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## Odor-Cued Grab Air Sampling for Improved Investigative Odorant Prioritization Assessment of Transient Downwind Environmental Odor Events

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**ABSTRACT:** A critical prelude to any community odor assessment should be the prioritization of specific chemical odorants that are most responsible for targeted downwind odors. Unfortunately, and historically, this is a step that has often been bypassed or overlooked. However, correct understanding of the specific impactful volatile organic compounds (VOCs) can inform the follow-on sampling, analytical, and remediation strategies that are most appropriate and efficient, based upon the chemistry behind the issue. With this understanding, the techniques and sampling strategies presented herein should be viewed as a qualitative prelude rather than an addendum to a follow-up routine, automated downwind odor monitoring.



Downwind odor characteristics can vary depending upon the size of the upwind source, interim topography, and wind conditions. At one extreme, the downwind odor plume from a relatively large source located on a flat open plain and under stable, near-straight line wind conditions can be rather broad, sustained, and predictable. 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 ("spikes" or "bursts"). These transient odor events can be surprisingly intense and offensive, despite their fleeting occurrence and perception. This work reports on improving and optimizing an environmental sampling strategy for odorant prioritization from such transient downwind odor conditions. This optimization addresses the challenges of (1) sampling of transient odor "spikes" and (2) prioritizing odors/odorants from multiple, closely colocated point sources under transient event conditions. Prioritizing is defined as identifying the key impactful odorants downwind. Grab air sampling protocol refinement has emerged from actual community environmental odor assessment projects. The challenge of assessing transient odor events has been mitigated by utilizing (a) rapid, odor-cued whole-air grab sampling (i.e., activated by and synchronous with the perceived sensory spikes) into metalized fluorinated ethylene polymer (m-FEP) gas sampling bags; (b) immediate transfer from bags onto solid-phase microextraction (SPME) fibers or sorbent tubes; and (c) maintaining refrigerated storage and shipment conditions between field collection and in-laboratory analysis. Results demonstrated approximately 11-fold increases in target odorant yields for 900 mL air sample capture on sorbent tube transfers from 2 to 3 s "burst" odor event bag captures compared to equivalent direct collections (with sorbent tubes) at the same downwind receptor location but during perceived (stable) odor "lull" periods. An application targeting general odor sampling and point-source differentiation utilizing tracer gases is also presented.

## 1. INTRODUCTION

Industrial zoning locates potential odor sources in relative proximity to each other and with downwind residential areas. Capturing, analyzing, and prioritizing the specific chemicals responsible for a community downwind odor issue can be an arduous task. Unfortunately, this odorant prioritization<sup>1</sup> is the critical qualitative, first step, which, historically, has been ignored, minimized, or bypassed in investigating community downwind odor issues. This first step is the discovery and assignment of the specific chemical odorants which are primarily responsible for specific citizen complaint. If and when the critical odorant prioritizations have been correctly assigned, targeted and automated sampling/analytical systems can be put into place for routine monitoring, accurately guided

by the qualitative odorant prioritization findings which precede.

As a recent example of this differentiation, we point to three recent publications in ACS Omega, Koziel et al.<sup>2</sup> and Oswald et al.<sup>3,4</sup> two research teams that, independently, correctly discovered and assigned the chemical identity of 3-methyl-2-butene-1-thiol (321-MBT) to the downwind "skunky" odor of

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cannabis and cannabis grow operations.<sup>2,3</sup> Historically, the cause had been incorrectly assigned to some combination of unspecified "skunky" terpenes.

Likewise, finding and identifying an offending odor source from multiple potential upwind sources can be a challenge. These are both exploratory, investigative challenges that must, typically, be qualitative in nature and undertaken by directly linking the human sensory response to sampling and analytical strategies. Of necessity, this dictates a qualitative, manual endeavor. It is important to note that current international environmental odor regulatory limitations are also based on linking human sensory panelists with odor events.<sup>5</sup>

Downwind odor sampling can be challenging due to the transient (perceived as randomly on/off) "spike" nature of characteristic odors. Typically, these odor spikes are momentary "bursts" of odor sensations, lasting only a few seconds, interspersed with long periods where the odor is undetectable or only faintly detectable. This characteristic can be the result of (1) a relatively small point source(s) responsible for the priority downwind impact and (2) frequent and rapid shifts in the wind direction. A well-documented characterization of this challenge was encountered in the Carthage Bottoms Industrial Area (i.e., CBIA) in Carthage, MO, in 2007 and is described elsewhere.<sup>6</sup> High-impact downwind odors relative to the CBIA appeared to be traceable to comparatively smaller point sources (i.e., 0.3-2 m-diameter roof or elevated stack vents).<sup>6</sup> It should be noted that this challenging situation, while commonly experienced by many affected communities, differs from that associated with many large area sources such as confined animal feeding operations (CAFOs) that are often isolated from other potential colocated sources.

