Article

Practical Application of a Multi-Bed Adsorbent Tube Coupled with GC-MS for Low-Level VOCs Identification to Achieve Comprehensive Odor Management

Yelim Choi 1, Kyunghoon Kim 2, Taeho Lee 3 and Daekeun Kim 1,*

1 Department of Environmental engineering, Seoul National University of Science and Technology, Seoul 01811, Korea
2 Transportation Environmental Research Department, Korea Railroad Research Institute, Uiwang 16105, Korea
3 Department of Chemical Engineering, Soongsil University, Seoul 06978, Korea
* Correspondence: kimd@seoultech.ac.kr; Tel.: +82-2-970-6606

Abstract: We investigated the effectiveness of a multi-sorbent tube (M-Tube) to improve the sampling method for a wide range of odor-causing volatile organic compounds (VOCs) at low concentrations. The M-Tube applied in this study was a fixed tube packed with three adsorbents (Carboxen®, Carbopack™, and Tenax®-TA) in series. To verify the efficiency of the M-Tube, a comparative study was conducted against a single tube (S-Tube, Tenax®-TA). A total of 42 target compounds were selected, including eight different chemical groups: terpenes, hydrocarbons, aldehydes, ketones, alcohols, esters, furans, and alkanes, to verify the effectiveness of the M-Tube. In the laboratory test, response factors, which are the ratios between output signals of gas chromatography by the sorbent-tube sample and the liquid-standard sample, for the M-Tube were higher than those for the S-Tube. The breakthrough volume of the M-Tube was higher than that of the S-Tube, indicating that the M-Tube had a relatively lower method detection limit. In the field application to the sewage treatment plant, 29 compounds were identified, and their concentration ranged from 0.3 to 98 ppbv (above MDL). The detected compounds were considered odor-causing VOCs, and the odor contribution of the compounds could be assessed. We ultimately concluded that comprehensive odor management could be established by determining trace VOCs.

Keywords: odor-causing VOCs; GC-MS; multi-sorbent tube; odor management

1. Introduction

Odors are caused by one or more volatilized chemical compounds affecting physiological symptoms and psychological stress [1]. Odor-causing compounds originate from odor sources (e.g., wastewater treatment, landfill, livestock, and industrial facilities) redistributing into a gas phase in the environment [2,3]. The pollutants should be accurately monitored for proper control and management [4]. The odorous compounds often include volatile organic compounds (VOCs) such as alcohols, aldehydes, esters, aromatics, terpenes, or ketones, that could contain sulfur or nitrogen. Most odorants have low odor threshold concentrations (down to ppbv; in some cases, it can go down to pptv) and exist at low concentrations (from ppmv down to pptv) in the environment [1–3,5], which leads to potential difficulty in the chemical analysis of odorants. Sulfur- or nitrogen-containing compounds (i.e., hydrogen sulfide and ammonia) have been widely studied in odor management [6–10], whereas VOCs have been less studied. As VOCs are a large group of organic chemicals with different chemical and physical properties [11,12], analysis of odorous VOCs is still challenging.

Sample collection and quantification of odorous VOCs are critical to establish a plan for odor management and develop control technologies, which will mitigate odor emissions [5]. The accuracy of the VOCs measurement largely depends on choosing the appropriate...
sampling method [13]. Traditional sampling techniques for VOCs includes canisters, bags, solid sorbents, and liquid solvents [14]. Sorbent materials usually packed in a tube have high surface areas, and the sampling method with the sorbent tube is easy to handle [15]. However, this measurement requires preconcentration prior to VOC analysis [16] and encounters problems of breakthroughs in sampling [17].

Previous studies have reported that VOC could be analyzed using various sampling and analysis methods such as online sampling with a proton transfer reaction quadrupole interface time-of-flight mass spectrometer (PTR-QiTOF-MS) [18,19], canister sampling with a solid-phase extraction-gas chromatography-mass spectrometry/pulsed discharge helium ionization detector (SPE-GC-MS/PDHID/FID) [20], TD-GC-MS [21–23], and SPME-GC-MS [19,21,24–27]. The ISO 16000 series has been widely accepted as the international standard for the determination of VOCs and recommends the use of the sorbent Tenax®-TA (Poly (2,6-diphenyl-p-phenylene oxide)) and gas chromatography (GC) followed by mass spectrometry (MS) or a mass spectrometry-flame ionization detector (MS-FID) [28]. Tenex-based polymer adsorbents have a low retention volume for high volatility VOCs, and the approximate analyte volatile range of commercialized Tenax®-TA is n-C7 to n-C26, including aromatics compounds (excluding benzene), nonpolar compounds, and less volatile polar compounds [29]. Many studies of VOC analysis have applied a Tenax®-TA single-sorbent tube [30,31]. Still, some studies reported that the Tenax®-TA single sorbent tube was inappropriate for analyzing odorous VOCs, especially for polar, very volatile, and low concentrated compounds [32,33].

To improve the sampling methods using the Tenax®-TA single tube, some studies have suggested the multi-sorbent tube, which packs more than one adsorbent material in series according to the characteristics of analytes [16,34–42]. They included two or three adsorbents for their multi-sorbent tubes to analyze VOCs in the gas phase. However, the previous studies [37,40,41] discussed a relatively narrow range of VOCs, which might cause difficulty in understanding the applicability of their multi-sorbent tubes to a wide range of VOCs. Sources of offensive odor may have different emission conditions against general air pollutants, and the proposed sampling method needs to be applied in the field. In particular, odorous compounds are generated in humid conditions from environmental facilities such as wastewater treatment plants. Therefore, further studies of multi-sorbent tubes are needed to cover a wide range of VOCs and, at the same time, the applicability of multi-sorbent tubes to humid field conditions must be checked.

This study aimed to achieve effective odor management by analyzing odorous VOCs generated at low concentrations. This purpose was to be achieved by comparing between the performance of a single sorbent tube (Tenax®-TA) and that of a multi-sorbent tube in the analysis of odorous VOCs using thermal desorption (TD) coupled with a capillary gas chromatography/mass spectrometry detector (GC-MS). The multi-sorbent tube contained Carboxen® 1003, Carbopack™ B, and Tenax®-TA in series to collect samples for the analysis of odorous VOCs. The laboratory-based study assessed the analytical sensitivity of the multi-sorbent tube over the single-sorbent tube. It also evaluated the breakthrough volume (BV) to identify the safe sampling volume. A field test with the multi-sorbent tube suggested in this study was also conducted to quantify odorous VOCs generated from sludge storage in a wastewater treatment plant. Lastly, the odor contribution of the quantified VOCs and the effect of gas humidity pretreatment on field sampling were investigated.

