

VOL. 68, 2018



Seasonal Variations in Odorous Compounds Emission from A Municipal Solid Waste Disposal Plant

Chuandong Wu^a, Shihua Liu^b, Mushui Shu^c, Chen Qu^a, Jiemin Liu^{a,*}, Martin Piringer^d, Günther Schauberger^e

^aSchool of Chemistry and Biological Engineering, University of Science and Technology Beijing, Beijing, China ^bChina Building Material Test & Certification Group Co., Ltd, Beijing 100024, China,

^cKey Laboratory of Occupational Health and Safety, Beijing Municipal Institute of Labor Protection, Beijing, China ^cEnvironmental Meteorology, Central Institute of Meteorology and Geodynamics, Vienna, Austria

^dWG Environmental Health, Unit for Physiology and Biophysics, University of Veterinary Medicine, Vienna, Austria liujm@ustb.edu.cn

Waste treatment plants are among the major sources of odor nuisances and health risk to workers and nearby residents. In this work, we present an assessment of the seasonal variations in volatile compounds emission and the odor nuisance effects from a waste treatment plant. Air samples were seasonally collected in four different processing units in the plant, and analyzed by both instrumental and sensory methods. Results showed that a total of 17, 27, 23 and 14 volatile compounds were detected in the air samples collected in the four seasons, with average total chemical concentration of 1515.4, 5364.7, 3282.5 and 1067.6 μ g m⁻³. On the other hand, the non-carcinogenic risk of H₂S (1.7 and 1.3 in summer and autumn) and dichloromethane (1.7 in summer) exceeded the acceptable risk levels (HI = 1). Carcinogenic risk of ethylbenzene ranged from 2.1E-05 to 4.2E-05 in spring, autumn and winter, exceeding the acceptable carcinogenic risk level (1.0E-06). Moreover, the carcinogenic risk of tetrachloroethylene and ethylbenzene was larger than 1.0E-04 and reached the level of "definite risks" in summer.

KEY WORDS: Municipal solid waste, Odor intensity, health risk

1. Introduction

The social and environmental aspects of odorous gas emitted from municipal solid waste (MSW) treatment facilities have received special attention in recent decades. People are concerned with potential health risks and odor nuisances produced by waste gas emissions (Wu et al. 2017) (Brancher et al. 2016; Schauberger et al. 2008). Waste gas emitted from waste treatment plant consists of volatile compounds such as nitrogenous compounds, oxygenated compounds, aromatics, halogenated compounds, sulfur compounds, and terpenes, which are major air pollutants due to their malodorous and hazardous properties (Brancher et al. 2016; Carioua et al. 2016; Wu et al. 2017).

Workers and the nearby residents are directly exposed to the volatile compounds emitted from the plant through inhalation. Long-term exposure to these volatile compounds has been associated with potential health risks. Moreover, prolonged exposure to odors can generate unpleasant reactions ranging from emotional stress to physical symptoms, including anxiety, unease, headaches, vomiting, eye irritation and respiratory problems (Capelli et al. 2011; Wu et al. 2015). Growing concerns and complaints (Liu et al. 2015) highlight the need for the evaluation of odor nuisances and health risks of volatile compounds in waste treatment plants.

In the current study, we characterized the odorous volatile compound emissions from an MSW treatment plant in China by combing the instrumental and sensory methods. By monitoring the volatile compounds from four different units in the treatment plant during a one-year period, we analyzed the concentration distributions of the odorants. In addition, risks for carcinogenic, non-carcinogenic and cumulative effects were assessed based on the concentrations of the total components.

85

2. Materials And Methods

2.1 Site description

The study was conducted in an MSW treatment plant in Beijing, China. The plant is located in the southeast of Beijing, approximately 15 km from the city center and near two busy highway and large villages within a 3-km radius. Use of the MSW treatment plant began in 2004, and about 200-300 tons of MSW has been processed per day. The disposed MSW originated from nearby districts and was mainly food waste, paper, cans, plastic bags and bottles. The MSW was transported and dumped into the waste inlet. Inorganic materials was removed by the workers, while the organic waste were crushed and beaten by the crusher and beater. Afterwards, and waste components was conveyed to the outlet pool by a conveyor. At last, a solid-liquid separator was used to deliver the solid residue in the pool to a residue tank. Volatile compounds emitted from these units could diffuse to the whole plant, causing odor nuisance effects to workers and nearby residents.

