Part 2: Odor-Cued Grab Sampling of Transient Environmental Odor Events; Mapping the 'Rolling Unmasking Effect' of Downwind Odor Dispersion

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Abstract: Downwind odor characteristics can be very different depending upon the size of the upwind point-source, interim topography, and wind conditions. At one extreme, the downwind odor plume from a relatively large, confined animal feeding operation (CAFO), located on a flat open plain and under stable, near-straight-line wind conditions can be rather broad, sustained and predictable relative to a fixed receptor site downwind. In contrast, the plume from a small point-source (e.g., a roof vent stack) located on irregular topography and under rapidly shifting wind conditions can be intermittent and fleeting. These transient odor events can be surprisingly intense and offensive, in spite of their fleeting occurrence and perception. This work reports on efforts to optimize an environmental odor sampling strategy, which is optimized for the challenges of (1) sampling of such transient odor ‘spikes’ and (2) the prioritization of odors/odorants from multiple, closely co-located point-sources, under such transient event conditions. Protocol refinement has emerged by way of 2 environmental odor assessment projects which have been undertaken on behalf of the Missouri Department of Natural Resources. The challenge of transient odor events has been mitigated utilizing rapid, odor cued whole-air grab capture sampling into metalized-FEP gas sampling bags, followed by immediate adsorption transfer onto SPME fibers or sorbent tubes for stabilization during the shipment and storage interval between collection and final analysis. Initial results demonstrated approximately 11 fold increases in target odorant yields for 900 mL sorbent tube transfers from 2-3 second ‘burst’ odor event bag-captures, as compared to equivalent direct collections at the same downwind receptor location but during perceived (stable) odor ‘lull’ periods. Results-to-date targeting refinement and field trials of this integrated environmental odor assessment strategy are presented. Preliminary application targeting general odor sampling and point-source differentiation utilizing tracer gases is also presented.

Keywords: malodor analysis, agricultural odor, turbulent dispersion, GC-Olfactometry, GC-O, solid-phase microextraction, SPME, multidimensional gas chromatography, MDGC, process odor, dispersion modeling, transient odor events, rolling unmasking effect, odor-cued grab sampling

1. Introduction

The authors previously reported on downwind odor sampling challenges encountered relative to a study focused on the Carthage Bottoms Industrial Area (i.e., CBIA) located on the northern edge of Carthage, Missouri [1]. As summarized in the previous report, much of the challenge associated with these downwind assessments resulted from the surprisingly transient, odor ‘spike’ characteristic encountered. These odor spikes were typical, momentary ‘hits’ or odor sensations of only a few seconds duration interspersed with long periods where the odor was undetectable or only faintly detectable. This characteristic appeared to be the result of (1) the at-distance downwind assessment format of a dispersed plume from the primary odor source; (2) relatively small point-source(s) carrying primary responsibility for the priority downwind impact and (3) frequent and rapid shifts...
in wind direction. It should be noted that this situation differs from that associated with many CAFO sources [2] in that CAFOs as odor sources can be rather broad (e.g., large manure piles, compost heaps, lagoons or field manure applications). In contrast, high-impact odor sources relative to the CBIA were believed to be traceable to comparatively small (i.e., approximately 1 to 6 ft diameter) roof or elevated stack vents.

These transient odor events are believed to be manifestations of the non-gaussian plume dynamic, which some dispersion modeling researchers have previously attempted to address [3,4]. In fact, these efforts suggest that current mathematical models that describe downwind plume dynamics as uniform Gaussian distributions [5] may be limiting, especially with respect to the issue of downwind odor impact. Regarding air toxics, for example, time-weighted average exposures of downwind citizenry can carry real significance with respect to predicting the cumulative impact on health. In contrast, from the standpoint of these same citizens, odor impact is best characterized as pass / fail or on/off events. Priority odorant concentrations are either below or above the recognition (i.e., or annoyance) threshold at any given moment-in-time. In the case of the former, the citizen-receptor is not impacted in the least; with respect to the latter, the frequency and intensity of these above-threshold excursions will determine the perceived quality-of-life impact.

