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An environmental air sampler to evaluate personal exposure to volatile organic compounds

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Abstract

A micro fabricated chip-based wearable air sampler was used to monitor the personnel exposure of volatile chemical concentrations in microenvironments. Six teenagers participated in this study and 14 volatile organic compounds (VOCs) including naphthalene, 3-decen-1-ol, hexanal, nonanal, methyl salicylate and limonene gave the highest abundance during routine daily activity. VOC exposure associated with daily activities and the location showed strong agreements with two of the participants results.One of these subjects had the highest exposure to methyl salicylate that was supported by the use a topical analgesic balm containing this compound. Environmental based air quality monitoring followed by the personnel exposure studies provided additional evidence associated to the main locations where the participants traveled. Toluene concentrations observed at a gas station were exceptionally high, with the highest amount observed at 1213.1 ng m-3. One subject had the highest exposure to toluene and the GPS data showed clear evidence of activities neighboring a gas station. This study shows that this wearable air sampler has potential applications including hazardous VOC exposure monitoring in occupational hazard assessment for certain professions, for example in industries that involve direct handling of petroleum products.

Graphical Abstract

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Conflicts of interest

There are no conflicts to declare.

†Footnotes relating to the title and/or authors should appear here.

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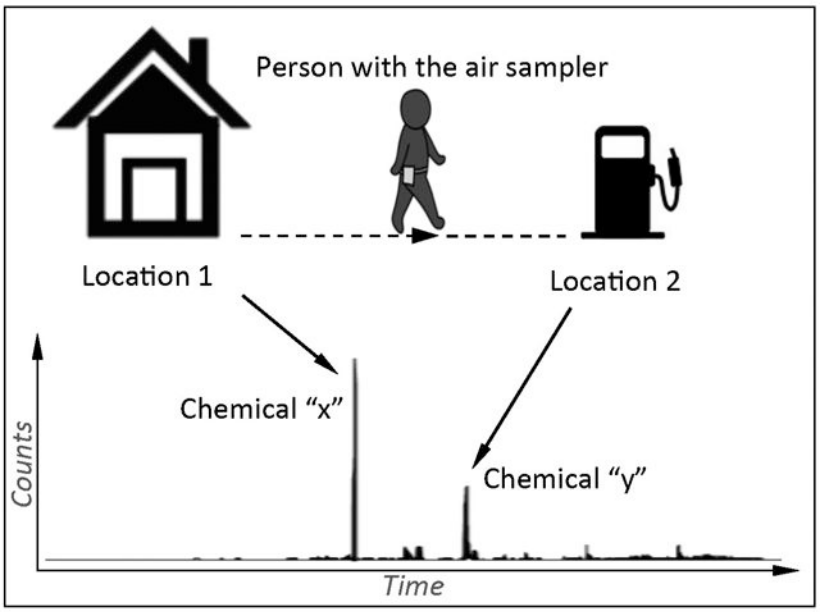

Introduction

Air pollution involving hazardous volatile organic compounds (VOCs) is a major concern due to their adverse effects on the human body[1–4]. Some VOCs directly impact human health by triggering respiratory disorders while others can be indirectly harmful by contributing to environmental imbalance and global warming[1]. VOCs can be found in a large number of chemical families such as aromatic hydrocarbons, aliphatic, aldehydes, ketones, ethers, acids and alcohols. Atmospheric research has revealed that considerable amount of the total composition of VOCs found in urban area are benzene related BTEX (benzene, toluene, ethyl benzene and xylene) constituents[5, 6]. Benzene is present in gasoline as well as in vehicle exhaust[7]. Besides gasoline, benzene related compounds are produced by other fossil fuel burning and several chemical and, industrial processes[8]. BTEX and other damaging VOCs can be found in both indoor and outdoor settings. For example, the VOCs emitted by building materials, paints, air fresheners, perfumes, cooking/food related products are found in closed poor ventilated indoor environment at higher concentrations than outdoors[9–11]. Otherwise, burning fossil fuel, tobacco smoke, pesticides and wildfires can be mostly considered as major contributors to outdoor VOC level elevations. Health effects due to the exposure of some damaging VOCs range from minor skin, nose, and eye irritation to critical consequences like organ failure or increased cancer risk. Due to the many adverse effects of these volatiles, it is necessary to have a mobile VOC monitoring technology that can evaluate personal VOC exposure from specific locations as a "chemical exposure monitor" that is independent of region-wide air quality assessments that do not account for microenvironment.

Currently, the majority of the real time detection of these harmful chemicals is done by mobile sensors that are based on electrochemical, metal oxide semiconductors (MOS), infrared (IR) and photoionization based detectors[12]. Advanced analytical technologies such

as gas chromatography (GC) and mass spectrometry (MS) are used, but are limited due to higher manufacturing, operational costs and mobile application difficulties due to bulky systems[13]. Additionally, direct measurement of a broad spectrum of these chemicals in an ambient environment by a single detector is challenging due to the low chemical concentrations (often < 1 ppb) present in the ambient environment[14–16].

Several versions of pre-concentration methods with both active and passive sampling have emerged in the past years offering advancements in chemical detection[17–19]. During pre-concentration, air passes actively or passively across or through a sorbent. The sorbent retains analytes of interest, while main constituents of air like nitrogen and oxygen are not trapped. After the gas phase chemical pre-concentration step, the loaded chemical trap is commonly analyzed using a laboratory-based detector. The pre-concentrated chemicals are desorbed, often thermally or through solvent extraction, and ran through a detector. Several research teams have made progress by using commercial pre-concentrators or by manufacturing their own sample traps[18]. However, most of these are passive samplers with no control of proper sampling flows or sampling durations. Furthermore, these sampling traps do not have the potential of integrating into a single handheld unit, having both sample pre-concentration and detection capabilities. If these samplers can offer features such as GPS data, temperature and humidity of the environment that will give additional benefits the users. Therefore, it is essential to have a lightweight, portable, easy to use device with different sensors integrated into the same device to carry out accurate environmental studies.