2.2 Air sampling

Air sampling was conducted during the working hours of selected days from 2012 to 2013 and represented the four different seasons of a one-year period. Sampling sites were set in the four different units in the treatment plant: the waste inlet (WI), conveyor opening (CO), outlet pool (OP), and residue tank (RT). Air samples from these units were collected in 5 L Tedlar bag by the vacuum pump method which was adopted in many similar studies (Duan et al. 2014; Wu et al. 2017). In addition, absorption solutions were used to collect ammonia (NH₃) and hydrogen sulfide (H₂S), absorption tube (filled with glass bead (60/80 mesh) coated with oxalic acid and glycerol) was used to collect trimethylamine according to the national standard method in China. Details of the sampling method have been described by the authors elsewhere (Wu et al. 2015). The samples were then carefully transported to the lab in a dark box and analyzed within 24 h.

2.3 Instrumental and olfactometric analyses

Instruments such as gas chromatography-mass spectrometry/flame photometric detector (GC-MS/FPD, Trace DSQ, Thermo Fisher, USA) were used to analysis the chemical concentration of compounds in the air samples, preceded by pre-concentration with solid-phase micro extraction/cryogenic trapping. The absorption solutions of hydrogen sulfide and ammonia were analyzed by a UV/vis spectrophotometer (Shimadzu, Japan), according to the national standards of China. Olfactometric analyses were conducted to assess the odor nuisance effects of the air samples by 6-8 panellists. Odor intensity of the air samples were measured by a group of sniffing panelists with the using a subjective scale (0: no odor, 1: scarce odor, 2: weak odor, 3: clear odor, 4: strong odor, and 5: extremely strong odor). The details of the analyses are similar to those reported in our previous work (Wu et al. 2015; Wu et al. 2017).

2.4 Risk assessment

For volatile compounds in waste treatment plant, inhalation is the main human exposure route. Thus, carcinogenic effect and non-carcinogenic effect are assessed by combining the workers' inhalation exposure to air in the treatment plant with the toxicological parameters derived from the USEPA database (USEPA 2009). In general, inhalation exposure to volatile compounds was calculated by estimating the exposure concentration (EC, $\mu g m^{-3}$) for each receptor exposed to pollutants via inhalation, as shown in the equation (1) (USEPA 2009):

$$EC = \frac{C_a \times ET \times EF \times ED}{AT \times 365 \times 24}$$
(1)

where C_a is the concentration of volatile compounds in the air($\mu g m^{-3}$); ET is the exposure time (2 hours day ⁻¹ for the waste inlet units and 1 hours day ⁻¹ for the conveyor opening, outlet pool, and residue tank since it is automatically operated); EF is the exposure frequency, 335 days year ⁻¹ (considering 30 days of annual vacation); ED is the exposure duration, which is assumed to be 20 years for the workers in the treatment plant; and AT is the averaging time, which is 20 years for non-carcinogenic effects and 70 years for carcinogenic effects (Martí et al. 2014).

For non-carcinogenic effects, the hazard index (HI) is expressed as equation (2) (USEPA 2009):

$$HI = \frac{EC}{RfC \times 1000 \, \mu g/mg} \tag{2}$$

where RfC is the reference concentration (mg m^{-3}) (USEPA 2009).

For carcinogenic effects, the risk (R) is defined as the probability to develop cancer during a lifetime and is calculated by equation (3) (USEPA 2009):

$$R = EC \times IUR \tag{3}$$

86

where IUR is the inhalation unit risk in (µg m⁻³)⁻¹ (USEPA 2009). Both RfC and IUR values were cited from RAIS (Risk Assessment Information System) and IRIS (Integrated Risk Information System) databases (Wu et al. 2018).

3. Results and Discussion

3.1 Chemical concentrations of detected compounds in the MSW treatment plant

Volatile compounds detected in air samples from the MSW treatment plant could be divided into seven categories, including seven aromatics, seven oxygenated compounds, four reduced sulfur compounds, three nitrogenous compounds, three halogenated compounds, one terpenes and three alkanes. The concentrations of each compound category are shown in Table 1. Compounds with the highest concentrations were limonene, phenol, ammonia, N,N-dimethylacetamide, and styrene, with detected frequency of 100%.

