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Odor composition analysis and odor indicator selection during sewage sludge composting

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ABSTRACT

On the basis of total temperature increase, normal dehydration, and maturity, the odor compositions of surface and internal piles in a well-run sewage sludge compost plant were analyzed using gas chromatography–mass spectrometry with a liquid nitrogen cooling system and a portable odor detector. Approximately 80 types of substances were detected, including 2 volatile inorganic compounds, 4 sulfur organic compounds, 16 benzenes, 27 alkanes, 15 alkenes, and 19 halogenated compounds. Most pollutants were mainly produced in the mesophilic and pre-thermophilic periods. The sulfur volatile organic compounds contributed significantly to odor and should be controlled primarily. Treatment strategies should be based on the properties of sulfur organic compounds. Hydrogen sulfide, methyl mercaptan, dimethyl disulfide, dimethyl sulfide, ammonia, and carbon disulfide were selected as core indicators. Ammonia, hydrogen sulfide, carbon disulfide, dimethyl disulfide, methyl mercaptan, dimethylbenzene, phenylpropane, and isopentane were designated as concentration indicators. Benzene, m-xylene, p-xylene, dimethylbenzene, dichloromethane, toluene, chlorobenzene, trichloromethane, carbon tetrachloride, and ethylbenzene were selected as health indicators. According to the principle of odor pollution indicator selection, dimethyl disulfide was selected as an odor pollution indicator of sewage sludge composting. Monitoring dimethyl disulfide provides a highly scientific method for modeling and evaluating odor pollution from sewage sludge composting facilities.

Implications: Composting is one of the most important methods for sewage sludge treatment and improving the low organic matter content of many agricultural soils. However, odors are inevitably produced during the composting process. Understanding the production and emission patterns of odors is important for odor control and treatment. Core indicators, concentration indicators, and health indicators provide an index system to odor evaluation. An odor pollution indicator provides theoretical support for further modelling and evaluating odor pollution from sewage sludge composting facilities.

PAPER HISTORY

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Introduction

The amounts of sewage sludge generated in China have increased dramatically with the rapid development of sewage treatment plants. These wastes can cause hygiene hazards, groundwater pollution from the leaching of pollutants, and odor pollution. China is an agricultural country, and cultivated arid and semiarid soils need organic matter to ensure sustainable production (Aggelides et al., 2000). Composting is one of the most important methods for waste treatment and improvement of the low organic matter content of many agricultural soils (Alexandros et al., 2012).

Odor is inevitably produced in the composting process, and leads to high symptom prevalence, such as

affective, gastrointestinal, head-related, cardiac, cognitive, neuromuscular, and musculoskeletal symptoms (Tian et al., 2013). Odor pollution has become a hindrance in the promotion of compost technology in treating sewage sludge from industries (Anderson et al., 2009). Odor compositions are complicated and can be divided into volatile inorganic compounds (VICs) and volatile organic compounds (VOCs). VICs mainly refer to ammonia and hydrogen sulfide, and VOCs generally refer to sulfur organic compounds, alcohols, terpenes, carbonyls, aromatics, volatile fatty acids, alkanes, alkenes, ketones, and esters (Fang et al., 2015; He et al., 2012). The Chinese regulation “Emission Standards for Odor Pollutants” (GB4554-1993) regulates only eight odor pollutants, namely, ammonia, trimethylamine, hydrogen sulfide,

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methyl mercaptan, dimethyl sulfide, dimethyl disulfide, carbon disulfide, and styrene (China Environmental Protection Agency, 1993). A previous study has shown that more than 50 types of odors are produced during solid waste treatment, and most of these have low odor thresholds and can be detected by the human nose at parts per million (ppm) or even parts per billion (ppb) concentration range (Zhang et al., 2013b).

Given the limitation of technical analyses, most current odor pollution research studies focused only on one or several pollutants, such as ammonia, hydrogen sulfide, and carbon disulfide (Shen et al., 2011; Wu et al., 2010), and are thus inadequate. Odors are a result of the interactions, such as antagonism and synergism, of various stinky substances (Blazy et al., 2014; Wu et al., 2010). Olfactometry and chemical analysis are recommended and extensively used to assess odor. The dynamic olfactometry and triangle odor bag methods are the most common olfactometry approaches (Lu et al., 2015). Olfactometry methods require panelists who passed the selection test to form a group for that would smell odor gas samples. The mood state and health state of panelists influence the results. Chemical analysis that utilizes instruments has difficulties in qualitatively and quantitatively assessing many odor pollutants because of the backwardness of test analysis instruments. Therefore, several researchers proposed the selection of one pollutant to describe complex odors. For instance, *Escherichia coli* is utilized as a single metric to describe environmental microorganisms in the food safety industry, whereas *m*-xylene is employed in landfill fields as a malodor pollution indicator, with its concentration denoting the intensity of odor pollution (Lu et al., 2011).

Previous studies focused on the compositions and production of odor from laboratory-controlled composting or pilot-scale landfills using different combinations of organic wastes (Elwell et al., 2001; He et al., 2010), rather than investigating odor production and release in sewage sludge composting plants. The main purposes of sewage sludge composting are minimization and recycling of nontoxic wastes, and hazardous odor substances are inevitable by-products. Therefore, studies on odor should be based on the successful completion of waste minimization and recycling. Shen et al. (2012) found that the production of VOCs within the pile was different from emission on the pile surface. However, the authors failed to provide details of the VOCs. The parameters were set to ensure successful composting. The surface and internal odor gases of the pile were collected and analyzed qualitatively and quantitatively at the mesophilic, thermophilic, and cooling phases. In the present study, the core indicators, concentration indicators, and health indicators

were discussed. According to the principle of odor pollution indicator selection, the odor pollution indicator of sewage sludge composting was further determined, which provides theoretical support to further modeling and evaluation of odor pollution from sewage sludge composting facilities.