We previously developed a microsystems-based chemical pre-concentrator “chip” fabricated using cleanroom approaches[20]. The micro pre-concentrator chip was initially presented as a stationary sampler[20] and then used with a handheld mobile sampler with limited tests in situations that may trigger asthma exacerbations, e.g. indoor cooking environments, exposure to indoor commercial cleaning products, and scented pet care products[12]. In this study, for the first time, we demonstrate the successful practical use of the micro fabricated chips with the air samplers to monitor environmentally-relevant VOCs in a personnel exposure pilot study that involved late adolescent aged participants. The teenagers wore wearable air samplers with the micro pre-concentrator chips for five days during their daily activities over ~1 week and the chips were returned to the lab for chemical analysis at the end of each day. VOCs were targeted during this analysis using GC-MS, and reported amounts are from integrated exposure sampling across each day. This novel technology has the potential to be widely deployed for personal exposure monitoring, and could potentially aide studies to understand the chemical exposure effects in various populations.

Material and Methods

Micro fabricated pre-concentrator chip (μPC) and the sampler

A micro fabricated pre-concentrator chip (μPC) with a sorbent bed having Tenax TA (Sigma-Aldrich, St. Louis, MO) was used in our wearable environmental sampler for this study, as described previously[20]. Briefly, the μPC was fabricated using lithography followed by etching the cavities for the sorbent bed into glass substrates. Heaters were added to the backside of the bonded μPC to achieve rapid heating of the sorbent cavity to desorb the VOCs for detection. The sampler is small and light enough to use as a wearable device and

μPCs can be easily interchanged for sampling over discrete time intervals. The sampler can be programmed for a desired duration of sampling at different flow rates and records GPS, temperature and humidity data into a SD card during each sampling session. Detailed engineering design of our wearable environmental sampler and the micro-fabrication of the pre-concentrator chip (μPC) are published previously[12, 20].

Sample collection

a) Personnel Exposure Study.—This study was carried out with informed consent under IRB approval by the University of California, Davis (# 1048328). A pre-programmed sampler and multiple μPCs were handed to six late adolescent teenage volunteers aged 14–16 (average age 15). These participants were instructed on how to use the sampler with an initial demonstration and a written standard operating procedure. A brief interview with each participant was completed before the study to help correlate some of the chemical exposure results with participants' daily activities. Questions such as their daily routines that participants are willing to explain (exposure to tobacco smoke, using a new car, living next to an active construction site) and their health conditions that could limit their daily activities to carry a sampler were asked. If such special cases were observed, additional questions were asked after the study to get more information to correlate chemical exposure to that situation (Example: participant 4, who was injured and not able to carry the sampler on during the whole experiment). Participants had the option to wear the sampler or keep the sampler next to them for the 5 days they used the sampler.

The environmental sampler was programmed to sample continuously for 30 min and then turned off for 30 min. This on/off cycle was repeated every hour for 12 hours per one single μPC chip. Each subject used two μPCs every day, one in the morning (AM) and one in the evening (PM), see Figure 1. Chips were retrieved from the participants, kept in a refrigerator prior to analysis and analyzed within 48 hours. A total of 60 samples were collected the study from six participants, with 10 samples collected per participant. Chips were blanked before deployment by desorbing them at ~260 °C for 15 min with a flow of 25 mL/min helium.

The sampler automatically recorded GPS coordinates, temperature and humidity every 10 sec and data was saved to the SD card during sampling. The sampling flow rate was 60 or 80 mL/min. The optimal sampler performance was previously assessed at the lab with researchers using the samplers at different experimental parameters, which included flow rates and sampling durations to simulate real sampling event.

b) Environmental Study.—After the personnel exposure study, some outdoor sites were chosen for further air sampling. Four principal locations were considered after studying the GPS data, the duration each participant spent at the location and know information from previous studies[13, 21–23]. The selected locations include a quiet street during the daytime, a parking garage at busy hours, a gas station, and a freeway overpass. Static environmental samples were collected for 30 minutes twice at the street and parking garage, thrice at the freeway and the sampling time was reduced to 15 minutes twice at the gas station due to presumed high VOC concentrations.

Table 1 summarizes the locations according to their proximity to the participants' homes, and duration spent in those. Values ranged between 0 and 5. A value of 5 was used when a participant spent more than 75% of their time less than 250 m from a location. Values decreased for every additional 250 m the participant was far from the location for the same amount of time. For example, participant 6 lived (spent more than 75% of exposed time) close to a supermarket with a relatively busy lot (within 100 m) and close to a gas station (within 500 m). However, participants 1 and 4 lived in and moved around quiet areas where the closest garages were located at approximately at 1 mile distance.

Desorption, GC-MS and data analysis

The μPCs were loaded onto a custom test fixture that is connected to the injector of a GC-MS for a chemical analysis, as previously described[20]. In brief, the chip was heated and held at ~260 °C for 15 min under a 25 mL/min flow of helium using a custom aluminum test fixture. A borosilicate transfer line connected desorbed analytes to the GC-MS inlet (Varian 3800 GC coupled to a 4000 ion trap MS). The inlet operated in splitless mode at 235 °C and was connected to a VF-5 MS column (30 m x 0.25 mm x 0.25 μm, Agilent Technologies Inc., Santa Clara, CA) using helium at 1 mL/min. A gradient of temperature was set in the oven, starting from 40 to 170 °C at 10 °C/min, and then a step ramp raised the temperature to 250 °C at 30 °C/min, holding it for 6 min. Transfer line was set at 250 °C and the mass spectrometer operated in scan mode, measuring 35 to 249 m/z.

Raw data files were initially checked using Varian Workstation software. After that, peaks were deconvoluted using AMDIS (version 2.71, NIST.gov) and aligned using Agilent's Genespring (version B.14.9). Putative chemical identifications were made by comparing the extracted mass spectra for each compound to the NIST '14 MS database. Additional peak confirmation was performed using commercial standards by matching the retention times and corresponding spectra. Multivariate data were studied using principal component analysis (PCA)[24], an exploratory method that compresses the data by reducing the variables keeping the original information. The condensed data can be visually interpreted to check the repeatability of measurements, detect outliers, and recognize patterns in sample distributions.

