AMBIENT AIR MONITORING OF

HAZARDOUS VOLATILE ORGANIC COMPOUNDS

IN SEATTLE, WASHINGTON NEIGHBORHOODS:

TRENDS AND IMPLICATIONS

By

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To the Faculty of Washington State University:

The members of the Committee appointed to examine the dissertation of DORIS

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AMBIENT AIR MONITORING OF HAZARDOUS VOLATILE ORGANIC COMPOUNDS IN SEATTLE, WASHINGTON NEIGHBORHOODS: TRENDS AND IMPLICATIONS

Abstract

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Urban areas generally have higher levels of air pollutants than rural or remote areas. People living in these urban communities have higher risks of suffering from diseases linked to these air pollutants. In 2001, the United States Environmental Protection Agency conducted an Urban Air Toxics Pilot Study at various monitoring sites across the country. Seattle, the largest city in the state of Washington, was selected as one of four urban areas to participate in the study. The 2001 study established a network of monitoring sites that provided baseline concentrations of hazardous air pollutants including benzene, 1,3-butadiene, carbon tetrachloride, chloroform, perchloroethylene, trichloroethylene, formaldehyde, and acetaldehyde. The Washington State University Laboratory for Atmospheric Research, in cooperation with the Washington Department of Ecology, began measuring air toxics at Beacon Hill and Georgetown sites in Seattle in 2000 with collection of 24-hour integrated samples every sixth day through the EPA Pilot Study. The network was expanded to six sampling sites in 2001 with the same sampling frequency. Of the six sites,

the Beacon Hill sampling station has a continuous record of hazardous VOC concentrations for the period 2000 to 2005.

The first part of this research was aimed at characterizing the spatial and temporal trends in the ambient air concentrations of these hazardous air pollutants in Seattle, Washington. Statistical analysis showed that benzene, chloroform, perchloroethylene, trichloroethylene and acetaldehyde concentrations exhibited significant spatial variability while only temporal variability was observed for 1,3-butadiene and formaldehyde concentrations. A 67% reduction in ambient benzene levels observed in 2005 relative to the 2000 levels provided the motivation for further characterization of mobile source hazardous VOCs. The ambient levels of benzene, toluene, ethylbenzene and xylenes, which are primarily from mobile sources, were linked to various control programs implemented in Seattle. Elevated chloroform levels observed at sites close to water reservoirs prompted us to quantify the chloroform emissions from water reservoirs, which were found to be about 335 lb/yr. It is hoped that this study will provide baseline data and tools to evaluate the success or failure of current and future control programs in the Seattle area.

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ATTRIBUTION

This dissertation is composed of five separate chapters. Chapter 1 provides an overview of the ambient air monitoring study and general introduction to the three manuscripts presented in Chapters 2-4. These manuscripts will be submitted for publication. Chapter 5 summarizes the various findings presented in the manuscripts and recommendations for future studies. The author is listed as the primary author in all these papers for the significant role played in sample analysis, data analysis and writing.

All the ambient air samples from 2000 to 2005 were collected by the Washington Department of Ecology under the leadership of John Williamson. These air samples were analyzed in the laboratory by Gene Allwine, Lee Bamesberger, Jenny Filipy and the author. Dr. Hal Westberg was responsible for the quality assurance/quality control of the reduced data and the reports submitted quarterly and annually to the US EPA. Statistical analysis was performed by the author with assistance from Dr. V. Krishna Jandhyala. From the chromatograms obtained in the analysis of whole air samples, concentrations of toluene, ethylbenzene and xylenes were extracted. Data extraction was done by the author except for the 2005 data set, which was done by Jenny Filipy. Simulations of chloroform emissions were done by the author based on a Simflux model developed by Dr. Brian Rumburg. Dr. Westberg and Dr. Lamb provided expertise in the analysis of the data and interpretation of the trends observed.

DEDICATION

Dedicated to my mother, Nelia, and my late father, Arsenio whose unconditional love and

support sustained me through all the seasons of my life

CHAPTER 1: INTRODUCTION

A consequence of urban development is the emission of hazardous air pollutants

(HAPs). HAPs or air toxics are those pollutants that are known or suspected to be

carcinogenic, mutagenic, teratogenic, or which are acutely or chronically toxic (EPA

1998). The 1990 Amendments to the Clean Air Act gave the United States

Environmental Protection Agency (US EPA) the mandate to reduce air toxic emissions

from major sources of air pollution using a technology-based and performance-based

approach. A risk-based approach is now being used to address any residual or remaining

risks. The amendments list 188 compounds as air toxics that EPA is required to control.

Section 112(k) of the 1990 Clean Air Act Amendments mandated the EPA to list at least

30 HAPs from area sources that present the greatest risk to public health in urban areas.

EPA made use of available toxicity, ambient air monitoring and emissions inventory data.

In 1996, EPA conducted the first National Scale Air Toxics Assessment (EPA

2002) which provided county level HAPs exposure summaries based on modeling and

1996 emissions data. Based on the results of the assessment, succeeding monitoring

efforts were concentrated on a list of priority HAPs. The 1999 National-Scale Air Toxics

Assessment identified 33 of the 188 air toxics that pose the greatest health risk at ambient

levels. Of the 33 priority HAPs, 13 are from mobile sources and comprise 38% of total

HAPs (EPA 2006).

In 2000, Seattle was selected as one of four urban areas to participate in EPA's

National Air Toxics Pilot Study (NATPS). This study is part of EPA's national air toxics

monitoring program designed to characterize, prioritize, and evaluate the impacts of

HAPs to public health and the environment (US EPA 2000). In order to meet this goal, three objectives have been set for the monitoring program. The first objective is measurement of key HAPs in selected sites to provide trends in space and time as well as an accounting of program progress. The second objective is to provide support to exposure assessments by having a comparison with personal measurements. The third objective is to provide measurements for model evaluation.

The initial monitoring in Seattle's Beacon Hill and Georgetown neighborhoods in 2000 was expanded to include Lake Forest Park, Maple Leaf Reservoir, Lake Sammamish, and Sea-Tac sites in 2001 (Fig. 1). In 2002, only three monitoring sites were maintained (Beacon Hill, Georgetown, and Lake Forest Park). From 2003 to 2005, monitoring continued only at the Beacon Hill site. The Beacon Hill site has been included in the National Air Toxics Trends Stations (NATTS) network. Measurements at this site will be included in the assessment of nationwide trends which could be the basis of future control programs introduced at the federal level and implemented at the state and local levels.

Our project was designed to capture spatial and temporal trends in ambient air toxics concentrations. Spatial variability was determined using 2001 data and seasonal and annual trends were evaluated for the measurements taken at the Beacon Hill site from 2000 to 2005. Summaries of annual averages measured at the six Seattle sites in 2001 have been presented previously (Westberg, 2004). Chapter 2 thus focuses on the seasonal and annual trends observed for the volatile organic compound and carbonyl air toxics. The results of the statistical analyses performed on the data collected at the six Seattle sites in 2001 and at Beacon Hill from 2000 to 2005 are presented also.

Figure 1: Sampling sites in Seattle for 2001

Analysis of benzene measurements taken at Beacon Hill showed a decreasing trend over the six year monitoring period. In 2005, the benzene annual average was found to be 67% less than the 2000 level. Benzene is primarily from mobile sources as a component of fuel and also a product of engine combustion. The observed abatement in ambient benzene concentration was the motivation for investigating the relationship between ambient concentration and mobile source emissions in Seattle. The decreasing trend in ambient benzene levels nationwide (McCarthy, 2007; Harley, 2006; Reiss, 2006; Touma, 2006; Aleksic, 2005; Fortin, 2005) was generally attributed to various control programs at the federal, state and local levels. The investigation presented in Chapter 3 is

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aimed at showing that changes in ambient levels of mobile source air toxics can be linked to the success or failure of control programs.

Statistical analysis of the 2001 data set showed that although chloroform concentrations do not have much seasonal or annual variability, there is spatial variability in chloroform concentrations. The two sites located near water reservoirs, Beacon Hill and Maple Leaf, have elevated annual average chloroform concentrations. Furthermore, the nearest residential neighborhood is about 200 meters from the Beacon Hill site. Simulation of chloroform emissions from the water reservoir at the Beacon Hill site was performed to determine any possible health impacts and the results are presented in Chapter 4. Ambient concentrations were modeled using these emissions and compared with actual measurements.

Monitoring the ambient levels of volatile organic compound and carbonyl air toxics is a critical component for evaluating the success or failure of control programs implemented at the federal, state and local levels. The results of six years of monitoring in Seattle, Washington are presented here to provide baseline data on which to evaluate current and future control strategies.

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CHAPTER TWO

Ambient Air Toxics Concentration Trends in Seattle, Washington

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ABSTRACT

Ambient levels of hazardous air pollutants including benzene, 1,3-butadiene, carbon tetrachloride, chloroform, perchloroethylene, trichloroethylene, acetaldehyde, and formaldehyde were measured in Seattle from 2000 to 2005. The spatial and temporal trends were determined for each species using statistical analysis. Benzene, chloroform, perchloroethylene, trichloroethylene and acetaldehyde were found to have statistically significant spatial variability among the six Seattle neighborhoods. Seasonal variability was observed for benzene, 1,3-butadiene, and formaldehyde. Annual variability was also exhibited by benzene, 1,3-butadiene, and perchloroethylene. A decreasing trend was generally observed for all species, with benzene levels in 2005 dropping to 67% of the 2000 baseline. The observed trends were related to emissions inventories and implemented control programs in Seattle.

INTRODUCTION

Hazardous air pollutants (HAPs) that are deemed to adversely affect human health and welfare are regulated under the Clean Air Act. Currently, there are 188 HAPs that are designated for control. However, relatively little is known about human exposure to these toxic materials in the ambient environment. As a result, the U.S. EPA has developed a national air toxics program with the objective being to characterize the impacts of HAPs on public health and the environment. Ambient measurement data are needed to estimate human and environmental exposures to toxics. Several cities/regions across the U.S. are currently determining or soon will be measuring the levels of toxic materials in their environs.

At present, it is not feasible to measure all 188 of the HAPs listed in Section 112 of the 1990 Clean Air Act Amendments. Consequently, EPA has identified a subset comprised of 33 HAPs that should receive the greatest attention. The 33 compounds fall into four chemical categories: volatile organic compounds (VOCs); carbonyl compounds (aldehydes); semi-volatile organic compounds (SVOCs); and metals. Collection and analytical methodologies are constantly evolving for these urban HAPs. At present, several of the HAPs lack approved ambient collection/analytical techniques. The SVOCs are troublesome because they can exist both as gases and as aerosols in the troposphere. Some of the less stable urban HAPs such as acrolein and ethylene oxide are easily lost during collection and storage prior to analysis. This has led to an even shorter list of toxic compounds that can be reliably measured in the urban environment. EPA has categorized these as urban air toxic (UAT) "core" species. There are nine VOCs, two carbonyls, and seven metals listed as "core" toxics (Table 1).

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Benzene is widely used as an industrial solvent as well as being a component of gasoline and auto exhaust. 1,3-Butadiene is used in rubber manufacturing processes and is emitted from combustion sources. The main source of 1,3-butadiene in Seattle is expected to be mobile source emissions. Carbon tetrachloride usage has been greatly curtailed in recent years due to its contribution to stratospheric ozone depletion and toxicity to human health, but its long atmospheric lifetime accounts for its ambient concentration. Trichloroethylene (TCE) and perchloroethylene (PCE) are used as metal degreasers and dry cleaning solvents.

Table 1. Urban air toxic "core" species.

VOCs	Carbonyls	Metals
Benzene	Acetaldehyde	Arsenic
1,3-Butadiene	Formaldehyde	Beryllium
Carbon tetrachloride		Cadmium
Chloroform		Chromium
Dichloromethane		Lead
1,2-Dichloropropane		Manganese
Perchloroethylene		Nickel
Trichloroethylene		
Vinyl chloride		

Seattle is the largest city in the state of Washington. In 1995, Seattle was one of the three cities, together with Chicago and Houston, used by the US EPA in its Model City HAP Analysis Memorandum (Campbell, 1995). Combined portions of the area source emissions from these cities were used to create an area source HAP emissions inventory for a "model" city in the US. A simple ranking scheme was used in this HAP analysis that led to a list of 33 urban air toxics, a subset of the 188 HAPs listed in the 1990 Clean Air Act Amendments. In 2001, EPA conducted its Urban Air Toxics Pilot Study at various monitoring sites across the country (US EPA, 2000). Seattle was

selected as one of four urban areas to participate in the study. The 2001 study established a network of monitoring sites that provided baseline concentration information for air toxics on a national scale. Washington State University's Laboratory for Atmospheric Research (WSU LAR), in cooperation with the Washington Department of Ecology (WA DOE), began measuring air toxics in Seattle in 2000. Two sites were employed in the initial studies with 24-hr integrated samples collected every sixth day. The network was expanded to six sampling sites in 2001 with the same sampling frequency. During 2002, three Seattle area sites were employed and from 2003 to the present time, one site has been active. The Beacon Hill sampling station is now a National Air Toxic Trends Station (NATTS). A continuous record of air toxic concentrations for the period 2000-2005 is present at Beacon Hill.

The purpose of this manuscript is to provide a description of the year-to-year VOC and carbonyl air toxics behavior in Seattle. We will briefly summarize data that has been previously reported concerning spatial patterns at six neighborhood sites in Seattle (Westberg, et.al., 2004). The focus will then shift to a discussion of temporal patterns during the 2000 to 2005 time period.

