172–2180 μg/m³), oxygenated compounds (50–2708 μg/m³), aromatics (8–319 μg/m³), and terpenes (23–450 μg/m³) were detected at the MSW landfill (Cheng et al., 2020; Fang et al., 2012; Lu et al., 2015). In general, the organic sulfides, with the low threshold comparable to H₂S, would generate from the anaerobic digestion of cysteine and methionine (Ko et al., 2015; Long et al., 2017). The NH₃, which was irritative for eyes and respiratory tract, would produce from the biodegradation of amino acids, purines and their derivatives (Duan et al., 2014; López et al., 2016). The oxygenated compounds was one of main intermediates of the hydrolysis and acidification. The aromatics, the well-known health threaten substances, would volatilize from the coatings and paints in the CDW (Cheng et al., 2020; Liu et al., 2016). And there were complex interaction effects among the odorants in mixtures, e.g., the additive, antagonistic and synergistic interaction (Cheng et al., 2019; Wu et al., 2015). Whereas, the recent studies relevant to the emissions from CDW landfills were almost focused on the H₂S (Eun et al., 2007; Inoue, 2005; Ko et al., 2015; Xu and Townsend, 2014). The wider species of odorants should be investigated, especially when there were some organic matters leaved in the CDW.

Different techniques have been utilized to evaluate the odor pollution. The chemical concentration of odorous compounds was always analyzed by the instruments, e.g., the special gas detectors and gas chromatography/mass spectrometers (GC/MS) (Conti et al., 2020; Hayes et al., 2014; Wu et al., 2015). At present, the studies of CDW landfills just paid attentions to the concentration of sulfides, especially H₂S (Asakura, 2015; Xu et al., 2011; Yang et al., 2006). There was lack of a comprehensive analysis of odor pollutants, which contributed to the identification of main odor pollutants and specific deodorization. The olfactory assessment was essential, because some odorants would make strong olfactory impacts at a low concentration (e.g., H₂S, methyl mercaptan (CH₃SH)), and vice versa (Lu et al., 2015; Wu et al., 2017). The sensorial analysis could directly reflect the olfactice effects of odors, but required specific equipment (e.g., dynamic olfactometers) and trained panelists (Cheng et al., 2019; Conti et al., 2020). The analysis of theory odor concentration (TOC), the ratio of an odorant’ chemical concentration to its odor threshold, was an alternative approach that could relate the chemical levels to the odor potential (Hayes et al., 2014; Wu et al., 2015). Significant correlations between TOC and chemical
concentration of odorants were reported in the study of MSW landfill (Wu et al., 2017), waste transfer station (Sun et al., 2017), and slaughterhouse sludge compost (Blazy et al., 2015). Besides, the electronic nose (e-nose), which mimicked the human olfaction system using an array of sensors and the patterns recognition system, has received growing concerns due to the lower costs, rapid response and continuous detection (Blanco-Rodriguez et al., 2018; López et al., 2016). It was applied as the real-time odor monitoring tools in wide fields, e.g., waste disposal, wastewater treatment and livestock farm (Conti et al., 2020; Orzi et al., 2010; Sironi et al., 2007; Sun et al., 2017).

To comprehensively assess the impact of organic matters on odor emission patterns from the CDW landfill process, in this work, several simulative landfills, with the real inert CDW components and different ratios of residual organic matters (from 5% to 30%), were conducted. The chemical concentrations of 94 odorants during the landfill process were analyzed using the three-stage cold trap concentrator coupled with the GC/MS. The potential olfactory effects of odorants were evaluated using the theory odor concentration and e-nose concentration. And the correlations between waste properties (e.g., DOC, sulfate, pH) and odor emission were also analyzed.

1. Materials and methods

1.1. Waste samples

In 2018, the amount of CDW collected in Shanghai reached 7.6 million tons (SMBS, 2020). The raw CDW of this study was taken from three typical CDW transfer stations located in the Xuhui, Huangpu, and Minhang district of Shanghai, allowing for the population, industrial structure, and waste composition (Appendix A Table S1). After transferring to the laboratory, the raw CDW was manually crushed into a size of about 1.0 cm and uniformly mixed to minimize the inhomogeneity. The inert CDW components were subsequently sorted and used in the experiment. The total carbon (TC), total nitrogen (TN), and total sulfur (TS) of inert components were 3.2% ± 0.8%, 0.03% ± 0.01%, and 1.8% ± 0.4%, respectively (Table 1). The content of Ca, Fe, and Al was 20.8%, 3.7%, and 1.4%, respectively (Appendix A Table S2). The organic matters leaved or mixed in CDW, to a degree, were homologous with the domestic waste, and the typical prescription of China (i.e., 64% food waste, 19% plastics, 13% papers and 4% woods) was simulated in this research (Yang et al., 2018). The detailed physical and chemical characteristics of solid waste were shown in Appendix A Tables S1 and S3.

