SUPPORTING INFORMATION

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

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Figure S1. Collected air sample (during odor-cued air sampling into m-FEP bags (right)) is immediately transferred onto a sorbent tube (center). An operator uses manual syringe (left) and facilitates transfer of odor-cued sample collection from m-FEP bags to two sorbent tubes connected in series. Prototype Peltier cryo-trapping device (center bottom) shown clamped onto a Tenax TA packed fore-trap. Set to chill the fore-trap to ~2 °C to increase the trapping efficiency toward the high impact semi-volatile odorants.

Figure S2. First-generation prototype scale-model transient odor event generator. The generator mixes three odorants and releases them through a single stack. A black wind strip-indicator mast shows the wind direction & velocity and informs the immediate downwind odor-cued sample collection.

Figure S3. Integrated two point-source transient odor event generator systems [3]. A black wind strip-indicator mast visualizes the wind direction and velocity. To the right are the two contrasting odor point sources with vent stacks. To the left background is the tripod-mounted weather data station. Odor-cued sampling (not shown) occurs downwind to the left from the photo frame.

Figure S4. Second generation prototype odor-cued grab air sampling assembly. Air sample inlet located near the breathing zone of the operator. The operator observes the wind strip-indicator mast visualizing the wind direction and velocity and likely odor plume location. An m-FEP sampling bag chamber 'cartridge' and the syringe (behind the chamber) 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.

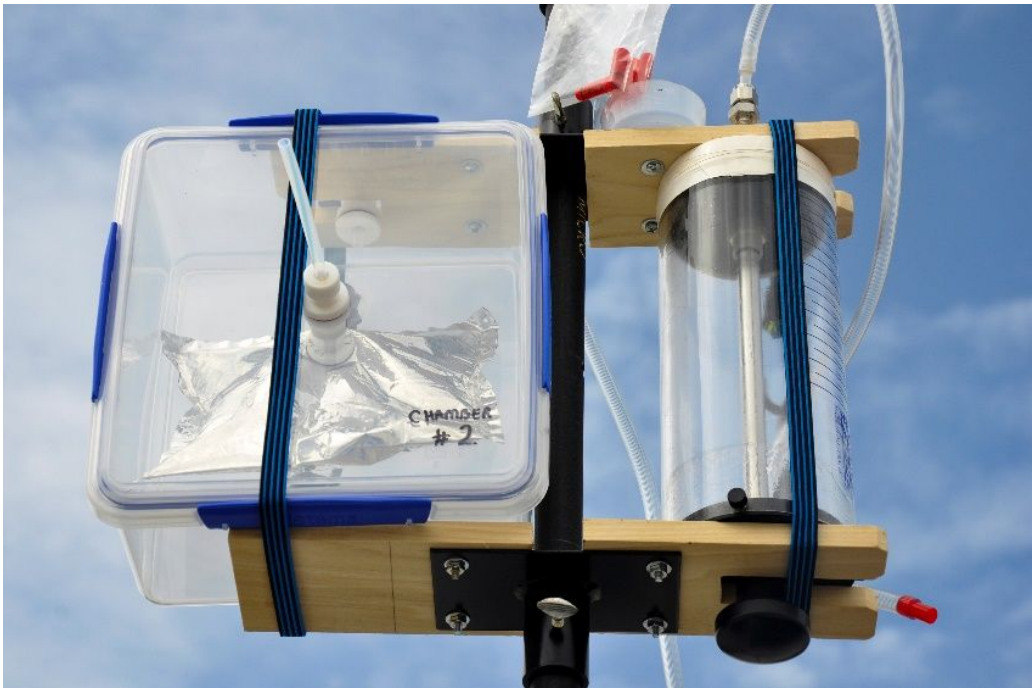

Figure S5. Second-generation prototype odor-cued grab sampling assembly: Close-up of syringe and sampling bag chamber 'cartridge' assemblies. Photo was taken 90 degrees (leftwise / counterclockwise) from ~ the operator's location on Figure S4.

Figure S6. A smartphone captured moment-in-time of the wind strip-indicator mast orientation/wind direction is shown relative to the orientation of the sampling bag/chamber assembly. The captured video of inflating bag provides the timestamp for odor-cued air sampling and the corresponding plume direction.

Figure S7. Truck-mounted prototype odor-cued grab sampling assembly. Added mobility is advantageous for transient odor events relocation and downwind air sampling.