EXPERIMENTAL METHODS

Twenty-four hour integrated ambient air samples were collected at a frequency of every six days at all air toxics monitoring sites. Ambient air samples collected at each of the sites in stainless steel canisters were analyzed for VOCs using Compendium Method TO-14A (GC-FID/ECD). Ambient air samples collected on 2, 4-dinitrophenyl hydrazine (DNPH)-coated silica cartridges at each site were analyzed for carbonyl compounds using Compendium Method TO-11A (HPLC). The VOC and carbonyl analyses were performed by WSU LAR. Commercial ZonTech instruments were employed for VOC and carbonyl field sample collections at all of the sites.

Sampling site

Sampling locations employed in Seattle air toxic studies were selected to reflect potential "community-oriented" population exposure. Samplers represented average concentrations within a 0.5 to 4.0 km^2 area, which is termed "neighborhood-scale". Neighborhood-scale measurements provide population exposures that can be used to estimate potential long-term risk since they are thought to reflect units of typical urban population exposures. All sampling stations met US EPA's guidelines for set back distances, inlet heights, and other siting considerations. This population-oriented approach is analogous to the core network for $PM_{2.5}$ and the National Air Monitoring Station (NAMS) trend network for the criteria pollutants. The air toxics monitoring stations were sited to provide air quality information relative to mobile, industrial, wood smoke, and other area sources. Stations were located in distinctly different sub-regions within the urban area, so that spatial variability of air toxics concentrations could be characterized. Emphasis in this manuscript is on Washington Department of Ecology's

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Beacon Hill (BH) sampling site, which is located in a controlled-access, water reservoir impoundment at the top of a hill 5 km southeast of downtown Seattle. Seattle's main industrial area lies to the west of Beacon Hill (Fig.1). Based on an analysis of air toxic data collected during the 2001 Pilot Cities Study, it was found that the annual mean concentrations of most species were quite similar at the six Seattle area sites. Based on these results and the fact than Beacon Hill served as a PM speciation network site, it was chosen as a NATTS for air toxics. There is a continuous record of "core" air toxic concentrations beginning in January 2000 until the present at this site. The six sites (see Figure 1) were located as follows:

- Lake Forest Park (LF) is a suburb approximately 24 km north of downtown Seattle. The site had been employed as a $PM_{2.5}$ monitoring station in past years. Emissions from residential wood burning and mobile sources were expected to be prominent at this site.

- The Maple Leaf Reservoir (ML) site was in the middle of the Maple Leaf residential community approximately 16 km north of downtown Seattle. It was surrounded by a region of high population density that included a mix of urban emission sources.

- Washington Dept. of Ecology's Beacon Hill (BH) sampling site is located in a controlled-access, water reservoir impoundment at the top of a hill southeast of downtown Seattle. An observer looking to the west can see King County Airport, Interstate Highway 5, and Seattle's main industrial area.

- The Georgetown (GT) site was established in a WA Dept. of Transportation (DOT) facility that is located a short distance north of the Georgetown residential

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neighborhood. Seattle's main industrial complex lies to the north of the Georgetown site.

- The South Seattle site was located just north of the Seattle-Tacoma International Airport (ST), which is approximately 32 km south of downtown Seattle. The site was impacted by mobile sources from a network of nearby freeways and congested streets.

- The easterly site was located roughly 16 km from downtown Seattle near Lake Sammamish (LS). This site was intended to measure air quality in the rapidly expanding residential areas to the east of the urban center.

Figure 1. Location of the 2001 sampling sites in Seattle, WA

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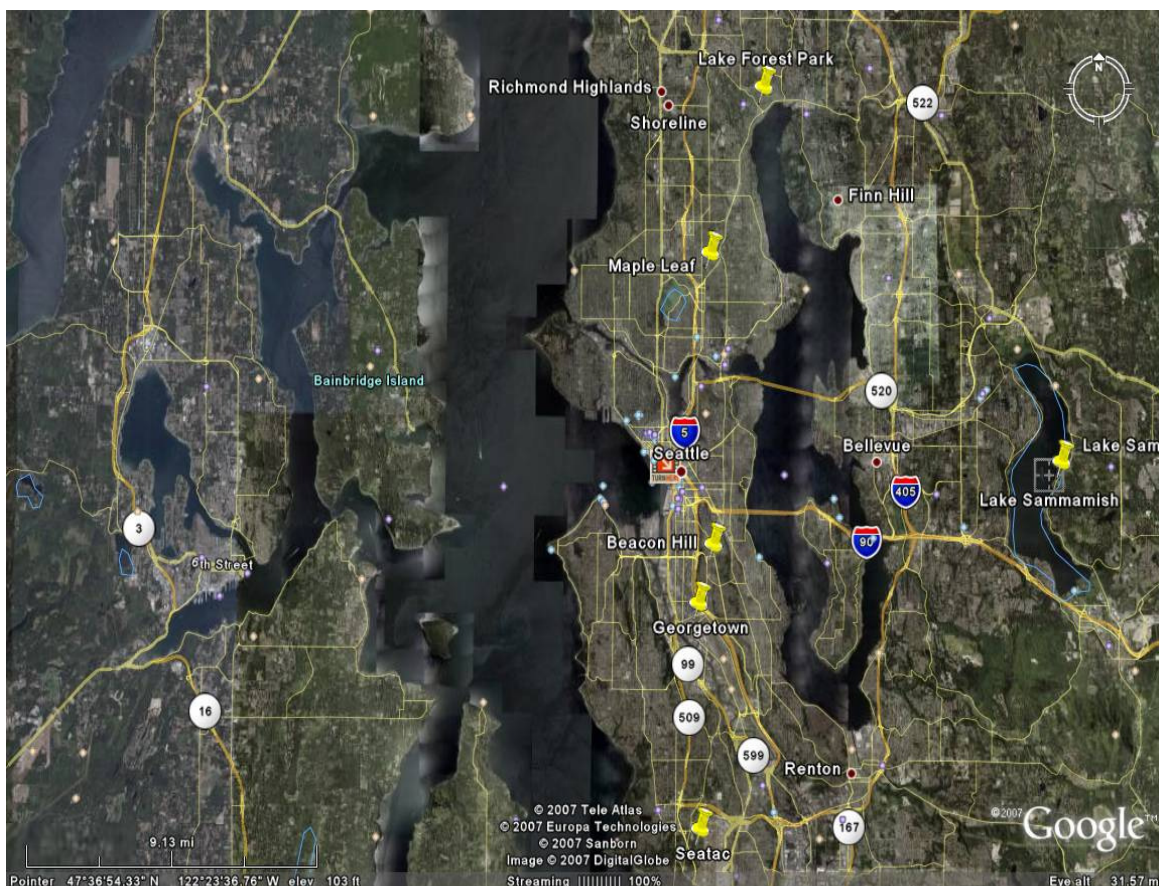
Sampling

VOC Sampling. The XonTech 910A samplers were programmed to fill a 6-liter passivated, stainless steel canister to about 1.5 atm. (~ 10 L) over the collection period. At the end of the 24-hour collection period, sample canisters were removed from the collection system and shipped to Pullman, Washington for VOC analysis.

Carbonyl Sampling. XonTech 925PC carbonyl samplers were employed for determination of formaldehyde and acetaldehyde. A measured amount of air was passed through a silica gel cartridge impregnated with DNPH. The cartridges were sealed and shipped to Pullman for analysis. An ozone scrubber was attached to the inlet line.

Analysis

VOC Analyses. A Hewlett Packard 5890 gas chromatograph was used for VOC analyses. A DB-1 fused silica capillary column (J & W Scientific) was employed to resolve VOCs in the C_3-C_{12} molecular weight range. The column effluent was split on the downstream end with about 90% of the flow to an FID and 10% to an ECD. The normal carrier gas flow system was modified to include a freeze-out trap for concentrating organics in the ambient air sample. Nitrogen at 1 cm^3 min^{-1} was used as the carrier gas with the DB-1 fused silica capillary column. Optimum results were obtained by temperature programming the column oven from -50 to 150 °C at 4 °C min^{-1}.

Air from the sample canister was drawn through the cryogenic trap into an evacuated cylinder. The sample volume was determined by measuring the pressure change in the cylinder. Normally, 750 ml of air was passed through the freeze-out trap, which was maintained at -186 °C (liquid oxygen). The trap itself consisted of a 3.18 mm

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x 15.24 cm stainless steel tube containing 60-80 mesh glass beads. This trap was attached to the gas chromatograph via a mini-volume gas-sampling valve (Valco Inst.).

Peak identities for the pure hydrocarbons (e.g. benzene and 1,3-butadiene) were based on comparison of retention times and mass spectra with known standards. The concentration of the hydrocarbons was determined by ratioing the instrument response for each peak to that recorded for a known concentration of 2,2-dimethylbutane. The concentration of the 2,2-dimethylbutane standard was assigned through comparison with a purchased National Institute of Standards and Technology propane Standard Reference Material. Determination of the levels of the halogenated hydrocarbons was based on a comparison of peak area responses to a certified TO-14 standard purchased from a commercial supplier. Each chromatogram was visually examined to ensure data quality. *Carbonyl Analyses.* Exposed DNPH cartridges were eluted with acetonitrile (ACN), the eluent volume was measured, and the hydrazones in the eluted samples were quantified by a Hewlett Packard 1090 series II High Performance Liquid Chromatograph with a diode array detector (DAD) operated at 360 nm. Peak separation was accomplished with a 10 cm OD-MPS reverse phase column (Supelco) with a gradient elution ranging from 50:50 to 30:70 H_2O:ACN over the period from 5 to 17minutes. A 20 μL sample loop was employed and the total solvent flowrate was 0.8 mL min^{-1}. Qualitative identification of the hydrazones was performed by matching the retention times with those of known standards. For quantitation, pure carbonyl hydrazone derivatives were prepared or purchased. High concentration master standards were prepared for each carbonyl of interest and these were then used to prepare a set of working standards ranging from 0.2 to 5 mg mL^{-1}. A running calibration for relating peak areas to hydrazone concentrations

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was formed by taking the running mean of the standard analyses (area counts for each analyte) over the time period the analyses were conducted. Ambient carbonyl concentrations were calculated from the recorded peak area, eluent mass, and air volume sampled.

Quality Assurance

Quality assurance activities during the UAT sampling program included duplicate sample collections at the Beacon Hill site. This provided a measure of sampling uncertainty. In addition, many replicate analyses were performed which were used to judge analytical precision. Relative percent difference (RPD) was the statistical measure used to judge comparability of duplicate and replicate analyses. Often a replicate analysis was carried out on the sample and/or the duplicate. This then gave as many as four analyses (sample and replicate plus duplicate and replicate) for a single 24-hr collection period at Beacon Hill. When comparing the results from three or more analyses, relative standard deviation (RSD) was used to calculate precision. Table 2 shows precision results determined during the 2003 calendar year. These values are representative of the entire 2000 – 2005 sampling period.

Statistical Analysis

All statistical analyses were performed using SAS statistical software version 9.0 (SAS Institute). A generalized linear model (GLM) was run for the 2001 data set to determine spatial variability (site effects). Only dates with no missing data for all HAPs were included in the analysis. To determine seasonal effects, a regression model was used for the 2000 to 2005 data set measured at Beacon Hill. Missing data were accepted by model and all sampling dates were included. Winter was defined as the period from

December to February; spring was from March to May; summer was from June to August and fall was from September to November.

Table 2. Precision statistics and minimum detection levels (MDL) for VOC species measured in Seattle during 2003.

	Sampling (%)	n	Analytical (%)	n	MDL (ppbv)
Benzene	15.0	46	10.3	58	0.009
1,3-Butadiene	36.5	45	27.7	56	0.018
Carbontetrachloride	19.2	46	12.2	57	0.010
Chloroform	16.1	46	10.3	58	0.021
Perchloroethylene	15.0	46	8.0	58	0.010
Trichloroethylene	16.2	46	9.2	58	0.009
Acetaldehyde	5.5	60	0.6	61	0.009
Formaldehyde	8.5	60	1.6	61	0.016

RESULTS AND DISCUSSION

Summaries of the Pilot Cities 2001 air toxic measurements in Seattle have been presented (Westberg, 2004; Westberg, 2003). Annual means together with other statistics for each of the "core" species were reported in these manuscripts. These data were the air toxic concentrations reported in the Pacific Northwest's largest city and provided a baseline for comparing air toxic levels in Seattle to other cities in the Pilot Cities Network (US EPA, 2001). Table 3 lists annual average concentrations and the 95% confidence interval measured at the six Seattle sites in 2001. With a few exceptions, annual means for the individual VOCs varied by less than a factor of two throughout the network. Annual means close to 0.05 parts per billion by volume (ppbv) for 1,3-butadiene were recorded at the six sites. Carbon tetrachloride exhibited negligible spatial variation with an annual mean of 0.10 ppbv at all six sites. The acetaldehyde's annual

average varied between 0.63 and 0.76 ppbv while formaldehyde and benzene annual means showed somewhat more variability but still less than a factor of two.