2. Materials and Methods

2.1. Materials

Standards of VOCs with a purity of no less than 98% are summarized in Table S1. The standards included alcohols, aldehydes, alkanes, esters, furans, hydrocarbons, ketones, and terpenes. The standards of VOCs were diluted with methanol (99.99%, Honeywell-Burdick & Jackson, Muskegon, MI, USA) prior to the analysis. To dilute VOCs standard gas in the analytical calibration procedure, pure dry nitrogen gas (99.999%, Air Korea Co., Ltd., Gimhae, Korea) was used.
2.2. Sorbent Tubes

The sorbent materials were selected in this study by considering the adsorption properties (i.e., adsorption strength, surface area of sorbent, hydrophilic-hydrophobic property) of the compounds to be tested. The adsorbents used in this study are Tenax®-TA, Carbopack™ B, and Carboxen®-1003. Tenax®-TA is known to be advantageous for adsorption of 7–26 carbons, having relatively weak adsorption strength (a surface area of 35 m²/g), among the three adsorbents, with hydrophobic adsorbates. Carbopack™ B is advantageous for adsorption of 5–12 carbons, having medium adsorption strength (a surface area of 100 m²/g) with hydrophobic adsorbates. Carboxen®-1003 is advantageous for capturing 2–5 carbons, having high adsorption strength (a surface area of 1000 m²/g) with adsorbates of medium hydrophilic property. Sorbent materials were placed in the tube to allow sample gas to pass through the weaker adsorbent first and then the most strongly adsorbing materials [43]. Sorbents were carefully weighted considering any loss during the fabrication of sorbent tubes (Table S2).

Single-sorbent and multi-sorbent tubes were prepared and referred as S-tube and M-tube, respectively. The S-tube (Tenax®-TA 200 mg, APK Sorbent Tubes) was purchased from KNR (KNR Co., Ltd., Seongnam, Korea). The M-tube was packed with 59.5 mg of Carboxen®-1003, 109.2 mg of Carbopack™ B, and 181.4 mg of Tenax®-TA in series (Figure S1). The adsorbents’ packing ratio was adjusted to collect a wide range of VOCs most efficiently according to the adsorbent properties (e.g., adsorption strength and surface area). All sorbents were placed in a stainless-steel tube with a stainless-steel mesh and end plugs, and glass wool was placed between sorbents to separate them. Tenax®-TA (60/80 mesh, 35 m²/g), Carbopack™ B (60/80 mesh, 100 m²/g), Carboxen®-1003 (40/60 mesh, 1000 m²/g), and glass wool (Non-treated, GC suitable) were purchased from Sigma-Aldrich (St. Louis, MO, USA). (The properties of the selected adsorbent are shown in Table S3.) Stainless-steel tubes in the thermal desorption unit (TDU tubes, SS, Empty, 6 mm external diameter, 89 mm long) were purchased from RESTEK (Bellefonte, PA, USA). After tube packing and before each use, all tubes were conditioned using a tube conditioner (APK-1200, KNR Co., Ltd., Korea) for 120 min at a maximum temperature of 300 °C under 100 mL/min of a pure nitrogen gas (99.9999%, Air Korea Gas Co., Ltd., Yeoju, Korea) flow. Conditioned tubes were immediately sealed using tube caps (UC-Tube Cap, Unilok Co., Ltd., Ansan, Korea) fitted with PTFE ferrules.

2.3. Experiments

2.3.1. Analytical Sensitivity

To test for GC-MS response sensitivity of the M-Tube, GC signals for standard VOCs were compared between S-Tube and M-Tube. Standard stock solutions from neat chemicals were prepared and further diluted in methanol to obtain VOC standards with concentrations ranging from 0.198 to 695.8 ng/µL, which is the typical range in the VOCs concentrations generated in the sewage treatment plant, found in our previous study [44]. All standards were newly prepared on the day of use. The calibration curves (4 calibration points) of the VOC standards were made by loading 1 µL of the previously prepared standard dilutions into the sorbent tubes (both S-tube and M-tube). Chemical analysis was performed by using TD-GC/MS in scan mode and SIM (selected ion monitoring) mode, respectively.

In order to verify the loss of analytes during the thermal desorption process, the liquid-phase VOCs standard solutions (78.008 to 170.379 ng/µL) were analyzed with 1 µL direct injection using GC/MS. The recovery percentage was calculated after analyzing liquid direct injection, M-tube, and S-tube, using the same concentration sample, respectively, and the recovery percentage formula was as follows.

\[
\text{Recovery percentage} = \frac{\text{GC signals of } M \text{ (or } S) \text{ tube sample}}{\text{GC signals of liquid direct inject sample}} \times 100
\]
2.3.2. Breakthrough Volume

In order to evaluate safe sampling volumes (SSV) for the given sorbent tubes, a breakthrough volume (BV) experiment was conducted. The term BV refers to the volume of gas that will purge any chemicals through the sorbent tube. In this study, a backup tube was used, by placing an identical tube in series with the first tube (both S-Tube and M-Tube). This setup could capture any sample breakthrough in the backup tube. The breakthrough percentage was estimated as the percentage of the mass detected in the backup tube to the total mass analyzed. The BV was estimated as the sample volume when the breakthrough percentage was 5% [17,43]. The SSV was calculated as half of the experimentally determined BV [45] and applied to the sampling conditions of the field study.

Standard gas samples were prepared by volatilizing liquid samples with pure nitrogen gas in the Tedlar® bags (KNR Co. Ltd., Namyangju, Korea). Standard gas concentrations for each compound were set up differently, ranging from 50 to 100 µg/m³, based on a previous study of VOC concentrations from sewage treatment plants [44]. It was assumed that the relative humidity (RH) of the standard gas sample was zero because the nitrogen gas used for dilution was 99.999% pure gas and a liquid standard sample does not contain any water. The gas standard sample in the Tedlar® bag flowed through a sampler (KMS-200, KEMIK Co. Ltd., Seoul, Korea) with a flow rate of 100 mL/min into the two tubes connected in series. In Table S4, VOCs loss was not observed at 100 mL/min of gas sampling flow rate.

