



## Characterization and control of odorous gases at a landfill site: A case study in Hangzhou, China

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### ABSTRACT

Municipal solid waste (MSW) landfills are one of the major sources of offensive odors potentially creating annoyance in adjacent communities. At the end of May 2007, an odor pollution incident occurred at the Tianziling landfill site, Hangzhou, China, where the residents lodged complaints about the intense odor from the landfill, which drew a significant attention from the government. In this study, ambient air monitoring was conducted at the Tianziling landfill site. The main odor composition of the gas samples collected on June 1st 2007 and the reduction of various odorous gases from the samples collected on June 1st 2009 due to the applied odor control techniques were determined using gas chromatography-mass spectrometry (GC-MS). In addition, variations of primary odorous gaseous ( $\text{NH}_3$  and  $\text{H}_2\text{S}$ ) concentrations at different locations in the landfill site from July 2007 to June 2009 were also investigated by using classical spectrophotometric methods. Results showed that a total of 68 volatile compounds were identified among which  $\text{H}_2\text{S}$  (56.58–579.84  $\mu\text{g}/\text{m}^3$ ) and  $\text{NH}_3$  (520–4460  $\mu\text{g}/\text{m}^3$ ) were the notable odor components contributing to 4.47–10.92% and 83.91–93.94% of total concentrations, respectively. Similar spatial and temporal shifts of  $\text{H}_2\text{S}$  and  $\text{NH}_3$  concentrations were observed and were significantly affected by environmental factors including temperature, air pressure and wind direction. Odor pollution was worse when high temperature, high humidity, low air pressure, and southeast, northeast or east wind appeared. Moreover, the environmental sampling points of the dumping area and the leachate treatment plant were found to be the main odor sources at the Tianziling landfill site. The odor control technologies used in this project had a good mitigating effect on the primary odorous compounds. This study provides long-term valuable information concerning the characteristics and control of odors at landfill sites in a long run.

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### 1. Introduction

Municipal solid waste (MSW) landfills are a potential source of offensive odors that can create annoyance in urban areas. Although these odorous gases generated by anaerobic decomposition of wastes account for less than 1% of the total emissions, they exert a disproportionately adverse effect on the environment because of their unique physical and chemical properties (Allen et al., 1997; Dincer et al., 2006; Zou et al., 2003; Fernandez-Martinez et al., 2001). As a result, odor problems have become a growing concern during the last few decades for both MSW operators and communities located close to MSW landfills (Sarkar et al., 2003; Dincer et al., 2006).

On the Keller's postulation, all landfill gases contain the following six classes of compounds: saturated and unsaturated hydrocarbons, acidic hydrocarbons and organic alcohols, aromatic hydrocarbons, halogenated compounds, sulfur compounds such as carbon disulfide

and mercaptans, and inorganic compounds (Allen et al., 1997). Over the last few decades, attentions to characterization of volatile organic compounds (VOCs) in landfill gas have been paid by many scientists since VOCs have detrimental effects on human and animal health (psychological stress, irritation of mucous membranes, long-term toxic reactions and causing cancer) and these air pollutants have been known as precursors of photochemical smog formation and the cause of uncomfortable odor problems (Atkinson, 2000; Belpomme et al., 2007; Gallego et al., 2008; Hutter et al., 2006; Irigaray et al., 2007; Liang and Liao, 2007; Peng et al., 2006; Wolkoff and Nielsen, 2001). Allen et al. (1997) examined the trace VOCs in landfill gas at seven UK waste disposal facilities by using gas chromatography-mass spectrometry (GC-MS) and identified over 140 compounds, of which more than 90 were common to all seven sites. James and Stack (1997) investigated the ambient VOCs at landfill sites with and without a leachate pool. Thirty-three VOCs were identified with 11 of the most hazardous compounds quantified. Schuetz et al. (2003) determined non-methane organic compounds (NMOCs) at two different areas at a French landfill site and 37 NMOCs were quantified. Subsequently, 47 NMOCs in the landfill gas samples

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including primarily alkanes, alkenes, halogenated hydrocarbons and aromatic hydrocarbons were quantified (Scheutz et al., 2008). Bogner et al. (2010) measured the concentrations and mitigation of nonmethane hydrocarbon (NMHC) emissions from a biocover placed above an existing intermediate soil cover at a Florida landfill. Dincer et al. (2006) identified and quantified 53 odorous gases at five sampling sites emitted from a municipal landfill in the city of Izmir, Turkey. Chiriac et al. (2009) studied the dispersion of 16 VOCs released from a MSW landfill over a period of one year. Zou et al., 2003 found that the VOC emission from the Datianshan landfill site in Guangzhou was quite serious with the number of VOCs released from that site varying between 38 and 60 from winter to summer seasons (Zou et al., 2003).

Odor perception itself is a complex event understandably because it is affected by many factors such as physiology, weather patterns, subjective perception, inurement and interaction among different odors (Firestein, 2001; Noble et al., 2001; Davoli et al., 2003). Environmental factors influencing odor emission were studied by some researchers including seasonal changes and weather conditions (Zou et al., 2003; Capelli et al., 2008; Gallego et al., 2008). However, few studies have been conducted on the environmental behavior of inorganic odorous gases. And there's little published information on primary odor levels associated with seasonal variations in landfill sites affected by many influencing factors mentioned above.

Landfilling is a popular disposal method for MSW in China (Zou et al., 2003). Statistical data showed that the total generation of MSW was approximately  $1.52 \times 10^8$  ton in 2007 with an annual growth rate of 8–10%. Hangzhou is the central city of Zhejiang Province with a population of 6.6 million, which has a world famous tourist attraction, known as the West Lake, visited by tens of thousands of tourists from all over the world every year. The annoying odors released to the atmosphere from the Tianziling landfill site, the largest one in Hangzhou, has the potential to decrease the quality of life in Hangzhou and cause possibly negative consequences on human health and welfare (Park et al., 2009; Saral et al., 2009). Unfortunately, there are limited studies on landfills, especially the odor data concerning landfill sites, in Hangzhou, as well as in China as a whole.

The main objectives of this research were to (1) identify the composition of the primary odorous gases in the Tianziling landfill site, which may pose health concerns to nearby neighborhoods; (2) investigate the seasonal and horizontal variations of the primary odors with respect to environmental influencing factors; and (3) examine the effect of odor control engineering technologies on the attenuation of primary odors concentrations. The results of the present study may provide long-term valuable information concerning the characteristics of primary odorous gases in landfill sites.

## 2. Materials and methods

### 2.1. Site description and odor problem

The Tianziling landfill site located to the north of Hangzhou City (120.2E, 30.3N) is the first standardized valley-style sanitary landfill in China, which has been in operation from 1991 to 2007 before the second landfill site was commissioned ever since with a designed filling capacity of  $2.2 \times 10^7$  m<sup>3</sup>. The site does not accept medical, industrial and hazardous waste. The capacity of landfill is 2000 ~ 4000 t/d of domestic wastes, which accounts for more than 60% of the municipal solid waste in Hangzhou. A wastewater treatment plant with a capacity of 1500 t/d is simultaneously operated for leachate treatment. However, near the landfill site was a residential area, Shitang, which was apparently susceptible to the landfill gas because an odor complaint was recorded at the end of May 2007 that drew significant attention from the government.

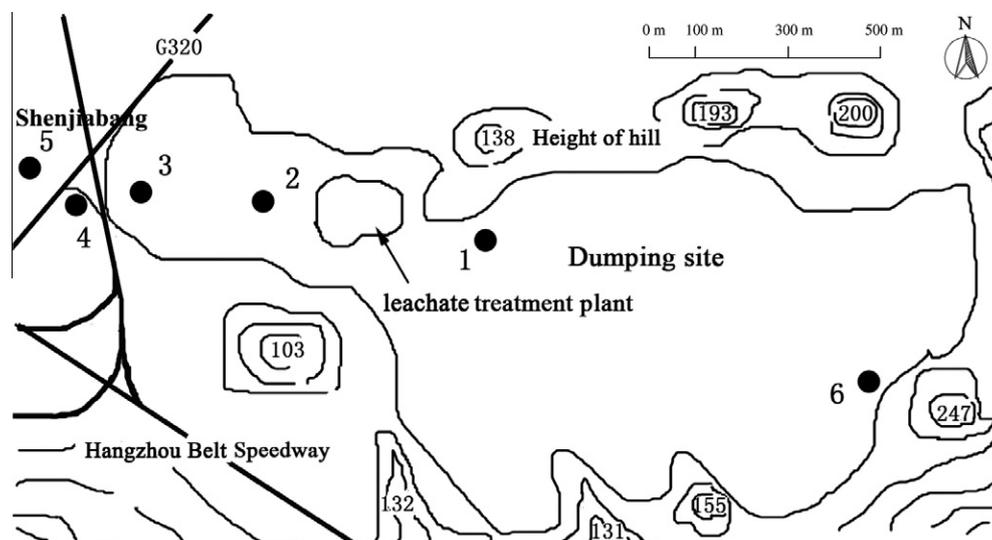
### 2.2. Odor control engineering

The conventional landfilling and cover practices at this site were carried out according to the "Municipal Solid Waste Landfill Technical Specifications" (CJJ17-2004, China). After the odor pollution incident occurred, a comprehensive odor control engineering project has been carried out since July 2007 to especially rein in the two main sources described early. In the dumping area, the cover soil thickness was increased and the High density polyethylene (HDPE) membrane was used to prevent direct exposure of fresh wastes to the ambient air. Meanwhile, the landfill gas was collected for electricity generation. In the leachate treatment plant, the treatment facilities such as the regulating reservoir and aeration tank were all covered with the odorous gas collected and removed by biofiltration.