Materials and methods

Experimental design

The experiments were conducted in Songjiang Sewage Sludge Composting Plant in Shanghai (China). The experiment began on January 12 and complete on January 30, 2015. The plant has 24 fermentation tanks, and each tank is 30 m in length, 5 m in width, and 1.6 m in height. Two stages aeration strategy were used to accelerate the degradation process, which was set under the parameters shown in Table 1. The aeration strategy was controlled through an innovated static forced-aeration process, which is a control technology based on a combination of temperature and O₂ concentration feedback from temperature and oxygen sensors. Aeration can provide oxygen for microorganisms to release heat, making temperature increase. Meanwhile, the air transferred through the composting pile results in composting pile heat loss because that air temperature is lower than the pile temperature (Zhou et al., 2014). Compared with traditional composting, a higher aeration rate was used to strengthen water removal (Zhou et al., 2014), during which the temperature was reduced. The objectives of aeration varied during different stages of composting. At the mesophilic phase (<50°C, 0–2 days), the temperature is low, and the first stage of the aeration strategy was used to avoid heat loss and provide oxygen for accelerating temperature increasing. At the thermophilic (>50°C, 2–11 days) and cooling (11–18 days) phases, microorganisms propagated quickly and produced a large amount of water. The second stage of the aeration strategy was used to remove large amounts of water in the pile. The aeration rate of the first and second stages was approximately 1.44 and 1.93 L min⁻¹ kg⁻¹ VS (dry basis), in the range of 0.04–3 L min⁻¹ kg⁻¹ VS (Ahn et al., 2007).

Wood chips and mature compost were used as bulking agents to modify the properties of sewage sludge with high moisture content (MC), low C/N ratio, and high density. The proportion of sewage sludge, wood chips, and mature

Table 1. Aeration parameters of the experiment.

Composting stages	Hours (hr)	On/off (min)	Frequency (Hz)	Volume (m ³ /hr)
First stage	72	6/32	30	4,800
Second stage	360	10/30	40	5,900

Table 2. Properties of the raw materials and initial mixtures.

	MC (%) ^a	TOC (g/kg) ^b	TN (g/kg) ^b	TS (g/kg) ^b	VS (%) ^b
Sewage sludge	80.34	390.1	57.6	20.1	73.62
Sawdust	13.27	497.7	5.2	1.9	98.34
Mature compost	51.23	400.3	27.2	11.2	83.72
Mixture	62.96	434.5	28.3	10.6	85.21

^aWet weight basis.^bDry weight basis.

compost was 3:1:2. The weight of the pile was approximately 120 t. The MC, total organic carbon (TOC), total nitrogen (TN), total sulfur (TS), and volatile solid (VS) were measured before and after mixing. The properties of the raw materials and initial mixtures are shown in Table 2. A turning instrument was utilized to turn the compost on days 11 and 13 to ensure the uniformity of the materials. Temperature sensors were inserted at the upper, middle, and lower layers at the center axis of the experiment region. Temperature sensors can autorecord the data. The three layers were set 0.4, 0.8, and 1.2 m below the surface. A schematic of sludge composting is presented in Figure 1a. The structure of the fermentation tank is shown in Figure 1b.

Sampling and analysis

Pile surface and internal gases were obtained on days 0, 2, 5, 8, 10, 14, and 18. The gas sampling points were set 0.8 m

above the pile surface floor and 0.8 m below the pile surface floor. The middle layer can best represent odor gas in the pile (Akdeniz, et al., 2010). The surface gas sampling point was set at 0.8 m (same distance to the floor as the internal sampling point). Internal gases were obtained, followed by the surface pile gases. Air samples were collected at the static stage because the high humidity and high temperature caused difficulty in obtaining samples at the aerated stage. Solid samples (approximately 1,000 g) were taken on days 0, 2, 5, 8, 10, 14, and 18. These samples were collected from three layers at nine points and divided into two parts, with one part stored at 4°C and the other analyzed for water content and pH. Gas samples (8 L) were collected through a negative pressure sampling method and analyzed for volatile organic odor pollutants using gas chromatography–mass spectrometry (Agilent 7890A GC, 5975C MS) with liquid nitrogen cooling system (Entech 7100). The sampling apparatus (SOC-01) was manufactured by Environmental Science and Technology Development Co. Ltd. in Tianjin Company. To accomplish gas collection, a polyethylene terephthalate sampling bag was connected to the side of the inlet port of the sampling device and sealed inside the sampling device. The air within the sampling device was extracted by a vacuum at 15 L/min. To balance the pressure of the sampling device, the composting gas sample was pressed into a dedicated gas sampling bag connected directly to the sample injector. The injector tube was made by Tedlar. The odor gas was

