

THESIS

QUANTIFYING COMMUTER EXPOSURES TO VOLATILE ORGANIC COMPOUNDS

Submitted by

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In partial fulfillment of the requirements

For the Degree of Master of Science

Colorado State University

Fort Collins, Colorado

Spring 2014

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ABSTRACT

QUANTIFYING COMMUTER EXPOSURES TO VOLATILE ORGANIC COMPOUNDS

Motor-vehicles can be a predominant source of air pollution in cities. Traffic-related air pollution is often unavoidable for people who live in populous areas. Commuters may have high exposures to traffic-related air pollution as they are close to vehicle tailpipes. Volatile organic compounds (VOCs) are one class of air pollutants of concern because exposure to VOCs carries risk for adverse health effects. Specific VOCs of interest for this work include benzene, toluene, ethylbenzene, and xylenes (BTEX), which are often found in gasoline and combustion products. Although methods exist to measure time-integrated personal exposures to BTEX, there are few practical methods to measure a commuter's time-resolved BTEX exposure which could identify peak exposures that could be concealed with a time-integrated measurement.

This study evaluated the ability of a photoionization detector (PID) to measure commuters' exposure to BTEX using Tenax TA samples as a reference and quantified the difference in BTEX exposure between cyclists and drivers with windows open and closed. To determine the suitability of two measurement methods (PID and Tenax TA) for use in this study, the precision, linearity, and limits of detection (LODs) for both the PID and Tenax TA measurement methods were determined in the laboratory with standard BTEX calibration gases. Volunteers commuted from their homes to their work places by cycling or driving while wearing a personal exposure backpack containing a collocated PID and Tenax TA sampler. Volunteers completed a survey and indicated if the windows in their vehicle were open or closed. Comparing pairs of exposure data from the Tenax TA and PID sampling methods determined the suitability of the PID to measure the BTEX exposures of commuters. The difference between BTEX exposures of cyclists and drivers with windows open and closed in Fort Collins was determined.

Both the PID and Tenax TA measurement methods were precise and linear when evaluated in the laboratory using standard BTEX gases. The LODs for the Tenax TA sampling tubes (determined with a

sample volume of 1,000 standard cubic centimeters which is close to the approximate commuter sample volumes collected) were orders of magnitude lower (0.04 to 0.7 parts per billion (ppb) for individual compounds of BTEX) compared to the PIDs' LODs (9.3 to 15 ppb of a BTEX mixture), which makes the Tenax TA sampling method more suitable to measure BTEX concentrations in the sub-parts per billion (ppb) range. PID and Tenax TA data for commuter exposures were inversely related. The concentrations of VOCs measured by the PID were substantially higher than BTEX concentrations measured by collocated Tenax TA samplers. The inverse trend and the large difference in magnitude between PID responses and Tenax TA BTEX measurements indicates the two methods may have been measuring different air pollutants that are negatively correlated. Drivers in Fort Collins, Colorado with closed windows experienced greater time-weighted average BTEX exposures than cyclists ($p: 0.04$). Commuter BTEX exposures measured in Fort Collins were lower than commuter exposures measured in prior studies that occurred in larger cities (Boston and Copenhagen). Although route and intake may affect a commuter's BTEX dose, these variables are outside of the scope of this study. Within the limitations of this study (including: small sample size, small representative area of Fort Collins, and respiration rates not taken into account), it appears health risks associated with traffic-induced BTEX exposures may be reduced by commuting via cycling instead of driving with windows closed and living in a less populous area that has less vehicle traffic.

Although the PID did not reliably measure low-level commuter BTEX exposures, the Tenax TA sampling method did. The PID measured BTEX concentrations reliably in a controlled environment, at high concentrations (300-800 ppb), and in the absence of other air pollutants. In environments where there could be multiple chemicals present that may produce a PID signal (such as nitrogen dioxide), Tenax TA samplers may be a better choice for measuring BTEX. Tenax TA measurements were the only suitable method within this study to measure commuter's BTEX exposure in Fort Collins, Colorado.

ACKNOWLEDGEMENTS

This thesis was supported by Grant Number T42OH009229-04 from CDC NIOSH and Mountain and Plains Education Research Center and the National Institutes of Health R01ES020017. Its contents are solely the responsibility of the author and do not necessarily represent the official views of the CDC NIOSH, MAP ERC, or NIH.

I would like to give a special thanks to the researchers at the National Center for Atmospheric Research, specifically John Ortega, Andrew Turnipseed, and Jim Smith.

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LIST OF NOMENCLATURE

BTEX- Benzene, toluene, ethylbenzene, and xylenes
BTX- Benzene, toluene, and xylenes
PID- Photoionization detector
GC- Gas chromatograph
MS- Mass spectrometer
FID- Flame ionization detector
LOD- Limit of detection
 R^2 - Coefficient of determination
 R_s - Spearman correlation coefficient
S- Sample standard deviation
VOC- Volatile organic compound
CNS- Central nervous system
MRL- Minimum recommended limit
NM- Not measured
ND- Not discernible after multiple volatiles were grouped together
PTR-MS- Proton transfer reaction – mass spectrometry
NIOSH- National Institute of Occupational Safety and Health
EPA- Environmental Protection Agency
IRB- Institutional Review Board
CSU- Colorado State University
NCAR- National Center for Atmospheric Research
TD- Thermal desorption
GPS- Global positioning system
GLM- Generalized linear model
SAS- Statistical Analysis Software
TVOC- Total volatile organic compounds
ppb- Parts per billion
ppm- Parts per million
TWA- Time-weighted average

1.0 INTRODUCTION

1.1 Traffic-related air pollution exposures in the U.S.

Exposure to traffic-related air pollution is frequent and widespread in the United States. Individuals may be exposed to high levels of traffic-related air pollution by living in close proximity to roads and also while driving. Motor vehicles are a major source of air pollution in the United States (HEI 2010); vehicular pollution may be unavoidable for approximately 80% of Americans (249 million) who live in urban environments (U.S. Census Bureau 2013a). Approximately 42% (132 million) of Americans commute to work (U.S. Census Bureau 2013b). These individuals are exposed to traffic-related air pollution on a nearly daily basis for the duration of their working lifetimes.

1.2 Air pollutants within vehicle exhaust

Vehicular exhaust consists of an array of air pollutants including carbon dioxide, carbon monoxide, nitrogen oxides, particulate matter, and volatile organic compounds, among others (HEI 2010). The presence of vehicle exhaust in the ambient environment results in an inhalation exposure pathway. This study focused on volatile organic compounds, one of many hazardous traffic-related air pollutants. The term volatile organic compounds (VOCs) encompass thousands of individual chemicals. There are three common sources of VOCs in outdoor air: 1) biogenic (e.g., odorous plants), 2) industrial (e.g., refineries, coal power plants), and 3) traffic (i.e., vehicle exhaust). Although these sources emit many common VOCs, certain VOCs have been used as tracers for a given source type (Baldasano, Delgado, and Calbó 1998).

Benzene, toluene, ethylbenzene, and xylenes (BTEX) are often considered the VOC “fingerprint” of petroleum products, including combustion byproducts. BTEX is often measured as a proxy for traffic-related VOCs. BTEX can be found in numerous other products including solvents, glues, paints, building materials, and various other materials. Numerous adverse health effects have been linked to BTEX exposure (U.S. HHS 2007a) (U.S. HHS 2000) (U.S. HHS 2010)(U.S. HHS 2007b).

1.3 Health risks associated with BTEX inhalation

Inhaling BTEX may cause adverse health effects in humans. Although the health effects following benzene inhalation are understood better than toluene, ethylbenzene and xylenes, studies have yet to find safe levels of benzene exposure. Toxicological studies have found concentrations of toluene (U.S. HHS 2000), ethylbenzene (U.S. HHS 2010), and xylenes (U.S. HHS 2007b) associated with minimal health risks, but few studies have observed low-level human inhalation exposures. Concentrations of benzene, toluene, ethylbenzene, and xylenes found on road in Fort Collins could be causing adverse health effects in commuters.

Epidemiological studies have found that low-level exposures to benzene are associated with an elevated risk of leukemia (Glass et al. 2003)(Bollati et al. 2007). Chronic exposure to benzene increased the risk of leukemia in Australian refinery workers at exposure levels as low as 1 part per million (ppm) - year (Glass et al. 2003). Chronic benzene inhalation has been associated with low blood count, bone marrow aplasia, aplastic anemia (a precursor to fibrosis), damage to the immune system, cytopenia, non-Hodgkin lymphoma, acute myelogenous leukemia, and acute non-lymphocytic leukemia (U.S. HHS 2007a) (Glass et al. 2003) (Bulka et al. 2013) (WHO International Agency for Research on Cancer 1998). Acute exposure to high concentrations of benzene can cause death from central nervous system depression (U.S. HHS 2007a) (Avis and Hutton 1993). Short exposures to concentrated benzene and BTX (100% benzene and 100% benzene, toluene, and xylenes) among refinery workers increased the risk of leukemia greater than the risk of experiencing the same total exposure at a lower concentration and over a greater amount of time (Glass et al. 2003). Several researchers conclude that even a small exposure to benzene could increase health risks and therefore no safe level of benzene exposure exists (Glass et al. 2003) (Bollati et al. 2007).

Chronic toluene exposure (via inhalation) can cause irreversible damage to the central nervous system (CNS) (U.S. HHS 2000). Acute toluene inhalation may cause reversible or irreversible CNS damage (U.S. HHS 2000). Pregnant women who are exposed to toluene are at an increased risk of fetal damage (U.S. HHS 2000). Studies on the health effects people experienced following toluene inhalation during

recreational drug use has contributed to the breadth of knowledge pertaining to high-level toluene inhalation toxicity. Toluene substance abusers and people exposed to high levels of toluene at work are at an increased risk of mortality due to cardiovascular, CNS, and respiratory system complications (U.S. HHS 2000). The air concentration of toluene associated with acute human fatality is currently estimated at 2,000 ppm (Nomiyama and Nomiyama 1978). Few observable effects have been reported following toluene inhalation at concentrations less than 50 ppm (U.S. HHS 2000). On-road concentrations of toluene in Fort Collins, Colorado (estimated between 1-10 ppb) are most likely below the minimum observational threshold for CNS depression (1 ppm (U.S. HHS 2000)).

Few human epidemiological and toxicological studies have been conducted for ethylbenzene exposure as these exposures rarely occur exclusively (OEHHA 2013). Ethylbenzene exposures often occur concurrently with other VOCs (OEHHA 2013). Animal health effects following ethylbenzene inhalation include: skeletal retardation, weight reduction, and kidney tumors (rodent model); lung and liver tumors and necrosis (mouse model); and reduced offspring count (rabbit model) (OEHHA 2013). Little is known about human health effects associated with inhaling ethylbenzene, however, animal studies suggest inhalation would likely have an adverse health effect on humans.

Xylene inhalation exposures primarily affect the human respiratory system and CNS (U.S. HHS 2007b). There are many xylene isomers, all of which are thought to have similar toxicity levels (U.S. HHS 2007b). Changes in pulmonary physiology and CNS effects, including short-term memory loss and a reduction in reaction time, have been linked with chronic xylene exposure (U.S. HHS 2007b). Acute xylene inhalation by humans is associated with impaired pulmonary function, adverse liver effects, and various CNS impairments: short-term memory, reaction time, and balance (U.S. HHS 2007b). Very high, acute exposures can lead to loss of consciousness, amnesia, brain hemorrhage, seizures, and death (U.S. HHS 2007b).

1.4 Minimum Risk Levels for BTEX inhalation exposure

Minimum risk levels (MRLs) have been identified by the Agency for Toxic Substances and Disease Registry as, “an estimate of the daily human exposure to a hazardous substance that is likely to be without

appreciable risk of adverse non-cancer health effects” (ATSDR 2013). MRLs are based on acute health effects that occur after short exposures and chronic health effects that occur after extended or repeated exposures. BTEX has been measured on-road within multiple studies (Table 1); all known studies observed benzene exposures above the chronic MRL.

Table 1: BTEX maximum time-integrated exposures observed during driving commutes and accompanying acute and chronic Minimum Risk Levels (MRLs) for inhalation exposures in micrograms per cubic meter ($\mu\text{g}/\text{m}^3$)

Compound	Acute MRL ¹	Chronic MRL ¹	West Yorkshire ²	Amsterdam ³	Boston ⁴	Raleigh ⁵	Copenhagen ⁶
Benzene	29	9.6	265.5	193	64.0	42.8	17.5
Toluene	3,800	300	NM	554	105.1	118.9	82.9
Ethylbenzene	22,000	260	NM	NM	21.6	21.8	ND
Xylenes	8,700	220	NM	287	100.7	103.9	ND

Notes:

MRL values were reported in ppb and were converted to $\mu\text{g}/\text{m}^3$ using a standard temperature of 25° Celsius

¹: Acute and chronic MRL references: benzene (U.S. HHS 2007a), toluene (U.S. HHS 2000), ethylbenzene (U.S. HHS 2010), xylenes (U.S. HHS 2007b)

²: West Yorkshire values were measured in September-October 1996 (Kingham et al. 1998)

³: Amsterdam values were measured in January and May of 1990 (Wijnen et al. 1995)

⁴: Boston values were measured in the winter of 1989-1990 (C.-C. Chan et al. 1991)

⁵: Raleigh values were measured in the summer of 1988 (C. C. Chan et al. 1991)

⁶: Copenhagen values were measured in July and August 1998 (Rank, Folke, and Homann Jespersen 2001)

NM: Not measured

ND: Not discernible after multiple volatiles were grouped together

Health risks associated with BTEX exposures can be affected by time-weighted average (TWA) exposure quantities, total exposure quantities (cumulative exposure quantities), exposure time durations, and the amount of pollutants inhaled (intake quantity). MRLs were established to be compared to time-weighted average exposures. Cumulative exposure quantities are important because exposure to a greater quantity of toxins may increase health risks. Extended exposure durations could increase health risks.

Increased inhalation rates may also affect health risks; a cyclist with a higher inhalation rate could experience a greater dose of air pollution than a driver with a lower inhalation rate. The amount of pollutants that are inhaled (i.e., the intake) and deposit within the body (i.e., the uptake) is often less than the concentration of pollutants in air (exposure) (EPA 2011). Because of the large inter-person intake variation including lung capacity, respiration rate, and body mass and the complex nature of the respiratory system pertaining to gas-exchange processes, intake was not evaluated within this study.

1.5 Commuter exposures to VOCs

Previous studies investigating VOC exposure while commuting have all occurred in urban areas. Commuting studies in West Yorkshire, Amsterdam, Boston, Raleigh, and Copenhagen, all reported benzene exposures on road (Table 1) (Kingham et al. 1998) (Wijnen et al. 1995) (C.-C. Chan et al. 1991) (C. C. Chan et al. 1991) (Rank, Folke, and Homann Jespersen 2001). However, little is known about personal exposures to BTEX on midsize city roadways.

1.6 Fort Collins Commuter Study

Few studies have measured commuter's exposure to traffic-related BTEX in non-urban settings. Commuters in large cities may be exposed to potentially harmful levels of benzene (see Table 1) but the benzene exposure of midsize city commuters remains relatively unknown. The Fort Collins Commuter Study was initiated to improve our understanding of midsize city commuters' air pollution exposures. The Fort Collins Commuter Study aims to evaluate the magnitude of various air-pollutant exposures spatiotemporally, identifying when and where exposures occur and how such exposures may vary between different commute modes (cycling vs. driving).

Previous commuter studies have noticed a marked difference between BTEX exposure levels observed for cyclists and vehicle drivers. Although cyclists are often in closer proximity to a vehicle's tailpipe than drivers, within large cities cyclists have experienced lower BTEX exposures than drivers (Kingham et al. 1998) (Rank, Folke, and Homann Jespersen 2001). The interior of new vehicles have elevated concentrations of many VOCs including but not limited to toluene and xylenes due to off-gassing of materials and the "new car smell" (Chien 2007); these VOC emissions are expected to decrease

with the life of a vehicle (Chien 2007). In-cabin fugitive emissions and exhaust from both personal and nearby automobiles may contribute to elevated VOC exposures for motorists while driving and are reasons cyclists could experience lower BTEX exposures than drivers. Drivers have greater time-integrated BTEX exposures than cyclists (C.-C. Chan et al. 1991) (Rank, Folke, and Homann Jespersen 2001), but the dynamic range of exposures throughout a commute remains unknown.

1.7 Past and present methods for measuring BTEX

There are few methods that can measure BTEX in real time. Real-time measurements are needed to characterize peak exposures that may be more harmful to human health than the same exposure spread out over more time (Glass et al. 2003). Proton transfer reaction – mass spectrometry (PTR-MS) and online gas chromatographs (GCs) are instruments that can measure BTEX in a time-resolved fashion; these instruments are not suitable for use in a personal exposure study, however, as they are prohibitively large, heavy, and expensive. A photoionization detector (PID) is a time-resolved instrument that can measure total VOCs (any chemical that can ionize within a specific photon-energy input) on or within a person's breathing zone. Several commercially available PIDs are size and weight appropriate for commuters to carry inside of a backpack. PIDs would be ideal to measure commuter exposures within the Fort Collins Commuter Study, however, they lack the ability to speciate individual VOCs.

Ambient air contains background VOCs that are indiscernible from BTEX when measured by a PID. Industrial sites and biogenic sources can contribute a large percentage of background VOCs. The absence of large industrial sites nearby Fort Collins, Colorado means that background VOCs are likely the result of biogenic sources (primarily isoprenes) which may contribute an unknown quantity of ambient VOCs.

Prior studies reported inconclusive results when evaluating the suitability of PIDs for measuring occupational VOC exposure. Oftentimes, PIDs are collocated with a time-integrated sampling method so that measurements can be compared (Poirot 2004) (Coy et al. 2000) (Coffey et al. 2008). Although many PIDs experience interference with high temperatures and humidity (Barsky, Hee, and Clark 1985) (LeBouf, Slaven, and Coffey 2013) (Coffey et al. 2008), the manufacturers of the Ion Science Tiger claim to have minimized this effect by adding a Fence Electrode (Geoff Hewitt 2013). The performance of the

PID containing a Fence Electrode has not been evaluated in the literature. Because the Tiger PID has not been tested by a third party, it should be compared against a standard method. Another limitation of PIDs is the variability of signal strength, which is dependent upon the ionization potential of the compound of interest. Compounds ionize preferentially at varying potentials and an ancillary compound could produce a stronger PID signal than the compound of interest. Speciation is necessary to measure BTEX within the variety of VOCs amid traffic exhaust. A major limitation of using PIDs in a commuter study is the lack of individual VOC speciation.

Studies of personal VOC exposure often use time-integrated measurement methods because they allow for VOC speciation. Standard methods to measure BTEX concentrations have been published by the National Institute of Occupational Safety and Health (NIOSH) and the U.S. Environmental Protection Agency (EPA); these methods were developed to evaluate time-integrated occupational and environmental exposures, respectively. The NIOSH and EPA BTEX measurement methods generally require sampling for a minimum of four hours, making them inappropriate to measure briefer commuting exposures. Time-integrated measurements cannot resolve temporal fluctuations in exposure concentrations across the sampling duration. Pairing a time-resolved measurement method with a standard time-integrated measurement method can determine if the time-resolved measurement method works; a time-resolved exposure profile can identify times (and potential locations) midsize city commuters experience elevated VOC exposures during a commute.

1.8 Study aims

The aims of the VOC sub study within the Fort Collins Commuter Study were to (1) quantify BTEX exposures of drivers and cyclists during midsize city commutes and (2) evaluate the effectiveness of PIDs at measuring commuter's exposure to BTEX. Assessing the relationship between time-resolved measurements of total VOCs and time-integrated measurements of speciated VOCs (BTEX) will determine if values measured by the PID are representative of true BTEX exposures.

2.0 METHODS

2.1 Measuring air pollution exposures within the Fort Collins Commuter Study

Volunteers participating in the Fort Collins Commuter Study commuted to and from work while wearing a backpack containing a suite of time-resolved instruments. Air pollution monitors within each backpack measured the following pollutants: VOCs (PhoCheck Tiger, IonScience, Fowlmere, UK), particulate matter (Personal DataRAM 1200, Thermo Scientific, Waltham, MA, USA), elemental carbon (microAeth, AethLabs, San Francisco, CA, USA), carbon monoxide (T15n, Langen Products, Inc., San Francisco, CA, USA), ultrafine particles (DiSCmini, Matter Aerosol AG, Wohlen, CH), and nitrogen dioxide (Series 500 IAQ, Aeroqual Ltd., Auckland, NZ). In addition to air pollution monitors, the backpacks contained instruments to measure situational variables such as location (BT Q1000XT, Qstar International Co. Ltd., Taiwan, R.O.C.), air temperature (MSR145, MSR Electronics GmbH, Seuzach, CH), relative humidity (MSR145, MSR Electronics GmbH, Seuzach, CH), light (MSR145, MSR Electronics GmbH, Seuzach, CH), acceleration (MSR145, MSR Electronics GmbH, Seuzach, CH), and noise (Model 703+, Larson Davis, PCB Group Inc., New York, USA). Situational variables can be used to account for situational effects within a generalized linear model (GLM) or to identify when people are entering or leaving a location. Volunteers also wore a heart rate monitor (Actiheart, CamNtech Ltd., Cambridge, UK) which was equipped with a three-axis accelerometer to approximate respiration and activity level.