### 2.3. Sampling and analytical methods

The gas sampling was conducted at 6 points (Fig. 1) immediately after the odor pollution incident occurred (on June 1st, 2007). The average air temperature was about 21 C and the relative humidity was 70–72%. Point 1 and 2 were selected to represent the odors from the dumping area of the second municipal waste landfill site and the landfill leachate treatment plant, respectively. The other 4 points were the spots in or adjacent to the two odor sources, among which point 3 was the administration office area, point 4 was the factory boundary, point 5 was the residential area near the landfill possibly affected by the odors, and point 6 was the 165 platform belonging to the first dumping site which had gone out of service. All six sampling points selected to represent different odor levels in the ambient air were arranged into a straight line. Sampling was carried out following recommendations described in the European Standard EN 13725. Gas samples in triplicate were collected into 1L Nalophan<sup>®</sup> bags using a special sampler based on the "lung" principle. Samples were transported to the laboratory and analyzed within 24 h after collection by SPME and GC-MS. After the primary odors were identified, long-term monitoring of NH<sub>3</sub> and H<sub>2</sub>S at four sampling points (point 1–4) was performed from July 2007 to June 2009. Sampling was conducted one day a week at two hour intervals and the NH<sub>3</sub> and H<sub>2</sub>S concentrations were evaluated by the spectrophotometric method. The weather data (including average temperature, relative humidity and air pressure) during the third quarter of 2007 to the second quarter of 2009 (2007-3rd to 2009-2nd) were also collected in the sampling days (Table 1). After 2-year operation of odor control engineering, the field sampling was conducted again at 6 points on June 1st, 2009 and were analyzed by SPME (Davoli et al., 2003) and GC-MS (Dincer et al., 2006), in order to evaluate the effectiveness of the odor control technologies.

The gas samples obtained on June 1st, 2007 and June 1st, 2009 were analyzed using a gas chromatography (GC) (Agilent 6890N, Agilent, USA) equipped with a mass selective detector (Agilent 5973 inert MSD, Agilent, USA) and a thermal desorber (Tekmar, Aerotrap 6000, USA) as described by Dincer et al., 2006, with some running conditions adjusted. Odor samples were desorbed for 5 min at 250 C using helium flowing at the rate of 35 mL/min. The internal trap temperature during sample desorption was 30 C. The trap was desorbed for 5 min at 250 C. The carrier gas was helium provided at 0.8 mL/min. The split ratio was 1:50. The inlet temperature was 250 C. The temperature program for odors was: initial oven temperature 30 C, hold for 2 min, then 30–125 C at 10 C/min, hold for 30 min. The samples obtained from long-term monitoring of NH<sub>3</sub> and H<sub>2</sub>S at four sampling points were analyzed by the spectrophotometric method. The gaseous components were transferred into aqueous solution by bubbling the gases in a solution of sulfuric acid and zinc acetate, respectively. NH<sub>3</sub>



**Fig. 1.** The sampling points in Tianziling landfill (point 1: dumping area, point 2: leachate treatment plant, point 3: office area, point 4: factory boundary, point 5: residential area, point 6: first dumping site).

**Table 1**

Different environmental factors and odor occurrence number during the quarters 2007-3rd to 2009-2nd at office area.

Quarter	Environmental factors			Odor occurrence number		
	Temperature (°C)	Humidity (%)	Pressure (Kpa)	No odor	Slight odor	Strong odor
2007-3rd	28.4 ± 2.8	68.3 ± 3.1	100.3 ± 0.5	349	65	14
2007-4th	13.3 ± 5.1	62.5 ± 1.9	102.2 ± 0.4	349	48	3
2008-1st	5.2 ± 4.2	61.6 ± 4.5	102.4 ± 0.4	400	25	3
2008-2nd	21.6 ± 4.9	66.6 ± 4.1	101.7 ± 0.5	465	72	14
2008-3rd	28.5 ± 1.9	72.0 ± 3.8	100.9 ± 0.3	494	46	12
2008-4th	13.3 ± 5.6	67.5 ± 0.0	102.2 ± 0.6	349	17	0
2009-1st	7.2 ± 2.9	63.4 ± 4.9	102.4 ± 0.7	343	57	6
2009-2nd	20.4 ± 5.8	69.9 ± 3.2	101.0 ± 0.7	532	13	27

concentration was evaluated by the spectrophotometric method using Nessler reagent. H<sub>2</sub>S concentration was monitored by using the Methylene-blue colorimetric method.

Sensory databases, which can be built to measure the scale of annoyance and the potential sources of emissions, are one method designed for odor control in a targeted area (Gallego et al., 2008). In order to obtain significant data about the origin of episodes over regular 24 h periods, special organizations such as social participation must be employed, which, in this case, consisted of obtaining sensory and occurrence data, and the collectors of NH<sub>3</sub> and H<sub>2</sub>S during episodes when medium and high odor intensity and nuisance were perceived. The database was built using questionnaires, monitoring, and recording. The workers of the Tianziling landfill site completed questionnaires individually, including the date of the odor episode, the times when the odor episode began and ended, the location of the odor, and a description of the odor and its intensity. The questionnaires required recording the odor occurrence every 2 h using the following scale: no odor, slight odor, and strong odor. Simultaneously, the wind directions were monitored and recorded for determining the relationship between odor emissions and wind directions.

#### 2.4. Statistical analysis

Data were analyzed and compared statistically by the Tukey's *t*-test at the 5% level using SPSS 11.5 (SPSS for Windows, Version 11.5, USA).

### 3. Results and discussion

#### 3.1. Characterization of odorous gases in the landfill site during odor pollution incident

On June 1st, 2007, a total of 68 odorous gases species were identified. The qualitative and quantitative results of analytes of interest are reported in Table 2. Little variation in the type and number of odors was observed among different sampling points. The measured odorous gases included inorganic compounds (e.g., ammonia and hydrogen sulfide), halogenated compounds (e.g., chlorobenzene and dichloroethylene), aromatics (e.g., benzene, toluene and naphthalene), volatile fatty acids (VFAs) (e.g., formic acid and acetic acid), aldehydes (e.g., propanal and butanal), ketones (e.g., cyclohexanone), esters (e.g., butyl formate), hydrocarbon (e.g., hexane and octane), other sulfur and nitrogen compounds (e.g., dimethyl sulfide, methyl mercaptan and pyridine). These results were similar to those obtained by other researchers (Allen et al., 1997; Zou et al., 2003; Dincer et al., 2006).

Among all these compounds, NH<sub>3</sub> and H<sub>2</sub>S were dominant and their concentrations were in the range of 520.00–4020.00 µg/m<sup>3</sup> and 56.58–514.52 µg/m<sup>3</sup>, respectively. The average concentration of NH<sub>3</sub> at the factory boundary was 2020.00 µg/m<sup>3</sup>, which was above the secondary standard value (1500 µg/m<sup>3</sup>) stated in "The Emission Standards for Odor Pollutants in China (GB14554-93)". The average concentration of H<sub>2</sub>S at the factory boundary was 178.46 µg/m<sup>3</sup>, which was almost three times the secondary standard value (60 µg/m<sup>3</sup>). In order to identify specific markers of odor

**Table 2**The mean and S.D. values of odor concentrations ( $\mu\text{g}/\text{m}^3$ ) in the emissions from 6 sampling points at Tianziling landfill site on June 1st, 2007.