1.2. Experimental equipment and reactor operation

The polymethyl methacrylate reactor with a volume of about 11.5 L (15 cm i.d. × 65 cm height) was utilized to simulate the landfill process (Fig. 1). The internal surface of reactor was coated with polytetrafluoroethylene to decrease the adsorption of walls. In order to calculate the emission rate of odorants (ER), a special gas collection system, i.e., the alike flux chamber, was developed according to the previous studies
(Eun et al., 2007; Gallego et al., 2014; Xu and Townsend, 2014). It consisted of the nitrogen distributor and empty chamber. The nitrogen distributor, a ring-shaped perforated pipe, was installed above the surface of solid waste and a headspace of about 2 L was reserved. Before sampling, each reactor was flushed with high purity nitrogen for 15 min (about 7 L) to exhaust the retention gas and ensure a steady flow rate (500 mL/min, the optimal result of pretests) (Eun et al., 2007; Liu et al., 2016). And gas samples were subsequently collected from the gas outlet using the Tedlar® bag (volume of 4 L, Restek Inc., USA). The gas outlet was open during the pre-flush period, and the volume of gas collected was kept as the same of nitrogen inserted, thereby avoiding the pressure increase or vacuum in the headspace. After sampling, the gas outlet was closed, and the reactor was well sealed. Gas samples were collected every two or four days regularly. Waste samples were collected at the start and end of the experiment, respectively.

According to the results of field investigation (Appendix A Table S1) and literature review (Chung et al., 2019; Lee et al., 2006; Montero et al., 2010), the residual organic matters of raw CDW were fluctuating from 2.9% to 28.9%. Therefore, five groups of CDW landfills were simulated in the study, with the ratios of organic matters to inert CDW components (O/I) being 5% (5OIL), 10% (10OIL), 15% (15OIL), 20% (20OIL) and 30% (30OIL), respectively. The reactor only with inert CDW components (IL) or organic matters (OL) was set as the control group. And the group only with organic matters (OL) was taken as the point of reference, because the MSW landfills have developed lots of reliable and mature deodorization technologies and criteria (Brancher et al., 2017). For each group, three parallel tests were conducted. The water content of all solid waste was adjusted to 40% (Yang et al., 2006). And 3.0 kg of solid waste was loaded in each reactor, with a typical compacted density of about 600 kg/m³ (Long et al., 2017). Each reactor was flushed with nitrogen from the leachate outlet for 15 min to quickly establish the anaerobic environment before the test. The ambient temperature was controlled at 35 °C, which was suitable for the growth of microorganisms, including the SRB (Ko et al., 2015; Yin et al., 2020).

1.3 Analysis methods

92 kinds of volatile odor compounds (VOC), including aromatic (13), organic sulfides (6), nitrogen compounds (1), oxygenated compounds (25), terpenes (3), halogenated compounds (36), and hydrocarbons (8), were analyzed based on the USEPA TO-15 methodology using the preconcentration system coupled with GC/MS (Cheng et al., 2020; US-EPA, 1999). Gas samples, ranging from 20 to 100 mL, were successively dehydrated at -50°C, trapped at -40°C, and focused at -160°C in the three-stage cold trap concentrator (7200, Entech, USA). It removed almost all water and concentrated the target VOC. Then, the pretreated gas was injected into the GC/MS (QP 2010, Shimadzu, Japan) for separation with a DB-624 capillary column (60 m × 0.25 mm × 1.4 μm). The flow rate of carrier gas (helium) was 1.2 mL/min. The oven temperature of GC was kept at 35°C for 5 min, and then increased to 140°C at 4°C/min with a hold of 3 min, following by an increase to 220°C at the same rate. The temperature of MS interface, EI source, and quadruple were 200°C, 220°C, and 150°C, respectively. The full scan mode and single ion monitor mode was utilized for the qualitative and quantitative analysis, respectively. VOC were identified with the standard mass spectra of NIST 147 Library and quantified with the combination of internal standard calibration (1,4-difluorobenzene, chlorobromomethane and chlorobenzene-d5) and external calibration (92 mixed standard gas, Linde Group Inc., Germany) (Appendix A Table S4). The related QA/QC profiles were shown in Appendix A Table S4.