Forty six volunteers commuted twice (on separate days) along four routes for a total of eight commutes per volunteer while driving and cycling for a study total of 376 commutes. The order in which volunteers completed their routes and modes was randomized. All commutes occurred on Tuesdays and Thursdays between September 12, 2012 and February 3, 2014. The Fort Collins Commuter Study obtained Institutional Review Board (IRB) approval from Colorado State University (CSU) and all volunteers gave informed consent prior to participating (Appendix A). Commuters were asked to complete a questionnaire inquiring about the details of each commute which included questions about but

were not limited to weather, commuting times, and if vehicle windows were up or down during the commute. VOC measurements were collected for a subset of Fort Collins Commuter Study volunteers due to resource limitations.

Nine volunteers participated in the VOC sub-study (15 total commutes) between September 9, 2013 and October 2, 2013; four volunteers repeated at least one route and five volunteers commuted a single time. Volunteers were chosen by using people already participating in the study, during their predetermined commute routes and days. Vehicles used in the sub study include: 1991 Ford Ranger 4x4, 1998 Oldsmobile Achieva, 2002 Chevrolet Silverado, 2005 Honda Odyssey, 2005 Subaru Impreza, 2005 Honda Pilot, 2009 Honda Civic, 2008 Subaru Outback, and 2012 Nissan Versa. These volunteers carried additional instruments to measure VOC concentrations during commuting. In addition to the instruments previously outlined (including a PID), participants in the VOC sub-study carried stainless steel tubes that were filled with Tenax TA sorbent resin and connected to a personal sampling pump (Pocket Pump, SKC Inc., Eighty Four, PA, USA). Volunteers participating in the sub-study agreed to a supplemental informed consent, which was approved by the CSU IRB (Appendix A). Volunteers manually started and stopped a pre-programmed personal sampling pump so that VOCs were sampled exclusively during commutes.

2.2 Time-integrated sampling method: Tenax TA sample tubes with subsequent GC/MS/FID analysis

A sampling apparatus (Figure 1) containing Tenax TA sorbent resin collected time-integrated VOC samples following a modified version of the National Institute of Occupational Safety and Health (NIOSH) Method 2549 (NIOSH 1996). The NIOSH Method 2549 specifies a humidity test, which was not conducted because the sorbent we chose to use (Tenax TA) was hydrophobic, unlike other available sorbents (SKC Inc. 2013). Tenax TA is a sorbent resin that adsorbs VOCs when used in conjunction with a sample pump. Sample volume is specified by NIOSH Method 2549 (NIOSH 1996) to range between one and six liters. Commute times were estimated prior to sampling and each sampling pump was calibrated with an inline Tenax TA tube to a flow rate between 100 and 235 milliliters per minute (modification from NIOSH Method 2549) to obtain the target sample volume (one-six liters). The

stainless steel tubes were prepared and filled by Andrew Turnipseed and John Ortega at the National Center for Atmospheric Research (NCAR).

If Tenax TA is left out and exposed to ambient air, any VOCs present may adsorb to the Tenax TA. To prevent ambient VOCs from contaminating sample media while the pump was not running, Swagelock caps were installed on the inlet of each sampling tube. Each volunteer unscrewed the Swagelock cap from the sample tube prior to starting their pump. Tube inlets were placed on the outside of the backpack, close to the breathing zone. After samples were collected the tubes were stored in an airtight container at 3° Celsius (C).



Figure 1: Tenax TA sampling apparatus: a stainless steel tube filled with Tenax TA sorbent media and connected to a personal sampling pump with a push-to-connect adapter

Collected VOCs were thermally desorbed (TD) from the Tenax TA tubes using a Series 2 Ultra™ TD autosampler (MARKES International, Llantrisant, UK) and analyzed sequentially using an Agilent 7890A gas chromatograph (GC) equipped with a flame ionization detector (FID) and an Agilent 5975C

mass spectrometer (MS) detector (Agilent Technologies, Santa Clara, CA, USA). The tubes were first purged for 7 minutes with helium followed by a 15 minute desorption at 275 °C. During this time, the analytes were transferred to a Markes Unity two-stage cold trap filled with Tenax TA followed by Carbograph 5. The cold trap temperature was maintained at 0 °C. The cold trap was rapidly heated from 0 to 285 °C as the analytes were transferred to the GC. Each sample was injected into the GC in split mode with a 25:1 split ratio. Helium was used as the carrier gas. A Restek Rxi-5Sil MS GC column was used for separation (0.25 mm inner diameter × 30 m length × 0.25 micron film thickness). The temperature inside the GC oven was initially held at -30 °C for one minute (min), and the temperature within the GC oven was then increased as follows: 20 °C min⁻¹ to 0 °C, 6 °C min⁻¹ to 80 °C, 3 °C min⁻¹ to 190 °C, 30 °C to 260 °C, and held at 260 °C for 5.87 minutes (total analysis time of 60.7 minutes). The GC/MS/FID system generates a chromatogram exhibiting peaks corresponding to chemical compounds that exited the column at distinct retention times. VOCs were identified based on GC retention times and mass to charge (m/z) values and were quantified using integrated FID peak areas of selected quantification ions.

Blank samples were collected for every round of samples analyzed so that any background concentration, contamination, or TD artifact could be accounted for. Blank samples were prepared the same as other samples and were treated the same way (attaching to fittings, calibration devices, storage, etc.) as non-blank sample tubes, with the exception that they never left the laboratory. Benzene and toluene peaks were identified in the chromatograms of blank samples; all measurements were corrected by subtracting the average of the blank peak-integrated areas within the round of samples. Benzene was produced during the TD process and blank corrections accounted for this artifact in actual field samples. The limit of detection (LOD) for the Tenax TA sampling method was established by evaluating Tenax TA tubes that measured known concentrations. Tenax TA tubes of varying concentrations (0.26, 0.40, 0.84, 1.0, 2.0, and 5.0 ppb benzene) of a BTEX standard were prepared using FC-260 Mass Flow Controllers (Tylan Corporation, Torrance, CA, USA) and analyzed. LODs were determined using 3-5 replicates. Sample means and standard deviations were used to construct calibration curves for each compound

(available in Appendix B, Figures 12 - 21). Equation 2.1 (ICH 2005) was used with the slope from each calibration curve (Appendix B, Figures 12 - 21) and the standard deviation of the concentration of the smallest value to determine the concentration where the GC/MS/FID signal (peak height) was greater than the signal from the TD artifacts.

$$\text{LOD} = 3 \cdot (s) / m \qquad \text{Equation 2.1}$$

Notes: s = sample standard deviation of blank or smallest signal visually detected; m = slope of calibration curve (Appendix B, Figures 12 - 21).

2.3 Time-resolved sample method: PID

Two Ion Science Tiger PIDs were used to obtain time-resolved VOC exposure data. The PIDs required minor adaptation to be used in the Fort Collins Commuter Study. An external battery was connected to each PID to extend instrument run time. The PIDs are sensitive to back pressure on the outlet, which resulted in occasional flow faults. A Teflon elbow (with five holes drilled in it) was added to the outlet to prevent flow faults while the PID was carried inside the backpack. The factory-installed PID inlet was not long enough to stick out of the backpack; therefore, a three inch Teflon extension was attached to each of the factory PID inlets. Four holes were drilled into the last half inch of the inlet extension to prevent the inlet from being accidentally blocked (another source of flow faults). A piece of brass was bent to contour the back side of the PID to reinforce the inlet extension. Although the modifications substantially reduced the number of flow faults that occurred, they did not prevent all flow faults.

To determine the PID response range of total VOC exposures experienced by commuters in Fort Collins, a preliminary study was conducted within the Fort Collins Commuter Study. Commuters carried PIDs inside of the personal exposure backpack; PIDs recorded a measurement every 10 seconds. The frequency of VOC measurements during four commutes chosen by the study coordinator determined the seven most frequent VOC concentrations observed on road. During this preliminary study, it became apparent that PIDs required frequent maintenance to retain accuracy and avoid instrument drift.

The PIDs required weekly maintenance to sustain their performance. PIDs produce a layer of contamination on the lamp as an artifact of the photoionization process. Ion Science recommends cleaning the lamp after every 100 hours of use (Ion Science 2013). Lamp contamination must be managed to produce reliable PID responses. Every week each PID was disassembled, the lamp was cleaned, and the internal pieces were blown out with commercial duster as per Ion Science specifications (Ion Science 2013). After cleaning, each PID was recalibrated using an Ion Science charcoal filter and 10 ppm BTEX standard. Instrument response was verified by conducting span checks at BTEX concentrations ranging from 100- 800 ppb.

2.4 Evaluating instrument response in the laboratory

A dilution chamber was built for calibrating the PIDs and verifying the accuracy of the PIDs and Tenax TA measurement methods (Figure 2). A 66 cm³ dilution chamber was fabricated from a Teflon tube, stainless steel and brass fittings, a needle valve, and a rotameter. Ultra-zero air was used to dilute BTEX calibration gas (originally 10.5 ppm benzene, 10.4 ppm toluene, 10.1 ppm m- xylene, 10.1 ppm p- xylene, and 10.1 ppm o- xylene). BTEX flow was controlled using calibrated critical orifices (20 and 50 µm) that were calibrated using a bubble meter (7373 500 ml, Bubble-O-Meter LLC., Dublin, OH, USA). Ultra-zero air flow was controlled with an adjustable needle valve and the flow was read on a rotameter that was calibrated using a DC-Lite DryCal primary flow standard (BIOS, Mesa Labs, Butler, NJ, USA). The ultra-zero air and BTEX standard converged in a T-junction that discharged into the dilution chamber. This dilution chamber setup could produce the range of BTEX concentrations observed most frequently during the preliminary PID study (100 to 800 ppb). The 100 ppb BTEX concentration was verified using the Tenax TA method and because of this agreement concentrations between 200-800 ppb were assumed to be accurate. One air exchange within the chamber took between 1 and 30 seconds depending on the flow of ultra-zero air. The dilution chamber was used to evaluate instrument drift, precision, and accuracy of the PID and Tenax TA measurement methods.

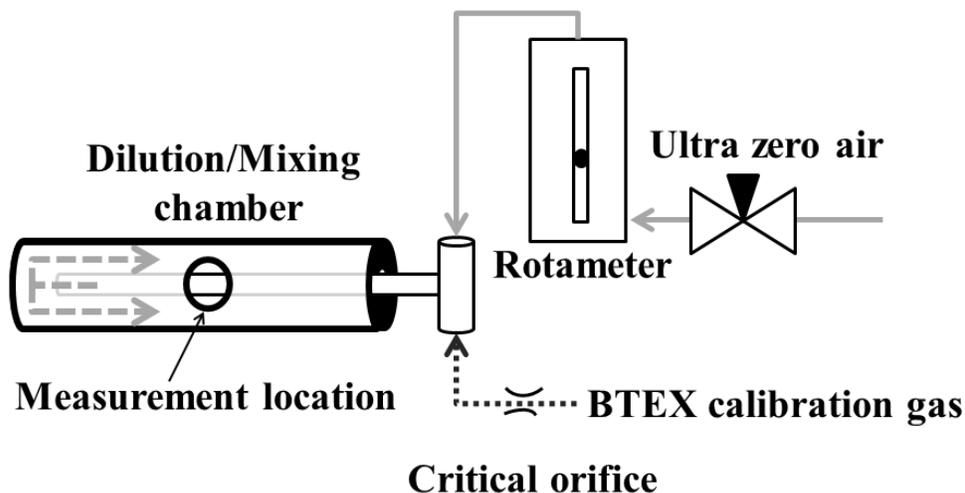


Figure 2: Diagram of dilution chamber

Precision, limit of detection, and linearity of the PIDs were evaluated by collocating the inlets of two PIDs inside the dilution chamber (Figure 3). The response of the PIDs was determined at the seven most frequently observed concentrations from the preliminary study (100, 200, 300, 400, 500, 600, and 800 ppb). The concentrations were evaluated in a randomized order to minimize the effects of hysteresis. Measurements were conducted within a fume hood at room temperature. The only known VOC signal in the chamber was from the BTEX calibration gas. The PIDs recorded measurements at 10 second intervals. The time required for a PID to reach equilibration within the chamber was dependent on the amount of contamination present on the internal lamp. The PID signals typically reached equilibration within 4-6 minutes. Following the equilibration delay, two minutes of 10 second measurements (n=12) were recorded. If the PID reading experienced additional drift after 6 minutes, the data were discarded. Summary statistics for PID measurements were used to build a calibration curve (Appendix C, Figures 22 - 28).

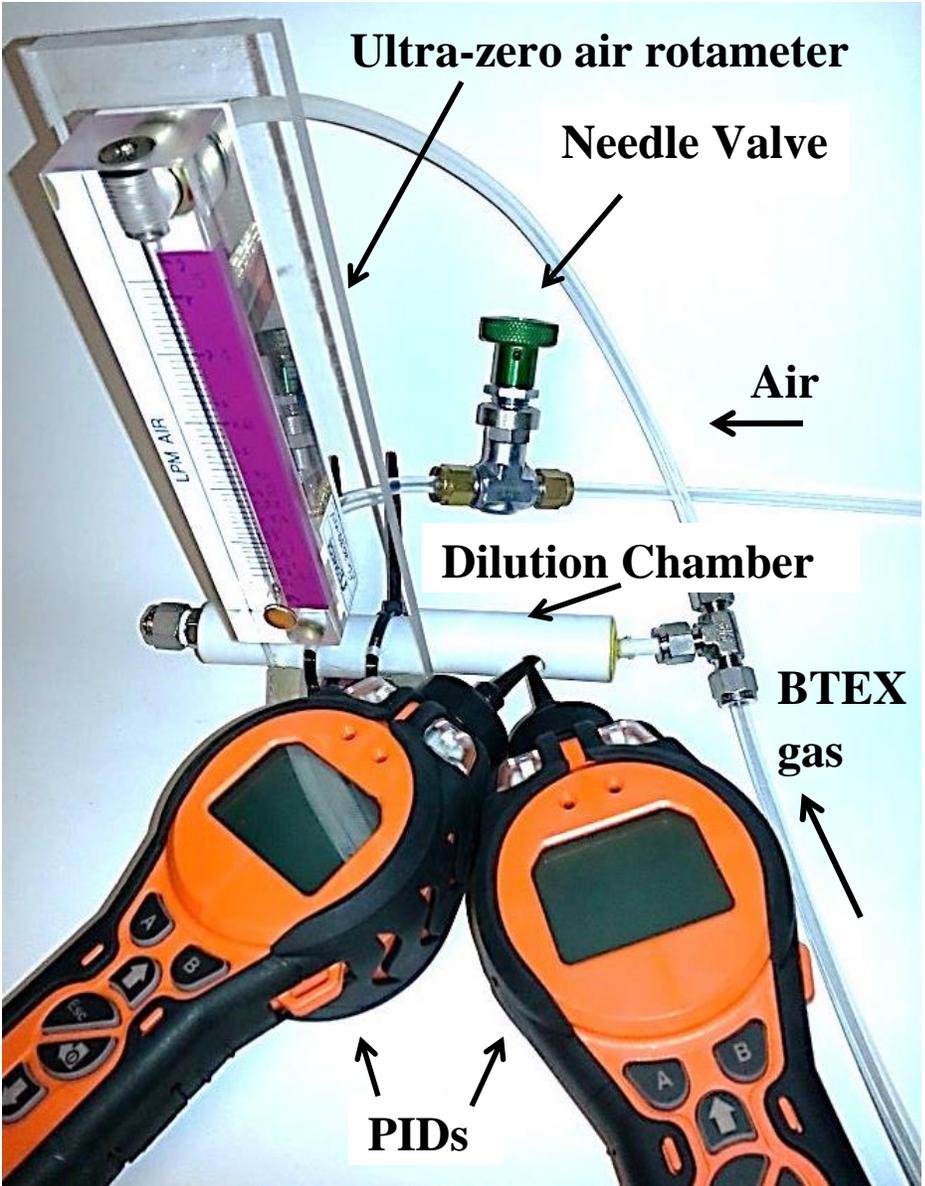


Figure 3: Collocated PID inlets measuring BTEX concentrations inside the dilution chamber

The dilution chamber was also used to evaluate the Tenax TA sampling method (n=4). Only 100 ppb concentrations were evaluated because fronting of peaks occurred at greater concentrations. Fronting is a phenomena characterized by poor peak shape and occurred because the VOC mass collected within a sample saturated the GC column. A fronting peak indicates inaccurate quantification. Calibration curves (described in section 2.2) were used to assess the precision, accuracy, and linearity of Tenax TA method responses to BTEX samples (see Appendix B Figures 12 - 21).

2.5 Evaluating PID and Tenax TA measurements during commutes

PID response was tested weekly to identify instrument drift from lamp contamination. After resetting the PID's internal calibration, a calibration curve (described in section 2.4) was compiled for each PID at the beginning of the week and once again at the end of the week (Appendix C, Figures 22 - 28). To account for instrument drift, the PID responses were adjusted to the average of the before and after calibration curves from that week. Pooling the variance measured at 100 ppb (or the lowest concentration that did not experience drift) between each set of weekly calibration curves provided a sample standard deviation to calculate a LOD for each instrument. PID responses below the LOD were adjusted to one half of the LOD. Other methods of adjusting PID values below the LOD were explored, however, the difference between PID responses above the LODs and below the LODs were greater by orders of magnitude so LOD adjustments made little difference. The TWA of the PID measurements sampled during commutes were compared against TWA Tenax TA data.

PID and Tenax TA measurements produced time-resolved total VOC concentrations and time-integrated, speciated VOC concentrations, respectively. A PID was placed in the backpack with the inlet extending above the exterior of the backpack (Figure 4). Placement of the PID in the backpack resulted in the inlet located behind the commuter's head. The inlet of the Tenax TA sampling tube was attached to the PID inlet to ensure samples were collected from a similar air space (Figure 4). The pump was placed in the outside pocket (accessible to volunteers) and Tygon tubing extended from the pump to the Tenax TA sampling tube. Although there were typically four volunteers commuting per study day, there were only two PIDs. Some backpacks did not have a PID but still had a Tenax TA tube attached to the outside of the bag at approximately the same location as the other tubes.

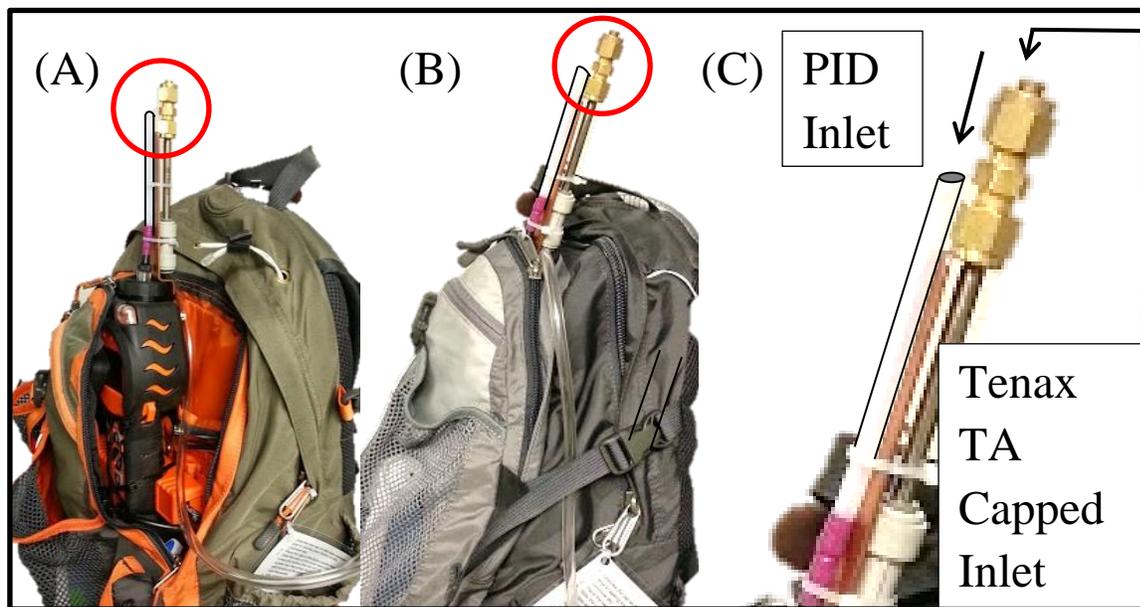


Figure 4: Location of PID and Tenax TA inlets; section (A) depicts the personal sampling backpack open with the PID and Tenax TA sampling inlets circled in red; section (B) depicts the backpack closed with PID and Tenax TA sampling inlets circled in red; section (C) depicts an enlarged image differentiating the two sampling inlets.

