A Spatial Investigation of Highly-Resolved Environmental Benzene Concentrations Using Passive Sampling

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INTRODUCTION

Benzene is a volatile organic compound that is emitted primarily from on-road mobile sources. This source category contributes to its classification as an urban air toxic since concentrations of benzene are approximately doubled in urban environments when compared to rural environments.[1] Benzene has also been found at higher concentrations in street canyons than in nearby parks in urban areas of Sweden.[2] Proximity to traffic of the home residence has been found to be associated with increased incidence of health outcomes, such as respiratory effects, cancers and birth effects.[3] These studies suggest that benzene and other traffic related pollutants vary spatially and that these spatial differences in exposure are large enough to be associated with increased health effects.

Benzene is a known human carcinogen for leukemia and lymphoma, and it is associated with non-cancer health effects such as respiratory, cardiovascular, gastrointestinal and neurological outcomes.[4] In children living in SE Texas, higher incidence rates of lymphoma were associated with census tracts containing the highest modeled concentrations of benzene and 1,3-butadiene.[5] The U.S. Environmental Protection Agency (EPA) has denoted in their toxicological support documents that benzene carcinogenicity differs between children and adults, but not enough data are available to quantify these observed differences.[6]

Benzene is currently monitored at approximately 50 sites nationwide by the Urban Air Toxics Monitoring Program (UATMP) and National Air Toxics Trends Stations (NATTS).[7] These networks do not measure benzene at the spatial resolution necessary for understanding differences in exposure. In order to better understand the differences in susceptibility of children and adults to environmental benzene it is necessary to obtain finer spatial resolution data of benzene concentrations. However, due to the expense of current active monitors research into using passive samplers for ambient monitoring of benzene is needed.

The objectives of this study were to develop protocols for the sampling and analysis of benzene using passive samplers, to evaluate these protocols, and to investigate the spatial variation in benzene concentrations and uncertainties in resultant calculated health effect risk levels over a small spatial area. While studies previously mentioned have measured spatial variation in benzene concentrations, this study describes variation over an area rather than variation with distance from roadways.

The Radiello RAD130 passive sampler is used here to investigate environmental benzene concentrations over a small spatial area (with twelve sampling sites separated by distances of tens of meters).

The concentrations observed at these sites are used to calculate the resultant risk for cancer effects in both children and adult populations. While the U.S. EPA method for risk calculation does not incorporate differences between children and adults,[6] the California EPA provides guidance for calculating differences in dose between these two populations;[8] these two methods are used and compared. Since this study is not taking into account the activity patterns of individuals, these calculations are meant to be a representation of uncertainty in risk due to sampler placement rather than actual risk of a child or adult in the area. The results from this study will provide useful insight for future epidemiological studies as well as help gauge the distribution of passive samplers needed to effectively monitor benzene concentrations where people are.

METHODS

Sampler Selection

The Radiello RAD130 sampler was chosen through a thorough literature review of passive samplers. It has been validated at environmental levels in previous studies, has an appropriate detection limit when compared to previously observed values in Hillsborough County, and can be used with solvent desorption (as opposed to thermal desorption, which requires additional instrumentation). Protocols for the use of this sampler, solvent desorption and gas chromatography/mass spectrometry (GC/MS) analysis were developed with the aid of the U.S. EPA methods TO-15[9] and TO-17,[10] the Radiello manual,[11] and published studies that have used the sampler.[12,13]

Sampling Protocol

The sampling protocol that was developed describes the processes of sampler deployment and retrieval to take place at each of twelve sampling locations. A Radiello shelter is put together, and then placed at the sampling location on a pole or tree at a height of 3 m. This is done 24 hours before sampler deployment to test the safety of the location from tampering or theft. During sampler deployment, a RAD130 sampling cartridge is placed in a white diffusive body, which is attached to a support plate and hung inside the shelter. At one sampling site, two samplers are placed in the same shelter for duplicate analysis to assess precision. Field blanks are taken at two of the sampling sites for calculation of the limit of detection. Separate from these twelve sites, one sampler is co-located with the existing active sampler run by the Hillsborough County Environmental Protection Commission (EPC) in Sydney, FL for evaluation. The samplers are left out for seven days, and then are transported back to the laboratory in a cooler with ice packs for extraction and analysis.