NH₃ was absorbed with sulfuric acid (0.01 mol/L) and detected by the Nessler’s reagent spectrophotometry (Cheng et al., 2019). H₂S was absorbed with zinc acetate solution and measured by the methylene blue spectrophotometry (Ding et al., 2012). The e-nose concentration (Cₑnₑ) was analyzed according to our previous methodology.


1.4. Data analysis

The emission rates of e-nose concentration (\(ER_{ENC}\)) and certain odorant (\(ER\)) were calculated by Eqs. (1) and (2), respectively (Sun et al., 2017; Liu et al., 2016).

\[
ER_{ENC} = \nu C_{ENC}/A
\]

\[
ER_i = \nu C_i/A
\]

where \(ER_{ENC}\) (OU/min) was the emission rate of e-nose concentration; \(ER\) (µg/min) was the emission rate of certain odorant; \(\nu\) was the flow rate of flushing gas (m³/min, \(5.0 \times 10^{-4}\) in current study); \(A\) was the covered area of the alike gas chamber (m², \(17.7 \times 10^{-3}\) in current study); \(C_{ENC}\) (OU/m³) was the e-nose concentration; \(C_i\) (µg/m³) was the concentration of certain odorant.

The theory odor concentration (TOC) was introduced to correlate the chemical level of certain odorant with its olfactory effects and defined by Eq. (3) (Cheng et al., 2019).

\[
TOC_i = C_i/OT_i
\]

Where \(TOC_i\) was the theory odor concentration of certain odorant; \(C_i\) (µg/m³) was the concentration of certain odorant; \(OT_i\) (µg/m³) was the odor threshold of certain odorant (Appendix A Table S4).

Besides, Spearman correlation analysis was conducted using the SPSS 18.0 software to test the linear correlation coefficient between the odor emissions (e.g., \(ER_{ENC}, ER_{total}, TOC_{total}, ER_{SUL}, ER_{MTR}, ER_{WBG}, ER_{AROM}, ER_{QUA}, ER_{HYD}, ER_{ERP}\)) and waste properties (e.g., DC, DOC, TN, pH, TC, TS, \(SO_4^{2-}, NH_4^+, NO_3^-\)) (Cheng et al., 2019; Sun et al., 2017).

2. Results and discussion

2.1. Chemical characteristics of odor emissions from different simulative CDW landfills

The average emission rate of 94 odors (\(ER_{total}\)) increased with the rise of O/l and reached the maximum level at the 200IL (4.4 ± 2.2 mg/m³/min), which was 7.6 and 1.4 times more than the IL (0.6 ± 0.2 mg/m³/min) and OL (3.1 ± 1.8 mg/m³/min), respectively (Fig. 2, Appendix A Fig. S2). The nutrition deficiency (TC of 3.2% ± 0.8%, TN of 0.03% ± 0.01%) and alkaline condition (pH of 9.8 ± 0.8) probably inhibited the growth of microorganism and resulted in the low level of \(ER_{total}\) in IL group, which was in agreement with the results of previous reports (Allen et al., 1997; O’Flaherty et al., 1998; Yang et al., 2006). The organic fractions would be biodegraded into numbers of small-molecular dissolvable substances (e.g., fatty acids, alcohols, ketones, etc.), especially the 200IL and 300IL (DOC of 231.0 ± 13.8 and 382.0 ± 21.6 mg/L, respectively). They were favorable carbon sources and acidity regulators and would facilitate the microbial metabolism (Asakura, 2015; Lou et al., 2015). The \(ER_{total}\) increased by 10.9 times as the O/l raising from 5% to 20%. The methanogens might prevail in the presence of some organics, e.g., the 300IL, which had a higher level of DOC and pH than the 200IL (Table 1) (Li et al., 2020; Omil et al., 1998; Yin et al., 2020). It was reported that the methanogenesis process would produce alkalinity relating to degradation of fatty acids and increase the pH value (O’Flaherty et al., 1998; Yin et al., 2020). Thus, amounts of bigas (e.g., methane, hydrogen), rather than the VOC, were likely to be yielded (Omil et al., 1998; Sun et al., 2016). The acid accumulation was a common phenomenon in the initial stage of MSW landfilling, which would restrain the activity of enzyme and microorganisms (Long et al., 2017). It was also observed in this research, for instance, the pH of OL was 5.4 ± 0.4 at the 30th day. And there appeared Lactobacillus genus with an abundance of 12.0% (Appendix A Fig. S7), which could ferment sugar into lactic acids and acetic acids (Gänzle, 2015).

