Carthage Bottoms Area Odor Study: A Missouri Test Case for Odorant Prioritization as a Prelude to Instrument Based Downwind Odor Monitoring Protocol Development

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ABSTRACT

Past experience with crisis-driven odor investigations has shown that there is an odor impact priority ranking which is definable for virtually every malodor issue; whether from natural or synthetic source. An accurate definition of such odorant priority ranking is, in turn, critical to the development of accurate and objective instrument-based methods for odor assessment and monitoring relative to that source. This paper reports on the results-to-date relative to the Carthage Bottoms Area Odor Study; a test case undertaken by the Missouri DNR to evaluate the concept of odorant prioritization by MDGC-MS-Olfactometry. The ultimate goal of this study was to explore the utility of odorant prioritization as a first step toward the translation of sensory-only odor monitoring protocols to sensory-directed but instrument based alternatives. The Carthage Bottoms Area was selected by the Missouri DNR for this exploratory effort based upon a number of factors: including; (1) an intermittent but long-standing unresolved odor issue with respect to downwind citizenry; (2) a uniquely complex, diverse and densely co-located source industry mix within the combined Bottoms Area; (3) limited past success in point-source differentiation utilizing sensory-only protocols and (4) a past history of cooperation between citizenry, community officials, industry leaders and regulatory agencies in the exploration and implementation of technologies targeting enhanced mutually beneficial co-existance. MDGC-MS-O odorant profile and prioritization results are presented for SPME collections taken near and at-distance downwind as well as reference upwind with respect to the combined Bottoms Area.

Keywords: malodor analysis, agricultural odor, downwind odor, GC-Olfactometry, GC-O, solid phase microextraction, SPME, multidimensional gas chromatography, MDGC, process odor, rendering odor

INTRODUCTION

Currently, downwind odor monitoring of agricultural and industrial sources is primarily limited to whole-air assessment utilizing human sensory panelists and variations of dynamic dilution olfactometry (ASTM E-679, 2004; ASTM E-1432, 2004; CEN/TC 264, 19990). Variations in these methodologies range from direct, on-site assessments by human sensory panelists to indirect, in-laboratory assessments of remotely collected air samples contained in plastic bags. Although these techniques are extensively utilized for downwind odor assessment, monitoring and regulation, they each carry challenges and limitations relative to this application. For example, remote sampling and storage of whole-air samples in plastic bags has been shown to be particularly problematic as a result of the loss of high impact semi-volatile odorants due to wall adsorption effects (Kenner et al, 2002; Koziel et al, 2005). Likewise, a significant, secondary issue relative to gas bag sampling is background odor contamination from out-gassing of the plastic film itself (Kenner et al, 2002; Koziel et al, 2005). Direct, on-site assessment is assumed to address theses limitations. However, it carries a number of disadvantages associated with having to rely on human detectors for routine odor monitoring. These limitations include, but are not limited to, (1) the subjective nature of odor measurements; (2) the practical limitation to the number of panelists applied to a specific odor event; (3) the transient nature of many downwind odor events and (4) the relatively high cost for training and maintenance of the human sensors. It is for these reasons that many entities involved in odor remediation and regulation are interested in exploring the potential of instrument based alternatives to human sensory protocols.

Such is the case with respect to the downwind odor issues surrounding the focus of this current study; the Carthage Industrial Bottoms Area (CBIA). Located on the northern edge of Carthage, Missouri, the challenges associated with monitoring the downwind odor impact of the combined CBIA are exacerbated by several factors. Primary among these is the number and diversity of potential odor sources and their density within the relatively small footprint of this industrial site. It is this site density which amplifies the challenges associated with attempting to trace specific downwind odor events back to a primary source or sources. Unfortunately, whether intentional or unintentional, this obscuring of the source field enables primary offenders to avoid or delay responsibility for initiating corrective action. Conversely, this obscuring of the source field also prevents the primary sources from efficiently gauging effectiveness of corrective actions which they do initiate.

In the fall of 2007, the principal investigator was engaged by the Missouri DNR to undertake a feasibility study targeting alternative assessment and monitoring strategies to deal with the unique challenges such as presented by the CBIA. Specifically, this study explored the utility of MDGC-MS-Olfactometry; a sensory directed but instrument based approach which has widely proven success in resolving complex malodor and malflavor issues relating to food, beverage, packaging and consumer products (Eaton et al, 2007). The results reported herein, summarize the progress-to-date with respect to this exploratory effort. In a process analogous to that successfully applied to consumer product issues, these reported Phase I results have focused on efforts to prioritize the individual odorant(s) representing the greatest impact to at-distance, downwind citizenry. If ultimately proven successful in this prioritization, subsequent Phase II efforts will attempt to differentiate the individual industries within the CBIA with respect to relative contribution of these high-impact emissions.