Modeling researchers have previously attempted to address the transient odor events as manifestations of the non-Gaussian plume dispersion.<sup>8,9</sup> These efforts suggest that current mathematical models describing plume dynamics downwind as uniform Gaussian distributions<sup>10</sup> may be limited, especially concerning odor impact downwind. Adding to this complexity is the fact that odor is not necessarily "conserved" as other conventional air pollutants, and the same source can result in different odor "characteristics" (i.e., "what it smells like"), depending upon the source-to-receptor distance separation. This effect was termed "rolling unmasking effect" (RUE) and was recently documented in ref 1.

Regarding air toxics (i.e., often of concern in the context of environmental odor complaints), time-weighted average exposures of downwind citizens can carry real significance for predicting the cumulative impact on health. In contrast, the odor impact is best characterized as on/off or pass/fail events. The characteristic offending odor is often caused by small subsets of priority odorants (odorous chemicals) from complex source emissions. These priority odorant concentrations, downwind, can be either below or above the recognition threshold at any given moment in time. In the case of the below odor threshold case, the citizen receptor is not impacted. However, in the above-threshold case, the frequency and intensity of the odor sensations determine the perceived quality-of-life impact.

As a result of the transient nature of the downwind odor events (e.g., observed in the CBIA  $project^{6}$ ), it was shown to be very difficult to achieve reasonable volatile organic compound (VOC) loadings (and therefore electronic detection) in downwind air samples collected for subsequent odorant prioritization analysis. This was especially true utilizing the preferred sampling technique for downwind odor assessment, i.e., direct extraction and preconcentration of VOCs from air with solid-phase microextraction (SPME).

Thus, the integrated, two-step odor-cued grab sampling strategy was developed and tested on a pilot demonstration scale as a potential alternative for greater target odorant yields in air sampling of such transient odor spikes. The initial concept was developed by Wright et al.<sup>11</sup> The proposed method was then compared for odorous VOC yields from (i) odor-cued grab sampling with bags and immediate transfer to sorbent tubes with (ii) conventional direct air sampling on sorbent tubes. Specifically, the paper integrates the critical findings and strategies, including (1) adoption of a metalized fluorinated ethylene polymer (m-FEP) for fabrication of gas sampling bags and for maximum recovery of the highest odor impact, polar semivolatile compounds; (2) minimizing wholeair sample storage time to minimize the potential for sample loss to the surface in the m-FEP bags; and (3) integration of SPME or sorbent tube sample transfer/storage from the m-FEP bag "grab" collection, to achieve constraint (2). The results present a proof of concept for the technology and approach for improved assessment and odor problem solving for those situations marked by transient events.

## 2. MATERIALS AND METHODS

2.1. Multidimensional Gas Chromatography–Mass Spectrometry–Olfactometry (MDGC-MS-O). Air samples collected on SPME and sorbent tubes were analyzed on an MDGC-MS-O system. MDGC-MS-O facilitates an integrated chemical and sensory approach combining olfactometry and multidimensional separation techniques with conventional GC-MS instrumentation. The integrated system consisted of an Agilent 6890 GC/5975B MS modified for MDGC-MS-O utilizing an AromaTrax control system from Volatile Analysis Corporation (Grant, AL). Details regarding general hardware and AromaTrax operation have been described in detail elsewhere.<sup>1,11-14</sup> Specific operational parameters utilized for the targeted odorants, as well as their associated tracer compounds during dual point-source prioritization experiments, are summarized as follows: injection mode: split-less with SPME sample collection and delivery; injection temperature: 250 °C; detector #1: flame ionization detector (FID); FID temperature: 280 °C; detector #2: Agilent 5975B MSD in MS-SCAN or MS-SIM acquisition mode; column # 1: 12 m x 0.53 mm ID BPX 5–1.0  $\mu$ m film (precolumn 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 modes): 40 °C initial, 3 min hold, 7 °C/min, 220 °C final, and 20 min hold.