Laboratory Analysis Protocol

A protocol for the extraction and subsequent analysis of each cartridge was also prepared. Each cartridge (including the 14 exposed cartridges, two field blanks, and one laboratory blank) is extracted with 2 ml of carbon disulfide (CS_2) and an additional 0.08 ml of a 10.4 µg ml^{-1} solution of 2-fluorotoluene in CS_2 as an internal standard (producing a final concentration of 0.40 µg ml^{-1} 2-fluorotoluene). The cartridges are left in the solvent for 30 minutes, the cartridge is removed, and the solution is placed in a GC/MS vial for analysis. Solutions are stored at 4°C.

The analysis is done on a Varian CP-3800 GC with Saturn 2000 MS and Varian capillary column CP-Sil 8 CB (50m x 0.25mm x 0.25µm; #CP7453). Helium is used as the carrier gas at a rate of 1.2 ml min^{-1} with a split ratio of 0.5. The injector temperature is 240°C and injection volume is 1.0 µl. The temperature program is as follows: start at 35°C and hold for nine minutes, raise to 60°C at 5°C min^{-1} and hold for 46 minutes. The concentration of benzene in each sample is obtained from calculations using the calibration curve created from the initial calibration. After subtraction of mean blank mass, the mass of benzene found in each sampling cartridge (m) is used to calculate the air concentration (C), using the temperature adjusted sampling rate (Q) and the sampling interval (t):

$$Q\left[\frac{ml}{min}\right] = 80.1\left[\frac{ml}{min}\right]\left(\frac{K}{298}\right)^{1.5}$$

$$\mathrm{C}\left[\frac{\mu g}{m^3}\right] = \frac{\mathrm{m}\ [\mu g]}{\mathrm{Q}\left[\frac{ml}{min}\right]\cdot \mathrm{t}\ [min]}\cdot 10^6\left[\frac{ml}{m^3}\right]$$

The variable *K* is the average temperature during the seven day sampling period calculated from hourly weather data that is available from the Hillsborough County EPC for the network monitoring site.

Five calibration standards of benzene at concentrations of 0.15, 0.50, 1.0, 2.5 and 4.0 µg ml^{-1} are made through serial dilutions, each containing the internal standard 2-fluorotoluene at a concentration of 0.40 µg ml^{-1}. This concentration range was determined by using equations 1 and 2 to calculate the mass of sample that would be present from exposure to ambient concentrations experienced in Hillsborough County[14] and other urban areas.[1] These calibration standards are analyzed first to generate the calibration curve. Each of the blanks and samples are analyzed in triplicate. For quality assurance, the percent relative standard deviation (%RSD) for the relative response factor of benzene, the difference of the relative retention time of benzene from the average, the percent difference of the area of the internal standard from the mean, and the difference of the retention time of the internal standard from the mean are calculated for the initial calibration data. These must meet predetermined criteria. Every 24 hour period of analysis, the 1.0 µg ml^{-1} calibration standard must be run as a daily calibration check.

Data Analysis

Once ambient concentrations are determined, several post analyses of the data are performed. First, the coefficient of variation over the sampling area is calculated to investigate homogeneity of concentrations over the area. The observed concentrations are also used to calculate the cancer risk level using two different methods for risk calculation. The U.S. EPA recommends calculating the exposure concentration and multiplying by a range of values of their Inhalation Unit Risk, which incorporate different susceptibilities.[6] The California EPA recommends a method of calculating the exposure dose, which takes into account the normalized breathing rate, and multiplying this dose by their Cancer Potency Factor for benzene.[8]

Protocol Testing

The sampling and laboratory analysis protocols were tested through preliminary work involving generation of the calibration standards and calibration curve, followed by the exposure of one test sampler for seven days. The test cartridge was extracted and analyzed according to the draft protocols and results were used to evaluate and improve the sampling and analysis protocols.