	Dumping area	Leachate treatment plant	Office area	Factory boundary	Residential area	165 platform
Ammonia	3960.00 ± 157.10	4020.00 ± 212.50	2320.00 ± 98.30	2020.00 ± 83.40	520.00 ± 46.15	3780.00 ± 175.84
Hydrogen sulfide	514.52 ± 23.41	488.24 ± 17.50	205.08 ± 9.26	178.46 ± 5.74	56.58 ± 2.78	179.92 ± 25.14
Chlorobenzene	1.28 ± 0.06	0.44 ± 0.01	0.76 ± 0.03	0.68 ± 0.02	0.22 ± 0.01	0.42 ± 0.03
1,2-Dichlorobenzene	0.06 ± 0.01	0.02 ± 0.001	0.06 ± 0.01	0.02 ± 0.001	0.02 ± 0.001	0.02 ± 0.001
1,3-Dichlorobenzene	0.08 ± 0.01	0.04 ± 0.001	0.10 ± 0.01	0.04 ± 0.001	0.02 ± 0.001	0.04 ± 0.001
1,4-Dichlorobenzene	1.40 ± 0.02	0.08 ± 0.01	0.04 ± 0.001	0.04 ± 0.001	0.04 ± 0.001	0.04 ± 0.001
1,2,4-Trichlorobenzene	0.02 ± 0.001	0.04 ± 0.001	0.02 ± 0.001	N.D.	N.D.	N.D.
1,2,4-Tribromobenzene	0.06 ± 0.01	0.10 ± 0.01	0.02 ± 0.001	N.D.	N.D.	0.04 ± 0.01
Chlorinated-dibenzo-pyran	0.62 ± 0.02	0.56 ± 0.01	0.38 ± 0.01	0.24 ± 0.01	N.D.	0.32 ± 0.01
1,2-Dichloroethane	0.44 ± 0.01	0.28 ± 0.03	0.22 ± 0.01	0.22 ± 0.02	0.14 ± 0.01	0.20 ± 0.01
1,2-Dichloropropane	13.92 ± 0.33	5.88 ± 0.21	4.06 ± 0.17	3.38 ± 0.08	1.04 ± 0.02	2.98 ± 0.05
1,1,1-Trichloroethane	4.98 ± 0.20	4.62 ± 0.19	4.02 ± 0.10	3.22 ± 0.07	1.92 ± 0.04	3.24 ± 0.09
1,1,2-Trichloroethane	0.62 ± 0.02	0.24 ± 0.01	0.26 ± 0.01	0.06 ± 0.002	0.08 ± 0.01	0.06 ± 0.01
1,1,2,2-Tetrachloroethane	0.92 ± 0.02	0.08 ± 0.01	0.46 ± 0.01	0.32 ± 0.01	0.12 ± 0.02	0.44 ± 0.01
1,2,3-Trichloro propane	0.04 ± 0.001	0.04 ± 0.001	0.04 ± 0.001	0.04 ± 0.001	0.04 ± 0.001	0.06 ± 0.01
Bromoform	0.44 ± 0.01	0.22 ± 0.01	0.38 ± 0.01	0.26 ± 0.01	0.02 ± 0.001	0.22 ± 0.01
Dichloroethylene	65.18 ± 2.98	43.92 ± 1.51	38.52 ± 1.56	26.52 ± 0.41	8.06 ± 0.03	25.82 ± 0.09
Trichloroethene	3.90 ± 0.12	3.48 ± 0.10	3.12 ± 0.08	2.38 ± 0.05	4.42 ± 0.01	2.02 ± 0.01
Tetrachloroethene	13.90 ± 0.50	8.32 ± 0.17	6.06 ± 0.21	4.72 ± 0.16	0.38 ± 0.01	4.32 ± 0.15
cis-1,4-Dichloro-2-butene	0.08 ± 0.01	0.10 ± 0.01	0.02 ± 0.001	0.04 ± 0.001	0.02 ± 0.001	0.10 ± 0.01
trans-1,4-Dichloro-2-butene	0.06 ± 0.002	0.04 ± 0.001	0.04 ± 0.001	0.08 ± 0.003	0.02 ± 0.001	0.06 ± 0.001
Dichloro acetaldehyde	0.06 ± 0.002	0.10 ± 0.01	0.08 ± 0.01	0.06 ± 0.002	0.04 ± 0.001	0.06 ± 0.001
Hydrogenated hydrocarbon	0.70 ± 0.03	0.52 ± 0.02	0.38 ± 0.01	0.46 ± 0.01	0.02 ± 0.001	0.22 ± 0.01
2,4,6-Trichloroaniline	0.02 ± 0.001	0.10 ± 0.01	0.04 ± 0.001	0.06 ± 0.002	0.06 ± 0.001	0.04 ± 0.001
Benzene	3.82 ± 0.11	0.42 ± 0.01	0.52 ± 0.01	0.06 ± 0.001	0.04 ± 0.001	0.22 ± 0.01
Toluene	60.04 ± 2.77	16.82 ± 0.62	4.12 ± 0.02	3.30 ± 0.14	1.92 ± 0.06	3.12 ± 0.12
Ethylbenzene	23.30 ± 1.10	10.46 ± 0.04	1.54 ± 0.05	1.38 ± 0.02	0.84 ± 0.01	1.62 ± 0.08
Xylenes	0.08 ± 0.01	0.02 ± 0.001	0.10 ± 0.001	0.02 ± 0.001	0.02 ± 0.001	0.02 ± 0.001
<i>o,m</i> -Xylene	0.58 ± 0.01	0.16 ± 0.01	0.08 ± 0.01	0.06 ± 0.01	0.04 ± 0.001	0.02 ± 0.001
<i>p</i> -Xylene	0.06 ± 0.001	0.02 ± 0.001	0.01 ± 0.001	0.01 ± 0.001	0.01 ± 0.001	0.01 ± 0.001
Isopropylbenzene	2.10 ± 0.01	2.06 ± 0.01	1.48 ± 0.01	1.38 ± 0.01	1.02 ± 0.01	1.14 ± 0.01
Naphthalene	0.08 ± 0.001	0.02 ± 0.001	N.D.	N.D.	N.D.	N.D.
Methyl mercaptan	5.30 ± 0.22	2.64 ± 0.09	2.22 ± 0.08	2.04 ± 0.04	1.56 ± 0.06	1.96 ± 0.07
Dimethyl sulfide	18.52 ± 0.87	15.92 ± 0.64	9.30 ± 0.39	10.46 ± 0.41	4.64 ± 0.02	11.12 ± 0.48
Dimethyl disulfide	0.04 ± 0.001	0.004 ± 0.001	0.02 ± 0.001	0.004 ± 0.001	0.002 ± 0.001	0.01 ± 0.001
Ethyl mercaptan	0.48 ± 0.02	0.22 ± 0.01	0.32 ± 0.01	0.04 ± 0.001	0.04 ± 0.001	0.06 ± 0.001
Carbon disulfide	0.66 ± 0.03	0.38 ± 0.02	0.26 ± 0.01	0.32 ± 0.01	0.04 ± 0.001	0.38 ± 0.01
Formic acid	2.78 ± 0.12	2.44 ± 0.10	0.32 ± 0.01	0.52 ± 0.01	0.24 ± 0.01	0.62 ± 0.03
Acetic acid	2.22 ± 0.08	1.10 ± 0.05	0.46 ± 0.02	0.18 ± 0.01	0.12 ± 0.01	0.22 ± 0.01
Propionic acid	0.30 ± 0.01	0.28 ± 0.01	0.22 ± 0.01	0.28 ± 0.01	0.30 ± 0.01	0.30 ± 0.01
Butyric acid	0.18 ± 0.01	0.02 ± 0.001	0.02 ± 0.001	0.02 ± 0.001	0.02 ± 0.001	0.02 ± 0.001
Isobutyric acid	0.42 ± 0.02	0.26 ± 0.01	0.22 ± 0.01	0.06 ± 0.002	0.04 ± 0.001	0.04 ± 0.001
Valeric acid	0.10 ± 0.01	0.02 ± 0.001	0.02 ± 0.001	0.06 ± 0.002	0.02 ± 0.001	0.06 ± 0.002
Isovaleric acid	0.12 ± 0.004	0.04 ± 0.002	0.04 ± 0.001	0.04 ± 0.001	0.02 ± 0.001	0.04 ± 0.001
Caproic acid	1.08 ± 0.05	0.34 ± 0.01	0.02 ± 0.001	0.10 ± 0.003	0.02 ± 0.001	0.22 ± 0.01
Heptanoic acid	0.02 ± 0.001	0.06 ± 0.002	0.06 ± 0.001	0.10 ± 0.01	0.10 ± 0.004	0.06 ± 0.001
Propanal	0.38 ± 0.01	0.46 ± 0.02	0.16 ± 0.01	0.14 ± 0.01	0.04 ± 0.001	0.18 ± 0.01
Butanal	0.66 ± 0.03	0.36 ± 0.01	0.06 ± 0.002	0.04 ± 0.001	0.02 ± 0.001	0.04 ± 0.001
Heptanal	0.12 ± 0.01	0.10 ± 0.01	0.04 ± 0.001	0.06 ± 0.001	0.06 ± 0.001	0.04 ± 0.001
Nonanal	0.44 ± 0.02	0.48 ± 0.02	0.62 ± 0.03	0.42 ± 0.01	0.22 ± 0.01	0.44 ± 0.01
Decanal	0.28 ± 0.01	0.10 ± 0.01	0.06 ± 0.001	0.04 ± 0.001	0.02 ± 0.001	0.04 ± 0.001
Acrolein	0.32 ± 0.02	0.04 ± 0.001	0.10 ± 0.002	0.12 ± 0.01	0.06 ± 0.002	0.16 ± 0.01
2-Butanone	0.42 ± 0.02	0.28 ± 0.01	0.38 ± 0.01	0.24 ± 0.01	0.02 ± 0.001	0.18 ± 0.01
Cyclohexanone	0.66 ± 0.03	0.08 ± 0.004	0.22 ± 0.01	0.18 ± 0.003	0.02 ± 0.001	0.14 ± 0.001
4-Methyl-2-pentanone	0.22 ± 0.01	0.22 ± 0.01	0.18 ± 0.01	0.02 ± 0.001	0.06 ± 0.001	0.02 ± 0.001
Butyl formate	0.10 ± 0.01	0.02 ± 0.001	0.02 ± 0.001	0.02 ± 0.001	0.04 ± 0.001	0.02 ± 0.001
Butyl acetate	0.08 ± 0.002	0.14 ± 0.01	0.14 ± 0.01	0.10 ± 0.01	0.08 ± 0.004	0.10 ± 0.01
Methyl propionate	0.38 ± 0.02	0.04 ± 0.001	0.04 ± 0.001	0.02 ± 0.001	0.02 ± 0.001	0.02 ± 0.001
Vinyl acetate	0.22 ± 0.01	0.22 ± 0.01	0.10 ± 0.01	0.06 ± 0.002	0.12 ± 0.01	0.06 ± 0.001
Hexane	0.06 ± 0.002	0.06 ± 0.002	0.04 ± 0.001	0.04 ± 0.001	0.02 ± 0.001	0.04 ± 0.001
Heptane	0.06 ± 0.001	0.02 ± 0.001	0.02 ± 0.001	0.02 ± 0.001	0.12 ± 0.001	0.02 ± 0.001
Octane	0.08 ± 0.004	0.04 ± 0.001	0.08 ± 0.003	0.02 ± 0.001	0.02 ± 0.001	0.02 ± 0.001
1-Nitro butane	0.02 ± 0.001	0.08 ± 0.004	0.02 ± 0.001	0.02 ± 0.001	N.D.	0.02 ± 0.001
Pinene	0.04 ± 0.001	0.02 ± 0.001	0.04 ± 0.001	0.002 ± 0.001	N.D.	0.02 ± 0.001
Camphene	0.06 ± 0.001	0.02 ± 0.001	0.02 ± 0.001	0.04 ± 0.001	N.D.	0.04 ± 0.001
Acenaphthylene	0.04 ± 0.001	0.02 ± 0.001	0.02 ± 0.001	0.02 ± 0.001	0.02 ± 0.001	0.04 ± 0.001
Acrylonitrile	0.78 ± 0.04	0.38 ± 0.03	0.32 ± 0.01	0.22 ± 0.01	0.10 ± 0.001	0.18 ± 0.01
Pyridine	0.38 ± 0.02	0.16 ± 0.01	0.02 ± 0.01	N.D.	N.D.	N.D.