Chloroform, perchloroethylene and trichloroethylene exhibited the largest spatial differences. Annual average chloroform concentrations at Maple Leaf and Beacon Hill were approximately double the values recorded at the other four sites. The two sites with elevated chloroform levels are located close to drinking water treatment facilities. It is well known that trihalocarbons, such as chloroform, are produced when water containing humic substances is chlorinated (Abd El-shafy, 2000; Garcia-Villanova, 1997a,b). Chloroform emissions from the water reservoirs are a major contributor to ambient levels measured at these sites. For example, when the BH sampling site is downwind of the reservoir for most of a 24-hr sampling period, chloroform levels often exceed 0.10 ppbv. When winds advect urban air from directions away from the reservoir, chloroform levels are generally in the 0.02 ppbv range. Thus, the chloroform annual means observed at Beacon Hill reflect levels close to the water treatment facility, but are not representative of the Seattle area in general.

Perchloroethylene and trichloroethylene annual average concentrations were significantly higher at the Georgetown neighborhood site. The trichloroethylene annual average was nearly twice that observed at the other five sites. The elevated levels of these two chlorocarbons at the Georgetown site are likely the result of its close proximity to Seattle's main industrial area.

Table 3. Spatial variation of hazardous air pollutants in Seattle, WA

Site	Mean (ppbv)	95 % CI (ppbv)	Max (ppbv)	Min (ppbv)	n	Pr > F (n=189)
benzene						
Lake Forest	0.52	0.09	1.65	0.14	61	
Maple Leaf	0.35	0.04	0.67	0.12	62	
Beacon Hill	0.41	0.06	1.70	0.1	69	
Georgetown	0.54	0.11	2.22	0.1	66	
Sea-Tac	0.33	0.04	0.95	0.1	63	
Lake Sammamish	0.37	0.04	0.68	0.11	57	
Seattle Average	0.43	0.03	2.22	0.1	378	0.0202
1,3-butadiene						
Lake Forest	0.06	0.01	0.50	0.01	61	
Maple Leaf	0.04	0.01	0.24	0.01	62	
Beacon Hill	0.04	0.01	0.27	0.01	63	
Georgetown	0.05	0.01	0.23	0.01	60	
Sea-Tac	0.05	0.01	0.33	0.01	63	
Lake Sammamish	0.05	0.01	0.37	0.01	57	
Seattle Average	0.05	0.01	0.5	0.01	366	0.1807
carbon tetrachloride						
Lake Forest	0.102	0.004	0.162	0.062	61	
Maple Leaf	0.097	0.003	0.124	0.068	62	
Beacon Hill	0.096	0.003	0.127	0.07	69	
Georgetown	0.103	0.004	0.182	0.072	65	
Sea-Tac	0.099	0.003	0.14	0.067	63	
Lake Sammamish	0.099	0.004	0.148	0.066	55	
Seattle Average	0.099	0.004	0.182	0.062	375	0.5723
chloroform						
Lake Forest	0.03	0.004	0.080	0.011	61	
Maple Leaf	0.047	0.009	0.185	0.008	62	
Beacon Hill	0.044	0.007	0.143	0.011	69	
Georgetown	0.029	0.005	0.11	0.01	65	
Sea-Tac	0.026	0.004	0.062	0.007	63	
Lake Sammamish	0.026	0.004	0.093	0.001	55	
Seattle Average	0.034	0.003	0.185	0.001	375	< 0.0001

Site	Mean (ppbv)	95 % CI (ppbv)	Max (ppbv)	Min (ppbv)	n	Pr > F (n=189)
perchloroethylene						
Lake Forest	0.036	0.011	0.267	0.004	61	
Maple Leaf	0.031	0.008	0.181	0.005	62	
Beacon Hill	0.023	0.005	0.116	0.003	69	
Georgetown	0.054	0.012	0.280	0.004	65	
Sea-Tac	0.021	0.006	0.113	0.003	63	
Lake Sammamish	0.026	0.008	0.185	0.004	55	
Seattle Average	0.032	0.004	0.28	0.003	375	<0.0001
trichloroethylene						
Lake Forest	0.031	0.006	0.107	0.003	60	
Maple Leaf	0.039	0.006	0.119	0.007	62	
Beacon Hill	0.035	0.005	0.138	0.003	69	
Georgetown	0.071	0.018	0.462	0.01	65	
Sea-Tac	0.032	0.013	0.408	0.004	63	
Lake Sammamish	0.026	0.007	0.181	0.004	55	
Seattle Average	0.04	0.006	0.462	0.003	374	<0.0001
acetaldehyde						
Lake Forest	0.66	0.07	1.50	0.21	60	
Maple Leaf	0.63	0.08	2.30	0.13	56	
Beacon Hill	0.74	0.14	2.50	0.11	58	
Georgetown	0.67	0.11	2.61	0.14	59	
Sea-Tac	0.76	0.09	2.09	0.21	61	
Lake Sammamish	0.71	0.12	3.34	0.33	57	
Seattle Average	0.69	0.07	3.34	0.11	351	0.0032
formaldehyde						
Lake Forest	0.89	0.1	2.30	0.14	61	
Maple Leaf	1.03	0.13	2.39	0.22	54	
Beacon Hill	1.35	0.17	3.70	0.2	66	
Georgetown	1.20	0.17	3.77	0.08	67	
Sea-Tac	1.08	0.12	2.44	0.04	63	
Lake Sammamish	0.85	0.15	3.12	0.07	59	
Seattle Average	1.08	0.06	3.77	0.04	370	0.0688

Based on results from the 2001 air toxic Pilot Study in Seattle, the Beacon Hill site was chosen to serve as a future air toxics trends site. Measurements were made continuously from January 2000 until the spring of 2006. There was a sampling gap through most of 2006 with sampling commencing again in 2007 and continuing until the present. We now have a continuous record of air toxics concentrations from January 2000 through December 2005 at the Beacon Hill site and can use these data to better understand temporal patterns and concentration trends over the six-year period.

A time series analysis was performed for each VOC species. Table 4 lists the annual mean concentration for each of these species from 2000-2005. There appears to be a decreasing trend in benzene, 1,3-butadiene and trichloroethylene relative to the year 2000 levels. Formaldehyde annual means decreased with the exception of 2003, when a six-week period of very high concentrations during the summer greatly enhanced the annual average values for that year. Carbon tetrachloride annual means remained constant at continental background levels (~0.10 ppbv). As noted earlier, the Beacon Hill site is located adjacent to a reservoir that treats drinking water. Emissions from the water treatment facility tended to maintain nearly constant annual average chloroform concentrations during the six-year period. Annual averages for perchloroethylene did not change much between 2000 and 2005.

Table 5 summarizes the year-to-year percentage change in each VOC relative to their 2000 concentration. Significant decreases in concentration were observed for benzene (67%), 1,3-butadiene (56%), trichloroethylene (43%) and formaldehyde (42%). Carbon tetrachloride, chloroform, perchloroethylene and acetaldehyde exhibited much smaller changes over the six-year period. With the exception of acetaldehyde and

formaldehyde, most of the HAPs exhibited their maximum concentrations during the

winter months (Fig. 2a-h).

Table 4. Annual mean concentrations in ppbv and $\mu g/m^3$ (in parentheses) measured at
the Beacon Hill site in Seattle.

	2000	**2001**	**2002**	**2003**	**2004**	**2005**
Benzene	0.53(1.69)	0.45(1.43)	0.38(1.22)	0.39(1.24)	0.40(1.27)	0.18(0.56)
1,3-Butadiene	0.08(0.17)	0.06(0.13)	0.04(0.09)	0.04(0.09)	0.06(0.13)	0.03(0.08)
CCl$_4$	0.10(0.65)	0.10(0.65)	0.10(0.65)	0.11(0.68)	0.10(0.65)	0.10(0.65)
Chloroform	0.06(0.27)	0.05(0.23)	0.05(0.23)	0.05(0.23)	0.05(0.23)	0.05(0.23)
PCE	0.03(0.20)	0.02(0.15)	0.04(0.25)	0.02(0.15)	0.03(0.20)	0.03(0.20)
TCE	0.05(0.28)	0.04(0.21)	0.02(0.10)	0.02(0.10)	0.02(0.10)	0.03(0.16)
Acetaldehyde	0.85(1.5)	0.77(1.4)	0.83(1.5)	1.1(1.8)	0.80(1.4)	0.81(1.5)
Formaldehyde	1.8(2.3)	1.5(1.8)	1.3(1.6)	3.1(3.8)	0.87(1.1)	1.1(1.3)

Table 5. Decrease (%) in air toxic VOC concentrations relative to 2000 levels in Seattle.

	benzene	1,3-butadiene	CCl4	chloroform	PCE	TCE	acetal	formal
2001	-16	-22	-4	-16	-19	-27	-10	-21
2002	-28	-47	2	-15	26	-56	-3	-28
2003	-27	-50	5	-2	-26	-64	19	70
2004	-25	-27	1	-15	-13	-68	-7	-52
2005	-67	-56	-3	-14	15	-43	-5	-42
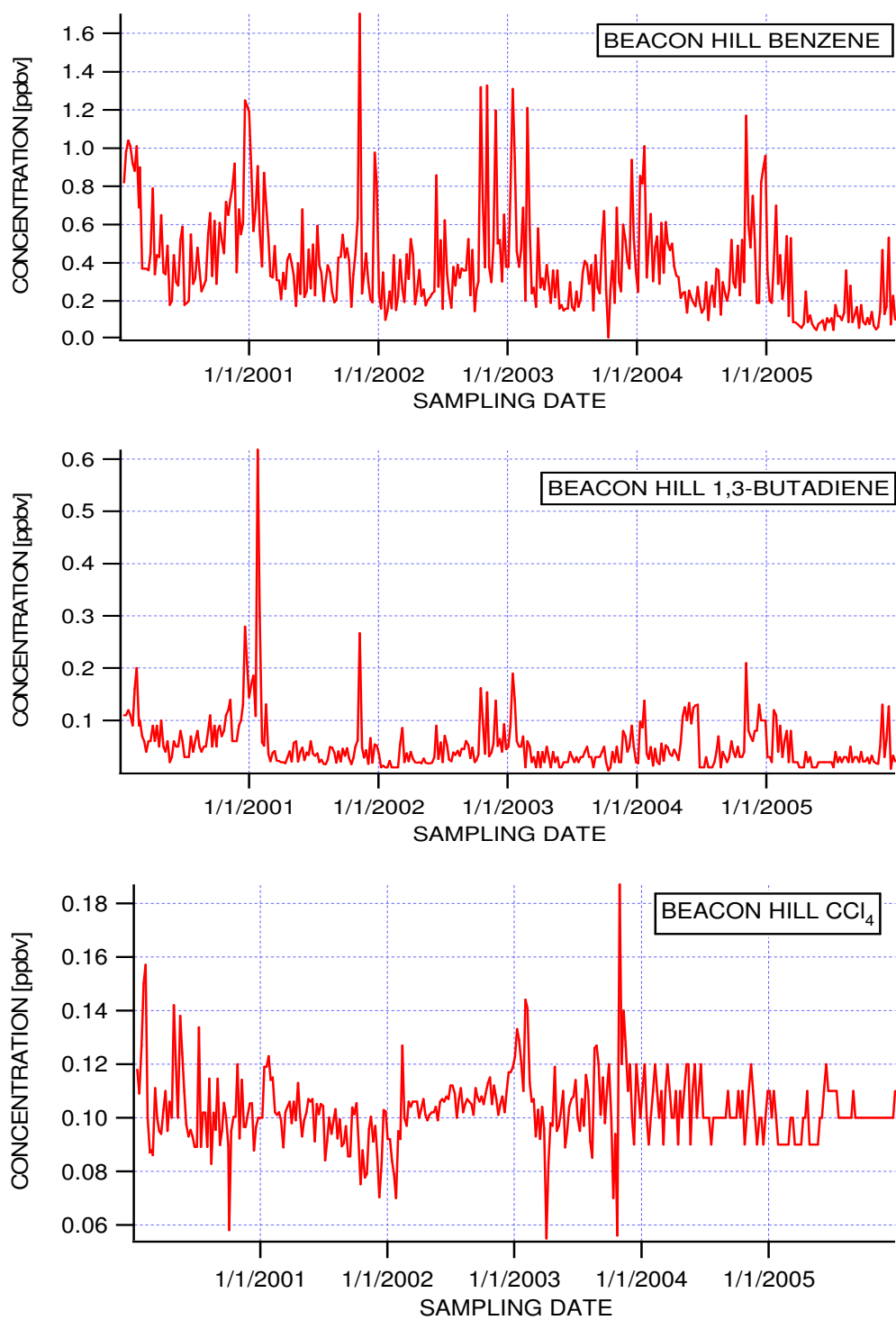
Figure 2a-c. Time series plots of ambient levels of HAPs at Beacon Hill, Seattle (a) Benzene (b) 1,3-Butadiene (c) Carbon Tetrachloride