Figure S8: Odor-cued sampling of a transient odor event [3]. To the right is the left-most generator (early prototype) configured for controlled release of the naphthalene / chloroform odorant / tracer pair (shown in Figure S3; the second odor generator is to the right of the picture frame (not shown). The wind strip-indicator mast helps with the selection of downwind sampling location. The first author is shown awaiting the characteristic sensory cue for the targeted transient event. Utilizing the 1 L manual gas-tight syringe, the 1 L m-FEP gas sampling bags could be completely filled in 1-2 sec during the sensory cued events.

The following is the Background Section taken from the Final Summary Report for USDA-CREES SBIR Phase II Grant [1]:

Background Section

> *"Extensive comparative odorant recovery results to-date consistently point to FEP as the most inert sample contact surface examined; especially with respect to the family of high-impact, polar, semi-volatile odorants commonly associated with CAFOs. Unfortunately, these results also confirm that the odorant recovery advantages which are directly attributable to sample contact surface materials, or surface modifications, represent relatively limited, incremental improvements only [1]. In retrospect, this limitation appears to be consistent with the thermodynamic limitations as driven by Van der Waals intermolecular attractive forces and described by the Maxwell – Boltzmann energy distribution relationship. Van der Waals forces are relatively weak with respect to intermolecular bonding; especially when compared to those which are driven by the electron sharing reflected in covalent bonds. They are composed of the combined intermolecular forces from three types of attractions: (a) relatively strong hydrogen bonds; (b) weaker dipole-dipole interactions and (c) weaker still, dispersion forces. Despite their relative weakness, Van der Waals forces are strong enough such that they are responsible for holding liquids together in a unified mass, determining vapor pressures above that liquid mass and the associated boiling point of that mass. The amount of energy input required to break these weak attractive forces and allow individual molecules to escape into the vapor space is, in turn, determined by the strength of the combined Van der Waals forces acting on the molecules at the surface. As a result, there is a minimum escape energy requirement which is specific for each molecule type, relative to the attractive forces holding it within the liquid mass. This escape energy requirement will be directly proportional to molecular weight alone; even if only weaker dipole-dipole and dispersion forces are involved (i.e. evidenced by ascending boiling points within a homologous series of hydrocarbons). The escape energy requirement will be further increased if much stronger, hydrogen bonding is added to the combined Van der Waals mix (i.e. evidenced by the relatively high boiling point for water which would otherwise be considered disproportionately high if based solely upon its molecular weight). The combined effects of the Van der Waals forces, described above for liquids, also drive the challenge of whole-air sampling of environmental odors. There is an analogous, surface escape energy requirement for each molecule which is a function of its molecular mass, functional affinity for the containment surface and the absolute temperature. Given the constancy of the Van der Waals forces (i.e. even the weak dipole-dipole and dispersion types), 'inertness' or 'inertizing' of the sample containment surface can only be expected to exert a limited effect on a target odorant's Phase Ratio (i.e. odorant concentration in the gas phase relative to its concentration adsorbed to the inner container surface). Stated another way; regardless of the material of construction, some level of odorant loss or 'scalping' from the vapor phase to the wall surface should always be expected; beginning immediately upon (or during) sample containment. The impact of such odorant loss-to-surface (i.e., 'scalping' effects) on odor assessment, rapidly increases in significance for polar, semi-volatile odorants which reflect diminishing Phase Ratio values; especially when acting in concert with high downwind odor impact priorities. As a result of these challenges, it became apparent, early on in this project, that sampling and extended storage of environmental odor samples in whole-air form is ill-advised; especially for situations where the target odor has not been characterized with respect to chemical composition and odorant impact-priority. This precaution conflicts with the common 'bag-capture and transport' approach to odor sampling, which has been historically practiced and is currently permitted by many regulatory and enforcement protocols. As a result of the various, intractable challenges working against the efficacy of whole-air sampling for <u>delayed</u> odor assessment, these investigators proposed to approach the challenge with a novel integrated strategy. From this perspective, the sample containment device, reflecting optimized inertness toward the targeted odorants, represents only one of the key elements. These results integrate the findings and strategies, including (1) adoption of metalized-polymeric (fluorinated ethylene polymer, FEP) for gas sampling bags for maximum recovery of the highest impact, polar semi-volatile odorants; (2) minimizing sample storage time in whole-air form in the metalized-FEP bags and (3) the integration of SPME fiber or sorbent tube sample collection/storage from the metalized-FEP bag vapor 'grab' collection, to achieve constraint (2)."*

The following is the Executive Summary taken from the Final Summary Report for Bridgeton Landfill Downwind Odor Assessment and Odorant Prioritization for the Missouri Attorney General's Office (dated August 27, 2015) [2].