2.6 Statistical analyses

Statistical analyses were conducted to evaluate instrument response and to quantify and compare commuter exposures. First, the two measurement methods (PID and Tenax TA) were compared to BTEX standards within the laboratory environment to determine their suitability of measuring the compounds of interest. Next, both measurement methods were collocated and sampled commuter exposures to determine how the PID method performs within the real world. Finally, the effect of mode on commuter exposures was evaluated. To make these comparisons, statistical models were used and statistical assumptions were evaluated.

Tenax TA and GC/MS/FID response within the controlled laboratory environment was evaluated. The correlation between the GC/MS/FID signal response and known, low-level BTEX concentrations was evaluated; the calibration curve (Appendix B, described in section 2.2) was used to determine the accuracy, precision, and linearity of the GC/MS/FID response to BTEX. A paired t-test was used to determine the difference between Tenax TA responses and high-level (100 ppb) BTEX standards.

Statistical assumptions for the paired t-test were verified prior to analyses. Similar analyses were conducted for the PID method.

The Pearson's correlation between PID responses and BTEX concentrations within the dilution chamber was evaluated. The time-resolved PID data was auto correlated so to meet the statistical assumption of independence, an arithmetic mean (TWA) was used for each set of time-resolved PID data; all other statistical assumptions were met. Calibration curves (Appendix C Figures 22 - 28, described in section 2.4) for each PID were used to determine the precision and linearity of PID response to a BTEX standard. Laboratory tests were used to objectively identify the performance of both PIDs in the best case scenario.

In addition to laboratory tests, the ability of the PID to measure traffic-related commuter exposures to BTEX was evaluated by comparing TWA PID measurements to the standard TWA Tenax TA method. Statistical assumptions (independence, interval variable, normality, linearity, and homoscedasticity) were verified for all samples; all commuter exposure data from the PID measurements were log-transformed prior to any analyses. In order to compare the total response of all VOCs sampled within a Tenax TA tube to PID measurements, we assumed the PID can only ionize compounds with retention times less than acrylonitrile (ionization potential: 12.19 eV) because its ionization potential is much greater than the 10.6 eV lamp inside the PID. Within each chromatogram, all peak areas with a retention time greater than acrylonitrile were discarded. Spearman's correlation was used to compare the correlation between PID and Tenax TA measurements considering individual BTEX compounds, the sum of BTEX compounds, and the integrated peak areas of total VOCs assumed to be within the ionization potential of the PID. PID measurements were also adjusted using published Response Factors and the methods described by Ion Science (Factory Direct 2013), which explains how to account for different PID responses to VOCs of a known composition. PID values adjusted for response factors were compared to Tenax TA measurements. After determining the competence of the PID to measure commuter's BTEX exposures, commuter exposures within mode were evaluated.

Additional effects considered within this study were: commute time, outside temperature, outside relative humidity, and mixing height of the atmosphere (the latter measurement made twice a day in Denver, Colorado). Commute time was measured by the GPS unit. The outside temperature and relative humidity were measured by a third party (CSU) at a stationary weather station on the CSU campus (CSU 2013). The mixing height was calculated by another third party (University of Wyoming) from sounding data in Denver, Colorado (UWYO 2013). Mixing height was assumed to be constant between Fort Collins and Denver.

A GLM was developed using Statistical Analysis Software (SAS, version 9.3) to determine if there is was a difference (at a 95% confidence one-tailed test) in BTEX exposure (measured with Tenax TA) between cycling or driving with open or closed windows. The GLM was used to determine the following effects on BTEX exposure during a commute: volunteer, commute time, outside temperature (CSU 2013), outside relative humidity (CSU 2013), and mixing height of the atmosphere (UWYO 2013). The significance of effects were evaluated by eliminating each covariate one at a time if the p-value within the GLM was greater than 0.05. BTEX exposures while cycling and driving with open or closed windows in Fort Collins were compared against commuter exposures from peer-reviewed, published studies in Boston and Copenhagen. Statistical analyses allowed for an objective evaluation of the exposure differences between cyclists and drivers with windows open and closed and the suitability of measuring commuter's BTEX exposure with a PID.

3.0 RESULTS AND DISCUSSION

3.1 Laboratory evaluation of Tenax TA and PID methods

The Tenax TA measurement method was tested at high (100 ppb) and low (0.10- 5 ppb) BTEX concentrations in the laboratory. A bar chart comparing concentrations measured via Tenax TA to laboratory-generated concentrations of BTEX is shown in Figure 5. Above concentrations of 200 ppb, the Tenax TA sampling method could not accurately resolve BTEX concentrations because the column within the GC became saturated resulting in peak fronting within chromatograms (peak fronting is an indication of inaccuracy). The samples were analyzed by NCAR and peak fronts were not identified until after the samples were discarded. At lower concentrations (0.10- 5 ppb), the GC/MS/FID response to each BTEX compound was linear with an R^2 value of 0.99 (calibration curves are located in Appendix B). The LOD for each compound was determined from the GC/MS/FID calibration curves (Appendix B): benzene: 0.69 ppb, toluene: 0.050 ppb, ethylbenzene: 0.40 ppb, p- and m- xylenes: 0.49 ppb, and o-xylene: 0.43 ppb. The Tenax TA method produced repeatable and accurate measurements at both high and low BTEX concentrations.

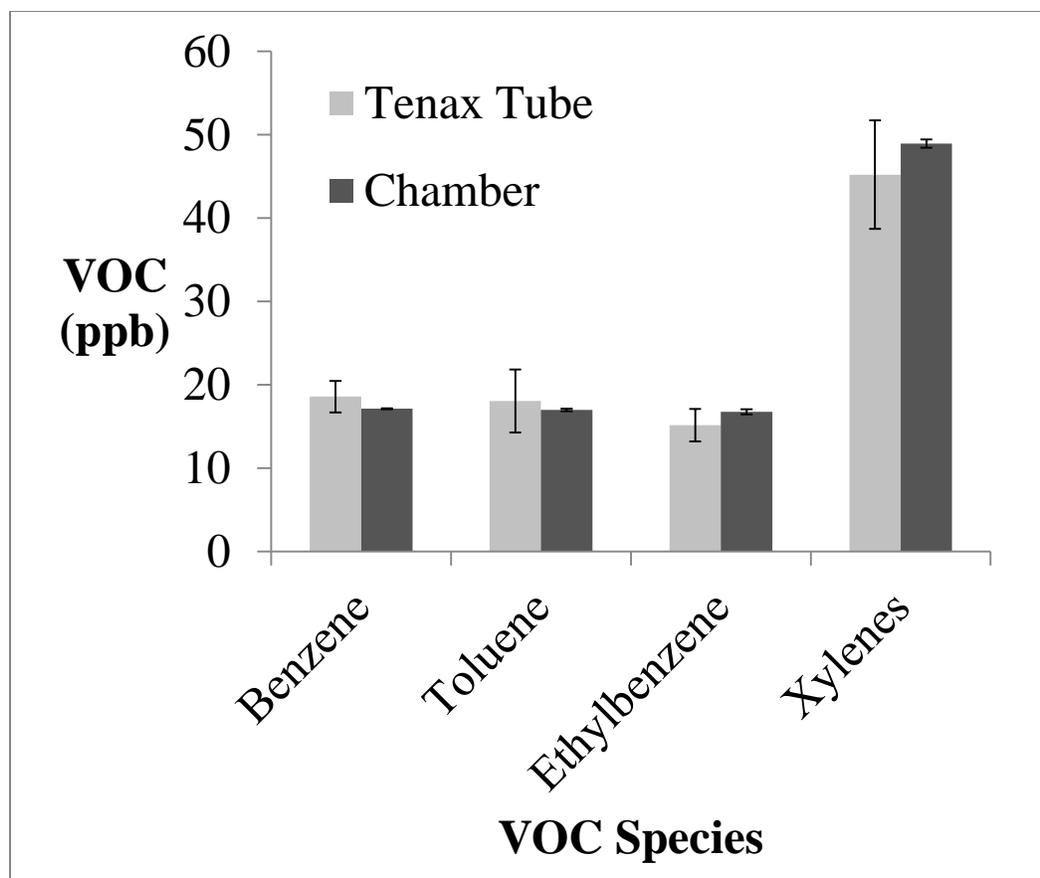


Figure 5: Tenax TA mean response to BTEX standard (100 ppb total) within a dilution chamber (n=4). Error bars represent one standard deviation.

When evaluated in the laboratory, the Tenax TA measurement method was accurate and precise. Measurements from the Tenax TA sampling were not statistically different from dilution chamber concentrations at 100 ppb; p-values of benzene: 0.2, toluene: 0.7, ethylbenzene: 0.2, xylenes: 0.2 and the sum of BTEX: 0.6 determined accuracy. Standard deviations were equal to or less than 0.5 ppb for each BTEX compound and the sum of BTEX compounds. The Tenax TA method was not suitable for sampling BTEX at large volumes (> 1.5 standard liters) and high concentrations (> 200 ppb BTEX) because column saturation occurred, which was indicated by peak fronting. Limits of detection for BTEX using the Tenax TA method were below 0.7 ppb, which was lower than anticipated on-road measurements (Gilman 2012). At low concentrations (0.1-5 ppb), the Tenax TA measurement method was accurate, precise, and linear (Appendix B Figures 12 - 21). Low variability within the Tenax TA

method combined with low LODs, accuracy, and linearity proved this measurement method was suitable to measure commuter's BTEX exposure.

Throughout the commuter study, laboratory evaluations identified similarities and differences between the individual PIDs' performances (Figure 6). Both PIDs responded linearly and had similar LOD ranges calculated from equation 2.1; however, the practical LODs varied greatly between PIDs. The variation between PID responses within the chamber was similar between the two PIDs (PID 1 standard deviation range: 3.9 – 9.1 ppb, PID 2 standard deviation range: 3.1- 4.7 ppb). The range in variation resulted in different LODs for different weeks. The range of LODs for PID 1 was between 9.6- 15 ppb BTEX and the range of LODs for PID 2 was 9.3- 12 ppb BTEX. PID 1 reported a negative response three times at BTEX concentrations above the LOD (twice at 100 ppb and once at 200 ppb, Figure 6) which means the chamber contained less VOCs than the IonScience provided charcoal filter that was used to zero the instruments. Despite these issues, the PIDs exhibited strong linearity with concentration (R^2 values of 0.96 and above, Appendix C Table 6). The responses of the PIDs changed between PID maintenance and also before and after sampling; the degree of drift, however, was inconsistent and may be an artifact of lamp contamination (Appendix C).

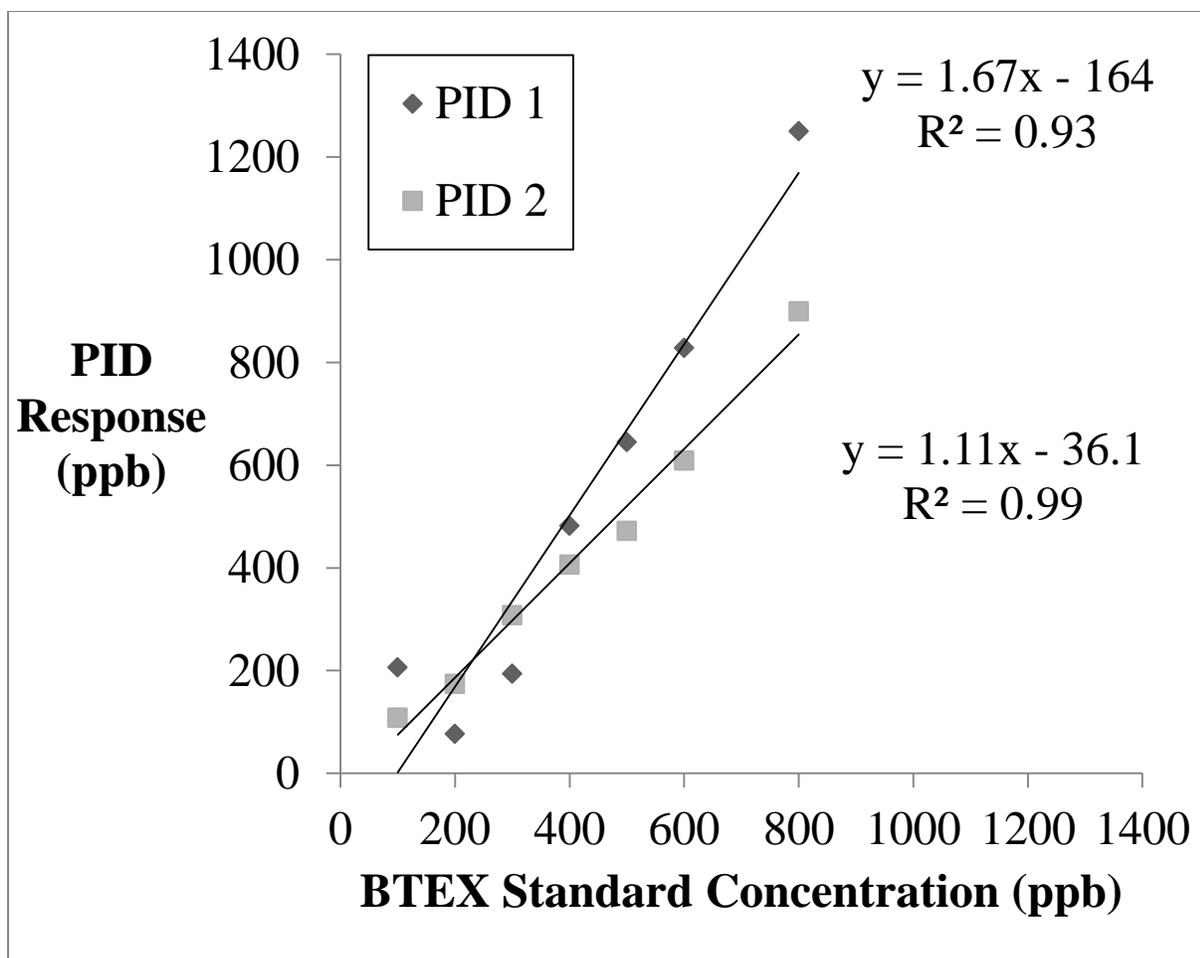


Figure 6: PID Response (mean) to a BTEX Standard, error bars are small and represent one standard deviation. Sample sizes were PID 1 n=4-6 and PID 2 n= 7-8. Any measurement that drifted for more than 6 minutes was discarded (PID 1: n=1) and PID 1 stopped operating and was removed from the study. PID 1 also experienced three negative values (100 ppb: n= 2 and 200 ppb: n= 1) which were treated as one half of the limit of detection.

PID performance was continually monitored in the laboratory before and after sampling while the PIDs were employed for the commuter exposure study (Appendix C). According to the manufacturer, the Tiger PID has a measurement range between 1 ppb- 20,000 ppm for specific compounds (Ion Science 2013); however, studies were conducted and within controlled conditions the lowest LOD for BTEX was 9.3 ppb. PID 1 produced negative measurement values three times at concentrations up to 200 ppb, at BTEX concentrations up to 200 ppb this particular instrument could not differentiate a signal from noise. The inconsistent response of PID 1 implies that without additional, more in-depth testing and instrument troubleshooting the practical LOD of this particular instrument is closer to 300 ppb BTEX. PID 2

responses were more accurate than PID 1 responses (Figure 6). Without conducting instrument testing at lower BTEX concentrations, the practical LOD for PID 2 is around 100 ppb BTEX. The difference between PID responses is likely an artifact of the individual lamp performance. Instrument drift varied between maintenance because the instruments were cleaned and the internal calibration was reset. Sample sizes for the two instruments are unequal because of instrument failure (PID 1) and excessive instrument drift during calibration (PID 1). The accuracy and precision of Ion Science Tiger PIDs were not consistent between the two units tested; however, both instruments had linear responses above the practical LODs (R^2 : 0.93 and 0.99).

Within the laboratory setting, both the Tenax TA and PID measurement methods appeared suitable to measure BTEX compounds, however the PIDs could only reliably measure concentrations above 300 ppb. The Tenax TA sampling method measured BTEX accurately, precisely, and linearly under laboratory conditions. Both PID units had linear responses to BTEX concentrations; however, PID 1 was less accurate. The Tenax TA method was able to accurately quantify BTEX at concentrations orders of magnitude smaller than either PID. The PIDs were less accurate and precise when measuring 100 ppb BTEX concentrations than the Tenax TA method.

3.2 Comparing PID and Tenax TA methods within the Fort Collins Commuter Study

The sample size of PID measurements was much smaller than planned as a result of multiple failures. Prior to having access to Tenax TA sample media, 65 PID measurements were attempted and 54 failed. Five measurements recorded all negative values, even after being corrected using calibration curves. Twenty eight measurements were discarded because there were no quality data for PID responses. PIDs were not maintained correctly; after the dilution chamber was built and the PIDs were tested, the instruments experienced substantial drift and noise. Eleven measurements were not recorded because the PID experienced a flow fault while in the personal exposure backpack before the commute. Three times the PID turned off before the commute began. The recording was not started or the PIDs did not start recording seven times. Following weekly performance evaluation, adjustments were made to the PIDs to prevent flow faults and to extend battery life, 18 consecutive measurements were attempted and

successfully recorded. Two of these 18 measurements recorded all negative values (median values: -33 and -36 ppb) and were substituted with one half of the LOD. The factory-equipped PIDs had a failure rate of 83% that made them unpractical for use in this study; however, after making adjustments to the PIDs and censoring data with calibration curves, the failure rate was reduced to 0%.

Some routes within the sub study were repeated. All commuters that completed a cycling commute completed either one or three driving commutes (Table 2 and Figure 7). Five volunteers commuted without cycling and drive only once. Two volunteers commuted once by cycling and once by driving. One volunteer commuted only by driving twice and another volunteer commuted once by cycling and three times by driving. Commutes encompassed a portion of the Fort Collins city limits (Figure 7).