RESULTS AND DISCUSSION

Figure 1 shows the initial calibration curve obtained as a result of the protocol evaluation. As shown in the graph, the coefficient of determination for the calibration line was greater than 0.99. These calibration data also met all of the quality assurance criteria upon calculation of the relative response factors and relative retention times. This calibration curve was used to calculate the amount of benzene in the test cartridge.

Figure 2 is the chromatogram from the analysis of the test cartridge. Peaks for benzene and the internal standard are present. Using this result, the mass of benzene on the test cartridge was 0.32 µg, which corresponds to an ambient concentration of 0.41 µg m^{-3} benzene. This concentration is around the same levels as those measured at the Sydney, FL site over the previous two years.[14] This preliminary run suggests that the range of the calibration standards may need to be broadened to include lower values, as the concentration for the test sample was only 0.152 µg ml^{-1}, near the lower calibration standard level. A range that begins at 0.10 µg ml^{-1} may be more appropriate for the pilot study.

Figure 1. Initial calibration curve generated during testing of the analysis protocol.

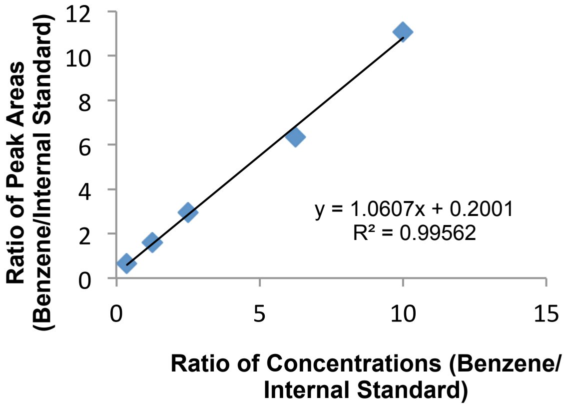
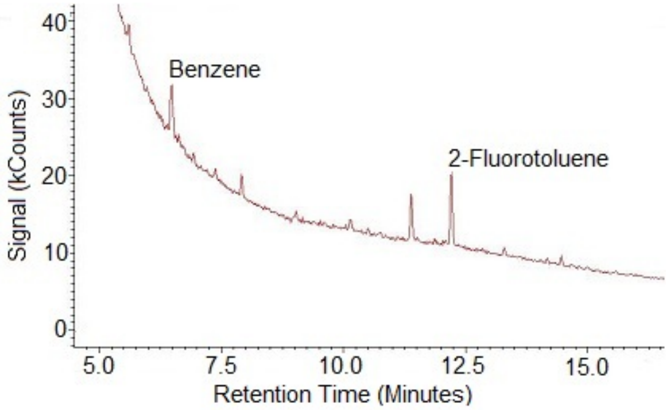


Figure 2. Chromatogram from the test sample.



SUMMARY

This study aims to use passive samplers to investigate the spatial variation of environmental benzene concentrations over a small area of Hillsborough County, Florida. Protocols for sampling and analysis were developed. Calibration standards were created and a calibration curve was generated. A preliminary sampling run with one sampler gave an ambient concentration of 0.41 $\mu g\ m^{-3}$ benzene, which is comparable to previously measured values in the county. This result also provides insight into the calibration range used in the draft protocol, and indicates that a lower range should be used. The preliminary run was crucial in preparing for the forthcoming pilot study, which will provide information on spatial variation in benzene concentrations and the resultant health risks over a small area. Results from the pilot study will provide guidance for a larger passive sampling campaign of the county as well as contribute knowledge that may facilitate future epidemiological studies on health effects of benzene at environmental levels.

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