The sampling volumes of the S-Tube were 0.5 L, 1 L, and 3 L. M-Tube was sampled with the sampling volumes of 1 L, 5 L, 10 L, 15 L, 20 L, 25 L, 30 L and 35 L. After sampling each volume, the main and backup tubes were analyzed with TD/GC/MS, respectively.

2.3.3. Analysis

Liquid standards were prepared by diluting in methanol with a concentration range of 0.1 ng/tube to 1000 ng/tube. In the calibration process, for loading the adsorbent tube with the liquid standard solution, a liquid standard injector (APK-6100L, KNR Co., Ltd., Namyangju, Korea), which can set a vaporizing temperature and purge gas flow rate, was used to vaporize the different liquid standard solutions before entering the adsorbent tubes. Liquid standards were vaporized at 250 °C and purged with 100 mL/min of pure nitrogen gas flow rate for five minutes and then introduced into the adsorbent tubes. VOCs analysis was performed with thermal desorption (Markes Unity Series 2, Markes International Ltd., Llantrisant, UK) coupled with gas chromatography (Agilent 7820 A) mass spectrometry (Agilent 5977 E, Santa Clara, CA, USA). In the TD, the conditions were set as follows: pre-purge, one minute; desorption temperature, 330 °C for eight minutes; desorption trap helium flow rate, 50 mL/min; inlet split, 1:1; cold-trap (U-T11GPC-2S, general purpose trap, Markes International Ltd.) temperature, −10 °C; transfer-line temperature, 180 °C. In the GC/MS, split ratio was 20 and column flow rate was 1 mL/min of helium (99.9999% purity). GC oven temperature was set as 35 °C for the first ten minutes, increased to 200 °C with the increment rate of 5 °C per minute, and then was kept at 200 °C for 10 min (total 48 min). Column used in the analysis was DB-5 (60 m x 0.320 mm x 1 µm, Agilent technologies, Santa Clara, CA, USA). The ion-source temperature and the quadrupole temperature were 230 °C and 150 °C, respectively. The mass range of scan mode analysis, which was conducted to confirm the retention time and major ions of each compound, was 31 to 400 m/z. Quantitative analysis was performed in SIM mode. In the case of liquid direct injection, all GC-MS analysis conditions, only without the TD part, were applied identically with the adsorbent tube method. The correlation coefficients of the calibration curves were equal or higher than 0.98. All samples taken in the adsorbent tube were analyzed in the same manner as described above. Details of the basic information and detection limits for all compounds are available in the Supplementary Materials (Table S1).

2.3.4. Application to a Field Test

To examine the application of the M-Tube to field conditions, a field test was conducted. A sewage treatment plant in Seoul, Korea, was selected for the site. The plant treats
wastewater flowing from a city and generates energy from the resulting biogases. This site has a very humid environment, with RH close to 100% (detected by Hygro-Thermometer Clock, 811CE, Daekwang, Inc., Hwaseong, Korea). Since the M-Tube contains a hydrophilic adsorbent, a pretreatment process for removing moisture was added to the sampling process using the M-Tube. In the case of S-Tube, the pretreatment process was not added in the entire sampling process.

For the M-Tube, humidity control with silica gel was implemented by putting the silica gel into the 30 mL of impinger and passing the gas to be sampled through the impinger. Humidity control with calcium chloride was also implemented by putting 500 mg of calcium chloride, mixed with 100 mg of diatomaceous earth, into the impinger and passing the sample gas through the impinger.

The headspace gases of the concentration facility were sampled using three types of sampling processes. The sampling-gas flow rate was set at 100 mL/min with a gas sampler (KMS-200, KEMIK Co. Ltd., Seoul, Korea). The SSVs resulting from our BV experiment were applied to the field test. We named the samples as shown in Table 1 according to the sampling procedure. M1-Sample was analyzed with a sampling volume of 0.5 L using the M-Tube with humidity pretreatment of silica gel. M2-Sample and M3-Sample were analyzed with sampling volumes of 0.5 L and 5 L, respectively, using the M-Tube pretreated by calcium chloride mixed with diatomaceous earth.

Table 1. Experimental setup of humidity control for different samples.

| Sample | Materials Used for Humidity Control | Sampling Volume (mL) | Flow Rate (mL/min) | Sampling Time (min) |
|--------|------------------------------------|----------------------|-------------------|--------------------|
| S      |                                    | 500                  | 100               | 5                  |
| M1     | Silica gel                          | 500                  | 100               | 5                  |
| M2     | CaCl₂ + Diatomaceous earth          | 500                  | 100               | 5                  |
| M3     | CaCl₂ + Diatomaceous earth          | 5000                 | 100               | 50                 |

1 Humidity pretreatment was not conducted for the S-Tube.

As for the gas-phase VOCs emitted in the field, qualitative analysis (MS scan mode) and quantitative analysis (MS SIM mode) were performed. Calibration curves made for standard VOCs were used to calculate the concentration of quantitative analysis.

2.4. Odor Assessment

To quantitatively evaluate the odor, we calculated an odor quotient (OQ) of each compound. The odor quotient is the value obtained by dividing the concentration of each odor substance by its odor threshold [46–48]. Moreover, a sum of odor quotients (SOQ) was compared in each sample. A previous study investigated the relationship between dilution to the threshold (D/T) ratio concentration and the odor quotient value and confirmed that log(SOQ) and log(D/T) values were linearly proportional (r = 0.86) [49].

\[
\text{Odor Quotient} = \frac{\text{Odor Concentration}}{\text{Odor Threshold}}
\]  

3. Results

3.1. TD/GC/MS Sensitivity

Figure 1 shows the responses to the corresponding retention concentrations of S-Tube and M-Tube. The responses obtained from S-Tube and M-Tube were compared at four concentrations ranging from 21.3 ng/tube to 21,302 ng/tube. The y-axis and the x-axis represent the intensity (abundance) of the signal by GC analysis with the S-Tube and the M-Tube, respectively. In all four concentrations, the slopes of the graphs were less than one, indicating that the response sensitivity of the S-Tube was smaller than that of the M-Tube. Less analyte was lost in the M-Tube than in the S-Tube because the adsorbent with high adsorption strength was used in the M-Tube. The S-Tube showed low responses in the relatively low concentrations (Figure 1a,b), while the responses of the S-Tube were similar
to those of the M-Tube in the higher concentrations (Figure 1c,d). Detailed chromatograms are provided in Figure S2a. These results imply that the M-tube is more applicable for analyzing samples with relatively low concentrations than the S-Tube. For samples with relatively low concentrations, the analyte loss in the M-tubes was less than that in the S-tubes. In all the analysis results, the GC-MS peak area ratio of the M-Tube to the S-Tube was 26 on average, demonstrating that analysis using the M-Tube was effective for analysis of low-concentration samples. Detailed recovery percentages of each compound showed in Table S5 (Supplementary Materials).