Table 2: The number of volunteers who performed 0 or 1 cycling commutes and 1 to 3 driving commutes

Cycling commutes	Driving commutes	Volunteer count
0	1	5
1	1	2
0	2	1
1	3	1

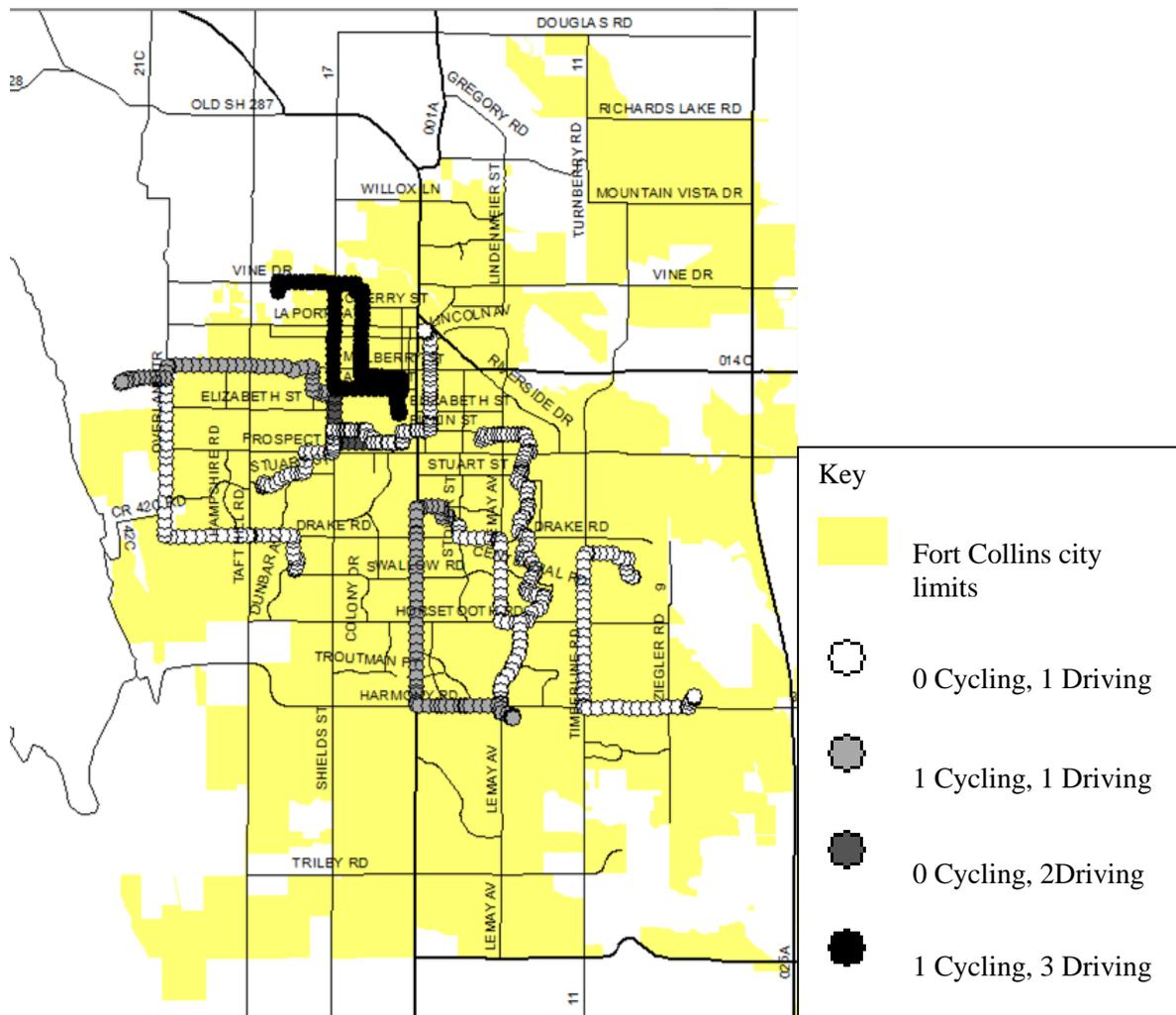


Figure 7: The distribution of routes within Fort Collins city limits and locations of repeated commutes. Sample sizes are as follows: 0 cycling and 1 driving n = 5, 1 cycling and 1 driving n = 2, 0 cycling and 2 driving n = 1, and 1 cycling and 3 driving n = 1.

Of the nine volunteers that commuted in the sub study, four volunteers repeated at least one route. With only nine volunteers participating in this study, we were unable to provide a thorough representation of every area within the Fort Collins city limits; however, commutes were performed across the central area of Fort Collins. The small sample size of this study was an inherent limitation to making generalized statements about commuter’s VOC exposures in Fort Collins.

During commuting, PID responses did not correlate well to the responses from the Tenax TA sampling method. When the total VOC response from a PID was compared to the Tenax TA response using the sum of the BTEX concentrations measured during commutes, there was a pronounced negative

trend (Figure 8). To determine if the PIDs were measuring VOCs other than BTEX, PID response was compared to the total integrated area of VOCs sampled by Tenax TA within the ionization potential of the PID. The total VOC response from a PID compared to the total VOC response from Tenax TA exhibited a weak negative trend (Figure 9). PID responses changed greatly with changing BTEX concentrations (Figure 8), yet were not very sensitive to a change in the sum of integrated peak areas (Figure 9).

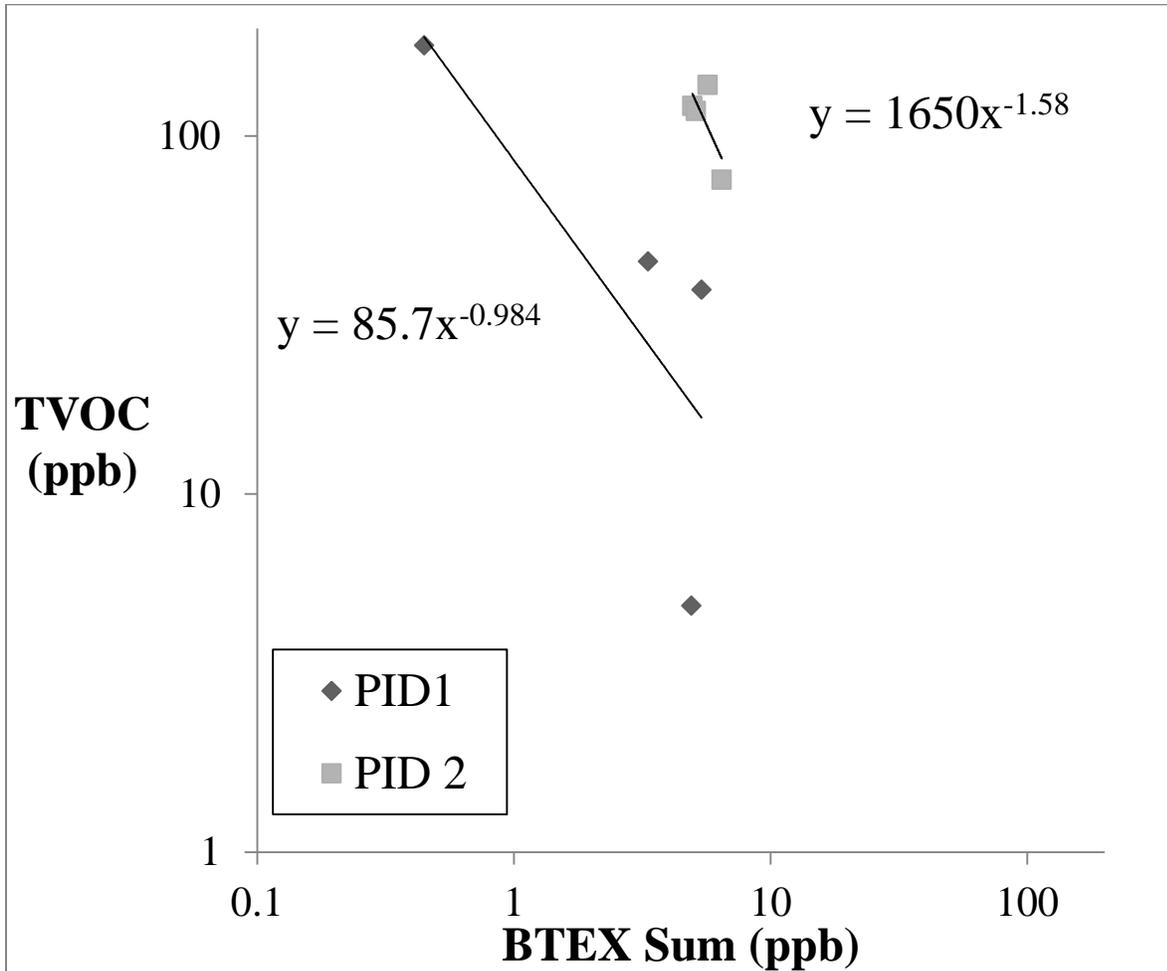


Figure 8: Relationship of PID (TVOC) to Tenax TA (BTEX Sum) methods collocated during commutes. PID data is represented as the time-weighted average of each sample. Sample sizes were PID 1: n=4, PID 2: n=4. Spearman's Correlations (r_s) are PID 1: -0.80 and PID 2: -0.40. Sample sizes are PID 1: n= 4, PID 2: n=4.

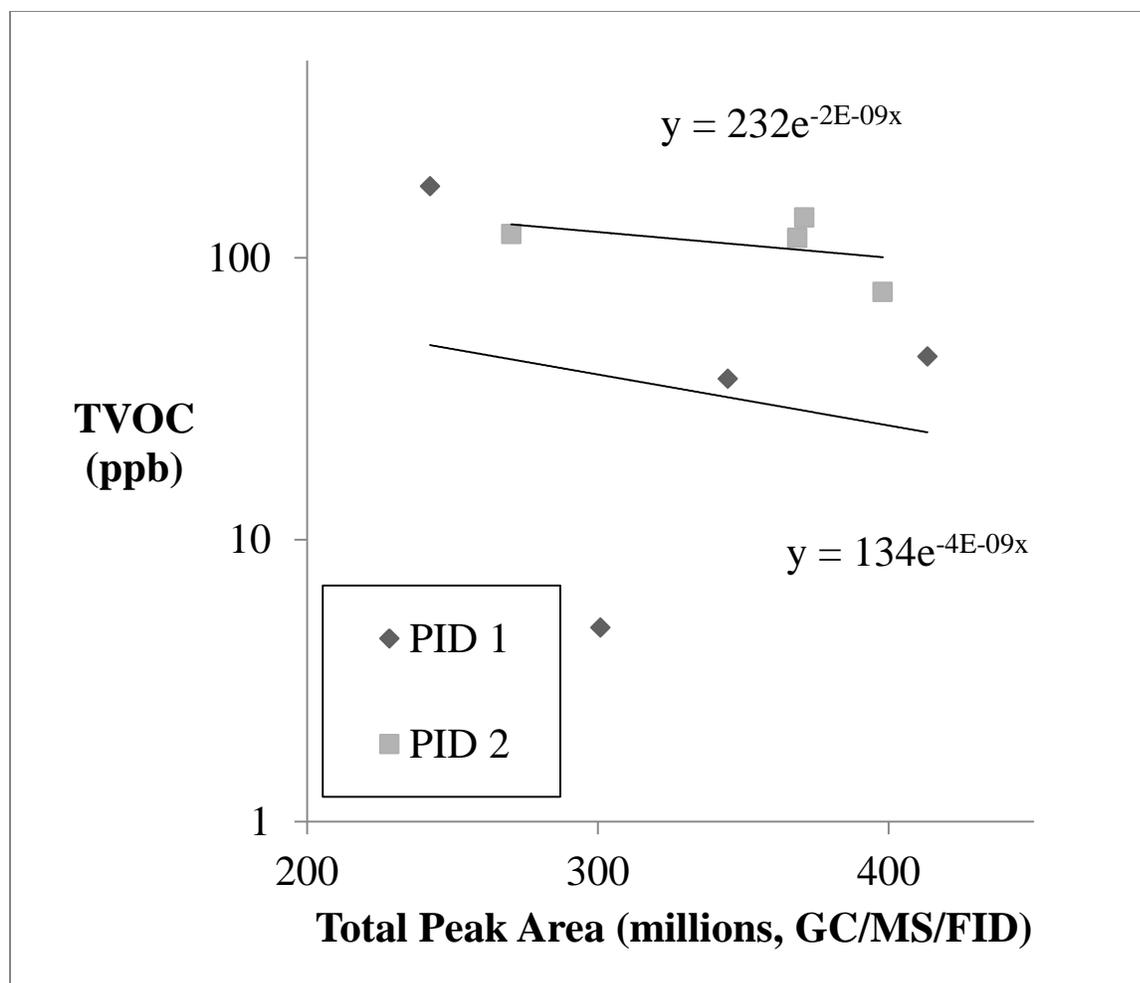


Figure 9: Responses of PID (TVOC) and the total hydrocarbon signal (Total Peak Area) from the Tenax TA sampling methods collocated during on road commutes. PID response is characterized by the time-weighted average of the TVOC for each sample. Total Peak Area is the sum of total integrated peak area of hydrocarbon responses from the Tenax TA sampling method that is assumed to be within ionization potential of the PID (only compounds with a retention time less than acetonitrile (ionization potential: 12.19 eV) were assumed to be within the ionization range of the 10.6 eV PID). Spearman's Correlations (r_s) are PID 1: -0.20 and PID 2: -0.40. Sample sizes are PID 1: n= 4, PID 2: n=4.

Neither PID's responses had a positive correlation with Tenax TA responses. PID responses were not very sensitive to a change in the total VOC peak areas from Tenax TA measurements. If a PID was primarily measuring the same VOCs as the Tenax TA method, there should be a positive correlation between the two sets of data; however, there was an inverse trend between the total VOCs measured by the PIDs and the sum of BTEX concentrations measured by Tenax TA (Figure 8). The PID responses were an order of magnitude greater than the BTEX Sum from the Tenax TA sampling method (Figure 8).

If the BTEX measured was from traffic, the inverse trend between the PID and Tenax TA responses suggests the PID signal could also be from a traffic-related air pollutant that has an inverse relationship to BTEX concentrations.

The total VOC concentrations measured by PIDs were found to have a negative trend to VOCs measured using the Tenax TA method (Table 3). With the exception of xylenes, there was a poor and negative correlation between the total VOCs measured by PIDs and every VOC measurement sampled by the Tenax TA method (Table 3, Figures 8 and 9). Correlations were not improved by correcting PID measurements with BTEX Response Factors based on the percentage of BTEX and non-BTEX compounds within each Tenax TA sample. With the exception of ethylbenzene, all individual BTEX compounds measured using the Tenax TA sampling method were correlated (at 95% confidence, two-tailed test) with total BTEX (Table 3). The sum of all VOC peak areas (BTEX + other compounds) was correlated with toluene concentrations and with total BTEX (Table 3).

Table 3: Spearman Correlation Coefficients (r_s) for commuter VOC exposures measured by Tenax TA (benzene, toluene, ethylbenzene, xylenes, BTEX sum, and TVOC_a, the sum of integrated peak areas within PID ionization potential) and PIDs (PID 1: TVOC and PID 2: TVOC). Sample sizes for PID comparisons are n=4 and for non-PID comparisons n=15.

	Benzene	Toluene	Ethylbenzene	Xylenes	Total BTEX	TVOC _a
Benzene	1					0.49
Toluene	0.68*	1				0.58*
Ethylbenzene	0.21	0.23	1			0.34
Xylenes	0.34	0.26	0.66*	1		0.41
Total BTEX	0.81**	0.85**	0.33	0.53*	1	0.71*
PID 1: TVOC	-0.80	-0.80	-0.77	-1.0**	-0.80	-0.20
PID 2: TVOC	0	0.20	0.26	-0.80	-0.40	-0.40

Note: *p < 0.05; **p < 0.001

The time-resolved total VOC measurement method (PIDs) could not measure commuter BTEX exposures as well as the time-integrated Tenax TA method. The correlation between individual BTEX constituents and the sum of all of the BTEX constituents suggests the BTEX source is consistent and that benzene, toluene, and xylenes are predictors of the BTEX sum. The statistically significant correlation between both benzene and toluene concentrations and ethylbenzene and xylenes concentrations (Table 3) suggests there is a consistent source of benzene and toluene and ethylbenzene and xylenes. A statistically significant correlation was not found between ethylbenzene and the BTEX sum; however, ethylbenzene was identified in only 5 of 15 Tenax TA samples. Within Tenax TA measurements of commuter VOC exposures, benzene and toluene concentrations were correlated (p-value: <0.05) and ethylbenzene and xylenes were significantly correlated (Table 3).

The lack of significant correlation but negative trend between PID responses and the Tenax TA responses to the BTEX sum (Figure 8) indicates the PIDs were responding to something other than BTEX, yet possibly from the same source because of the trend. The PIDs may be responding to another pollutant such as nitrogen dioxide which has previously been known to have an inverse relationship with BTEX (EPA 2008). Ion Science reports the Tiger PID will respond to nitrogen dioxide however the response is approximately two orders of magnitude less than the response from BTEX (Factory Direct 2013). PIDs produce signals of varying strength for VOCs with different ionization energies. The PID's compound-specific responses are termed Response Factors; both PIDs were calibrated to a standard that contained BTEX to compensate for this effect. The correlation between PID and Tenax TA measurements was not improved after adjusting the PID responses proportionately to the response factors of BTEX which indicates the BTEX response factors were not hindering the PID signal. The FID signal (part of the GC/MS/FID output) produces a linear response to the number of carbons within the compound of interest which is why Tenax TA sampling with GC/MS/FID analysis quantifies VOCs more reliably than the PID. The inability of the PID method to resolve BTEX at on road concentrations in Fort Collins by default makes the Tenax TA the method of choice to evaluate commuter exposures to BTEX.

Very little nitrogen dioxide (NO₂) exposure data was collected in this study, but there was a positive correlation between the PID and Series 500 IAQ NO₂ monitor. Only three commutes had data for both the PID and the Series 500 IAQ because there were only two of each instrument and the Series 500 IAQ struggled to remain on for the time preceding the commute. The PID and Series 500 IAQ responses showed a positive correlation although the Series 500 IAQ responses were much larger than the PID responses (Figure 10).

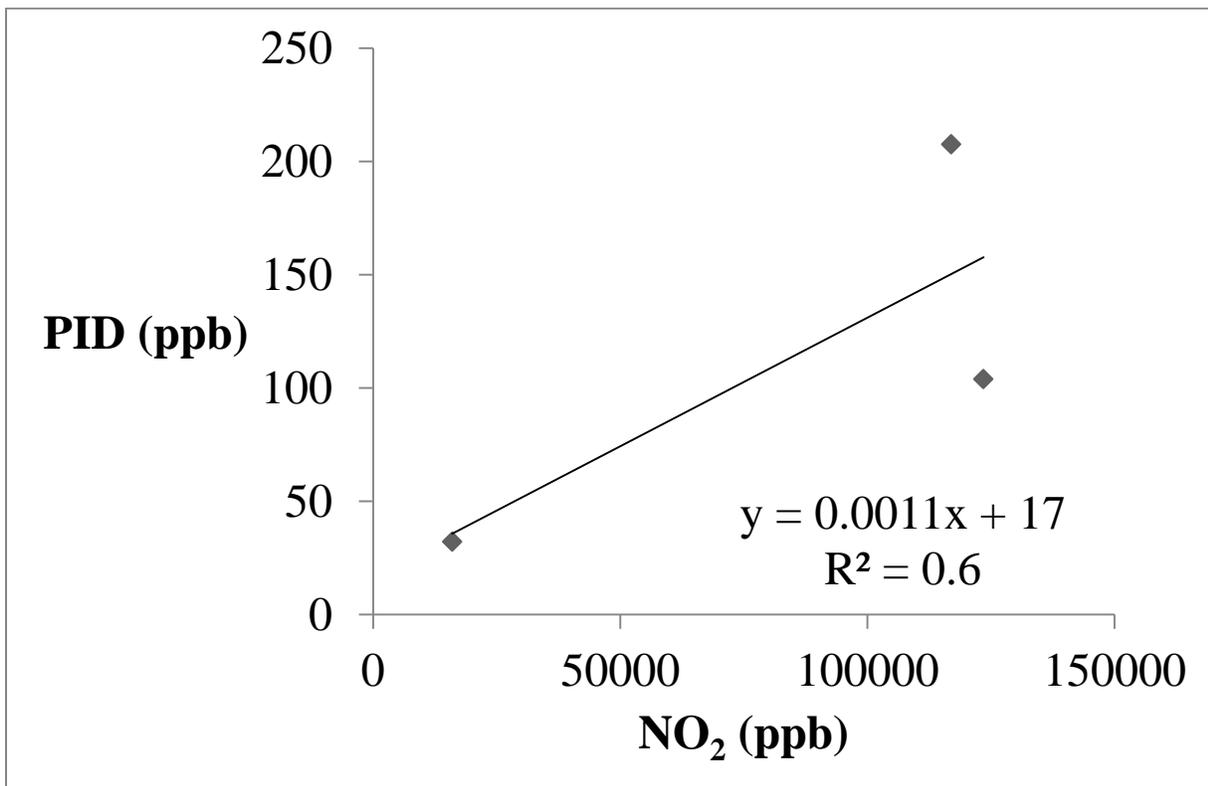


Figure 10: Correlation between PID and 500 IAQ (NO₂) responses (n = 3).

Unfortunately there were only three commutes that had both PID and Series 500 IAQ data. Within the very small sample, there was a positive correlation which means these two instruments could be responding to the same signal. The large discrepancy in response values could be a mechanism of one or both of the instruments' ability to resolve NO₂. The PID was calibrated using a BTEX standard, not isobutylene which has published response factors, so the only way to determine the response factor of the

PID with the current calibration setting to NO₂ would be to determine it empirically or to calibrate the PIDs with an isobutylene standard.

3.3 Evaluating commuter exposures within Fort Collins, Colorado

Tenax TA data were used to evaluate commuter BTEX exposures; PID data were not used for these analyses due to the uncertainties surrounding the PID data. Cycling and driving exposures with windows open and closed were compared using a GLM. The underlying assumptions inherent to the GLM calculations were met prior to conducting analyses. Although the model considered numerous factors including commute time, date, outdoor temperature, outdoor relative humidity, mixing height, and the sum of total VOC peak areas, no factors were significant contributors and the final model did not include any covariates. Subject was treated as a fixed variable for all analyses because volunteers were not randomly selected, however, repeated commutes within a volunteer were accounted for; inter-person commutes were assumed to be independent. Driving commuters with closed windows experienced significantly greater TWA BTEX exposures than cyclists (Figure 11, one-tailed test at 95 % confidence p-value: 0.04).