As a result of the transient nature of the CBIA odor events, it was shown to be very difficult to achieve reasonable odorant / VOC loadings in downwind air samples collected for subsequent odorant prioritization analysis. This was especially true utilizing the preferred, direct solid-phase micro-extraction (i.e., SPME) sampling approach. The integrated strategy reported below was developed as a potential alternative for greater target odorant yields in sampling of such transient odor spikes. These results integrate some of the findings and strategies emerging from the USDA funded SBIR project referenced in the Acknowledgements section which follows, including (1) metalized-FEP gas sampling bags for maximum recovery of the highest impact polar semi-volatile odorants; (2) the necessity for minimizing sample storage time in the vapor state in the metalized-FEP bags and (3) the integration of SPME fiber or sorbent tube transfer collection/storage from the metalized-FEP bag vapor ‘grab’ collection, to achieve constraint (2).

2. Materials and Methods

2.1 Multidimensional Gas Chromatography-Mass Spectrometry-Olfactometry

MDGC-MS-Olfactometry is an integrated approach combining olfactometry and multidimensional G.C. separation techniques with conventional GCMS instrumentation. A commercial, integrated Multidimensional-Gas Chromatography-Mass Spectrometry-Olfactometry (i.e., MDGC-MS-O) system was used for the target odorant analysis work as presented herein. The integrated system consisted of an Agilent 6890 Gas Chromatograph / 5975B Mass Spectrometer modified for MDGC-MS-O utilizing an AromaTrax™ control system from Volatile Analysis Corporation of Round Rock, Texas. Details regarding general hardware and AromaTrax™ operation have been described in detail in past publications [6], [7], and are not restated here. Specific operational parameters utilized for the targeted odorants, as well as their associated tracer compounds during dual point-source prioritization experiments, is summarized as follows: injection mode: split-less with solid-phase microextraction (SPME) sample collection and delivery; injection temperature: 250 °C; detector #1: Flame Ionization Detector (FID); detector #1 temperature: 280 °C; detector #2: Agilent 5975B MSD in MS-SCAN or MS-SIM acquisition mode; column # 1: 12 m x .53 mm ID BPX 5 - 1.0 µm film (pre-column from SGE); column # 2: 25 m x 0.53 mm ID BPX 20 - 1.0 µm film (analytical column from SGE); column temperature program (overview survey and MDGC-MS-O): 40 °C initial, 3 min hold, 7 °C/min., 220 °C final, 20 min hold.

A series-coupled sorbent tube pair was utilized for this testing. The fore tube was packed with @ 2 cm (0.022 g) of Tenax TA, an adsorbent of moderate strength. The aft tube was packed sequentially, with @ 1 cm (0.009 g) Carbopack B and @1 cm (0.009 g) Carboxen; adsorbents representing sequentially increasing adsorbent strength. The integrated tracer gas injection/sample
bag to sorbent tube transfers were carried out utilizing a prototype Peltier cryotrap device. This device was set to control at $@ 2 \, ^\circ \text{C}$ for increasing the trapping efficiency of the Tenax TA fore trap.

2.2 SPME Sampling

Solid-phase microextraction [7-12] utilizing a 1 cm Carboxen modified PDMS - 75 µm fiber was the headspace sampling technique that was utilized for the initial efforts. SPME collections were carried out by direct fiber exposure, downwind of the scale-model transient odor event generators. The SPME fibers which were prepared for this segment of the project were: (a) preconditioned $@ 260 \, \text{deg C}$ by the first author; (b) transported by the first author, under dry-ice storage conditions, to the field-trial site for execution of the reference and peak-event odor collections by direct SPME fiber exposure and (c) return transported by the first author, under dry-ice conditions back to the laboratory for execution of the analytical segment of the experiment. Figure 1 below presents a general image of the environmental sampling fixture utilized for direct SPME fiber exposure. In this case, the preconditioned SPME samplers are shown secured within a field-support stand; the preconditioned adsorbent coated fiber tips shown retracted back into their protective needle sheaths, in preparation for exposure to the environment to initiate sample collection. Volatiles loadings on the SPME fibers were varied by altering the length of time the SPME fibers were exposed to the air environments.

![Figure 1. SPME sampler stand with 4 field SPME fibers in place.](image)

2.3 Weather Monitoring

A Kestrel 4500 Pocket Weather Tracker was used during the transient event, and source differentiation experiments with the prototype scale model transient event generators described below. This unit is tripod mounted, configured for wind direction monitoring, and incorporates comprehensive data logging capabilities.