N.D.: not detected.

sources, the concentration data were grouped into classes representative of the most odor-impacting compounds by summing up some concentration data presented in Table 3. For all sampling

points, the most abundant gas was  $\text{NH}_3$  (84.05–93.94% of total odorous gases concentrations) followed by  $\text{H}_2\text{S}$  (4.47–10.92%).  $\text{NH}_3$  has an unpleasant pungent odor even at extremely low

**Table 3**

Percent contributions of groups of compounds to the emission from 6 sampling points at Tianziling landfill site.

	Dumping area	Wastewater treatment plant	Office area	Factory boundary	Residential area	165 platform
Ammonia	84.05	86.74	88.95	89.24	86.47	93.94
Hydrogen sulfide	10.92	10.53	7.86	7.88	9.41	4.47
Halogenated compounds	2.29	1.48	2.25	1.87	2.11	1.01
Aromatics	1.91	0.65	0.30	0.27	0.65	0.15
Other sulfur compounds	0.53	0.41	0.46	0.57	1.04	0.34
Volatile fatty acid	0.15	0.10	0.05	0.06	0.15	0.04
Aldehydes	0.05	0.03	0.04	0.04	0.07	0.02
Ketones	0.03	0.01	0.03	0.02	0.02	0.01
Esters	0.02	0.01	0.01	0.01	0.04	0.00
Hydrocarbon	0.02	0.02	0.02	0.03	0.03	0.01
Other nitrogen compounds	0.02	0.01	0.01	0.01	0.02	0.00

concentrations with the threshold of 500–1000  $\mu\text{g}/\text{m}^3$ . The levels of  $\text{NH}_3$  were found to be above the odor threshold at all sampling points, especially at the leachate treatment plant. Often present at high levels, the  $\text{NH}_3$  gas was also described as a toxic constituent of landfill leachate (Clément and Merlin, 1995).  $\text{H}_2\text{S}$  has a distinctive “rotten egg” smell at low concentrations and its reported threshold ranges from 1.5–150  $\mu\text{g}/\text{m}^3$ . Exposure to concentrations above 150  $\text{mg}/\text{m}^3$  quickly paralyzes human olfactory senses, which is considered immediately hazardous to life and health (Flynn, 1998; Lee et al., 2006). Therefore,  $\text{H}_2\text{S}$  is the head compound with an important factor of odor of 10 within the main 25 compounds concerning the odorant impact listed by USEPA. Since Tianziling landfill site treats domestic wastes, ever accepted wastewater treatment sludges and does not accept medical, industrial and hazardous waste, the formation of  $\text{H}_2\text{S}$  probably results from the biological conversion of sulfate from gypsum-rich soils and landfilled wastewater treatment sludges by sulfate-reducing bacteria (SRB) which can utilize dissolved sulfate as an electron acceptor (Lee et al., 2006). This may be the reason that the concentrations of  $\text{H}_2\text{S}$  and other sulfur compounds were higher at dumping area than that at leachate treatment plant. Recent studies have also shown that  $\text{H}_2\text{S}$  is an important trace component of landfill gases (Kim et al., 2005; Shon et al., 2005; Lee et al., 2006). The presence of  $\text{NH}_3$  and  $\text{H}_2\text{S}$  has several implications for landfill owners and operators with respect to human health risk, the control of their emission is therefore important for protecting public health and welfare.

Twenty-two halogenated compounds were detected in the samples and they contributed to 1.01–2.29% of total odorous gases concentrations (Table 2 and 3). The average concentration ranges of some chlorinated species such as 1,2-dichloropropane, 1,1,1-trichloroethane, dichloroethylene, trichloroethene, and tetrachloroethene were 1.04–13.92  $\mu\text{g}/\text{m}^3$ , 1.92–4.98  $\mu\text{g}/\text{m}^3$ , 8.06–65.18  $\mu\text{g}/\text{m}^3$ , 0.42–3.90  $\mu\text{g}/\text{m}^3$ , and 0.38–13.90  $\mu\text{g}/\text{m}^3$ , respectively, which were relatively higher than other halogenated compounds. The presence of chlorinated organics in the landfill might be related to the solvents that are widely used as cleaners and disinfectants (Dincer et al., 2006). The manufactured trichloroethene is used for metal cleaning and tetrachloroethene is commonly present in textiles, dry cleaning workplaces, and chemical manufacturing units. This would suggest that both tetrachloroethene and trichloroethene were probably not derived from domestic refuse. Degradation of tetrachloroethene via anaerobic hydrogen–halogen substitution can lead to the formation of trichloroethene, dichloroethene and chloroethene (Allen et al., 1997). The results from our study seemed to support this theory as a relatively high level of tetrachloroethene was observed, accompanied by elevated levels of both trichloroethene and dichloroethene.

High levels of aromatics were observed at several sampling points such as the dumping area and leachate treatment plant. Among these aromatics, toluene (1.92–60.04  $\mu\text{g}/\text{m}^3$ ) had the

highest average concentrations followed by ethylbenzene (0.84–23.30  $\mu\text{g}/\text{m}^3$ ) and benzene (0.04–3.82  $\mu\text{g}/\text{m}^3$ ). The benzene-to-toluene (B:T) ratio has been commonly used as an indicator of combustion engine emissions (Zou et al., 2003; Dincer et al., 2006). Studies on vehicular exhaust generally report a B:T ratio of 0.5 (Sweet and Vertmette, 1992; Scheff and Wadden, 1993). As we all know, the odor compounds are produced during the waste degradation processes and their levels in landfill gas are thus dependent upon both the waste composition and the stage reached in the decomposition process. In this study, the B:T ratios ranged from 0.02 to 0.12 in the landfill air, indicating that the waste emissions were a dominant toluene source and the presence of higher amounts of toluene than benzene in landfills was comparable to that in urban areas having rich vehicular exhausts. This is in agreement with the findings obtained by Dincer et al. (2006) at the Izmir landfill.

Some other sulfur compounds, VFAs, aldehydes, ketones, esters, hydrocarbon, and other nitrogen compounds were also identified and quantified in this study but their concentrations were relatively low except for dimethyl sulfide (4.64–18.52  $\mu\text{g}/\text{m}^3$ ) and methyl mercaptan (1.56–5.30  $\mu\text{g}/\text{m}^3$ ). The odor threshold values for dimethyl sulfide and methyl mercaptan has been reported to be 2.77  $\mu\text{g}/\text{m}^3$  and 2.14  $\mu\text{g}/\text{m}^3$ , respectively (Lee et al., 2006). Dimethyl sulfide was found to be above the odor threshold at all sampling points, while methyl mercaptan only at several locations. However, the average concentration of methyl mercaptan at the factory boundary was 2.04  $\mu\text{g}/\text{m}^3$ , which was below the primary standard value (4.0  $\mu\text{g}/\text{m}^3$ ) stated in “the Emission Standards for Odor Pollutants in China (GB14554-93)”. Moreover, the average concentrations of the sulfur compounds such as dimethyl sulfide, dimethyl disulfide and carbon disulfide were all lower than the limits listed in the above Standards (GB14554-93).

Based on the data in Table 2, the total odor concentrations at different sampling points were calculated, which were 4711, 4635, 2608, 2264, 601, and 4024  $\mu\text{g}/\text{m}^3$  at point 1 through 6, respectively. It was found that the odor concentration levels at the dumping area and leachate treatment plant were much higher than the rest while the odor composition was almost similar. And the odor concentrations at point 3–5 were declining along with the distance to point 2. Results showed that the dumping area was the main odor source, but the odor concentration, especially  $\text{NH}_3$ , from the leachate treatment plant was quite high. In addition, surface diffusion from the dumping area and leachate treatment plant was probably the source of ambient odors in the Tianziling landfill site.

