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A Pilot Study of Small-Scale Spatial Variability in Aldehyde Concentrations in Hillsborough County, Florida, to Establish and Evaluate Passive Sampling and Analysis Methods

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A Pilot Study of Small-Scale Spatial Variability in Aldehyde Concentrations in Hillsborough County, Florida, to Establish and Evaluate Passive Sampling and Analysis Methods

by

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of the requirements for the degree of
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A Pilot Study of Small-Scale Variability in Aldehyde Concentrations in Hillsborough County, Florida to Establish and Evaluate Passive Sampling and Analysis Methods

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ABSTRACT

Formaldehyde and acetaldehyde are listed by the United States Environmental Protection Agency (U.S. EPA) as urban air toxics. Health effects due to significant exposure to these air toxics include increased incidence of nasopharyngeal cancer, myeloid leukemia, and exacerbation of asthma. Determining the spatial variation of air toxics, such as acetaldehyde and formaldehyde, is important for improving health risk assessment and evaluating the effectiveness of source control and reduction programs.

Here, a pilot study was designed and performed to investigate small-scale spatial variability in concentrations of aldehydes using passive samplers. A literature review was first completed to select and evaluate current passive sampling and analysis methods. Radiello Aldehyde Samplers and high performance liquid chromatography (HPLC) were selected for sampling and analysis, respectively. An HPLC instrument was then set-up for separation with an Allure AK (aldehyde-ketone) column and for detection of aldehyde-derivatives via ultraviolet-visible (UV-Vis) spectrometer at 365 nm. Samplers were deployed in an (approximately) 0.7 km resolution grid pattern for one week in January 2010. Collected samples and blanks were eluted with acetonitrile and analysis was performed with the HPLC. Aldehyde samples were quantified using calibration standards.

Mean aldehyde concentrations were 3.1 and 1.2 $\mu g/m^3$ for formaldehyde and acetaldehyde, respectively, and mean acetaldehyde/formaldehyde concentration ratios were 0.4. The concentration ratios showed very little variation between sites, and correlation of aldehyde concentrations by site was high (r=0.7). Therefore, it is likely that both aldehydes have similar sources. Spatial variation of aldehyde concentrations was small within the sampling area, as displayed by low coefficients of variation (13 and 23% for formaldehyde and acetaldehyde, respectively) and small concentration differences between sites (average of both aldehydes less than 0.5 $\mu g/m^3$). Thus, one sampler may be representative of this sampling area and possibly other areas of the same spatial scale. Methods established during this pilot study will be used in a larger field campaign to characterize the spatial distribution of concentrations throughout the county, for analysis of environmental equity and health impacts.

CHAPTER 1:

INTRODUCTION

Background and Significance

Hazardous air pollutants (HAPS), or air toxics, are a group of 187 pollutants recognized by the United Stated Environmental Protection Agency (U.S. EPA) as having serious health or ecological effects (EPA, 2008). A subset of HAPs that are especially abundant in urban environments and pose a significant threat to those living and/or working in urban areas are urban air toxics (U.S. EPA, 2008). Although air toxics can have natural and anthropogenic sources, the majority of emissions in urban areas are from mobile sources (HEI, 2010; U.S. EPA, 2008; HEI, 2008). Mobile source air toxics (MSATs) have been estimated by the U.S. EPA to be associated with nearly half of the cancers attributable to outdoor sources of air toxics (U.S. EPA, 1994). Air toxics are therefore ubiquitous in urban atmospheres and exposures occur regularly.

Two such air toxics, classified as both urban air toxics and MSATs, are formaldehyde and acetaldehyde (U.S. EPA, 2008; U.S. EPA, 2010a). The International Agency for Research on Cancer (IARC) has labeled formaldehyde as a human carcinogen—associated with an increased risk of nasopharyngeal cancers, and acetaldehyde as a suspected or probable human carcinogen (WHO, 2006; WHO, 1999). The U.S. EPA and the National Toxicology Program are in the review process of

updating formaldehyde to a known human carcinogen (NTP, 2010; U.S. EPA, 2010b). Additionally, both are irritants (eyes, nose, throat, and skin) and formaldehyde exacerbates asthma and may be associated with incident asthma (McGwin, et al., 2010; WHO, 2006; DHHS, 2003; HEI, 2008). Not only are they emitted as primary pollutants from both biogenic and anthropogenic sources, they can also be formed as secondary pollutants due to the photooxidation of hydrocarbons (Tanner, Miguel, de Andrade, Gaffney, & Streit, 1988; IARC, 1999; HEI, 2010; Anderson, Lanning, Barrell, Miyagishima, Jones, & Wolfe, 1996; Altshuller, 1993; HEI, 2008). Formaldehyde and acetaldehyde are precursors to free radicals, peroxyacetyl nitrate and ozone (Grosjean, Grosjean, & Gertler, 2001). Thus, they have been identified as important to atmospheric chemistry, urban air quality and public health.

Air toxics are regulated by the U.S. EPA via National Emissions Standards for Hazardous Air Pollutants (NESHAPs) (U.S. EPA, 2009). In addition to NESHAPs, the EPA has established the Integrated Urban Air Toxics Strategy and Control of Hazardous Air Pollutants from Mobile Sources rule (U.S. EPA, 2010a; U.S. EPA, 2009). Currently, there are no ambient air standards for air toxics as there are for criteria air pollutants. The U.S. EPA monitors air toxics concentrations at several sites throughout the United States and data from these monitors are used to support programs that have a unifying goal of public health protection (U.S. EPA, 2009). In support of the above goal, the U.S. EPA has outlined three monitoring objectives: exposure assessment, trends, and air quality model evaluation (U.S. EPA, 2009).

There are usually only one to a few monitors throughout an area to characterize pollutant concentrations. Air pollution exposure assessments often use data from central

monitors as surrogates for personal exposures (Blanchard, Carr, Collins, Smith, Lehrman, & Michaels, 1999; Clougherty, Houseman, & Levy, 2009; Delfino, 2002; Isakov, Touma, & Khlystov, 2007; Zou, Wilson, Zhan, & Zeng, 2009). Due to their low density, monitors can generally not estimate the spatial variation within a city (i.e. over a small spatial scale) of many air toxics. Consequently, study results based on these exposure estimates are susceptible to exposure misclassification bias (Zou, Wilson, Zhan, & Zeng, 2009; Ozkaynak, Palma, Touma, & Thurman, 2008; Ozkaynak, Glenn, Qualters, Strosnider, Mcheehin, & Zenick, 2009). Exposures may be over or under estimated due to this bias depending on the area, spatial scale and pollutants under study. Understanding how concentrations of air toxics vary within a city will not only improve exposure assessments but will also be important for evaluations of source control programs and useful for urban and transportation planners.

The reformulated fuel program is one such source control program for which knowing intraurban variations of air toxics would be beneficial. Reformulated, or alternative, fuels initially were implemented to reduce emissions of carbon monoxide (CO) and ozone forming hydrocarbons (HCs) via oxygenated gasoline additives (i.e. ethanol and methanol) (Yacobucci, 2008; National Research Council, 1999). Ethanol has recently replaced methyl *tert*-butyl ether (MTBE) as the oxygenate of choice. This change was due to the public health scare caused by MTBE contaminating groundwater from leaks in underground storage tanks (Yacobucci, 2008; National Research Council, 1999). Although some air toxic emissions decrease (e.g. benzene) with the use of ethanol reformulated gasoline; others have been shown to increase (e.g. acetaldehyde and formaldehyde) (Niven, 2005; Hoekman, 1992; Yacobucci & Womach, 2008; Grosjean, et

al., 1990; Tanner et al., 1988). Acetaldehyde emissions have been estimated to increase by 100-200% in areas where ethanol use is widespread, such as Brazil; with some reports of increases up to 700% (Niven, 2005; Grosjean, Miguel, & Tavares, 1990). Knowing the concentrations of these air toxics before ethanol use was widespread would provide valuable quantitiave information on the effect of emissions changes on air quality and public health.

Although vehicles produce around 70% less pollution than they did two decades ago (due largely to better control technology and cleaner burning fuels) emissions have continued to increase (HEI, 2008). This increase in emissions is due to an increase in vehicles miles traveled (VMT) and is projected to offset the air quality benefit of technological and fuel improvements (Walters & Ewing, 2009). The Energy Information Administration (EIA) of the U.S. Department of Energy has projected that VMT will increase 59% by 2030 (Energy Information Administration, 2007). Population increases contribute only a small portion of this increase, with development patterns as the main driving force (Walters & Ewing, 2009; Marshall, 2008). Current urban development increases urban sprawl and encourages people to drive more and farther. This trend could be reversed through the design of neighborhoods that promote walking, biking, and public transit (Walters & Ewing, 2009; Marshall, 2008). Compact development has been estimated to decrease VMT by 30% (Walters & Ewing, 2009; Marshall, 2008). Spatial variability of air toxics at neighborhood scales could be used in assessments of different urban plans and to inform planners of future urban designs that could be implemented to improve air quality and public health

High-resolution data is necessary to estimate the spatial variability of pollutants. Monitoring networks that measure pollutants at a fine spatial scale can accomplish this. Using the current active sampling methods is impractical because they require an energy source and costly equipment. Mobile platforms have been successfully used to measure the spatial variability of pollutants, but this requires specialized, expensive equipment and spatial distributions over the same sampling time cannot be compared (Isakov, Touma, & Khlystov, 2007). Therefore, a cost effective sampling and analysis method is desirable. Passive samplers have been successfully used to measure aldehyde in indoor air and workspaces. This method could also be used to generate high-resolution data for use in spatial variability estimates and health assessments.

Specific Aims

There are three specific aims of the current thesis: 1) establish and test sampling and analysis protocols for aldehydes, 2) evaluate Radiello diffusive aldehyde samplers, and 3) assess the variability of formaldehyde and acetaldehyde concentrations at the census block group scale . A literature review was performed to identify established methods of sampling and analysis for aldehydes. A pilot study was designed and carried out to address the last two goals. A secondary aim of this work is to determine the minimum number of passive samplers that would be necessary to represent the census block group spatial scale in future, large-scale studies.

Organization of Manuscript

This manuscript has been organized into the following sections: preliminary research, sampling design, a draft scientific manuscript, and overall conclusions. Chapter 2 (preliminary research) discusses the development of the sampling and analysis

protocols, set-up and calibration of the laboratory equipment (high performance liquid chromatography instrument). Chapter 3 provides details on the sampling design. Chapter 4 is a scientific paper, including methods and results, to be submitted to a journal. Chapter 5 discusses how this pilot study fits into a larger ongoing research project and how the results of this study add to the literature and can be used in future projects to more fully understand small-scale spatial variation of urban air toxics and health effects.

CHAPTER 2:

DEVELOPMENT OF SAMPLING AND ANALYSIS METHODS

Methods of sampling and analysis of aldehydes were reviewed in the literature and standard operating procedures (SOP) were developed and evaluated during the pilot study. Once the analytical method had been selected, the laboratory needed to be set-up and all instruments calibrated as per quality control criteria in the SOP. The following sections detail the rationale used for the protocol development and laboratory set-up procedures. The sampling and analysis SOPs are included in Appendices A and B, respectively.

Sampling and Analysis Protocols

Aldehydes have most often been collected in ambient air as hydrazone derivatives via 2,4-dinitrophenylhyrazine coated media (Fuselli, Zanetti, & Santarsiero, 2007; EPA, 1999; Arnts & Tejeda, 1989; Grosjean, 1991). Radiello Diffusive Aldehyde Samplers were selected for use in the pilot study due to their high sampling rates, low detection limits and minimal interferences. These samplers and provided sampling rates have been used to determine aldehyde concentrations in a variety of environments (i.e. workplace, indoor, and outdoor) (Gonzalez-Flesca, Cicolella, Bates, & Bastin, 1999; Fuselli, Zanetti, & Santarsiero, 2007; Meininghaus, Kouiali, Mandin, & Cicolelle, 2003). They are currently being used by the CARB in a community-scale risk assessment of aldehydes

(Fujita, Campbell, Mason, & Zielinska, 2009). These samplers have an outer diffusive body made of microporous polyethylene 1.7 mm thick and are opaque to light. The diffusive body is reusable and washable. The adsorbing cartridge for aldehydes is stainless steel net mesh filled with DNPH coated Florisil. Although ozone concentrations were not an issue during the pilot study, the samplers have reported interferences with ozone concentrations greater than 50 and 100 ppbv for acetaldehyde and formaldehyde, respectively (Fondazione, Salvatore, & Maugeri, 2008). Sampling rates under environmental conditions listed in Radiello manual and averaged over sampling interval are listed in Table 2.1.

Table 2.1 Sampling rate parameters

	Wind Speed (m/s)	**% RH**	**Temp (K)**	**Ozone (ppbv)**		**Sampling Rate (ml/min)**	
				AA[b]	**FA[b]**	**AA[b]**	**FA[b]**
Radiello	0.1-10	15-90	298	50	100	84	99
Field Study[a]	4	70	317	29		86	101

[a] Environmental parameters were averaged over sampling interval and provided by the Hillsborough County Environmental Protection Commission
[b] AA=Acetaldehyde, FA=Formaldehyde

As can be noted in Table 2.1, sampling rate corrections were only necessary for temperatures experienced during the sampling interval. Using Equation 2.1 the sampling rate for each aldehyde was corrected for the average temperature (K) over the study interval.

$$Q_K = Q_{298}\left(\frac{K}{298}\right)^{0.35} \qquad \textbf{Equation 2.1}$$

The sampling SOP was written based on the Radiello manual as well as other studies that have used and evaluated these samplers (Fuselli, Zanetti, & Santarsiero, 2007; Fujita,

Campbell, Mason, & Zielinska, 2009; Gonzalez-Flesca, Cicolella, Bates, & Bastin, 1999; Meininghaus, Kouiali, Mandin, & Cicolelle, 2003). The SOP details the storage of samplers before and after deployment, set-up of samplers for deployment and actual deployment and retrieval procedures. Sampling design is not discussed in the SOP but will be discussed briefly in a Chapter 3.