2.2. Air Sampling with SPME, m-FEP Bags, and Sorbent Tubes. SPME,<sup>15–19</sup> utilizing a 1 cm Carboxenmodified polydimethylsiloxane (PDMS) 75  $\mu$ m sampler, was applied for initial downwind-direct air sampling. SPME collections were carried out by direct SPME fiber exposure downwind of the scale-model transient odor event generators. The SPME fibers that were prepared for air sampling were (a) preconditioned at 260 °C, (b) transported under dry ice storage conditions, to the field-trial site for execution of the reference and "spike" odor collections, and (c) transported back under dry ice conditions to the laboratory for analysis.

Figure 1 presents a general image of the support fixture utilized for direct SPME fiber exposure and air sample



Figure 1. Direct air sampling with four field SPME samplers, weather station, and wind-strip indicator mast.

collection. The SPME samplers are shown secured within a field-support stand; the preconditioned SPME sorbent-coated fiber tips are shown retracted back into their protective needle sheaths in preparation for exposure to the air for direct sample collection. Volatile loadings on the SPME fibers were varied by altering the length of time the SPME fibers were exposed to the air being sampled.

Series-coupled sorbent tube pairs were used for direct air sampling and indirect, two-step sampling from odor-cued collections into m-FEP bags and subsequent thermal desorption and analysis on an MDGC-MS-O. 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) of Carbopack B and 1 cm (0.009 g) of Carboxen, adsorbents representing sequentially increasing adsorbent strength.

While this research focuses on the extremes of sample capacity (i.e., (1) traditional, low-capacity, thin-film SPME and (2) high-capacity series-coupled multibed thermal desorption devices), a number of alternate, innovative sorption-based sampling devices have subsequently emerged within the industry. It is reasonable to assume that newer innovations to both SPME (i.e., TF-SPME and SPME Arrow) and tubular thermal desorption could also benefit from the odor-cued strategy in overcoming the unique challenge of moving-target sample isolation when investigating the targeted fleeting transient odor events.

Whole odor-cued air sampling was accomplished with 1 L of metalized m-FEP gas sample bags. The integrated m-FEP sample bag to sorbent tube transfers were carried out utilizing a prototype Peltier cryo-trapping device (Figure S1, Supporting Information). This device was set to control at 2  $^{\circ}$ C for increasing the VOC trapping efficiency of the sorbent tube fore trap.

**2.3. Weather Monitoring.** A Kestrel 4500 Pocket Weather Tracker (Kestrel Meters, Boothwyn, PA) was used during the transient odor event and source differentiation experiments with prototype-scale model event generators. This unit is tripod-mounted, is configured for wind direction and speed monitoring, and incorporates data logging capabilities.

**2.4. Transient Odor Event Generator.** A prototype odor generator was built to conduct controlled experiments to test the effectiveness of the proposed odor-centered air sample collection strategy (Figure 2). The odor generator was designed and configured to permit up to three target odorants to be mixed at fixed ratios prior to ejection from the small vent stack under controlled release conditions. The target odorants



**Figure 2.** Prototype odor generator used for the release of target odorants from a model vent stack. The schematic presents a single odorant and single tracer release. Multiple odorant mixing and release through a single vent stack or individual odorant release through separate generator stacks is possible (Figures S2 and S3). Odor generators were used for controlled release experiments to collect the downwind "odor-cued" and direct air samples for comparisons. Test odorants are released from permeation tubes or cartridges (solid form). Optional tracer release can be used for the proper location and timing of downwind air sampling.

were placed into one of three PVC generator cartridges in an appropriate form depending upon the targeted odorant and the experiment's goal. These forms included (1) measured amounts of high-purity solids (e.g., naphthalene); (2) permeation tubes for odorants of high volatility; and (3) odorant-saturated polymeric materials, in the film or fiber form, to serve as odor carrier materials for "spike" odor release simulation. Each cartridge was affixed with a blower, operating under independent rheostat control. In the first-generation prototype form, the blowers used were inexpensive hair dryers. The vent stack and odorant cartridge assemblies were fabricated from 7.6 cm-diameter Schedule 40 PVC and associated fittings (i.e., see photos/diagrams in Figures S2 and S3). The stack vent terminated at 2.1 m above ground. Alternately, individual test odorants can be mixed and released from separate generators/vent stacks (Figures 3 and S3). The latter configuration was used to simulate a multisource scenario.