![Figure 1](image_url)

**Figure 1.** Comparison of GC-MS response intensity between the S-Tube (y-axis) and the M-Tube (x-axis) with four different retention concentrations ranging from 21.3 ng/tube to 21,302 ng/tube. Analysis was performed by thermal desorption coupled with GC/MS in scan mode and SIM mode: (a) Total mass: 21.3 ng/tube; (b) Total mass: 2130 ng/tube; (c) Total mass: 10,651 ng/tube; (d) Total mass: 21,302 ng/tube.

3.2. Breakthrough Volume

Figure 2 shows the adsorbed mass of the main and backup tubes of the S-Tube in three different retention volumes (i.e., 0.5 L, 1 L, 3 L) and two different inlet concentrations of total volatile organic compounds (i.e., 440 ppbv, 880 ppbv). In the S-Tube, some compounds experienced breakthrough from 1 L of retention volume. As the retention volume increased, the amount of mass adsorbed on the backup tube also increased. In Figure 2a, the breakthrough did not occur in 0.5 L and 1 L. In the 3 L of retention volume, the breakthrough percentage was 1.6% (data not shown). In Figure 2b, the breakthrough occurred at 1.5% at 0.5 L, 6.1% at 1 L, and 8.7% at 3 L retention volume, indicating that the BV of the S-Tube was 5 L/g of adsorbent at the inlet gas concentrations of 880 ppbv. The safe sampling volume of the S-Tube was calculated as 2.5 L/g, which is half of the BV. As the concentration of the
inlet gas increased, the BV decreased. Thus, the BV we obtained in this study cannot be applied to inlet gas at different concentrations.

![Figure 2](image_url)

**Figure 2.** Adsorbed mass of the main and backup tubes of S-Tube for two different inlet gas concentrations of total volatile organic compounds; (a) 440 ppbv, and (b) 880 ppbv. The open circles represent the adsorbed mass of the main tubes and the closed circles represent the adsorbed mass of the backup tubes.

Figure 3 shows the chromatograms of the main and backup tubes of the M-Tube at 35 L retention volume when the inlet gas concentration of TVOCs was 440 ppbv (detailed chromatograms are provided in Figure S2b). Some peaks seen in the chromatogram of the backup tube were below the detection limit and breakthrough did not occur in the backup tube at 35 L retention volume. Conversely, some overloaded peaks were observed in the chromatogram of the main tube, suggesting that analytical errors might occur. Since there was no overloaded peak in the 10 L retention volume, the BV of the M-Tube was estimated as 10 L (converted to 28.6 L/g of adsorbent). The SSV in our M-tubes was determined to be 14.3 L/g of adsorbent, which is half of 28.6 L/g of adsorbent.

![Figure 3](image_url)

**Figure 3.** The chromatogram of the main (left) and backup (right) tube of the M-Tube at 35 L retention volume. The inlet gas concentration of total volatile organic compounds was 440 ppbv. For the comparison of GC peaks between the main tube and backup tube, y-axis was shown in the same scale for both chromatograms.
3.3. Field Study

Figure 4 shows the composition of each group of chemicals in our field study, detected with different tube types and methods for humidity pretreatment. As we estimated the SSV of the S-Tube as 0.5 L in this study, 0.5 L of headspace gas of the concentration facility was sampled using the S-Tube without humidity pretreatment. Likewise, as we estimated the SSV of the M-Tube as 5 L in this study, we sampled 0.5 L (for comparison with S-tube) and 5 L of the headspace gas in the same facility using the M-Tube with either silica gel or calcium chloride for humidity pretreatment. As a wide range of substances was detected, the substances were grouped into different classes.

![Figure 4](image_url)

**Figure 4.** Composition of analytes sampled from the headspace gas in the concentration facility of wastewater treatment plant. Different sampling conditions (i.e., tube type, sampling volume, humidity pretreatment) were applied to each sample (Table 1). (Tube types: S-Tube or M-Tube, sampling volume: 0.5 L or 5 L, humidity control (in the M-Tube sampling): silica gel or CaCl₂ with diatomaceous earth).

In Figure 4a–c, field sampling results of the S-Tube and M-Tube with the 0.5 L sampling volume are shown. The total mass of the S-Tube was 357 ng/tube, which was higher than those of the M-Tube with silica gel (172 ng/tube) and calcium chloride (183 ng/tube). Half of the analyte was lost due to humidity pretreatment (Figure 4b,c). The sample pretreated with calcium chloride had a lower sample loss. However, the sample loss rate was quite large, indicating that the humidity pretreatment had a negative effect on the stable sampling of VOCs gas. Further studies, such as sample stability, oxidant control, and humidity control, are recommended for investigating appropriate methods to overcome this problem.
The M3-Sample was observed to have a higher TVOCs concentration (912 µg/m³) than that of the S-Sample (713 µg/m³) (Figure 4a,d), with the same headspace gas from the concentration facility. The low detection limit of the M-Tube might account for the higher concentrations by the M3-Sample because trace compounds are more likely to be detected in the M3-Sample. For this reason, it is recommended to use the M-Tube for the analysis of trace compounds. Twenty-nine compounds were detected above the MDL using the M3-Sample, while only five compounds were detected above the MDL using either the M1-Sample or M2-Sample (data not shown). When using the M3-Sample, the highest concentration was observed in toluene (371 µg/m³, corresponding to 98.5 ppbv), followed by n-decane (122 µg/m³, corresponding to 20.9 ppbv), methyl pentanoate (74 µg/m³, corresponding to 15.6 ppbv), 3-pentanone (58 µg/m³, corresponding to 16.5 ppbv), n-undecane (57 µg/m³, corresponding to 8.9 ppbv), and ethyl pentanoate (51 µg/m³, corresponding to 9.6 ppbv). The concentrations of the remaining 23 compounds ranged from 2 to 22 µg/m³ (up to 0.3 ppbv).