Within this study, commuting on a busy street appeared to have an effect on BTEX exposures while cycling but not while driving. The greatest exposure that occurred while cycling (4.6 ppb, Table 4 and Figure 11) occurred during a commute along College Avenue, a busy street; the two other cycling routes occurred mainly along side streets and had lower exposures. The third lowest BTEX exposure that occurred while driving (in a 2005 Honda Pilot) with closed windows (3.6 ppb) occurred while driving along College Avenue. The two greatest BTEX exposures (10.3 and 11.3 ppb) occurred while driving with windows closed inside of a 2002 Chevrolet Silverado truck and a 2005 Subaru Impreza, respectively; one route was along Shields, a busy street and the other route travelled through side streets. Another commuter who drove (in a 1998 Oldsmobile Achieva) along Shields once with windows closed and once with windows open experienced relatively low BTEX exposures of 3.3 and 4.9 ppb, respectively.

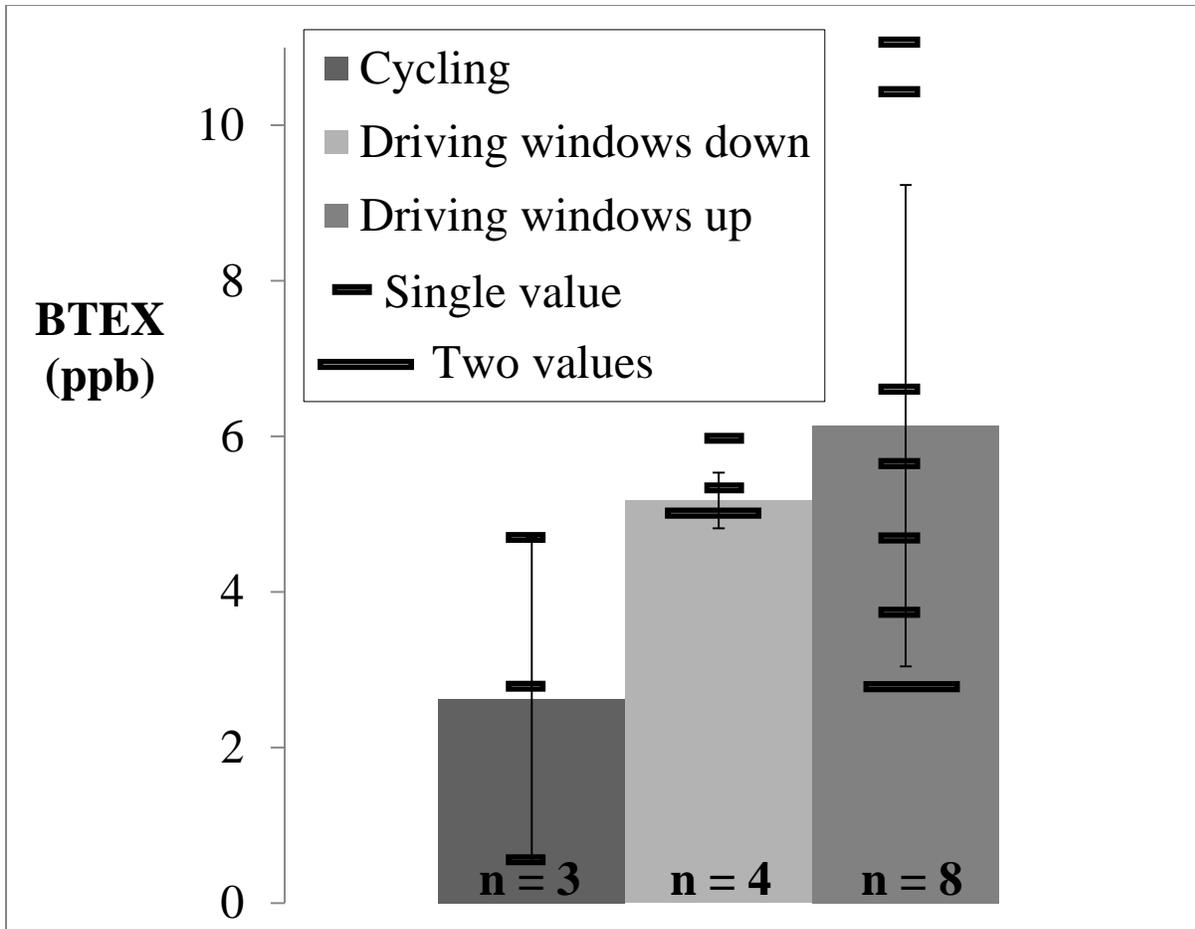


Figure 11: Commuter BTEX exposure (measured with Tenax TA) between cyclists, drivers with open windows (windows down), and drivers with closed windows (windows up). Drivers with closed windows experienced greater BTEX exposures than cyclists (p-value: 0.04 at 95% confidence, one-tailed test). Individual measurements and means (cycling: 2.62, driving windows down: 5.17, and driving windows up: 6.14 ppb) are shown and error bars represent one standard deviation. Sample sizes are cycling n = 3, driving windows open n= 4, and driving windows closed n = 8.

Table 4: Commuter BTEX exposures (ppb) by volunteer, mode, and window position.

Volunteer	Mode	Windows	Benzene	Toluene	Ethylbenzene	Xylenes	BTEX sum
A	Car	Closed	0.8*	1.2	0.0	1.4	2.5
A	Car	Open	1.0	1.9	0.3	1.8	4.9
B	Car	Open	1.8	3.9	0.0	0.0	5.7
C	Car	Closed	1.7	1.9	0.0	1.7	5.4
D	Car	Closed	2.9	3.8	0.4	3.2	10.3
D	Car	Open	1.0	2.3	0.2	1.5	5.0
D	Car	Open	2.1	2.6	0.0	0.4	5.1
D	Bike	-	1.1	1.9	0.0	1.6	4.6
E	Car	Closed	2.5	5.5	0.6	2.7	11.3
F	Car	Closed	0.7*	2.4	0.0	0.2*	2.4
G	Bike	-	0.1*	0.3	0.0	0.0	0.3
G	Car	Closed	2.2	1.4	0.0	0.2*	3.6
H	Car	Closed	1.1	3.7	0.0	0.4*	4.8
H	Bike	-	0.6	1.1	0.1	0.9	2.8
I	Car	Closed	1.3	3.6	0.0	1.5	6.5

Note: * indicates the measured value was below the limit of detection for that sample. Values were used as is within the statistical analyses.

Driving commuters with closed windows were exposed to greater TWA BTEX concentrations than cyclists (TWA p-value: 0.04), which is consistent with other studies that found drivers experienced greater exposures than cyclists and were conducted in larger cities (Table 5). The consistent trend of drivers experiencing greater TWA BTEX exposures than cyclists, regardless of the city size where the studies were conducted, suggests that vehicles were the predominant BTEX source within all of these studies. Drivers that had closed windows experienced greater (although not significantly) BTEX exposures than drivers with open windows. On average, both driving and cycling commuters in Fort Collins experienced lower BTEX exposures in 2013 than commuters in Boston and Copenhagen in 1989 and 1998, respectively (Table 5). The lower BTEX exposures of commuters in Fort Collins may be attributable to the smaller population density of the city. The findings of this study indicate that commuters in Fort Collins may be able to make a conscious choice to reduce their TWA BTEX exposure on the outside of their bodies by choosing to cycle instead of drive to work (Figure 11, Table 4), however,

further studies with larger sample sizes should be conducted to confidently accept or refute this preliminary finding.

Table 5: A comparison of the time-weighted average of commuter BTEX exposures while driving and cycling in Fort Collins, Colorado (Summer 2013), Boston, Massachusetts (Winter 1989) (C.-C. Chan et al. 1991), and Copenhagen, Denmark (Summer 1998) (Rank, Folke, and Homann Jespersen 2001). Units are expressed in $\mu\text{g}/\text{m}^3$ and sample standard deviations are indicated in parentheses.

	Fort Collins (s)		Boston (s)		Copenhagen (s)	
	Driving (n=12)	Cycling (n=3)	Driving (n=40)	Cycling (n=11)	Driving (n=4)	Cycling (n=4)
Benzene	5.14 (2.32)	1.97 (1.60)	17.0 (10.0)	9.2 (7.2)	14.4 (2.8)	5.23 (0.49)
Toluene	10.7 (4.80)	4.28 (2.99)	33.1 (20.4)	16.3 (11.4)	69.3 (19.0)	20.6 (1.6)
Ethylbenzene	0.55 (0.905)	0.178 (0.309)	5.8 (3.9)	2.4 (2.0)		
m-, p- Xylenes			20.9 (13.8)	10.0 (7.2)		
o- xylenes			7.3 (4.8)	3.0 (2.5)		
m-, p-, o- xylenes	5.39 (4.43)	3.60 (3.42)				
Ethylbenzene and Xylenes					66.7 (16.1)	18.1 (5.8)

4.0 CONCLUSION

This study compared two methods of measuring commuter BTEX exposures in Fort Collins: time-resolved PID measurements and time-integrated Tenax TA measurements (analyzed with GC/MS/FID). The Tenax TA sampling method was used to determine the effect of commute mode (driving or cycling) on commuter BTEX exposures. The Ion Science Tiger PID measures time-resolved VOCs and is affordable and mobile enough to measure commuter exposures. There is no literature that has evaluated the accuracy and precision of the Ion Science Tiger PID when measuring low concentrations (ppb level) of BTEX. Prior studies have found city drivers experience greater BTEX exposures compared to cyclists, but this relationship had not been evaluated within a midsize city with little traffic-related air pollution. While cities may have substantial populations and elevated air pollution, many Americans live in midsize cities and it is important to evaluate the air pollution exposures of this population.

4.1 Study limitations

Intake was not considered within this study. Cyclists may experience greater ventilation than drivers which may increase their intake of air pollutants and thus may increase their risk of adverse health effects associated with air pollutant exposure while commuting. Future work should include a more comprehensive evaluation of intake by incorporating ventilation rates for individuals. This study also did not evaluate physiologic changes indicative of pollutant uptake, dose, or adverse health effects. Future work should consider inclusion of biomarkers to determine both air pollutant doses and short-term markers of effect on the body. This study was also limited by a small sample size. This sample (n = 9) may not be representative of all Fort Collins residents' BTEX exposures. Commuter routes were spread across central Fort Collins; no routes covered the northern or southern areas. Increasing the number of volunteers and commuting locations would give a more accurate representation of commuter BTEX exposures in Fort Collins.

The response of the PID to NO₂ was unknown at the onset of this study. PID readings may have been inflated because they were measuring NO₂ in addition to VOCs. The evaluation of PID response to NO₂ was outside the scope of this study.

Peak VOC exposures were not evaluated within this study because we were not convinced the time-resolved measurement method (PIDs) was measuring VOCs. The source of PID response remains unknown but was not solely BTEX. Measuring peak BTEX exposures is an important step to understanding commuter's BTEX exposures.

4.2 Study findings

Two measurement methods (PIDs and Tenax TA) were compared in the laboratory to determine if they can resolve the compounds of interest (BTEX) in a controlled environment. The Tenax TA sampling method with subsequent GC/MS/FID analysis was evaluated at BTEX concentrations ranging from 0.1 to 100 ppb. The Tenax TA method was accurate, precise, linear, and had LODs for BTEX below expected on-road concentrations in Fort Collins. PID testing occurred in the laboratory at BTEX concentrations ranging from 100 to 800 ppb, because of the great frequency of PID responses that were observed between this range during a preliminary study. The response between the two PIDs was inconsistent (one instrument had a practical LOD of at least 200 ppb lower than the other instrument), yet instrument response above the LODs was precise and linear. Lamp performance should be tested before and after each use. Within the laboratory both the Tenax TA and the PID measurement methods measured BTEX although the practical Tenax TA method LODs (< 1 ppb for BTEX) were much lower than the practical PID LODs (100- 300 ppb, instrument dependent).

Commuter TWA BTEX exposures ranged from 0.45 to 11.3 ppb; the majority of commuter BTEX exposures were below PID LODs. The PIDs did not reliably measure commuter BTEX concentrations in Fort Collins. Although commuter BTEX exposures measured in Fort Collins by Tenax TA was below the PID LODs for 13 of 15 samples, the PIDs measured something else at a much greater concentration. An inverse relationship was observed between Tenax TA responses and PID responses. The negative trend observed between PID responses and Tenax TA responses suggests the PIDs were measuring something

contained within vehicle exhaust that was not BTEX, such as other VOCs or NO₂. When choosing a measurement method, it is important to consider all compounds (including non-VOCs) a PID may measure, especially if they could be present in greater concentrations than the VOC (s) of interest.

Commuters who drove with their windows closed experienced greater TWA BTEX exposures than commuters who cycled. Because there is no safe level of benzene exposure, lowering diurnal BTEX exposures experienced while commuting may reduce the health risks associated with these exposures. The significance of mode when evaluating BTEX exposures experienced by commuters in central Fort Collins is consistent with commuter exposures from prior studies that occurred in more populous areas. People who live in midsize cities and choose to cycle to work instead of drive with their windows closed may be able to reduce their TWA BTEX exposures. Lowering chronic BTEX exposures may reduce the risk of adverse health effects associated with BTEX exposures; however, vehicle exhaust contains many air pollutants other than BTEX which can be inhaled and could be more harmful to human health than BTEX and cyclists with increased respiration could experience an increased risk.

On average, Fort Collins commuters experienced lower TWA BTEX exposures than commuter exposures observed in prior studies which were conducted in larger cities (Boston and Copenhagen). Living in an area with less vehicle traffic could lower traffic-related BTEX exposures that occur on road as well as in residential areas. The health risks associated with chronic BTEX exposures may be reduced by living in a less populous area with less traffic and traffic-related air pollution exposures.

4.3 Future directions

The BTEX source within a vehicle should be determined. Drivers with closed windows experienced greater BTEX exposures (although not significantly) than drivers with open windows which suggests a driver's BTEX exposure could be coming from the vehicle being driven. If in-car BTEX comes from a point source such as a ventilation system or an exhaust leak, lowering drivers' BTEX exposures could be a relatively simple task. There are activated charcoal filters that will remove VOCs and could be placed inline of a vehicle ventilation system; to our knowledge none of the vehicles used in this study had an activated carbon filter to remove VOCs. Exhaust leaks can be patched. If the BTEX exposure of drivers

can be reduced, health risks associated with BTEX exposure could theoretically be reduced for drivers all over the world.

Elevated BTEX exposures could increase health risks for commuters. Although PIDs could not measure commuter BTEX exposures, a more sensitive and reliable time-resolved instrument could identify locations, habits, or trends that are associated with elevated VOC exposures that occur while commuting. Identifying associations between commuters and scenarios that are associated with elevated health risks could empower commuters, home buyers, and car buyers to make informed decisions pertaining to their personal VOC exposures.

To improve the results of this study, a different technology could be used to resolve commuter BTEX exposures. A portable GC (such as the FROG-4000) would be an improved method to measure BTEX exposures because individual VOC species could be quantified in real time, which could be used to identify locations, habits, or trends that are associated with elevated BTEX exposures. Conducting a year-round commuter study with a larger sample size and better representation of Fort Collins would determine how sensitive commuter's BTEX exposures are to seasonal and other environmental changes. The inverse association between PID and Tenax TA BTEX measurements was not expected or explained within this study; further exploration of this phenomenon is recommended.

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APPENDIX A: IRB APPROVALS

Appendix A includes the IRB approval for the Fort Collins Commuter Study and for the sub study investigating commuter's VOC exposures.

NOTICE OF APPROVAL FOR HUMAN RESEARCH

DATE: October 26, 2012
TO: Peel, Jennifer, 1681 Env & Rad Health Sciences
Voldkens, John, 1681 Env & Rad Health Sciences, Clark, Maggie, Nickoloff, Jac, 1681 Env & Rad Health Sciences
FROM: Barker, Janell, Coordinator, CSU IRB 1
PROTOCOL TITLE: The Commuter Exposure Study: Linking Exposure, Source-Receptor Models, and Health
FUNDING SOURCE: NONE
PROTOCOL NUMBER: 11-2911H
APPROVAL PERIOD: Approval Date: November 14, 2012 Expiration Date: November 13, 2013

The CSU Institutional Review Board (IRB) for the protection of human subjects has reviewed the protocol entitled: The Commuter Exposure Study: Linking Exposure, Source-Receptor Models, and Health. The project has been approved for the procedures and subjects described in the protocol. This protocol must be reviewed for renewal on a yearly basis for as long as the research remains active. Should the protocol not be renewed before expiration, all activities must cease until the protocol has been re-reviewed.

If approval did not accompany a proposal when it was submitted to a sponsor, it is the PI's responsibility to provide the sponsor with the approval notice.

This approval is issued under Colorado State University's Federal Wide Assurance 00000647 with the Office for Human Research Protections (OHRP). If you have any questions regarding your obligations under CSU's Assurance, please do not hesitate to contact us.

Please direct any questions about the IRB's actions on this project to:

Janell Barker, Senior IRB Coordinator - (970) 491-1635 Janell.Barker@Colostate.edu
Evelyn Swiss, IRB Coordinator - (970) 491-1381 Evelyn.Swiss@Colostate.edu

Barker, Janell



Barker, Janell

Approval is to continue to recruit the remaining 94 participants for Aim 1 of the study with the approved recruitment & consent material. The above-referenced project was approved by the Institutional Review Board with the condition that the approved consent form is signed by the subjects and each subject is given a copy of the form. NO changes may be made to this document without first obtaining the approval of the IRB.

Approval Period: November 14, 2012 through November 13, 2013
Review Type: EXPEDITED
IRB Number: 00000202
Funding: National Institute of Health : 110174

NOTICE OF APPROVAL FOR HUMAN RESEARCH

DATE: September 11, 2013
TO: Peel, Jennifer, 1681 Env & Rad Health Sciences
Voldkens, John, 1681 Env & Rad Health Sciences, Clark, Maggie, Nickoloff, Jac, 1681 Env & Rad Health Sciences
FROM: Barker, Janell, Coordinator, CSU IRB 1
PROTOCOL TITLE: The Commuter Exposure Study: Linking Exposure, Source-Receptor Models, and Health
FUNDING SOURCE: Funding - Grants/Contracts, Other Funding
PROTOCOL NUMBER: 11-2911H
APPROVAL PERIOD: Approval Date: September 11, 2013 Expiration Date: November 13, 2013

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Amendment approval is to add a sub-study to be conducted under Ashleigh Kayne by adding a tube and pump to measure the volatile organic compound air pollution exposure using the consent addendum to obtain consent from 10 participants.

Approval Period: September 11, 2013 through November 13, 2013
Review Type: EXPEDITED
IRB Number: 00000202
Funding: National Institute of Health, CSU CVMS College Research Council, NIOSH Mountain and Plains, Education and Research Center

APPENDIX B: BENZENE, TOLUENE, ETHYLBENZENE, AND XYLENE CALIBRATION CURVES
FOR THE TENAX TA SAMPLING METHOD WITH SUBSEQUENT GC/MS/FID ANALYSIS

Appendix B includes calibration curves of BTEX concentrations sampled with Tenax TA and analyzed with GC/MS/FID. The GC/FID Peak Height represents the FID signal height of the areas that were used for quantification at each concentration. Each Tenax TA sample was loaded with 1,000 standard cubic centimeters of calibration gas to approximate the average volume sampled during each commute. The odd-numbered graphs contain all measured values and the even-numbered graphs include the aforementioned data with the exception of the greatest value. Linear regression equations, correlation coefficients (R^2), and LODs are located within each graph. Each point represents a mean and error bars represent one standard deviation of test replicates. Additional notes and details pertaining to the figures can be found at the end of this document.