Finally, to assess the quality and to quantify the compounds of interest, blank samples (containing clean unused μPCs) were injected before each batch of samples. Blanks were used to determine background levels and signals coming from the sorbent and device. A commercial BTEX mixture (Restek, Bellefonte, PA) was used to build calibration curves to quantify the amounts of these specific VOCs collected by the μPC chip during sampling times. Curves contained triplicates at five concentration levels and standard solutions were prepared in methanol and directly injected into the GC-MS. Detection limits were determined by five replicates at 1.5 pg for each compound (at a signal to noise ratio 3:1). This calibrated the mass spectrum response to a known injected mass of analyte in the GC inlet. Final concentrations were expressed in ng m^{-3} using the known volume of air captured by the μPC sampler and the average for all days and times was calculated to assess the overall quality of the air from the surroundings of each participant during the personnel exposure study.

Results and Discussion

Data from the personnel exposure study

Sixty environmental samples were collected in total from six participants wearing the portable μPC sampler. Teenaged participants were allowed to proceed with their normal life, collecting the air information from their surroundings over a 24 h time course. The chips were changed every 12 h by the participant for new-cleaned chips. All μPC chips were analyzed using the GC-MS methodology previously described (Figure 1). All the participants reported that they carried daily activities without any interference from the sampler and it was lightweight, easy to use with negligible sound from the sampling pump.

Figure 1 shows the combined total ion chromatograms (TIC) obtained from all the samples. Data from most of the participants presented visually similar chromatographic profiles, except for participant 1 (P1) and 4 (P4), who had higher signals compared from the other subjects. Specifically, a sample from P4 (day 3 - AM) contained a high intensity peak corresponding to methyl salicylate. The health/activity questionnaires revealed that this participant was recovering from a muscle injury and stayed home during the study. This explanation corresponded with the GPS data that showed P4 stayed mostly at home. Subject P4 also reported using topical analgesic balm containing methyl salicylate, and the high intensity methyl salicylate peak could be attributed to that.

a) Total VOCs detected per participants—After inspection of the initial data, raw files were analyzed after deconvolution and alignment of the peaks. The resulting peak table was normalized and main signals were putatively identified by the NIST database. Table 2 shows the list of the peaks detected with the retention time (in min), calculated and literature kovats indexes (KI), formula and CAS number. An additional confirmation of some of the compounds was preformed using commercial standards.

A final 48 compounds were identified after filtering from a total of approximately 150 peaks detected during the study. The number of times each peak was detected is also described in Table 2. Most of the compounds appeared in the majority of the samples, such as naphthalene, 3-decen-1-ol, hexanal, nonanal, methyl salicylate or limonene. These are VOCs with high abundance in the day-to-day environment coming from plants, cleaning products, and/or personal hygiene products[25]. Furthermore, BTEX compounds were present in most samples. Other compounds were only detected by in samples of a few participants. This was the case for 2-ethylhexyl acrylate and octyl propionate found only in day 1 for P2 (AM and PM), or 3-ethenyl-1,2-dithi-4-ene (only in day 2 for P1) and 3,7-dimethyl-1,3,6-octatriene, found in high intensities in single days from P1 and P4. Di-isopropyl adipate, commonly used in food additives and personal care products, was also detected only in P3, but over most days. Similarly, compounds like (E)-3,7-dimethyl-2,6-octadienal, b-pinene and terpinolen were detected in some of the participants, but in samples from few days.

Additionally, the similarities and the differences between the participants' day and night samples were evaluated. The obtained dataset was logarithm transformed and normalized using pareto-scale before performing multivariate analysis. These treatments reduced the skewedness and help interpretation of possible non-normal distributions. PCA establishes

the similarities and differences between groups of samples using reduction of the GC-MS data dimension by making data more interpretable without losing information (Figure 2). For that, the original dataset is translated to new variables, which are linear functions called principal components (PCs) that maximize the data variance and are uncorrelated within each other. Figure 2A and 2B show PCA scores plots, which describe individual ambient environment differences between all the study participants. We observed that VOC profiles were similar between participants 1 and 4 and their profiles differed from the rest of the subjects (P2, P3, P5 and P6). Moreover, the latter four participants had some similarities in their profiles, but the VOC profiles were most alike between P5 and P6. Although the presented PCA shows low explained variance (around 20 % from PC2 and PC3, Fig 2B), the highest variability (51.73 % first principal component, PC1) is due to unknown differences that are non-related to the participants or days of analyses (Fig 2A).

When differences between days or morning (AM) / evening (PM) were studied, there were no clear tendencies or clusters observed when considering all participants (data not shown). The only trend was observed using data from participant 2 (Figure 2C), which showed some differences between AM/PM samples (except for day 1). In this case, morning samples had higher intensities of compounds such as methyl salicylate, limonene, hexanal and toluene for most of the days. This could be related to VOCs that are commonly released in daytime such as plant aroma or personal care products. At the same time, it also showed that evening (PM) samples had higher levels of butylated hydroxytoluene, a compound related with slightly musty odor.

Since there were no major differences explained by the day and time of the samples, we summarized the intensities detected of VOCs for each participant in the study. The percentage of area detected for the 14 most abundant compounds is presented (Figure 3). Percentages were calculated by normalization of all the peaks and average within the same participant. From this analysis, we observed high abundance of methyl salicylate for participant 4 (41.5%, confirming the note from the initial visualization) with low levels presented by participant 3 (2.6%). Other VOCs with high presence were limonene-3-denen-1-ol and nonanal for most of the participants (except P4). Other compounds more specific for each individual were: 1,4-dichlorbenzene for P1; octanal and butylated hydroxytoluene for P2; and 1,2,3-trimethylbenzene for P3. Some of the compounds were detected in similar percentages through all the participants such as with naphthalene, hexanal, 2-methyl naphthalene, octanal, heptanal, and (E)-2-nonenal.

b) Air quality during the personnel exposure study – BTEX concentrations— We determined the average concentration of benzene and its derivatives: toluene, ethylbenzene and xylene that the participants were exposed to. These BTEX VOCs are highly relevant for air quality and provide information about the ambient pollution during the sampling experiments[8]. Calibration curves were built to determine the final amount of each BTEX compound in the samples. The final concentration (in ng m^{-3}) was calculated using chromatographic peak areas, calibration curves and corrected by the known volume of air captured by the μPC sampler (Table 3).