### 3.2. Effect on the attenuation of odor concentrations by odor control engineering

The  $\text{NH}_3$  and  $\text{H}_2\text{S}$  concentrations at four representative sampling points (the dumping area, the office area and the factory boundary from 2007 to 2009, and the leachate treatment plant

from 2007 to 2008 due to the plugging engineering) are shown in Fig. 2 and Fig. 3, respectively.

As shown in Fig. 2a and b, the average concentrations of NH<sub>3</sub> ranged from 24 to 213 µg/m<sup>3</sup> at the dumping area, while

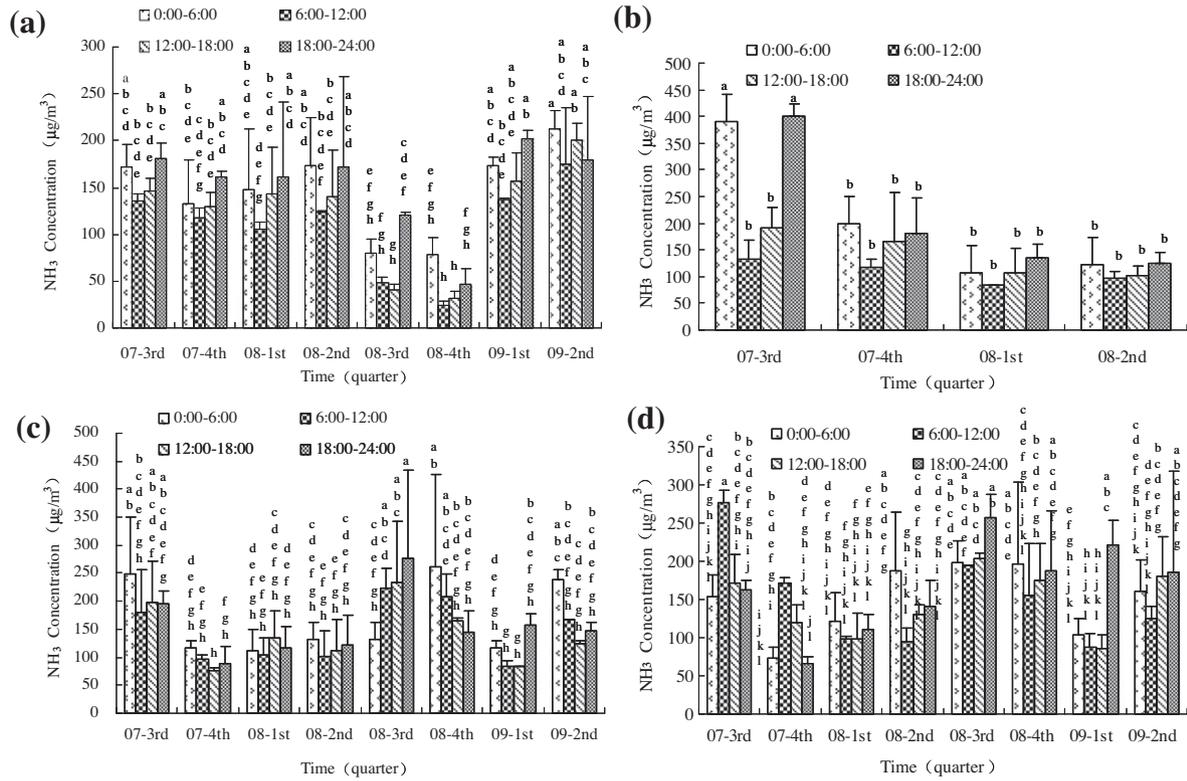


Fig. 2. NH<sub>3</sub> concentration profile during the quarters from 2007-3rd (07-3rd) to 2009-2nd (09-2nd) at following areas: (a) dumping area; (b) leachate treatment plant, (c) office area; (d) factory boundary. Error bars are standard errors of at least three independent experiments.

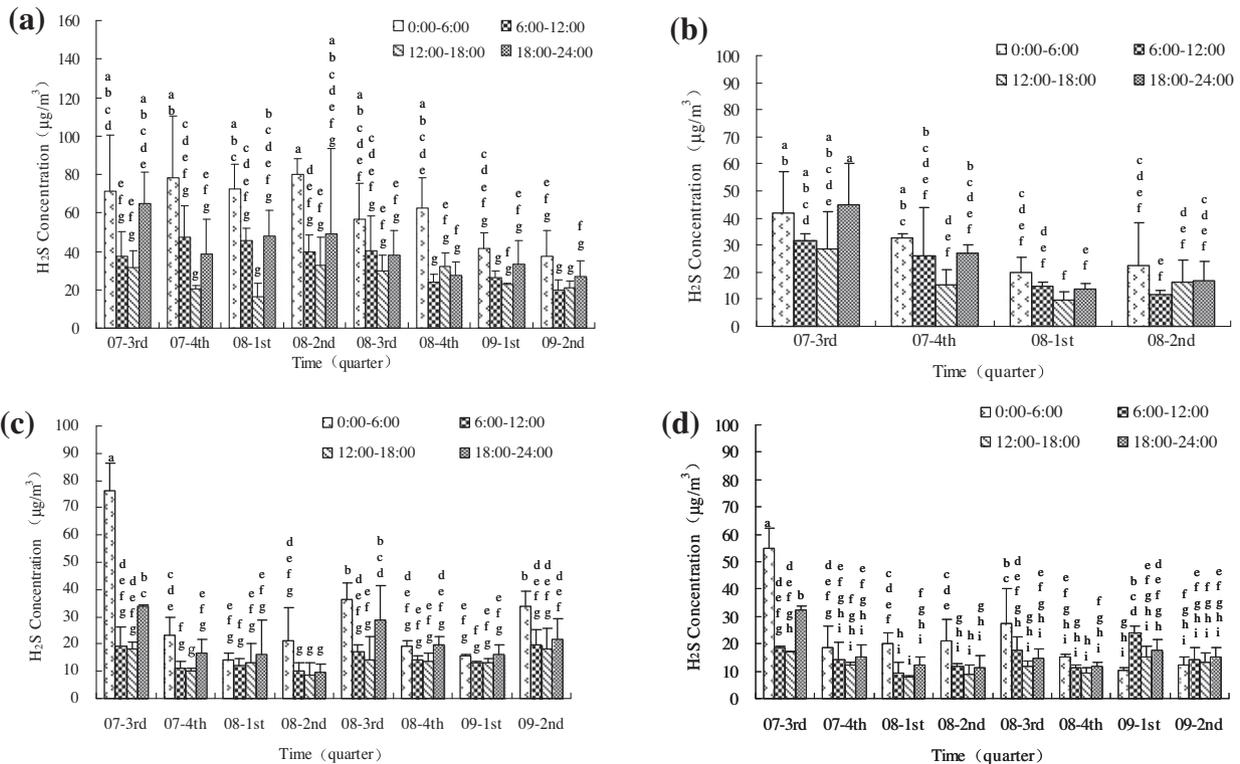


Fig. 3. H<sub>2</sub>S concentration profile during the quarters from 2007-3rd (07-3rd) to 2009-2nd (09-2nd) at following areas: (a) dumping area; (b) leachate treatment plant; (c) office area; (d) factory boundary. Error bars are standard errors of at least three independent experiments.

83–401  $\mu\text{g}/\text{m}^3$  at the leachate treatment plant. The latter was relatively higher mainly due to the high ammonia–nitrogen ( $\text{NH}_4^+\text{-N}$ ) concentration in the leachate. Our previous study showed that the  $\text{NH}_4^+\text{-N}$  concentration of raw leachate from the Tianziling landfill was  $2158 \pm 266 \text{ mg}/\text{L}$  (Wu et al., 2009). The presence of

$\text{NH}_4^+\text{-N}$  in the leachate is one of the big problems normally faced by landfill operators (Aziz et al., 2004). James and Stack's study (1997) had demonstrated that an action, designed to prevent the release of potentially polluting wastewaters to the aquatic environment, has actually adversely impacted air quality. The average

**Table 4**

The mean values ( $\mu\text{g}/\text{m}^3$ ) and removal efficiencies (%) of odor concentrations in the emissions from 6 sampling points at Tianziling landfill site on June 1st, 2009.