MATERIALS and METHODS

Multidimensional Gas Chromatography-Mass Spectrometry-Olfactometry:

MDGC-MS-Olfactometry (MDGC-MS-O) is an integrated approach combining multdimensional GC separation techniques with parallel olfactory detection by a human sensory investigator and conventional electronic detection by mass spectrometry. A commercial, integrated AromaTrax™ system from Microanalytics (a MOCON

Company) of Round Rock, Texas was used for the MDGC-MS-O work in support of the efforts directed at odorant identification and prioritization. General details regarding integrated hardware and operational parameters have been described in detail elsewhere (Wright et al., 1997; Bulliner et al, 2006; Cai et al. 2006) and are not restated here. With respect to MS operation; the Agilent 5975 B was operated in selected ion monitoring mode (SIM) and targeted several suspect odorants which are common to agricultural communities and environments. Representative target odorants included: H2S, methyl mercaptan, dimethyl sulfide, trimethylamine, dimethyl disulfide, dimethyltrisulfide, acetic acid, butyric acid, isovaleric acid, p-cresol, 2-aminoacetophenone, indole and skatol. In parallel with these targeted electronic signals, sensory detection by the investigator was applied to screen for other odorants of significant impact.

SPME Sampling:

Solid Phase Microextraction (i.e. SPME) (Pawliszyn, 1997; Chai and Pawliszyn, 1995 Chai and Tang, 1997; Koziel and Pawliszyn, 2001; Koziel et al, 2006) utilizing a 1 cm Carboxen modified PDMS - 85 µm fiber was the headspace sampling technique which was utilized for the initial, Phase I efforts. SPME collections were carried out by direct fiber exposure at-distance and downwind of the combined CBIA and utilized variations in exposure time for cross-comparison purposes. All SPME downwind collections were carried out under ambient conditions present at the time of target odor detection by the principal investigator. Reference or control samples were subsequently collected generally upwind of the combined CBIA source.

Weather Monitoring:

A Weather Monitor II portable data logging weather station from Davis instruments was carried by the principal investigator during the Phase I downwind odor survey work. However, as a result of the logistical challenges associated with the transient, ‘moving target’ character of the typical odor events, attempts to use the system were abandoned early on. Subsequent area meteorlogical conditions were monitored through the local offical data as posted on www.weather.com. In addition, for monitoring of the most critical parameter, wind direction, a small plastic strip wind direction indicator (Lomax et al, 1995) was attached to the top of the pole mounted SPME support assembly at the various individual odor event locations.

A Kestrel 4500 Pocket Weather Tracker was used for subsequent off-site experiments with a prototype scale model transient odor event simulator described in the sections below. Being tripod mounted and configured for wind direction monitoring, this data logging unit is rapidly deployable and will therefore be employed for future full scale assessments.

Downwind Odor Assessments of the Combined Carthage Bottoms Industrial Area:

The Phase I at-distance downwind odor assessments were carried out during three separate visits to the area. The first was an announced visit between Sunday, October 28, 2007 @ 1500 hrs and Thursday, November 01, 2007 @ 1300 hrs. The second was an unannounced visit between Monday, December 03, 2007 @ 1100 hrs and Wednesday, December 05, 2007 @ 1000 hrs. The separation distances from the approximate geometric center of the combined CBIA to the sites of the downwind odor event encounters ranged from @ 300 meters to @ 1770 meters. The composite downwind odor characterizations were performed by Don Wright, the principal investigator and Helen, his wife and associate. A final one-day follow-up site visit was carried out on January 15, 2008.

Prototype Scale Model Transient Odor Event Simulator:

In response to the challenges encountered during attempts to sample the charactistic, transient odor events encountered in Phase I, a scale model odor event simulator was designed, constructed and carried through initial experimental evaluation. The prototype 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. The target odorants are placed into one of three generator cartridges in an appropriate form depending upon the target odorants and the goal of the experiment. These forms ranged from measured amounts of high purity solids such as naphthalene to permeation tubes for odorants carrying high vapor pressures to odorant saturated film or fiber carriers. Each cartridge is affixed with a blower under independent rheostat contol. In this case the blowers used are relatively inexpensive hair dryers. The vent stack and odorant cartridge assemblies were fabricated from 3 inch schedule 40 PVC and associated fittings. The stack vent terminates @ 7 feet above ground level in the prototype system.