2.4 Scale Model Transient Odor Event Generator

A prototype odor generator was designed to permit up to 4 target odorants to be combined at selected ratios prior to ejection from the small vent stack under controlled flow conditions. The target odorants were placed into one of three PVC generator cartridges in an appropriate form depending upon the targeted odorant and the goal of the experiment. These forms include: (1) measured amounts of high purity solids such as naphthalene; (2) permeation tubes for odorants of high volatility and (3) odorant saturated polymeric materials, in film or fiber form, were used as odor carrier materials for odorant ‘surge release’ simulation. Each cartridge was affixed with a blower, operating under independent rheostat control. In the first generation prototype form, the blowers
used were relatively inexpensive hair dryers. The vent stack and odorant cartridge assemblies were fabricated from 3-inch Schedule 40 PVC and associated fittings (i.e., see photos/diagrams in the Supplemental Materials Section). The stack vent terminated @ 7 ft above ground level and is shown in Figure 5.

2.5 Sampling for Transient Odor Events; Odor Cued Whole-Air Grab Form

A sampling variation was applied during the sampling sessions in an effort to off-set the challenges brought about by transient odor events (i.e., the momentary, fleeting nature of environmental odor events; brought about by shifting wind conditions and associated shifting of targeted odor plumes). In addition to the direct, SPME fiber air sample collections summarized above, alternate collections were taken in which the SPME fiber exposures were applied to momentary whole-air grab-capture air samples. These grab samples were collected over 2-3 second intervals (i.e., Figure 2), attempting to coincide those momentary collections with perceived momentary peak odor events. The odor-cued air sample collections were captured within 1L metalized FEP (i.e., metalized fluorinated ethylene polymer) gas sampling bags before immediate transfer to SPME fibers or adsorbent tubes for stabilization during the storage interim between collection and analysis. In the case of SPME fiber collection/storage, the fibers were quickly exposed to the captured odorous air contents within the bag. All other SPME fiber preconditioning and logistics handling parameters were as described above for direct environmental air sampling. First and second-generation prototype odor grab sampling assemblies are shown in Figures 2, 3, 4. As shown, refinements in the second generation prototype assembly included: (1) rigid mount of a battery-powered vacuum/pressure pump system for control of gross bag inflate/deflate; (2) rigid mounted 1L gas-tight syringe for final m-FEP sample bag evacuation before sample collection; (3) integrated, cartridge-form quick-change vacuum chamber + m-FEP sample bag assembly; (4) A smartphone mounting platform extension between the vacuum chamber and pump assemblies; positioned to permit time / date-stamped video recording of the orientation and movement of the wind strip indicator mast, accompanying the momentary grab sample collections and (5) a low-speed wind strip indicator mast [13].

Figure 2. Second generation prototype grab sampling assembly: Syringe and sampling bag chamber 'cartridge' assemblies are shown rigid-mounted near the top of the pole-support assembly. A selectable, vacuum/pressure air pump assembly is positioned below this syringe/bag chamber bracket assembly. A smartphone mounting platform extension is mounted between the two, positioned to permit video recording of the orientation and movement of the wind strip-indicator mast, accompanying the momentary grab sample collections. The first author is shown awaiting a characteristic odor-cue for a targeted odor event.
2.6 Tracer Gas Injection Strategy for Point-Source Prioritization

Each of two, independent, transient event generators was configured to permit steady-state emission of one characteristic odorant and one associated tracer gas. Generator #1 was configured for the controlled release of the odorant/tracer pair, naphthalene, and chloroform. Generator #2 was configured for the controlled release of the contrasting odorant/tracer pair, 1,4-dimethoxybenzene / methylene chloride. The tracer compounds were injected under controlled conditions utilizing a variation of the automated vaporizing injection technique as previously described by the first author for the vinyl chloride purity assay analysis (ASTM D-5507-08).

3. Results

3.1 Transient odor simulator trials
Significant challenges were encountered in 2007 when, on behalf of the Missouri DNR, the authors attempted sampling of the transient downwind odor events which were characteristic of the CBIA in Carthage, Missouri. In an effort to expedite the development of an improved approach to overcome these challenges, a small scale transient odor event simulator was designed, constructed, and carried through initial experimental evaluation. The first-generation prototype, shown in Figure 5 below, was designed to permit up to 4 target odorants to be combined at selected ratios prior to being ejected from the small vent stack under controlled flow conditions.

Figure 5. First-generation prototype scale-model transient odor event simulator.

The goal of this follow-up effort was, to the extent possible, compress the distance and time cycle factors responsible for drawing out the transient odor sampling process optimization. Based on initial results, the system successfully achieved the following: (1) compressed the assessment area from @ 1 sq. mile at the CBIA to @ 0.5 acres; (2) compressed the maximum source to receptor distance from @ 1 mile at the CBIA to @ less than 100 ft; (3) compressed the average event frequency from < 2 per hour at the CBIA to > 20 per h and (4) compressed travel time to survey site from several hours to < 10 min.