	Dumping area	Leachate treatment plant	Office area	Factory boundary	Residential area	165 platform
Chlorobenzene	0.59 (53.9)	0.23 (47.7)	0.41 (46.1)	0.35 (48.5)	0.11 (50.0)	0.26 (38.1)
1,2-Dichlorobenzene	0.04 (33.3)	0.02 (0.0)	0.03 (50.0)	0.01 (50.0)	0.03	0.01 (50.0)
1,3-Dichlorobenzene	0.06 (25.0)	0.02 (50.0)	0.04 (60.0)	0.03 (25.0)	0.03	0.02 (50.0)
1,4-Dichlorobenzene	0.71 (49.3)	0.04 (50.0)	0.09	0.02 (50.0)	0.03 (25.0)	0.03 (25.0)
1,2,4-Trichlorobenzene	0.02 (0.0)	0.02 (50.0)	0.01 (50.0)	0.009	N.D.	N.D.
1,2,4-Tribromobenzene	0.03 (50.0)	0.06 (40.0)	0.02 (0.0)	0.01	N.D.	0.03 (25.0)
Chlorinated-dibenzo-pyran	0.35 (43.6)	0.28 (50.0)	0.19 (50.0)	0.13 (45.8)	N.D.	0.16 (50.0)
1,2-Dichloroethane	0.26 (40.9)	0.14 (50.0)	0.13 (40.9)	0.2 (9.1)	0.09 (35.7)	0.13 (35.0)
1,2-Dichloropropane	6.69 (52.0)	2.92 (50.3)	2.24 (44.8)	1.69 (50.0)	0.59 (43.3)	1.53 (48.7)
1,1,1-Trichloroethane	2.65 (46.8)	2.23 (51.7)	2.39 (40.6)	1.75 (45.7)	1.06 (44.8)	1.75 (46.0)
1,1,2-Trichloroethane	0.31 (50.0)	0.12 (50.0)	0.16 (38.5)	0.03 (50.0)	0.06 (25.0)	0.04 (33.3)
1,1,2,2-Tetrachloroethane	0.44 (52.2)	0.05 (37.5)	0.28 (39.1)	0.16 (50.0)	0.08 (33.3)	0.26 (40.9)
1,2,3-Trichloro propane	0.03 (25.0)	0.01 (75.0)	0.02 (50.0)	0.02 (50.0)	0.03 (25.0)	0.03 (50.0)
Bromoform	0.28 (36.4)	0.11 (50.0)	0.19 (50.0)	0.16 (38.5)	0.02 (0.0)	0.15 (31.8)
Dichloroethylene	33.65 (48.4)	21.95 (50.0)	20.68 (46.3)	14.23 (46.3)	4.12 (48.9)	13.54 (47.6)
Trichloroethene	2.45 (37.2)	1.75 (49.7)	1.65 (47.1)	1.31 (45.0)	0.29 (31.0)	1.11 (45.1)
Tetrachloroethene	6.67 (52.0)	4.13 (50.4)	3.23 (46.7)	2.65 (43.9)	0.22 (42.1)	2.31 (46.5)
Cis-1,4-Dichloro-2-butene	0.03 (62.5)	0.05 (50.0)	0.03	0.03 (25.0)	0.03	0.06 (40.0)
Trans-1,4-Dichloro-2-butene	0.05 (16.7)	0.02 (50.0)	0.02 (50.0)	0.03 (62.5)	0.02 (0.0)	0.04 (33.3)
Dichloro acetaldehyde	0.02 (66.7)	0.04 (60.0)	0.04 (50.0)	0.03 (50.0)	0.03 (25.0)	0.03 (50.0)
Hydrogenated hydrocarbon	0.33 (52.9)	0.25 (51.9)	0.16 (57.9)	0.29 (37.0)	0.02 (0.0)	0.13 (40.9)
2,4,6-Trichloroaniline	0.03	0.04 (60.0)	0.02 (50.0)	0.03 (50.0)	0.03 (50.0)	0.04 (0.0)
Benzene	1.97 (48.4)	0.22 (47.6)	0.35 (32.7)	0.09	0.04 (0.0)	0.15 (31.8)
Toluene	29.65 (50.6)	8.39 (50.1)	2.34 (43.2)	1.91 (42.1)	1.09 (43.2)	1.71 (45.2)
Ethylbenzene	11.98 (48.6)	5.23 (50.0)	0.85 (44.8)	0.74 (46.4)	0.56 (33.3)	0.85 (47.5)
Xylenes	0.05 (37.5)	0.02 (0.0)	0.03 (70.0)	0.03	0.03	0.03
<i>o,m</i> -Xylene	0.23 (60.3)	0.08 (50.0)	0.05 (37.5)	0.03 (50.0)	0.03 (25.0)	0.03
<i>p</i> -Xylene	0.03 (50.0)	0.04	0.012	0.009 (10.0)	0.006 (40.0)	0.004 (60.0)
Isopropylbenzene	1.21 (42.4)	1.12 (45.6)	0.85 (42.6)	0.71 (48.6)	0.59 (42.2)	0.61 (46.5)
Naphthalene	0.05 (37.5)	0.02 (0.0)	0.02	0.01	N.D.	N.D.
Methyl mercaptan	2.56 (51.7)	1.54 (41.7)	1.32 (40.5)	1.32 (35.3)	0.86 (44.9)	1.12 (42.9)
Dimethyl sulfide	9.32 (49.7)	7.98 (49.9)	4.65 (50.0)	5.02 (52.0)	2.78 (40.1)	6.12 (45.0)
Dimethyl disulfide	0.018 (55.0)	0.003 (25.0)	0.014 (30.0)	0.004 (0.0)	0.002 (0.0)	0.005 (50.0)
Ethyl mercaptan	0.25 (47.9)	0.13 (40.9)	0.19 (40.6)	0.03 (25.0)	0.02 (50.0)	0.05 (16.7)
Carbon disulfide	0.27 (59.1)	0.15 (60.5)	0.16 (38.5)	0.19 (40.6)	0.02 (50.0)	0.22 (42.1)
Formic acid	1.16 (58.3)	1.23 (49.6)	0.23 (28.1)	0.25 (51.9)	0.13 (45.8)	0.35 (43.6)
Acetic acid	1.03 (53.6)	0.53 (51.8)	0.28 (39.1)	0.12 (33.3)	0.08 (33.3)	0.13 (41.0)
Propionic acid	0.16 (46.7)	0.14 (50.0)	0.16 (27.3)	0.17 (39.3)	0.19 (36.7)	0.19 (36.7)
Butyric acid	0.07 (61.1)	0.02 (0.0)	0.03	0.03	0.03	0.03
Isobutyric acid	0.15 (64.3)	0.13 (50.0)	0.13 (40.9)	0.04 (33.3)	0.03 (25.0)	0.03 (25.0)
Valeric acid	0.05 (50.0)	0.01 (50.0)	0.02 (0.0)	0.02 (66.7)	0.03	0.04 (33.3)
Isovaleric acid	0.07 (41.7)	0.02 (50.0)	0.03 (25.0)	0.03 (25.0)	0.02 (0.0)	0.03 (25.0)
Caproic acid	0.46 (57.4)	0.16 (52.9)	0.05	0.04 (60.0)	0.02 (0.0)	0.16 (27.3)
Heptanoic acid	0.03	0.03 (50.0)	0.02 (66.7)	0.03 (70.0)	0.07 (30.0)	0.03 (50.0)
Propanal	0.19 (50.0)	0.16 (65.2)	0.12 (25.0)	0.08 (42.9)	0.02 (50.0)	0.12 (33.3)
Butanal	0.27 (59.1)	0.16 (55.6)	0.03 (50.0)	0.03 (25.0)	0.02 (0.0)	0.03 (25.0)
Heptanal	0.08 (33.3)	0.05 (50.0)	0.05	0.04 (33.3)	0.03 (50.0)	0.03 (25.0)
Nonanal	0.22 (50.0)	0.21 (56.3)	0.21 (66.1)	0.23 (45.2)	0.13 (40.9)	0.25 (43.2)
Decanal	0.18 (35.7)	0.05 (50.0)	0.05 (16.7)	0.03 (25.0)	0.02 (0.0)	0.03 (25.0)
Acrolein	0.16 (50.0)	0.02 (50.0)	0.05 (50.0)	0.05 (58.3)	0.04 (33.3)	0.11 (31.3)
2-Butanone	0.21 (50.0)	0.15 (46.4)	0.21 (44.7)	0.13 (45.8)	0.02 (0.0)	0.09 (50.0)
Cyclohexanone	0.41 (37.9)	0.04 (50.0)	0.15 (31.8)	0.11 (38.9)	0.03	0.09 (35.7)
4-Methyl-2-pentanone	0.13 (40.9)	0.12 (45.5)	0.11 (38.9)	0.02 (0.0)	0.03 (50.0)	0.02 (0.0)
Butyl formate	0.06 (40.0)	0.01 (50.0)	0.01 (50.0)	0.01 (50.0)	0.02 (50.0)	0.01 (50.0)
Butyl acetate	0.04 (50.0)	0.06 (57.1)	0.05 (64.3)	0.05 (50.0)	0.05 (37.5)	0.06 (40.0)
Methyl propionate	0.21 (44.7)	0.02 (50.0)	0.05	0.03	0.02 (0.0)	0.02 (0.0)
Vinyl acetate	0.16 (27.3)	0.11 (50.0)	0.09 (10.0)	0.03 (50.0)	0.07 (41.7)	0.03 (50.0)
Hexane	0.04 (33.3)	0.03 (50.0)	0.02 (50.0)	0.02 (50.0)	0.02 (0.0)	0.05
Heptane	0.05 (16.7)	0.01 (50.0)	0.03	0.02 (0.0)	0.06 (50.0)	0.03
Octane	0.05 (37.5)	0.02 (50.0)	0.03 (62.5)	0.02 (0.0)	0.02 (0.0)	0.03
1-Nitro butane	0.02 (0.0)	0.03 (62.5)	0.01 (50.0)	0.01 (50.0)	N.D.	0.01 (50.0)
Pinene	0.02 (50.0)	0.012 (40.0)	0.01 (75.0)	0.001 (50.0)	N.D.	0.01 (50.0)
Camphene	0.03 (50.0)	0.02 (0.0)	0.03	0.02 (50.0)	N.D.	0.02 (50.0)
Acenaphthylene	0.03 (25.0)	0.01 (50.0)	0.02 (0.0)	0.02 (0.0)	0.05	0.03 (25.0)
Acrylonitrile	0.34 (56.4)	0.18 (52.6)	0.18 (43.8)	0.14 (36.4)	0.08 (20.0)	0.11 (38.9)
Pyridine	0.23 (39.5)	0.07 (56.3)	0.07	0.05	N.D.	N.D.