In Figure 4, the composition of substances was different depending on the sampling methods, meaning that the substances that the S-Tube and M-Tube collected differed. From comparing field sampling results between the M1-Sample and M2-Sample, alcohols might be adsorbed by the humidity pretreatment material of the M2-Sample (i.e., CaCl₂ + diatomaceous earth) before arriving at adsorbents. In the case of M3-Sample, substances of various chemical groups were detected because the larger sampling volume of M3-Sample (5 L) led to a stronger preconcentration of trace compounds.

Figure 5 shows the odor quotients of the detected compounds. The odor quotient is a quantitative index of odor, calculated by the ratio of the odor substance concentrations to the odor threshold concentration of each substance. The sum of odor quotient (SOQ) was 5.08 in S-Sample, 7.82 in M1-Sample, 45.76 in M2-Sample, and 93.24 in M3-Sample. The M3-Sample had the highest odor quotient because the M3-Sample had the highest adsorbed mass of detected compounds. The lowest SOQ value of 5.08 in S-Sample and the highest value of 93.24 in M3-sample differed by more than 18 times. Moreover, the odor quotient of terpenes was less than 1 from S-Sample, M1-Sample and M2-Sample, while that of terpenes was close to 10 from M3-Sample.

![Figure 5. Distribution of odor quotients for each chemical group (bar graph, left side) and sum of odor quotient for each sample in the field study (line graph, right side) for four different sampling conditions (Table 1). Odor quotients were calculated as the ratio of the measured concentrations at headspace gas to the odor threshold concentrations. Odor quotient is 1 when humans begin to sense the odor from a specific substance.](image-url)
Hydrocarbons had the highest composition among the seven chemical groups (Figure 4), while ester and glycol ethers had the highest odor quotient (Figure 5). The reason is that ester and glycol ethers have lower odor threshold concentrations than hydrocarbons, further implying that glycol ethers contribute more to odor than hydrocarbons. It is recommended to consider the odor contribution of each chemical group and give priority to chemical groups with higher odor contribution in the removal process.

4. Discussion

Commercial multi-tubes combined only for analyzing odorous substances do not yet exist. The manufacturer provides information about each adsorbent, but multi-sorbent tubes still have limited options. The manufacturer also provides a service that manufactures multi-tubes if the analyst selects adsorbents and configures them. However, the selection guide is very limited, and all the analysis results from the selected combination’s adsorbent are the analyst’s responsibility, making it difficult to use the desired adsorbent combination in terms of the reliability of the results. Therefore, it is necessary to increase the research on the validation of multi-sorbent tubes.

Since odorous VOCs exist at low concentrations, the sensitivity of the analytic method and the capacity of sampling volume are critical to evaluating VOCs emission, which can be allowed by applying the analytical method proposed in this study. We observed that the M-tube is better for collecting VOCs with lower concentrations and boiling points and has a bigger SSV than the S-tube.

Our results were consistent with previous studies showing that breakthroughs are more likely to occur with lower boiling points or carbon numbers [40,41]. Of compounds with a 100 °C or lower boiling point, the breakthrough occurred in 76% of them. Only 48% of compounds with boiling points higher than 100 °C experienced the breakthrough, indicating that the compounds with higher boiling points had lower breakthrough percentages. Therefore, the physical properties, such as the boiling point of compounds, should be considered when they are analyzed. For example, breakthroughs are likely to occur when sampling very volatile compounds and smaller sampling volumes should be collected accordingly.

However, it is practical to increase the sampling volume to lower the detection limit when analyzing substances that are not highly volatile. Odor-causing VOCs tend to have a more irritating odor at higher vapor pressures [42]. The adsorbent packed in the sorbent tube can significantly affect odor-causing VOCs analysis, demonstrating that the adsorbent type should be carefully selected for practical VOC analysis.

The SSV was higher in the M-Tube than in the S-Tube because the packing adsorbents had a larger surface area and stronger adsorption force than the S-Tube. Compared to the M-Tube, the S-Tube might easily desorb the analytes back when it is purged for desorbing. This observation can be supported by previous studies reporting that polymeric adsorbents such as Tenax tended to have lower SSVs for highly volatile compounds [31,43]. As the sampling volume increases, it might be advantageous to use our M-Tubes to analyze trace compounds because of their larger SSVs. Several studies compared the breakthrough percentage of the S-tubes with that of multi-sorbent tubes. They found that the multi-sorbent tubes showed relatively large BVs compared to the single-sorbent tubes [18,31,44], consistent with our results. The maximum volume of gas that can be sampled without a significant breakthrough of VOCs must be known before use, which directly correlates to the effectiveness of the sampling method for VOCs analysis.

However, the actual breakthrough volumes in the field study decreased under extreme environmental conditions (e.g., high humidity). Humidity control is necessary for the field study when using multi-tubes containing hydrophilic adsorbents, which are easily affected by humidity in the air sample. Research on moisture control in field sampling is still limited and challenging. In this study, silica gel and calcium chloride were used to control moisture. The silica gel adsorbs moisture through physical adsorption, and calcium chloride absorbs water molecules in the air to liquefy them since it is deliquescent.
and ionizes itself to remove moisture. Other methods include purging the tube with dry nitrogen gas just before TD-GC-MS analysis, or heating the tube, setting the temperature of the tube to high during sampling, to prevent condensation of water molecules. In the purging case, the compounds are already lost by moisture during sampling because it is a follow-up process. The heating tube’s sample loss was big because the heat applied to prevent water from being condensed so that other VOCs, particularly very VOCs (with lower boiling points than water), are not adsorbed. However, in the case of silica gel, some VOCs, such as acetaldehyde, tend to be adsorbed together, which is consistent with the results of papers published by several researchers [50–53]. Calcium chloride, which is very deliquescent, can be better for removing water from the air, resulting in the loss of volatile compounds being less than that of silica gel. It is worthwhile to note that some VOCs were easily dissolved in moisture.