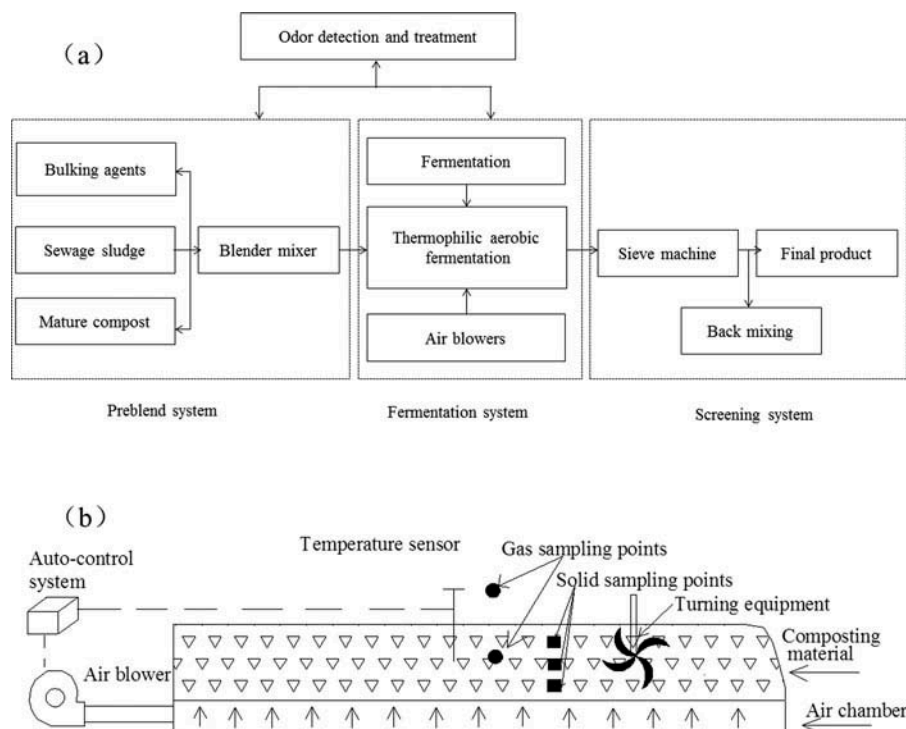


Figure 1. (a) Schematic of sewage sludge composting. (b) Structure of the composting system.

collected in 2 min at a flow of 3.5 L/min. The detailed sampling method has been described by a previous study (Zhang et al., 2013a). Connecting a hard Teflon tube to the apparatus sampling port, a tube with tiny holes ($d = 4$ mm) in the forepart was inserted into the internal pile to collect internal pile gas.

Before the formal sampling, the bag was prewashed twice with field gas. Gas samples were transported to the State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry for analysis within 24 hr after collection. The gas samples should be kept under dark conditions. A portable odor detector that uses sensors was employed to measure odor concentration, ammonia, and hydrogen sulfide for in situ measurement. The odor detector was manufactured by Korea Science Lab Center Co. Ltd. The ranges are 1–10,000 OU for odor units (OU), 1–75 ppm for H_2S , 5–150 ppm for NH_3 . The OU sensor is a semiconductor type, and H_2S and NH_3 sensors are electrochemistry types. The models are as follows: OU ($y = 1.4317e^{-0.0266x}$, $R^2 = 0.9953$), H_2S ($y = 39.477x - 11.584$, $R^2 = 0.9994$), and NH_3 ($y = 45.318x - 13.24$, $R^2 = 0.9991$).

Chemical analysis

The VOC_s were determined with the U.S. Environmental Protection Agency (EPA) TO-15 method. A 50-mL sample was concentrated in a three-stage preconcentration system (Entech 7100, USA). Oxygen and nitrogen in the sampling gas were removed in the first stage. Water and most carbon dioxide were removed in the second stage. The third stage aims to rapidly heat the gas and lead it to the gas chromatography (GC) system. The VOC_s were further focused with a capillary focusing trap for rapid injection prior to the analytical column. The trap was filled with carbon molecular sieves, which can adsorb most volatile compounds in samples by a cycle of increasing pressure and decreasing pressure. When the temperature increased to 400°C, volatile compounds were desorbed and spilt flowed into the GC system. A DB-560m column (60 m × 0.32 μm × 1.0 μm) was utilized in the GC system (Agilent 7890A). The temperature increase program was set as follows. First, the temperature was maintained at 35°C for 5 min and then increased to 150°C at a rate of 5°C/min. Second, the temperature was increased to 220°C at a rate of 15°C/min and maintained for 10 min. The temperature of the injection port was 100°C. The identification of each compound was based on its retention time and mass spectrum. Full scan and selected ion monitoring modes were utilized for quantitative determination. Target compounds were quantified through a multipoint external calibration method. To generate the calibration curves, VOC_s (TO-15, PAMs,

and sulfur-containing standards) were initially diluted with pure nitrogen to approximately 1 ppm as a primary standard mixture. This standard mixture was further dynamically diluted with pure nitrogen to 0.05, 0.1, 0.2, 0.4, and 0.8 ppm by using mass flow controllers and a mixing chamber. The carrier gas was high-purity helium (99.999%).

Statistical analysis

Correlation analyses were performed with SPSS 17 software for Windows. Correlation analysis was used to test the linear correlation relation among odor concentration, chemical classes, and special compounds. The value of r^2 was obtained with the values calculated at 95% and 99% confidence levels by the regression model. Origin 16 software was utilized to draw the diagrams.

Results and discussion

Temperature, moisture content, and pH

Microorganisms absorb small degradable organic molecules by catabolism and release large amounts of heat in the initial stage (0–2 days), which induced the temperature of the compost pile to increase significantly to 67°C on the second day at an average rate of 13.5°C/day. The maximum temperature of the experiment was more than 50°C and lasted for 7 days, which meets the requirements of the sanitation standard. The turning operation increases the free air space, so oxygen was provided to microorganisms. The metabolism of microorganisms was improved, which led to an increase in pile temperature. The pile internal temperature was close to the ambient temperature at the end of aerobic fermentation.