Table 1 Concentrations of detected compound categories in samples from the waste treatment plant in each season (mean concentration from the four sampling sites).

| Categories | Concentration (µg m ⁻³) | | | | | |
|--------------------------|-------------------------------------|--------|--------|--------|--|--|
| | Spring | Summer | Autumn | Winter | | |
| Aromatics | 319.6 | 1795.5 | 1304.4 | 258.2 | | |
| Oxygenated compounds | 96.2 | 862.2 | 243.1 | 21.0 | | |
| Reduced sulfur compounds | 27.6 | 98.0 | 72.4 | 14.2 | | |
| Nitrogenous compounds | 359.2 | 1115.9 | 811.5 | 144.9 | | |
| Halogenated compounds | 18.5 | 267.6 | 71.0 | 11.1 | | |
| Alkanes | 66.8 | 102.5 | 58.8 | 62.6 | | |
| Terpenes | 627.8 | 1123.1 | 721.3 | 555.6 | | |
| Total | 1515.5 | 5364.7 | 3282.5 | 1067.6 | | |

The concentrations of the seven categories in different seasons were significantly different (Friedman's test, p < 0.01, n = 24, SPSS 18.0 software). Averages of the total concentrations of the air samples decreased in the following order: summer (5364.7 μ g m⁻³) > autumn (3282.5 μ g m⁻³) > spring (1515.6 μ g m⁻³) > winter (1067.6 μ g m⁻³). This is due to the fact that under higher temperatures, the release of volatile compounds in the MSW treatment plant, especially those with relatively small molecules, can be significantly accelerated (Wenjing et al. 2015; Wu et al. 2015).

3.2 Olfactometric measured odor intensity of the air samples

To assess the level of odor pollution in the MSW treatment plant, odor intensity of air samples from the four units in the four seasons were measured. Results showed that the highest odor intensity was observed at the outlet pool (Figure 1). This is due to the fact that the waste went through hydrothermal process in the outlet pool, releasing more odorous compounds through physical and chemical reactions. On the other hand, the lowest odor intensity was at the waste inlet areas, since there was a regular drip washing procedure at the inlet area. Moreover, in summer, the odor intensity could be over 4, indicating that the odor stimuli is of the level of strong. These results suggest that the MSW treatment plant can indeed act as a potential source of odor pollution for workers.



Figure 1 Odor intensity of air samples in the four units of the waste treatment plant. WI: the waste inlet, CO: conveyor opening, OP: outlet pool, and RT: residue tank.

3.3 Health risk

In the present study, we compared the concentrations of the detected compounds with the occupational exposure limits (OELs) in China (GBZ 2.1-2007), and found that the concentrations were 2-3 orders of magnitude lower than the permissible concentration-time weighted average (PC-TWA) and the permissible concentration-short term exposure limit (PC-STEL). To further evaluate the health risks of these compounds, methodology recommended by the USEPA were used. Three compounds with carcinogenic risks (R) and 13 compounds with non-carcinogenic risks (HI) were assessed according to the USEPA database (Table 2 and 3). Moreover, cumulative non-carcinogenic and carcinogenic risks (sum of individual HI and R values) of each compound category and the total compounds were also calculated to account for simultaneous exposure to the detected volatile compounds considered in this study. The HI and R values were averaged by the sampling seasons.

| Compounds | CAS No. | RfC mg m ⁻³ | Spring | Summer | Autumn | Winter |
|---------------------|-----------|------------------------|--------|--------|--------|--------|
| Toluene | 108-88-3 | 5' | 0.01 | 0.2 | 0.17 | - |
| Ethylbenzene | 100-41-4 | 1 ¹ | - | - | - | - |
| o-xylene | 95-47-6 | 0.1 ¹ | - | 0.01 | 0.01 | - |
| m-xylene | 108-38-3 | 0.1 ^I | - | 0.05 | 0.03 | - |
| p-xylene | 106-42-3 | 0.1 ¹ | 0.01 | 0.07 | 0.05 | - |
| Styrene | 100-42-5 | 1 ¹ | - | 0.02 | 0.02 | - |
| ∑Aromatics | | - | 0.02 | 0.4 | 0.3 | - |
| Phenol | 108-95-2 | 0.2 ^R | 0.03 | 0.1 | 0.1 | 0.02 |
| Ethyl acetate | 141-78-6 | 0.07 ^R | - | 0.04 | - | 0.01 |
| ∑Oxygenated | | - | 0.03 | 0.1 | 0.1 | 0.03 |
| Hydrogen sulfide | 7783-06-4 | 0.002 | 0.5 | 1.7 | 1.3 | 0.3 |
| ∑Sulfur | | | 0.5 | 1.7 | 1.3 | 0.3 |
| Ammonia | 7664-41-7 | 0.5 ¹ | 0.02 | 0.04 | 0.02 | 0.01 |
| ∑Nitrogenous | | | 0.02 | 0.04 | 0.02 | 0.01 |
| Chlorobenzene | 108-90-7 | 0.05 ^R | - | 0.05 | 0.01 | - |
| Tetrachloroethylene | 127-18-4 | 0.04 ¹ | 0.02 | 0.06 | 0.06 | 0.01 |
| Dichloromethane | 75-09-2 | 0.6 | - | 1.7 | - | - |
| ∑Halogenated | | - | 0.02 | 1.8 | 0.07 | 0.01 |
| Cumulative | | - | 0.6 | 4.1 | 1.8 | 0.3 |

Table 2 Non-carcinogenic risks (HI) and the cumulative values from volatile compounds through inhalation in the waste treatment plant.