RESULTS and DISCUSSION

Experience with scores of odor investigations over the past 15 years (Wright, 1997; Eaton et al, 2007) has shown that there is an odor impact priority ranking which is definable for virtually every odor source; whether natural or synthetic. This consideration is widely recognized by flavor chemists who understand that the characteristic aroma and flavor of many common food products are primarily driven by individual or limited numbers of high impact odorants (Mistry et al, 1997; Belitz and Grosch, 1999). This ‘character-defining’ effect is often the case in spite of their presence within a very complex overall odorant and volatile emission field. Common examples of this ‘character- defining’ effect include: (1) geosmin and the aroma / flavor of beets (Belitz and Grosch, 1999); (2) 2-acetyl-1-pyrroline and the aroma / flavor of Basmati rice (Buttery et al, 1983); (3) diacetyl and the aroma / flavor of buttered popcorn; (4) 1-octene-3-one / 1-octene-3-ol and the ‘earthy’ mushroom aroma / flavor (Belitz and Grosch, 1999) and (5) 3-methyl-2-butene-1-thiol and the ‘skunky’ aroma / flavor defect of light-struck beer (Goldstein et al, 1993). In some cases, over time, individual chemicals have taken on descriptive common names which are based upon this ‘character- defining’ relationship; including, for example, coconut lactone, peach lactone and whisky / oak lactone among others. Past and recent work by these authors has shown that this ‘character-defining’ relationship carries over to many common animal odor sources; including, (1) 2-amino acetophenone and the at-distance, downwind odor character of high density Mexican Free-tail bat colonies (Nielsen et al, 2006); (2) p-cresol and its high at-distance, downwind odor impact with respect to hog barns and cattle feedlots (Wright et al, 2005) and (3) felinine, an amino acid unique to the cat family, as the source (i.e. albeit indirect) of the characteristic odor of cat urine marked areas (Wright et al, 2006; Miyazaki et al, 2006). The ability to define such odorant priorities is the critical first step toward the ultimate goal of developing objective, instrument based odor monitoring protocols. This is true regardless of whether the odor source under consideration is a food, beverage, consumer product or, as in the case of the combined CBIA, a high density industrial center.

CBIA Downwind Odor Impact Challenge

Pinpointing and monitoring primary downwind odor sources and their odorous emissions can be challeging under the best of conditions. The complicating factors responsible for this challenge include continuously shifting meteorological conditions as well as variations in source operations and emissions. The ‘moving target’ aspect of these challenges is magnified with respect to the combined CBIA as a result of the additional factors of: (1) multiple, independent source entities; (2) the diversity of these independent entities and (3) the high-density co-location of these entities within the CBIA boundries. For example, included within the @ 0.10 sq. mi. CBIA industrial mix are 5 ‘potential’ odor sources, including: (1) a municipal sewage pumping station; (2) a cheese production operation; (3) a poultry processing operation; (4) a grain storage and distribution center and (5) a renewable energy production operation based upon poultry processing waste as feed-stock.

Against this background complexity and its attendant challenge to odor assessment, monitoring, and regulation, three fundamental questions drive the decision to explore instrument based alternatives to sensory based protocols. These include: (1) is there a priority composite odor which is definable when comparing the diverse odors from the combined CBIA source; (2) if yes, are there priority odorants which are definable with respect to this priority composite odor and, finally; (3) is it possible to differentiate the individual ‘potential’ sources within the CBIA, based upon their relative contribution of these high impact odorants. A decision was made by officials with the Missouri DNR that, given the stated background issues, these questions were worthy of exploration through an appropriate feasibility study. Concomitant with the decision to proceed with this feasibility study, however, was a decision that the study should be broken up into two sequential, experimental phases.

Driven by project costs and other considerations, it was determined that Phase I should address only the first two of the fundemental questions stated above and those should be outsourced to Microanalytics (a MOCON Company) as the agent of the principal investigator. Based upon results from the Phase I effort, it was reasoned, subsequent Phase II efforts addressing the third question (i.e. regarding relative odorant contribution by individual industries within the CBIA) could be addressed utilizing expertise and resources within the Missouri DNR agency itself. Therefore, the results presented here represent a progress-to-date report which addresses the Phase I, at-distance downwind assessment and odorant prioritization effort with respect to to the CBIA as a combined source.