High performance liquid chromatography (HPLC) with ultraviolet/visible detection is the usual method used for analysis of aldehyde-DNPH derivatives and is used by the U.S. EPA, the California Air Resource Board (CARB), and the National Institute of Occupational Safety and Health (NIOSH). Thus, standard operating procedures were written using the U.S. EPA's Method TO-11A and CARB's Method 430 as templates (EPA, 1999; CARB, 1991). The analytical protocol developed here, provides step-by-step instructions about how to prepare samples for analysis, run a sample, and calculations used to quantify concentrations. The protocol also contains detailed quality assurance and control procedures, including establishing a control chart, cartridge blanks, calibration procedures, and calculating the analytical limit of detection.

Laboratory Set-up

Once the analysis method was selected, the HPLC instrument needed to be set-up and calibrated. This was a fairly involved process, as the HPLC had been stored for several years and was not operational. The HPLC used was a Varian ProStar with two independent pumps and a UV/vis detector. The pumps are automatically controlled by software (Star Workstation) on a nearby computer. Set-up was completed using reference materials (including instrument manuals, books, and published literature) and phone assistance from Varian personnel. Once the HPLC was successfully set-up, all

work was verified by a certified Varian technician during a preventive maintenance review. The following is an overview of the procedures completed to set-up the HPLC.

All tubing and associated fittings were replaced to ensure that tubing had the appropriate diameter in all places and there were no leaks due to improper storage or previous usage. The manual injector was rebuilt due to a leak and a 20 µl stainless steel injection loop was replaced by a 10 µl loop. A backpressure regulator was purchased and installed to minimize interference from air bubbles that were entering the line as depressurized solvent exited. The UV light was also replaced after the backpressure regulator was installed because the baseline was still very noisy.

Once the HPLC was operational, a control chart was established to track instrument performance over time; warning and control limits were set after 20 daily calibration runs had been completed on multiple days. The instrument was calibrated using aldehyde-DNPH standards purchased from Sigma Aldrich.

Linear Calibration

The range for the calibration curve was determined by identifying an expected range of aldehyde concentrations in the field sampling domain. The expected ambient concentrations were estimated from air toxic monitoring data reported by the U.S. EPA and the Hillsborough County Environmental Protection Commission (EPC). The range of the linear curve was determined by the aldehyde with the lowest and highest estimated yearly average. The actual curve includes values 10% below and above the aforementioned range to account for variations in the concentrations that may be experienced over the shorter averaging time of the pilot study. Replicate samples of ten selected concentrations, calibration standards, were injected into the HPLC for analysis.

A plot of sample concentration (µg/ml), versus the detector response (area counts) was carried out using Microsoft Excel 2007. Linearity was confirmed with correlation coefficients greater than or equal to 0.99, as can be seen in Figure 2.1.

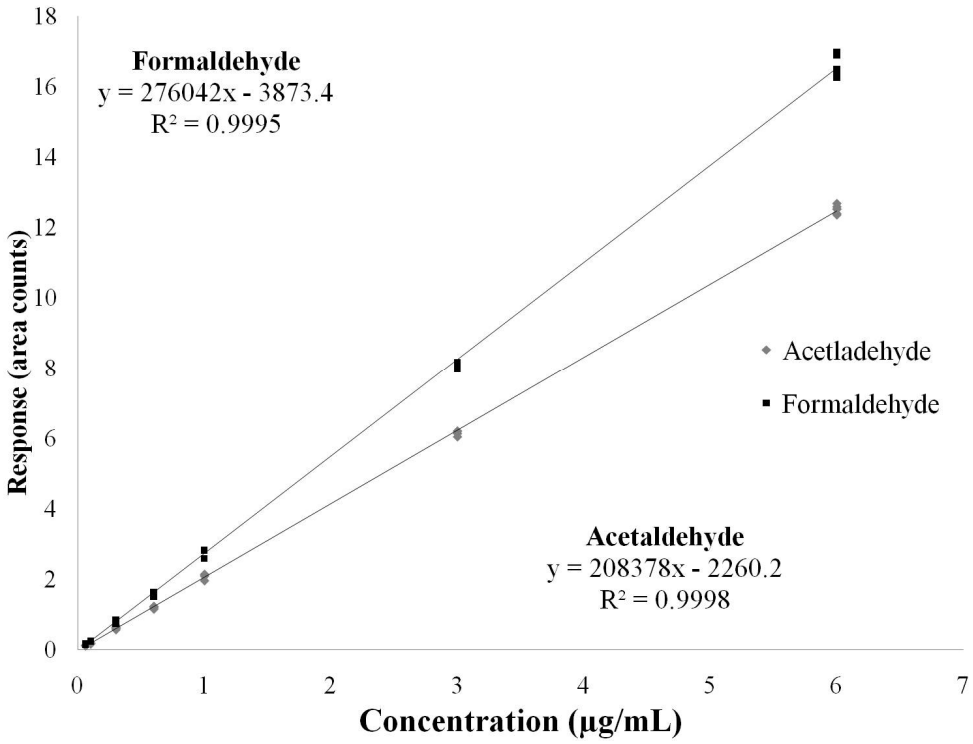

Figure 2.1 Calibration curves of acetaldehyde and formaldehyde.

Analytical Detection Limit

Typically analytical detection limits are calculated by analyzing a number of blank cartridges and using the average of this value. For the pilot study, there were a limited number of samplers available. Therefore, only one blank cartridge was analyzed and an alternative method was used for calculating the analytical detection limit, as outlined in CARB 430. A low-level concentration curve was constructed and the detection limit was calculated using the standard deviation of the lowest concentration,

the slope of the line and the student's t score (one sided, 99% confidence level, 9 degrees of freedom) . The standard deviation (SD) is first converted from area counts to concentration (㎎/ml) using Equation 2.2.

$$SD\ (㎎/ml) = SD\ (area\ counts)/slope \qquad \textbf{Equation 2.2}$$

Next the detection limit (DL) is calculated using the above student's t score according to Equation 2.3.

$$Analytical\ DL\ (㎎/ml) = t\ value * SD\ (㎎/ml) \qquad \textbf{Equation 2.3}$$

Values below the analytical detection limit are reported as non-detects. However all values in the pilot study were above this limit. Calibration curves used for calculating the analytical detection limit are shown in Figure 2.2.

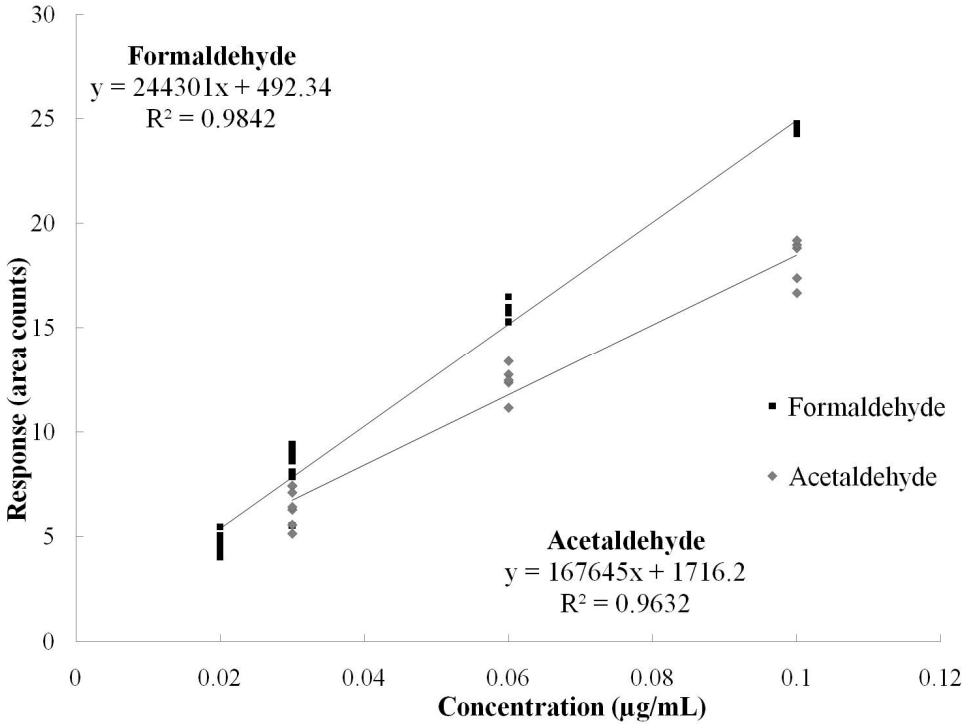

Figure 2.2 Calibration curves of formaldehyde and acetaldehyde used to calculate analytical detection limits.

Sample Quantification

A brief overview of sample quantification is provided below, a detailed description of the protocols used are in Appendix B. Concentrations of field samples were quantified by comparison with the daily calibration standard for each analysis day. A response factor (RF) was first calculated using Equation 2.4.

$$RF = \frac{response\ (area\ counts) - intercept\ (area\ counts)}{calibration\ standard\ concentration\ (\frac{mg}{ml})} \qquad \textbf{Equation 2.4}$$

The mass of cartridge blanks and field samples was calculated by Equation 2.5. The mass of each field sample was corrected by subtracting the average mass of the cartridge blanks.

$$Mass\ (mg) = \frac{response\ (area\ counts) \times volume\ of\ exract\ (ml)}{RF} \qquad \textbf{Equation 2.5}$$

Sample mass (mg) is then used in conjunction with the aldehyde-specific sampling rate and site-specific sampling time to determine the ambient concentration (mg/m^3) as shown in Equation 2.6. Details of sampling rate parameters and corrections are discussed in Chapter 4.

$$Sample\ Concentration\ \ \frac{mg}{m^3} = \frac{Mass\ (mg)}{Sampling\ rate\ \frac{ml}{min} \times sampling\ time\ (min)} x\ \frac{10^6\ ml}{m^3} \qquad \textbf{Equation 2.6}$$

Quality Assurance and Control

Control charts were implemented after twenty calibration samples were analyzed and the instrument was deemed in good operating condition by the certified Varian technician. Control charts were used to track instrument performance over time; both detector responses and retention times were used. Control and warning limits were

calculated as outlined in the SOP and shown in Figures 2.3 and 2.4. A cartridge blank was analyzed and calculated mass subtracted from field samples. Baseline and solvent blanks were run at the start of each analysis day and after the analyses of 10 field samples.

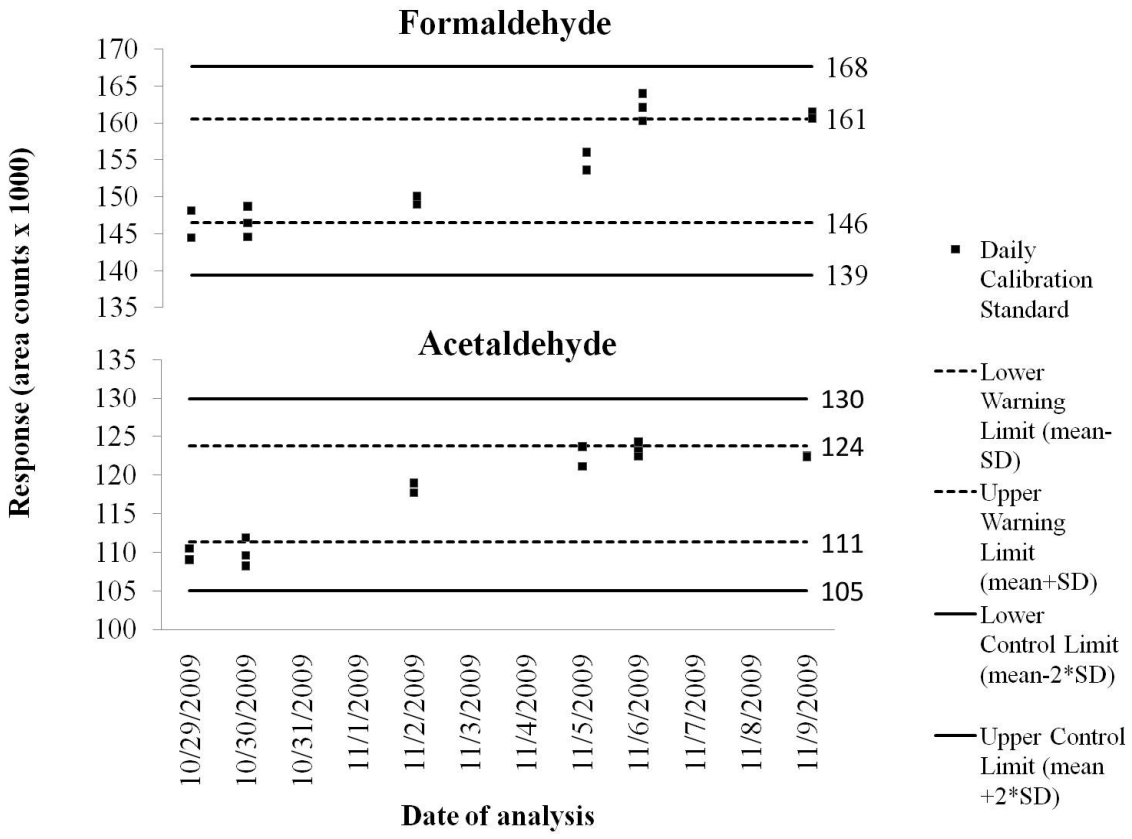

Figure 2.3 Control charts of detector response for formaldehyde and acetaldehyde.