As one of the important parameters of composting, the moisture content (MC) of compostable materials determines whether the composting process can proceed smoothly. Moisture affects the composting process from three aspects, namely, microbial activity, potential energy of water, and O_2 mass transfer (Cai et al., 2013). In this study, the MC of the compostable material exhibited change laws that increased slightly during the mesophilic period and then decreased significantly during the thermophilic and cooling periods. Water content increased from 62.97% to 63.92% and then decreased to 47.66%. When air passed through the compostable materials after being blown from the bottom of the pile, the air temperature gradually increased, resulting in an increase in water saturation vapor pressure (Wang et al., 2011). The air then became wet as it traveled through the pile, resulting in the inability to

remove water molecules from the upper layer, and causing the compost pile to dry from the bottom (Sugni et al., 2005, Zhao et al., 2010). Water was extracted from the compostable material, and moisture was evaporated. Water in the compostable material can be divided into free water and bound water, and the main evaporated water in the early composting stage was free water. After entering the heating period, the microbial activity increased (Hassen et al., 2001), the bound water in the compostable material was released, and MC increased with the increase in temperature. As the biochemical reactions developed further, the windrow temperature and the dehydrated amount increased. The windrow dehydration process mainly occurred in the thermophilic and cooling periods (Zhou et al., 2014). The dynamic changes in temperature and MC during sewage sludge composting are shown in Figure 2a.

pH was maintained at 6.4–7.2 during the composting process, as shown in Figure 2b. pH increased from 6.4 to 7.2 in 5 days and then decreased to 6.4 at the end of composting. The increase in the compost pH is caused by the decomposition of nitrogen-containing organic matter, which leads to the accumulation of NH_3 that dissolves in moisture to form alkaline NH_4^+ (Guo et al., 2012; Wong et al., 2001). In addition, the intermediate organic acids are decomposed biologically to form gaseous carbon dioxide and water. The fatty acids formed from the decomposition of fat may also be further decomposed into small molecular acids to evaporate. The decrease in pH is mainly due to the reduced production and increased release of NH_3 and the subsequent release of hydrogen ions (Wong et al., 2001).

Dynamic changes in odor concentration

The internal and surface odor concentrations reached 664.8 and 132.5 within the first 0–1 days, respectively, because of the metabolism of the psychrophilic and mesophilic aerobic

microbes. The internal odor concentration was approximately five times higher than the surface odor concentration, as shown in Figure 3. After the easily degradable compounds were depleted, the composting process entered the cooling period and the odor concentration decreased significantly. However, the decreased magnitude of internal odor concentration was larger than that of the surface. At the end of the composting process, the internal odor concentration was close to the surface concentration. The turning operation promoted odor concentration increase, but the magnitude of the increase decreased gradually. The internal odor concentration was not equal to that of the surface, possibly because the production and release processes are two different processes (Shen et al., 2012). Odor production is the process in which anaerobic microorganisms utilize organics, whereas odor release is the process in which odor pollutants migrate through the pile. The release of odor pollutants was influenced by their inherited concentrations, production, degradation, adsorption, dissolution, and retention in free air space (He et al., 2010). The concentrations of inherited odor pollutants were related to the characteristics of the composting material, and the production, release, and degradation were affected by microbial metabolisms, odor properties, pH, temperature, and water content. Retention time is influenced by porosity, aeration, temperature, and so on. Dissolution is affected by water content and the key properties of odor, for example, boiling point, vapor pressure, and solubility. Surface odors have a significant effect on workshop staff and neighboring plant community residents, so these should be the focus of attention.

Odor compositions

Sewage sludge composting can be divided into seven classes, namely, VICs, sulfur organic compounds, benzenes, alkanes, alkenes, halogenated compounds, and others. However, the current experiment analyzed

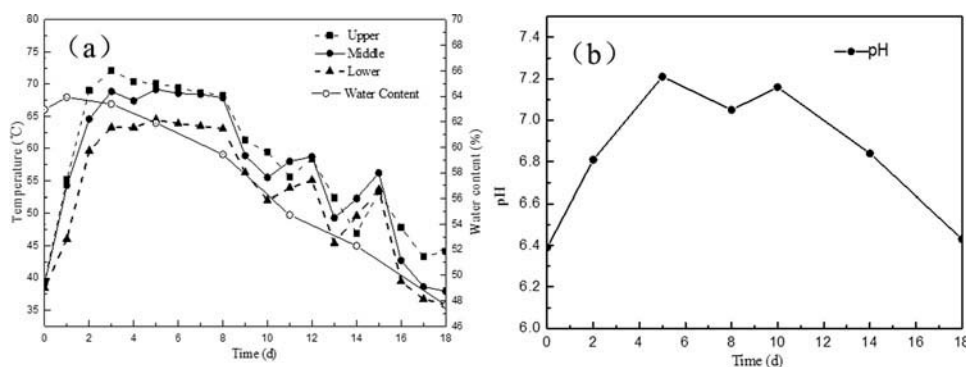


Figure 2. (a) Dynamic changes in temperature and MC during sewage sludge composting. (b) Dynamic changes in pH during sewage sludge composting.