N.D.: not detected.

concentrations of  $\text{NH}_3$  ranged from 76 to 278  $\mu\text{g}/\text{m}^3$  at the office area and 66–277  $\mu\text{g}/\text{m}^3$  at the factory boundary (Fig. 2c and d). Compared to the dumping area point, the office area and factory boundary points had relatively higher  $\text{NH}_3$  levels. This could be explained by the fact that these two sampling points were downwind and close to the leachate treatment plant. However, the  $\text{NH}_3$  concentrations at all sampling points were lower than the primary standard value (1000  $\mu\text{g}/\text{m}^3$ ) stated in the Standards (GB14554-93). As compared to the  $\text{NH}_3$  level during the odor incident, the  $\text{NH}_3$  levels here were reduced by 94.6–99.4%, 90.0–97.9%, 88.0–96.7% and 86.3–96.7% at the dumping area, the leachate treatment plant, the office area, and the factory boundary, respectively.

In contrast to  $\text{NH}_3$ , the corresponding average concentrations of  $\text{H}_2\text{S}$  at the dumping area (17–80  $\mu\text{g}/\text{m}^3$ ) were higher than that at the leachate treatment plant (10–45  $\mu\text{g}/\text{m}^3$ ) (Fig. 3a and b). The average concentrations of some samples from 0:00–6:00 at the dumping area were above the secondary standard value (600  $\mu\text{g}/\text{m}^3$ ) stated in the Standards (GB14554-93). In MSW landfills, large amounts of  $\text{H}_2\text{S}$  are produced as a result of anaerobically degrading refuse at the dumping area and studies of the MSW landfill gas commonly report measurable concentrations of  $\text{H}_2\text{S}$  and other reduced sulfur compounds (RSC) (Shin et al., 2002). It is reasonable for  $\text{H}_2\text{S}$  concentrations at the office area and the factory boundary to be much lower than those measured at the dumping area (Fig. 3c and d), as  $\text{H}_2\text{S}$  is emitted from the landfill surface and becomes diluted as it mixes with air. The degree of dilution is a function of wind speed, direction and other climatic conditions (Lee et al., 2006). In comparison with the same time/quarter of last year, the average  $\text{H}_2\text{S}$  concentrations at the dumping area were decreased (Fig. 3a). At the leachate treatment plant, both  $\text{NH}_3$  and  $\text{H}_2\text{S}$  concentrations were reduced significantly over time. Compared to the  $\text{H}_2\text{S}$  level during the odor incident, the  $\text{H}_2\text{S}$  levels dropped by 91.3–96.7%, 90.8–98.0%, 62.9–95.6% and 69.1–95.5% at the dumping area, the leachate treatment plant, the office area, and the factory boundary, respectively.

The GC-MS results of air samples collected on June 1st, 2009 are shown in Table 4. Compared with the results in June 2007, little variation in the type and number of odors was observed from samples collected in 2009. However, the average concentrations of

odors were largely decreased in 2009. For example, the average concentration ranges of some chlorinated species such as 1,2-dichloropropane, 1,1,1-trichloroethane, dichloroethylene, trichloroethene, and tetrachloroethene were reduced to 0.59–6.69  $\mu\text{g}/\text{m}^3$ , 1.06–2.65  $\mu\text{g}/\text{m}^3$ , 4.12–33.65  $\mu\text{g}/\text{m}^3$ , 0.29–2.45  $\mu\text{g}/\text{m}^3$ , and 0.22–6.67  $\mu\text{g}/\text{m}^3$ , respectively. The removal efficiencies of these chlorinated compounds were 43.3–52.0%, 40.6–51.7%, 46.3–50.0%, 31.0–49.7%, and 42.1–52.0%, respectively. Other odorous gases including aromatics, VFAs, aldehydes, ketones, esters, hydrocarbon, and other sulfur and nitrogen compounds were also kept at very low levels. Although monitoring the odor annoyance generated by a landfill area is difficult due to multiple area sources with a discontinuous odor emission (Nicolas et al., 2006), the results suggest that the odor control technologies applied have a good effect on the reduction of primary odor concentrations. The proposed strategy proves to be reliable for diffusive sources, such as the dumping area and the leachate treatment plant.

### 3.3. Odor emission linked to the various ambient conditions

As shown in Figs. 2 and 3, the variations of  $\text{NH}_3$  and  $\text{H}_2\text{S}$  concentrations at nearly all sampling points in four periods of time during a day (0:00–6:00, 6:00–12:00, 12:00–18:00 and 18:00–24:00) exhibited a similar trend with a decline followed by an increase (Figs. 2 and 3). That implies that the average odor concentrations were usually low in daytime (6:00–18:00), but relatively high in nighttime (18:00–6:00). The observed trend was thought to be due to changes in atmospheric pressure. It was found that the decrease of odor level was associated with high atmospheric pressure and the most annoyance was perceived in the hours of early morning or towards evening. This is in agreement with the findings obtained by Gallego et al. (2008). In contrast to other research outcomes in landfill, the seasonal variation of average  $\text{NH}_3$  and  $\text{H}_2\text{S}$  concentrations were not obvious. This could be attributed to the different running mode (e.g., landfill gas extraction) and the effective odor control techniques (e.g., the dumping area covered by HDPE membranes) in the Tianziling landfill site.

The odor occurrence numbers from the third quarter of 2007 (2007-3rd) to the second quarter of 2009 (2009-2nd) were

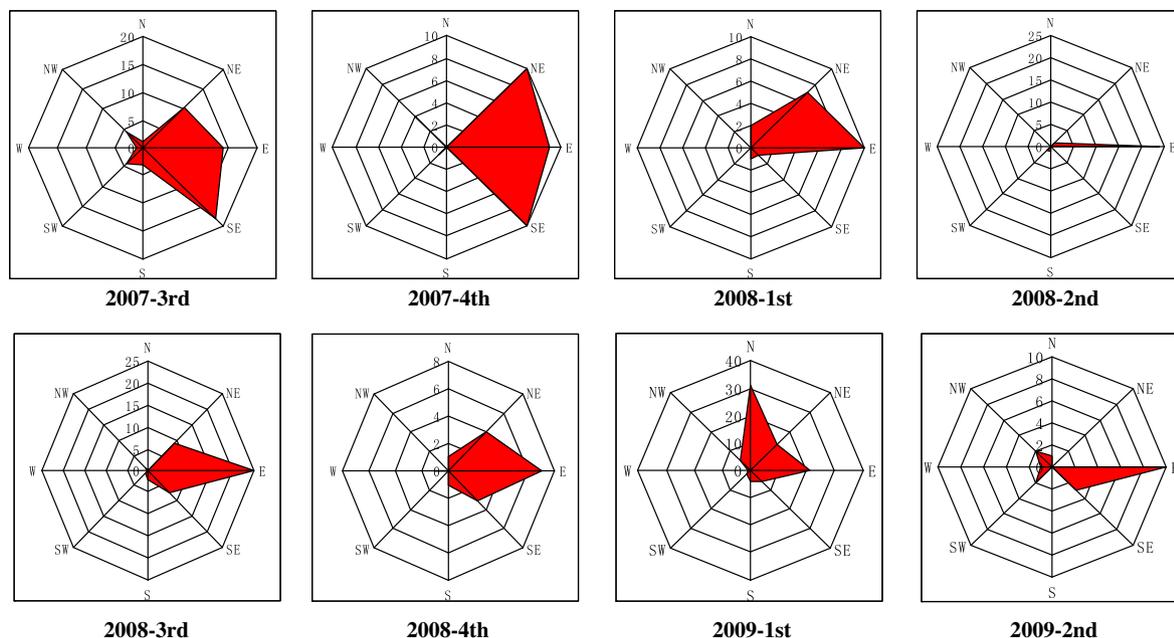


Fig. 4. Odour episode roses during the quarters from 2007-3rd to 2009-2nd at office area.

recorded in Table 1. The strong odor occurrence numbers in the second and third quarter of a year were much larger than those in other quarters. For example, the strong odor occurrence number in 2007-3rd, 2008-2nd, 2008-3rd and 2009-2nd was 14, 14, 12 and 27, respectively. This could result from the major influence of climate condition such as temperature, humidity and air pressure on odor transport from the landfill. Usually, high temperature, high humidity and low air pressure were observed in the second and third quarter of a year in the Tianziling landfill site. Capelli et al. (2008) found similar results at an Italian landfill where the highest odor values were measured during the high temperature season. It was also found that the decrease of odor level was associated with high air pressure. In addition, researchers also reported that wet weather (high humidity) likely played a role in increasing odor concentrations (Lee et al., 2006).

A common observation obtained by other researchers was that odors were sporadic, especially on windy days. A strong odor would be noted in one location at a given time, but a short time later the odor could be gone (Lee et al., 2006). The correlation between odor episode and wind direction in the Tianziling landfill site was investigated by creating episode roses. Episode roses, which are circular in shape, show the frequencies of different wind directions when an odor episode occurs (Gallego et al., 2008). As shown in Fig. 4, the odor episodes mainly occurred accompanied by southeast, northeast or east wind in different quarters, which could be explained by the downwind position of the Tianziling landfill site because in these wind directions, the leachate treatment plant and the dumping area were both exposed (Fig. 1). This emphasizes the critical influence of atmospheric condition such as wind direction on odor transport from the landfill site.