Phase I Downwind Composite Odor Assessment

Phase I downwind odor assessment and sampling efforts were performed by the principal investigator during three separate visits to the area. The primary effort was carried out during a four day site visit between October 28 and November 01, 2007. Subsequent follow-up assessments were performed during a two day visit between December 03 and December 05 and a final one day visit on January 15, 2008. Downwind assessments were carried out utilizing a combination of approaches, including: (1) overview odor survey utilizing vehicle patrolling of a public road network circling the CBIA target area; (2) local area foot patrols were used for refined odor assessments subsequent to significant event encounters during gross vehicle survey and (3) stationary, point surveys carried out at fixed downwind locations during periods of generally stable wind conditions. The overview vehicle surveys generally utilized a route ~ 3.76 miles in length and encompassed a total area of approximately 1.0 square mile (i.e. beginning US 96 at Central Ave; north to MO CR V; west to Garrison Ave; south to Central Ave and east back to US 96). This primary route resulted in source-to-receptor separations ranging from approximately 320 meters to 1800 meters (i.e. referenced to the approximate geometric center of the CBIA). Foot patrols and fixed location surveys were found to be necessary as a result of the surprisingly transient and fleeting characteristic of the odor events as typically encountered.

A summary of the significant odor events is listed in **Figure 1** and **Table I** below. **Figure 1** is a Google Earth aerial photograph of the CBIA and downwind assessment sites. The CBIA geometric center (i.e. balloon A) and odor event sites (i.e. balloons B through L) are marked accordingly. The event encounters are in approximate chronological order, B to L reflecting a generally continuous wind direction shift accompaning the arrival of a cold front which closely bracketed the assessment period. During the assessment period the wind direction ranged from: (1) generally southerly at B; (2) generally westerly at F and G; (3) generally northerly at I and J and (4) generally easterly at K and L.

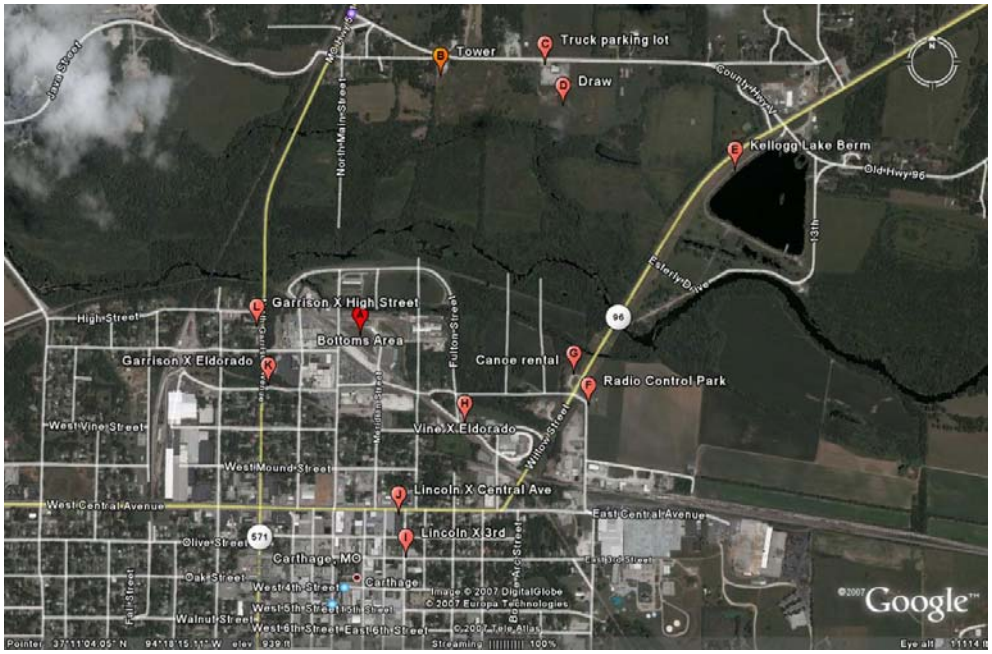

Figure 1 – Google Earth Photo of CBIA and odor assesment vicinity – first visit

Table I below summarizes the composite odor assessment results and characterizations which correspond to the encounter locations which are shown in **Figure 1** above.

