Composition and Distribution of Non-Methane Organic Compounds at Municipal Solid Waste Landfill Surfaces

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Abstract. The non-methane organic compounds (NMOCs) released from municipal solid waste (MSW) landfills impose significant impact on the environment and human health. It is necessary to investigate the fugitive emission of NMOCs from MSW landfills for helping control NMOC emissions and reduce the environmental impacts. This study was focused on the concentration distribution of NMOCs on the operating and soil covered landfill areas. The NMOCs at the surfaces were measured with the static chamber method at two typical landfill sites located in northern China. Organosulfur compounds, oxygenated compounds, halogenated hydrocarbons, aromatics, aliphatic hydrocarbons and terpene compounds were all detected at both landfills. Aliphatic hydrocarbons and oxygenated compounds were predominant substances in the NMOCs. Ethanthiol, dimethyl disulfide and dimethyl sulfide were the main odorous pollutants on the operating area. Higher concentrations of odorous pollutants were found on the operating area than on the covered one.

Introduction

Around 77% of municipal solid waste (MSW) collected in China was disposed of in landfills in 2011 [1]. Most facilities dealing with MSW are facing a odorous problem, which could be caused by hydrogen sulfide [2] and ammonium [3]. In the process of anaerobic degradation in a landfill, non-methane organic compounds (NMOCs) are always produced as well as methane and carbon dioxide. NMOCs could be generated and emitted during the process of biodegradation of organics [4-8]. The composition of NMOCs varied with different degradation stages [9]. Aerobic pretreatment prior to landfilling could reduce the quantity of the NMOCs generated during anaerobic landfilling [10,11].

Although the volume concentration of them is usually less than 1% [12], NMOCs are generally considered as the main source of the odorous problem at MSW landfills, because they include many compounds with very low odor thresholds, such as dimethyl sulfide and diethyl sulfide [13,14]. It has been reported that the inhabitants living close to MSW landfills are more likely to get cancer than people from other areas, for cancerigenic substances, such as benzene and vinyl chloride, can also be detected in the adjacent ambient [15]. Moreover, the volatile compounds, e.g. long chain fatty hydrocodone, produce ozone leading to secondary pollution [16].

It is necessary to take appropriate measures to control NMOCs at landfills. The landfills in the US must be equipped with landfill gas collection facilities if the annual NMOC emissions yield 50 tons [17]. In the UK, MSW landfills are required to monitor the concentration of odorous substances to estimate their environmental risks [18]. The emissions of NMOCs from landfills are not being paid much attention to in China, from perspectives of both management and research.
This study aims to characterize NMOC emissions with field campaigns from different areas at two typical MSW landfills in China.

Materials and Methods

Landfill sites. The field campaigns were conducted at landfills A and P in northern China, located in Beijing and Liaoning, respectively. Landfills A and P were started in 1995 and 2009, receiving about 4000 and 600 metric tons of MSW each day, respectively. The composition of MSW is shown in Table 1.

<table>
<thead>
<tr>
<th>Components</th>
<th>Food waste%</th>
<th>Paper%</th>
<th>Plastics &amp; rubber%</th>
<th>Textiles%</th>
<th>Wood%</th>
<th>Ceramics &amp; tiles%</th>
<th>Glass%</th>
<th>Metals%</th>
<th>Other%</th>
<th>Residue%</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>50.7(23.9)</td>
<td>16.3(7.6)</td>
<td>8.3(3.3)</td>
<td>2.1(2.9)</td>
<td>0.3(0.2)</td>
<td>2.7(3.7)</td>
<td>4.7(6.5)</td>
<td>0.3(0.8)</td>
<td>-</td>
<td>14.3(9.9)</td>
</tr>
<tr>
<td>A</td>
<td>59.8(6.4)</td>
<td>13.5(4.3)</td>
<td>10.7(2.4)</td>
<td>0.8(0.3)</td>
<td>0.8(0.7)</td>
<td>0.5(0.4)</td>
<td>2.8(3.2)</td>
<td>0.1(0.1)</td>
<td>0.6(0.6)</td>
<td>10.3(4.4)</td>
</tr>
</tbody>
</table>

- A Percentage of wet weight. Standard deviations are presented parenthetically.
- The data represent the averages of five samples collected through September to November of 2008.
- The data represent the averages of two samples collected in October and November of 2011.

Sampling method. Gas emissions from surface of waste or covered waste were collected by means of static flux chambers. Gas sampling was carried out at surface of operating area (SOA) and surface of soil-covered area (SSA) for surface emissions. Gas samples were collected by self-extracting equipment, stored in special plastic bags and then sent for analysis within 24 hrs. Five campaigns were carried out in fall and winter of 2012 (from September to December).

Analytical methods. Gas samples was analyzed by State Environmental Protection Key Laboratory of Odour Control of China in Tianjin, referring to USEPA method TO-15. The detection limit was below 1 ppb. Totally 118 species of NMOCs could be quantitatively detected. The surface concentrations were averaged after removal of extreme values using the Grubbs method.