**2.5. Sampling for Transient Odor Events: Odor-Cued Whole-Air Grab Collections.** 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 samples (Figures S4-S8). Utilizing m-FEP gas sampling bags for interim containment, odor-cued grab samples were collected over 2-3 s intervals (at the odor sampling station, Figure 3), attempting to coincide those momentary collections with perceived spike or peak odor events. The odor-cued bag-containing samples were then immediately stabilized for transport by either (1) direct insertion of SPME fibers into the bags for collection/preconcentration of odors or (2)



**Figure 3.** Schematic of the two odor generator stacks set up simulating a multisource scenario for field odor-cued experiments to capture transient specific offending odor from one source.

evacuation through preconditioned sorbent tubes (Figure S1). Both approaches aimed for stabilized sample storage between collection and analysis. In the case of SPME collection/storage, the fibers were quickly exposed to the captured odorous air within the m-FEP bag via insertion through the septum port. All other SPME fiber preconditioning and logistic handling parameters were as described above for direct environmental air sampling.

To date, extensive comparative odorant recovery results consistently indicate FEP as the most inert sample contact surface examined, especially concerning the family of high-impact, polar, semivolatile odorants commonly associated with CAFOs.<sup>20–22</sup> Unfortunately, these results confirm that odorant recovery advantages directly attributable to sample contact surface materials or modifications represent relatively limited incremental improvements only. On the other hand, the impact of odor-cued sample loss in m-FEP bags appears to be compensated by the proposed immediate sample transfer and stabilization on SPME or sorbent tubes. Additional background information regarding surface scalping of high-impact semivolatile odorants from contained whole-air samples is included in the Supporting Infomation.

The prototype schematic for the odor-cued grab sampling station is shown in Figure 4. As pictured in Figures S4–S7, the prototype included (1) a rigid mount of a battery-powered vacuum/pressure pump system for control of gross m-FEP bag inflation/deflation; (2) rigid mounted 1 L gastight 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) 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) low-speed wind-strip indicator mast.<sup>23</sup>

2.6. Tracer Gas Injection Strategy for Point-Source Prioritization. Each of the 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



**Figure 4.** Schematic of the odor-cued sampling station. 2-3 s grab samples captured in m-FEP bags are immediately stabilized by transfer onto sorbent tubes or SPME from the bag (not shown in the schematic).

injection technique as previously described by the first author (D.W.W.) for the vinyl chloride purity assay protocol (ASTM D-5507-21a).<sup>24</sup>

#### 3. RESULTS AND DISCUSSION

3.1. Transient Odor Simulator Trials. The firstgeneration prototype odor generator (Figure S2) was used to mix target odorants at fixed ratios prior to being ejected from the small vent stack under controlled flow conditions and nearby downwind sample collection. The resulting pilot-scale format enabled minimizing the distance and sample collection challenge of the full-scale CBIA source, i.e., speeding up the transient odor sampling process development and optimization. The initial trials confirmed that the pilot-scale system successfully (1) compressed the odor assessment area to @ 0.5acres (14 m × 14 m) (from, e.g., 1 sq. mi (1.6 m × 1.6 km) of a full-scale CBIA source as described<sup>6</sup>); (2) compressed the maximum source-to-receptor distance to <30.5 m (from, e.g., 1 mile (1.6 km) at the CBIA); (3) improved the average odor event frequency to >20 per h (from, <2 per h at the CBIA); and (4) compressed travel time from the survey site to the lab to <10 min from at least several hours for field-scale work.

A two-odorant trial consisted of contrasting odorants, i.e., naphthalene/"mothball" odor and 1,4-dimethoxybenzene/ "bluebonnet-field" aroma. It was possible to quickly achieve a steady-state odor release condition for several hours with the following characteristics: (i) odor frontal boundary @ 70 ft ( $\sim$ 21 m); (ii) the odor character at the odor frontal boundary (i.e., 50–70 ft,  $\sim$ 15 to 21 m) was clearly dominated by the 1,4-dimethoxybenzene/"bluebonnet field"; and (iii) the near-source (i.e., 5–10 ft, 1.5–3 m) odor character was clearly dominated by naphthalene/"mothball".