There was variability per participant through the different days of VOC sampling, which resulted in high standard deviations in some cases. These high values are related to the individual samples with unusually high or non-detectable concentrations for certain compounds. This is the case of toluene in participant 6, with sample values of 30–60 ng m^{-3} for most of the samples, but with two samples (day 3 and 4, both PM) with values around 120 ng m^{-3}. When the GPS data were analyzed for both afternoons, the user was at a gas station for about 15–20 minutes on day 4 PM and mostly outdoors in an urban area on day 3 PM.

The m,p-xylene and toluene compounds were most abundant in the analyzed samples, followed by o-xylene. In most of cases, participant 6 achieved the highest concentrations of these compounds, with values around 45–58 ng m^{-3}. Similar values of these compounds were also detected for participant 3, but with lower values for toluene (16 ng m^{-3}). However, toluene and xylenes were detected in much lower concentrations for participants 2 and 4, with values ranging from 10 to 24 ng m^{-3}. In general, ethylbenzene was detected in low concentrations (between 4 and 34 ng m^{-3}), with P6 on the high end of exposure. Benzene was detected in smallest amounts for all the participants, not exceeding 1.1 ng m^{-3}.

Figure 4 presents the differences between participants using BTEX data. Scores plot from a PCA (Figure 4A), previously log transformed and normalized, shows main differences were determined by P6 and P1 compared to the rest of the participants. In this case PC2 and PC3 explained no clear differences for the participants, and PC4 allowed a clear separation between these two participants from the rest. As observed before, P6 showed higher concentrations for most of the BTEX compounds, but also for the T/B ratio. P1 had a higher X/E ratio than the rest of the participants. When these BTEX ratios were evaluated we could notice that their differences between the participants were also reflected in the PCA. While T/B ratios (Figure 4B) were relatively consistent for participants 1 to 5 (between 14 and 30), it was considerably larger for participant 6.

The T/B ratio is used to study vehicle emissions and it commonly decreases when samples are far from these pollution sources[26]. This occurs because toluene is more photochemically reactive with the atmosphere which leads to low T/B ratios for samples collected far from traffic exhaust emissions. This information is in good agreement with the fact that P6 lived close to a gas station and a busy lot, clear sources of pollutants that increase the level of T/B ratio and toluene concentration. Similarly, lower T/B ratios were obtained by the rest of the subjects, which mainly lived and moved around quiet traffic areas.

The (*m*+*p*)-xylenes/ethylbenzene ratio (X/E ratio) (Figure 4C) also indicates the distance from emission sources to the collected VOC sample. Since xylenes are more reactive in this case, higher concentrations of xylenes (and higher X/E ratio) show the proximity to pollutant sources (not vehicular related). Xylene, is mainly related to petroleum industries, but it can also be found in dyes, paints, medical technology and different industries as a solvent[27]. In this case, participant 1 was closer to a source of emission of these compounds, but no data from the personnel exposure study support that observation. The participants P4 to P6 had low X/E which indicates they were far from the emission sources of these compounds.

Data from the environmental study

Multiple samples from each environmental location were collected and are summarized in Figure 5. Twenty volatiles were detected and identified through all the locations, and (apart from the BTEX compounds) these included high levels of aldehydes ((E)-2-octenal and nonanal) and alcohols (5-methyl-1-heptanol and 3-decen-1-ol). Less harmful and scented VOCs, such as 2-octenal (green leafy), 5-methyl-1-heptanol and 3-decen-1-ol were detected at higher amounts in quiet streets, while benzene derivatives, such as (m+p)-xylene, o-xylene, toluene and ethylbenzene where detected in higher amounts in busy garages and gas stations. A mixture of car exhaustion related gases like toluene and (m+p) xylene, and aromatic fragrant VOCs like limonene, 3-decen-1-ol and nonanal (citrus smell) were detected close to the freeway. These aromatic scented VOCs from quiet streets and freeway can be associated to the VOCs emitted from wood chips of newly landscaped areas located nearby.

BTEX compounds were detected in all the locations and Table 4 shows the calculated concentrations. Toluene was found in higher amounts in all cases, especially at the gas station where levels reached concentrations of 1213.1 ng m^{-3}, followed by the busy garage at 120 ng m^{-3}. Also, toluene had the highest concentrations of the BTEX compounds in the quiet street and the freeway. Similarly, (m+p)-xylene was detected in the gas station and the busy garage, with concentrations of 508 and 150 ng m^{-3} respectively. Overall, the gas station had the highest levels of BTEX compounds. B/T ratio had the higher values at the gas station and the busy garage, both places having high presence of vehicle exhaust.

VOC exposure of the participants

From all the volatile compounds detected in the previous sections, 17 VOCs were common among the different locations and the participants in the study. Because we worked with specific locations and participants where averaged through 5 days of moving near or further the locations, no clear correlations were found from those common VOCs. However, for the BTEX amounts a slight trend could be observed (Fig. 6).

Figure 6 shows a bi-plot of the PCA obtained with all the averaged BTEX concentrations from all participants considered in the study. In Fig. 6 scores are presented as diamonds for participants and as circles for locations. Simultaneously, loadings are included in the PCS plot as stars, which represent the BTEX compounds that explain the differences and similarities between samples plotted. For example, PC1 (74.5%) separates samples by the amounts of the individual compounds and ratio (T/B) in the positive side of the scores plot axes, and by ratio X/E in the negative side. However, only ratio X/E explains PC2 (13.73%) differences.

The gas station presented an overall higher concentration of all the BTEX compounds and ratio T/B, followed by the busy garage. Interestingly, with slightly higher PC1 positive values (x-axis Fig. 6), P6 showed more similarities to the named locations (compared to the rest of the subjects), matching the values indicated in Table 1. BTEX values for quiet street and freeway are very similar, as well as P2, P4 and P5, also in accordance of the values presented in Table 1. Among the participant 5 was closer to the freeway, corresponding to

the previous results obtained by the BTEX amounts per participants. Participant 1, however, showed more differences compared to the rest of the subjects (PC2) for the ratio X/E, which cannot be related to any of the locations studied. Despite all subjects participated in the study are living within Davis, CA, specific environmental signatures unique for certain participants (P1, P3, and P6) were captured. This study was mainly focused on detecting a broad number of volatiles from different families, which included BTEX (one indicator for air quality). It is important to acknowledge that the performance of the sorbent, Tenax TA, has been reported good results for capturing volatiles and semi-volatiles from air, however, it has low specificity for absorbing low level of benzene and some derivatives. However, during this study such evidence was not clearly observed.