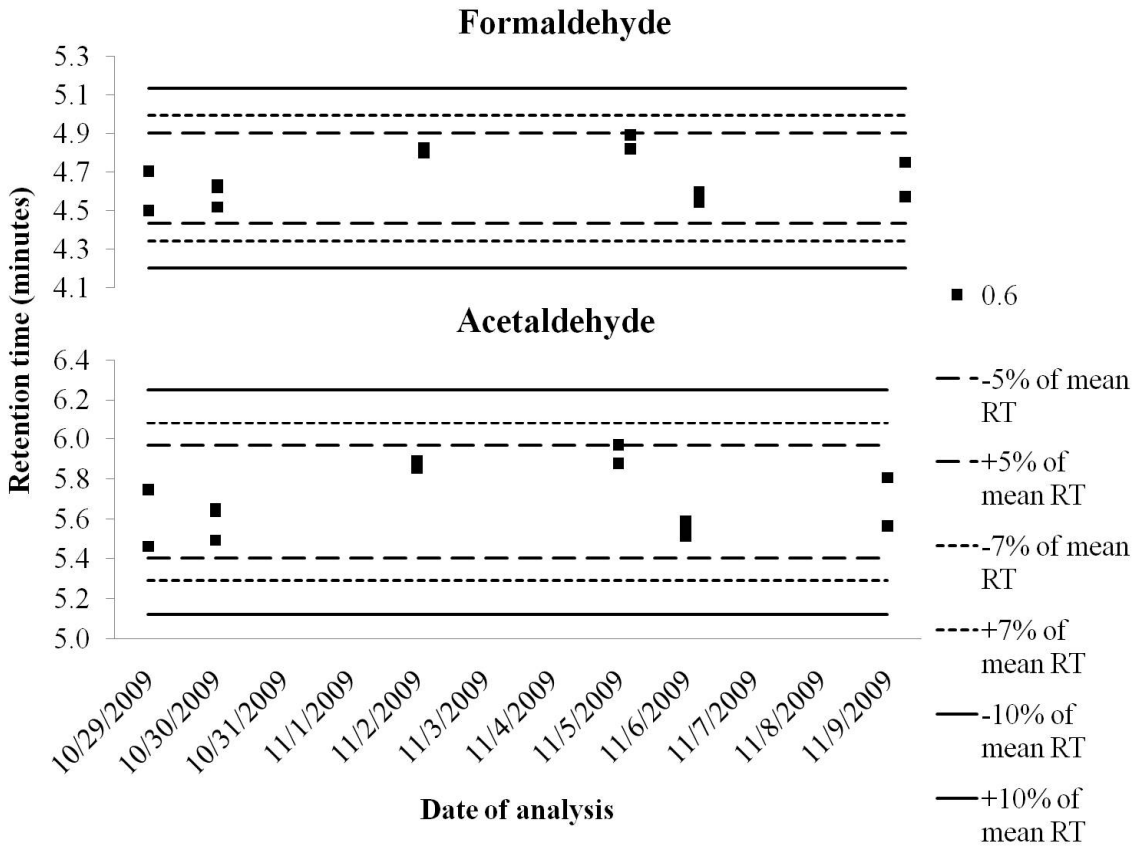

Figure 2.4 Control charts of detector retention time for formaldehyde and acetaldehyde.

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CHAPTER 3:

SAMPLING DESIGN DEVELOPMENT

Case Study: Hillsborough County

Hillsborough County, FL was selected as a case study for assessing spatial variations of urban air toxics in a larger overarching funded study. This county is located on the west coast of Florida in a growing metropolitan area, Tampa –St. Petersburg-Clearwater, FL Metro Area and has an estimated population of over 1 million (U.S. Census Bureau, 2010). In 2000 the county had a population density of approximately 1000 people per square mile. Since 2000 there has been a population increase of almost 20% (U.S. Census Bureau, 2010). This county was chosen due to its accessibility for field sampling. The diversity and magnitude of sources (including interstates, power plants, a large port, phosphate manufacturing processes, and agriculture) is also important as well as the potential impact these sources have on the community (densely populated areas located close to sources). Figure 3.1 displays point and mobile sources of acetaldehyde for the county. Table 3.1 displays a summary of emissions data for acetaldehyde and formaldehyde. From this table it can be seen that over 90% of emissions of both aldehydes are due to mobile sources. This area has also been consistently monitoring air toxics, including aldehydes, at a minimum of one site for almost 10 years.

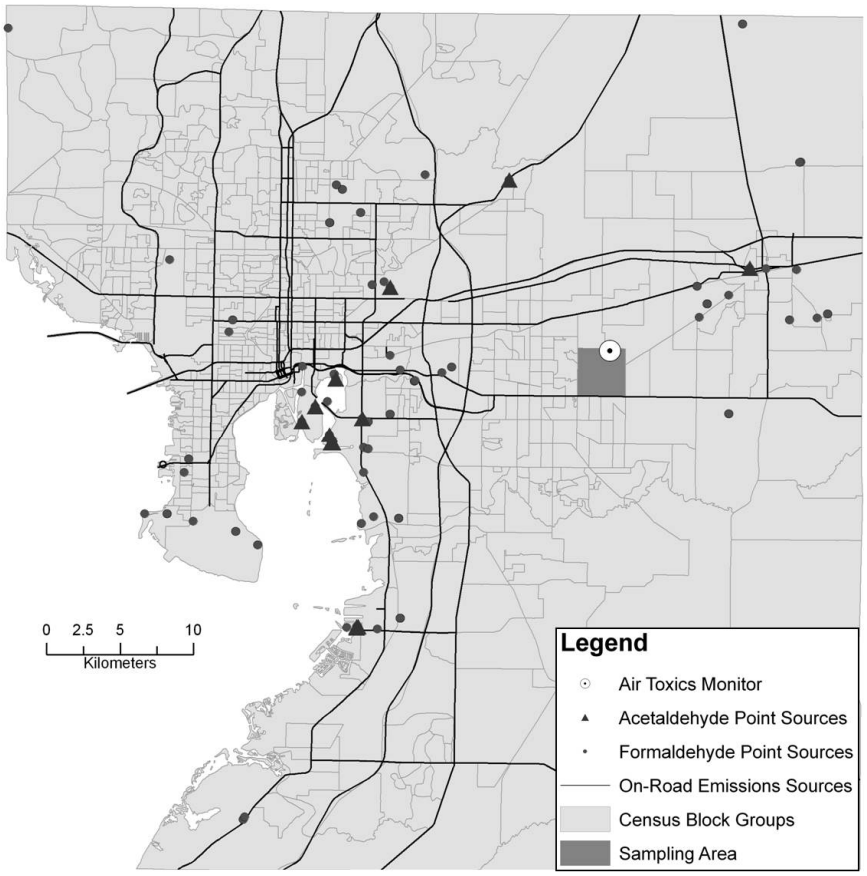


Figure 3.1 Census block groups in Hillsborough County superimposed over aldehyde emission sources (roadways and point sources).

A goal of the overarching case study is to quantify concentrations of select air toxics at the census block group level. This will allow for adequate data to assess spatial variations throughout the county and additional analyses including concentration variations by race, socioeconomic status, or susceptibility status (children and elderly)—which are important with respect to environmental justice. Here, the focus is to develop and evaluate passive sampling methods for aldehydes and to determine the approximate number of samplers needed for each sampling area (census block group).

Table 3.1 Aldehyde emissions data[a] for Hillsborough County

Pollutant	Stationary		Mobile		Total	
	Point	Nonpoint	Nonroad	Onroad	TPY[b]	%[c]
Formaldehyde	1%	3%	54%	42%	455.00	3%
Acetaldehyde	1%	2%	49%	48%	172.00	1%
Total Urban HAP	1%	8%	62%	29%	1902.00	13%
Total HAP	26%	21%	39%	15%	14765	

[a] Calculations based on data from the 2002 U.S. EPA National Emissions Inventory
[b] Tons per year
[c] Percentage of total HAPs for Hillsborough County

Spatial Scale: Census Block Group

To assess the extent of spatial variation over small spatial scales, a census block group inside Hillsborough County, Florida was used for a pilot study. The census block group was chosen as an appropriate spatial scale due to its use as a proxy for neighborhood level estimates (U.S. Census Bureau, 2005). A census block group is a cluster of census blocks that contains about 1,500 people (U.S. Census Bureau, 2005). A block group was identified as a potential sampling area if there was a currently operational central site carbonyl and ozone monitor located in the block group, only one site met this criteria.

A saturation style sampling approach was utilized with a grid-based sampling design in order to quantify the spatial variation. This sampling approach has been utilized in previous studies for assessing intra-urban spatial variation (Blanchard, et al., 1999; Zhu, et al., 2008). For the pilot study, there were 15 samplers available for field sampling and the sampling area was approximately 10 km^2; therefore, a sampler was placed around every 0.7 km, as can be seen in Figure 3.2. The sampling design included

the collocation of two field samplers (Site 2) to assess the precision of the overall sampling method. A sampler was also collocated with the active regulatory carbonyl monitor (Site 3) to evaluate the passive sampler.

Description of Sampling Area

Using the above criteria for choosing the sampling area, there was only one block group currently monitoring carbonyls in the county, located in Plant City, FL. This site has been used as an U.S. EPA National Air Toxics Trends Station (NATTS), to estimate background levels of HAPs, including formaldehyde and acetaldehyde. The monitoring equipment and data are managed by the local environmental protection agency, Environmental Protection Commission of Hillsborough County (EPC). Local emissions are mainly from mobile sources. On-road mobile sources include four roadways creating the boundary of the study area—Sydney Road, Dover Road, Hwy 60, and Valrico Rd. Substantial off-road emissions may be due to agricultural equipment associated with farming in the area, local development including two subdivision, and residential and commercial (e.g. golf course) lawn equipment.

Sampling Sites

The sampling area was surveyed by vehicle to identify all potential sampling sites. Sited were identified as appropriate if they were publicly accessible and had an appropriate place to mount the sampler (i.e. telephone or electric pole)—safety of study personnel and potential for sampler tampering was also considered. Nearly 30 sites were identified and tracked using a Global Positioning System (Garmin *eTrex* Venture-HC) with coordinates uploaded and saved to Garmin MapSource. Final sites were selected to have samplers evenly spaced within the sampling area according to the aforementioned

sampler spacing scheme. There was large wastewater treatment plant in the northeast quadrant of the sampling area that limited the number of samplers in this area. For this reason, a sampler (Site 4) was placed outside of the original sampling area in an attempt to represent concentrations in this area. There was also a large golf course in the northeast quadrant that was unavailable for sampling. On the whole, the samplers should be representative of concentrations throughout the area that may lead to exposures of those living and/or working in this area.

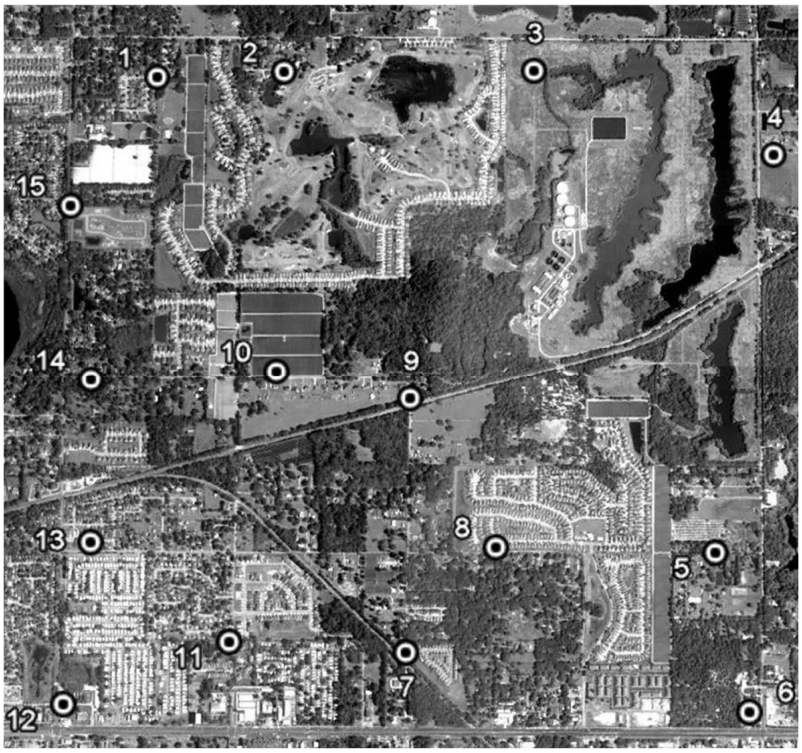


Figure 3.2 Overview of sampling area

CHAPTER 4:

A PASSIVE SAMPLING STUDY OF SMALL-SCALE VARIATIONS IN AMBIENT ACETALDEHYDE AND FORMALDEHYDE CONCENTRATIONS

Abstract

Formaldehyde and acetaldehyde are urban air toxics whose emissions from vehicles are expected to increase with the use of ethanol as a fuel additive. Understanding of concentration variations over small spatial scales is needed for determining exposures and health effects of traffic. Here, Radiello passive diffusive aldehyde samplers were used to measure ambient formaldehyde and acetaldehyde in a 10 km^2 sampling area in Hillsborough Co., Florida from January 21 to 28, 2000. Samples were analyzed for aldehyde-DNPH derivatives via high performance liquid chromatography with ultraviolet detection. Concentrations were compared with values at a regulatory fixed-site monitor for evaluation. Distribution statistics, concentration ratios, and spatial contours were calculated to investigate spatial variability. Mean aldehyde concentrations were 3.1 and 1.2 $\mu g/m^3$ for formaldehyde and acetaldehyde, respectively. Observed spatial variation was small, with coefficients of variation (CV) of 13 and 23%, respectively. Similar spatial concentration trends were observed for both aldehydes measured. Results suggest that one sampler may be relatively representative of this sampling area, which is on the scale of a U.S. Census block group. Hence, this approach could be used for future studies of within-county spatial variability for exposure assessment or hot spot analyses.

Introduction

Aldehyde emissions have been noted to increase by as much as 200% with the use of oxygenated fuels (Niven, 2005; Yacobucci, 2008). However, limited monitoring data exist to evaluate exposures and health impacts associated with such increases. Formaldehyde and acetaldehyde, specifically, are ubiquitous in the environment (Altshuller 1993; Anderson et al. 1996) and have known health effects (ATSDR, 1999; U.S. EPA, 1994). Formaldehyde is a human carcinogen associated with increased risk of nasopharyngeal cancers (International Agency for Research on Cancer [IARC], 2006). Acetaldehyde is a suspected human carcinogen (IARC, 1999). In addition, formaldehyde exacerbates asthma and may be associated with incident asthma (Health Effects Institute (HEI), 2008; McGwin et al. 2010). Both are known irritants (eyes, nose, throat, and skin) (HEI, 2008; National Toxicology Program [NTP], 2009). Both also contribute to ozone formation and, hence, photochemical smog (Altshuller, 1993; Anderson, et al. 1996; Grosjean, et al. 1990; HEI, 2008; Yacobucci, 2008).