Compared with the OL, the ratio of residual organic matters in CDW should be less than 15% (i.e., DOC of 119.5 ± 9.1 mg/L) in terms of the chemical amount of odorants. It was close to limit value for the percolation test (160 mg/L) for inert waste defined by the EU Council Decision (EC, 2003). Whereas, Asakura (2015) suggested that the DOC should be lower than 200 mg/L to avoid the acute toxicity of \(H_2S\) (<1518 mg/m³). Ono and Tanaka (2003) thought that limitation should be below 30 mg/L. The \(H_2S\) content of all CDW landfills in this research was lower than 885 mg/m³ during the whole test period (Appendix A Fig. S4). The previous studies were conducted by the SBR culture experiment, where the test conditions (e.g., water content, microbial biomass, alkalinity) were greatly differed from the practical landfills and the simulated ones in this research (Asakura, 2015; Ono and Tanaka, 2003). For instance, the easy biodegradable substrate (yeast and lactose at 1:1) and neutral condition (pH of 7.0 ± 0.1) were adopted by Asakura (2015), which would significantly enhance the growth of SRB and overstate the \(H_2S\) generation (Hao et al., 2014; Inoue, 2005; O’Flaherty et al., 1998).
Besides, the main contributors to ER\textsubscript{total} was greatly affected by the residual organic matters in the CDW (Fig. 2). For the control group (IL), NH\textsubscript{3} accounted for about 93.0% of ER\textsubscript{total}. For the group with the presence of organic matters, sulfides (41.6%), NH\textsubscript{3} (31.0%) and oxygenated compounds (25.9%) were the major contributors to ER\textsubscript{total}. It might require the next researchers to pay more attentions to the emissions of NH\textsubscript{3} and oxygenated compounds from CDW landfills. NH\textsubscript{3} was irritative for eyes and respiratory tract and might exert a synergistic interaction on the olfaction of H\textsubscript{2}S (Cheng et al., 2019; Wu et al., 2015).

### 2.1.1. Sulfur compounds

For the inorganic sulfide (i.e., H\textsubscript{2}S), the reduction of sulfate and decomposition of sulfur-containing organics were the main formation pathways at CDW landfills (Eun et al., 2007; Yang et al., 2006). The SO\textsubscript{4}\textsuperscript{2-} of filtrate in IL group reached 34.1 ± 2.1 mg/L, but there was a little H\textsubscript{2}S detected during the test period (0.0-0.9 µg/(m²·min)) (Appendix A Fig. S4). López and Lobo (2014) found the similar results at some CDW landfills in European, where the gypsum board was not acceptable. The inhibitions of alkaline environment (pH of 9.6–9.8) and insufficient carbon source (TC of 2.6%–3.2%) might be responsible for the phenomenon (Reis et al., 1992; Xu and Townsend, 2014). The optimal pH for the growth of SRB was about 7.0 (Ko et al., 2015). Yang et al. (2006) found that the alkalic substances (pH of 9.0–11.2) could restrain the activity of SRB and the volatilization of H\textsubscript{2}S. The combination of sulfides and metals probably was the other reason, as reported by Xu et al. (2011) and Galvín et al. (2012). The content of Fe, Cu and As in inert CDW components reached 3.7%, 87.4 mg/kg and 25.3 mg/kg, respectively (Appendix A Table S5). In the presence of organic matters, the bacterial reduction of sulfate would be enhanced due to the preferable pH value and carbon source relating to the hydrolysis process (e.g., amino acids, fatty acids) (Long et al., 2017; Lou et al., 2015). With the rise of O/I from 5% to 20%, the average ER\textsubscript{H2S} increased from 6.5 ± 0.1 µg/(m²·min) to 1.5 ± 0.7 mg/(m²·min) (Appendix A Fig. S4). The range of pH was from 6.8 to 9.6, and that of DOC was from 55.5 to 231.0 mg/L (Table 1). And there existed Desulfotomaculum genus with the abundance from 4.2% to 8.9%, a typical chemoheterotrophic SRB found in the lake sediment and sludge digestion (Appendix A Fig. S7) (Hao et al., 2014; Spring et al., 2012). The H\textsubscript{2}S generation of 300IL might be restrained by the competition of methanogens for organic substances (Sun et al., 2016; Yin et al., 2020). It was reported that the substrate competition between SRB and methanogens would occur when the ratio of DOC to sulfate was higher than 0.67 during the wastewater anaerobic treatment (Omil et al., 1998). Besides, Reis et al. (1992) found that the activity of SRB...
would be completely inhibited by the long presence of high H$_2$S (>871 mg/m$^3$). The H$_2$S content of reactors’ headspace gas was not analyzed in this study. But that inhibition probably was not strong here, because the dynamic sampling method (described in Section 1.2) would discharge the H$_2$S in the headspace timely. As reported by Sun et al. (2016), the sparging of nitrogen could effectively reduce the H$_2$S toxicity to SRB at the CDW landfill. Moreover, Asakura (2015) suggested that the SO$_4^{2-}$ of filtrate should be less than 50 mg/L to avoid the acute toxicity of H$_2$S (~1518 mg/m$^3$). The SO$_4^{2-}$ in this study (~34.1 mg/L) was lower than that limit. There was probably no potential health harm, but the olfactive impact of H$_2$S was remarkable (discussed in Sections 2.2 and 2.4).