A three-odorant trial integrated *p*-cresol/"barnyard" to the two-odorant setup and resulted in the following observations: (i) the odor frontal boundary immediately shifted outward to  $\sim 100$  ft (30 m), i.e., it was detectable at much longer distance from the source; (ii) the odor character approaching the shifted odor frontal boundary was perceived as that of pure *p*-cresol/"barnyard"; seemingly unaffected by the 1,4-dimethoxybenzene/"bluebonnet field" odor; the limited loading of *p*-cresol in the source (i.e., as a result of the *p*-cresol "source"



**Figure 5.** Generic pictorial representation of the "rolling unmasking effect" (RUE) applied to the transient odor simulator trials with multiodorant sources. The odor frontal boundary (e.g., *p*-cresol/"barnyard") represents the farthest downwind reach relative to the odor source, while the internal (closer to the source) bands represent the distances of sequential odor unmasking as the secondary-impact odorants are diluted below their detection/masking concentration levels (e.g., *1*,4-dimethoxybenzene-driven "bluebonnet field").

being a saturated latex film) resulted in a slow, exponential decay of the "barnyard" odor boundary back toward the source; (iii) upon approaching the 70 ft (21 m) reach point of the "bluebonnet field" odor (e.g., secondary boundary interface as shown in Figure 5), the odor character "confusion" commonly associated with blending of odorants occurred but over a relatively narrow band of distance; and (iv) as the diminishing p-cresol-driven "barnyard" odor continued its migration back toward the source, the 1,4-dimethoxybenzenedriven "bluebonnet field" odor was observed to re-emerge to the point that, eventually, there was no discernible impact from p-cresol. In this case, 70 ft (21 m) became the odor secondary boundary where, owing to the RUE,<sup>1</sup> the odor frontal boundary transitions to the odor character of the "next-inline" impact-priority odorant. Stated another way, the selective elimination of the initial masking effect of the p-cresol/ barnyard odor reduced the downwind reach of the priority "barnyard" odor from  $\sim 100$  to  $\sim 70$  ft (30-21 m). This reduction in downwind reach was accompanied by a corresponding change in the odor character at the "new" odor frontal boundary, from "barnyard" to "bluebonnet field". This "next-in-line" boundary is the odor secondary interface boundary (Figure 5).<sup>1</sup> The observed RUE underlines the practical challenges encountered when sampling odor downwind from multiodorant sources due to apparent changes of the odor character with the distance.

**3.2. Two-Step Strategy for Air Sampling of Transient Downwind Odor Events.** Sampling yield improvements were achieved by applying the odor-cued two-step sampling process to the challenge of downwind air sampling of transient odor events. The rapid 2 s grab samples were manually drawn into m-FEP gas sampling bags, cued by the investigator's perception of odor event peak intensity (Figures S4 and S8). As quickly as possible, this was followed by sampling the captured bag contents through extended SPME fiber exposure to the air sample in the m-FEP bag for up to 0.5 h. As shown in Table 1, utilizing this two-step strategy, it was possible to achieve an approximately fourfold MS detector response (in SIM mode) increase for the targeted naphthalene odorant compared to reference 3 min direct SPME fiber exposures to the same downwind environment.

An alternate two-step transient event odorant sampling strategy was developed and compared with direct air sampling via sorbent tubes. Like direct SPME, the direct sorbent tube sampling works well for odor event sampling that is somewhat sustained, e.g., downwind from a large CAFO. However, due to Table 1. Two-Step Strategy (i.e., 2 s Odor-Cued Grab Sample into the m-FEP Bag Grab Sample Followed by Immediate Extraction of the Bagged Air Sample with SPME) Enhanced Analytical Detection of Odor-Causing Odorants

two-step, odor-cued grab sample into the m-FEP bag followed by	MS detector response to	~response		
SPME	naphthalene	differential		
sample #1	10,524			
sample #2	10,318			
mean	10,421	$4 \times \text{direct}$		
Direct Air Sampling with SPME				
sample #1	2624			
sample #2	2451			
mean	2538	$0.25 \times \text{two-step}$		

the flow restrictions of packed sorbent tubes, there is still a limit to the volume of air that can be processed during such brief transient events. For example, assuming a 30 mL/min peak flow rate through a packed sorbent tube under full vacuum (e.g., 1 atm (~14.7 psi) pressure differential), approximately 30 min is still required for concentrating odorants from a 1000 mL air sample. Unfortunately, this is a relatively long period in relation to being effective at capturing transient odor events (a few sec to min) such as those encountered at the CBIA.<sup>6</sup>