Understanding spatial variations of air toxics, including aldehydes, within urban areas has been identified as a research priority (Mckone et al. 2009; Ozkaynak et al., 2009; Ozkaynak et al., 2008; Jerrett, et al., 2005). Results from modeling, such as the United States Environmental Protection Agency's (U.S. EPA) ASPEN model, indicate variability of these and other urban air toxics at neighborhood and community scales (Ozkaynak et al. 2008), However, low-resolution measurement data available from sparsely located fixed-site regulatory monitors cannot adequately characterize spatial variations over small scales. This has been cited as a significant uncertainty in health effects studies, whose results can be biased due to exposure misclassification (Ozkaynak,

et al. 2009; Wilson et al. 2005; Zou et al. 2009). Furthermore, the magnitude and direction of bias cannot be known without more-resolved data (Isakov et al. 2007; Wilson et al. 2005; Zou et al. 2009).

Models can be informative at small scales, but monitoring data is still necessary to evaluate modeling results (Jerrett, et al. 2005; Ozkaynak et al. 2008). Yet, only a few studies have attempted to quantify concentrations of air toxics at high resolution within cities where local sources (i.e. major roadways) can impact personal exposures (Isakov et al. 2007; Logue et al. 2010; Zhu, et al. 2008). High-resolution monitoring is often impractical due to the high costs of active sampling instruments. Mobile measurements have been used to gather high-resolution data, but this also requires expensive equipment (Isakov et al. 2007; Ott et al. 2008). Spatial characterization is further limited by resulting data that is not coincident in time. Conversely, passive sampling does not require electricity or costly equipment. Therefore, it can be a cost-effective strategy for obtaining high-resolution data and has been successfully used for assessing spatial variations of air toxics within urban areas (Ott et al. 2008; Jerrett et al. 2005; Zhu et al. 2008).

Here, a pilot passive sampling study was conducted to measure ambient formaldehyde and acetaldehyde in a small sampling area on the approximate scale of a neighborhood. The aims were to assess spatial variations in concentrations at this scale and to evaluate the approach for application in a full campaign.

Experimental Methods

Sampling

This pilot study is part of a larger investigation to understand spatial variations of traffic-related pollutants within Hillsborough County, FL for environmental equity and health effects analyses. The county is located on the west coast of Florida in a growing metropolitan area (Tampa –St. Petersburg-Clearwater Metro Area). It has an estimated 2009 population of over 1 million (U.S. Census Bureau, 2010). A diverse mix of air pollution sources in areas of high population density make this county an interesting case study. Hillsborough county has also been consistently monitoring air toxics for approximately 10 years. Figure 4.1 shows the location of emission sources and the one active monitoring site for formaldehyde and acetaldehyde.

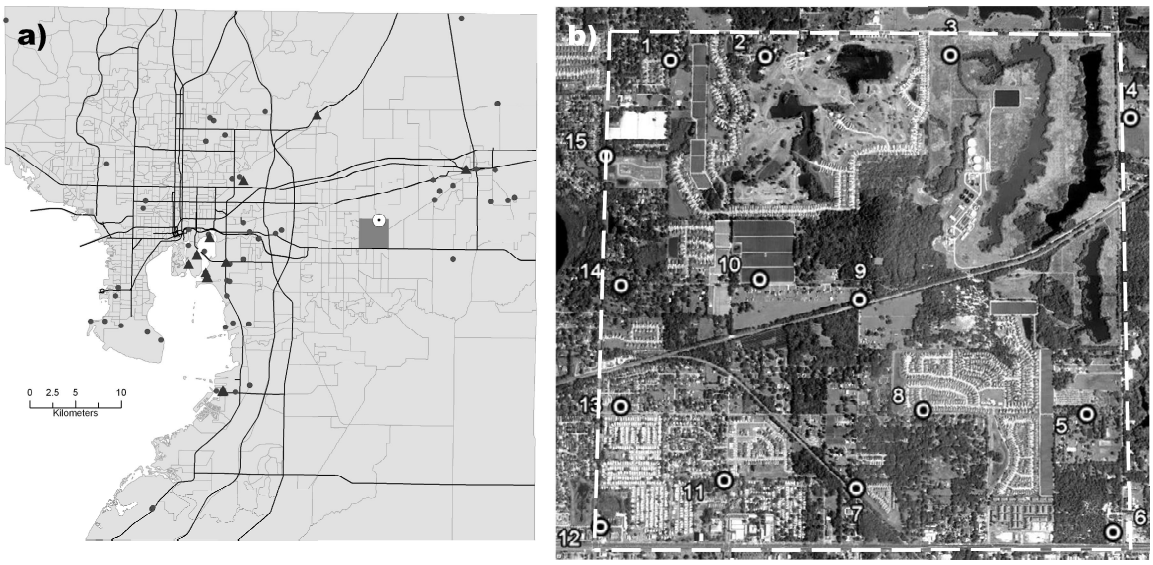


Figure 4.1 Study area. **a)** Map of Hillsborough County, FL with aldehyde sources and reference method monitor site. Air toxics monitor (EPA Air Quality System ID 120573002) is operated and maintained by the Hillsborough County Environmental Protection Commission. Emissions data are from the 2002 National Emissions Inventory. **b)** The sampling area (3.2 x 3.2 km) with locations of sampler placements. The numbers indicate the site ID. Site 3 is the location of the reference method fixed-site monitor where a passive sampler was collocated. Duplicate passive samplers were located at Site 2. The sampler at Site 6 was found on the ground and excluded from all analyses. The satellite image is from Google Earth. The white dashed box in b) is the area shown in Fig.ure 4.3.

Here, a 10 km^2 area in Plant City, FL was chosen as the study area to assess small-scale spatial variations of the target aldehydes. Information on variation at this scale is needed to inform sampler placement for the larger study. The area corresponds to three census block groups. The block group is the smallest spatial scale at which detailed demographic information is routinely available and is often used a proxy for a neighborhood (U.S. Census Bureau, 2005). The specific area here was chosen to allow collocation with the only active reference method monitor in the county. To determine spatial variations, a saturation sampling approach, with grid-based sampler placement, was used. This approach has been utilized previously to assess intra-urban spatial variation (Blanchard et al. 1999; Zhu et al. 2008). Here, samplers were placed approximately 0.7 km apart throughout the sampling area, in accessible locations (utility poles) in residential areas. Figure 4.1 shows the location of the sampling area and individual sampler placement. Note that two field samplers were collocated.

Ambient aldehydes were collected using Radiello diffusive samplers (Sigma-Aldrich). These samplers are impregnated with 2,4-dinitrophenylhydrazine (DNPH) coated Florisil, to which the aldehydes chemisorb, creating stable aldehyde-DNPH hydrazones. For the seven-day sampling interval used here, the samplers have a limit of quantitation of 0.1 mg/m^3 for each aldehyde (Fondazione et al. 2008). Samplers (n=15) were deployed for one week from January 21 to 28, 2010. Samplers were placed at a height of 2.5 m and shelters were used for protection from inclement weather and direct sunlight (Fondazione et al. 2008; Ott et al. 2008; Olson et al. 2009). All samplers were successfully deployed and retrieved; however, one sampler (located at site ID 6) was found on the ground and excluded from analyses.

Analysis

Analytical protocols were adapted from U.S. EPA Method TO-11A (U.S. EPA, 1999) and California Air Resources Board (CARB) SOP104 (CARB, 2006), with modifications for specific equipment and materials. An Allure AK column (200 x 4.6 mm, Restek) was employed to achieve separation of the aldehyde-DNPH derivates using only two solvents. The mobile phase was a mixture of acetonitrile and water (both HPLC-grade) with gradient elution as follows: 40:60 (acetonitrile:water) for 0-8 min, 30:70 min for 8-10 min, and reaching 100% acetonitrile by 10 min. A constant flow rate of 1.0 ml/min was used. Following Radiello protocols (Fondazione et al. 2008), cartridges were eluted with 2 mL of acetonitrile. 10 µl aliquots of filtered eluate were then analyzed. Absorbances were measured at 360 nm. Calibration was performed over the range of 0.06-6.0 µg/ml using 100 µg/ml aldehyde-DNPH stock (Restek). Calibration curves for each aldehyde had coefficients of determination (R^2) greater than 0.99. Analytical detection limits were determined using a low concentration calibration curve (0.01-1.0 µg/ml), following CARB SOP 104 (CARB, 2006). Ambient concentrations were calculated from the blank corrected mass, the sampling time at each sampling site, and the sampling rate for each aldehyde (99 and 84 ml/min for formaldehyde and acetaldehyde, respectively) (Fondaziione et al., 2008). The sample rates are specific to local environmental conditions (relative humidity, temperature, wind speed, and ozone concentration). Local environmental data at the regulatory reference site were used.

Data Analysis

Descriptive statistics, ratios between acetaldehyde and formaldehyde, and correlations were calculated to summarize the data and compare results to those from

other sites. Concentrations between the two collocated field samples and between the reference method monitor and a collocated passive sampler were also compared. To investigate spatial variation in the study area, concentrations were interpolated by kriging to produce contour maps, using ArcGis (Desktop 9.3, Redlands, CA). Coefficients of variation (CV) and concentration differences between sites were also determined. All statistics were calculated using SAS 9.2 (Cary, NC).

Results and discussion

Measured levels of acetaldehyde and formaldehyde in the study area

Descriptive statistics are summarized in Table 4.1, with values and ratios at each site provided in Figure 4.2. All samples (n=14) contained levels greater than the analytical detection limit for both aldehydes.

Table 4.1 Summary statistics[a] for formaldehyde and acetaldehyde measured at Sydney, Florida from January 21-28, 2010.

	Formaldehyde	**Acetaldehyde**	**Ratio[b]**
Mean	3.1	1.2	0.39
Standard Deviation	0.41	0.28	0.06
Coefficient of Variation (%)	13	23	14
Minimum	2.3	0.67	0.29
Maximum	3.8	1.6	0.47

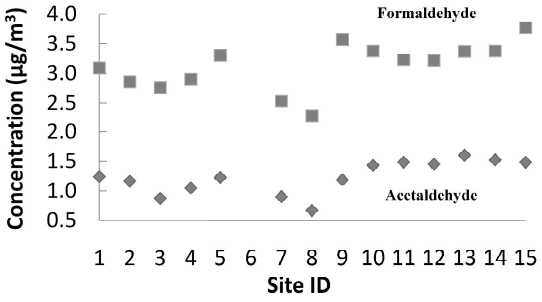
[a] All units $\mu g/m^3$, unless otherwise stated
[b] Ratio of acetaldehyde to formaldehyde concentration

Mean values for the study area are comparable to the 2009 annual average concentrations from the reference fixed-site monitor for formaldehyde and acetaldehyde, of 2.6 and 1.2 $\mu g/m^3$, respectively (U.S. EPA, 2008). Dasgupta et al. (2005) also reported a similar value for formaldehyde, 3.2 $\mu g/m^3$, during May 2002 at a nearby intensive measurement site that was part of the Bay Region Atmospheric Chemistry Experiment.

Values from other urban areas are comparable, within the range of 1 to 5 mg/m^3 (Anderson et al. 1996; Baez et al. 1995; Bakeas et al. 2003; Grosjean, 1991; HEI, 2008).

In an effort to quantify the risk associated with lifetime exposure to ambient concentrations of pollutants, the U.S. EPA has established inhalation reference concentrations (RfC). Lifetime population exposures (including sensitive populations) that occur at or below the RfC are not expected to result in adverse health effects (U.S. EPA, 1994). The RfC for formaldehyde and acetaldehyde are 9.8 and 9 mg/m^3, respectively (U.S. EPA, 1994). The maximum study values (3.8 and 1.6 mg/m^3, respectively) are at least a factor of 2 lower than the RfCs. Hence, health risks associated with lifetime exposure to these levels is expected to be low, though they only represent the time period studied here.

a)



b)

Site	Formaldehyde (µg/m³)	Acetaldehyde (µg/m³)	Ratio
1	3.01	1.24	0.40
2	2.86	1.16	0.41
3	2.76	0.87	0.32
4	2.90	1.05	0.36
5	3.30	1.23	0.37
7	2.53	0.90	0.36
8	2.28	0.67	0.29
9	3.58	1.19	0.33
10	3.38	1.44	0.42
11	3.23	1.49	0.46
12	3.22	1.46	0.45
13	3.38	1.61	0.48
14	3.38	1.53	0.45
15	3.78	1.49	0.39

Figure 4. 2 Measured formaldehyde and acetaldehyde concentrations by sampler location. **a)** Trend in concentrations by site. **b)** Data values for concentrations and the acetaldehyde to formaldehyde ratio. Samplers were deployed for one week from January 21 to 28, 2010. All samples were above the analytical detection limits of 5 and 10 ng/ml for formaldehyde and acetaldehyde, respectively. The sampler at Site 6 has been excluded due to possible contamination as it was found on the ground upon retrieval. Site locations are shown in Figure 4.1

As shown in Figure 4.2, acetaldehyde was lower than formaldehyde (by about a factor of 2) at every site in this study, with an average acetaldehyde to formaldehyde ratio of 0.4. Grosjean et al. (1990, 1996) reported that average acetaldehyde/formaldehyde

ratios from multiple studies in urban areas of the U.S. were about 0.44. Similar ratios have also been found in more recent work (Lee et al. 2001; Ho et al. 2002; Possanzini et al. 2002; Bakeas et al, 2003). Data from Brazil provide an interesting exception. Historically, Brazil has had very high ethanol fuel content, with resulting high acetaldehyde to formaldehyde ratios (Correa et al., 2003; Grosjean et al., 1990; Grosjean et al., 2002). The data here are consistent with urban ratios, and ethanol fuel content, in the U.S.