Organic sulfides were the other critical part of sulfide odorants for CDW landfills, accounting for 12.1%-98.3% of ER$_{sulf}$. (Appendix A Fig. S4). The organic sulfides mainly originated from the decomposition of sulfur-containing organics, and their emission rates increased along with the rise of O/I (Duan et al., 2014; Long et al., 2017). The mean emission rate of organic sulfides in 200IL (0.2 ± 0.1 mg/m$^3$-min) was about 2.9 times more than that of the 50IL (0.5 ± 0.1 mg/m$^3$-min). The main organic sulfides for the IL group were dimethyl sulfide (2.5 ± 1.7 μg/(m$^3$-min)) and dimethyl sulfide (1.0 ± 0.9 μg/(m$^3$-min)), which was in accordance with the results of field study (Lee et al., 2006). With the rise of O/I, the ratio of dimethyl disulfide to total organic sulfides declined from 64.0% (IL) to 24.0% (300IL), while that of CH$_3$SH increased from 7.4% (IL) to 300IL (60.8%) (Appendix A Fig. S4). Overall, dimethyl sulfide, CH$_3$SH, and dimethyl disulfide were the major organic sulfides for the CDW landfill process, with the average emission rate of 30.8-639.4 μg/(m$^3$-min), 129.7-181.5 μg/(m$^3$-min) and 18.5-117.6 μg/(m$^3$-min), respectively (Appendix A Fig. S4). Besides, the sulfide compounds were one of main chemical contributors for the 50IL (2-5 days), 100IL (2-10 day), 150IL (1-10 day), 200IL (2-30 day), 300IL (1-13 day) and OL (1-5 day) with the ratio of ER$_{sulf}$ to ER$_{total}$ above 29.7% (Appendix A Fig. S3).

2.1.2. Nitrogen compounds

NH$_3$ was usually released from the ammonification of nitrogen-containing organics (Lou et al., 2015). There was a small difference for the ER$_{NH3}$ between the IL (548.1 ± 342.7 μg/(m$^3$-min)) and OL (813.2 ± 203.1 μg/(m$^3$-min)) (Fig. 2, Appendix A Fig. S3), though the DOC of OL (1204.0 ± 77.8 mg/L) was much higher than that of IL (665.5 ± 5.7 mg/L). The pH value relevant to the volatilization of NH$_3$ might be responsible for the phenomenon (Ding et al., 2012; Duan et al., 2014).