Thus, the two-step odor-cued sampling process was used for sorbent tubes (Figures 4 and S1) and involved (i) rapid, 2-3 s 1 L grab samples being drawn into m-FEP gas sampling bags during the perceived momentary peak odor events and (ii) immediate transfer of the bag contents to packed sorbent tubes for refrigerated transport and storage between sample collection and analysis in the lab. The alternative two-step strategy achieved a reasonable compromise between sample volume requirements and transient event-induced time constraints (Table 2). An average 11-fold increase in MS detector response to the target odorant was achieved compared to 900 mL direct collections onto sorbent tubes at the same downwind receptor site during perceived transient odor periods. It is noteworthy that this comparison was made during an extended period of relatively stable wind conditions, and it was possible to select the sampling locations to be at the approximate geometric center between the plume lateral downwind boundaries.

3.3. Tracer Gas Integration to a Pilot-Scale Model of Stack Odor Emissions. The optimized transient event

Table 2. Two-Step Strategy (i.e., 2 s Odor-Cued Grab Sample into the m-FEP Bag Grab Sample Followed by Immediate Extraction of the Bagged Air Sample with Sorbent Tubes) Enhanced Analytical Detection of Odor-Causing Odorants

two-step, odor-cued grab sample into the m-FEP bag followed by extraction of bagged air with sorbent tubes	MS detector response to naphthalene	~response differential		
sample #1	83,915	13.5 × direct		
sample #2	54,851	$8.8 \times \text{direct}$		
mean	69,383	$11.5 \times \text{direct}$		
Direct Air Sampling with Sorbent Tubes				
sample #1	6216	$1 \times \text{two-step}$		

sampling strategy described above is potentially applicable to a number of downwind odor assessment challenges. One of these challenges is the downwind impact prioritization of multiple, closely colocated upwind point sources. Simply stated, if an investigator successfully prioritizes the specific odorants most responsible for the negative impact at the odor frontal boundary, he/she should be able to quickly narrow down the most likely source among multiple "potential" upwind point sources.

The odor-cued grab sampling strategy was demonstrated to be helpful in the process of narrowing down the likely source by incorporating the signature odorant or tracer spiking at discrete upwind point sources. Sulfur hexafluoride (SF<sub>6</sub>) and perfluorocarbon tracer (PFT) compounds have been widely referenced<sup>25,26</sup> for such VOC dispersion and air movement profiling studies. However, for this application, other tracers could be selected on the basis of the following criteria: (i) relatively low odor impact; (ii) high chemical stability; (iii) relative absence from the typical environmental background in the target area; and (iv) safety and environmental impact.

Chloroform and methylene chloride were selected as tracer compounds for this exploratory scale model experiment. These selections were made solely based on the availability and appropriateness of physical and analytical properties rather than any perception of applicability to expanded full-scale studies. The liquid-phase tracers were injected into the odor generator and vaporized under controlled conditions utilizing a variation of the automated vaporizing injection technique (ASTM D-5507-21 $a^{24}$ ) to ensure a high degree of precision in the rate of tracer compound introduction into odor generators. This technique was previously described for the industrystandard vinyl chloride purity assay analysis and has been used extensively to achieve a high degree of precision. The ASTM D-5507-21a variation, in summary, was (i) the liquid tracer feed reservoir was pressurized with  $N_2$  (Figure 2), well beyond the compound's vapor pressure; (ii) the overpressured liquid was fed through a fixed restrictor, which terminated in the heated vaporization chamber; and (iii) control and limitation of the tracer feed rate were achieved by matching the liquid feed head pressure with the restriction (i.e., length and I.D.) of the tubular fixed restrictor.

Prior to the pilot-scale trials with the tracers, a controlled experiment utilizing naphthalene/chloroform was conducted to prove that the tracer can be reliably integrated into the odor generators. Five, two-step, odor-cued grab sample collections into the m-FEP bag followed by extraction of the bagged air with sorbent tubes from the model odor generator (Figure 2) were completed, and the precision of the naphthalene/ chloroform ratio is summarized (Table 3). 8.6% RSD was

# Table 3. Tracer Gas Integration to a Pilot-Scale Model ofStack Odor Emissions

two-step, odor-cued grab sample into the m-FEP bag followed by extraction of the bagged air with sorbent tubes	ratio of MS detector response to naphthalene (odorant)/chloroform (tracer)			
sample #1	0.84			
sample #2	0.98			
sample #3	0.96			
sample #4	0.95			
sample #5	1.07			
mean	0.96			
St. Dev.	0.082			
RSD	8.56%			
The ratio of MS detector response	to naphthalene (odorant)/			

chloroform (tracer) showed sufficient precision.

excellent considering the complete range of experimental variability that reflects (i) the odorant/tracer vaporization process; (ii) stack emission process; (iii) meteorological variability; (iv) transient event downwind sampling; and (v) analytical process. It is possible, despite being unproven at this point, that the general upward trend 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.