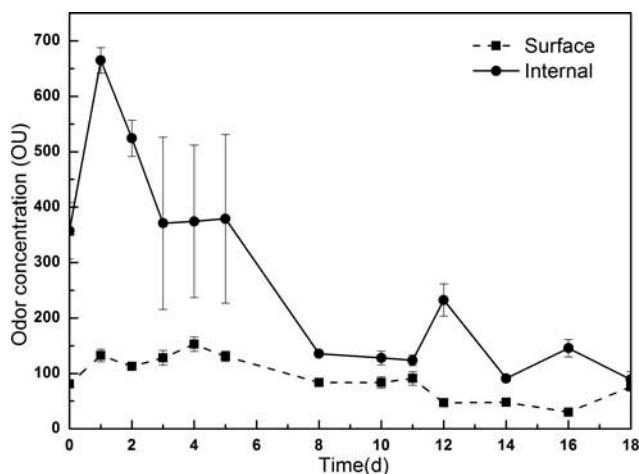


Figure 3. Dynamic changes in odor concentration during sewage sludge composting.

only the first six classes because of the limitations of the analysis technology. In total, 83 pollutants, including 2 VICs, 4 sulfur organic compounds, 16 benzenes, 27 alkanes, 15 alkenes, and 19 halogenated compounds, were detected and are shown in Table 3. VICs dominated in the produced and released odor, followed by sulfur organic compounds, benzenes, alkanes, alkenes, and halogenated compounds. The mass concentration ranges of critical odor pollutants are shown in Table 4. VICs and sulfur organic compounds were the main odor pollutants, and the sum of their mass concentration was approximately 80% that of the total odor. The mass concentration of the six classes and the odor concentrations at the mesophilic, thermophilic, and cooling periods are shown in Table 5. Ammonia emission was highly relevant to temperature (Pagans et al., 2006). A large amount of ammonia was released when pile temperature increased. The temperature reached its peak, and the oxygen content reached its lowest point (Zhang et al., 2013). Thus, abundant sulfur-containing pollutants were produced via anaerobic microorganisms. The relationship between odor group percentage and odor concentration is shown in Figure 4. The main odor pollutants in the mesophilic and thermophilic periods were VICs, sulfur organic compounds, and benzenes, whereas the main odor pollutants in the cooling period were VICs.

Pearson’s correlation coefficients between odor concentration and compound classes and between any classes were determined. Table 6 shows that odor concentration has a linear correlation with total odor, volatile organic sulfur compounds, and benzenes. Odor concentration has no linear correlation with the other compound classes. Volatile organic sulfur compounds also have an evident linear correlation with

Table 3. Odor composition during sewage sludge composting.

	Species	Pollutants
Volatile inorganic compounds	2	Hydrogen sulfide, ammonia
Sulfur organic compounds	4	Methyl mercaptan, dimethyl sulfide, dimethyl disulfide, carbon disulfide
Benzenes	16	Benzene, toluene, ethylbenzene, dimethylbenzene, <i>p</i> -xylene, isopropylbenzene, propylbenzene, <i>m</i> -ethyltoluene, <i>m</i> -xylene, 1,3,5-trimethylbenzene, <i>o</i> -ethyltoluene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, 1,2-diethylbenzene, 1,4-diethylbenzene, styrene
Alkanes	27	Isobutane, butane, isopentane, pentane, 2,2-dimethyl-butane, cyclopentane, 2,3-dimethyl-butane, 2-methyl-pentane, 3-methyl-pentane, <i>n</i> -hexane, methyl-cyclopentane, 2,4-dimethyl-pentane, cyclohexane, 2-methyl-hexane, 2,3-dimethyl-pentane, 3-methyl-hexane, 2,2,4-trimethyl-pentane, heptane, methyl-cyclohexane, 2,3,4-trimethyl-pentane, 2-methyl-heptane, 3-methyl-heptane, <i>n</i> -octane, nonane, decane, undecane, dodecane
Alkenes	15	1-Butene, 1,3-butadiene, <i>t</i> -2-butene, <i>c</i> -2-butene, 3-methyl-1-butene, 1-pentene, isoprene, <i>t</i> -2-pentene, <i>c</i> -2-pentene, 2-methyl-2-butene, cyclopentene, 4-methyl-1-pentene, 1-hexene, <i>t</i> -2-hexene, <i>c</i> -2-hexene
Halogenated compounds	19	Freon-12, dichloromethane, Freon-114, vinyl-chloride, chloroethane, freon 11, 1,1-dichloro-ethene, 1,1-dichloroethane, Freon-113, 1,1-dichloro-ethane, 1,2-dichloro-ethene (E), chloroform, 1,2-dichloroethane, carbon tetrachloride, 1,2-dichloro-propane, trichloroethane, chlorobenzene, 1,2-dichloro-benzene, 1,3-dichloro-benzene

Table 4. Concentration range of typical odor gas during sewage sludge composting.