We found that underestimated VOCs could also affect odor assessment. Figure 5 shows the broad range of SOQ from 5.2 (S-Sample) to 93.3 (M3-Sample); even though they are the same gas sample, they could be assessed very differently according to the different sampling tools. These differences can lead to a significant error in establishing the operation plan of the odor-reduction process. It is recommended to analyze the odorous substances through appropriate sampling methods. Olfactory and theoretical threshold tests have been generally used to evaluate odors [54]. When evaluating odor intensity using the olfactory test, the odor is subjectively judged through the individual’s sense of smell, so theoretical odor evaluation methods such as the threshold test are being studied to secure the objectivity of the odor evaluation. However, there is still some limitations in the theoretical threshold test due to the complexity of odor. For example, the olfactory test and threshold test results are often less correlated, which can provide substantially different results from each other, which is known to be because the odor threshold can represent different values in different literature [55]. However, in an approach based on the results of this study, the difference in results according to the odor assessment method may be due to the chemical analysis’s analytical limitation. For more advanced odor evaluation, it is essential to study the correct odor-threshold calculation and the sampling/analysis method, which can identify and quantify odor-causing compounds, specifically odorous VOCs which are still under study.

5. Conclusions

In this study, we made the multi-sorbent tube composed of three adsorbents of Carboxen® 1003, Carbopack™ B, and Tenax®-TA in series and compared their sampling performances with those of the single-sorbent tube packed with Tenax®-TA.

After VOCs were adsorbed on the adsorbent tubes (i.e., S-Tube, M-Tube), they were analyzed using thermal desorption coupled with gas chromatography/mass spectrometry under the scan mode and SIM mode.

Areas of the analysis were compared between the S-Tube and M-Tube among different concentrations ranging from 20 ng/tube to 20,000 ng/tube. In the analysis of compounds with relatively high concentrations, both types of tubes showed similar performance, but the S-Tube was not efficient in the analysis of compounds with relatively low retention concentrations (20–2000 ng/tube).

BV of the S-Tube and M-Tube were compared with standard gas concentrations of 50 µg/m³ and 100 µg/m³. BV of the S-Tubes was 1 L and SSV was 0.5 L, correspondingly. In the M-Tube, the BV experiments were performed up to 35 L of sampling volume, but breakthrough did not occur. SSV of the M-Tube was determined to be 5 L considering the peak overloaded on the gas chromatogram.

The samples collected from concentration facility in a wastewater treatment plant were compared among different types of tubes and humidity pretreatment methods. The highest adsorbed mass was observed in the analysis of the headspace gas with 5 L sampling volume using the M-Tube.
In conclusion, it is suggested that using the multi-sorbent tube composed of suitable adsorbents enables a more accurate and efficient analysis of trace compounds in gas samples, establishing more comprehensive odor management.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/atmos13091457/s1. Figure S1: Schematic drawing of multi-sorbent tube suggested in this study. Carboxen, Carbopack B, and Tenax TA were packed in series inside a stainless steel tube [46–48,56]; Figure S2a: Comparison of GC/MS responses between the single-sorbent tube and the multi-sorbent tube; Figure S2b: Chromatograms of the back-up tube and main tube in the single-sorbent tube (upper) and the multi-sorbent tube (bottom) sampling methods; Table S1: Quality assurance of the S-Tube and M-Tube sampling for 42 target compounds; Table S2: Mass of adsorbents (Tenax® TA, Carbopack™ B, and Carboxen® 1003) packed in multi-sorbent tubes; Table S3: Characteristics of adsorbents used in this study; Table S4: Capture efficiency (%) of specified VOCs by sorbent tubes on gas sampling flow rates; Table S5: Relative recovery rates between different standard phases (gas and liquid) in the analysis of VOCs using gas chromatography–mass spectrometry (Am: chromatographic peak area of gas samples in the multi-sorbent tube method, As: chromatographic peak area of gas samples in the single-sorbent tube method, Al: chromatographic peak area of liquid samples).

**Author Contributions:** Conceptualization, D.K.; methodology, Y.C. and D.K.; formal analysis, Y.C. and K.K; investigation, Y.C.; data curation, Y.C.; visualization, Y.C.; writing—original draft, Y.C. and K.K.; resource, D.K.; supervision, D.K.; project administration, D.K.; funding acquisition, D.K.; writing—review, T.L. and D.K.; editing, T.L. and D.K. All authors have read and agreed to the published version of the manuscript.

**Funding:** This study was financially supported by Seoul National University of Science and Technology.

**Conflicts of Interest:** The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

**References**

1. Brattoli, M.; Cisternino, E.; Dambruoso, P.R.; De Gennaro, G.; Giungato, P.; Mazzone, A.; Palmisani, J.; Tutino, M. Gas chromatography analysis with olfactometric detection (GC-O) as a useful methodology for chemical characterization of odorous compounds. *Sensors* 2013, 13, 16759–16800. [PubMed]
2. Gostelow, P.; Parsons, S.; Stuetz, R. Odour measurements for sewage treatment works. *Water Res.* 2001, 35, 579–597. [CrossRef]
3. Hayes, J.; Stevenson, R.; Stuetz, R. The impact of malodour on communities: A review of assessment techniques. *Sci. Total Environ.* 2014, 500, 395–407. [PubMed]
4. Shusterman, D.; Lipscomb, J.; Neutra, R.; Satin, K. Symptom prevalence and odor-worry interaction near hazardous waste sites. *Environ. Health Perspect.* 1991, 94, 25–30. [PubMed]
5. Schiffman, S.S.; Walker, J.M.; Dalton, P.; Lorig, T.S.; Raymer, J.H.; Shusterman, D.; Williams, C.M. Potential health effects of odor from animal operations, wastewater treatment, and recycling of byproducts. *J. Agromed.* 2000, 7, 7–81.
6. Yang, J.; Jiao, Y.; Yang, W.; Gu, P.; Bai, S.; Liu, L. Review of methods for determination of ammonia volatilization in farmland. In *IOP Conference Series: Earth and Environmental Science;* IOP Publishing: Bristol, UK, 2018; Volume 113, p. 012022.
7. Lin, K.; Zhu, Y.; Zhang, Y.; Lin, H. Determination of ammonia nitrogen in natural waters: Recent advances and applications. *Trends Environ. Anal. Chem.* 2019, 24, e00073. [CrossRef]
8. Lacey, R.; Mukhtar, S.; Carey, J.; Ullman, J. A review of literature concerning odors, ammonia, and dust from broiler production facilities: 1. Odor concentrations and emissions. *J. Appl. Poult. Res.* 2004, 13, 500–508. [CrossRef]
9. Xue, S.; Chen, S.; Hermanson, R. Measuring ammonia and hydrogen sulfide emitted from manure storage facilities. *Trans. ASAE* 1998, 41, 1125. [CrossRef]
10. Devai, I.; DeLaune, R.D. Emission of reduced malodorous sulfur gases from wastewater treatment plants. *Water Environ. Res.* 1999, 71, 203–208. [CrossRef]
11. Sin, D.W.-M.; Wong, Y.-C.; Sham, W.-C.; Wang, D. Development of an analytical technique and stability evaluation of 143 C3–C12 volatile organic compounds in Summa®canisters by gas chromatography–mass spectrometry. *Analyst* 2001, 126, 310–321.
12. Brancaleoni, E.; Scovaventi, M.; Frattoni, M.; Mabilia, R.; Ciccioli, P. Novel family of multi-layer cartridges filled with a new carbon adsorbent for the quantitative determination of volatile organic compounds in the atmosphere. *J. Chromatogr. A* 1999, 845, 317–328. [CrossRef]
13. Belgiorno, V.; Naddeo, V.; Zarra, T. *Odour Impact Assessment Handbook;* John Wiley & Sons: Hoboken, NJ, USA, 2012.
14. Król, S.; Zabiegala, B.; Namieśnik, J. Monitoring VOCs in atmospheric air II. Sample collection and preparation. *TrAC Trends Anal. Chem.* 2010, 29, 1101–1112. [CrossRef]
15. Brattoli, M.; De Gennaro, G.; De Pinto, V.; Demarinis Loiotile, A.; Lovascio, S.; Penza, M. Odour detection methods: Olfactometry and chemical sensors. *Sensors* **2011**, *11*, 5290–5322. [CrossRef]