Trends by site for both aldehydes are also similar. A Pearson correlation coefficient of 0.71 was found between acetaldehyde and formaldehyde. Values observed in other studies reporting correlations range from 0.77-0.97 (Anderson et al. 1996; Lee et al. 2001; Bakeas et al. 2003; Ho et al. 2006). High correlations between acetaldehyde and formaldehyde, along with similar concentration ratios at all sites, suggest similar emissions sources nearby (Bakeas et al. 2003; Ho et al. 2006; Wheeler et al. 2008). Since, no point souces of both aldehydes are located near the study area (see Figure 4.1), mobile sources may be important.

Spatial Variation

Spatial distributions of acetaldehyde and formaldehyde are shown in Figure 4.3. Similar patterns can be observed for both aldehydes. Little data exist on observed spatial variation of aldehydes at this spatial scale. Based on mobile measurements of formaldehyde for a 16 km^2 area in Wilmington Delaware, Isakov et al. (2007) suggested the importance of both local emissions sources and regional photochemical production. Here, the highest concentrations were found on the more densely populated western side of the sampling area near a busy road on the boundary (and where samplers were located

close to the roadway). For acetaldehyde, the high is located closer to the high volume intersection in the southwest corner than for formaldehyde. A local high is also seen near the southeast corner, adjacent to a high volume roadway intersection there. However, similar highs are not seen near the other roadways bounding the study area, including the highest volume roadway to the south (though the samplers were located further from that roadway). Local concentration lows are observed in a highly vegetated residential area in the southeast quadrant of the study area in addition to near the reference method monitor. These patterns indicate the potential importance of local mobile sources, particularly for acetaldehyde.

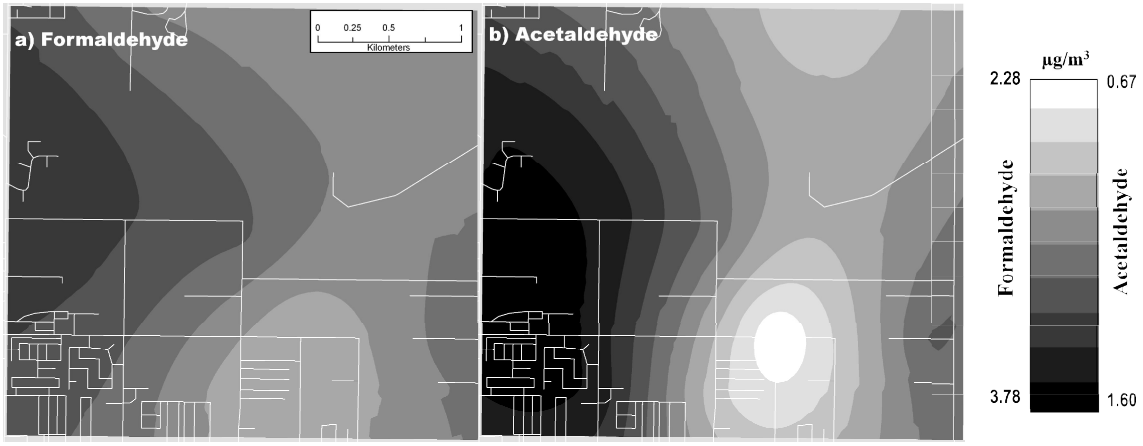


Figure 4.3 Spatial contours of **a)** formaldehyde and **b)** acetaldehyde concentrations in the sampling area. Contours are based on kriging interpolation performed in Arc GIS. The basic roadway network (U.S. Census Bureau, 2000) is provided as white lines. Figure 4.1 shows the location of the sampling sites. The white dashed box in Figure 4.1 corresponds to the area shown above.

Although there is no universally accepted method for quantifying spatial variation, the coefficient of variation (CV) has been used (Logue et al. 2010; Wilson et al. 2005; Zou et al. 2009). CVs calculated here indicate that the spatial variation is small in magnitude overall. However, acetaldehyde (CV of 23%) displayed slightly higher

variation than formaldehyde (CV of 13%). Isakov et al. (2007) reported similar values for formaldehyde (average daily CVs ranged from around 5 to 30%). They suggested the importance of photochemical production. Logue et al. (2010), in a recent study in Pittsburg PA, also saw less variation (CV less than 25%) for formaldehyde and slightly more variation (CV greater than 25%) for acetaldehyde. Higher variations for acetaldehyde versus formaldehyde could indicate larger impacts from local sources versus background photochemical production. This is also consistent with the comparative location of the high concentrations seen here.

A threshold variation of 20% has been used to indicate a homogenous spatial distribution (Blanchard et al. 1999; Wilson et al. 2005). CVs found here for each aldehyde are close to or less than this threshold. Interestingly, total aldehyde concentration (formaldehyde plus acetaldehyde) had a CV of 18%. This small degree variability suggests that one sampler may be somewhat representative of the study area. For example, using data from the site at the center of the sampling area (site ID 9) alone would result in formaldehyde and acetaldehyde concentrations within 15% and 4%, respectively, of the area mean. However, this threshold was based on expected health impacts for particulate matter (Blanchard et al. 1999), and hence may not be appropriate for the focus pollutants here. In addition, more research using different sampling areas within the county and multiple times of the year, need to be conducted to determine variability for other areas with similar spatial scales.

Sampler Evaluation

Table 4.2 provides data comparing concentrations from the reference method monitor with that from a collocated passive sampler (site ID 3). Note that the averaging

times are different (the reference monitor takes 24 hour samples every 6 days, while concentrations from this study are 7 day samples), so the comparison is indirect. Nonetheless, values are similar, with a percent difference (referenced to the fixed-site monitor weekly average value) of 31% for formaldehyde and -47% for acetaldehyde. If total aldehyde concentrations are compared, the percent difference is only -3%. sampling field studies (Wheeler et al., 2008; Clarisse et al., 2003).

Table 4.2 Sampler evaluation. Concentrations (g/m3) from passive and reference method fixed-site monitors during January 20-28, 2010 in Sydney, Florida

	Passive Sampler	**Reference Method Monitor[a]**			
	January 21-28	Jan 20	Jan 26[b]	Jan 26[b]	Weekly Avg[c]
Formaldehyde	2.76	2.38	1.73	1.91	2.10
Acetaldehyde	0.87	1.87	1.41	1.46	1.65

[a] Data provided by the Hillsborough County Environmental Protection Commission (Method TO-11A).
[b] Duplicate measurements were taken on January 26 for QA/QC purposes, as per EPA requirements.
[c] Average of values from the reference monitor from Jan 20 and Jan 26 (where that on the 26 is an average of the duplicate values).

Passive measurement values were comparatively high for formaldehyde and low for acetaldehyde compared with the reference monitor. Similar comparative values were observed in a study by Mason (2008). Additionally, comparatively low acetaldehyde values are consistent with recent results by Herrington et al. (2007), who found low acetaldehyde collection efficiencies on DNPH-coated solid sorbents for sampling intervals greater than 24 hr. Duplicate passive samplers at site 2 had good precision, with relative percent differences of 3 and 6% for formaldehyde and acetaldehyde, respectively. These precision values are similar to those from the January 26 regulatory fixed-site duplicate samples, shown in Table 4.2. They are also similar to precisions reported in other passive sampling field studies (Wheeler et al., 2008; Clarisse et al., 2003).

Conclusions

Here, a one-week pilot study using passive samplers was conducted to evaluate the measurement approach and to investigate spatial variations of acetaldehyde and formaldehyde on the neighborhood scale. Measured concentrations of both aldehydes in the study area were found to be in the range of values found in other urban areas in the US. Additionally, values collocated with a reference monitor were similar, though the collection efficiency by the samplers for acetaldehyde for this sampling period (one week) may be low. This work provides an ambient field application of the use of Radiello aldehyde passive samplers for high spatial resolution measurement. Use of these samplers for ambient studies has been limited in the U.S. Additionally, the method here demonstrates the use of the Allure AK HPLC column, which simplifies the laboratory analysis.

Spatial variations and concentration ratios found here suggest the potential influence of nearby mobile sources for both aldehydes. However, some differences in spatial patterns are seen between the two pollutants. Variations in concentration over the sampling area were small overall, potentially indicating relative homogeneity at this spatial scale (and temporal sampling interval). This suggests that one sampling site may be relatively representative for an area of similar size, sources, and meteorology. For example, the approach could be used to quantify concentrations for studies of intra-urban variability in aldehyde concentrations. Additionally, as few data are available on spatial variation of aldehydes at this scale, results here provide a case study. In addition, the data provide near baseline values regarding fuel ethanol content, as its use is increasing in the area.

However, in order for these results to be generalizable, further work is needed in different areas at similar scales. A sampling area close to the city center is suggested, to assess whether increased local mobile source emissions result in higher spatial variations. Sampling all census block groups within a tract could also lead to better understanding of the spatial scale needed for future sampling (block group versus tract) and lead to better placement of future regulatory fixed monitoring sites. High-resolution data on air toxics concentrations, such as that produced in this study, can help improve exposure assessment, inform city planners and policymakers, and ensure public health.

CHAPTER 5:

SUMMARY AND IMPLICATIONS

Results from epidemiologic studies are often used to inform policymakers of health risks associated with exposure. Due to lack of spatially resolved data, most of the exposure assessments in these studies assume concentrations are homogenous within an area and, consequently, may result in exposure misclassification. The magnitude, direction and significance of health outcomes can be altered due to this bias. Knowing how concentrations vary over small spatial scales would be useful improving epidemiology studies and risk assessments by reducing exposure misclassification bias. It is too costly and cumbersome to carry out current active sampling methods at the scale needed to produce high resolution data. Therefore, passive sampling has been used as a cost-effect alternative for performing high density sampling over a limited area. This type of sampling produces high resolution data that can then be used to evaluate the spatial variation. Information about how concentrations vary within a city can be useful for identifying "hot spots" of air pollution and sources that may increase personal exposures (residences close to roadways) and also for environmental equity assessments.

Here, a passive sampling and analysis method for aldehydes has been developed and evaluated through a pilot study. The pilot study had a secondary aim of determining spatial variations over small-scales. Samplers were deployed over a 10 km^2 sampling

area in Hillsborough County for one week in January 2010. Samplers were eluted, analyzed, and concentrations quantified. Mean aldehyde concentrations were 3.1 and 1.2 $\mu g/m^3$ for formaldehyde and acetaldehyde, respectively. Aldehyde concentrations were in the range of those found in others studies. Samplers were evaluated by collocating a field sampler with a reference sampler. Overall, samplers performed well and concentration differences were similar to those found in other field evaluations of same samplers. Spatial variation over this sampling area was small and one sampler may be relatively representative of the area.

These results imply that mobile sources are an important source of aldehydes but that the spatial variability at this spatial scale may be small. The conclusion that one sampler is representative of this spatial scale would need to be tested in areas where there are significant traffic emissions (downtown or urban areas) or closer to point sources. The sampling and analysis methods here allow for a cost-effective means of measuring aldehyde concentration at small spatial scales (i.e. within citites). The methods can be used to compare the concentrations of aldehydes within and between different census block groups and the spatial variation to be estimated for the entire county. Knowing the concentrations at a neighborhood level would be useful in environmental justice analyses to compare the air quality in areas of differing socioeconomic class or race/ethnicity. Hot spots of high air toxic concentrations could also be identified and risks assessed. In sum, knowing the spatial variability of air toxics improves health studies, can be used to evaluate the effectiveness of source reduction programs, inform urban and transportation planners and, ultimately, to protect and improve public health.

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APPENDICES

Appendix A : SOP 01 :

Standard Operating Procedure:

Passive Sampling for Aldehydes in Ambient Air Using Radiello Samplers

SOP 01

Date of issue: 12 May 2009

Number of Revisions: 0

by: Amanda Evans

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1. Purpose and Applicability

The purpose of this standard operating procedure (SOP) is to establish a uniform procedure for the passive diffusive sampling of various aldehydes in ambient air by their derivitization with 2,4-dinitrophenylhydrazine (DNPH) on silica gel filled cartridges provided by Radiello. Short-term exposures to aldehydes (specifically formaldehyde and acetaldehyde) can cause irritation of the eyes, skin and mucous membranes of the upper respiratory tract and are possible carcinogens. Active sampling is expensive and is generally sparse for hazardous air pollutants; there may be only one monitoring site for an entire state or county. In order to accurately quantify exposure to aldehydes and identify variations in exposure there needs to be multiple monitoring sites. Passive sampling is an inexpensive alternative to active sampling that allows measurements at multiple sites within an area. Enough data should be obtained for the area of interest to better estimate exposure levels and locate areas and populations that are exposed to different levels of the aldehydes of interest. SOP 01 is written specifically for the pilot study of the application of Radiello passive diffusive samplers for the identification of ambient aldehydes in a census block group area of Hillsborough County Florida. From this pilot study, problems with the sampling design, method, and/or the samplers should be identified and resolved before a larger scale application of this method is to be attempted.

2. Summary of Method

Ambient concentrations of two aldehydes (formaldehyde and acetaldehyde) will be determined by collecting the aldehyde-DNPH derivatives via passive samplers and separation via HPLC with UV detection– samplers and protocol can be used for the collection of additional aldehydes as well (benzaldehyde, acrolein, propanal, pentanal, isopentanal, and hexanal). The samplers contain pre-packed cartridges filled with DNPH coated Florisil®. The samplers will be contained in a protective shelter for the duration of the sampling interval, seven days. At the end of the seven-day sampling period, the cartridges will be removed from the diffusive body and placed in the glass tubes with polypropylenes caps and placed in cold storage (~4°C). The cartridges can remain in the glass tubes until analysis or can be immediately eluted. The compounds of interest (aldehyde-DNPH derivatives) will be eluted from the cartridges with 2 mL of acetonitrile (ACN). Analysis will be carried out by high performance liquid chromatography (HPLC) with an ultraviolet (UV/Vis) detector at 360 nm as described in SOP 02.