	Critical odor pollutants	Concentration range (mg/m ³)
Volatile inorganic compounds	Ammonia	10 – 150
	Hydrogen sulfide	2 – 40
	Carbon disulfide	0 – 15
Sulfur organic compounds	Dimethyl disulfide	0 – 12
	Dimethyl sulfide	0 – 13
	Methyl mercaptan	0 – 0.2
Benzenes	Toluene	0 – 10
	Ethylbenzene	0 – 1.5
	Dimethylbenzene	0 – 5
Alkanes	Isopentane	0 – 0.7
	Undecane	0 – 0.2
	Butane	0 – 0.4
Alkenes	1-Butene	0 – 1.3
	<i>t</i> -2-Butene	0 – 8
	1-Pentene	0 – 1.6
Halogenated compounds	Freon-11	0 – 0.1
	Carbon tetrachloride	0 – 0.1
	Trichloroethylene	0 – 0.8

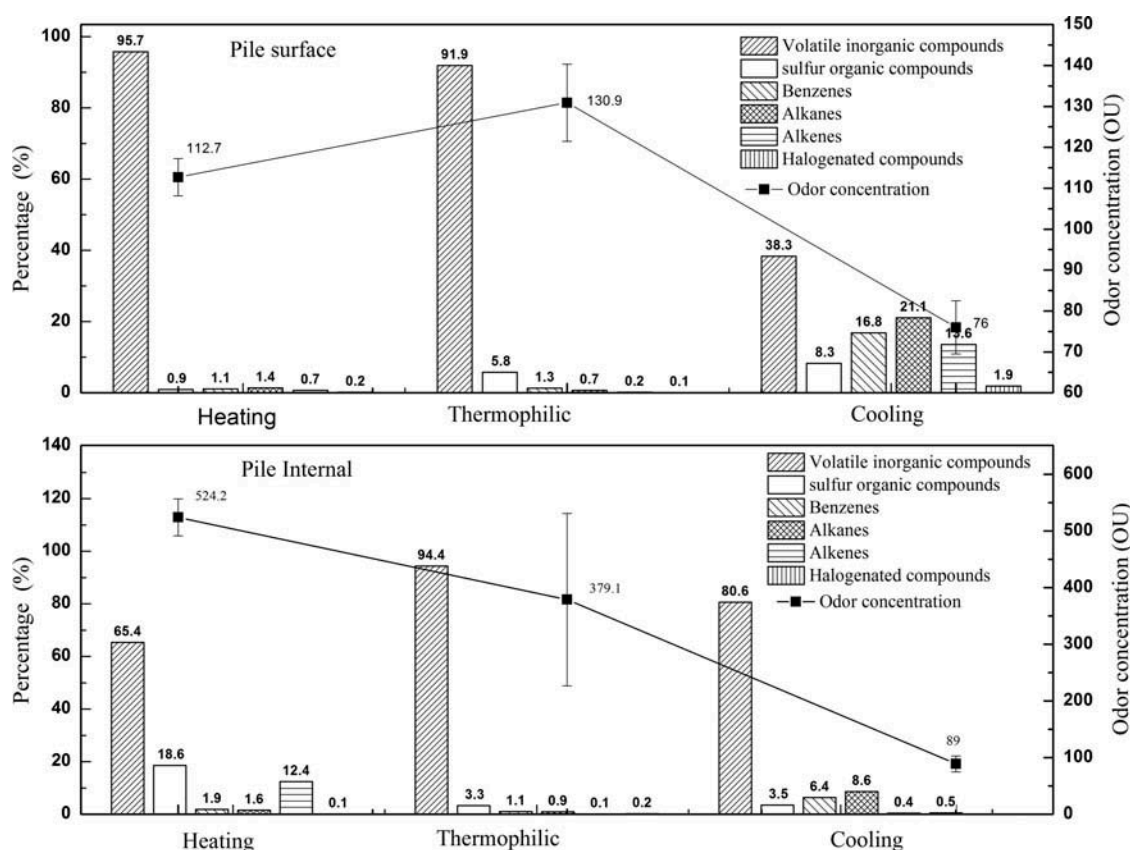
benzenes, alkanes, and alkenes. A previous study about odor on the landfill working face in four seasons has shown that the correlation of odor concentration and concentration of different chemical classes is

Table 5. Concentration of each compound class at different stages (unit: $\mu\text{g}/\text{m}^3$).

	Day 2		Day 5		Day 18	
	Internal	Surface	Internal	Surface	Internal	Surface
Volatile inorganic compounds	123,688	53,793	97,799	96,476	13,063	1,258
Sulfur organic compounds	35,142	515	3,420	6,095	574	272
Benzenes	3,611	609	1,159	1,371	1,031	552
Alkanes	3,107	787	932	687	1,396	694
Alkenes	23,365	403	125	187	61	448
Halogenated compounds	98	116	136	77	86	60
Total	189,010	56,222	103,572	104,893	16,211	3,283
Odor concentration	524.2	112.7	379.1	130.9	89	76

affected by the season. In spring, sulfur compounds, aldehydes, ketones, and alkenes have linear correlations with odor concentration. Esters, ethers, and alcohols are the major odor contributors in summer, and sulfur compounds are the major odor contributors in autumn

and winter (Lu et al., 2015). Carlos's study on VOCs in landfill odor emissions showed that odor concentration has no positive linear correlation with any compound class or any single compound (Carlos et al., 2013). Di's study demonstrated that odor concentration has a

**Figure 4.** Percentage of each class of compounds in relation to odor concentration.**Table 6.** Correlation analysis between odor concentration and emission of each class.

	Odor concentration	VICs	Sulfur organic compounds	Benzenes	Alkanes	Alkenes	Halogenated compounds	Total
Odor concentration	1	0.804	0.828*	0.841*	0.768	0.795	0.502	0.881*
Volatile inorganic compounds		1	0.690	0.719	0.487	0.579	0.449	0.961*
Sulfur organic compounds			1	0.987**	0.931**	0.985**	0.052	0.863**
Benzenes				1	0.936*	0.956*	0.082	0.878*
Alkanes					1	0.956**	0.079	0.699
Alkenes						1	0.033	0.782
Halogenated compounds							1	0.379
Total								1

*Denotes $p < 0.05$ significant relation.