Table I
Site Visit #1 Downwind Composite Odor Characterizations

Location	Date & Time	Coordinates	Distance / Elevation	Composite Descriptors
B	Tue, Oct 30th @1500 hrs	37°11’33.80” N 94°18’22.72” W	0.63 mi / 973 ft	‘characteristic’, ‘burnt’, ‘sulfurous’, ‘papermill’
C	Tue, Oct 30th @1520 hrs	37°11’34.65” N 94°18’07.89” W	0.73 mi / 983 ft	‘characteristic’, ‘burnt’, ‘sulfurous’, ‘papermill’
D	Tue, Oct 30th @1535 hrs	37°11’30.35” N 94°18’06.65” W	0.71 mi / 961 ft	‘characteristic’, ‘burnt’, ‘sulfurous’, ‘papermill’
B	Wed, Oct 31st @0805 hrs	37°11’33.80” N 94°18’22.72” W	0.63 mi / 973 ft	‘characteristic’, ‘burnt’, ‘sulfurous’, ‘papermill’
near C	Wed, Oct 31st @0815 hrs	37°11’35.19” N 94°18’16.35” W	0.88 mi / 977 ft	‘characteristic’, ‘burnt’, ‘sulfurous’, ‘papermill’
E	Wed, Oct 31st @0920 hrs	37°11’23.55” N 94°17’37.22” W	0.98 mi / 947 ft	‘characteristic’, ‘burnt’, ‘sulfurous’, ‘papermill’
F	Wed, Oct 31st @1030 hrs	37°10’55.13” N 94°18’01.87” W	0.53 mi / 945 ft	‘characteristic’, ‘burnt’, ‘sulfurous’, ‘papermill’
G	Wed, Oct 31st @1045 hrs	37°10’58.09” N 94°18’04.00” W	0.50 mi / 947 ft	‘characteristic’, ‘burnt’, ‘sulfurous’, ‘papermill’
H	Wed, Oct 31st @1400 hrs	37°10’52.84” N 94°18’20.27” W	0.30 mi / 948 ft	‘characteristic’, ‘burnt’, ‘sulfurous’, ‘papermill’
I	Wed, Oct 31st @1800 hrs	37°10’37.12” N 94°18’29.17” W	0.50 mi / 990 ft	‘characteristic’, ‘burnt’, ‘sulfurous’, ‘papermill’
B (ref)	Wed, Oct 31st @1540 hrs	37°11’33.80” N 94°18’22.72” W	0.63 mi / 973 ft	faint, non-descript, slightly ‘smoky’ background odor
J	Wed, Oct 31st @1845 hrs	37°10’41.90” N 94°18’29.71” W	0.44 mi / 990 ft	‘characteristic’, ‘burnt’, ‘sulfurous’, ‘papermill’
K	Thur, Nov 01st @1045 hrs	37°10’57.44” N 94°18’49.23” W	0.23 mi / 968 ft	‘poultry house’ and ‘landfill’ / ‘dumpster’ primarily
L	Thur, Nov 01st @1145 hrs	37°11’04.27” N 94°18’50.21” W	0.23 mi / 991 ft	‘characteristic’, ‘burnt’, ‘sulfurous’, ‘papermill’

H (ref)	Thur, Nov 01st @1200 hrs	37°10’52.84” N 94°18’20.27” W	0.30 mi / 948 ft	faint, non-descript, slightly ‘musty’ background odor

This data clearly indicates that the primary at-distance downwind odor events encountered during the test period were very consistent and, as perceived by the PI, describable as ‘characteristic’, ‘burnt’, ‘sulfurous’ and ‘papermill-like’. The data also clearly shows that, of the 13 significant downwind encounters (i.e. eliminating the 2 upwind references), only one significant event was shown to deviate from this odor character as originally encountered and described at location B. It is also believed to be noteworthy that this one exception, coincidentally, is the location which is closest in proximity to the CBIA. Specifically, this separation was only @ 370 meters from the approximate geometric center of the CBIA and only @ 200 meters from the approximate geometric center of two of the industrial operations within the CBIA. The two industrial entities in closest proximity to this site were the cheese production and poultry processing operations. In contrast, with respect to the dozen other encounters, the distance separation for the characteristic ‘papermill-like’ odor from the geometric center of the CBIA ranged from @370 meters for site L to @1577 meters for site E. These considerations appear to support prioritization of this characteristic odor with respect to at-distance downwind impact relative to the CBIA.