Initial experimental results with the model were very encouraging. Beginning with a binary odorant challenge system consisting of contrasting odorants (i.e., high purity naphthalene and its ‘mothball’ odor and 1,4-dimethoxybenzene and its character-defining ‘bluebonnet-field’ aroma), it was possible to quickly achieve a steady-state condition of several hours duration with the following characteristics: (1) odor frontal boundary @ 70 feet; (2) the odor character at the odor frontal boundary (i.e., 50 to 70 feet) was clearly dominated by 1,4-dimethoxybenzene / ‘bluebonnet-field’ and (3) the near-source (i.e., 5 to 10 feet) odor character was clearly dominated by naphthalene / ‘mothball.’ In addition: (4) later experiments integrated p-cresol as a third, limited, odorant challenge; limited in that it was delivered from a latex glove ‘carrier’ which had been placed overnight in a concentrated p-cresol headspace environment to approach saturation. Upon integration into the 3rd cartridge of the 3-odorant odor generator assembly: (a) the odor frontal boundary immediately shifted outward to ~100 feet; (b) the odor character approaching the outer boundary was that of pure p-cresol / ‘barnyard’; unaffected by the 1,4-dimethoxybenzene / ‘bluebonnet-field’ odor; (c) the limited loading of p-cresol in the latex glove carrier resulted in a slow, exponential decay of the ‘barnyard’ odor boundary back toward the source; (d) upon approaching the 70 ft to reach the point of the ‘bluebonnet-field’ odor (e.g., secondary boundary interface as shown in Figure 6 below) the odor-character ‘confusion’ commonly associated with blending of odorants occurred, but over a relatively narrow band; (e) as the diminishing p-cresol driven ‘barnyard’ odor continued its migration back toward the source, the 1,4-dimethoxybenzene driven ‘bluebonnet-field’ odor was observed to reemerge to the point that, eventually, there was no discernable impact from p-cresol. In this case, it
is that 70 ft secondary boundary where, owing to the Rolling Unmasking Effect (i.e., RUE), the odor frontal boundary transitions to the odor-character of the ‘next-in-line’ impact-priority odorant. Stated another way, the selective elimination of the initial masking effect of the p-cresol / ‘barnyard’ odor resulted in a reduction of the downwind reach of the priority ‘barnyard’ odor from ~100 feet to ~70 feet. This reduction in downwind reach was accompanied by a corresponding change in odor character at the ‘new’ odor frontal boundary, from ‘barnyard’ to ‘bluebonnet-field.’ This ‘next-in-line’ boundary is the secondary interface boundary, which is shown in Figure 6 below, a diagrammatic representation of the effect of the RUE on the outward progression of odor character relative to an odor source.

![Figure 6](image.png)

**Figure 6.** Generic pictorial representation of ‘rolling unmasking effect’ (RUE). The odor frontal boundary represents the farthest downwind reach relative to the odor source while the internal bands represent the points of sequential odor unmasking as the secondary-impact odorants are diluted below their detection/masking concentration levels.

### 3.2 A Two-Step Strategy for Sampling of Transient Downwind Odor Events

Encouraging sampling yield improvements were achieved by applying the odor-cued two-step sampling process to the challenge of transient odor events. The rapid grab samples of @ 2 seconds duration were manually drawn into metallic-FEP gas sampling bags, cued by the investigator’s perception of odor event peak intensity. This was followed, as quickly as possible, by sampling of the captured bag contents through extended SPME fiber exposure times of up to 0.5 h. As shown in Table 1 below, utilizing this approach, it was possible to achieve an approximate 4 fold ms-SIM response increase for the targeted naphthalene odorant, in comparison to reference 3 min direct SPME fiber exposures to the same downwind environment.