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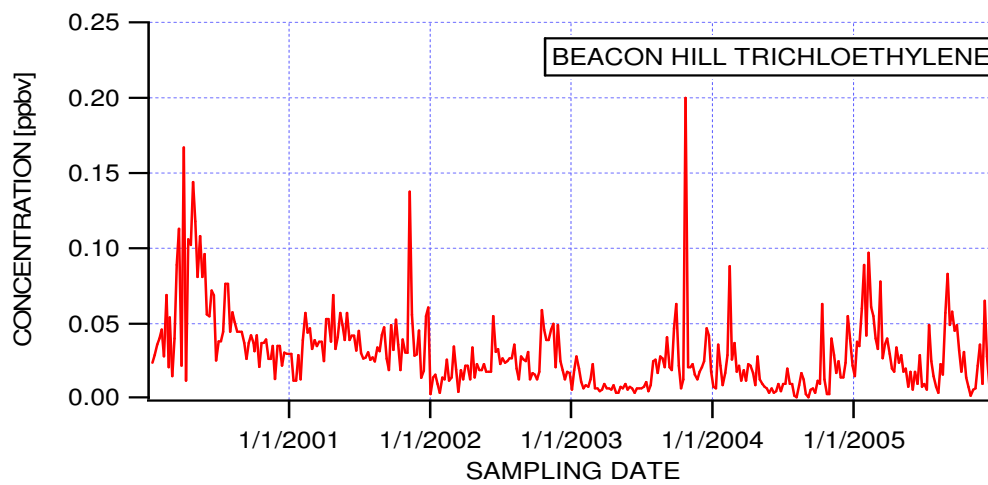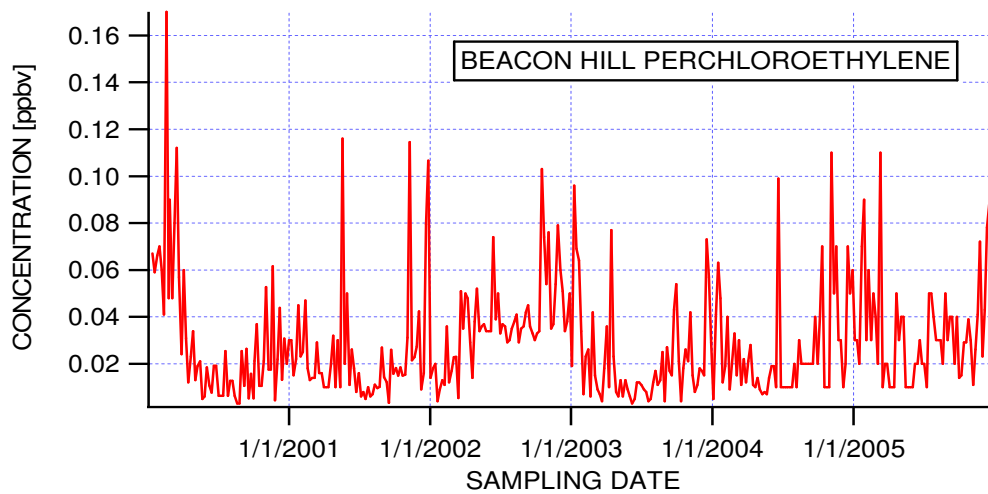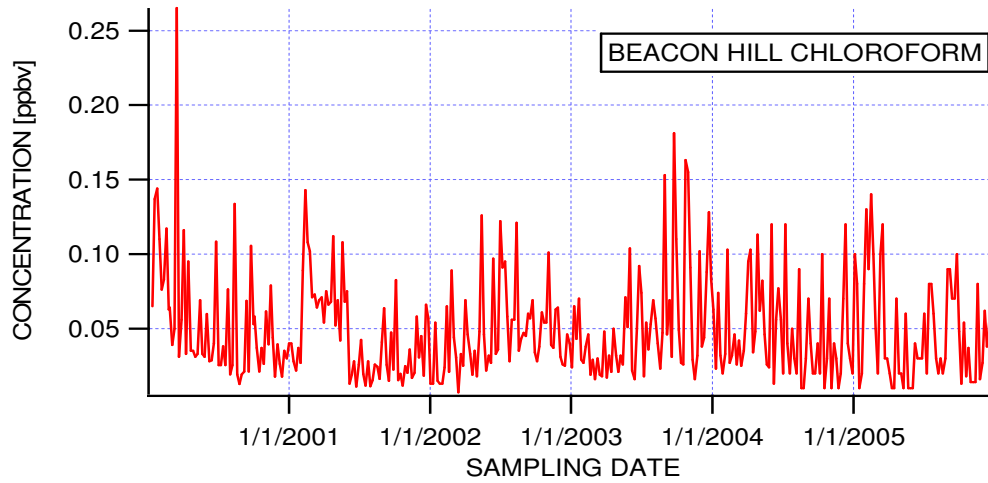
Figure 2d-f. Time series plots of ambient levels of HAPs at Beacon Hill (d) Chloroform
(e) Perchloroethylene (f) Trichloroethylene

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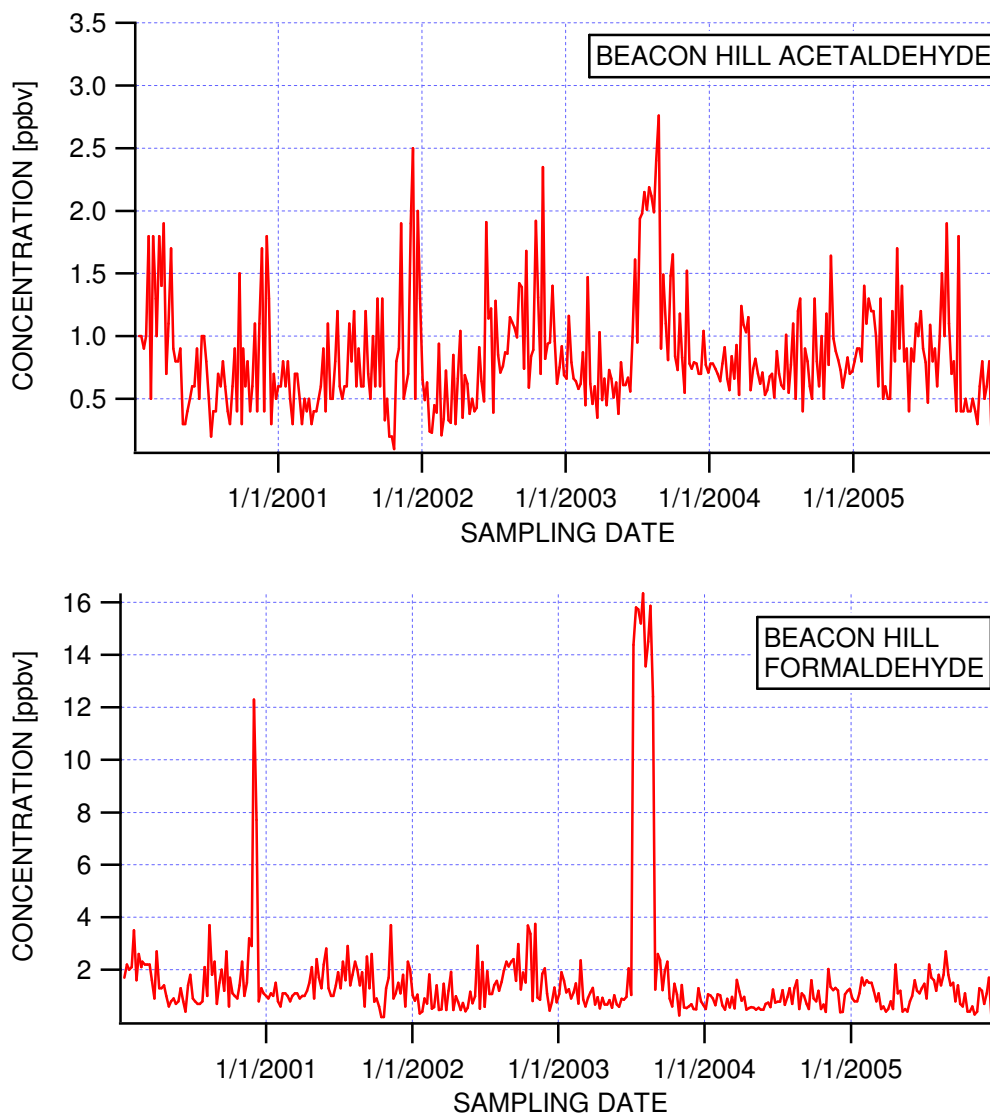
Figure 2g-h. Time series plots of ambient levels of HAPs at Beacon Hill (g) Acetaldehyde (h) Formaldehyde

Emission reductions, year-to-year meteorological changes and sampling/analytical factors all can influence temporal trends. It is our belief that the sampling and analysis had minimal influence on the observed 2000-2005 VOC trends. The field and laboratory procedures did not change during this period and the annual analytical and sampling precision statistics remained constant. We have utilized annual means for examining the changes in air toxic concentrations over time in Seattle. Annual

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means are used by toxicologists for assessing health risks due to exposure to air toxics and therefore are appropriate for the present discussion. However, annual means can be influenced by a few very high concentrations measured during the year. In Seattle, the high values are usually recorded during the winter months when meteorological mixing is limited. Thus, it is important to consider meteorology as well as emissions changes when evaluating trends in air toxic concentrations. One way to do this is to look at seasonal variations over the six-year period. Statistical analysis using a regression model in SAS shows that benzene, 1,3-butadiene and formaldehyde exhibit statistically significant seasonal variation while benzene, 1,3-butadiene and perchloroethylene exhibit some statistically significant annual variability as well (Table 6). In Seattle, mobile sources are the primary emitters of benzene and 1,3-butadiene, area and industrial sources release the chlorocarbons and the carbonyls have both primary and secondary sources.

Table 6. Seasonal and annual variability of HAPs at Beacon Hill

	n	Missing Data	Pr > F	
			year	season
Benzene	334	27	< 0.0001	0.0217
1,3-Butadiene	334	27	0.0001	0.0114
Carbon Tetrachloride	334	27	0.9969	0.1853
Chloroform	334	27	0.4430	0.8437
Perchloroethylene	334	27	< 0.0001	0.4889
Trichloroethylene	334	27	0.2437	0.1309
Formaldehyde	334	27	0.3235	0.0229
Acetaldehyde	334	27	0.1795	0.1039

Benzene and 1,3-Butadiene. Figure 2a shows benzene concentrations over the six-year time span. The seasonal cycle of concentration changes is readily apparent in this figure with high and quite variable wintertime values and lower summertime concentrations.

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Maximum and minimum values observed in the individual 24-hr integrated samples were 1.70 and 0.01 ppbv respectively.

The reason for the reduction in ambient benzene levels is most likely due to gasoline control measures implemented in the Seattle area. The decrease in ambient benzene levels correlates well with the decrease in benzene emissions from mobile sources (Fig. 3). Vapor recovery systems are now required at nearly all gasoline stations in Seattle and BP, a major supplier of gasoline for the Seattle market, lowered the benzene content of their fuel beginning in the fall of 2004 (Fridrich, 2006).
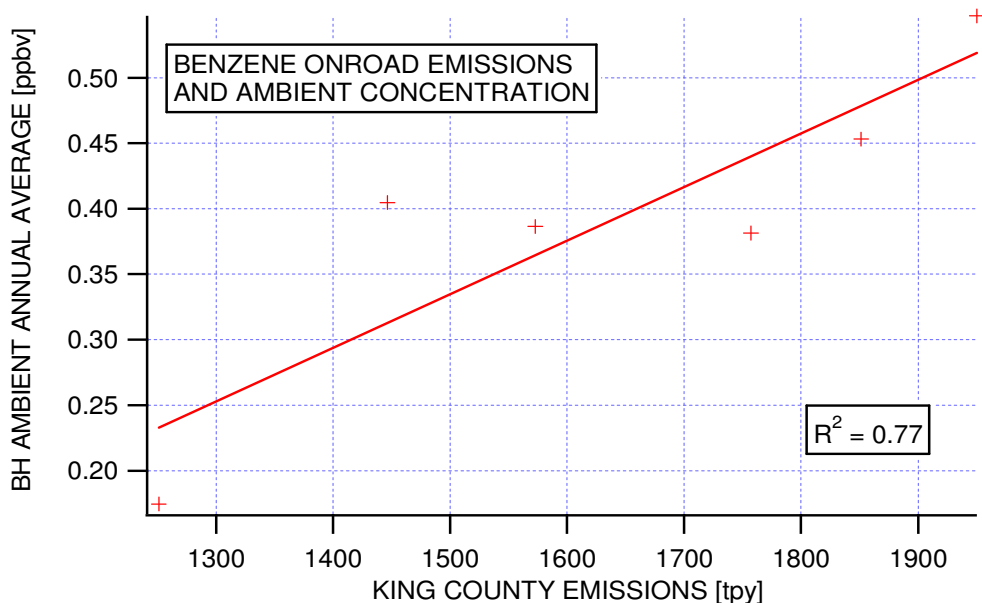
Figure 3. Relationship between onroad benzene emissions (King Co., WA) and ambient benzene concentrations recorded at Beacon Hill during the years 2000-2005.