16. Maceira, A.; Vallecillos, L.; Borrull, F.; Marce, R.M. New approach to resolve the humidity problem in VOC determination in outdoor air samples using solid adsorbent tubes followed by TD-GC–MS. *Sci. Total Environ.* **2017**, *599*, 1718–1727. [CrossRef]

17. Harper, M. Sorbent trapping of volatile organic compounds from air. *J. Chromatogr. A* **2000**, *885*, 129–151.

18. Kaser, L.; Peron, A.; Graus, M.; Strieding, M.; Wohlfahrt, G.; Jurait, S.; Karl, T. Interannual variability of terpene emissions in an alpine city. *Atmos. Chem. Phys.* **2022**, *22*, 5603–5618.

19. Capozzi, V.; Lonzarich, V.; Khomenko, I.; Cappellin, L.; Navarini, L.; Biasiol, F. Unveiling the molecular basis of mascarpone cheese aroma: VOCs analysis by SPME-GC/MS and PTR-ToF-MS. *Molecules* **2020**, *25*, 1242. [CrossRef]

20. Hernández-Fernández, J.; Lopez-Martinez, J.; Barceló, D. Quantification and elimination of substituted synthetic phenols and volatile organic compounds in the wastewater treatment plant during the production of industrial scale polypropylene. *Chemosphere* **2021**, *263*, 128027. [CrossRef]

21. Moufid, M.; Hofmann, M.; El Bari, N.; Tiebe, C.; Bartholmai, M.; Bouchikhi, B. Wastewater monitoring by means of e-nose, VE-tongue, TD-GC-MS, and SPME-GC-MS. *Talanta* **2021**, *221*, 121450. [CrossRef]

22. Kaikiti, C.; Stylianou, M.; Agapiou, A. TD-GC/MS analysis of indoor air pollutants (VOCs, PM) in hair salons. *Chemosphere* **2022**, *294*, 133691. [CrossRef]

23. Moufid, M.; Bouchikhi, B.; Tiebe, C.; Bartholmai, M.; El Bari, N. Assessment of outdoor odor emissions from polluted sites using simultaneous thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS), electronic nose in conjunction with advanced multivariate statistical approaches. *Atmos. Environ.* **2021**, *256*, 118449. [CrossRef]

24. Kalus, K.; Opalirski, S.; Maurer, D.; Rice, S.; Koziel, J.A.; Korczynski, M.; Dobrzanski, Z.; Kolacz, R.; Gutarsowska, B. Odour reducing microbial-mineral additive for poultry manure treatment. *Front. Environ. Sci. Eng.* **2017**, *11*, 7. [CrossRef]

25. Young Jeong, J.; Atikul Islam, M.; Khan, N.; Jamila, N.; Hong, J.H.; Kim, K.S. Simultaneous Distillation Extraction (SDE) and Headspace Solid-Phase Microextraction (HS-SPME) for the Determination of Volatile Organic Compounds (VOCs) by Gas Chromatography–Mass Spectrometry (GC-MS) in Perilla Frutescens Foliage from South Korea. *Anal. Lett.* **2022**, *55*, 1605–1622. [CrossRef]

26. Monedeiro, F.; Milanowski, M.; Ratti, I.-A.; Zmyslowski, H.; Ligor, T.; Buszewski, B. VOC profiles of saliva in assessment of halitosis and submandibular abscesses using HS-SPME-GC/MS technique. *Molecules* **2019**, *24*, 2977. [CrossRef]

27. Burgeon, C.; Markey, A.; Debliquy, M.; Lahem, D.; Rodriguez, J.; Ly, A.; Fauconnier, M.-L. Comprehensive SPME-GC-MS analysis of voc profiles obtained following high-temperature heating of pork back fat with varying boar taint intensities. *Foods* **2021**, *10*, 1311. [CrossRef]

28. Brown, V.M.; Crump, D.R. An investigation into the performance of a multi-sorbent sampling tube for the measurement of VOCs and VOC emissions from products used indoors. *Anal. Methods* **2013**, *5*, 2746–2756. [CrossRef]

29. Environmental Protection Agency. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. In *Method TO-17 Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes*; Environmental Protection Agency: Cincinnati, OH, USA, 1999; p. 45268.