3. Interferences

3.1 Solvents, reagents, glassware and other sample processing may yield discrete artifacts and/or elevated baselines causing misinterpretation of the chromatographs. All of these materials must be demonstrated to be free from interference, under the conditions of analysis, by analyzing method blanks.

- Glassware and plasticware must be scrupulously cleaned. Clean all glassware and plasticware as soon as possible after use by rinsing with the last solvent used in it. This should be followed by detergent washing with hot water and rinsing with tap water, organic-free reagent water, and aldehyde-free acetonitrile. After cleaning, glassware and plasticware should be stored in a clean environment to prevent any accumulation of dust or other contaminants.

- High purity reagents and solvents should be used to minimize interference problems. Purification of solvents by distillation in all-glass systems may be necessary.

3.2 Other carbonyl compounds will react with the DNPH but should not interfere with analysis as long as appropriate chromatographic parameters are selected.

3.3 Ozone at high concentration has been shown to interfere negatively by reacting with both DNPH and its hydrazone derivatives in the cartridge.

- The extent of interference depends on the temporal variations of both the ozone and the aldehyde during sampling. The presence of ozone in the sample stream is readily inferred from the appearance of new compounds with retention times shorter than that of the hydrazone of formaldehyde.

- With the current cartridges (Radiello code 165) ozone will only be an interference at concentrations of greater than 100 ppbv (the only exception being acetaldehyde, which shows interferences at ozone concentrations of 50 ppbv) averaged over the sampling interval. If these concentrations are experienced corrected sampling rates will be used according to the Radiello Manual Section C1.

  à Ozone concentrations will be obtained from the closest ozone monitor to the sampling site maintained by the Florida Department of Environmental Protection (FL DEP), or Hillsborough County Environmental Protection Commission (EPC) and the ozone concentration will be averaged for the sampling period.

3.4 Contamination of samples can occur during transportation, setup, or storage by diffusion of volatile organic compounds (VOCs) through the sample bottle septum seal. Analysis of field blanks will determine if sampling, transportation, and/or storage procedures have caused contamination. Field samples will be corrected by subtracting the average mass of the field blanks.

3.5 Matrix interferences may be caused by contaminants acquired during the sampling process. The extents of matrix interferences will vary considerable from source to source, depending upon the compounds that have the same retention time, altering the separation conditions by using alternative HPLC columns or mobile phase conditions may resolve the problem.

4. Equipment and Materials

4.1 Sampling Equipment

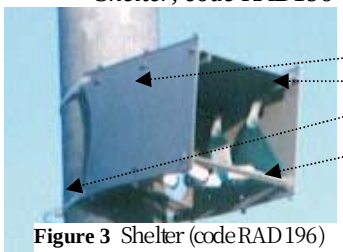
- Passive Diffusive Samplers for Aldehydes by Radiello® from Supelco, Inc
  - *Blue Diffusive Body, code RAD120-1*, 20 each (Fig. 1)
    - Made of microporous polyethylene 1.7mm thick with average porosity of 25±5 m
    - Diffusive path length is 18mm
    - Polypropylene containers for storage

Figure 1 Blue Diffusive Body (code RAD1201)

  - *Supporting plate, code RAD121, 20 each (Fig. 2)*
    - Made of polycarbonate with a clip and support for diffusive body
    - Transparent Adhesive pocket for label (to be attached)

Figure 1- Supporting plate (code RAD121)

  - *Shelter, code RAD196*, 20 each (Fig. 3)



Identical polypropylene panels (3)
Bars for suspending samplers (2)
Extra large "zip ties" (2)
Support bars (2)
**Number in parenthesis, is the quantity needed per sampler

Figure 3 Shelter (code RAD196)

- *Adsorbing cartridge for aldehydes, code RAD165* , 20 each (Fig. 4)
  - Stainless steel net cartridge filled with DNPH coated Florisil®
  - 60mm in length and 4.8mm in diameter
  - Glass tubes with polypropylene caps for storage
  - Set of 20 self-adhesive labels with printed barcode

Figure 4- Adsorbing cartridge code RAD165

4.2 **Reagents**

- *Acetonitrile* (CH_3CN) HPLC grade, Sigma-Aldrich

4.3 Personal protective equipment

- Laboratory coat
- Nitrile gloves
- Closed toed shoes
- goggles

5 Sample Collection, Preservation, and Handling

5.1 Maintenance of Equipment and Materials Prior to Deployment

§ *Adsorbing cartridge for aldehydes*

- Before exposure cartridges should be kept in a dark place at 4°C
  - If kept closed in their bags, they are stable for 6 months from the production date printed on outside of bag
- After exposure, the cartridges should be well capped and kept at 4°C
  - They are stable for 60 days
- After solvent desorption, discard the cartridge
  - Eluate should be stored well capped at 4°C and is stable for 42 days

5.2 Shelter Assembly

à Shelters will be assembled and placed in their field locations at least one day prior to the estimated day that field sampling will begin

à All components are snap-on assembled (no tools required)

1. Put on provided nitrile gloves

2. Use one polypropylene panel as the roof and attach both support bars to the underside, push up and slide forward
   - These will be used to suspend the samplers by the clips on the top of the supporting plate

3. Fix two walls (the other two polypropylene panels) to the sides of the roof panel, align the three tabs of the roof panel with the three slots on the side panels and slide forward

4. Insert the two support panes in the bottom front and back slots of the side panels and turn 90°
   - There may be some resistance felt when attempting to rotate the support bars, this is normal, continue rotating until a clicking sound is heard
   - The shelter should now be rigid

5. Insert plastic strips into the rear vertical slots of the side panels

- These will be used to attach shelters at appropriate heights (i.e. to trees or telephone poles) for the duration of the sampling interval

5.3 Supporting Plate Assembly

5.3.1 Supporting plates will be assembled at least one day prior to the estimated sate that field sampling will begin

1. Insert the clip strip in the slot, with the peg facing upwards
2. Ply the strip and insert the peg into the hole
3. Peel off the backing of transparent pocket to reveal the adhesive
4. Place pocket on the plate in a central position, preferable on the front but may also be located on the back
   - Be careful that the label insertion slot is on a side (not the top or bottom) to prevent rain damage or accidently loss

5.4 Sampler Assembly/Preparation

- Diffusive body and cartridge will be assembled the morning that field sampling is to begin in the laboratory so that all cartridges are exposed to the same environment and that environment will allow minimal exposure of the cartridges to VOC's. This is done to minimize both the possible contamination of samplers and the uncertainty in the measurements.

  - *Possible sources of VOCs include:* hairspray, perfume, deodorant, freshly painted surfaces, idling cars or machines, cigarette, pipe or cigar smoke, glue, cooking odors or vapors, etc.

  - Exposing the adsorbing cartridge to any exposures of these kinds should be minimized if not avoided. This also includes potential exposures from those handling the samplers à contact with any of these substances by all personnel that will be involved in preparation deployment, retrieval and analysis should be avoided

5.4.1.1 Put on provided nitrile gloves

5.4.1.2 Using a ballpoint pen give each provided label a unique sample ID and location ID, the sample ID's and corresponding location ID's will be determined before sample deployment.

- Only <u>ballpoint pens</u> should be used for all labeling because other marking instruments contain solvents that are sampled by Radiello samplers and if used could lead to increased uncertainty in the measurements

5.4.1.3 Place labels inside the transparent pocket located on the supporting plate (either front or back) without peeling them off
  - After the sampling interval the labels will be peeled off their backing and placed on the glass tube of their respective cartridges

5.4.1.4 Make note in the field log of the sample ID, location name and ID, and the cartridge lot ID that was recorded on the labels

5.4.1.5 In addition to the provided label, 2 extra sets of labels should be made, again using a ballpoint pen, and noting the sampler ID and location ID on the label
- One set of labels will be placed on the outside of the polypropylene containers of the diffusive samplers and the other on the plastic bag that contains the glass tubes for the adsorbing cartridges

5.4.1.6 Assemble samplers one at time to decrease time they are exposed

5.4.1.7 Open plastic bag containing adsorbent cartridge, remove cartridge from tube and invert tube to insert into diffusive body being careful not to accidently drop or touch the cartridge

5.4.1.7.1.1 DO NOT touch the cartridge with your fingers

5.4.1.8 Fully insert cartridge into diffusive body and set at the base of diffusive body, the lower part of the diffusive body holds a seat for the central positioning of the cartridge

5.4.1.8.1.1 To get the cartridge in a central position it may be necessary to gently tap on the diffusive body

5.4.1.8.1.2 A correctly placed cartridge should not stick out of the diffusive body

5.4.1.9 Reclose glass tube and store inside original plastic bag for future use

5.4.1.10 Transfer the diffusive body to the appropriate airtight polypropylene container for storage until deployment, sample and location ID on sampler container should match that on the glass tube and the plastic bag

Note: At all times during handling of the adsorbent cartridge, contact with the cartridge should be minimized. Solvents should NOT be used to clean any part of the sampler assembly or housing shelter, to minimize contamination. Tubes in which adsorbent cartridges were shipped are to be retained for storage of cartridges prior to analysis.

5.5 **Field Deployment**

5.5.1 Field deployment requires first that appropriate locations be identified and then housing shelters securely placed at these locations before the start of the sampling interval. Samplers will be transported to the locations inside their storage containers and attached securely to supporting plates and then placed inside mounted housing shelters and left at these locations for the sampling interval of seven days. After seven days, the samplers will be collected in the order they were set-up and transported back to the laboratory and stored under appropriate conditions until analysis.

1. The housing shelters need to be mounted on a suitable surface (tree, telephone or lighting pole etc.) at a height of 2.5 to 3 meters (8-10 feet) using the supplied plastic strips ("zip ties")
   - This will be done at least one day prior to the start of the sampling interval so that any problems with locations or mounting of shelters can be dealt with in advance.

2. Mount the shelter by inserting the two plastic strips (zip ties) into the back of the shelter assembly and tighten around pole (or other appropriate structure)
   - Do not tighten so much that the housing shelter becomes deformed under pressure
   - If the pole has a diameter greater than 20 cm, the shelter will lean on the curved edges at rear of the side walls
     - If the diameter is much greater than 20 cm, multiple zip ties can be attached to help support the shelter
   - If the pole has a diameter less than 20 cm, the shelter will lean against the curved edge of the roof panel and rear spacer
     - Diameters much less than 20 cm are not recommended due to possible slippage
   - In the event that a housing shelter is missing upon arrival for sampler placement, replace with a spare shelter
     - An alternate location may also need to be considered if tampering of sampler is suspected

3. Upon arrival at the field location, park the vehicle at a reasonable distance and downwind, if possible, from the sampling site

4. Wearing nitrile gloves, remove the diffusive body from the container that has the corresponding location ID for the current location. Do this away from, and upwind of, the automobile.

- Reclose diffusive body container and store for future use

5. Keeping the diffusive body in the vertical position, being careful not to dislodge the cartridge inside, screw the diffusive body into the appropriately labeled supporting plate (sample and location IDs of polypropylene container and label of supporting plate should match)
   - Using a ballpoint pen, mark the deployment time and date, location name and the sample and location ID that is on the label inside the supporting plate in the field log
     - Any changes to the field log should be denoted by a single line crossing out the incorrect information, initialing and then filling in the correct information

6. Using the clip provided on the supporting plate, attach the sampler assembly to the bars located near the roof of the shelter housing and as near to the pole as possible to prevent weather damage to samplers
   - The clip should attach to one of the two bars located at the top (roof) of the inside of the shelter housing
   - Some locations will have multiple samplers, these should be attached to the opposite support bar facing the first sampler

7. One field blank (assembled sampler kept inside polypropylene container) per cartridge lot should be transported to and from the sampling sites and treated just like the other samplers in every respect except that exposure to outside air should be minimal

Note: As noted previously, avoid contact with any VOCs that may be present in the non-sampling atmosphere; including ones present inside and directly around the vehicle and on those performing the sampler set-up and field deployment

5.6 Sample Retrieval

à Samplers should remain in the field for the entire sampling interval of seven days. At the end of seven days, retrieve samplers at approximately the same time and in the same order as which they were deployed. Make note in the field log of the date and time of retrieval, name of location, and the sample and location ID located on the label of the supporting plate. Also, make a note in the field log if the samplers that are missing, appear to have been tampered with and/or any other notable conditions (i.e. possible weather damage)

1. Wearing nitirle gloves, remove the sampler assemblies from the outdoor housing by unclipping the support plate from the housing support bar

2. Remove the diffusive body from the support plate by holding the assembly in the vertical position with the support plate up and unscrewing the diffusive body from the support plate

3. Place the diffusive body into the appropriately labeled polypropylene container for transport back to the lab

4. Note in the field log the date and time, location name, and sample and location ID found on the label of the supporting plate
   - Also, note the appearance of the sampler itself; if it was missing or appeared to have been damaged or tampered with

5. Once all samplers have been collected from sample sites and their retrieval noted in the field log, transport samplers back to lab for storage until analysis

6. Once back at the lab, line up the labeled plastic bags containing the glass tubes, the supporting plates, and the polypropylene containers with the samplers inside so that the sample and location IDs of all sets match

- Be careful that while attaching labels and removing cartridges the sample and location IDs always match from where they are coming from and where they are going.