Conclusion

This technology can provide detailed granular data for epidemiological studies to expand studies for risk groups. Potential other applications include hazardous VOC exposure monitoring in occupational hazard assessment for certain professions, for example in industries that involve direct handling of fossil fuels and professions that involve hazardous chemical exposure such as firefighting. However, depending on the chemical of target additional experiments may need to test different sorbent materials to minimize reactivity of certain chemicals with the sorbent hindering the accuracy of the results. Future work involves testing different sorbent materials for chemical reactivity, integrating this μPC chip with a chip based chemical detector to achieve a real-time chemical monitoring device and validate the device with a standard technology such as EPA method TO-14.

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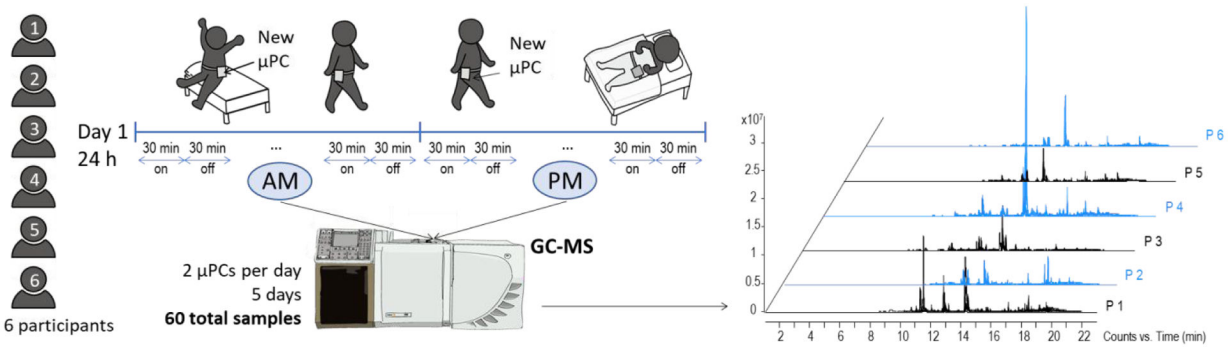

Figure 1.
Experimental setup for the personnel exposure study and obtained GC-MS data (right)

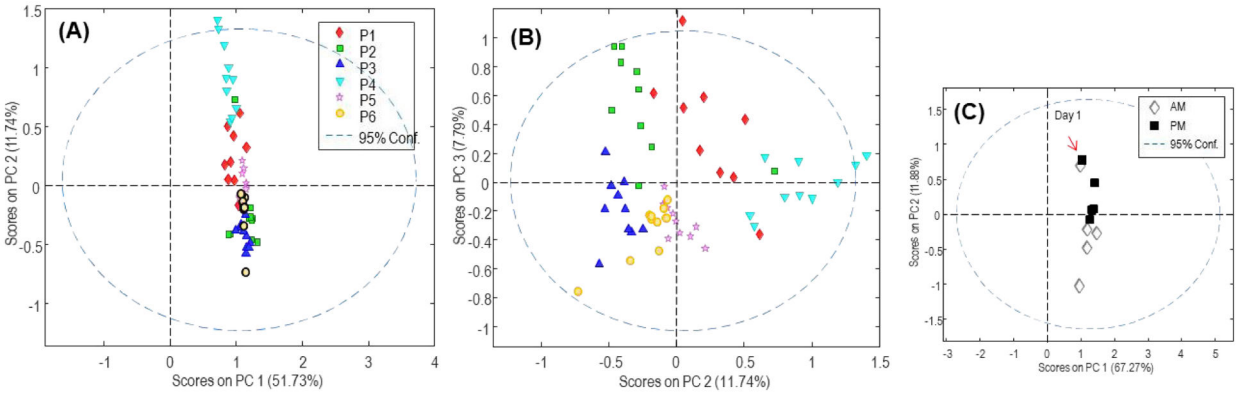

Figure 2.

Scores plot from Principal Component Analysis (PCA) using GC-MS data, showing differences between participants (panels A and B) and morning (AM) - evening (PM) for participant 2 (panel C). Different principal components are described: PC1 *vs.* PC2 (A) and PC2 *vs.* PC2 (B) including all participants. (C) describes PCA (PC1 *vs* PC2) just for the participant 2 (P2).

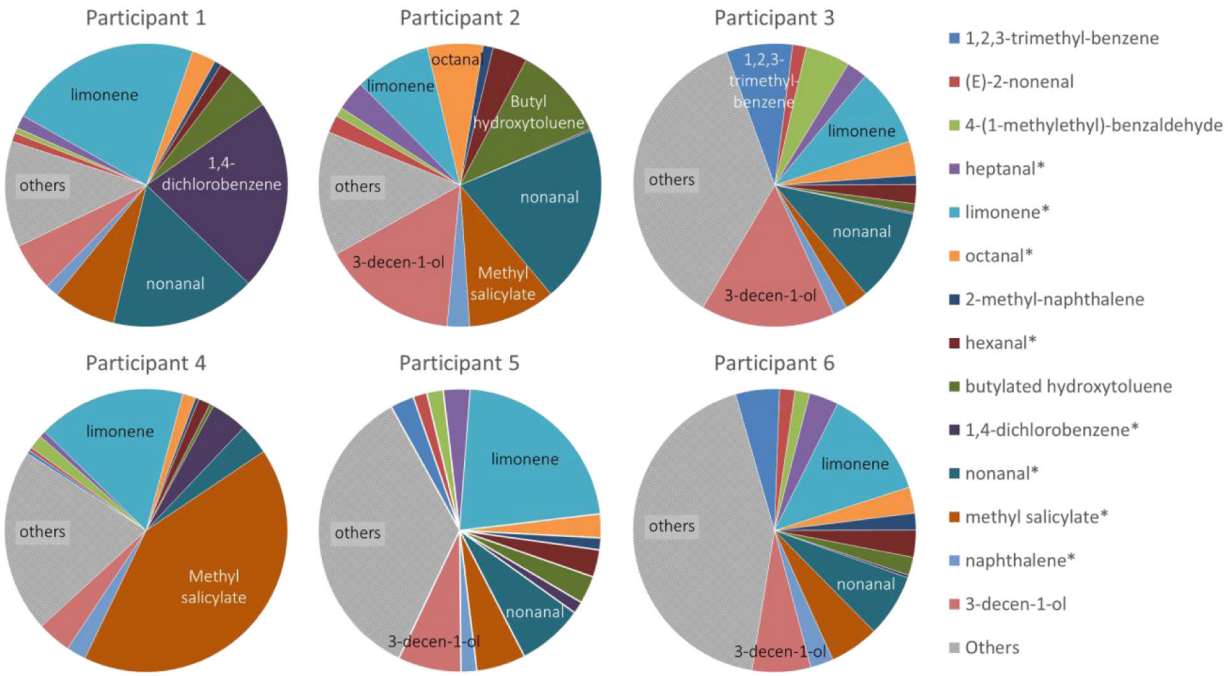

Figure 3.