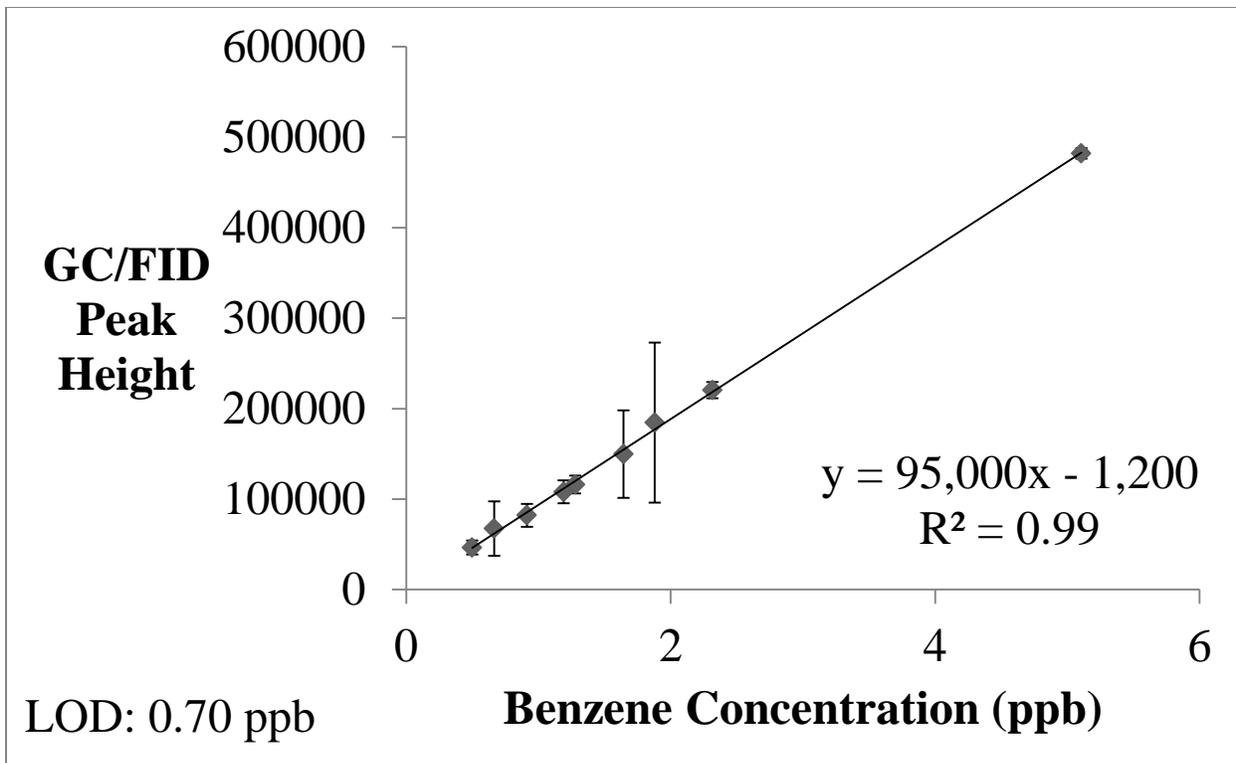


Figure 12: Calibration curve (linear regression) of Tenax TA GC/MS/FID sample method mean responses to benzene standard. Error bars represent one standard deviation of 3-5 replicates.

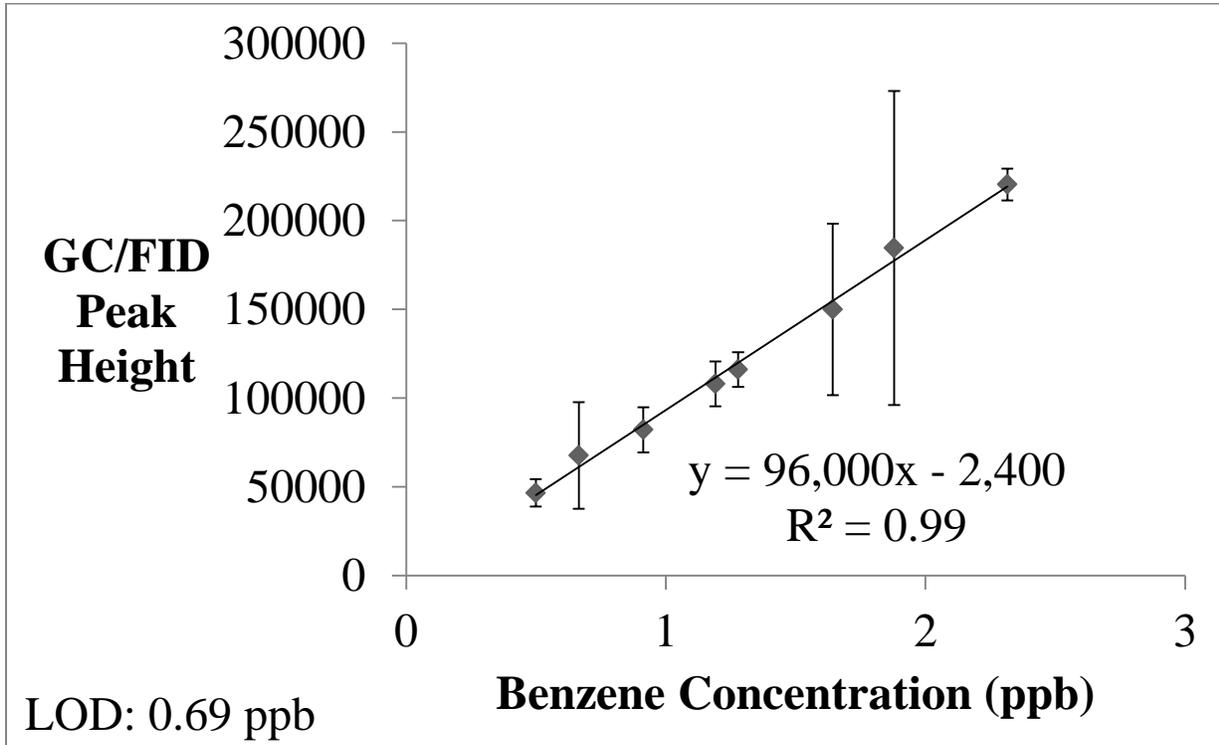


Figure 13: Calibration curve (linear regression) of Tenax TA GC/MS/FID sample method mean responses to benzene standard excluding the largest mean. Error bars represent one standard deviation of 3-5 replicates.

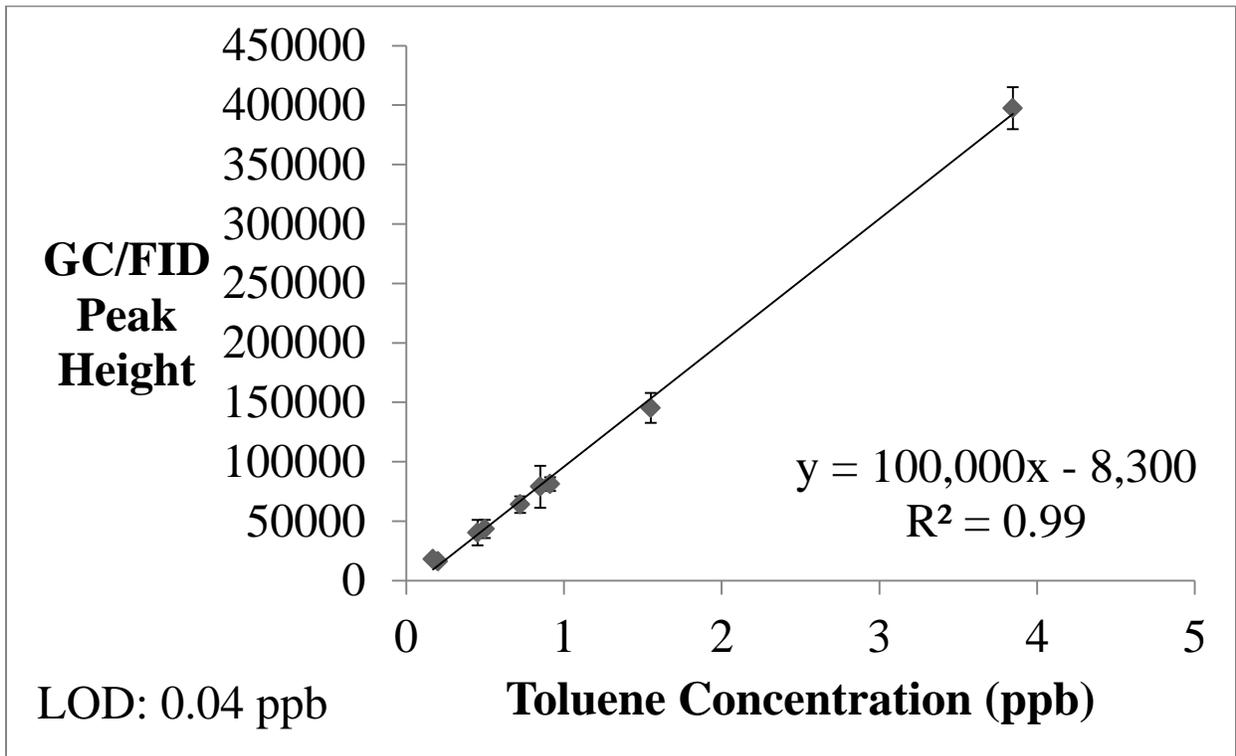


Figure 14: Calibration curve (linear regression) of Tenax TA GC/MS/FID sample method mean responses to toluene standard. Error bars represent one standard deviation of 3-5 replicates.

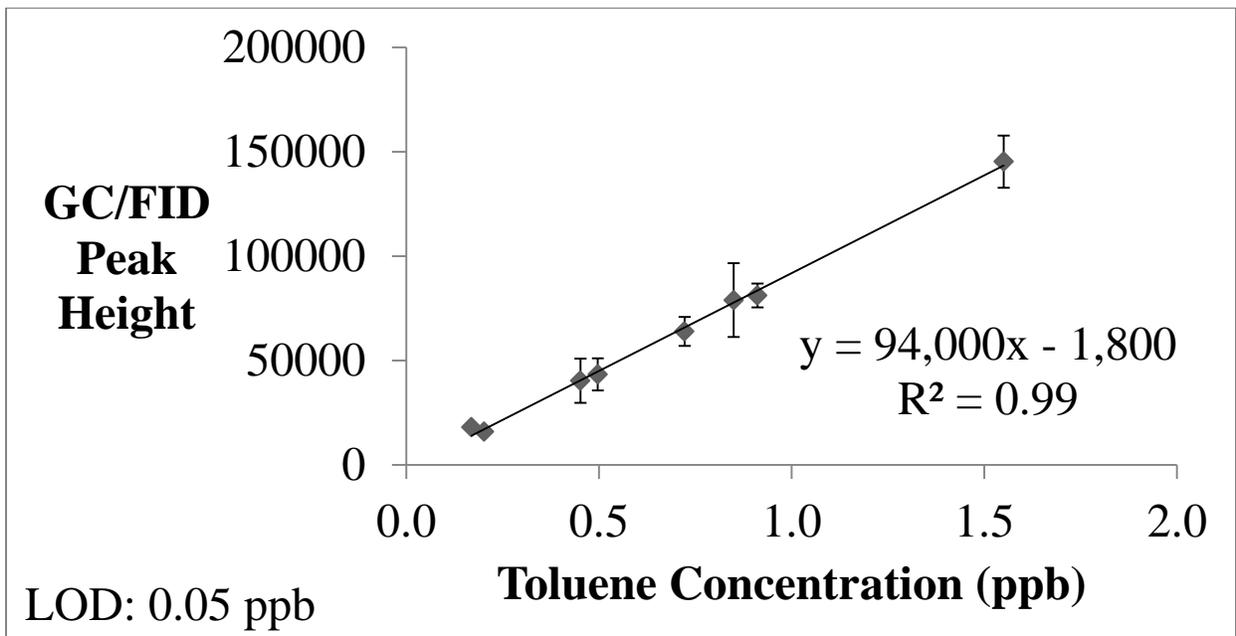


Figure 15: Calibration curve (linear regression) of Tenax TA GC/MS/FID sample method mean responses to toluene standard excluding the largest mean. Error bars represent one standard deviation of 3-5 replicates.

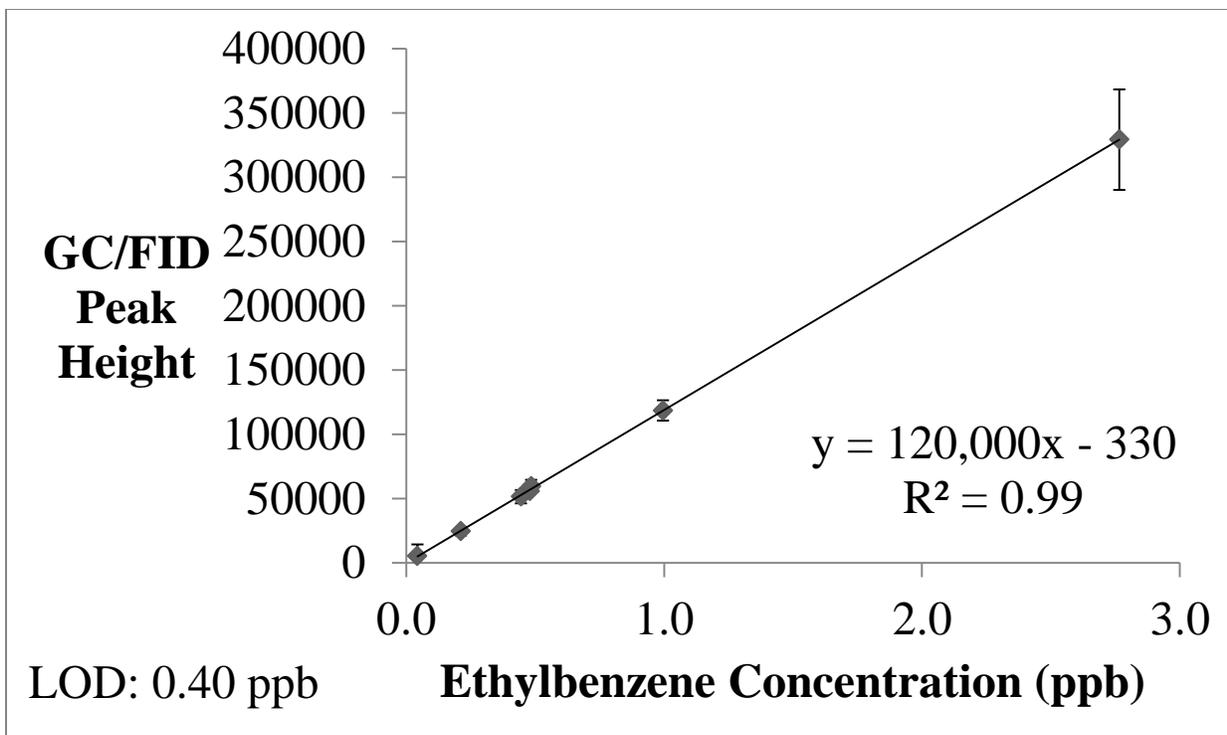


Figure 16: Calibration curve (linear regression) of Tenax TA GC/MS/FID sample method mean responses to ethylbenzene standard. Error bars represent one standard deviation of 3-5 replicates.

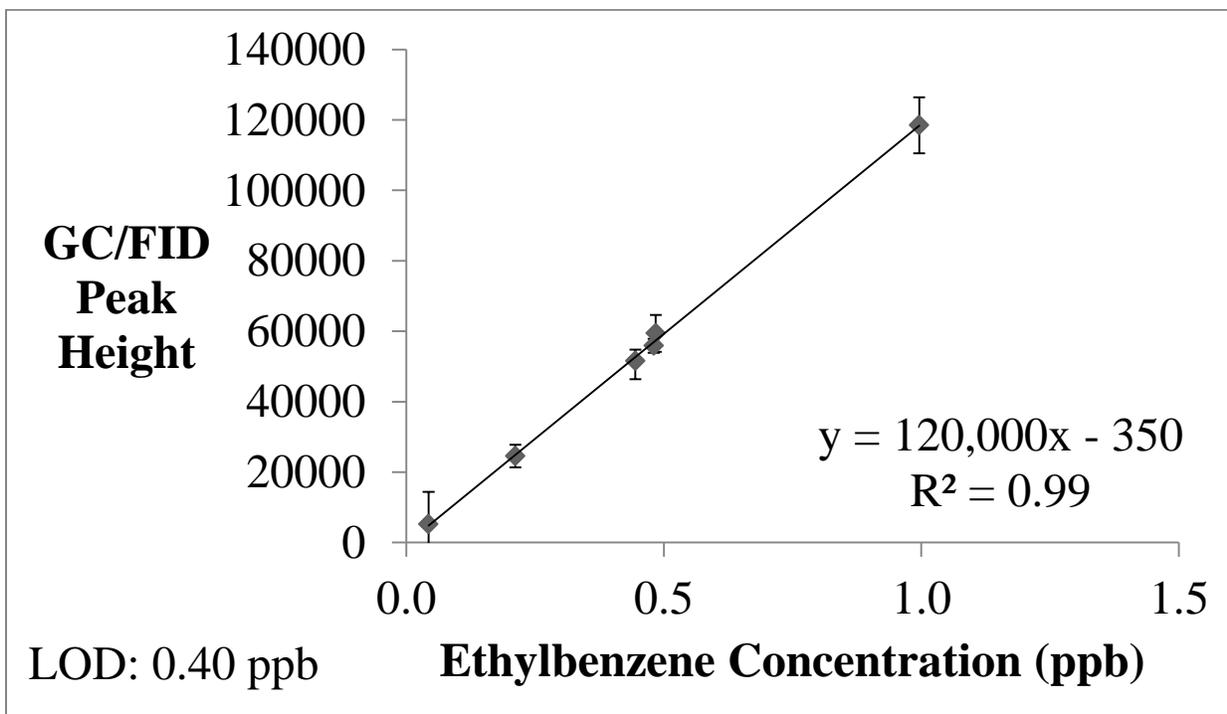


Figure 17: Calibration curve (linear regression) of Tenax TA GC/MS/FID sample method mean responses to ethylbenzene standard excluding the largest mean. Error bars represent one standard deviation of 3-5 replicates.

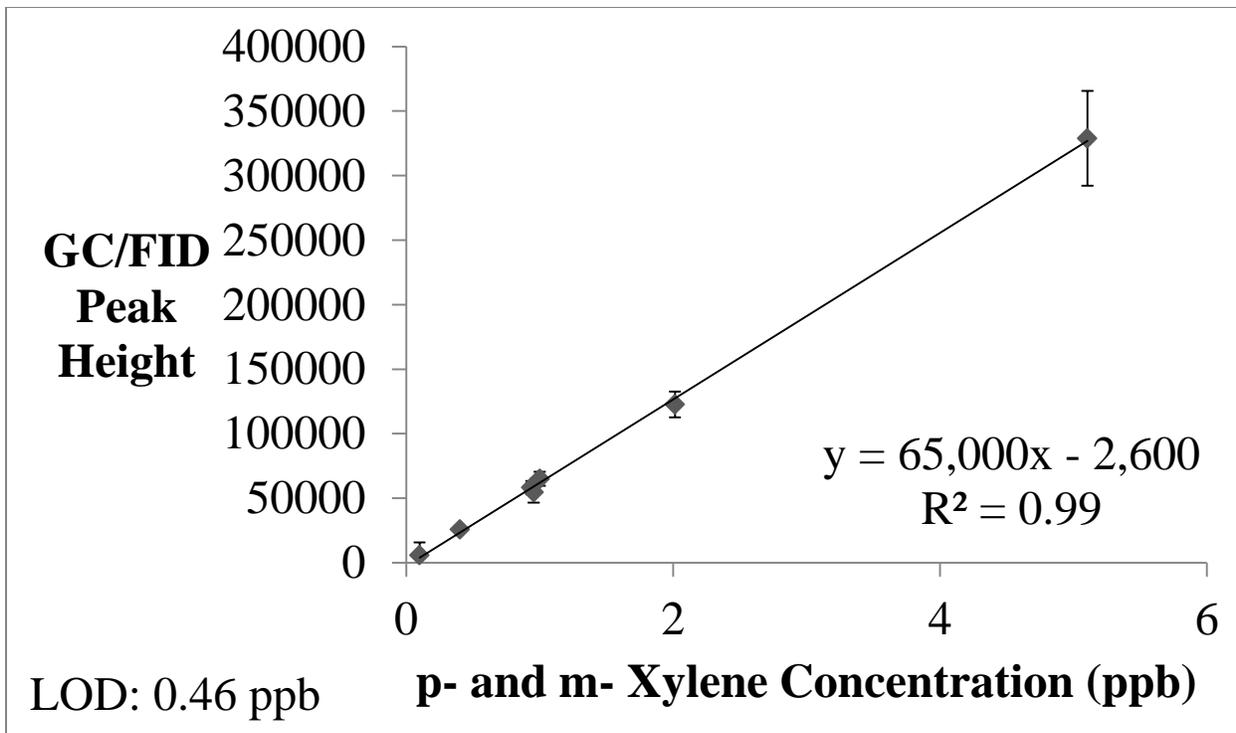


Figure 18: Calibration curve (linear regression) of Tenax TA GC/MS/FID sample method mean responses to p- and m- xylene standard. Error bars represent one standard deviation of 3-5 replicates.