30. Parker, D.B.; Gilley, J.; Woodbury, B.; Kim, K.-H.; Galvin, G.; Bartelt-Hunt, S.L.; Li, X.; Snow, D.D. Odorous VOC emission following land application of swine manure slurry. *Atmos. Environ.* **2013**, *66*, 91–100. [CrossRef]

31. Gómez, J.S.; Lohmann, H.; Krassowski, J. Determination of volatile organic compounds from biowaste and co-fermentation biogas plants by single-sorbent adsorption. *Chemosphere* **2016**, *153*, 48–57. [CrossRef]

32. Dettmer, K.; Engwald, W. Adsorbent materials commonly used in air analysis for absorptive enrichment and thermal desorption of volatile compounds. *Anal. Bioanal. Chem.* **2002**, *373*, 490–500. [CrossRef]

33. Borusiewicz, R.; Zięba-Palus, J. Comparison of the effectiveness of Tenax TA® and Carbotrapp 300® in concentration of flammable liquids compounds. *J. Forensic Sci.* **2007**, *52*, 70–74. [CrossRef]

34. Ho, S.S.H.; Wang, L.; Chow, J.C.; Watson, J.G.; Xue, Y.; Huang, Y.; Qu, L.; Li, B.; Dai, W.; Li, L. Optimization and evaluation of multi-bed adsorbent tube method in collection of volatile organic compounds. *Atmos. Res.* **2018**, *202*, 187–195. [CrossRef]

35. Ho, S.S.H.; Chow, J.C.; Watson, J.G.; Wang, L.; Qu, L.; Dai, W.; Huang, Y.; Cao, J. Influences of relative humidities and temperatures on the collection of C2-C5 aliphatic hydrocarbons with multi-bed (Tenax TA, Carbograph 1TD, Carboxen 1003) sorbent tube method. *Atmos. Environ.* **2017**, *151*, 45–51. [CrossRef]

36. Kim, Y.-H.; Kim, K.-H. A novel quantitation approach for maximizing detectable targets for offensive/volatile odors with diverse functional groups by thermal desorption-gas chromatography-mass spectrometry. *Sci. Rep.* **2016**, *6*, 29248. [CrossRef] [PubMed]

37. Dutta, T.; Kim, K.-H.; Brown, R.J.; Kim, Y.-H.; Boukhvalov, D. Metal-organic framework and Tenax-TA as optimal sorbent mixture for concurrent GC-MS analysis of C1 to C5 carbonyl compounds. *Sci. Rep.* **2018**, *8*, 5033. [CrossRef] [PubMed]

38. Wang, B.; Zhao, Y.; Lan, Z.; Yao, Y.; Wang, L.; Sun, H. Sampling methods of emerging organic contaminants in indoor air. *Trends Environ. Anal. Chem.* **2016**, *12*, 13–22. [CrossRef]

39. Ullah, M.A.; Kim, K.-H. Performance test of a sorbent tube sampler with respect to analyte loss in collecting biogenic volatile organic compounds. *Anal. Bioanal. Chem.* **2015**, *407*, 415–426. [CrossRef]
40. Brown, V.M.; Crump, D.R.; Plant, N.T.; Pengelly, I. Evaluation of the stability of a mixture of volatile organic compounds on sorbents for the determination of emissions from indoor materials and products using thermal desorption/gas chromatography/mass spectrometry. J. Chromatogr. A 2014, 1350, 1–9. [CrossRef]

41. Kim, K.-H.; Lee, M.-H.; Szulejko, J.E. Simulation of the breakthrough behavior of volatile organic compounds against sorbent tube sampler as a function of concentration level and sampling volume. Anal. Chim. Acta 2014, 835, 46–55. [CrossRef]

42. Salthammer, T. Very volatile organic compounds: An understudied class of indoor air pollutants. Indoor Air 2016, 26, 25–38. [CrossRef]

43. Woolfenden, E. Monitoring VOCs in air using sorbent tubes followed by thermal desorption-capillary GC analysis: Summary of data and practical guidelines. J. Air Waste Manag. Assoc. 1997, 47, 20–36. [CrossRef]

44. Choi, Y.L.; Lee, S.; Kim, D. Determination of volatile organic compounds and sulfur-based odorous substances from sewage treatment plants. J. Odor Indoor Environ. 2018, 17, 161–167. [CrossRef]

45. Woolfenden, E. Sorbent-based sampling methods for volatile and semi-volatile organic compounds in air. Part 2. Sorbent selection and other aspects of optimizing air monitoring methods. J. Chromatogr. A 2010, 1217, 2685–2694. [CrossRef] [PubMed]

46. Bingham, E.; Cohrssen, B.; Powell, C.H. Patty’s Toxicology. Volume 1: Toxicology Issues, Inorganic Particulates, Dusts, Products of Biological Origin and Pathogens; John Wiley and Sons: Hoboken, NJ, USA, 2001.

47. Leonardos, G.; Kendall, D.; Barnard, N. Odor threshold determination of 53 odorant chemicals. J. Environ. Conserv. Eng. 1974, 3, 579–585. [CrossRef]

48. Amoore, J.E.; Hautala, E. Odor as an aid to chemical safety: Odor thresholds compared with threshold limit values and volatilities for 214 industrial chemicals in air and water dilution. J. Appl. Toxicol. 1983, 3, 272–290. [CrossRef]

49. Kim, K.-H.; Park, S.-Y. A comparative analysis of malodor samples between direct (olfactometry) and indirect (instrumental) methods. Atmos. Environ. 2008, 42, 5061–5070. [CrossRef]

50. Sui, H.; Liu, J.; He, L.; Li, X.; Jani, A. Adsorption and desorption of binary mixture of acetone and ethyl acetate on silica gel. Chem. Eng. Sci. 2019, 197, 185–194. [CrossRef]

51. Sui, H.; Liu, H.; An, P.; He, L.; Li, X.; Cong, S. Application of silica gel in removing high concentrations toluene vapor by adsorption and desorption process. J. Taiwan Inst. Chem. Eng. 2017, 74, 218–224. [CrossRef]

52. Huang, W.; Xu, J.; Tang, B.; Wang, H.; Tan, X.; Lv, A. Adsorption performance of hydrophobically modified silica gel for the vapors of n-hexane and water. Adsorpt. Sci. Technol. 2018, 36, 888–903. [CrossRef]

53. Kutluay, S.; Temel, F. Silica gel based new adsorbent having enhanced VOC dynamic adsorption/desorption performance. Colloids Surf. A Physicochem. Eng. Asp. 2021, 609, 125848. [CrossRef]

54. Liu, Y.; Lu, W.; Wang, H.; Huang, Q.; Gao, X. Odor impact assessment of trace sulfur compounds from working faces of landfills in Beijing, China. J. Environ. Manag. 2018, 220, 136–141. [CrossRef]

55. Capelli, L.; Sironi, S.; Del Rosso, R.; Guillot, J.-M. Measuring odours in the environment vs. dispersion modelling: A review. Atmos. Envi. 2013, 79, 731–743. [CrossRef]

56. United States Environmental Protection Agency. Definition and Procedure for the Determination of the Method Detection Limit, Revision 2; United States Environmental Protection Agency: Washington, DC, USA, 2016; p. 20460.