Ambient benzene levels show some weekend-weekday variation (Fig. 4), which is to be expected if traffic is the major source. The benzene point source contribution is very small relative to mobile sources (Table 7). Thus, the decreasing trend in annual mean benzene levels is best attributed to emission changes in the transportation sector. Meteorological factors influence benzene seasonal concentrations most significantly during the winter months. Periods of low ventilation are more common during this time of year in Seattle and result in elevated benzene levels. The shift to lower mixing ratios between 2000 and 2005 can be seen in Table 8. The 2002 wintertime period showed an abnormally low mean concentration compared to the annual average (Table 8). Using wind speed as a measure of ventilation, it can be seen in Figure 5 that higher than normal wind speeds prevailed during the 2002 winter months. Roughly 90% of wind speed recordings during most of wintertime periods shown in Figure 5 fell in the less than 2 m s^{-1} range, while in 2002 this dropped to 70%.
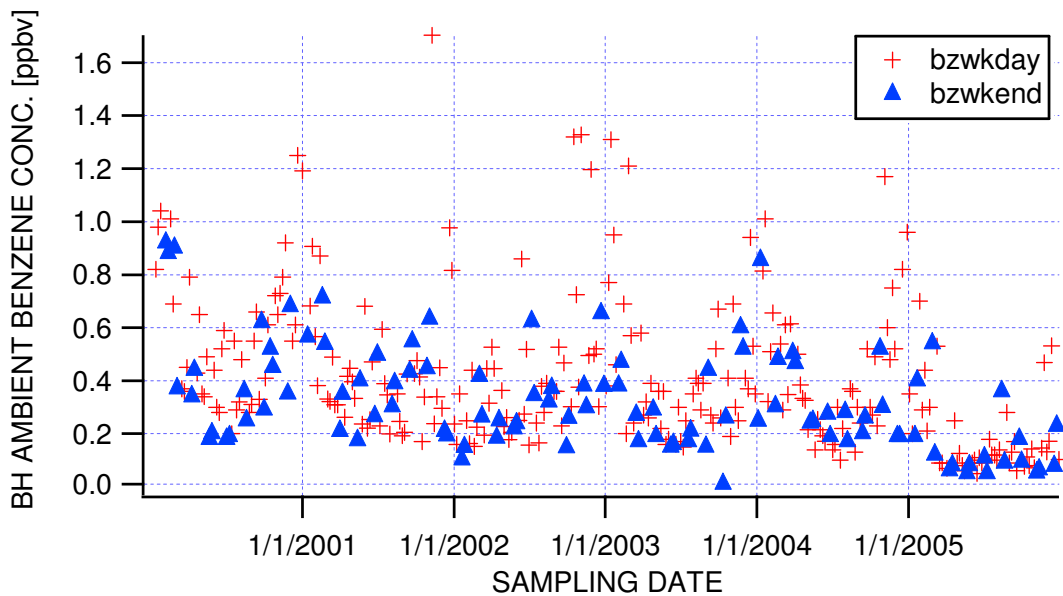
Figure 4. Weekday-weekend variation of benzene mixing ratio measured at Beacon Hill, Seattle

Table 7. VOC Emission estimates for Washington state (tons/yr)

Year		Onroad (King)	Point Sources	Nonroad (WA)	Nonroad (King)*	King/WA	Total**
2000							
	Benzene	1950	0.273	1527	436		2387
	1,3-Butadiene	194	0.038	197	59		254
	Formaldehyde	571	16.267	740	197		784
	Acetaldehyde	192	0.002	318	84		276
2001							
	Benzene	1851	0.328	1504	430		2282
	1,3-Butadiene	181	0.117	193	58		240
	Formaldehyde	533	12.590	719	191		736
	Acetaldehyde	180	0.002	308	82		262
2002							
	Benzene	1757	0.295	1475	432	0.29	2190
	1,3-Butadiene	169	0.037	189	56	0.30	226
	Formaldehyde	497	8.992	698	193	0.28	699
	Acetaldehyde	169	0.000	298	82	0.27	251
2003							
	Benzene	1573	0.448	1441	412		1985
	1,3-Butadiene	141	0.000	185	56		197
	Formaldehyde	411	7.865	677	180		599
	Acetaldehyde	144	0.001	288	77		221
2004							
	Benzene	1447	0.987	1396	399		1846
	1,3-Butadiene	128	0.001	180	54		182
	Formaldehyde	375	12.640	654	174		561
	Acetaldehyde	132	0.001	278	74		205
2005							
	Benzene	1251	2.584	1345	374	0.28	1628
	1,3-Butadiene	113	0.000	174	53	0.31	166
	Formaldehyde	293	14.254	630	161	0.25	468
	Acetaldehyde	108	0.001	267	69	0.26	177

* Estimated using average of 2002 & 2005 EI King/WA ratio
** Total for King County

Table 8. Seasonal mean benzene mixing ratios (ppbv)

	WINTER	SPRING	SUMMER	FALL	AVE
2000	0.91	0.41	0.35	0.57	0.55
2001	0.73	0.35	0.33	0.48	0.45
2002	0.31	0.30	0.36	0.56	0.38
2003	0.61	0.31	0.24	0.38	0.39
2004	0.56	0.36	0.22	0.46	0.40
2005	0.41	0.13	0.13	0.13	0.17
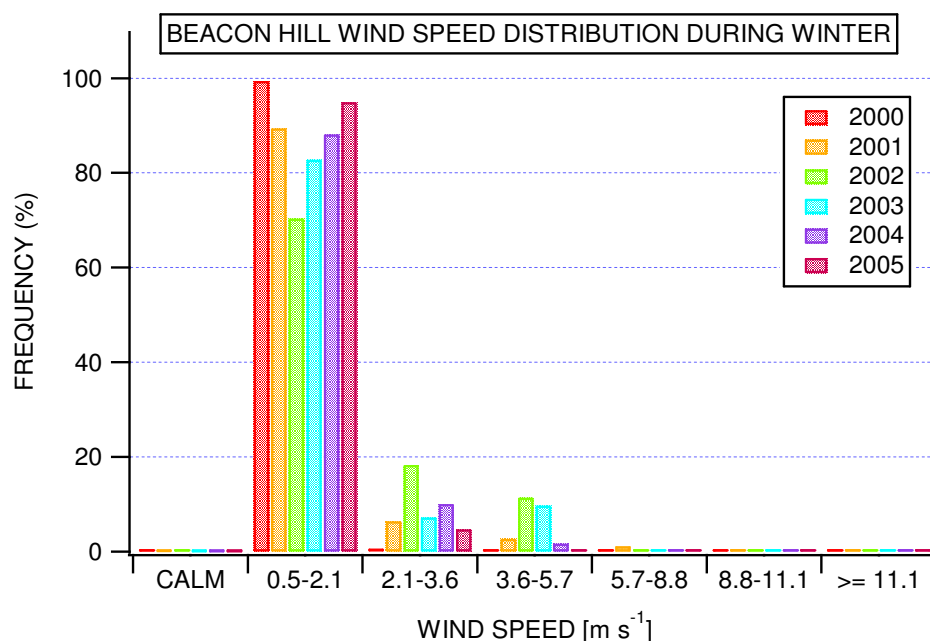
Figure 5. Frequency distribution of wind speeds during winter at Beacon Hill

Like benzene, 1,3-butadiene tends to exhibit some seasonal variability, with highest concentrations observed in winter and lowest concentrations in summer (Fig. 2b and Table 9). As shown in Tables 4 and 5, 1,3-butadiene concentrations and emissions have decreased over time in Seattle. The annual percentage changes between 2000 and 2005 are more variable than for benzene, which may be due in part to the much lower ambient levels for 1,3-butadiene. Because the ambient levels are near our detection limit, measurement precision for 1,3-butadiene is poor compared to benzene. The relatively good correlation between benzene and 1,3-butadiene suggest similar sources. However, a difference in their 2004-2005 trends (Table 5) suggests a control in benzene emissions that was not in effect for 1,3-butadiene.

Table 9. Seasonal mean 1,3-butadiene mixing ratios (ppbv)

	WINTER	SPRING	SUMMER	FALL
2000	0.12	0.06	0.05	0.08
2001	0.17	0.03	0.03	0.05
2002	0.02	0.03	0.04	0.07
2003	0.07	0.03	0.03	0.04
2004	0.05	0.06	0.05	0.06
2005	0.07	0.02	0.02	0.03

Carbonyls. As shown in Table 8, primary emissions of formaldehyde in the Seattle area are thought to originate mainly from the onroad and non-road mobile categories with a much smaller contribution from point sources. Overall, the formaldehyde emission estimates decreased by about 40% between 2000 and 2005. This is in good agreement with the six-year change (Table 5) in ambient concentrations (42%). Secondary formaldehyde formation via atmospheric photochemistry probably does not contribute much to the annual average at the Beacon Hill site. Since Beacon Hill is very near the urban core, it is undoubtedly NO_X rich most of the time, which limits oxidant production. The ozone design compliance site for the Puget Sound region is about 35 miles southeast of Seattle near Enumclaw WA. Earlier studies have show that formaldehyde levels are much higher at the Enumclaw site compared to Beacon Hill during summertime ozone episodes (Hopkins, 2002).

Formaldehyde concentrations have ranged between 0.10 and 16.34 ppbv during the six-year study period. Figure 2h shows formaldehyde concentrations recorded during the 2000-2005 time span. It is difficult to recognize a predictable pattern in the formaldehyde time series. In 2000 and 2001, formaldehyde concentrations peaked during the winter months; however, as time went on, the highest mean values were observed

during the summer and fall months (Table 10). Anomalously high formaldehyde

concentrations were recorded during a six-week period in the summer of 2003. Figure 6

shows the 24-hour ambient formaldehyde concentration for each sampling day from June

to August 2003. A ten-fold enhancement in formaldehyde concentrations is apparent

between July 8 and August 19. The step function pattern associated with the elevated

levels implies a temporary, local source. Close scrutiny of activities at the Beacon Hill

monitoring station and the adjacent water treatment plant, did not reveal a temporary

formaldehyde source. Thus, we are uncertain what caused the high values. Analytical

problems have been ruled out because there were no changes in DNPH sample cartridge

usage or analysis during the 2003 summertime period. Furthermore, cartridges that

showed high levels of formaldehyde at the start and end of the period were analyzed in

batches that included normal (lower) formaldehyde concentrations.

Table 10. Seasonal mean formaldehyde mixing ratios (ppbv)

	WINTER	SPRING	SUMMER	FALL
2000	2.20	1.13	1.33	1.77
2001	2.52	1.52	1.70	1.33
2002	1.10	0.85	1.52	2.08
2003	1.11	0.92	8.84	1.23
2004	0.78	0.73	0.93	1.02
2005	0.93	0.79	1.53	0.91
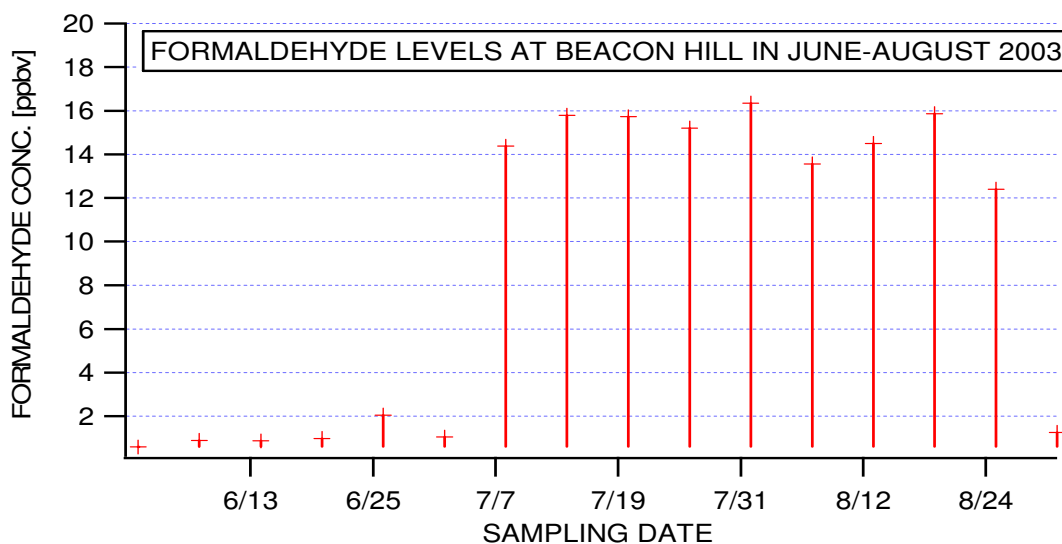
Figure 6. 24-hour ambient formaldehyde levels at Beacon Hill from June to Aug. 2003

Acetaldehyde concentrations did not change much over the six-year period even though the emissions inventory (Table 8) estimates a decrease of 36% between 2000 and 2005. EPA's analysis guidelines for carbonyls mandate that blank subtractions not be performed on DNPH cartridges; rather cartridges should be rejected if blank checks show elevated levels of acetaldehyde. Acetaldehyde contamination of commercial DNPH cartridges is much more significant than for formaldehyde. In fact, one entire batch of commercial cartridges supplied for this study was rejected because of elevated blank levels. Ambient formaldehyde and acetaldehyde have very poor correlation ($R^2 < 0.04$) with emission estimates. This indicates that secondary sources contribute significantly to their ambient levels.

Chlorocarbons. Carbon tetrachloride does not exhibit much variability, whether annual or seasonal (Table 11). Since its use has been banned in the US, the observed ambient level is due to its persistence in the atmosphere. The other chlorinated VOCs do not

exhibit a clear seasonal trends (Table 11) with high and low levels observed during any

of the seasons.