At the end of test, the pH of IL and OL was 9.6 ± 1.1 and 5.4 ± 0.4, respectively (Table 1). It was reported that the alkaline condition contributed to the volatilization of free ammonia from leachate at MSW landfills (Cheng et al., 2020; Galvin et al., 2012). The lime (e.g., Ca(OH)$_2$) and concrete (e.g., CaO) in inert CDW components were one of major alkalinity sources (Montero et al., 2010; Yang et al., 2006). Besides, the release of NH$_3$ from concrete additives was the other reason (Bai et al., 2006; Xu et al., 2011). It was found that the urea compounds from concrete antifreeze admixtures could be transformed to gaseous NH$_3$ under alkaline and warm condition (Bai et al., 2006; Montero et al., 2010). The ER$_{NH3}$ from concrete wall pieces could reach 240.0 μg/(m$^3$-min) on the condition that air exchange rate of 1.5 hr$^{-1}$, relative humidity of 45%, and temperature of 35°C (Bai et al., 2006). With the rise of O/I, ER$_{NH3}$ increased from 467.4 μg/(m$^3$-min) (SOIL) to 1052.6 μg/(m$^3$-min) (200IL). It might be attributed to the elevated nitrogen-containing substrate and enhanced microbial activity (Fang et al., 2012; Li et al., 2020; Lou et al., 2015). The abundance of Bacillus genus, one of ammonification bacteria found in the thermophilic compost, increased from 9% (SOIL) to 28% (200IL) (Appendix A Fig. S7) (Li et al., 2020). Moreover, the ratio of ER$_{NH3}$ to ER$_{total}$ increased along with the landfill time (Fig. S3), which was in accordance with the study of MSW landfills (Lu et al., 2015; Wu et al., 2015). For instance, in the initial period (1-10 days), the average ER$_{NH3}$/ER$_{total}$ ratio for IL, 50IL, 100IL, 150IL, 200IL and 300IL was 86.6%, 61.9%, 41.2%, 42.5%, 28.3% and 19.7%, while in the later period (13-30 days) it was 96.4%, 93.8%, 71.0%, 88.6%, 29.4% and 71.7%, accordingly (Appendix A Fig. S3).

2.1.3. Oxygenated compounds

There were 15 species of oxygenated compounds frequently detected and quantified in the research (Appendix A Table S1). The ethanol was excluded here due to its exceeding the protection limit of GC/MS at times. Tan et al. (2017) also reported that the ethanol could reach 2449.6 μg/(kg-day) in the initial decomposition stage of MSW. In general, oxygenated compounds primarily originate from the hydrolysis of organic fractions (Ding et al., 2012; Duan et al., 2014). The amount of ER$_{oxygen}$ increased with the rise of O/I (Fig. 2). The average ER$_{oxygen}$ of 200IL (1263.8 ± 403.5 μg/(m$^3$-min)) was 63.5 times more than that of IL (19.9 ± 12.5 μg/(m$^3$-min)) (Fig. 2). Besides, the ER$_{oxygen}$ of 300IL (1546.7 ± 2372.7 μg/(m$^3$-min)) and 200IL were comparable to the OL group (2061.8 ± 1665.1 μg/(m$^3$-min)). But the peak value of ER$_{oxygen}$ for 300IL (the 5th day) and 200IL (the 5th day) appeared at an earlier time than the OL (the 20th day) (Appendix A Fig. S3). The neutral condition of 200IL (pH of 6.8 ± 0.3) and 300IL (pH of 7.5 ± 0.7) might induce the enhancement of hydrolysis process (Yang et al., 2006). And some oxygenated substances (e.g., ketones, esters) might also be volatilized from the adhesives and coatings in CDW directly (Ding et al., 2012; López and Lobo, 2014).