**Denotes $p < 0.01$ extremely significantly correlation.

significant relationship with the total chemical concentration of sulfur and nitrogen compounds in food waste anaerobic fermentation (Di et al., 2013). These studies show that no consensus on odor concentration and odor pollutants mass concentration of odor pollutants has been achieved.

Core, concentration, and health indicators

By calculating the dilution multiple of 14 samples, the counts of the core indicators were determined. The dilution multiple is the ratio of chemical mass concentration to its odor threshold value. The dilution multiple elucidates the actual influence of odors on the environment. The core indicators (more than seven samples whose dilution multiples were higher than 1) were hydrogen sulfide, methyl mercaptan, dimethyl disulfide, dimethyl sulfide, ammonia, and carbon disulfide. The odor threshold values were obtained from the study results of EPA and Japan's Environmental Protection Agency (Nagata, 2003; EPA, 1992). The detection methods for the odor threshold values used in the United States and Japan are chemical analysis and triangle odor bag methods, respectively. The analysis method employed in China is similar to that used in Japan. Thus, this study adopted Japan's results when no equal value between the United States and Japan was obtained. The odor threshold values of sewage sludge composting odor pollutants are shown in Table 7. The core indicators were the main contributors to olfactory nuisance and should be considered.

The mass concentration indicators (more than seven samples whose mass concentrations are higher than 100 $\mu\text{g}/\text{m}^3$) were ammonia, hydrogen sulfide, carbon disulfide, dimethyl disulfide, methyl mercaptan, dimethylbenzene, phenylpropane, and isopentane.

The health indicators, which were listed in the *Directory of National Environmental Health Risks of China*, were toluene, chlorobenzene, trichloromethane, carbon tetrachloride, and ethylbenzene (China Environmental Protection Agency, 2009). Most of the

health indicators were benzenes. Although the production of benzenes was low, benzenes are harmful to human health. Thus, benzenes should not be ignored.

The core, concentration, and health indicators are shown in Table 8.

Selection of the odor pollution indicator

Sulfur-containing compounds are produced by bacteria through the reduction of sulfate and S-containing amino acids (Higgins et al., 2006; Zhu et al., 1999). Ammonia and volatile amines are produced by the decarboxylation and hydrolysis of amino acids (Spoelstra, 1980; Tsai et al., 2008; Zhu et al., 1999). Aldehydes are produced by the imperfect degradation of organics (Bonnin et al., 1990). When discussing the odor pollution indicator for sewage sludge composting treatments, that the alternative compounds are produced via biochemical activities or from intrinsic contaminations is taken into account. Most odors are produced because of microbe biochemical degradation of organic compounds under anaerobic conditions. For representation, the pollution indicator should be produced by biochemical activities.

The odor pollution indicator was selected by following several principles. The odor pollution indicator should be a representative compound in the vicinity of composting grounds, and should have a relatively low odor threshold, such that people are sensitive to it. The odor pollution indicator can also represent the dynamics of the composting process.

Despite its extensive emission and low odor threshold, hydrogen sulfide fails to represent the odor in the composting process because its main source is sulfate reduction rather than amino acid decomposition, whereas the majority of odor compounds with low odor thresholds are produced during the biochemical reactions of microbes (Zhu et al., 1999). Organic sulfur compounds resulting from anaerobic microbe activities in the anaerobic condition are listed as the second main emissions group in composting and have low odor thresholds. Therefore, volatile

Table 7. Odor threshold values of different compounds during sewage sludge composting (unit: ppm).

Pollutants	Molecular formula	Odor thresholds	Pollutants	Molecular formula	Odor thresholds
Ammonia	NH_3	1.5	Benzene	C_6H_6	2.7
Hydrogen sulfide	H_2S	0.00041	Toluene	$\text{C}_6\text{H}_5\text{CH}_3$	0.33
Methyl mercaptan	$(\text{CH}_3)\text{SH}$	0.00007	Ethylbenzene	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$	0.17
Carbon disulfide	CS_2	0.21	Styrene	$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$	0.035
Dimethyl disulfide	$(\text{CH}_3)_2\text{S}_2$	0.0022	1,3,5-Trimethylbenzene	$\text{C}_6\text{H}_3(\text{CH}_3)_3$	0.17
Propylene	$\text{CH}_2=\text{CHCH}_3$	13	1,2,4-Trimethylbenzene	$\text{C}_6\text{H}_3(\text{CH}_3)_3$	0.12
Isobutene	C_4H_8	10	<i>p</i> -Xylene	$\text{C}_6\text{H}_4(\text{CH}_3)_2$	0.058
Cyclohexane	C_6H_{12}	2.5	Isopropylbenzene	$\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2$	0.0084
Heptane	C_7H_{16}	0.67	Undecane	$\text{C}_{11}\text{H}_{24}$	0.87
<i>n</i> -Hexane	C_6H_{14}	1.5	Dodecane	$\text{C}_{12}\text{H}_{26}$	0.11
<i>n</i> -Octane	C_8H_{18}	1.7			

Note. During calculation, volume concentration should be converted to mass concentration with the formula of mass concentration ($\mu\text{g}/\text{m}^3$) = volume concentration (ppb) \times relative molecular mass/22.4.

Table 8. Core, concentration, and health indicators during sewage sludge composting.