Results and Discussion

Odor concentration (OC). Odor concentrations, calculated by dividing the concentration of a certain compound by its odor threshold [19], were applied to invest the most influencing odor substances (Table 2). The chemicals at SOA of landfill A exhibited the most obvious odorous impact, since landfill A was receiving much more MSW than landfill P. It is significant that the predominant odorous substances detected were mostly organosulfides, suggesting that landfill operators pay more attention to control of organosulfides [20].

Table 2 The main odorous substances detected at landfills A and P

<table>
<thead>
<tr>
<th>Species</th>
<th>P-SOA</th>
<th>A-SOA</th>
<th>P-SSA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl sulfide</td>
<td>16.6</td>
<td>1294.0</td>
<td>46.1</td>
</tr>
<tr>
<td>Dimethyl Disulfide</td>
<td>12.7</td>
<td>579.9</td>
<td>6.4</td>
</tr>
<tr>
<td>Dimethyl Sulfide</td>
<td>3.9</td>
<td>244.8</td>
<td>1.1</td>
</tr>
<tr>
<td>Butyraldehyde</td>
<td>3.4</td>
<td>88.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Hydrogen sulphide</td>
<td>2.0</td>
<td>32.8</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Distribution of NMOCs. All detected NMOCs were grouped into six categories according to different functional groups, and the concentrations are shown in Fig. 1. From perspective of mass...
quantity, oxygenated compounds and aliphatic hydrocarbons dominated the NMOCs detected at the SOA of landfill A and at the SSA of landfill P, respectively, and both of them were the top two chemical groups found at the SOA of landfill P. The concentrations of halogenated compounds, aromatics, and aliphatic hydrocarbons at SSA of landfill P were slightly higher than those at SOA, while organosulfur, terpene, and oxygenated compounds were in the opposite way. The MSW at SOA were under an aerobic condition, and the degradation of complex organic matter would form many kinds of intermediates and final products, including alcohols, ketones, aldehydes, esters, and so on. Terpene compounds were mainly released from plant residues [9]. The organosulfur compounds were generated from degradation of organic compounds that contain sulfur.

![Fig. 1 Concentrations of NMOCs on different surfaces at landfills A and P. (SOA: Surface of Operating Area; SSA: Surface of Soil-covered Area)](image)

The concentrations of all detected NMOCs at the SOA of landfill A were higher than those at landfill P’s SOA, and the difference was up to 40 times for oxygenated compounds. It might be attributed to the distinction in landfill properties. Landfill A was receiving a MSW stream about 10 times larger than landfill P, while the SOA of the former landfill was much smaller than that of the latter. Furthermore, the landfill gas was not being collected at landfill P, and the emission of landfill gas might cause obvious dilution of the trace chemicals in air.

Organosulfur compounds are one of the most important sources of odors and most halogenated compounds and aromatics may be toxic and carcinogenic, both of which should be paid attention to during the operation of a MSW landfill.

**Sulfides.** Organosulfur compound emissions from SOA and SSA of landfill P and SOA of landfill A are shown in Fig. 2. Hydrogen sulfide and carbon disulfide were included, since they exhibit similar environmental impact. All detected sulfide emissions from the SOA were higher than from the other (SSA), except ethyl sulfide. It could be attributed to the low level anaerobic process at operating area, where very little landfill gas (mainly consisting of methane and carbon dioxide) were generated and emitted, causing a relatively high concentration of trace compounds. Having been operated much longer and receiving much more MSW each day, landfill A was generating and emitting much more sulfide emissions than landfill P.
Fig. 2 Sulfide concentrations on different surfaces at landfills A and P. (SOA: Surface of Operating Area; SSA: Surface of Soil-covered Area)

**Halogenated compounds.** Chlorinated hydrocarbons and chlorofluorocarbons were detected, while bromine-containing substances were not detected. Composition and concentrations of grouped halogenated substances are shown in Fig. 3. Chlorinated hydrocarbons containing chlorinated aliphatic hydrocarbons and chlorinated aromatic hydrocarbons. The concentrations of halogenated groups at the operating surface of landfill A were always higher than those at landfill P’s surface, and the difference was up to 23 times for chlorofluorocarbons. Chemicals widely used in households, such as tetrachloroethylene and dichloroethane (cleaning agents), were found with very high concentrations at the SOA of landfill A, which was serving several core urban areas for MSW treatment. The predominant species detected at landfill P comforted reasonably with the industries of the oil based city, since the major chemicals, such as vinyl chloride and carbon tetrachloride, are important industrial materials.

Fig. 3 Concentrations of halogenated compounds on different surfaces at landfills A and P. (SOA: Surface of Operating Area; SSA: Surface of Soil-covered Area)

**Conclusions**

Field campaigns were conducted at two typical Chinese MSW landfills in this study to characterize the composition and concentrations of NMOCs on the operating and soil covered surfaces. The results showed that the NMOCs detected at the landfill surfaces could be grouped into organosulfur compounds, oxygenated compounds, halogenated hydrocarbons, aromatics, aliphatic hydrocarbons and terpene compounds. Aliphatic hydrocarbons and oxygenated compounds were predominant substances in the NMOCs. Organosulfur compounds were the major odorous source of the two landfills, and the concentrations at the SOA were higher than at the SSA.
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