A number of challenges to the at-distance odor assessment process were encountered during the first site visit. The most significant of these was the surprisingly transient nature of the event encounters. This transient character was observed to be typical, even for events marked by significant peak odor intensity. The typical encounter was characterized by a single or series of detectable odor events with individual peak durations ranging from a few seconds to a minute or less. These event peaks were typically followed by relatively longer periods ranging from several minutes to hours during which the odor was detectable only faintly or not at all. During these extended odor lull periods, local foot patrols and extended vehicle patrols were used in conjunction with various wind direction indicators to relocate the shifting plume. This characteristic presented an unexpected challenge to assessment, both from the standpoint of composite odor and SPME sampling for MDGC-MS-O analysis. This ‘moving-target’ characteristic appeared to be consistent throughout the study and in sharp contrast to that observed during past downwind assessments relative to large, high density animal sources such as CAFOs and Mexican Free-tail bat colonies.

A second issue resides with the fact that the timing of the on-site assessment was widely known in advance of the site visit. This factor set up a situation in which the motives behind potentially complicating actions were, whether real or perceived, placed in question. The most prominent of these potentially complicating actions was that two of the five CBIA operations were shut-down during the first two of what was originally scheduled to be a one day on-site odor assessment. These shut downs were both reported as, and in all likelihood were, the result of maintenance or repair requirements. However, the end result was an absence of significant at-distance downwind odor events during the scheduled two day assessment period. Extending the scheduled visit by two additional days enabled this potential complication to be off-set and the assessment to be completed.

To eliminate both the potential for and perception of intentional hinderence, an unannounced two day follow-up visit was scheduled and carried out between December 3rd and December 5th. An aerial photo summary of significant odor events during that follow-up visit is shown in **Figure 2** below. The noted event sightings are in approximate chronological order, B to I, reflecting a generally continuous clockwise wind direction shift accompaning the arrival of a cold front which closely bracketed the second day assessment period. As shown, the wind direction ranged from: (1) generally WSW at sightings B through D to (2) generally northerly at F through I. Location H was an upwind reference site.

Figure 2 – Google Earth Photo of CBIA and odor assesment vicinity – second visit

The odor assessment results for the unannounced second site visit proved to be remarkably similar to those described for the first visit, albeit abbreviated. Specifically, it was marked by: (1) the absence of significant at-distance downwind odor events during the first day of the two day assessment period; (2) the return of significant, trackable odor events on the second day of the period; (3) cold weather front arrival coincident with odor detection and tracking during the second day and (4) an odor character for the at-distance downwind events which was consistent with the primary 'sulfurous' / 'papermill' odor events from the previous assessment visit. It is noteworthy that there were no significant odor events detected during this follow-up assessment period which deviated from this priority odor character. As a result of assessment timing being unannounced, the absence of significant at-distance odor events during the first day was clearly the result of normal source operational factors rather than any intentional influence.

A final, one day follow-up site visit was made on January 15, 2008. The characteristic at-distance odor events were found to be immediately detectable upon arrival at the CBIA site. Likewise, the odor events, as detected, were found to be consistent with the primary ‘sulfurous’ / ‘papermill’ odor character which was consistently encountered and described for the previous two site visits. As was the case with the previous visit, there were no at-distance downwind odor events which were shown to deviate from the primary ‘sulfurous’ / ‘papermill’ odor.

Phase I MDGC-MS-Olfactometry Based Odorant Prioritization

Unfortunately, the challenges to composite odor assessment due to the transient nature of at-distance events appeared to be even more problematic for the MDGC-MS-O odorant prioritization efforts. The continuously shifting of the wind direction during the assessment period and the resulting ‘moving target’ situation increased the difficulty of achieving an extended and relatively continuous sampling of the plume core. In concert, the increased wind speed and direction variability resulted in increased dilution of the odorant density in the plume (Pasquill et al, 1976). With respect to the SPME sample collection process, the end result was a sampled volatiles / odorant density which was well below optimum for differentiation of odorants between the general area background and those from the targeted industrial sources. As a result, the unstable conditions dictated that, from an analytical standpoint, it was necessary to work just above the ‘noise level’ in terms of MDGC-MS-O odor profile development. As a result of increased dilution, the complexity of the combined odorant suite and the trace levels of many of the key odorants it was not possible to develop tentative GC-MS identification or odor impact priority ranking for many of the perceived secondary priority odor contributors. To do so will require additional efforts utilizing modified sampling strategies and MDGC techniques to refine the separation and identification of these trace level, high impact odor carrier compounds.