¹: cited from IRIS (Integrated Risk Information System) database

^R: cited from RAIS (Risk Assessment Information System) database

The cumulative HI in the four seasons ranged from 0.3 to 4.1 (Table 2). The highest cumulative HI value was observed in summer, followed by autumn. The high risks in these seasons were mostly contributed by H_2S (1.7 and 1.3 in summer and autumn) and dichloromethane (1.7 in summer). These two species in the waste treatment plant require special attention since the risk exceeded the acceptable risk levels (HI = 1). Furthermore, from the point of cumulative effect, the cumulative HI values were over the acceptable level in summer and autumn, while under the acceptable level in spring and winter. Hence, high levels of non-carcinogenic deserve to be paid more attention in summer and autumn when considering all the target compounds in the air samples as a whole. Moreover, as shown in the Figure 2, the non-carcinogenic risks were mainly contributed by sulfur compounds with average contribution of 71%.

88



Fiure. 2 Percentage of non-carcinogenic risks (HI) contribution for the total non-carcinogenic risks

The carcinogenic risks (R) of the 3 compounds ranged from 1.3E-07 to 1.1E-04 (Table 3). The USEPA acceptable R level of individual compounds is 1.0E-06. Compounds with R values larger than 1.0E-04 and 1.0E-03 are marked as "definite risks" and "significant risks", respectively (Bari and Kindzierski 2017; Durmusoglu et al. 2010; Liu et al. 2016). In the present study, the carcinogenic risk of dichloromethane is lower than the acceptable level. Yet the carcinogenic risk of ethylbenzene ranged from 2.1E-05 to 4.2E-05 in spring, autumn and winter, exceeding the acceptable carcinogenic risk level (R = 1.0E-06). Moreover, the R values of tetrachloroethylene and ethylbenzene was larger than 1.0E-04 and reached the level of "definite risks" in summer. These results suggest that the risk of compounds causing adverse health effects could concern the workers, especially in summer. From the point of cumulative effect, the cumulative R values were over the acceptable level. Hence, high levels of carcinogenic risks should not be neglected when considering all the target compounds in the air samples as a whole.

| Compounds | CAS No. | IUR (µg m ⁻³) ⁻¹ | Spring | Summer | Autumn | Winter |
|---------------------|----------|---|---------|---------|---------|---------|
| Ethylbenzene | 100-41-4 | 2.5E-06 ^R | 2.6E-05 | 1.1E-04 | 4.2E-05 | 2.1E-05 |
| ∑Aromatics | | | 2.6E-05 | 1.1E-04 | 4.2E-05 | 2.1E-05 |
| Tetrachloroethylene | 127-18-4 | 2.6E-07 ¹ | - | 1.2E-04 | - | - |
| Dichloromethane | 75-09-2 | 1.0E-08 ¹ | 2.1E-07 | 6.1E-07 | 6.7E-07 | 1.3E-07 |
| ∑Halogenated | | - | 2.1E-07 | 6.1E-07 | 6.7E-07 | 1.3E-07 |
| Cumulative | | - | 2.7E-05 | 2.3E-04 | 4.2E-05 | 2.1E-05 |

Table 3 Carcinogenic risks (R) and the cumulative values from volatile compounds through inhalation in the waste treatment plant.

¹: cited from IRIS (Integrated Risk Information System) database

^R: cited from RAIS (Risk Assessment Information System) database

4. Conclusions

Waste treatment plants are a source of odorous volatile compounds. By combining the instrumental and olfactometric analyses, we concluded that the volatile compounds and the odor intensity was higher in summer than in other seasons. Moreover, the health risk assessment reveal that the HI of H_2S and dichloromethane, and R of tetrachloroethylene and ethylbenzene in the waste treatment plant require special attention. Furthermore, high levels of R and HI should not be neglected when considering all the target compounds in the air samples as a whole.