7. Remove glass tubes from their labeled plastic bags and place on top of the appropriately labeled plastic bag

8. Remove the label from the inside the protective sleeve of supporting plate, peel off backing to reveal adhesive and place label on the appropriate glass container

9. Remove cartridge from diffusive body and store inside the appropriately labeled glass tube
à Cartridges should be removed from diffusive bodies one at a time and placed into appropriately labeled glass tubes to keep exposures and associated uncertainties to a minimum

10. Holding the glass tube so that it covers the opening of the diffusive body, invert sampler so that cartridge will transfer into glass tube
- Diffusive body may need to be gently tapped to loosen cartridge from base
- Be careful not to drop the cartridge during this process and try not to handle with fingers

11. Put original polypropylene cap on glass tube.

12. Store labeled glass tubes in the dark at 4°C until analysis à cartridges are stable for 60 days

6 Quality Control

6.1 Field Blanks

6.1.1.1 Method Blank - a method blank must be prepared for each set of analytical operations to evaluate contamination and artifacts that can be derived from glassware, reagents and sample handling in the laboratory
- One method blank per cartridge lot should be analyzed.
  - Cartridges should have blank value of less than 0.15 g/cartridge for formaldehyde
- Radiello cartridges have a certified blank value of formaldehyde of 0.1 g, as long as used by expiration date printed on plastic bag
  - If used after this date, this concentration will increase over time

6.1.1.2 Field Blank - the number of filed blanks should be equivalent to 10% of the field samples. For the pilot study only 15 field samples will be used (excluding duplicates) and therefore only one field blank will be necessary. The field blank will be assembled and analyzed identical to other samplers. Once leaving the lab to disseminate the field samples the field blank will be removed from protective tube and left exposed in the transport container to and from the lab and carried to and from each sampling site. This same procedure will be repeated using the same field blank when the field samples are collected. This should allow for calculation of maximum uncertainty of the measurements.

6.2 General QA/QC Requirements

1. Sampling
- Radiello samplers
  - § Cartridges have a certified blank value of formaldehyde of 0.1 g, as long as used by expiration date printed on plastic bag
- If used after this date, this concentration will increase over time
- 10 percent of field samples are collocated to help calculate method precision and evaluate biases
- Field blank cartridges are included with each field sample collection program to evaluate background levels and interferences

2. Reagents
- Only HPLC-grade acetonitrile (ACN) is to be used for elution

References

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Appendix B : SOP 02

Standard Operating Procedure:

High Performance Liquid Chromatography Analysis and Quantitation of Ambient Aldehyde-DNPH Samples Collected via SOP01

SOP 02:
Date of issue: 10 January 2010
Number of Revisions: 0

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1. Purpose and Applicability

The purpose of this standard operating procedure (SOP) is to establish a uniform procedure for the analysis of samples collected via SOP 01 to determine ambient concentrations of various aldehydes in the ambient air of Hillsborough County, FL. Analysis of aldehyde-DNPH derivatives will be carried out by high performance liquid chromatography (HPLC) with ultraviolet-visible (UV/Vis) detection. The method described here is based on the Environmental Protection Agency (EPA) Compendium Method TO-11A, California Air Resources Board (CARB) Method 430 and CARB Method 1004 with modifications made for the specific equipment and materials that will be used.

2. Summary of Method

Ambient air samples are collected via SOP 01. After field sampling, sample cartridges and field blank cartridges are either stored immediately at 4°C until analysis or can be washed by gravity feed elution with acetonitrile (ACN) and the eluate stored at 4°C until analysis. Analysis of the aldehyde-DNPH derivatives is carried out by reverse phase HPLC/UV-vis at 360nm. The mass of the aldehydes in the samples is determined via quantified comparison of the aldehyde-DNHP sample's retention times and peak areas with those of standard solutions.

3. Definitions

DNPH- 2,4-dinitrophenylhydrazine

HPLC – high performance liquid chromatography

Laboratory Blanks -provide information about controlling and quantifying contamination due to analysis

System Blank-measurement of instrument background, or baseline, in the absence of a sample; a preliminary check for system contamination

Solvent Blank- consists only of the solvent used to dilute the sample; used to identify or correct for signals produced by the solvent or by impurities in the solvent; can also be used as a calibration blank which is used to set the instrument response to zero (an analyte concentration of zero)

Method Blank (also referred to as cartridge blank)-a sample cartridge that has never been to the field, but is carried through the same analytical procedure in the same manner as an actual sample would be; should include all steps involved in sample preparation, such as cleanup, elution, filtration, extraction, and concentration. Provides a measure of contamination that may be introduced during sample preparation and analysis; may also be called a reagent blank

Field Blank - Provides information about contaminants that may be introduced during sample collection, storage, and transport. Cartridge is taken out of container and placed inside diffusive body upon arrival at each sample site, removed from diffusive body and returned to container once field sample is in place. This is done for both the deployment and retrieval using the same cartridge. The concentration from the field blank will be subtracted from field sample concentrations to correct for possible contamination from both sampling and analysis.

Limit of Quantitation (LOQ) – the lowest mass that can be measured and reported with acceptable precision; the mass that can be reported with 95% confidence that the value is above zero (also called the method quantitation limit, MQL)

Limit of Detection (LOD) - the mass of analyte which gives a mean signal three sample standard deviations (3s) above the mean blank signal (also called the method detection limit, MDL)

Certification Blank- the mean value of the cartridge blank plus three standard deviations; should be less than 0.15 µg/cartridge for formaldehyde

4. Interferences and Limitations

4.1 This method is subject to interference by compounds in the acetonitrile extract (eluate) having the same retention time as one of the target compounds and detectable by UV adsorption at 360nm.

4.2 If samples are not analyzed the same day as received, they must be refrigerates at temperatures of 4° C. Exposed cartridges are stable for 60 days if they refrigerated and capped immediately.

4.3 After solvent desorption and extraction of the cartridge from the tube, the eluate is stable for 42 days well capped and refrigerated at 4° C.

5. Equipment and Materials

5.1 Equipment

- Sterile, volumetric flasks (25mL) (Pyrex®)
- Calibrated, sterilized micropipettes (5mL-25mL) (Finnipipette®)
- Gas tight syringes, 25mL (Hamilton)
- Sterile, reaction tubes– to be used for sample extraction and storage (Pyrex)

5.2 HPLC analytical system consists of the following:

- Dual high-pressure pumps, ProStar Model #210 (Varian Inc.)
- Manual injection valve, with 10mL stainless steel sample loop, Rheodyne Model #7725i (Varian Inc.)
- Allure AK column, 200mm in length, 4.6mm internal diameter, 5µm particle size, 60Å pore size (Restek U.S., Bellefonte, PA)
- An ultraviolet/visible (UV/Vis) detector, ProStar Model #320 (Varian Inc.)
- Teflon tubing, peek tubing, various fitting and ferrules to connect tubing and column (Restek U.S., Bellefonte, PA)
- Back pressure regulator, attached to detector outlet line (Restek)
- Computer (Dell) with printer capability with Star Chromatography Workstation version V.6.3 (Varian Inc.) downloaded for HPLC system control (control mobile phase flow rate and gradient and setting the detector wavelength), peak integration and data analysis.

6. Reagents and Chemicals

6.1 Reagents

- Aldehyde-Ketone DNPH calibration standards, analytical grade, (Restek, Inc.)

6.2 Chemicals

- Acetonitrile, HPLC grade, (Sigma-Aldrich)
- Water, HPLC grade, (Fisher Scientific)

7. Sample Analysis

7.1 Sample Preparation

- Samples (and blanks) are retrieved from the field and stored in the laboratory until analysis according to SOP 01.
- The time between sampling and extraction should not exceed 2 weeks. Since background levels in the cartridges may change due to adsorption during storage, always compare field samples to their associated field blanks, which are stored under the same conditions.

7.2 Sample Extraction

- Label clean reaction tubes
- Remove the labeled glass tube containing the sample cartridge from its corresponding plastic bag.
- Fill a new plastic syringe with 2mL of HPLC grade acetonitrile. Use a new syringe on each sample (and blank) to avoid cross-contamination.
- Remove cap from labeled glass tube containing the sample cartridge and slowly expel acetonitrile from syringe into the glass tube and recap. Save syringe for future use during filtration of eluate.
- Leave acetonitrile in capped glass tube with cartridge for at least 30 minutes, stirring occasionally.
- After 30 minutes, remove cartridge from labeled glass tube and discard. The remaining solution contains the aldehyde-DNPH derivatives collected from the ambient air and will hereafter be referred to as the eluate.
- Filter the eluate, using the same syringe that was used earlier and the provided filter. Transfer contents of glass tube into syringe, making note in the field log of the volume in the syringe. Rinse glass tube with acetonitrile and allow it to dry. Attach filter to end of syringe and slowly force eluate through filter back into labeled glass tube, being careful not to dislodge the filter from the end of the syringe.
- Repeat process for all samples.

- Immediately store labeled glass tube with eluate at 4°C until analysis.
- Eluate is stable for 42 days well capped and refrigerated at 4°C.

7.3 HPLC Analysis

- The HPLC system (pumps and detector) should already be assembled according to manufacturer's specifications and calibrated as described in section 7.4.
- The HPLC system should already be primed with the desired mobile phase (water and acetonitrile). Mobile phase levels should be checked each analysis day to ensure that the solvent levels are high enough to complete analyses for that day, when either of the solvent levels fall below 50% check to see if more of solvent is in the lab or neighboring labs and can be used or if it will need to be ordered.
- The HPLC system is controlled by Varian Star Chromatography Workstation software that is downloaded on the computer next the HPLC instrument.
- Before each analysis, the detector baseline (system blank) is checked to ensure stable baseline conditions.

The operating parameters are as follows:
Column: Reverse phase Allure AK HPLC column (200 x 4.6 mm)
Detector: UV/VIS at 360 nm
Sample Volume: 10 mL
Flow: 1.0 mL/min
Mobile Phase: A) Water B) Acetonitrile

Time (min)	% Acetonitrile
0-8	60
8-10	70
10-13	100
13-15	100
15	50

7.3.5 A typical batch to be analyzed will consist of:

- Working standard (QC check and establishing daily RF values), field and method blanks, field samples (include duplicate samples) and replicate analyses of the same samples.
- If more than 20 field samples are to be processed on any day, the method should be checked after 15 field samples have been analyzed (not including blanks, duplicates and replicate analyses) à analyze a working standard sample and double check SD and RF à continue with analyses and repeat after 15 more field samples have been analyzed

7.3.6 Procedure to follow on any day that HPLC analysis is to be performed is as follows:

1. Turn on pumps and detector manually.

o The detector (UV lamp) needs to warm up for at least 45 minutes before any analysis are performed

2. Open Star Workstation on the computer by double clicking the system control icon that should be located in the upper left hand corner on the desktop. Alternately, it can be found by going to start à programs à double click Star Workstation.

3. Once system control is open, maximize the box in the bottom left labeled ProStar/Dynamx 2.4 à click on the manual control box à set the total flow and ramp time equal to zero à let UV lamp warm-up for about 30 min, after this time the baseline should be stabilized and the manual control box can be closed by clicking "exit manual control" in the bottom right hang corner

4. Once the baseline has become stabilized activate the method labeled "C1-C2 mth"

à Click on the long box on the system control toolbar that says "activate method options when the mouse is over it à method, "C1-C2 mth" should be selected, if not then select this method, and then activate the

method as above à monitor baseline again until stabilized (fairly even, not fluctuating by more than 10 mV)

5. If baseline does not become stabilized in one hour, research source of interference and remedy before continuing
a. Bubble in flow cell
b. Dirty flow cell
c. Electrical interference
d. Lamp has become dislodged
6. Open the sample list labeled "Aldehydes.smp"

à click the first open folder that says "open automation file" when mouse is over it and then click "open sampleList" and open folder labeled "mandi" on the system control toolbar and inside the oand type in the sample name, select the type of sample that is being run from the drop-down list (baseline, analysis, calibration, etc), set number of injections to one under and click "Begin" at the bottom left of the sample list box
7. The System control window should give you a message saying "wait for inject" if not reactivate the method in the same manner as before
8. Once you see the wait for inject message, check to see that the manual injection handle is in the "load" position (if not move to load position and continue) and then insert the syringe into the needle port and ensure that syringe is completely inserted (should feel slight resistance when almost completely inserted, continue inserting until the needle can be pushed in no further) slowly inject your sample, leave syringe in its slot and then quickly pull handle down into the inject position and leave syringe in slot for at least one complete minute (this is done to ensure that none of the sample is pulled out with syringe before it has been rinsed by mobile phase and carried to the column).
9. Monitor run for excess background noise or any other problems but allow run to complete regardless of how the chromatograph appears to look (many of the integration parameters can be alters later and the results recalculated)
10. Once the current run has completed, open up the file containing the results; which should be found in the box on the right of the screen.
11. Check that the run was saved correctly and that the results look acceptable (peaks of interest were detected) before running next sample.

7.4 HPLC Calibration

7.4.1 The working standard solution (0.6 mg/mL) is prepared as follows:

- Using a sterile, calibrated micropipette, transfer 0.4 mL of aldehyde/ketone DNPH stock solution (15 mg/mL) to a sterile 25 mL volumetric flask (or other acceptable sterile glass container).
- Dilute to 10 mL mark with 9.6 mL of acetonitrile.
- Immediately cover tightly with Parafilm® and labeled with the date prepared, concentration of solution, and initials of who prepared solution and store at 4°C until use.

7.4.2 Calibration standards are prepared from the aldehyde/ketone DNPH stock solution (15 mg/mL) in a range that will span the expected ambient concentration of acetaldehyde. The expected ambient concentration will be determined from the literature research, and for the pilot study was determined to be around 1.7 mg/m^3, as reported from the EPA's National Air Toxic Assessment modeled data for ambient acetaldehyde in Hillsborough County, FL from 1999. This corresponds to an expected mass of about 1.5 mg if the sampling is carried out for 7 days. The linear range was chosen to be 0.06 – 15 mg/mL (0.051 – 12.71 mg). This range will safely encompass concentrations well below or exceeding the estimated expected concentration.

7.4.3 Calibration standards used for linear range (0.06 – 15 mg/mL) and LOD determination (0.02 – 0.10 mg/mL) are prepared in as follows:

à All of the following steps assume the use of a sterile, calibrated micropipette, and a sterile 25mL volumetric flask (or other sterile, glass container that can be safely stored and sealed)
à All standards will be made from dilution of the most concentrate standard (except for the control standard)
à Label all tubes with concentration, date of preparation, and initials prior to preparing standards, this is to ensure that no samples are incorrectly labeled once prepared.