Table 11. Seasonal mean chlorocarbon mixing ratios (ppbv)

	WINTER	SPRING	SUMMER	FALL
carbon tetrachloride				
2000	0.11	0.11	0.10	0.10
2001	0.11	0.10	0.10	0.09
2002	0.09	0.10	0.11	0.11
2003	0.12	0.10	0.11	0.11
2004	0.11	0.11	0.10	0.10
2005	0.10	0.10	0.11	0.10
chloroform				
2000	0.09	0.06	0.04	0.05
2001	0.06	0.07	0.02	0.03
2002	0.04	0.04	0.06	0.05
2003	0.04	0.03	0.06	0.08
2004	0.06	0.05	0.05	0.04
2005	0.08	0.04	0.04	0.05
perchloroethylene				
2000	0.08	0.03	0.01	0.02
2001	0.03	0.03	0.01	0.02
2002	0.03	0.03	0.04	0.05
2003	0.04	0.02	0.01	0.02
2004	0.03	0.01	0.02	0.04
2005	0.04	0.03	0.03	0.03
trichloroethylene				
2000	0.04	0.09	0.05	0.03
2001	0.03	0.04	0.03	0.04
2002	0.02	0.02	0.03	0.03
2003	0.02	0.01	0.01	0.04
2004	0.03	0.01	0.01	0.02
2005	0.05	0.03	0.02	0.03

The triennial emission inventories for King County show a dramatic drop in

chloroform emissions between 1999 and 2002 and little further change in 2005 (Fig. 7).

This reduction in chloroform emissions must have occurred shortly after 1999 as we

observed no significant change in the annual average levels during the study period

(Table 4). Chloroform in the Seattle area is emitted primarily from area and point sources with the majority coming from wastewater treatment (79%) and the Boeing Company (20%) (Table 12). The median chloroform concentration of 0.038 ppbv for the six-year study period is higher than the median national annual average of 0.026 ppbv (McCarthy, 2007).
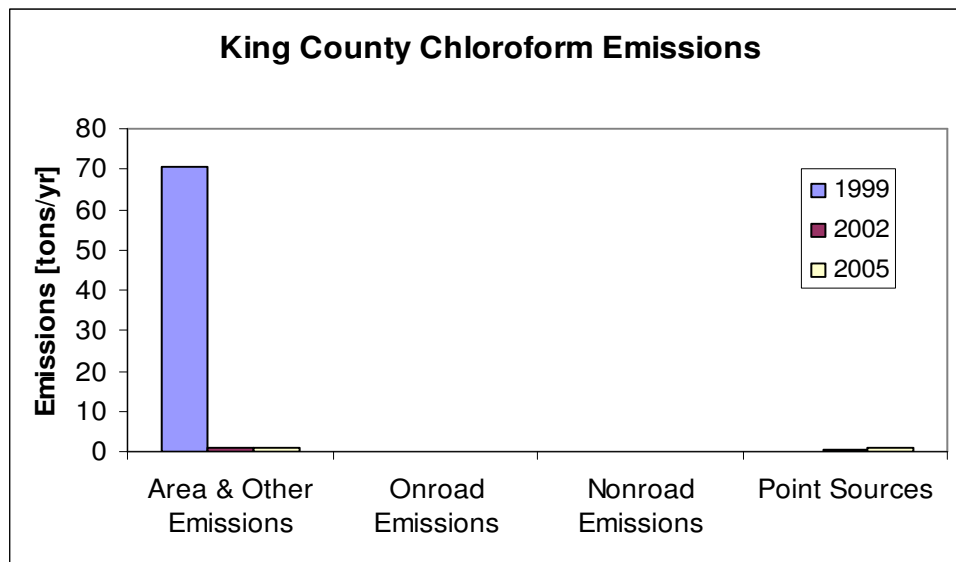
Figure 7. Chloroform emissions from King County Triennial Emission Inventories

Table 12. 1999 Emissions inventory sources of chloroform for King County, WA

Facility Name	Pollutant Emissions	% of Total Emissions	Number of HAPs
King Co Natural Resource Wastewater Treatment	1532	78.98	12
Boeing Space Center (BSC)	389	20.05	24
Cedar Hills Landfill	7.41	0.38	28
Kent Highlands Landfill	6.78	0.35	28
King Co Solid Waste Op Sec (Cedar Hills)	3	0.15	19
Duvall Landfill	0.939	0.05	28
Enumclaw Landfill	0.184	0.01	28
Coal Creek Development Landfill	0.184	0.01	28
Hobart Landfill	0.137	0.01	28
Vashon Landfill	0.0965	4.97E-03	28
Carnation Landfill	0.0306	1.58E-03	28
Midway Restricted Landfill	0.0306	1.58E-03	28

Perchloroethylene is widely used as a dry cleaning solvent and metals degreaser. Triennial emission inventories show that its source is primarily area and some point sources (Fig. 8). 1999 perchloroethylene emissions inventory for King County (Table 13) listed two facilities, Wescor Graphics Corporation (44%) and Leathercare Inc. (35%) as the source of the majority of PCE emissions. These commercial facilities are located in the downtown Seattle area. Ambient PCE levels remained fairly constant throughout the six-year period (Table 4). Unlike chloroform, the average of the median annual perchloroethylene concentration of 0.021 ppbv for the six-year study period is lower than the national median annual concentration of 0.038 ppbv (McCarthy, 2007).

Figure 8. Perchloroethylene emissions from King County Triennial Emission Inventories

Table 13. 1999 Emissions inventory sources of PCE for King County, WA

Facility Name	Pollutant Emissions	% of Total Emissions	Number of HAPs
Wescor Graphics Corporation	12520	44.44	1
Leathercare Inc.	9813	34.83	1
Boeing Commercial Airplane (Auburn)	2391	8.49	25
Cedar Hills Landfill	1281	4.55	28
Kent Highlands Landfill	1171	4.16	28
King Co Natural Resource Wastewater Treatment	477	1.69	12
Duvall Landfill	162	0.58	28
Web Press Corporation	90	0.32	15
Boeing Commercial Airplane (Renton)	63	0.22	35
Boeing Space Center (Bsc)	46	0.16	24
Rudd Company Inc	43	0.15	21
Enumclaw Landfill	31.8	0.11	28
Coal Creek Development Landfill	31.8	0.11	28

TCE levels show some decreasing trend (Fig. 2f). A look at its triennial emissions inventory (Fig. 9) shows a decrease in area source emissions from 1999 to 2005. Point sources did not change much from 1999 to 2005. Only two sources (Asko Processing Inc. and Art Brass Plating Inc.) identified in the 1999 TCE emissions inventory for King County (Table 14) are located in Seattle and comprise 19% of total emissions. The median trichloroethylene concentration of 0.025 ppbv for the six-year study period is higher than the median national annual concentration of 0.018 ppbv (Touma, 2006).
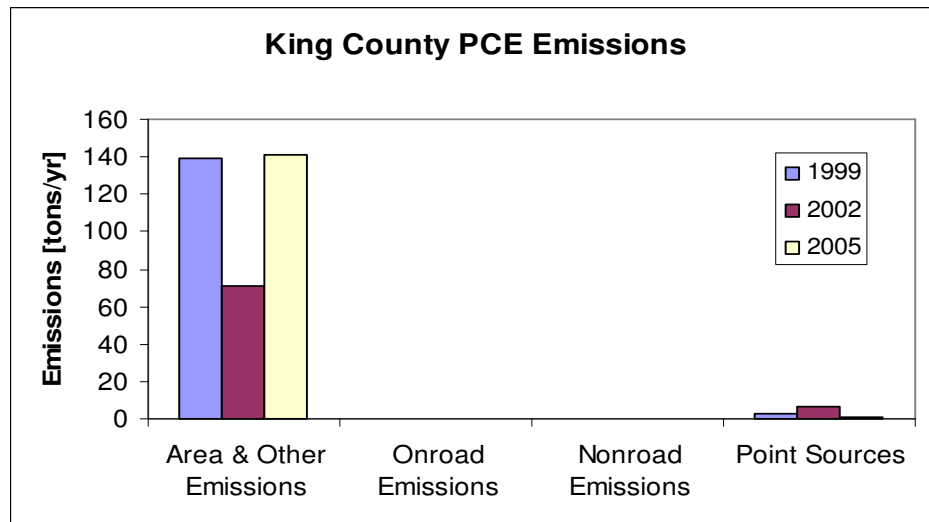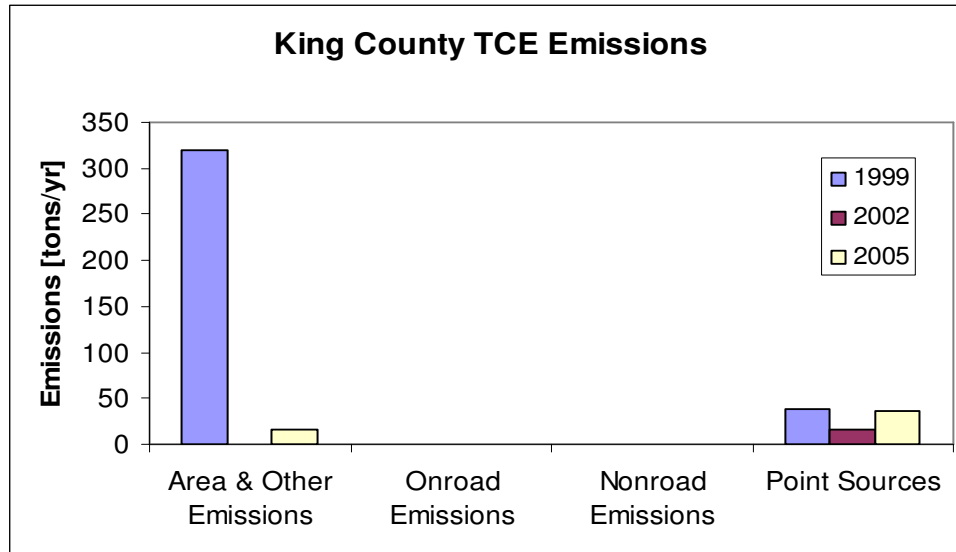
Figure 9. TCE emissions from King County Triennial Emission Inventories

Table 14. 1999 Emissions inventory sources of TCE for King County, WA

Facility Name	Pollutant Emissions	% of Total Emissions	Number of HAPs
Western Pneumatic Tube Company	49165	37.36	3
Red Dot Corp.	25080	19.06	1
Asko Processing Inc	12702	9.65	3
Protective Coatings Inc	12443	9.45	6
Art Brass Plating Inc	12300	9.35	1
Exotic Metals Forming Co	6886	5.23	6
Tubetronics (Kent Division)	6023	4.58	1
Web Press Corporation	4895	3.72	15
Cedar Hills Landfill	767	0.58	28
Kent Highlands Landfill	702	0.53	28
Boeing Space Center (BSC)	284	0.22	24

CONCLUSIONS

Benzene, chloroform, perchloroethylene, trichloroethylene and acetaldehyde exhibited spatial variation during the 2001 Urban Air Toxics Pilot City Study. The proximity of two sites to water reservoirs accounted for their elevated chloroform levels. Perchloroethylene and trichloroethylene are elevated in the site nearest to Seattle's industrial area. Continuous monitoring at the Beacon Hill site revealed a seasonal variability in ambient levels of benzene, 1,3-butadiene, and formaldehyde. Annual variability was found to be statistically significant for benzene, 1,3-butadiene, and perchloroethylene. Furthermore, monitoring of the ambient levels of HAPs relative to the 2000 levels appears to follow a decreasing trend. The observed reduction is highly correlated with the emissions inventory in King County. Nationally, it was found that benzene, 1,3-butadiene, chloroform and carbon tetrachloride measured at NATTS network from 2000 to 2003 declined significantly; PCE, TCE and acetaldehyde declined on average though not statistically significant and formaldehyde increased on average though not statistically significant as well (Touma, 2006). The trends observed at Beacon Hill seem to follow the national trends closely. The data collected over the six year period will provide baseline data to evaluate the success or failure of current and future control programs in the Seattle area.

ACKNOWLEDGMENTS

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CHAPTER THREE

Ambient BTEX Concentrations in Seattle, WA and their Relationship to Emission Controls

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ABSTRACT

Ambient benzene levels measured at Beacon Hill, Seattle in 2005 were 67% lower than the 2000 baseline. Since benzene is primarily from the transportation sector, the levels of other mobile source air toxics were examined as well. Toluene, ethylbenzene and the three xylene isomers, together with benzene, are indicators of vehicular emissions. More stringent standards for vehicle emission control systems, fuel sulfur content and use of reformulated gasoline are being enforced on the federal level. Installation of vapor recovery at fueling stations and a shift to low sulfur diesel fuel in state-owned fleet of highway vehicles and ferries were implemented in Washington state. Locally, there was modernization of the bus fleet, the use of biodiesel mixed with the conventional petroleum based diesel and the switch to reformulated gasoline. Thus, the observed abatement in ambient benzene level was linked with control programs implemented in Seattle during the time period.

INTRODUCTION

Mobile source air toxics (MSAT) are volatile organic compounds emitted by off-road and on-highway motor vehicles. These MSATs, which cause cancer or other serious health or environmental effects (EPA 2006), may be present in the fuel or produced during engine combustion and through atmospheric reactions of primary mobile emissions. MSATs are emitted in the exhaust as well as in evaporative emissions if they are components of fuel. Engine wear and impurities in the oil can yield MSATs, as well. Mobile source air toxics are of primary concern to people living or working near major roads and those who spend a lot of time in vehicles. MSATs include benzene, toluene, ethylbenzene, and the three xylene isomers. The United States Environmental Protection Agency (US EPA) is proposing a new gasoline rule to be implemented in 2011 that would decrease the nationwide levels of benzene from the current 0.97 percent by volume to 0.62 percent by volume. Furthermore, the rule would impose more stringent evaporative emission standards by 2009 for new vehicles and gasoline storage containers.