Percentage of area detected of the 14 VOCs with the highest abundances. For example, P1 had a presence of approx. 20% of each: limonene, 1,4-dichlorobenzene and nonanal; 30% of the rest of 11 identified VOCs and 10% of “others” as unidentified peaks.

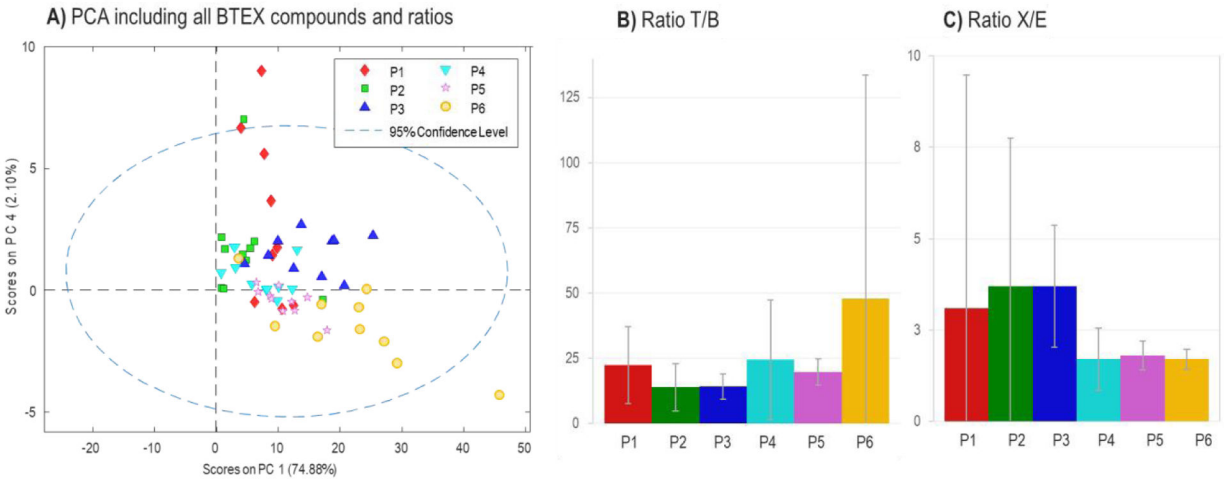

Figure 4.

BTEX results for the participants in the personnel exposure study. (A) PCA showing the separation between participants by all BTEX concentrations and their ratios toluene/benzene (T/B) and (m+p)-xylene/ethylbenzene (X/E). Data from Table 3 is described in Fig 4 B and C, where T/B (B) and X/E (C) are ratios for the averaged days per each participant. Error bars correspond to the standard deviation.

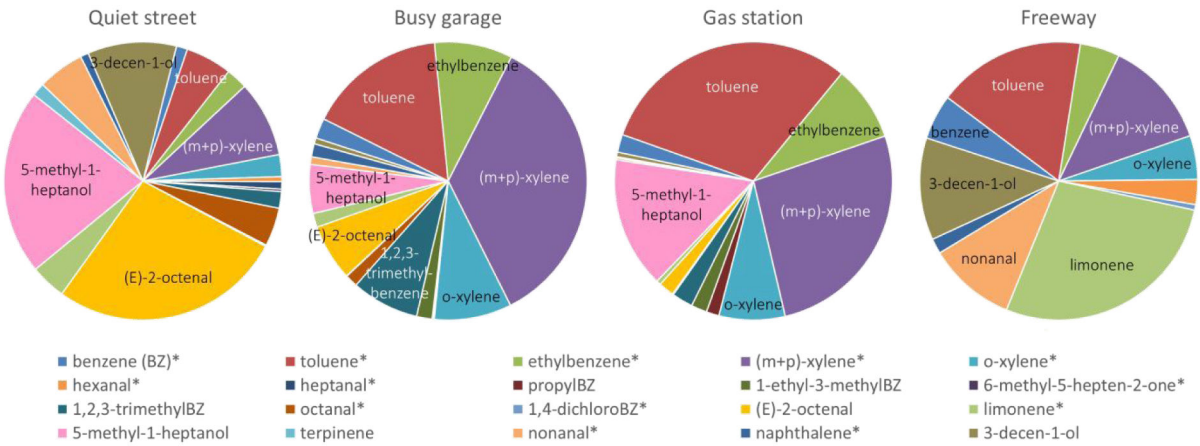

Figure 5.
Percentage of area detected of the main VOCs detected in the four locations studied.