A number of alternatives for transient event odorant sampling were considered in light of the challenges initially encountered for the direct SPME approach. One alternative approach for concentrating high-impact odorants is by sorbent tube directly, and, like SPME, this technique will work well for odor events that are somewhat sustained (e.g., CAFO). However, as a result of the normal flow restrictions of packed adsorbent tubes, there is still a limit to the volume of air which can be processed during such brief transient events. For example, assuming a 30 cc/min peak flow rate through a packed sorbent tube under full vacuum (i.e., ~14.7 psi pressure differential), approximately 30 min is still required for concentrating odorants from a 1000 cc air sample. Unfortunately, this is a relatively long period in relation to transient odor events such as those encountered relative to the CBIA. As shown above for SPME sampling, the two-step odor-cued sampling process was shown to achieve a reasonable compromise between sample volume requirements and transient event induced time constraints. With respect to the sorbent tube strategy, the two-step grab sampling variation integrates m-FEP gas-bag and sorbent tube techniques in the following manner: (1) rapid, 1 liter grab samples of 2 to 3 seconds duration are vacuum drawn into
m-FEP gas sampling bags during the perceived momentary peak odor events and (2) these whole-air collections are followed by immediate transfer of the bag contents to packed sorbent tubes for transport and storage in the interim between sample collection and lab analysis. As shown in Table 2 below, an average 11X increase in target odorant response was achieved for the 2-3 s grab captured odor events, as compared to 900 mL direct collections at the same downwind receptor-site during perceived interim odor ‘lull’ periods. It is noteworthy that this collection series was made during an extended period of relatively stable wind conditions. It is also believed noteworthy that the sample points were selected to be at the approximate geometric center between the plume lateral downwind boundaries.

Table 1. m-FEP Gas Bag Grab Sample / Extended SPME Exposure.

<table>
<thead>
<tr>
<th>Indirect Series</th>
<th>Naphthalene Response</th>
<th>Response Differential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run #1</td>
<td>10,524</td>
<td></td>
</tr>
<tr>
<td>Run #2</td>
<td>10,318</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>10,421</td>
<td>4 X Direct</td>
</tr>
<tr>
<td>Direct Series</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fiber #1</td>
<td>2,624</td>
<td></td>
</tr>
<tr>
<td>Fiber #2</td>
<td>2,451</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>2,538</td>
<td>0.25 X Indirect</td>
</tr>
</tbody>
</table>

Table 2. m-FEP Gas Bag Grab Sample / Sorbent Tube Transfer.

<table>
<thead>
<tr>
<th>Indirect 'Peak' Series</th>
<th>Naphthalene Response</th>
<th>Relative Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run #1</td>
<td>83,915</td>
<td>13.5 X</td>
</tr>
<tr>
<td>Run #2</td>
<td>54,851</td>
<td>8.8 X</td>
</tr>
<tr>
<td>Direct 'Lull' Reference</td>
<td></td>
<td>1X</td>
</tr>
</tbody>
</table>

3.3 Tracer Gas Integration to Controlled Model Stack Emissions

The optimized transient event sampling strategy described above is potentially applicable to a number of downwind odor assessment challenges. One of these challenges is in the downwind impact prioritization of multiple, closely co-located upwind point-sources. Simply stated, if an investigator is successful in prioritizing the specific odorants most responsible for negative impact at the frontal odor boundary, he should be able to use this information to shift focus back to prioritize from among multiple, ‘potential’ upwind point-sources. This current effort explores the use of optimized odor-cued grab sampling in conjunction with signature odorant or tracer spiking of discrete upwind point-sources. Sulfur hexafluoride (SF6) and perfluorocarbon tracer (PFT) compounds have been widely referenced (Dietz et al., 1982; Dietz, 1986) for such VOC dispersion and air movement profiling studies. However, with respect to this application, others may also be appropriate and could be selected based upon: (1) relatively low odor impact; (2) high chemical stability; (3) relative absence from the normal environmental background of the target area and (4) safety and environmental impact considerations. For the purposes of this exploratory scale-model effort, chloroform and methylene chloride were selected as the tracer compounds. These selections were made solely on the basis of availability and appropriateness of physical and analytical properties rather than any perception of applicability to expanded full-scale studies.

To ensure a high degree of precision in the rate of tracer compound introduction, the liquid form compounds were injected and vaporized under controlled conditions utilizing a variation of the automated vaporizing injection technique (ASTM D-5507-08). This technique was previously described for the industry-standard vinyl chloride purity assay analysis and has been used...
extensively to achieve a high degree of precision in that analysis. The process variation, in summary, are: (1) the liquid tracer feed reservoir is pressurized with nitrogen, well beyond the compound’s natural vapor pressure; (2) the over-pressured liquid is fed through a fixed restrictor which terminates in the heated vaporization chamber and (3) control and limitation of the tracer feed-rate is achieved by matching the liquid feed head pressure with the restriction (i.e., length and I.D.) of the tubular fixed restrictor. The naphthalene/chloroform ratio data summarized in Table 3 below was carried out to determine the precision which could be achieved utilizing this approach for tracer introduction into the model stack emission. The data reflects the results from 5 sequential sorbent tube collections from model Stack #1, which was configured for odorant/tracer pair emission. The 8.6% RSD value was felt to be excellent considering the fact that it reflects the complete range of experimental variability; (1) the odorant/tracer vaporization process; (2) stack emission process; (3) meteorological variability; (4) the transient event downwind sampling process and (5) the analytical process. It is possible, although unproven at this point, that the general upward trending of the ratio values (i.e., increasing naphthalene response relative to that of the chloroform tracer) stems from rushing the start of the collection series before achieving naphthalene emission equilibrium.