	Core indicators	Concentration indicators	Health indicators
1	Hydrogen sulfide	Ammonia	Benzene
2	Methyl mercaptan	Hydrogen sulfide	<i>m</i> -Xylene
3	Dimethyl disulfide	Carbon disulfide	<i>p</i> -Xylene
4	Dimethyl sulfide	Dimethyl disulfide	Dimethylbenzene
5	Ammonia	Methyl mercaptan	Dichloromethane
6	Carbon disulfide	Toluene	Toluene
7		Dimethylbenzene	Chlorobenzene
8		Propylbenzene	Trichloromethane
9		Isopentane	Carbon tetrachloride
10			Ethylbenzene

Note. The table shows that the contribution degree of the core indicators and the production concentration of the concentration indicators decreased.

organic sulfur compounds are most likely the odor pollution indicators.

Air samples were collected 1 km away from the composting plant in an upwind direction and tested as the background value. No odor source existed around the sampling point. The results showed that dimethyl sulfide, dimethyl disulfide, and carbon disulfide are representative compounds in the vicinity. Correlative relationships were observed in the concentrations of dimethyl sulfide, dimethyl disulfide, and carbon disulfide, as shown in Tables 9 and 10, where $p < 0.05$ indicates a significant correlative relationship. Dimethyl sulfide and carbon disulfide have a significant relationship with dimethyl disulfide. Thus, dimethyl disulfide was selected as the odor pollution indicator for sewage sludge composting. The concentration of dimethyl disulfide could represent the degree of odor pollution. The dynamic changes in dimethyl disulfide are shown in Figure 5. The initial dimethyl disulfide concentration inside the pile and on the pile surface was 12,182 and 5386 $\mu\text{g}/\text{m}^3$, respectively. It increased to 12,278 and 6135 $\mu\text{g}/\text{m}^3$ on the second day but decreased afterward. At the end of the composting, the dimethyl disulfide concentration inside the pile and on the pile surface decreased to 281 and 120 $\mu\text{g}/\text{m}^3$, respectively. The emission of odor increased as the composting process ensued, the temperature increased, and the activities of the microbes became extensive, which resulted in an anaerobic condition and thus the emission of organic sulfur compounds as the products of anaerobic microbe activities (Delgado et al., 2012). With the decrease in temperature and available organic compounds for microbes after the thermospheric phase, the production of organic sulfur compounds also decreased.

Conclusion

Approximately 80 types of pollutants, including 2 VICs, 4 sulfur organic compounds, 16 benzenes, 27 alkanes, 15 alkenes, and 19 halogenated compounds, were detected

Table 9. Correlation analysis for dimethyl sulfide, carbon disulfide, and dimethyl disulfide inside the pile.

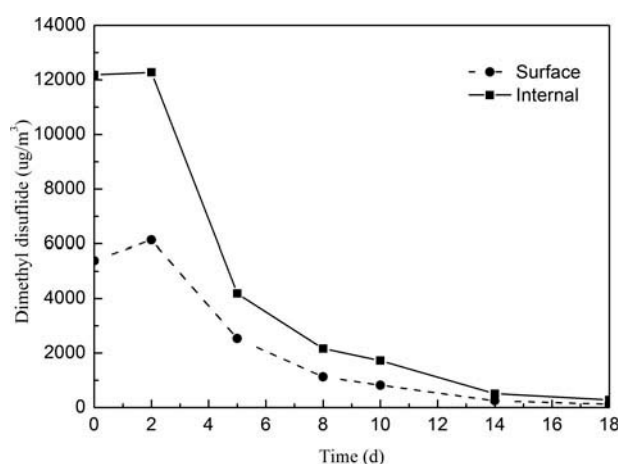
	Dimethyl sulfide	Carbon disulfide	Dimethyl disulfide
Dimethyl sulfide	1	0.568	0.932*
Carbon disulfide		1	0.808*
Dimethyl disulfide			1

*Denotes $p < 0.05$ significant relation.

Table 10. Correlation analysis for dimethyl sulfide, carbon disulfide, and dimethyl disulfide on the surface of the pile.

	Dimethyl sulfide	Carbon disulfide	Dimethyl disulfide
Dimethyl sulfide	1	0.906	0.788*
Carbon disulfide		1	0.973*
Dimethyl disulfide			1

*Denotes $p < 0.05$ significant relation.

**Figure 5.** Dynamic changes of the dimethyl disulfide during sewage sludge composting.

during the sewage sludge composting process. Most pollutants were mainly produced in the mesophilic and pre-thermophilic periods. The concentrations of pollutants and the odor of the internal pile were higher than those of the surface pile; in other words, production was not equal to release. Inorganic and sulfur organic compounds accounted for approximately 80% of the total odor pollutants. Sulfur VOCs contributed significantly to odor and should be controlled primarily.

Hydrogen sulfide, methyl mercaptan, dimethyl disulfide, dimethyl sulfide, ammonia, and carbon disulfide were selected as core indicators. Ammonia, hydrogen sulfide, carbon disulfide, dimethyl disulfide, methyl mercaptan, dimethylbenzene, phenylpropane, and isopentane were selected as concentration indicators. Benzene, *m*-xylene, *p*-xylene, dimethylbenzene, dichloromethane, toluene, chlorobenzene, trichloromethane, carbon tetrachloride, and ethylbenzene were designated as health indicators. According to the principle of odor pollution

indicator selection, dimethyl disulfide was selected as an odor pollution indicator of sewage sludge composting and its concentration represented the degree of odor pollution.

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