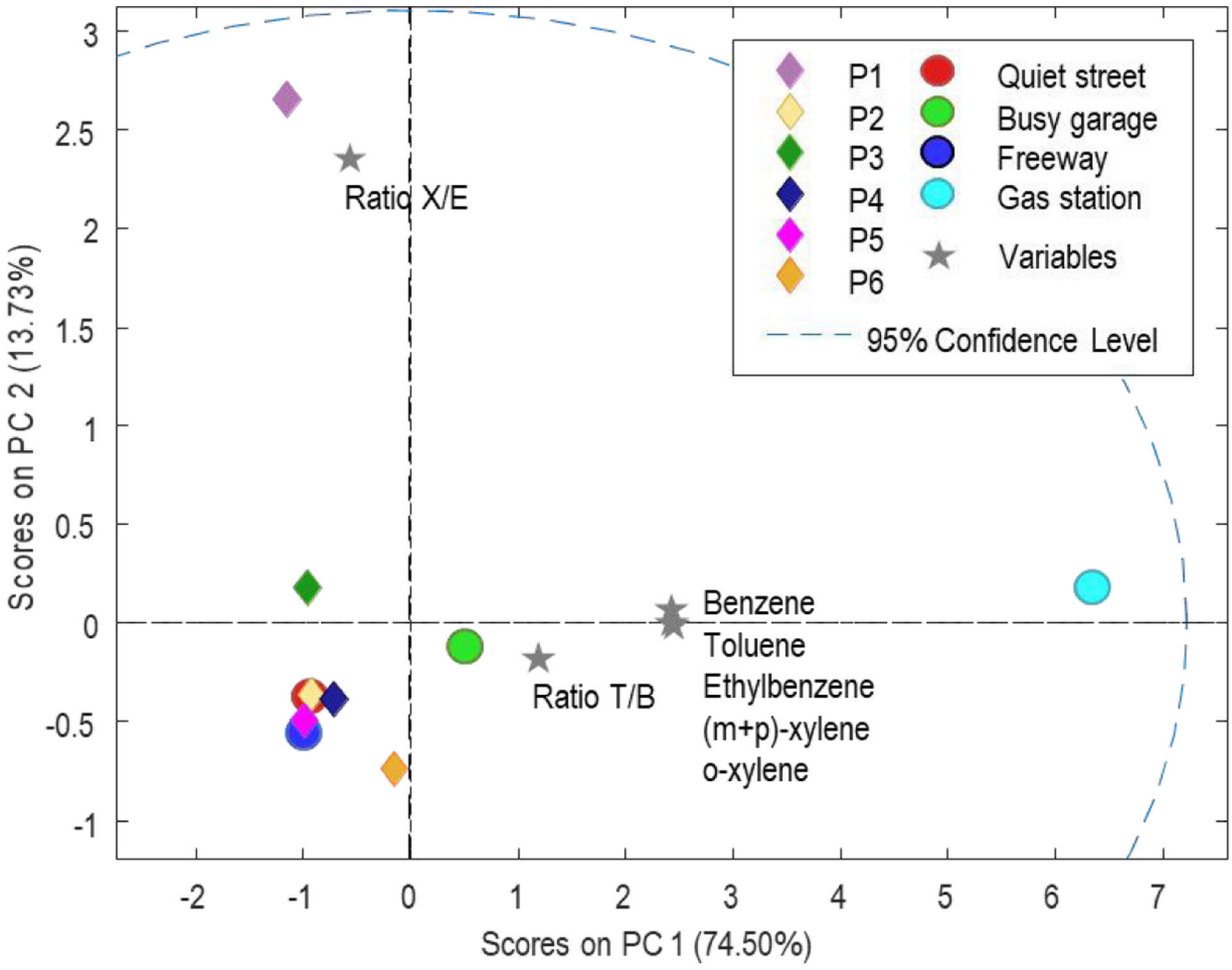

Figure 6.

Bi-plot from PCA using quantified BTEX compounds that shows differences and similarities between participants and locations. Variables are added as a bi-plot representation to show which BTEX compounds explain the distribution.

Table 1.

Connection between locations and participants. Values indicated the proximity and time spent close to the locations (0: not exposed, 5 very exposed)

Participant	P1	P2	P3	P4	P5	P6
Quiet street	5	4	4	5	4	4
Busy garage	1	1	1	2	1	5
Gas station	0	0	0	0	0	4
Freeway	0	0	3	0	3	1

Table 2.

List of identified peaks from the personnel exposure study. Compounds with * have been confirmed with a commercial standard

Peak	RT	Compound	KI calc	KI lit	Formula	CAS	Number of times detected						
							Total	P1	P2	P3	P4	P5	P6
1	3.0	benzene*	700	680	C6H6	71-43-2	54	8	8	9	10	10	9
2	5.1	toluene*	858	770	C7H8	108-88-3	57	9	8	10	10	10	10
3	7.9	ethylbenzene*	889	870	C8H10	100-41-4	54	8	8	10	9	10	9
4	8.2	(m+p)-xylene*	892	890	C8H10	106-42-3	56	8	8	10	10	10	10
5	8.7	o-xylene*	897	890	C8H10	95-47-6	55	8	8	10	9	10	10
6	6.4	hexanal*	872	815	C6H12O	66-25-1	56	8	8	10	10	10	10
7	6.7	butyl ester acetic acid*	875	815	C6H12O2	123-86-4	54	7	7	10	10	10	10
8	8.3	3-methyl-1-butanol acetate*	894	880	C7H14O2	123-92-2	27	2	3	7	8	5	2
9	8.9	heptanal*	905	900	C7H14O	111-71-7	53	8	7	9	9	10	10
10	9.2	2-butoxy ethanol	925	910	C6H14O2	111-76-2	29	1	0	0	8	10	10
11	9.8	1-butoxy-2-propanol	947	940	C7H16O2	5131-66-8	28	0	0	0	8	10	10
12	10.2	1-ethyl-2-methyl-benzene	966	965	C9H12	611-14-3	43	2	3	10	8	10	10
13	10.3	benzaldehyde*	971	980	C7H6O	100-52-7	54	7	9	10	8	10	10
14	10.7	b-pinene*	993	993	C10H16	127-91-3	14	2	0	0	5	7	0
15	10.8	6-methyl-5-hepten-2-one*	995	985	C8H14O	110-93-0	38	2	1	8	10	10	7
16	10.9	1,2,3-trimethyl-benzene	998	1005	C9H12	526-73-8	44	2	4	10	8	10	10
17	11.1	octanal*	1013	1005	C8H16O	124-13-0	55	7	8	10	10	10	10
18	11.4	1,4-dichlorobenzene*	1030	1020	C6H4Cl2	106-46-7	59	9	10	10	10	10	10
19	11.6	limonene*	1039	1035	C10H16	5989-54-8	53	8	6	10	10	10	9
20	11.8	3,7-dimethyl-1,3,6-octatriene	1051	1045	C10H16	3338-55-4	3	2	0	0	1	0	0
21	12.0	isoamyl butyrate	1061	1055	C9H18O2	106-27-4	33	1	1	5	8	10	8
22	12.1	terpinene	1065	1060	C10H16	99-85-4	32	2	0	5	8	9	8
23	12.6	terpinolen	1093	1090	C10H16	586-62-9	19	2	0	5	8	2	2
24	12.8	linalool*	1105	1100	C10H18O	78-70-6	36	2	2	5	8	10	9
25	12.9	nonanal*	1110	1095	C9H18O	124-19-6	59	9	10	10	10	10	10
26	13.0	disulfide, dipropyl	1117	1115	C6H14S2	629-19-6	20	2	0	9	9	0	0