Table 3. Odorant / Tracer Pair Response Ratio Precision.

<table>
<thead>
<tr>
<th>Run Number</th>
<th>Naphth / CCl₃ Response Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run #1</td>
<td>0.84</td>
</tr>
<tr>
<td>Run #2</td>
<td>0.98</td>
</tr>
<tr>
<td>Run #3</td>
<td>0.96</td>
</tr>
<tr>
<td>Run #4</td>
<td>0.95</td>
</tr>
<tr>
<td>Run #5</td>
<td>1.07</td>
</tr>
<tr>
<td>Mean</td>
<td>0.96</td>
</tr>
<tr>
<td>sd</td>
<td>0.082</td>
</tr>
<tr>
<td>%RSD</td>
<td>8.56</td>
</tr>
<tr>
<td>n</td>
<td>5</td>
</tr>
</tbody>
</table>

3.4 Integrated Sampling Strategy for Upwind Odor Point-Source Prioritization

Based on the precision reflected in the above odorant/tracer ratio data, it was felt that point-source prioritization should be relatively straightforward. These results suggest that by coordinating; (1) transient event peak odor-cued grab sampling; (2) priority odorant identification/detection; (3) tracer compound relative abundance (i.e., or relative absence) and (4) coincident meteorological conditions, a definitive source prioritization from among multiple ‘potential’ up-wind point-sources should be achieved. To explore and refine the process, an expanded field test was carried out utilizing two independently controlled and positionable transient odor event generator stacks. Stack #1, as described above, was configured for controlled emission of the naphthalene/chloroform, odorant/tracer pair. In contrast, Stack #2 was configured for controlled emission of the 1,4-dimethoxybenzene / methylene chloride odorant/tracer pair. Figure 7 below shows the integrated generator system, which was utilized for this point-source prioritization field test. Shown in the right foreground are the two point-source generators. To the left background is the data logging weather station.
Figure 7. Integrated multiple point-source transient odor event generator systems. To the right are the two contrasting point-sources. To the left background is the tripod-mounted weather data logger.

For the initial field trial, two contrasting conditions were targeted: (1) transient ‘mothball’ odor events, indicating a naphthalene concentration spike, and (2) transient ‘bluebonnet field’ odor events, indicating a 1,4-dimethoxybenzene concentration spike. Six, series-coupled sorbent tubes were distributed to reflect, triplicate naphthalene ‘peak’ events, and triplicate 1,4-dimethoxybenzene ‘peak’ events. Unfortunately, weather conditions turned un-favorable for initiating the test, but once the set-up was begun, a decision was made to continue. Specifically, an approaching cold front and degrading wind conditions forced accelerated initiation of the transient event sampling process. Under the rapidly deteriorating wind conditions (i.e., both wind speed and direction variability), the transient odor events were found to be particularly brief; approximately 1 to 3 sec in duration, typical. Under the rushed conditions, it was not possible to ensure that the generators were allowed to reach emission steady-state before starting the downwind collections. As surmised previously, the resulting non-steady-state condition appears to be reflected in the generally ‘ascending’ naphthalene/chloroform ratio values for the ‘mothball’ odor peak series (i.e., 1.10, 1.00 and 1.52). Adding to the weather-related challenge, another problem arose due to the fact that the second generator (i.e., 1,4-dimethoxybenzene / methylene chloride) had not been carried through a post-fabrication mechanical check-out prior to initiating this field trial. As a result, unexpected mechanical problems were encountered during set-up, which adversely affected control of both methylene chloride feed and stacks total flow.

Table 4. Transient Event Sampling with Tracer Gas Injection for Point-Source Prioritization.