**3.4. Integrated Transient Odor Sampling Strategy for Upwind Odor Point Source Prioritization.** The development of an integrated odor sampling strategy for the upwind point source prioritization process was relatively straightforward due to coordinated (i) transient event odor-cued grab sampling; (ii) priority odorant identification/detection; (iii) tracer compound relative abundance (or relative absence); and (iv) moment-in-time meteorological condition. A field trial was carried out utilizing two independently controlled and positioned transient odor event generator stacks (Figures 3 and S3). Stack #1 was configured for controlled release of the naphthalene/chloroform odorant/tracer pair. Stack #2 was configured for controlled release of the 1,4-dimethoxybenzene/ methylene chloride odorant/tracer pair.

Two contrasting conditions were targeted for the initial field trial: (i) transient "mothball" odor events, indicating a naphthalene concentration spike, and (ii) transient "bluebonnet field" odor events, indicating a 1,4-dimethoxybenzene concentration spike. Two-step, odor-cued grab sampling into the m-FEP bag followed by extraction of the bagged air with six sorbent tubes (each in-series-coupled) was used to reflect triplicate naphthalene "peak" events and triplicate 1,4dimethoxybenzene "peak" events. Unfortunately, weather conditions turned unfavorable for initiating the test, but once the setup was begun, a decision was made to continue. Specifically, an approaching cold front and degrading wind conditions forced an accelerated initiation of the transient event sampling process. It is noteworthy to mention that the encountered challenge was not different from that encountered in odor sampling practice. Under the rapidly deteriorating wind conditions (i.e., wind speed and direction variability), the transient odor events were particularly brief, approximately 1-3 s in duration. Under these challenging conditions, it was not possible to ensure that the generators were allowed to reach steady-state release before the downwind sample collections. As surmised previously, the resulting nonsteady-state condition

"mothball" transient odor event	naphthalene	chloroform	ratio of MS detector response to naphthalene (odorant)/chloroform (tracer)	1,4-dimethoxybenzene
sample #1	220,450	200,750	1.1	6592
sample #2	653,343	650,217	1.0	390
sample #3	584,887	386,036	1.5	480
mean	486,227	412,334	$1.21 \pm 0.28$	2487
			"Bluebonnet Field" Transient Odor Event	
sample #1	26,522	<mdl< td=""><td></td><td>4203</td></mdl<>		4203
sample #2	35,053	580	6.3	84,373
sample #3	17,428	2988	5.8	3771
mean	26,334	2889	6.1	30,782

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

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 (Table 4). Another problem arose relative to the second generator (i.e., 1,4-dimethoxybenzene/methylene chloride) not being carried through a postfabrication mechanical check-out prior to initiating this field trial. As a result, unexpected mechanical problems were encountered during the setup, which adversely affected control of both the methylene chloride feed and the stack's total flow.

As a result of the above complications, this experimental series is considered significant only 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 an alternate or reference source.

Within the constraints imposed by the above-stated context, the data shown do 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 22fold 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  $1.21 \pm 0.28$  (23.1% RSD). This level of variation is higher than expected (i.e., the previous field trial series results were an average of  $0.96 \pm 0.082$ , 8.56% RSD, n =5) or would normally be acceptable. However, given the abovementioned meteorological challenges, it should probably be expected.

**3.5. Transient Sampling Strategy Implications for Field Odor Assessments by Dynamic Dilution Olfactometry (DDO).** To date, conventional efforts to assess transient odor events have primarily utilized the analytical approach (i.e., direct sampling from the air) to begin the 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 (DDO) (ASTM E-679;<sup>27</sup> ASTM E-1432;<sup>28</sup> and CEN<sup>29</sup>). Typically, agency officials receive a complaint from downwind citizens and possibly assign an investigator to travel to the complaint site. This official response can often take hours (or days), and 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 accurately assess the "odor dilution number" or arrange a proper and representative sampling protocol when dealing with such a rapidly shifting impact.