Acknowledgments

This work was jointly supported by the National Key R&D Program of China (Nos. 2016YFE0115500, 2016YFC0700603 and 2016YFC0700601), the National Natural Science Foundation of China (21576023 and 21407008), and the Fundamental Research Funds for the Central Universities (No. FRF-TP-17-047A1). The cooperation between China and Austria was funded by the National Key R&D Program of China (No. 2016YFE0115500) and the OeAD-GmbH (No. CN 10/2016).

References

- Bari, M.A., Kindzierski, W.B. 2017. Concentrations, sources and human health risk of inhalation exposure to air toxics in Edmonton, Canada. Chemosphere 173, 160-171.
- Brancher, M., Schaubergerb, G., Francoa, D., De Melo, H. 2016. Odour impact criteria in South American regulations. Chemical Engineering Transactions 54.
- Capelli, L., Sironi, S., Del Rosso, R., Céntola, P., Rossi, A., Austeri, C. 2011. Olfactometric approach for the evaluation of citizens' exposure to industrial emissions in the city of Terni, Italy. Sci Total Environ 409, 595-603.
- Carioua, S., Chaignaudb, M., Montreera, P., Fagesa, M., Fanloa, J.-L. 2016. Odor Concentration Prediction by Gas Chromatography and Mass Spectrometry (GC-MS): Importance of VOCs Quantification and Odor Detection Threshold Accuracy. Chemical Engineering Transactions 54.
- Duan, Z.,Lu, W.,Li, D.,Wang, H. 2014. Temporal Variation of Trace Compound Emission on the Working Surface of a Landfill in Beijing, China. Atmos Environ 88, 230-238.
- Durmusoglu, E., Taspinar, F., Karademir, A. 2010. Health risk assessment of BTEX emissions in the landfill environment. J Hazard Mater 176, 870-877.
- Liu, Y.,Liu, Y.,Li, H.,Fu, X.,Guo, H.,Meng, R.,Lu, W.,Zhao, M.,Wang, H. 2016. Health risk impacts analysis of fugitive aromatic compounds emissions from the working face of a municipal solid waste landfill in China. Environ Int 97, 15-27.
- Liu, Y.,Lu, W.,Li, D.,Guo, H.,Caicedo, L.,Wang, C.,Xu, S.,Wang, H. 2015. Estimation of volatile compounds emission rates from the working face of a large anaerobic landfill in China using a wind tunnel system. Atmos Environ 111, 213-221.
- Martí, V., Jubany, I., Pérez, C., Rubio, X., Pablo, J.D., Giménez, J. 2014. Human Health Risk Assessment of a landfill based on Volatile Organic Compounds emission, immission and soil gas concentration measurements. Appl Geochem 49, 218-224.
- Schauberger, G.,Piringer, M.,Knauder, W.,Petz, E. Re-calculation of the odour emission of a thermal treatment plant for waste by using a Monte-Carlo based model. International Conference on Environmental Odour Monitoring and Control NOSE; 2008
- USEPA. Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (Part F, Supplemental Guidance for Inhalation Risk Assessment), EPA-540-R-070-002. Office of Superfund Remediation and Technology Innovation Environmental Protection Agency. Available from: https://www.epa.gov/sites/production/files/2015-09/documents/partf_200901_final.pdf; 2009
- Wenjing, L.,Zhenhan, D.,Dong, L.,Jimenez, L.M.C.,Yanjun, L.,Hanwen, G.,Hongtao, W. 2015. Characterization of odor emission on the working face of landfill and establishing of odorous compounds index. Waste Manage 42, 74-81.
- Wu, C.,Liu, J.,Liu, S.,Li, W.,Yan, L.,Shu, M.,Zhao, P.,Zhou, P.,Cao, W. 2018. Assessment of the health risks and odor concentration of volatile compounds from a municipal solid waste landfill in China. Chemosphere 202, 1-8.
- Wu, C.,Liu, J.,Yan, L.,Chen, H.,Shao, H.,Meng, T. 2015. Assessment of odor activity value coefficient and odor contribution based on binary interaction effects in waste disposal plant. Atmos Environ 103, 231-237.
- Wu, C.,Liu, J.,Zhao, P.,Li, W.,Yan, L.,Piringer, M.,Schauberger, G. 2017. Evaluation of the chemical composition and correlation between the calculated and measured odour concentration of odorous gases from a landfill in Beijing, China. Atmos Environ 164, 337-347.
- Wu, C.,Liu, J.,Zhao, P.,Piringer, M.,Schauberger, G. 2016. Determination of the Odour Concentration and Odour Intensity of a Mixture of Odorous Substances by Chemical Concentrations: a Comparison of Methods. Chemical Engineering Transactions 54.