<table>
<thead>
<tr>
<th>'Mothball' Event</th>
<th>Naphthalene</th>
<th>CCl3</th>
<th>DMB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run #1</td>
<td>220,450</td>
<td>200,750</td>
<td>6,592</td>
</tr>
<tr>
<td>Run #2</td>
<td>653,343</td>
<td>650,217</td>
<td>390</td>
</tr>
<tr>
<td>Run #3</td>
<td>584,887</td>
<td>386,036</td>
<td>480</td>
</tr>
<tr>
<td>Mean</td>
<td>486,227</td>
<td>412,334</td>
<td>2,487</td>
</tr>
<tr>
<td>'Bluebonnet Field' Event</td>
<td>Run #1</td>
<td>Run #2</td>
<td>Run #3</td>
</tr>
<tr>
<td>-------------------------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td></td>
<td>26,522</td>
<td>35,053</td>
<td>17,428</td>
</tr>
<tr>
<td></td>
<td>&lt;dl</td>
<td>5,580</td>
<td>2,988</td>
</tr>
<tr>
<td></td>
<td>4,203</td>
<td>84,373</td>
<td>3,771</td>
</tr>
</tbody>
</table>

As a result of the above complications, this experimental series is only considered significant from a system tuning perspective in advance of subsequent, fully integrated, field trials. Further, it should be viewed in the context of a 3 component strategy for point-source prioritization. In this context, naphthalene represents the ‘mothball’ transient odor event target; chloroform serves as the tracer gas for point-source #1 and 1,4-dimethoxybenzene serves as the sensory cue for timing the sampling event for reference point-source #2. This strategy is believed to be appropriate for those situations where the goal is to differentiate the relative downwind impact of a primary suspect point-source with respect to that of a ‘potential’ reference.

Within the constraints imposed by the above-stated context, the data shown does provide a number of observations that are believed to be significant. In particular, the first three collections, reflecting ‘mothball’ cued transient events, reflect consistent correlations between the sensory and analytical data. The chloroform average response during the ‘mothball’ peak events was 74 fold higher than for the highest individual chloroform response and 188 fold higher than the average chloroform response values during the contrasting ‘bluebonnet field’ cued transient events. Likewise, the naphthalene average response during the ‘mothball’ peak events was 14 fold higher than for the highest individual naphthalene response and 22 fold higher than the average naphthalene response values during the ‘bluebonnet field’ cued events. Unfortunately, the naphthalene/chloroform response ratio values were 1.10; 1.00 and 1.52 for an average of 1.21 and sd of 0.28 for a %RSD of 23.1%. This level of variation is higher than expected (i.e., the previous field trial series results were avg = 0.96, sd = 0.082, %RSD = 8.56% for n=5) or would normally be acceptable, but given the above stated meteorological challenges should probably be expected.

3.5 Transient sampling strategy implications for field odor assessments by Dynamic Dilution Olfactometry

Efforts-to-date relative to the assessment of transient odor events has primarily been directed at the analytical approach to priority odorant assessment. However, the transient event characteristic also magnifies the challenge associated with follow-up investigation of citizen odor complaints utilizing human ‘sensors’ and Dynamic Dilution Olfactometry (i.e., DDO), (ASTM E-679, 2004; ASTM E-1432; 2004 and CEN/TC264, 1999). Typically, agency officials receive a complaint from downwind citizens and put an investigator on the road to drive the miles to the complaint site. As often happens, in the minutes or hours that it takes for this official response, the odor impact will have shifted to a new location. Likewise, even if the event is still perceptible, it is likely to be difficult to get an accurate fix on the ‘odor dilution number’ when dealing with such a rapidly shifting target. Preliminary results indicate that, in addition to analytical assessment strategies, the odor-cued grab-capture strategy may be applicable to DDO assessment techniques as well (USDA NIFA SBIR Phase II final report). For example, the following narrative segment was taken from the final report, which was filed in February 2011 for this USDA SBIR funded study.

‘…That goal [of this Phase II project] can best be summarized as the development of a robust strategy for capture, transport, archiving, and deferred ‘re-play’ of environmental odor events. We believe that the integrated materials and sampling strategies which have emerged from our efforts begin to strike very close to that overall goal; in spite of the considerable challenges imposed by (a) the VOC emission complexity commonly associated with CAFOs and (b) the constraints imposed by Van der Waals attractive forces in concert with the Maxwell-Boltzmann energy distribution relationship. The progress-to-date toward this overall goal can best be illustrated by visual survey of the two figures which follow.'
Figure 8. Contrasting Volatile Organic Compounds (VOC’s) recoveries for chamber direct versus thermally reconstituted [from sorbent tube] after 7-day freezer storage; overview.

Figure 9. Contrasting VOC recoveries for chamber direct versus thermally reconstituted [from sorbent tube] after 7-day freezer storage; zoom-in view.