In 1996 and 1999, the US EPA conducted comprehensive evaluations of air toxics in the US. They found that more than 100 million people live in areas where the upper-bound lifetime cancer risk exceeds 10 in a million due to air toxics from mobile source emissions (1996 NATA, 1999 NATA). Benzene was the only national cancer driver in both risk assessments. Airborne benzene is predominantly from vehicular sources as a component of unburned gasoline and a product of combustion (Fortin, 2005; Harley, 2006). Benzene has been used, together with several compounds, as indicators of vehicular emissions (Fortin, 2005; Pankow, 2003; Gelencser, 1997). Toluene, ethylbenzene, and the xylenes are known to be closely associated with benzene and the

group is collectively referred to as BTEX compounds. Benzene may be formed by incomplete combustion of these aromatic compounds (EPA 1994). BTEX compounds have been used to characterize exhaust emissions (Martins, 2007; Gullet, 2006; Mohamed, 2002; Heeb, 1999; Guicherit, 1997), sources (Fernandes, 2002) and impact of alternative or reformulated fuel (Kado, 2005; Harley, 2000). Ratios of BTEX compounds have also been used to characterize traffic emissions in tunnel measurements (Hsieh, 1999) and age of air mass (Monod, 2001; Hsieh, 2003). Good correlation of the BTEX compounds was attributed to common petrochemical sources (Pankow, 2003; Monod, 2001). The ratio of toluene to benzene has been used to characterize air masses. Gelenczer et. al.,(1997) used the ratio to estimate the distance from a vehicular emission source.

Ambient benzene levels have been reported to be decreasing in recent years (McCarthy, 2007; Harley, 2006; Reiss, 2006; Touma, 2006; Aleksic, 2005; Fortin, 2005). These reductions have been attributed to various control strategies at the federal, state and local levels. One of these control strategies is fuel reformulation (Harley, 2006; Kirchstetter, 1999), which includes reduction of fuel volatility as well as benzene, aromatic, olefin, oxygen and sulfur content. Alternative technologies and fuels are expected to significantly reduce urban air toxics emissions (Winebrake, 2001). The national low emission vehicle (NLEV) program, Tier 2 motor vehicle emission standards and gasoline sulfur requirements are other federal programs aimed at reducing mobile source emissions (EPA 1994, EPA 2000).

In 2005, ambient monitoring at Seattle's National Air Toxics Trend Site (Beacon Hill) showed a dramatic drop in benzene levels (Table 1). This paper investigates

reasons for this observed abatement by examining relationships between ambient concentrations and mobile source emissions in Seattle. Thus, our goal is to show that changes in ambient levels can be linked to the success or failure of control programs and that continued monitoring of BTEX and other air toxics is a critical part of any control strategy.

EXPERIMENTAL METHODS

Twenty-four hr integrated whole air samples were collected in Summa canisters every sixth day at the Beacon Hill site in Seattle WA from 2000 through 2005. EPA Method TO-14A was employed for VOC analysis. Samples were shipped weekly from Seattle to WSU for analysis. BTEX levels were extracted from gas chromatograms obtained from the analysis of the samples. Additional samples were collected in 2001 at Georgetown, Lake Forest Park, Lake Sammamish, Maple Leaf, and SeaTac (Figure 1). Seattle, with a population of 582,454 (2006 Census Estimate), is located in King County which is part of the regional airshed referred to as the Puget Sound Basin.

Each chromatogram was visually examined to ensure data quality. Peak identities were established by comparison of retention times and mass spectra with known standards. The concentration of the hydrocarbons was determined by using the instrument response for each peak to that recorded for a known concentration of 2,2-dimethylbutane. The concentration of the 2,2-dimethylbutane standard was assigned through comparison with a purchased National Institute of Standards and Technology propane Standard Reference Material. The long term (2000-2005) sampling precision determined as relative percent difference (side-by-side collection) for benzene was 11%

(n = 274). Analytical precision (replicate runs) for the same period was 10% (n = 257).

During the sampling period, the WSU analytical laboratory participated in quarterly EPA

performance tests (US EPA 2002b, Caviston 2005a-d) and in the South Coast Air Basin's

annual multi-laboratory hydrocarbon inter-comparisons (Fitzell 2003).

Emissions inventory data were obtained from the EPA AIRS database and the

Washington Department of Ecology. Ambient nitrogen oxides, carbon monoxide, ozone,

and meteorological data were downloaded from the Puget Sound Clean Air Agency

website (www.pscleanair.org). Annual vehicle miles traveled (AVMT) data for King

County were obtained from annual reports on the Washington Department of

Transportation website (www.wsdot.wa.gov).
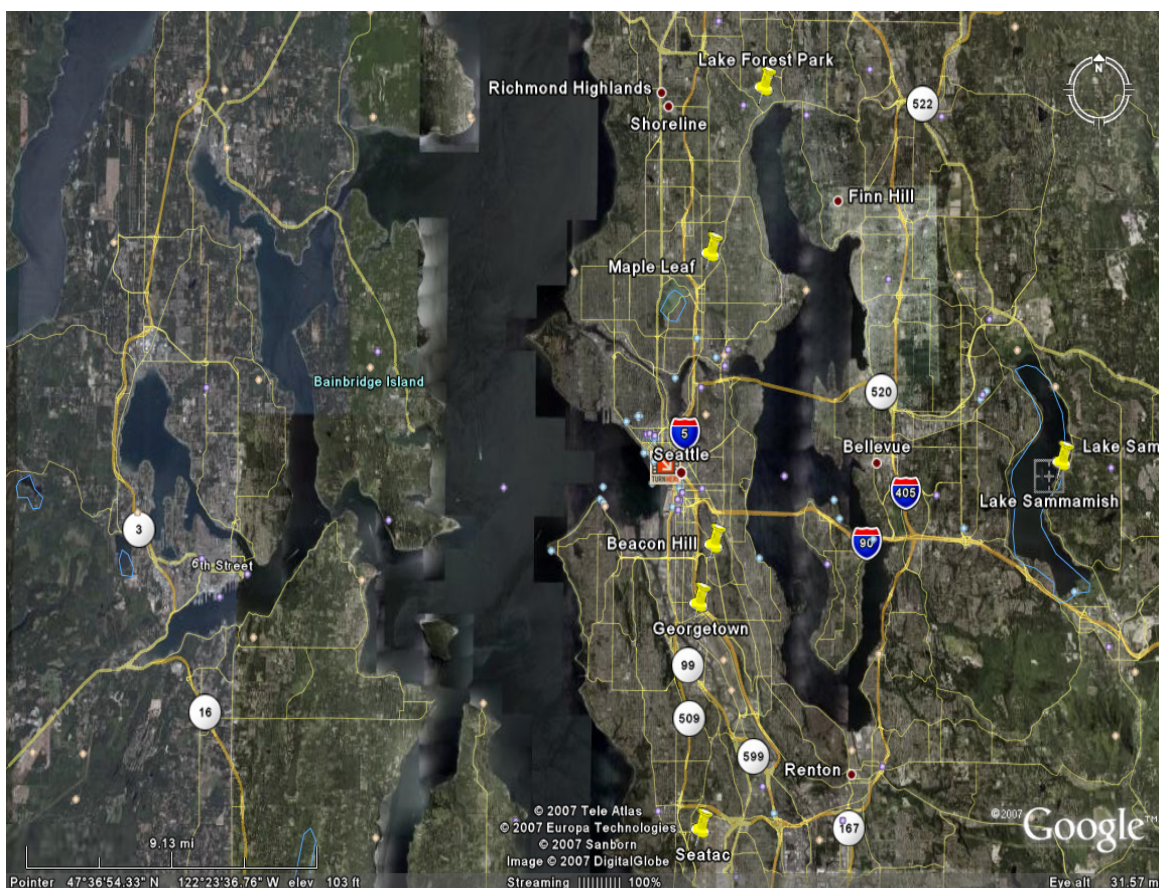
Figure 1. Location of the 2001 sampling sites in Seattle, WA

RESULTS AND DISCUSSION

Temporal Trends

The annual average benzene, toluene, ethylbenzene, and xylenes concentrations showed a decreasing trend from 2000 through 2005 (Table 1). As was described in a companion publication (Westberg *et. al.,*2004)**,** ambient benzene concentrations in Seattle exhibit a well defined seasonal pattern with high and variable wintertime values and lower, more constant summertime levels. Because of the relative constant summer concentrations, the most recognizable year-to-year changes can be seen during this period. Figure 2 shows the June-August average benzene concentrations along with

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variability for each of the six summers between 2000 and 2005. There is an obvious

decrease in the summertime benzene level in 2003 and again in 2005 compared to results

from previous years.
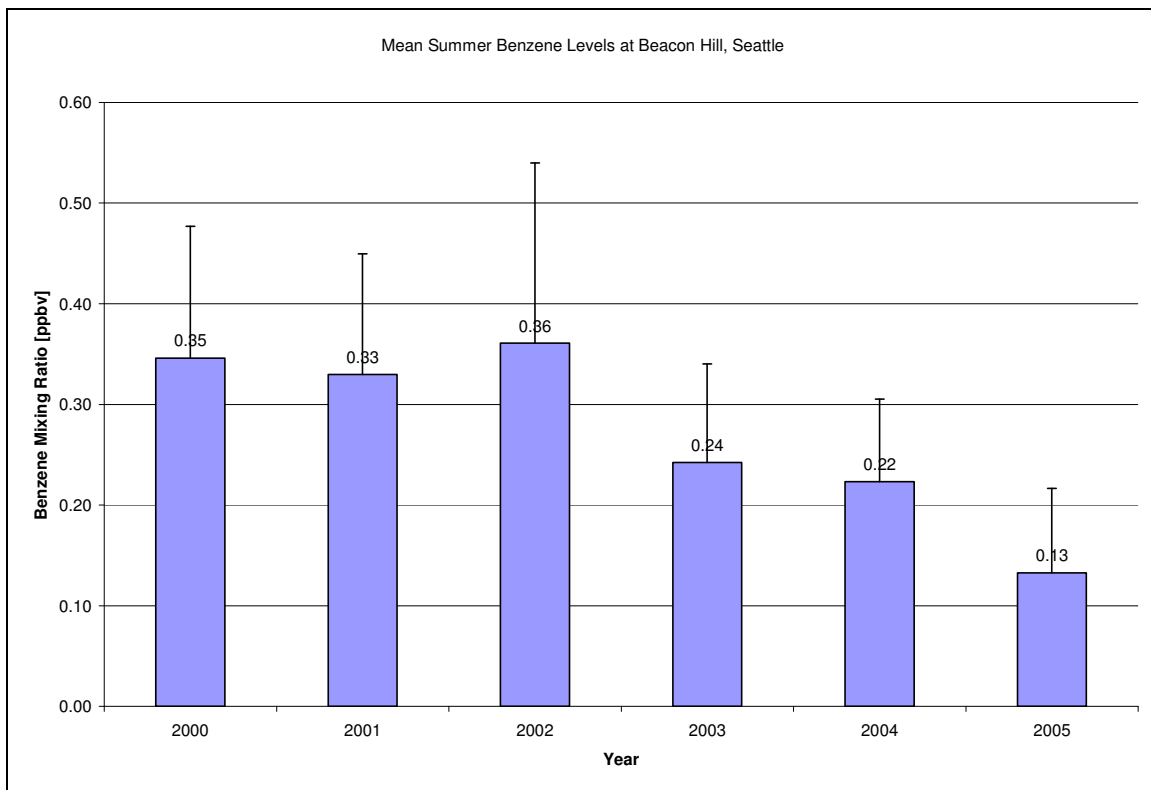
Figure 2. Average summer (June-August) benzene concentrations and variability from 2000 through 2005

Emissions estimates from the Washington State Department of Ecology's

Triennial Inventory show that BTEX emissions are predominantly from on-road mobile

sources (Table 2). With the exception of 2002, the on-road mobile emissions exhibit a

decreasing trend through this same time period. The higher emissions estimate in 2002 is

consistent with the Washington State Department of Transportation's (WSDOT) reported

total annual vehicle miles traveled (AVMT) shown in Table 3. This table shows an

increasing trend in AVMT from 2000 to 2003 followed by a decrease in 2004, possibly

due to increasing fuel prices. The AVMT again increased in 2005 from the 2004 level

but was lower than the 2002 AVMT. The emissions estimates for 2005 show a decrease,

which is consistent with the trend observed in ambient concentrations. The apparent

increase in emissions estimates for 2002 may be due to the incompleteness of the 1999

inventory. Outdoor burning was included as a category in 2002 and woodstoves and

fireplaces were added in 2005. Benzene, toluene, and the xylenes are released from

residential wood burning stoves (McDonald, 2000). The exclusion of these additional

sources in 1999 may have led to an underestimation of emissions.

Table 1. Annual mean ambient concentration (ppbv) measured at the Beacon Hill
site in Seattle, WA.

	2000	2001	2002	2003	2004	2005
benzene	0.55	0.45	0.38	0.39	0.40	0.17
toluene	1.48	1.31	1.17	1.00	0.86	0.80
ethylbenzene	0.29	0.18	0.18	0.18	0.21	0.12
xylenes	1.30	1.00	1.02	1.12	1.30	0.63

Table 2. On-road mobile BTEX emissions estimates (tons/yr) for King County, WA.