2.1.4. Other volatile odor compounds

Aromatics were mainly volatilized from the paints, solvents, print papers and their decomposed by-products (Cheng et al., 2019; Ding et al., 2012). And the IL (4.2 ± 1.5 μg/(m$^3$-min)) released a higher level of aromatics than OL group (1.6 ± 0.6 μg/(m$^3$-min)) (Fig. 2). The mean ER$_{hydro}$ (12.9 ± 6.9 μg/(m$^3$-min)) of 200IL was about 3.1 times more than that of IL (4.2 ± 1.5 μg/(m$^3$-min)). The high temperature of 200IL (42.1°C) might result in the higher level of aromatic emissions than other groups (35.8-39.1°C) (data not shown). For hydrocarbons, it mostly derived from the biodegradation of organic waste (Liu et al., 2017). The average ER$_{hydro}$ (26.1 ± 12.7 μg/(m$^3$-min)) of 200IL was 5.6 times more than that of IL (4.6 ± 4.2 μg/(m$^3$-min)). And most of hydrocarbons (56.4%-84.9%) were released in the initial stage (1-13 days) (Fig. 2, Appendix A Fig. S3). It was reported that the halogenated compounds had few direct relations with biological degradation (Duan et al., 2014; Lu et al., 2015). There was no obvious difference among the ER$_{halo}$ of test groups (Fig. 2). The average ER$_{halo}$ fluctuated from 7.4 to 10.4 μg/(m$^3$-min), which
was slightly lower than that detected at the MSW landfills (17.1–25.1 μg/(m²·min)) (Liu et al., 2017). For terpenes, there was also hardly any differences, with the range of 0.74–1.38 μg/(m²·min) (Fig. 2). Allen et al. (1997) believed that the terpenes were mainly volatilized from the vegetation when the ratio of α-pinene and β-pinene to total was more than 50.0%. And that ratio in this study was about 75.9%.

### 2.2. Variations of theory odor concentration at different simulative CDW landfills

The residual organic matters markedly facilitated the olfaction effects associated with TOC (Fig. 3). With the rise of O/I, the average TOC_{total} of 200IL (170546 ± 94726) increased 20.6 times than that of SOIL (8254 ± 5723) (Appendix A Fig. S6). Compared with the OL, the O/I should be limited to 10% in terms of TOC_{total} (i.e., DOC of 101.3 ± 8.3 mg/L), which was stricter than the evaluation value based on ER_{total} and ER_{ENC}.

For the IL, the sulfides (TOC_{sulf}) and NH₃ (TOC_{NH₃}) were the major odor contributors, accounting for 69.7% and 28.2% of TOC_{total}, respectively (Fig 3). CH₂SH (12.0%–93.8%) and dimethyl disulfide (5.4%–60.7%) were the major contributors towards TOC_{sulf} for the IL group. Apart from the sulfides (well-known for low odor thresholds), NH₃ was also regarded as one of key olfactory contributors in the studies of MSW landfill, compost and sludge drying, owing to its high chemical levels (Bai et al., 2006; Cheng et al., 2020; Fang et al., 2012). For the groups with residual organic matters, CH₂SH (71.7%) and H₂S (24.8%) were the major contributors to TOC_{total} (Appendix A Fig. S5). Lee et al. (2006) reported that the carbonyl sulfide and CH₂SH might make greater contributions to odor nuisance than H₂S in the CDW landfill accepting both CDW and other non-potable wastes.