The presented two-stage odor-cued air sampling addresses the limitation above. The presented two-stage approach has already been practiced, and the findings were presented in a final project report.<sup>30</sup> An example of such a project was the odor-cued grab-capture strategy application to DDO assessment techniques in addition to analytical assessment strategies (USDA NIFA SBIR Phase II final report<sup>22</sup>). The key recommendation relative to the use of 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 a very short time. Storage time should be just long enough for either immediate analysis or transfer to a sorbed form (e.g., onto a SPME fiber or packed sorption tube) for shipment/storage in the interim between collection and analysis. Semivolatile odorant recovery data to date suggest that this time limit should likely be less than 15 min, in marked contrast to the 24-36 h constraint reflected in many current odor sampling protocols and the practical considerations of shipment of bags to the lab.

3.6. Application of the Proposed Odor-Cued Grab Sampling Technique and Odorant Prioritization to Odor Assessment of a Missouri Landfill Odor Source. As stated in the Introduction, addressing the challenges associated with transient environmental odor events began with an investigation, on behalf of the Missouri DNR, in Carthage, Missouri, in 2007.<sup>6</sup> The techniques emerging from the subsequent addressing of these challenges were used to advantage for a second Missouri DNR-sponsored source investigation in 2015,<sup>30</sup> a landfill located in eastern Missouri. The latter project confirmed that (i) the challenge of downwind sampling of transient odor events, such as those previously encountered in Carthage, Missouri,<sup>6</sup> was also clearly reflected in this more recent case;<sup>30</sup> (ii) as a result, the most informative downwind sample collections were shown to be those utilizing the odor-cued grab sampling technique; (iii) the odor at the odor frontal boundary appeared, at the time of the assessment, to be reproducible and characteristic of the reported citizen complaint; (iv) the characteristic odor at the

odor frontal boundary quickly appeared, at the time of the assessment, to be dominated by a single character-defining odorant; (v) interestingly, although a clear mass spectral profile was easily developed for this trace-level, impact-priority odorant, ultimate chemical identification was not possible due to the absence of its spectral profile from any of the common mass spectral search databases employed; however, (vi) utilizing the mass spectral signal, it was possible to electronically monitor for the presence/absence of the impact-priority odorant, ultimately confirming that the odorant was common to the landfill source. The Executive Summary section from the final report for this investigation is included in the Supporting Information. In addition, the complete report for this MDGC-MS-olfactometry-based odorant prioritization effort can be accessed from the Missouri DNR website.<sup>30</sup>

## 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 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 stabilized transport and cold storage in the interim between field collection and inlaboratory analysis. Encouraging initial evaluation of the concept and device has been realized utilizing scale-model transient odor event generator devices. A fourfold increase in target odorant yield was realized for 30 min SPME fiber exposures to 2-3 s bag captures, when compared to 3 min direct exposures to the same downwind location. Likewise, an 11-fold increase in target odorant yield was shown for 900 mL adsorbent tube transfers from 2 to 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 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 tube transfer/stabilization to ensure odorant capture stability in the interim between sample collection, shipment, storage, and analysis.

## ASSOCIATED CONTENT

#### Data Availability Statement

The original contributions presented in the study are included in the article; further inquiries can be directed to the corresponding authors.

## Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c00531.

Collected air sample immediately transferred onto a sorbent tube, first-generation prototype-scale-model transient odor event generator, integrated two-point source transient odor event generator systems, second-generation prototype odor-cued grab air sampling assembly, smartphone-captured moment in time of the wind-strip indicator mast orientation/wind direction relative to the orientation of the sampling bag/chamber assembly, truck-mounted prototype odor-cued grab sampling of a transient odor event (PDF)

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Conceptualization: D.W.W.; methodology: D.W.W.; validation: D.W.W.; formal analysis: D.W.W.; investigation: D.W.W., F.W.K., D.K.E., and A.I.; resources, D.W.W. and F.W.K.; data curation: D.W.W.; writing—original draft preparation: D.W.W. and J.A.K.; writing—review and editing: D.W.W., J.A.K., and L.W.; visualization: D.W.W., L.W., and J.A.K.; supervision: D.W.W.; project administration: D.W.W. and F.W.K.; and funding acquisition: D.W.W. and F.W.K.

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## Notes

The authors declare the following competing financial interest(s): Three commercial entities are represented among

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