In spite of the these limitations, it was possible to develop a limited, first-pass approximation of odorant priority (i.e. as perceived by the PI and during the period of this assessment) relative to the at-distance survey. It appears that dimethyltrisulfide (i.e. DMTS) may represent a high impact priority relative to the characteristic ‘papermill-like’ downwind odor. This conclusion is based upon the following factors; (1) past experience with odor issues involving this odorant as priority; (2) direct experience with its individual odor character under different conditions and from different source types; (3) personal encounters with the composite odor character, at-distance and downwind of the CBIA during the final two days of the site visit; (4) feedback comments from a very limited number of local citizens regarding consistency with the historical problem and (5) MDGC-MS-Olfactometry analytical results which appear to support this impression. **Figure 3** below shows overlay downwind and upwind reference traces for MS SIM 126 amu ion targeting DMTS. DMTS is an odorous sulfur compound which carries a particularly potent and disagreeable odor which is alternately described as ‘sulfurous’, ‘fecal’, ‘burnt’ or ‘papermill’, among others. It is one of the suite of reduced sulfur compounds which are primarily responsible for the at-distance downwind odor historically associated with papermill operations which utilize sulfite based bleaching processes. The other commonly referenced members of this odorous suite include: (1) hydrogen sulfide; (2) methyl mercaptan; (3) dimethyl sulfide and (4) dimethyl disulfide among others.

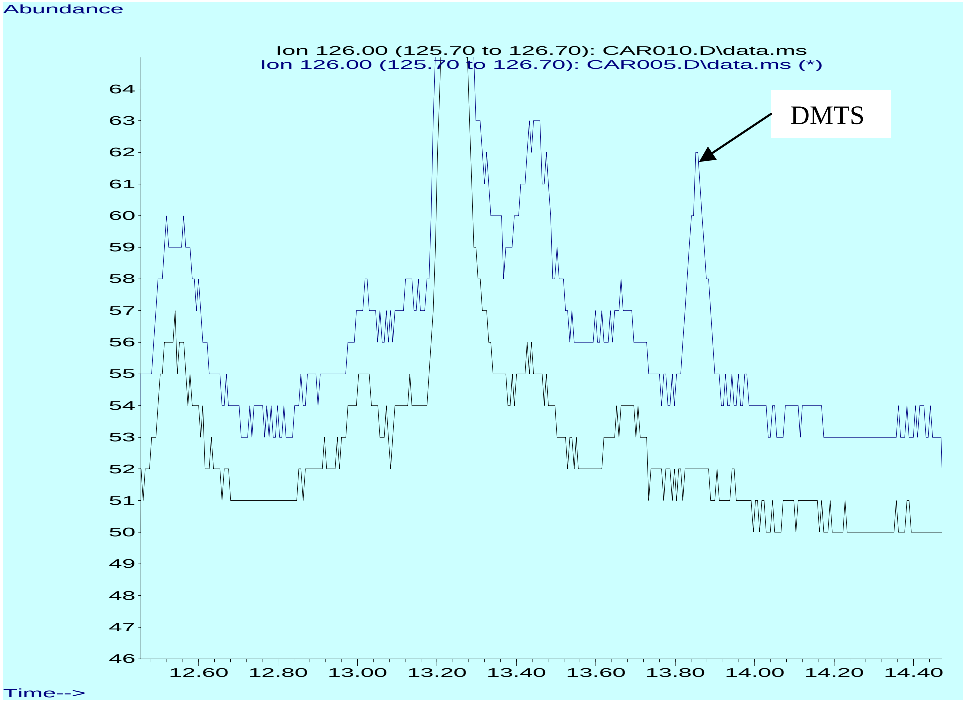

Figure 3 – MS-SIM 126 amu ion response overlay – CBIA downwind (blue upper) and upwind (black lower)

It is noteworthy that the several transient, at-distance odor events which were encountered during the three site visits were marked by a consistent odor character which was strongly reminiscent, to the PI, of the odor character associated with DMTS alone. As a result of the near ‘noise level’ limitation described above for this initial odor survey it is difficult to infer the secondary odorant priority ranking beyond DMTS as the apparent single highest impact odorant.

Phase I follow-up - downwind odor assessment and sampling optimization utilizing a prototype scale model point-source generator.