### 2.3. Characterization of odor emissions from different CDW landfills based on e-nose concentration

The ER_{ENC} was also enhanced by the residual organic fractions in CDW (Fig. 4). The trend of ER_{ENC} approximately agreed with the ER_{sulf}, ER_{altr}, ER_{hydr}, and ER_{arom}. It was reported that the aromatics and aliphatic compounds perhaps were two key explanatory factors for e-nose concentration in compost process (López et al., 2016). With the rise of O/I, the average ER_{ENC} increased from 588 ± 38 OU/(m²·min) (SOIL) to 1227 ± 544 OU/(m²·min) (200IL) (Appendix A Fig. S1). The extent of increase was much lower than the ER_{total} (10.9-fold) and TOC_{total} (20.6-fold), which was agreement with the previous reports about MSW (Sun et al., 2017). The average ER_{ENC} (570 ± 12
correlated with \( ER_{\text{ENC}} \) \( r=0.86, 0.86, -0.88, p<0.05, n=21 \) and \( \text{TOC}_{\text{total}} \) \( r=0.82, 0.79, 0.82, -0.82, p<0.05, n=21 \). It was agreement with the hypothesis that the carbon sources and acidity regulating substances relevant to the biodegradation of organics probably were the main reasons for the enhanced odor emission (discussed in Section 2.1). And there were similar relationships between the air-dried waste properties (e.g., TC, TN and TS) and \( ER_{\text{ENC}} \) and \( \text{TOC}_{\text{total}} \). It was reported that the electronic nose was effective to assess the maturity of compost (López et al., 2016). The good regressions between the oxygen uptake rate (an indicator of microbial activity) and \( C_{\text{ENC}} \) \( r=0.98, p<0.01 \) and chemical amount \( r=0.95, p<0.01 \) were founded in the MSW anaerobic digestion (Orzi et al., 2010). The \( ER_{\text{ENC}} \) had a significant correlation with the \( ER_{\text{Rust}} \) \( r=0.89, p<0.01, n=21 \), \( \text{TOC}_{\text{total}} \) \( r=0.96, p<0.01, n=21 \), \( ER_{\text{total}} \) \( r=0.86, p<0.05, n=21 \), \( ER_{\text{hydr}} \) \( r=0.96, p<0.05, n=21 \), and \( ER_{\text{terp}} \) \( r=0.79, p<0.05, n=21 \). It was agreement with the fact that sulfide compounds were one of main chemistry and olfactory contributors in CDW landfills (discussed in Sections 2.1 and 2.2). And the common source for the sulfides, hydrocarbons, and terpenes through biodegradation of organic fractions might be an explanation for the correlation (Duan et al., 2014; Orzi et al., 2010). It was reported that the correlation coefficient between total chemical concentration and hydrocarbons, oxygenated compounds, and \( \text{NH}_3 \) reached 0.95, 0.94, and 0.91 \( p<0.05, n=12 \), respectively, at the MSW landfills (Cheng et al., 2019). The good regression was also observed between the \( \text{TOC}_{\text{total}} \) and \( ER_{\text{total}} \) \( r=0.89, p<0.01, n=21 \), which was in accordance with the studies conducted at MSW landfills (Cheng et al., 2019; Wu et al., 2017) and waste compost plants (Cheng et al., 2019; Blazy et al., 2015). Besides, the \( ER_{\text{ENC}} \) was significantly correlated with \( \text{TOC}_{\text{total}} \) \( r=0.96, p<0.01, n=21 \) and \( ER_{\text{ENC}} \) \( r=0.86, p<0.05, n=21 \), indicating that electronic nose might be a promising methodology to forewarn odor pollution at CDW landfills. Similar results were reported in the study of odors from MSW transfer process (Sun et al., 2017), green waste compost (López et al., 2016) and anaerobic digestion (Blanco-Rodríguez et al., 2018).

### 3. Conclusions

The chemical and olfactory effects of organic matters on odor emission patterns from simulative CDW landfill process were comprehensively discussed in the study. The residual organic fractions in CDW significantly enhanced the emissions rate of 94 odorants \( (ER_{\text{total}}) \) e-nose concentration \( (ER_{\text{ENC}}) \) and theory odor concentration \( (\text{TOC}_{\text{total}}) \). When the ratio of organic matters to insert CDW components reached 20%, the odor emissions achieved the peak level under the test condition, with the \( ER_{\text{total}} \) of 4.4 ± 2.2 mg/(m²·min), \( \text{TOC}_{\text{total}} \) of 170546 ± 94726 and \( ER_{\text{ENC}} \) of 1227 ± 544 OUs/(m²·min). In terms of the \( ER_{\text{total}} \) and \( ER_{\text{ENC}} \), the residual organics content was suggested to below 15% (i.e., DOC of 119.5 ± 9.1 mg/L), which was close to the limit value for the percolation test for inert waste defined by the EU Council Decision. But that limitation became more stricter \( (<10%) \), upon considering the \( \text{TOC}_{\text{total}} \). And there were obvious changes for the main contributors to \( ER_{\text{total}} \) and

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**Fig. 4** - The emission rate of electronic nose concentration (\( ER_{\text{ENC}} \)) for different simulative CDW landfills.

**Fig. 5** - The relationships between odor emissions and the property of CDW \((*: p<0.05, **: p<0.01)\).
TOC$_{\text{total}}$, NH$_3$ was the major contributor to ER$_{\text{total}}$ for the inert CDW landfill (IL), while that for the CDW landfills with residual organics was sulfides, NH$_3$ and oxygenated compounds. CH$_3$SH and NH$_3$ were the major contributors towards TOC$_{\text{total}}$ for IL, while that for the CDW landfills with residual organics was CH$_3$SH and H$_2$S. It might require the next researchers to pay more attention to the emissions of NH$_3$, oxygenated compounds, and organic sulfides from CDW landfills, except for the H$_2$S. Besides, the correlation analysis indicated that the electronic nose might be a reliable tool to continuously monitor odor pollution from CDW landfills.

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**Appendix A Supplementary data**


**REFERENCES**