Executive Summary

> *"A unique and characteristic odor was noted by this investigator at-distance and downwind of the Bridgeton Landfill during a beyond-fence-line assessment visit which was carried out during the March 29 to March 31, 2015 time-frame. It is the opinion of this investigator, that the observed odor was emitted by and carried a considerable distance downwind from the Bridgeton Landfill source. It is also the opinion of this investigator that this characteristic odor is primarily traceable to a very small fraction of the total VOC emission field from the landfill source; an 8.4 s isolate from a complex gas chromatographic VOC profile which spans, at least, 1,260 s (i.e. less than 0.7% of the total VOC elution span). These opinions are based upon several factors, prioritized approximately as follows: (1) observation of a single, dominant odor response at the olfactory detector from direct environmental air samples which were collected by SPME (i.e. solid phase microextraction) during the Bridgeton Landfill area assessment visit of late March; (2) the odor character for this on-instrument sensory response was perceived, by this investigator, as virtually identical to that sensed directly within the Bridgeton Landfill downwind odor plume, at its outer boundary; (3) the suspect gas chromatographic fraction isolate, identified herein as Unk 12.86 (i.e. unknown @ 12.86 min retention on this investigator's instrument), was found to be common to: (a) the air environment within and beyond the fence line of the Bridgeton Landfill site; (b) the equilibrated headspace VOCs surrounding flexible geomembrane barrier sheeting material which had undergone extended barrier-service exposure to the Bridgeton Landfill site and (c) the equilibrated headspace VOCs above a leachate sample which had been extracted from the Bridgeton Landfill site on April 09, 2015. In contrast; (4) the Unk 12.86 chromatographic isolate fraction was found to be relatively absent from a control geomembrane sample which was taken from a roll stored on the Bridgeton Landfill site on July 22, 2015; a 'pristine' roll which had not seen barrier service on the site. In addition; (5) the combined odor character emitting from the site-exposed geomembrane sample of July 22, 2015 was perceived, by this investigator, as reflecting a substantial odor-match fidelity (i.e. estimated at >60%) to that which was sensed directly within the Bridgeton Landfill downwind odor plume, at its outer boundary during the area visit in late March; (6) the Unk 12.86 chromatographic isolate fraction, when collected in whole-air form from Bridgeton Landfill site-exposed geomembrane headspace, yielded an odor character which this investigator perceived as reflecting a relatively high-fidelity odor-match (i.e. estimated at >70%) to the combined odor which was sensed in late March directly within the Bridgeton Landfill downwind odor plume, at its outer boundary and (7) the Unk 12.86 chromatographic isolate fraction, when collected in whole-air form from site-exposed Bridgeton Landfill geomembrane headspace, and combined into an expanded, 3 component, odor-match formulation yielded an odor character which this investigator perceived as reflecting a relatively high-fidelity odor-match (i.e. estimated at ~80%) to the combined odor which was sensed in late March directly within the Bridgeton Landfill downwind odor plume, at its outer boundary. Independent sensory panel odor-match fidelity grading of the proposed formulation has not been possible as of the time of this writing. This results from a combination of: (1) the unknown chemical ID status of Unk 12.86 and (2) the potential constraints imposed by the NIH OHRP (i.e. Office of Human Research Protections) human subject testing guidelines in relation to that uncertainty. Efforts to address these constraints are on-going; both through the resolution of the chemical ID barrier and through pursuit of a protocol review / approval of an independent IRB (i.e. Institutional Review Board)."*

References

1. Final Summary Report for USDA-CREES SBIR Phase II Grant Award number 2007-33610-18619 to Microanalytics (a MOCON Company); *Metalized FEP – an Improved Alternative to Tedlar Bags for Downwind Odor and Volatiles Emission Sampling of Confined Animal Operations*; Feb 03, 2011.

2. Wright, D. Final Summary Report for Bridgeton Landfill Downwind Odor Assessment and Odorant Prioritization for the Missouri Attorney General's Office; Missouri Department of Natural Resources: Jefferson City, MO, USA, August 2015. Available online: https://dnrservices.mo.gov/bridgeton/docs/bridgetonodorassessment.pdf (accessed on 04 January 2024).

3. Wright, D.W.; Kuhrt, F.; Iwasinska, A.; Eaton, D.K.; Koziel, J.A. A novel downwind odor sampling strategy for transient events; combined metalized-FEP gas sampling bag, sorbent tube transfer and thermal reconstitution. ASABE Paper #097277. Proceedings of the American Society of Agricultural and Biological Engineers: Reno, NV, Unites States, 2009. DOI: https://doi.org/10.13031/2013.27238.