Shown in Figure 8 (overview) and Figure 9 (zoom-in view) are two dual-chromatogram comparisons which are presented in mirror-image format. The downward-pointing chromatogram in each figure reflects the direct SPME sampling of a well-equilibrated, odor chamber while the upward chromatogram reflects the contrasting, indirect SPME sampling [of that environment] from a 1 liter, whole-air, m-FEP bag sample which had been thermally reconstituted from sorbent tubes after a 7-day freezer storage period. It is important to note that execution of the two comparative sample collections (i.e., direct SPME chamber followed immediately by indirect sorbent tube collection) were, by experimental design, executed on the same day and within a very short timeframe (i.e., ~25 min total) to minimize compositional changes which might otherwise result from long delays. It is also noteworthy that, by design, the same SPME fiber was utilized for both sampling conditions, to off-set the normal variables associated with differences between individual SPME fibers. Intuitively, the ultimate goal for such an experiment would be a perfect symmetry shown for the total volatiles profile, with respect to both major and trace volatiles constituents. The reality, however, is that such symmetry’ perfection’ is not required to replicate the target odor, since most of the peaks shown in these complex profiles do not contribute significantly to the odor impact, but...
rather, are relegated to the status of 'background noise.' This being said and against the challenges imposed by the Maxwell-Boltzmann energy distribution relationship, the overall level of symmetry shown in these comparative profiles are believed to be quite remarkable. To illustrate, MDGC-MS-Olfactometry based odorant prioritization efforts by the segment lead investigator indicated that the odor character and intensity for the test chamber were defined, primarily, by a pair of trace-level semi-volatiles: (a) guaiacol @ 21.4 min and (b) p-cresol @ 24.6 min (i.e., both within a headspace concentration range of ~5 to 10 ppbv). In addition, secondary odor impact-priority for the chamber environment was indicated for (c) skatole @ 31.5 min in combination with the volatile free fatty acids: (d) butyric @ 17.0 min and (e) isovaleric @ 17.8 min. If the symmetry survey is limited to this proposed, minimum subset of odorous VOCs, the level of agreement between 'before and after' collection, long-term cold-storage, and thermal reconstitution are believed to be very significant…'

The key consideration relative to any gas bag based odor sampling strategy, whether analytical or sensory, is the constraint that samples must only be held in the whole-air form for very short periods of time; just long enough for either immediate analysis or transfer to an adsorbed form (e.g., SPME fiber or packed thermal desorption tube) for shipment/storage in the interim between collection and analysis. Semi-volatile odorant recovery data to-date suggests that this time limit should likely be in the range of 15 to 30 min, in marked contrast to the 24 to 36 h constraint reflected in many current protocols.

5. Conclusions

The challenge encountered and addressed in this work was the special case of transient downwind odor events; brief events of, typically, only a few seconds duration in spite of relatively significant peak odor intensities. Attempts to address this unique challenge have led to the development of a novel transient event sampling strategy. The novel odor-cued grab sampling concept is summarized as (1) rapid fill of a metalized-FEP bag at the instant of a perceived peak odor event followed by (2) immediate transfer of the bag-captured odorant contents onto SPME fibers or packed sorbent beds for transport and storage in the interim between field collection and laboratory analysis. Encouraging initial evaluation of the concept and device has been realized utilizing scale-model transient odor event generator devices. A 4 fold increase in target odorant yield was realized for 30 min SPME fiber exposures to 2-3 s bag-capture odor events; when compared to 3 min direct exposures to the same downwind location. Likewise, an 11 fold increase in target odorant yield was shown for a 900 mL adsorbent tube transfers from 2-3 s odor-cued bag-captures; when compared to equivalent 900 mL direct collections at the same downwind location during perceived interim odor 'lull' periods. Efforts, reported herein, have subsequently been directed at applying this transient event sampling strategy to the challenge of scale-model point-source prioritization. Despite a number of unexpected meteorological challenges during the initial field-trial attempt, preliminary data indicate that odor impact prioritization from among multiple 'potential' upwind point-sources is feasible. The critical elements of this strategic application are: (1) correct downwind odorant impact prioritization and detection; (2) contrasting tracer gas injection; (3) tracer odorant injections, as required for contrasting sensory cue purposes; (4) rapid, odor-cued transient event grab sample capture and (5) SPME fiber or adsorbent bed transfer/stabilization to ensure odorant capture stability in the interim during extended periods between the collection, shipment, and analysis.

Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1, Figure S1: title, Table S1: title, Video S1: title.


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