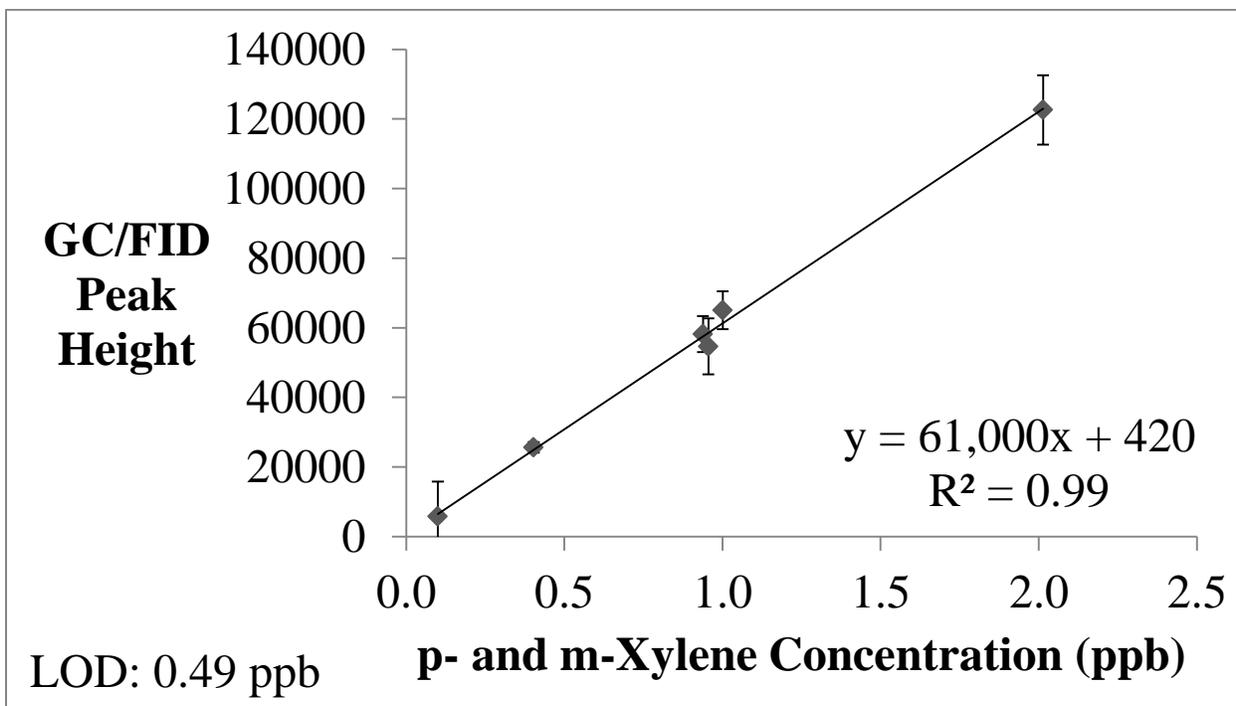


Figure 19: Calibration curve (linear regression) of Tenax TA GC/MS/FID sample method mean responses to p- and m- xylene standard excluding the largest mean. Error bars represent one standard deviation of 3-5 replicates.

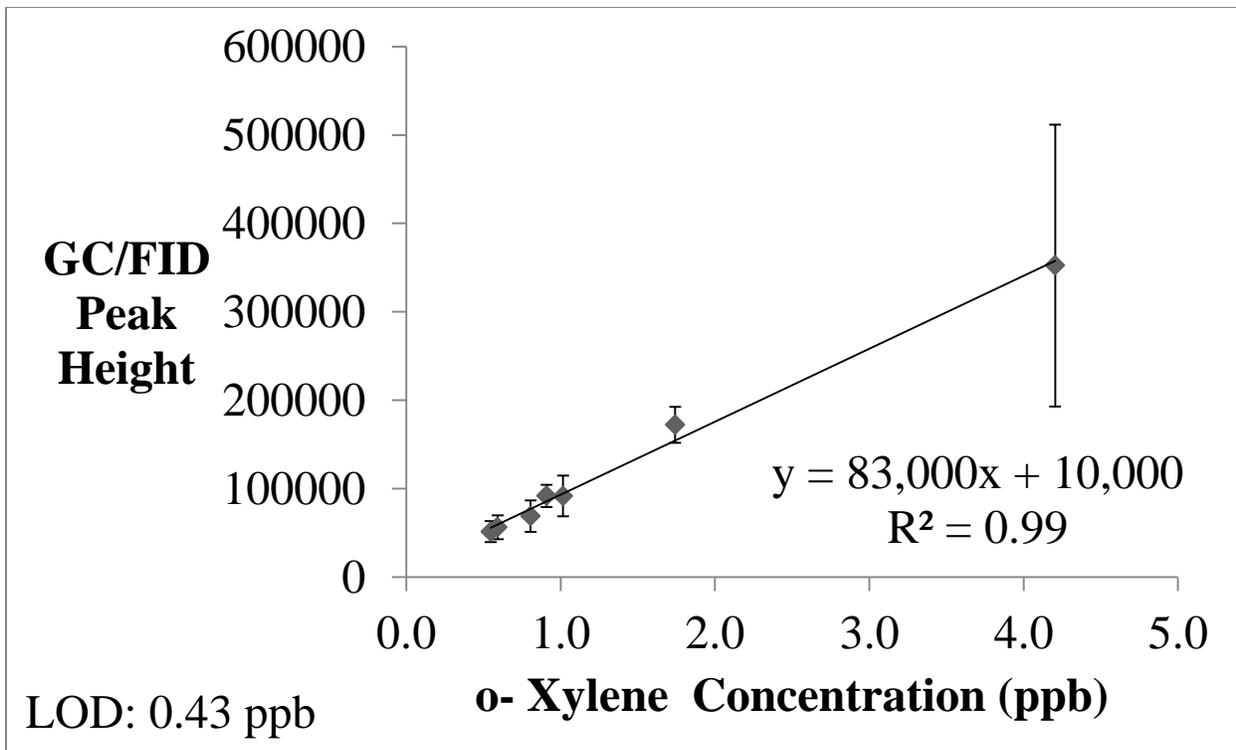


Figure 20: Calibration curve (linear regression) of Tenax TA GC/MS/FID sample method mean responses to o-xylene standard. Error bars represent one standard deviation of 3-5 replicates.

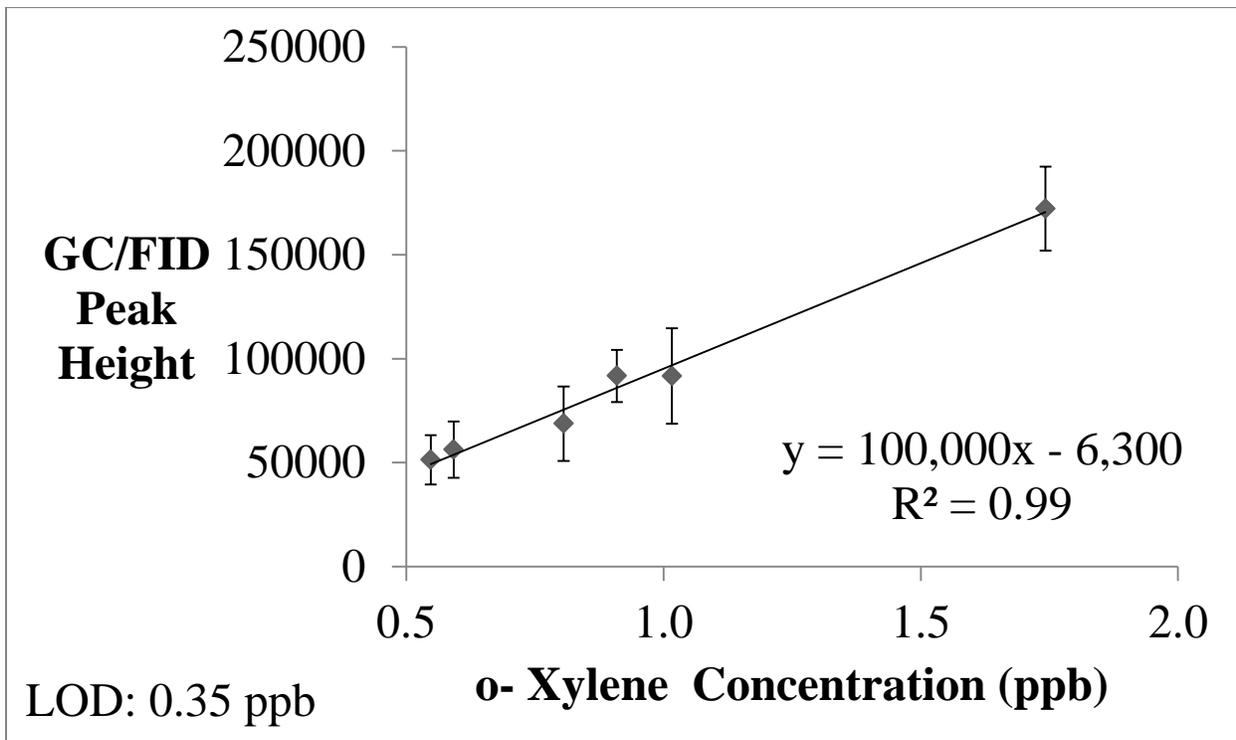


Figure 21: Calibration curve (linear regression) of Tenax TA GC/MS/FID sample method mean responses to o-xylene standard excluding the largest mean. Error bars represent one standard deviation of 3-5 replicates.

Notes:

GC/MS/FID: Gas chromatograph/ mass spectrograph/ flame ionization detector

GC/FID: Gas chromatograph/ flame ionization detector

LOD: Limit of detection

Ppb: parts per billion

Error bars represent one standard deviation

Sample volumes= 1,000 standard cubic centimeters

APPENDIX C: PID CALIBRATION CURVES, REGRESSION EQUATIONS, COEFFICIENTS OF DETERMINATION, LIMITS OF DETECTION, AND SAMPLE STANDARD DEVIATIONS

Appendix C contains calibration curves for each PID (1 and 2) after maintenance has been conducted (cleaning the instrument and resetting the internal calibration) yet before the instrument measures a sample (Before Sampling) and after samples have been measured yet before instrument maintenance (After Sampling). The average between before and after sampling values was calculated, a linear regression was applied and subsequently plotted as “Average between before sampling date and after sampling date”. Each calibration point is the average of 12 10-second measurements. All commuter samples were corrected using the “Average” calibration curve. Linear regression equations, coefficients of determination, standard deviations, and limits of detection are included in Table 6, found at the end of this document. Additional notes and details pertaining to the figures can also be found at the end of this document.

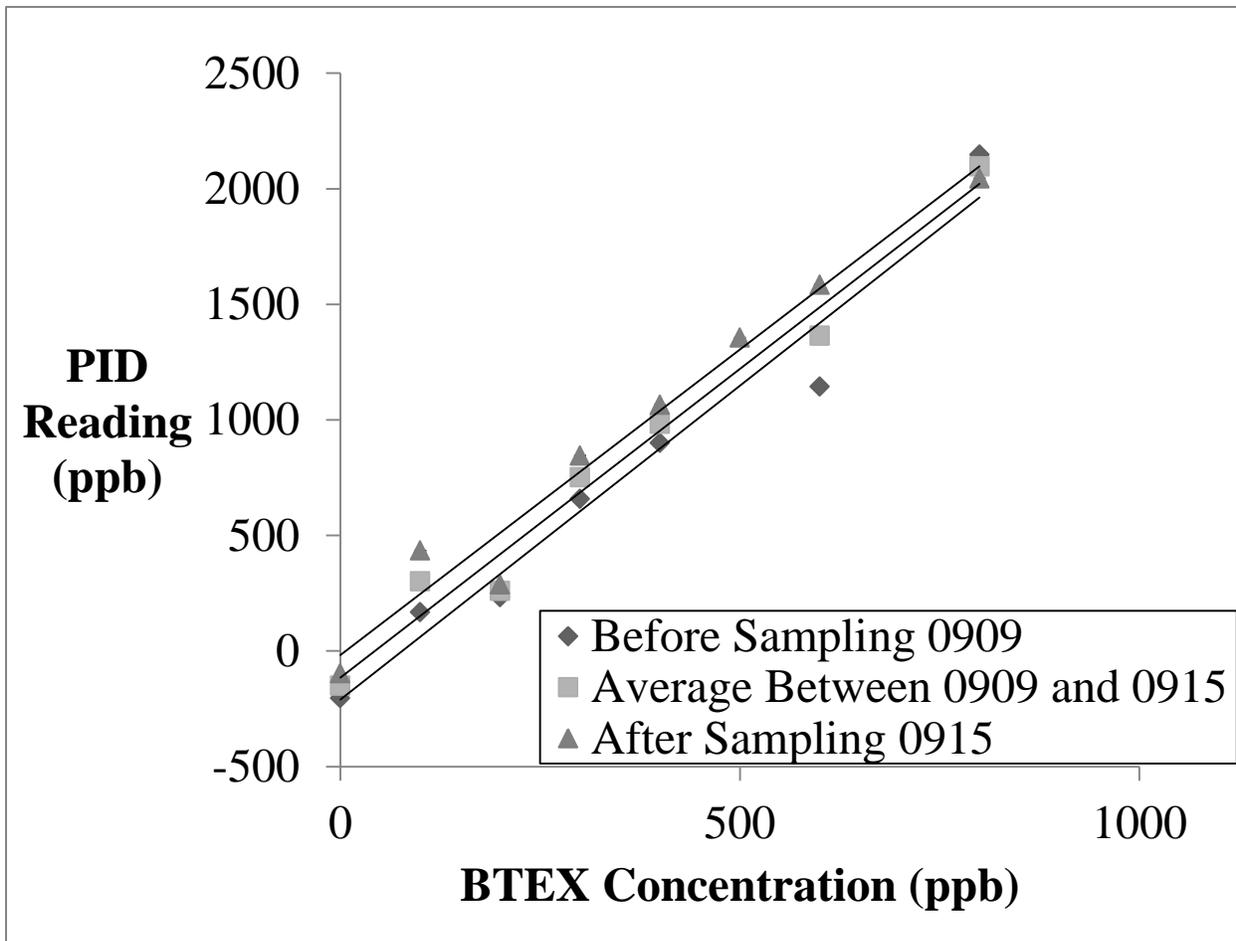


Figure 22: Calibration curve of PID 1 mean responses (before sampling, after sampling, and the average of the two days September 9- 15, 2013) to BTEX concentrations from Tenax tubes. Error bars represent one standard deviation.

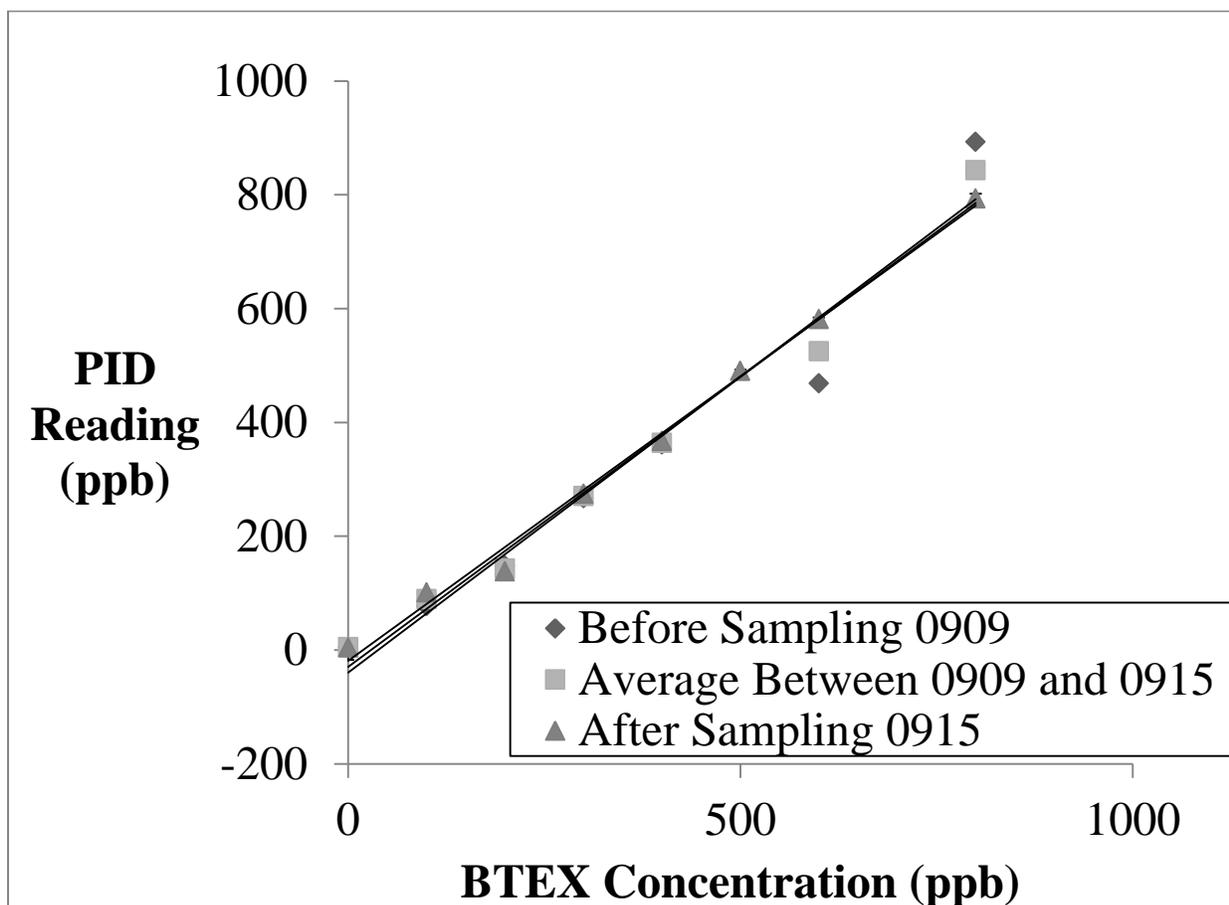


Figure 23: Calibration curve of PID 2 mean responses (before sampling, after sampling, and the average of the two days September 9- 15, 2013) to BTEX concentrations. Error bars represent one standard deviation.

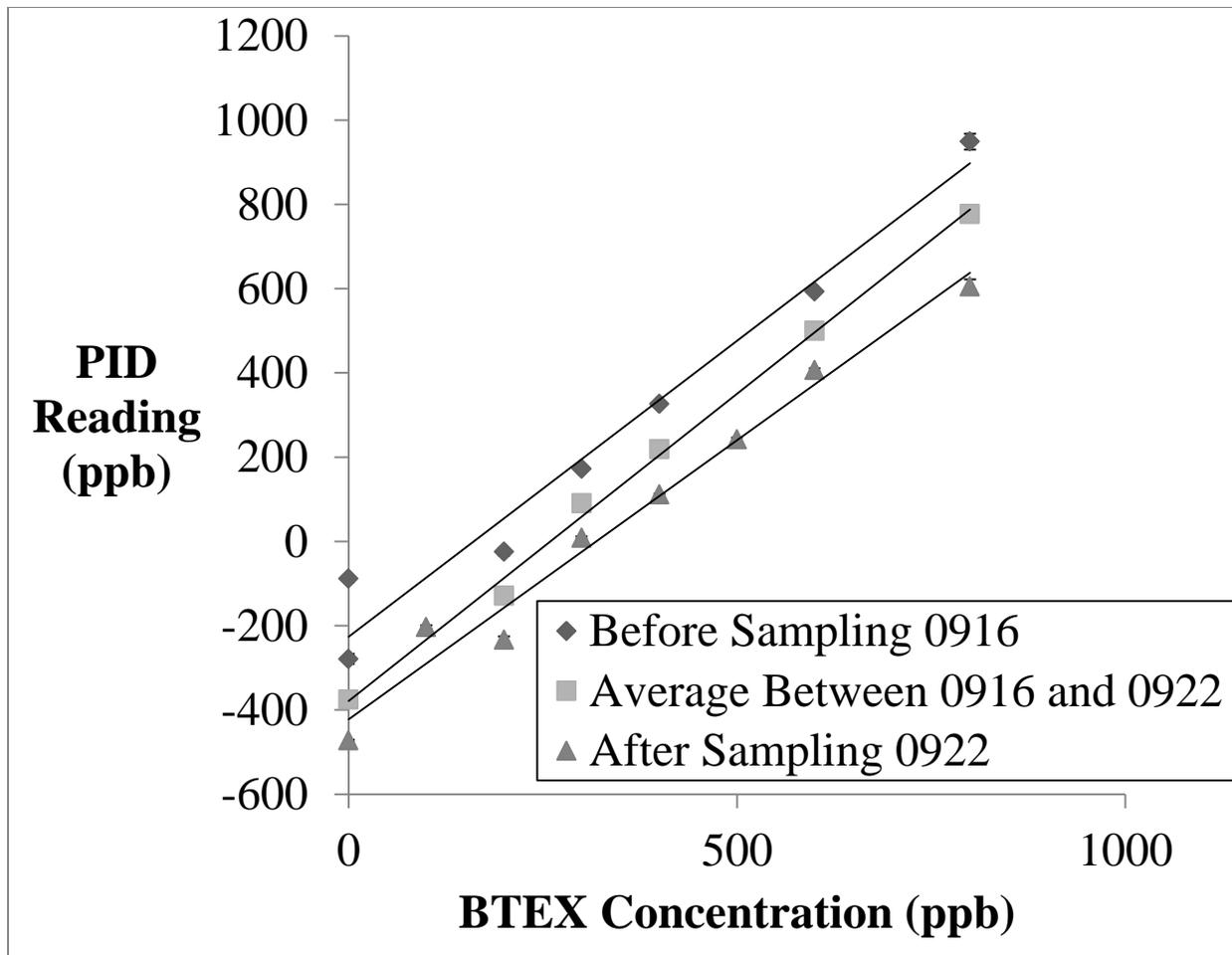


Figure 24: Calibration curve of PID 1 mean responses (before sampling, after sampling, and the average of the two days September 16- 22, 2013) to BTEX concentrations. Error bars represent one standard deviation.