#### 4. Conclusion

A complete characterization of primary odorous gases at a landfill site in Hangzhou, China was investigated. Up to 68 odorous gases in different classes (inorganic odorous compounds, halogenated compounds, aromatics, VFAs, aldehydes, ketones, esters, hydrocarbon, and other sulfur and nitrogen compounds) were identified and quantified during the period of odor pollution incident. Among all these compounds,  $\text{NH}_3$  and  $\text{H}_2\text{S}$  were the dominant gases and contributed to 83.91–93.94% and 4.47–10.92% of the total odorous gases concentrations, respectively. The environmental sampling points revealed that the dumping area and the leachate treatment plant were the main odor sources at the Tianziling landfill site. The results of long-term  $\text{NH}_3$  and  $\text{H}_2\text{S}$  concentrations monitoring indicated a combined effect of climate condition (e.g., temperature, humidity, air pressure, and wind direction), running practice (e.g., use of the HDPE membrane cover and landfill gas extraction), and the geographical position of landfill on the transport of these gases. Moreover, the odor control engineering technologies had a good effect on the attenuation of primary odor concentrations. The information obtained is helpful in understanding the odor characteristics in landfill sites, which plays an important role in seeking effective ways to enhance the level of odor control.

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#### References

- Allen, M.R., Braithwaite, A., Hills, C.C., 1997. Trace organic compounds in landfill gas at seven UK waste disposal sites. *Environ. Sci. Technol.* 31, 1054–1061.
- Atkinson, R., 2000. Atmospheric chemistry of VOCs and NOx. *Atmos. Environ.* 34, 2063–2101.
- Aziz, H.A., Adlan, M.N., Zahari, M.S.M., Alias, S., 2004. Removal of ammoniacal nitrogen ( $\text{N-NH}_3$ ) from municipal solid waste leachate by using activated carbon and limestone. *Waste Manage. Res.* 22, 371–375.
- Belpomme, D., Irigaray, P., Hardell, L., Clapp, R., Montagnier, L., Epstein, S., Saso, A.J., 2007. The multitude and diversity of environmental carcinogens. *Environ. Res.* 105, 414–429.
- Bogner, J., Chanton, J., Blake, D., Abichou, T., Powelson, D., 2010. Effectiveness of a Florida landfill biocover for reduction of  $\text{CH}_4$  and NMHC emissions. *Environ. Sci. Technol.* 44, 1197–1203.
- Capelli, L., Sironi, S., Rosso, R.D., Céntola, P., Grande, M.I., 2008. A comparative and critical evaluation of odour assessment methods on a landfill site. *Atmos. Environ.* 42, 7050–7058.
- Chiriac, R., Carré, J., Perrodin, Y., Vaillant, H., Gasso, S., Miele, P., 2009. Study of the dispersion of VOCs emitted by a municipal solid waste landfill. *Atmos. Environ.* 43, 1926–1931.
- Clément, B., Merlin, G., 1995. The contribution of ammonia and alkalinity to landfill leachate toxicity to duckweed. *Sci. Total Environ.* 170, 71–79.
- Davoli, E., Gangai, M.L., Morselli, L., Tonelli, D., 2003. Characterisation of odorants emissions from landfills by SPME and GC/MS. *Chemosphere* 51, 357–368.
- Dincer, F., Odabasi, M., Muezzinoglu, A., 2006. Chemical characterization of odorous gases at a landfill site by gas chromatography-mass spectrometry. *J. Chromatogr. A* 1122, 222–229.
- Fernandez-Martinez, G., Lopez-Mahia, P., Muniategui-Lorenzo, S., Prada-Rodriguez, D., Fernandez-Fernandez, E., 2001. Measurement of volatile organic compounds in urban air of La Coruna, Spain. *Water Air Soil Pollut.* 129, 267–288.
- Firestein, S., 2001. How the olfactory system makes sense of scents. *Nature* 413, 211–218.
- Gallego, E., Soriano, C., Roca, F.X., Perales, J.F., Alarcon, M., Guardino, X., 2008. Identification of the origin of odour episodes through social participation, chemical control and numerical modelling. *Atmos. Environ.* 42, 8150–8160.
- Hutter, H.P., Moshhammer, H., Wallner, P., Damberger, B., Tappler, P., Kundi, M., 2006. Health complaints and annoyances after moving into a new office building: a multidisciplinary approach including analysis of questionnaires, air and house dust samples. *Int. J. Hyg. Environ. Heal.* 209, 65–68.
- Irigaray, P., Newby, J.A., Clapp, R., Hardell, L., Howard, V., Montagnier, L., Epstein, S., Belpomme, D., 2007. Lifestyle-related factors and environmental agents causing cancer: an overview. *Biomed. Pharmacother.* 61, 640–658.
- James, K.J., Stack, M.A., 1997. The impact of leachate collection on air quality in landfills. *Chemosphere* 34, 1713–1721.
- Kim, K.H., Choi, Y.J., Jeon, E.C., Sunwoo, Y., 2005. Characterization of malodorous sulfur compounds in landfill gas. *Atmos. Environ.* 39, 1103–1112.
- Lee, S., Xu, Q., Booth, M., Townsend, T.G., Chadik, P., Bitton, G., 2006. Reduced sulfur compounds in gas from construction and demolition debris landfills. *Waste Manage.* 26, 526–533.
- Liang, H.M., Liao, C.M., 2007. Modeling VOC-odor exposure risk in livestock buildings. *Chemosphere* 68, 781–789.
- Nicolas, J., Crafte, F., Romain, A.C., 2006. Estimation of odor emission rate from landfill areas using the sniffing team method. *Waste Manage.* 26, 1259–1269.
- Noble, R., Hobbs, P.J., Dobrovin-Pennington, A., Misselbrook, T.H., Mead, A., 2001. Atmospheric pollutants trace gases: olfactory response to mushroom composting emissions as a function of chemical concentration. *J. Environ. Qual.* 30, 760–767.
- Park, S., Lee, C.H., Ryu, C.R., Sung, K.J., 2009. Biofiltration for reducing methane emissions from modern sanitary landfills at the low methane generation stage. *Water Air Soil Pollut.* 196, 19–27.
- Peng, Y.P., Chen, K.S., Lai, C.H., Lu, P.J., Kao, J.H., 2006. Concentrations of  $\text{H}_2\text{O}_2$  and  $\text{HNO}_3$  and  $\text{O}_3$ -VOC-NOx sensitivity in ambient air in southern Taiwan. *Atmos. Environ.* 40, 6741–6751.
- Saral, A., Demir, S., Yildiz, S., 2009. Assessment of odorous VOCs released from a main MSW landfill site in Istanbul-Turkey via a modelling approach. *J. Hazard. Mater.* 168, 338–345.
- Sarkar, U., Hobbs, S.E., Longhurst, P., 2003. Dispersion of odour: a case study with a municipal solid waste landfill site in North London, United Kingdom. *J. Environ. Manage.* 68, 153–160.
- Scheff, P.A., Wadden, R.A., 1993. Receptor modeling of volatile organic compounds. 1. Emission inventory and validation. *Environ. Sci. Technol.* 27, 617–625.
- Schuetz, C., Bogner, J., Chanton, J., Blake, D., Morcet, M., Kjeldsen, P., 2003. Comparative oxidation and net emissions of methane and selected non-methane organic compounds in landfill cover soils. *Environ. Sci. Technol.* 37, 5150–5158.
- Schuetz, C., Bogner, J., Chanton, J.P., Blake, D., Morcet, M., Aran, C., Kjeldsen, P., 2008. Atmospheric emissions and attenuation of non-methane organic compounds in cover soils at a French Landfill. *Waste Manage.* 28, 1892–1908.
- Shin, H., Park, J., Park, K., Song, H., 2002. Removal characteristics of trace compounds of landfill gas by activated carbon adsorption. *Environ. Pollut.* 119, 227–236.

- Shon, Z.H., Kim, K.H., Jeon, E.C., Kim, M.Y., Kim, Y.K., Song, S.K., 2005. Photochemistry of reduced sulfur compounds in a landfill environment. *Atmos. Environ.* 39, 4803–4814.
- Sweet, C.W., Vertmette, S.J., 1992. Toxic volatile organic compounds in urban air in Illinois. *Environ. Sci. Technol.* 26, 165–173.
- Wolkoff, P., Nielsen, G.D., 2001. Organic compounds in indoor air - their relevance for perceived indoor air quality? *Atmos. Environ.* 35, 4407–4417.
- Wu, W.X., Hao, Y.J., Ding, Y., Chen, Y.X., 2009. Denitrification capacity in response to increasing nitrate loads and decreasing organic carbon contents in injected leachate of a simulated landfill reactor. *Process Biochem.* 44, 486–489.
- Zou, S.C., Lee, S.C., Chan, C.Y., Ho, K.F., Wang, X.M., Chan, L.Y., Zhang, Z.X., 2003. Characterization of ambient volatile organic compounds at a landfill site in Guangzhou, South China. *Chemosphere* 51, 1015–1022.