As described in the preceeding sections, significant challenges were encountered in sampling the transient at-distance and downwind odor events characteristic of the CBIA. In an effort to expedite 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 prototype, as shown in the following photograph, 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 4 – Prototype scale model transient downwind 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 experimental optimization process. Based upon early results, the system appears to achieve the following: (1) compress the assessment area from @ 1 sq. mile to @ .5 acre; (2) compress the maximum source to receptor distance from @ 1 mile to @ less than 100 feet; (3) compress the average event frequency from < 2 per hour to > 20 per hour and (4) compress travel time to survey site from several hours to < 10 minutes.

Initial experimental results with the model have been very encouraging. Beginning with a binary odorant system consisting of contrasting odorants (i.e. high purity naphthalene and its ‘mothball’ odor and 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 recognition threshold @ 70 feet; (2) at-distance (i.e. 50 to 70 feet) odor character was clearly dominated by dimethoxybenzene and (3) near-source (i.e. 5 to 10 feet) odor character was clearly dominated by naphthalene. Encouraging sampling enhancement results were also achieved by appling a two stage sampling process. Utilizing gas sampling bags, rapid grab samples of @ 2 seconds duration were manually drawn based upon perceived odor event peak intensity. This was followed by sampling of the captured bag contents through extended SPME fiber exposure times of up to 0.5 hour. Utilizing this approach, it was possible to achieve an approximate 4 fold response increase in comparison to 3 minute direct SPME fiber exposures to the same downwind environment.

These early results suggest that this integrated system may be useful for evaluation of two different investigative strategies. The first of these strategies is with respect to evaluation of proposed odorant priority rankings through odor character matching utilizing synthetic odor blends (Wright et al, 2006). The second of these strategies is the use of optimizied odor event grab sampling in conjunction with signature tracer spiking of multiple suspect (i.e. or potential) point-sources. Sulfur hexafluoride (SF6) and perfluorocarbon tracer (PFT) compounds have been widely referenced 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. It is likely that by coordinating odor event peak grab sampling with priority odorant detection, tracer compound detection (i.e. or absence) and coincident meteorological conditions, a definitive source prioritization from among multiple 'possible' point-sources can be achieved. A detailed report of the evaluation, optimization and application of the odor modeling system and integrated sampling strategy will be reported at a later date.

Phase II: Priority odorant survey among the individual CBIA industries

The Missouri Department of Natural Resources is following up with the specific sources in the Carthage Bottoms area in an attempt to further refine the information and begin to explore strategies for mitigating odor. The initial ambient evaluation was followed by some limited sample collection at one of the sources in the area. This follow up investigation resulted in some qualitative information that should serve to provide direction for a more in-depth, directed investigation of individual point sources within the facility. The department will be working cooperatively with the facility on the next phase of the investigation, with the ultimate goal of designing targeted control measures.

CONCLUSIONS

This paper reports on the results-to-date relative to the CBIA odor study; a test case undertaken by the Missouri DNR to evaluate the concept of odorant prioritization by MDGC-MS-Olfactometry. Although limited to the at-distance downwind odor assessment phase of a planned two phase study, the authors believe that a number of conclusions can be drawn from the results which are summarized in the preceeding sections. Most importantly, based upon this limited survey, there does appear to be a characteristic odor which justifies assignment of an impact priority ranking. This conclusion appears to be warranted in spite of the fact that there are other, distinctly different odor emissions coming from the combined CBIA. As a result of its observed repeatability of odor character, greater frequency of encounter and greater reach the 'sulfurous' / 'papermill-like' odor appears to warrant that priority ranking. Likewise, preliminary MDGC-MS-O based odorant prioritization efforts indicate that dimethyltrisulfide is likely an individual priority odorant contributing to the high impact 'papermill' composite odor. The observed downwind encounters with this priority odor were found to be of a consistently and surprisingly transient nature. The resulting 'moving-target' character proved to be particularly challenging to the chosen analytical sampling technique, solid phase microextraction. SPME, being a passive, adsorption based technique, functions best as a trace odorant concentrator under conditions which permit extended fiber exposure times to the target environment (i.e. several minutes to hours). The transient nature of the observed CBIA events, with odor intensity peaks typically lasting only seconds, proved to be problematic, particularly with respect to attempts at SPME collection for analytical and sensory correlation. As a result of this challenge, a Phase I follow-up effort has been initiated which is aimed at the development of a scale-model odor generator to permit replication of the types of transient odor events such as consistently observed at-distance from the CBIA source. It is hoped that this device will enable development and optimization of a sampling strategy to deal with the challenges presented by odor events of such a transient nature. It is noteworthy that the challenges presented by such transient events will be problematic, regardless of whether the assessment approach is instrument or conventional sensory panel based.

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