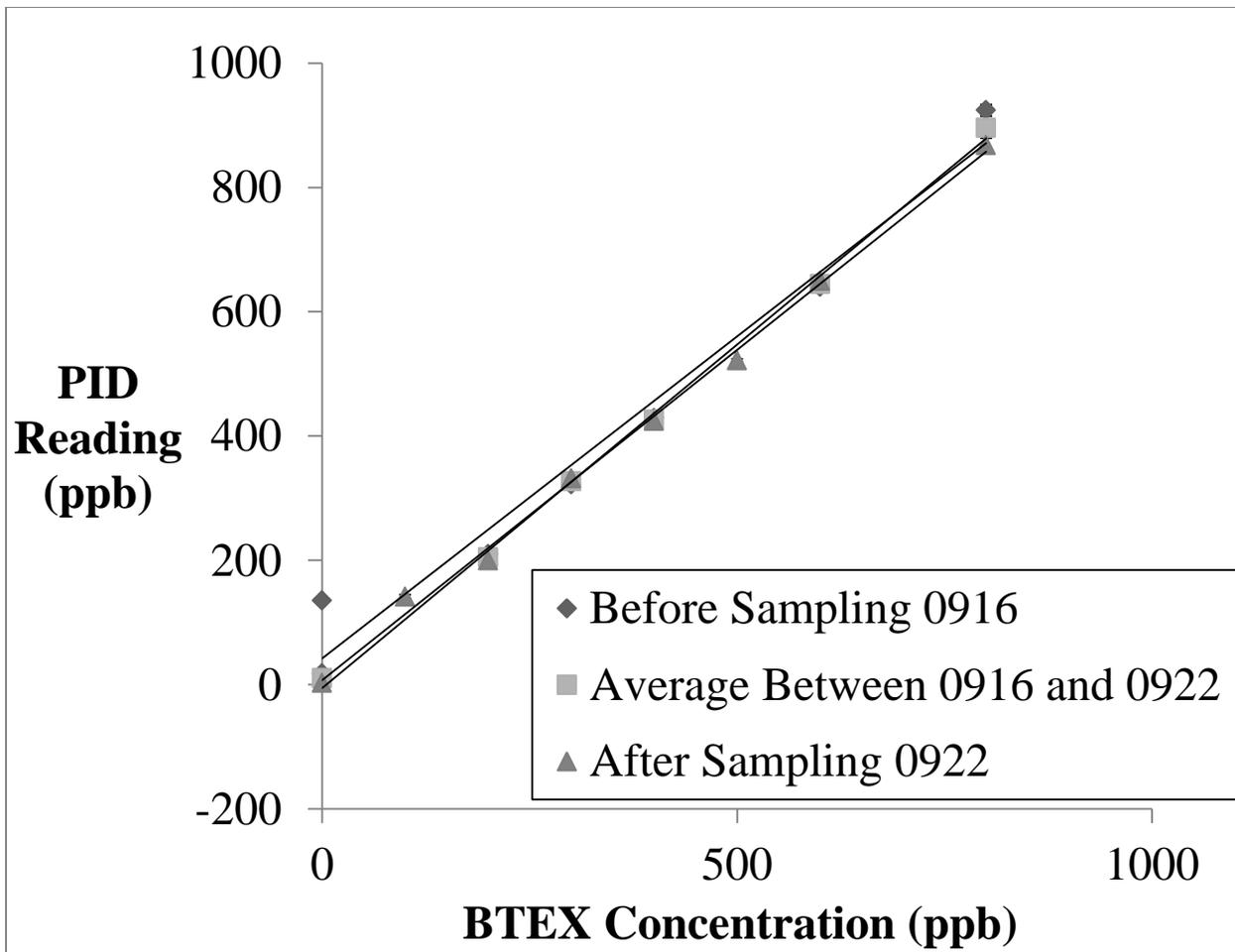


Figure 25: Calibration curve of PID 2 mean responses (before sampling, after sampling, and the average of the two days September 16- 22, 2013) to BTEX concentrations. Error bars represent one standard deviation.

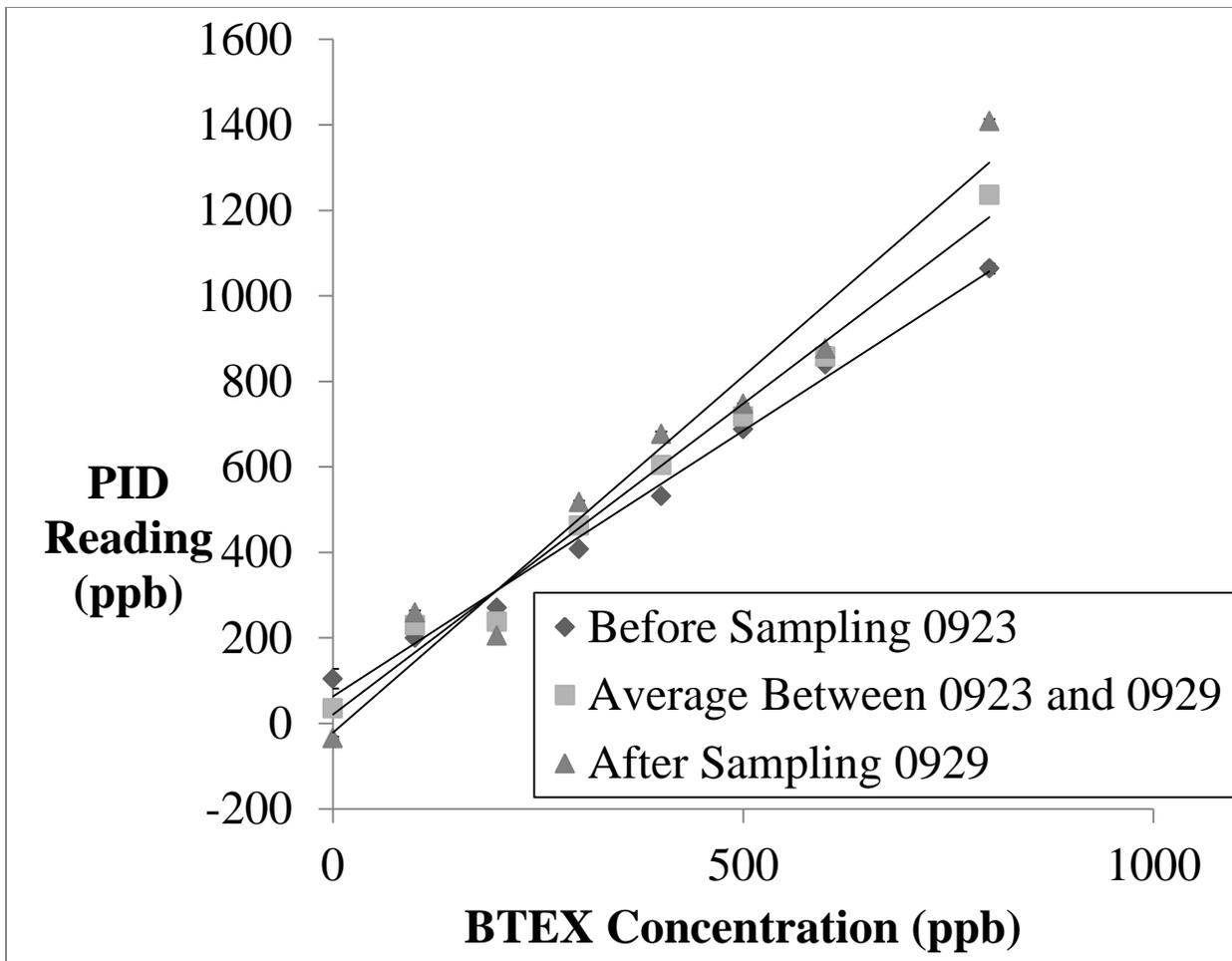


Figure 26: Calibration curve of PID 1 mean responses (before sampling, after sampling, and the average of the two days September 23- 29, 2013) to BTEX concentrations. Error bars represent one standard deviation.

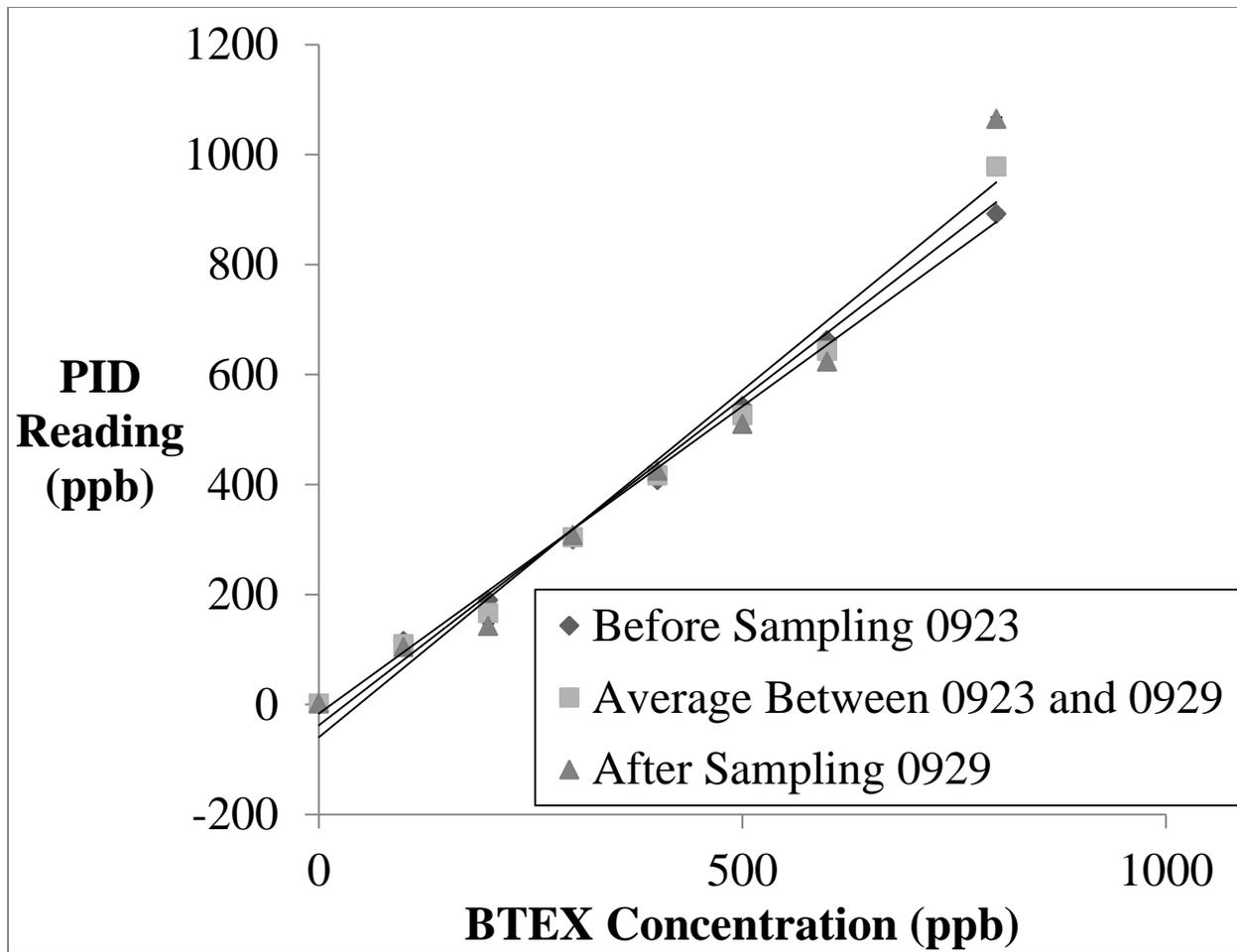


Figure 27: Calibration curve of PID 2 mean responses (before sampling, after sampling, and the average of the two days September 23- 29, 2013) to BTEX concentrations. Error bars represent one standard deviation.

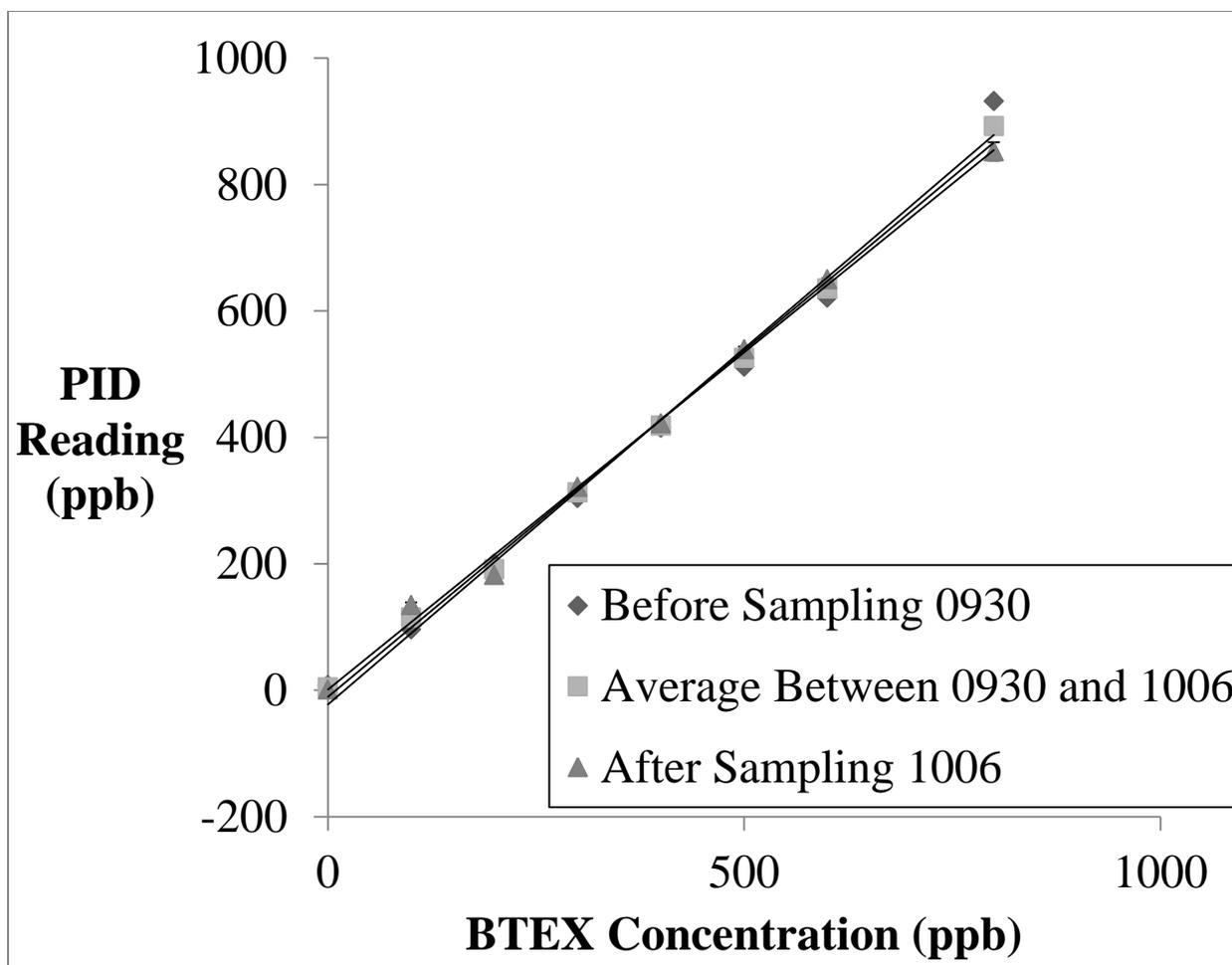


Figure 28: Calibration curve of PID 2 mean responses (before sampling, after sampling, and the average of the two days September 30- October 6, 2013) to BTEX concentrations. Error bars represent one standard deviation.

Notes:

PID: Ion Science Tiger Photoionization Detector equipped with a 10.6 eV lamp

BTEX: Calibration gas consisting of benzene (10.5 ppm), toluene (10.4 ppm), ethylbenzene (10.2 ppm), p- xylene (10.1 ppm), m- xylene (10.1 ppm), and o- xylene (10.1 ppm) diluted with ultra-zero air

Ppb: parts per billion

Error bars represent one standard deviation

Table 6: Regression Equations, Coefficient of Determination (R^2), Limits of Detection (LOD), and Standard Deviations (S) for PID Responses

PID	Calibration Curve	Regression Equation	R^2	LOD (ppb)	S
1	Before Sampling: September 9, 2013	$Y = 2.7x - 210$	0.96	9.6	6.9
1	Average Between September 9 and 15, 2013	$Y = 2.7x - 110$	0.98	9.6	8.5
1	After Sampling: September 15, 2013	$Y = 2.6x - 18$	0.97	9.6	9.1
2	Before Sampling: September 9, 2013	$Y = 1.0x - 40$	0.95	11	3.7
2	Average Between September 9 and 15, 2013	$Y = 1.0x - 29$	0.98	11	3.7
2	After Sampling: September 15, 2013	$Y = 1.0x - 19$	0.99	11	3.3
1	Before Sampling: September 16, 2013	$Y = 1.4x - 0.23$	0.97	15	9.0
1	Average Between September 16 and 22, 2013	$Y = 1.5x - 380$	1.0	15	7.3
1	After Sampling: September 22, 2013	$Y = 1.3x - 423$	0.98	15	3.9
2	Before Sampling: September 16, 2013	$Y = 1.0x + 42$	0.97	11	4.7
2	Average Between September 16 and 22, 2013	$Y = 1.1x - 5.3$	1.0	11	4.2
2	After Sampling: September 22, 2013	$Y = 1.1x + 7.1$	1.0	11	3.1
1	Before Sampling: September 23, 2013	$Y = 1.2x + 63$	0.99	10	4.6
1	Average Between September 23 and 29, 2013	$Y = 1.5x + 20$	0.99	10	4.8
1	After Sampling: September 29, 2013	$Y = 1.7x - 22$	0.96	10	4.6
2	Before Sampling: September 23, 2013	$Y = 1.1x - 16$	1.0	9.3	3.1
2	Average Between September 23 and 29, 2013	$Y = 1.2x - 38$	0.99	9.3	3.7
2	After Sampling: September 29, 2013	$Y = 1.3x - 60$	0.96	9.3	3.9

2	Before Sampling: September 30, 2013	$Y = 1.1x - 22$	0.99	12	3.6
2	Average Between September 30 and October 6, 2013	$Y = 1.1x - 11$	1.0	12	4.3
2	After Sampling: October 6, 2013	$Y = 1.1x + 1.1$	1.0	12	4.6

Notes:

R²: Coefficient of determination

LOD: Limit of detection, defined by equation 2.1

S: "Before" and "After" calibration curves: standard deviation at 100 ppb; "Average" calibration curve
"s" values are pooled variation from "Before" and "After" sampling curves

N= 12 measurements logged every 10 seconds