Peak	RT	Compound	KI calc	KI lit	Formula	CAS	Number of times detected						
							Total	P1	P2	P3	P4	P5	P6
27	13.8	(E)-2-nonenal	1168	1165	C9H16O	18829-56-6	44	6	6	6	8	10	8
28	13.9	benzyl acetate*	1172	1170	C9H10O2	140-11-4	51	8	7	9	8	10	9
29	14.4	methyl salicylate*	1206	1200	C8H8O3	119-36-8	59	9	10	10	10	10	10
30	14.4	naphthalene*	1190	1200	C10H8	91-20-3	59	9	10	10	10	10	10
31	14.5	3-decen-1-ol	1217	1230	C10H20O	10340-22-4	59	9	10	10	10	10	10
32	14.8	2-ethylhexyl acrylate	1234	1220	C11H20O2	103-11-7	2	0	2	0	0	0	0
33	14.8	3-ethenyl-1,2-dithi-4-ene	1236	1220	C6H8S2	62488-53-3	2	2	0	0	0	0	0
34	14.9	octyl propionate	1243	1300	C11H22O2	142-60-9	2	0	2	0	0	0	0
35	15.0	benzothiazole	1251	1230	C7H5NS	95-16-9	53	8	7	10	8	10	10
36	15.2	4-(1-methylethyl)-benzaldehyde	1261	1240	C10H12O	122-03-2	46	5	5	10	8	9	9
37	15.3	(E)-2-decenal	1275	1265	C10H18O	3913-81-3	32	2	1	8	2	9	10
38	15.4	(E)-3,7-dimethyl-2,6-octadienal	1281	1275	C10H16O	141-27-5	10	2	0	5	1	2	0
39	16.0	2-methyl-naphthalene	1320	1310	C11H10	91-57-6	55	8	8	10	9	10	10
40	16.0	di-2-propenyl trisulfide	1322	1300	C6H10S3	2050-87-5	22	1	0	10	8	2	1
41	16.9	2-ethyl-3-hydroxyhexyl 2-methylpropanoate	1386	1375	C12H24O3	74367-31-0	57	9	9	10	9	10	10
42	17.3	dodecanal	1420	1420	C12H24O	112-54-9	48	4	5	10	9	10	10
43	17.4	diphenyl ether	1424	1405	C12H10O	101-84-8	56	8	8	10	10	10	10
44	17.8	di-isopropyl adipate	1460	1464	C12H22O4	6938-94-9	9	0	0	9	0	0	0
45	17.8	geranylacetone*	1462	1455	C13H22O	3796-70-1	34	3	2	0	10	10	9
46	18.1	2,6-di-tert-butyl-1,4-benzoquinone	1483	1480	C14H20O2	719-22-2	58	9	9	10	10	10	10
47	18.5	butylated hydroxytoluene	1521	1510	C15H24O	128-37-0	58	9	9	10	10	10	10
48	19.2	1-(1,1-dimethylethyl)-2-methyl-1,3-propanediyl ester 2-methyl-propanoic acid	1600	1603	C16H30O4	74381-40-1	56	8	9	10	10	10	9

Table 3.

Concentration for BTEX compounds during the personnel exposure study. Concentration values expressed in ng m^{-3} of air and standard deviation inside parenthesis (SD)

	Participant 1	Participant 2	Participant 3	Participant 4	Participant 5	Participant 6
benzene	1.0 (0.8)	1.1 (0.9)	1.1 (1.2)	1.0 (0.4)	0.9 (0.7)	1.1 (0.7)
toluene	23.1 (8.2)	15.5 (17.3)	15.9 (15.6)	23.9 (16.1)	17.2 (10.0)	54.1 (42.0)
ethylbenzene	8.2 (8.4)	4.2 (4.4)	16.2 (10.8)	10.1 (6.4)	18.6 (8.6)	34.3 (19.6)
(m+p)-xylene	25.6 (5.2)	15.5 (15.4)	60.2 (24.6)	17.3 (12.5)	33.8 (12.2)	57.9 (42.1)
o-xylene	20.6 (10.8)	10.2 (9.5)	47.6 (21.0)	11.4 (7.1)	27.4 (10.1)	45.5 (35.2)
Ratio toluene/benzene (T/B)	22.3 (14.6)	13.9 (9.1)	14.1 (4.8)	24.5 (22.9)	19.6 (5.0)	47.8 (85.8)
Ratio (m+p-xylene)/ ethylbenzene	3.1 (6.4)	3.7 (4.1)	3.7 (1.7)	1.7 (0.9)	1.8 (0.4)	1.7 (0.3)

Table 4.

Concentration for BTEX compounds in the studies locations. Concentration values expressed in ng m^{-3} of air and standard deviation inside parenthesis (SD)

	Quiet street	Busy garage	Gas station	Freeway
benzene	1.7 (0.7)	16.5 (3.1)	69.9 (35.0)	2.1 (0.3)
toluene	6.9 (0.2)	120.1 (76.7)	1213.1 (115.0)	4.6 (0.4)
ethylbenzene	2.6 (0.1)	60.9 (6.7)	278.3 (20.0)	0.7 (0.2)
(m+p)-xylene	5.6 (0.0)	150.9 (1.7)	508.6 (2.9)	1.2 (0.1)
o-xylene	3.1 (0.7)	54.6 (7.7)	281.6 (24.8)	1.2 (0.3)
Ratio toluene/benzene (T/B)	4.0 (1.7)	7.3 (3.3)	17.4 (8.1)	2.2 (0.5)
Ratio (m+p-xylene)/ ethylbenzene	0.4 (0.0)	0.5 (0.3)	0.2 (0.1)	0.2 (0.6)