1. To determine what volume of the stock solution is needed for the preparation of the most concentrated standard (6.0mg/mL); multiply the desired end concentration by the desired end volume and then divide by the concentration of the standard starting solution

$$V_{starting\ standard} = \frac{(V_{end\ solution})\ (C_{end\ solution})}{C_{starting\ standard}}$$

2. Subtract the volume of the starting standard from the volume of the end solution to determine the volume of acetonitrile (ACN) to add.

v For example if one wanted to make a standard solution with end concentration of 6.0mg/mL and end volume of 2mL from a starting standard of 100mg/mL, one would need to add 0.12mL (120mL) of standard solution to 1.88mL of ACN.

3. Immediately cover all standards tightly with Parafilm® and label with date made, concentration of solution, and initials of who prepared solution and store in the dark at 4°C.
4. Calibration standards (to determine linear range of analytical method) will be made in the following concentrations:
- 0.06mg/mL
- 0.10mg/mL
- 0.30mg/mL
- 0.60mg/mL
- 1.00mg/mL
- 3.00mg/mL
- 6.00mg/mL

5. LOD standards (to determine the detection limit of the analytical method; below which values will be reported as zero) will be made in the following concentrations:
- 0.02mg/mL
- 0.03mg/mL
- 0.06mg/mL
- 0.10mg/mL

6. Any standards of the same concentration that will be used for both linear range and LOD need only be made once.

7.4.4 Each of the calibration standards is analyzed five times.
7.4.5 Average area response of each concentration level is tabulated against the mass concentration injected. The results are used to prepare a calibration curve. The slope of the calibration curve gives the response factor, RF. Linear response is indicated where a correlation coefficient, R, of at least 0.999 for linear least-squares fit of the data (mass concentration versus area response) is obtained. The intercept of the calibration curve should pass through the origin. If it does not, check the reagents and standards solutions preparation procedure for possible contamination. If the calibration curve does not pass through the origin, the equation of the calibration curve should include the intercept.
7.4.5 Each new calibration curve should be verified by analyzing a standard prepared from material obtained from a second source (or analysis of a prepared stock solution from a second source). This standard should show a recovery of ± 15%. If not, corrective action is required to eliminate the discrepancy between the two sources of the standard material.

7.4.6 Once linear response has been documented, a concentration standard near the anticipated level of acetaldehyde, but at least ten times the LOD, should be chosen for daily calibration. For the current pilot study, the daily calibration standard will be referred to as the control standard and is 0.60 mg/mL.

- The daily response for each aldehyde should be ± 10% of the calibration value. If greater variability is observed, prepare a fresh calibration check standard.
- If the variability using a freshly prepared calibration check standard is greater than ± 15%, a new calibration curve must be developed from fresh standards. A plot of the daily values on a Quality Control Chart (day versus concentration) should be kept to compare short- and long-term variability.

7.4.7 The response for each component in the daily calibration standard is used to calculate a response factor (RF) for each aldehyde according to the following equation:

$$RF = \frac{\text{peak area counts x calibration curve intercept}}{\text{concentration of aldehyde in the calibration standard in units of } \mu g/mL}$$

7.4.8 The aldehyde concentrations (mg/mL) are determined with the calibration curves for each component in the analyzed sample. Give an example calculation at end of document

8. Data Analysis and Calculations

Determination of the concentration of aldehydes in air requires three steps: (1) determination of the average blank and the standard deviation of the blank (2) determination of the collected aldehyde mass from the cartridge (3) calculation of the aldehyde concentration in air.

8.1 Blank Determination

Since the blank level for any arbitrary cartridge is unknown, an average value for the blank is used in the calculation. The average blank value is determined for each lot of cartridges. For a given lot size, N, a minimum of √ cartridge blanks (rounded to the next whole number) should be analyzed. For the current pilot study there are 20 cartridges all from the same lot (N=20; $\sqrt{20} = 4.47$). Four cartridges will be used for blank determination. The cartridges are pre-coated with DNPH and have a reported certified blank value of less than 0.15 µg for all aldehydes; therefore only one cartridge will be used to confirm the certified blank value of aldehydes.

The mass of each aldehyde on each blank cartridge (M_{BL}) is determined by multiplying the observed peak area for blank cartridge solution by the acetonitrile extract volume (2mL) and dividing by the RF for each aldehyde, and is given as:

$$M_{BL\text{-aldehyde}} = \frac{\text{area counts for each aldehyde in blank sample extract x 2mL}}{\text{RF for each aldehyde}}$$

Once all blank cartridges have been measured, the average blank value ($_{BL}$) for each aldehyde is determined by multiplying the inverse of the number of blank cartridges (1/4) by the sum of the mass of each aldehyde for all blank cartridges, and is given as:

$$M_{BL\text{-aldehyde}} = \frac{1}{4} * \Sigma M_{BL\text{-aldehyde}}$$

8.2 Aldehyde Analyte Mass

The calculation equation for the mass of the collected aldehydes on an individual cartridge is the same as that for the cartridge blanks. The gross measured aldehyde mass (M_{SA}) is determined by multiplying the peak area counts of each aldehyde for each cartridge by the extract volume (2mL) and then dividing by the RF for each aldehyde, and is given as:

$$M_{SA\text{-aldehyde}} = \frac{\text{peak area counts for each aldehyde for each cartridge} * 2mL}{\text{RF for each aldehyde}}$$

The net mass for an individual cartridge for each aldehyde is determined by subtracting the average blank value ($_{BL}$) from the gross mass (M_{SA}) obtained for each sample, and is given as:

$$M_{aldehyde} = M_{SA\text{-}aldehyde} - M_{BL\text{-}aldehyde}$$

8.3 Aldehyde Compound Concentration

The sample air concentration for each aldehyde cannot be determined directly from the mass measurement and requires conversion to units of volume. The following equation will convert the net mass of each aldehyde into a concentration in air in µg/mL ($C_{aldehyde}$) based on the sampling rate in mL/min (Q) at average temperature and ozone concentrations encountered during sampling period, provided by Radiello, and the total sampling time in minutes (t), and is given as follows:

$$C_{aldehyde} = \frac{M_{aldehyde}}{Q \times t} * 10^6$$

Where:

$M_{aldehyde}$ = mass of aldehyde = mg

- Q = sampling rate = mL/min
- Acetaldehyde = 84 mL/min
- Formaldehyde = 99 mL/min
- t = min
- 7 day sampling interval = 10080 min

9. Quality Control

8.1 Standard Operating Procedures (SOPs)

SOPs have been written and should be followed for the passive sampling of aldehydes in ambient air (SOP 01) and for the analysis of aldehyde collected above procedure by HPLC-UV/VIS and analysis of the associated data to generate average masses and ambient concentrations of appropriate aldehydes (SOP 02).

The SOPs provide specific stepwise instructions and should be read and understood by all personnel before sample collection and analysis occurs. SOPs will be readily available for all personnel throughout all procedures.

8.2 HPLC System Performance

HPLC system efficiency is calculated according the following equation, where N is the column efficiency in theoretical plates:

$$N = 5.54 \left(\frac{\text{retention time of analyte in seconds}}{\text{width of the component peak at half height in seconds}} \right)^2$$

A column efficiency of >5,000 theoretical plates should be utilized.

8.2.2 Precision of response for replicate HPLC injections should be ±10% or less, day to day, for analyte calibration standards at 150 ng/mL or greater levels (as the aldehyde-DNPH compound). At 75 ng/mL levels and below, precision of replicate analyses could vary up to 25%. Precision of retention times should be ±7% for same day analyses and ±10% for day to day analyses.

8.3 Blank Runs

8.3.1 Reagent Blanks-the solvents used are of the highest HPLC grade and are tested for impurities, when a new lot number is used. If this lot number is found to be acceptable, (no aldehydes present at concentrations at or above the LOD), daily blank analysis is not performed

8.3.2 Field Blanks-one cartridge is analyzed as a field blank for each emission test. If the file blank shows a peak greater than the LOD in the region of interest, the source of the contamination must be investigated and removed.

8.3.3 Cartridge Blanks-at least one cartridge per batch is analyzed as a batch blank. If the cartridge blank shows a peak great than the LOD in the region of interest, the source of the contamination must be investigated and removed.

8.3.4 At least one field blank should be used for each day of field sampling and analyzed with each group of samples. The number of samples within a group and/or time frame should be recorded so that a specific minimum number of blanks is obtained for a given cartridge lot used for filed samples. The field blank is treated identically to the samples except that it is not exposed to the sampling environment. It is also desirable to analyze trip and laboratory blank cartridges as well, to distinguish between possible field and lab contamination.

8.4 Calibration Run

The calibration standard, the working standard (0.60 mg/mL), is analyzed each analysis day to generate the response factors used to quantify the sample concentrations.

8.5 Control Standard Run

The quality control (QC) standard is analyzed at least once each analysis day. Measurements of all target compounds in the control standard, except acrolein, must fall within the control limits to ensure the validity of the sample analyses that day. To meet this requirement, it may be necessary, to rerun the calibration and control standards, and inspect and repair the HPLC

8.6 Control Charts

A quality control chart is maintained for each component of the control standard. The control charts, used on a daily basis, establish that the method is "in-control." The following described how to construct a typical control chart:

1. Obtain at least 20 daily control standard results

2. Calculate the control standard mean concentration, and standard deviation (s) for the target analyte

3. Create a control chart for the target analyte by placing the concentration on the Y-axis and the date on the X-axis. Establish an upper warning limit (UWL) and a lower warning limit (LWL) at two standard deviations (2s) above and below the average concentration. Establish an upper control limit (UCL) and a lower control limit (LCL) at three standard deviation above and below the average concentration (3s).

- If the method is in control then 95% of responses should fall between the average of the analyte response and the warning limit; and 99.7% of responses should fall within the average and the control limit.

4. Due to the low variability of the aldehyde control standard measurements, a control standard measurement is considered to be out-of-control when the analyzed value exceeds either the 3s limit, or the range of ±10% of the mean control measurement, whichever is greater, or if two successive control standard measurements of the same analyte exceed the 2s limit.

5. If 20 control standard measurements are not yet available to create a control chart, measurements must be within 10% of the assay concentration.

The measured concentration of all target analytes contained in the control standard chart must be within the control limits (in-control) for the sample results to be considered acceptable. No control requirements have been established for acrolein, since it has been shown to degrade over time.

8.7 Replicate Analysis

A random selection of 10% of samples will be reanalyzed each day analyses day of sample analyses. The relative percent difference (RPD) is calculated for each duplicate run as follows:

$$RPD\ (\%) = \frac{|\text{Difference between duplicate and original measurements}|}{\text{Average of duplicate and original measurements}} * 100$$

For each compound, the allowable RPD depends on the average concentration level for the duplicate runs, as shown in the following table:

Average Measurement for Duplicate Runs		Allowable RPD (%)
1 to 10	times the LOD	100
10 to 20	times the LOD	30
20 to 50	times the LOD	20
Greater than 50	times the LOD	15

If the results of the duplicate analyses do not meet these criteria for all target compounds, the sample may be reanalyzed. If reanalysis is not feasible or if the criteria are still not met on reanalysis, all sample results for that analysis day are invalid.

8.8 Linearity

A multipoint calibration to confirm instrument linearity is performed for all target analytes for new instruments, after making instrument modifications that can affect linearity, and at least once every year. The multipoint calibration consists of at least five concentration or mass loading levels (using smaller or larger volume sample sizes of existing standards is acceptable), each above the LOD, distributed over the range of expected sample concentration. Each concentration level is measured at least twice. A linear regression analysis is performed using concentration and average area counts to determine regression correlation coefficients, R. The r must be greater than 0.995 to be considered linear for one point calibrations.

8.9 Limit of Detection

The limit of detection (LOD) for the target analytes must be determined for new instruments, after making instrument modifications which can affect the LOD and at least once per year. To make the calculations, it is necessary to perform a multipoint calibration consisting of at least four "low" concentrations levels, each above the expected LOD. The two lowest concentrations are measured a minimum of five times while the other concentrations are measured a minimum of four times. The LOD determination can be performed concurrently with the linearity determination if the requirements listed above are satisfied.

8.9.1 A linear regression analysis is performed on this data set to identify slopes, m, for each of the target compounds.

8.9.2 For each of the target compounds, the standard deviation, s_a, in units of area counts is determined for the lowest concentration standard. The standard deviation is converted to concentration units (µg/mL), s, using the slope of the linear regression, as follows:

$$s = s_a / m$$

where m is the slope of the linear regression, s is the standard deviation (in µg/mL) of the lowest concentration standard and s_a is the standard deviation (in area counts) of the lowest concentration standard.

8.9.3 The LOD can now be calculated using the following equation:

$$LOD = t * s$$

Where s is the standard deviation (in µg/mL) of at least five replicate determinations of the lowest concentration standard and t is the Student's t value associated with a 99% confidence interval.

8.9.4 The Student's t value is dependent upon the degrees of freedom associated with the analysis. This "degrees of freedom" is equal to the number of replicate measurements for the lowest concentration standard, n, minus one. For the pilot study, the lowest concentration standard will be analyzed five times, which will correspond to 4 degrees of freedom and a Student's t value equal to 3.7 with a 99% confidence.

Other levels of confidence and number of replicate analyses can be substituted for these, one must reference a Student's t table to find the correct t value to use in the above calculation.

8.9.5 The concentration of the lowest standard must be greater than the calculated laboratory LOD, and not more than five times the maximum allowable LOD (5*0.0075 µg/mL = 0.0375 µg/mL).

8.9.6 The maximum allowable LOD is 0.0075 µg/mL for each aldehyde, not the aldehyde-DNPH derivative. The calculated laboratory LOD must be equal to or lower than the maximum allowable LOD for sample analysis to be considered valid.

8.9.7 For sample analysis, all peaks identified as target compounds that are equal to or exceed the maximum allowable LOD must be reported. If the calculated laboratory LOD is less than the maximum allowable LOD, the laboratory may choose to set its reporting limit at the maximum allowable LOD, the calculated laboratory LOD, or any level in between.

8.9.8 For the purpose of calculating the total mass of all aldehydes, the concentrations of the compounds below the LOD are considered to be zero.

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