	Total			On-Road		
	1999	*2002*	*2005*	*1999*	*2002*	*2005*
benzene	2169	2305	1884	1397	1798	1234
toluene	5040	5618	4372	2925	4020	2527
ethylbenzene	795	944	645	433	593	382
xylenes	2347	3688	2869	1643	2258	1415

Table 3. Annual vehicle miles traveled (thousands of miles) in King County, WA (Source: WSDOT Annual Reports).

	Total					
	2000	2001	2002	2003	2004	2005
Principal Arterials	2915526	2900236	2954939	2971469	2991087	3009676
Minor	570931	563114	561058	558623	486100	468515
Collector	207	207	213	253	247	256
Interstate	5200066	5237016	5266661	5269481	5188067	5240002
Total	8686730	8700573	8782870	8809826	8665511	8718449

The downward trend in Seattle's ambient benzene and other BTEX levels between 2000 and 2005 is suspected to result from a combination of emission control measures that occurred in the Puget Sound region. In 2004, a phasing in of the more stringent Tier 2 vehicle standards and gasoline sulfur control requirements (Table 4) was required (EPA 2000). The desulfurization process in a refinery also reduces the aromatic content since the heavier sulfur-containing compounds in naphtha have similar endpoint temperature in the fluid catalytic cracking (FCC) unit (Nafis, 2004). Although this program was designed to reduce ozone and particulate matter, the technologies involved consequently reduced the air toxics through controls of non-methane organic gases (NMOG).

Table 4. Tier 2 Gasoline Sulfur Standards for Refiners, Importers and Individual Refineries (EPA 2000)

Compliance as of:	2004	2005	2006
Refinery Average, ppm	---	30	30
Corporate Pool Average, ppm	120	90	---
Per-Gallon Cap, ppm	300	300	80

The 1999 emissions inventory shows that toluene, ethylbenzene and the xylenes are also predominantly from mobile sources (Table 5). However, the non-mobile source (major point, area and others) contribution to toluene and ethylbenzene emissions is greater than for benzene and xylenes. This is reflected in their poorer correlation with CO (Table 6).

Table 5. 1999 Emissions inventory (tons/year) for King County, WA.

	On-road	Off-road	Major Point	area & others
Benzene	1397	361	2	409
Toluene	2925	816	211	1089
Ethylbenzene	433	219	5	139
Xylenes	1643	864	43	698

Table 6. BTEX correlation and mean ratio with CO (ppbv/ppmv)

	Correlation Coefficient					
	2000	2001	2002	2003	2004	2005
benzene	0.78	0.81	0.84	0.79	0.82	0.78
toluene	0.90	0.91	0.79	0.69	0.52	0.76
ethylbenzene	0.37	0.84	0.64	0.38	0.76	0.76
xylenes	0.83	0.90	0.75	0.42	0.74	0.74
	Ratio					
	2000	2001	2002	2003	2004	2005
benzene/CO	1.15	1.31	1.05	0.98	0.68	0.26
toluene/CO	2.71	3.58	3.11	2.56	1.53	1.25
ethylbenzene/CO	0.63	0.51	0.47	0.44	0.34	0.19
xylenes/CO	2.61	2.78	2.79	2.93	2.22	0.99

On October 1, 2004, the New Gas Station Rule was implemented in the Puget Sound area (PSCAA 2004). This rule required gas stations to install a vapor recovery system on all storage tanks with a rated capacity of at least 1,000 gallons. This control

requirement reduces evaporative emissions from gasoline stations. Together with on-board recovery systems in model 2004 vehicles, this control strategy reduces BTEX but not CO emissions. This could account for the decrease of the ratio of each hydrocarbon to CO in 2004 and 2005 (Table 5).

The federal maximum reformulated gasoline (RFG) standard for benzene was 1.3% in 2000 (EPA 2000b). Summertime conventional gasoline (CG) parameters reported to the EPA in 2000 had 28.5% aromatics and 1.15% benzene by volume (Table 7). The summertime RFG in 2000 had 19.3% aromatics and 0.59% benzene by volume. Sulfur content was 320 ppm in 2000 for CG and 126 ppm for RFG. Reid vapor pressure (RVP) was 8.27 psi for CG and 6.78 psi for RFG. These parameters did not change much in 2005. However, if more RFG than CG was distributed by refineries starting in 2004 to comply with the Tier 2 gasoline sulfur control requirements, benzene content in gasoline would have been reduced by about 50%. Harley *et. al.* (2006) reported a step change in benzene emissions that coincided with the introduction of Phase 2 reformulated gasoline in California. They stated that a 35% decrease in aromatics overall was dominated by changes in the more abundant C_7-C_9 compounds, with toluene as the least changed among the aromatics. Durana *et. al.* (2006) also reported a 50% reduction in ambient benzene levels after implementation of benzene content reduction in fuel. It has been suggested that reduction in benzene emission rates is due both to a reduction of gasoline aromatics and overall VOC mass emission rates (Harley, 2006).

Table 7. Reported Compositional Content for Conventional and Reformulated Gasoline (EPA 2007a,b)

	2000	2001	2002	2003	2004	2005
Summertime Conventional Gasoline						
Oxygen (wt%)	0.66	0.63	0.71	0.81	0.97	0.95
Ethanol (% vol)	0.84	0.74	0.93	0.98	1.52	1.75
Sulfur (ppm)	320	304	296	303	118	106
Aromatics (%vol)	28.5	28.3	28.0	27.9	28.0	27.7
Olefins (%vol)	11.8	12.8	12.1	12.1	11.2	12.0
Benzene (%vol)	1.15	1.17	1.10	1.15	1.15	1.21
RVP (psi)	8.27	8.27	8.27	8.31	8.31	8.30
Summertime Reformulated Gasoline						
Oxygen (wt%)	2.24	2.21	2.25	2.30	2.55	2.49
Ethanol (% vol)	1.14	1.10	1.30	1.50	3.04	3.03
Sulfur (ppm)	126	127	124	110	80	71
Aromatics (%vol)	19.3	20.1	20.4	20.1	20.1	20.7
Olefins (%vol)	10.6	11.8	10.8	11.0	11.4	11.9
Benzene (%vol)	0.59	0.62	0.59	0.61	0.59	0.66
RVP (psi)	6.78	6.79	6.80	6.83	6.87	6.91

A sample of low sulfur diesel was found to contain about 21% aromatics and less than 15 parts per million of sulfur and BTEX emissions from buses running on low sulfur diesel fuel were found to be about an order of magnitude lower than gasoline-powered vehicles (Kado, *et. al.* 2005). Since emissions of lighter hydrocarbons from diesel vehicles are said to be similar to light duty gasoline vehicle emissions (Lough, *et. al.*, 2005), the lower BTEX emissions may be attributed to the low sulfur diesel fuel.

In late 2004, Seattle Metro Transit added 236 hybrid buses to its fleet of 1300 vehicles and replaced the 14 year-old dual-mode Breda buses that had exceeded their 12 year lifetime (Chandler, 2006). These hybrid buses were found to emit 50% less hydrocarbons than the conventional diesel bus with both buses running on ultra-low sulfur diesel (ULSD). The Washington State Ferries (WSF) system shifted its entire fleet to low-sulfur diesel fuel in mid-2004 (WSDOT 2007). In addition, they tested the use of ULSD in some of their ferries for a year starting in the summer of 2004. Since sulfur poisons the catalyst in catalytic converters, sulfur reduction in fuels allows for greater conversion of unburned and partially burned hydrocarbons to carbon dioxide. This, in effect, reduces VOC and BTEX emissions.

Another VOC control strategy implemented in King County was the use of biodiesel. Biodiesel does not contain aromatics and, when mixed with petroleum based fuels, will lower the aromatic content by volume of the fuel. In 2005, WSDOT started using 5% biodiesel mixed with regular diesel in maintenance vehicles operating in King and the surrounding counties in Washington (WA ECY 2006).

Spatial Trends

The trend data provided in the previous section was acquired at the Beacon Hill site. The ambient concentrations measured at Beacon Hill appear to be representative of most Seattle neighborhoods based on the measurements made at several sites in 2001. The ambient BTEX levels measured at Beacon Hill, Lake Sammamish, Maple Leaf and Sea Tac sites (Figure 1) were similar in 2001 and about a factor of two

lower than those recorded at Georgetown and Lake Forest Park (Table 8). The Georgetown neighborhood is located immediately adjacent to Seattle's Duwamish industrial area. so its higher ambient BTEX likely includes a contribution from area source emissions not present at the other Seattle neighborhood sites. The toluene/benzene ratio of 4.1 at Georgetown (Table 9) is indicative of toluene sources in addition to mobile emissions. The mobile source toluene/benzene ratio in Seattle during 2001 was about 2.8 based on measurements at the four sites (LF, LS, ML and ST) predominantly influenced by mobile emissions. Vehicle exhaust emissions measured in a tunnel (μg/m^3) are reported to have a toluene/benzene ratio of about 2 (Gelencser, 1997). Both toluene and benzene were found to be formed in the three-way catalyst and emitted at 416 $\pm$ 25 mg/km and 206 $\pm$ 22 mg/km respectively (Bruehlmann, 2005). The toluene/benzene ratio from reformulated gasoline headspace vapor (wt%) is between 2.4 and 4.8 (Kirchstetter, 1999).

The toluene/benzene ratio of 3.3 at Beacon Hill is between those at Georgetown and the other three sites. Since Beacon Hill is typically downwind and closest to Georgetown, it likely is influenced to some extent by diluted area source emissions from the industrial sector. The LF sampling station was located in a shallow valley where restricted ventilation could lead to elevated pollutant levels compared to stations located on higher ground. As can be seen in Figure 3, daily average wind speeds were lower at Lake Forest Park than Beacon Hill in 2001. As a consequence, the toluene/benzene ratio at Lake Forest Park was indicative of mobile emissions, but the annual average BTEX concentrations were on a par with those recorded at Georgetown

Based on the 2001 spatial study results, ambient air toxic levels measured at Beacon Hill were deemed representative of Seattle and the site is currently part of the NATTS network.

Table 8. BTEX mean and standard deviation at various Seattle sites from February 2001 to February 2002

	BH		GT		LF		LS		ML		ST	
	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
benzene	0.43	*0.25*	0.73	*0.61*	0.73	*0.67*	0.46	*0.31*	0.41	*0.33*	0.41	*0.24*
toluene	1.31	*0.81*	2.69	*1.97*	1.86	*1.57*	1.31	*0.90*	1.09	*0.77*	1.12	*0.76*
ethylbenzene	0.18	*0.10*	0.36	*0.29*	0.25	*0.18*	0.18	*0.12*	0.16	*0.11*	0.16	*0.10*
m,p-xylenes	0.77	*0.43*	1.55	*1.16*	1.03	*0.76*	0.77	*0.49*	0.71	*0.42*	0.69	*0.38*
o-xylene	0.23	*0.14*	0.43	*0.36*	0.32	*0.26*	0.24	*0.16*	0.20	*0.14*	0.19	*0.12*

Table 9. Mean and Median Toluene/Benzene Ratios (ppbv/ppbv) at Seattle Sites in 2001

	Mean	Median
Beacon Hill	3.3	3.1
Georgetown	4.1	3.8
Lake Forest Park	2.6	2.7
Lake Sammamish	2.9	2.7
Maple Leaf	2.9	2.7
Sea Tac	2.8	2.6
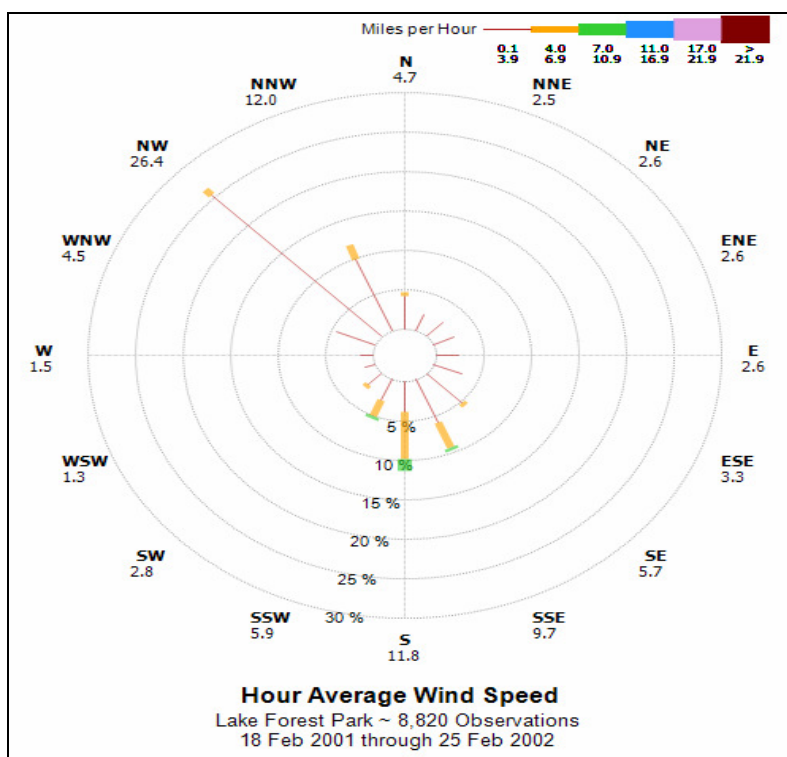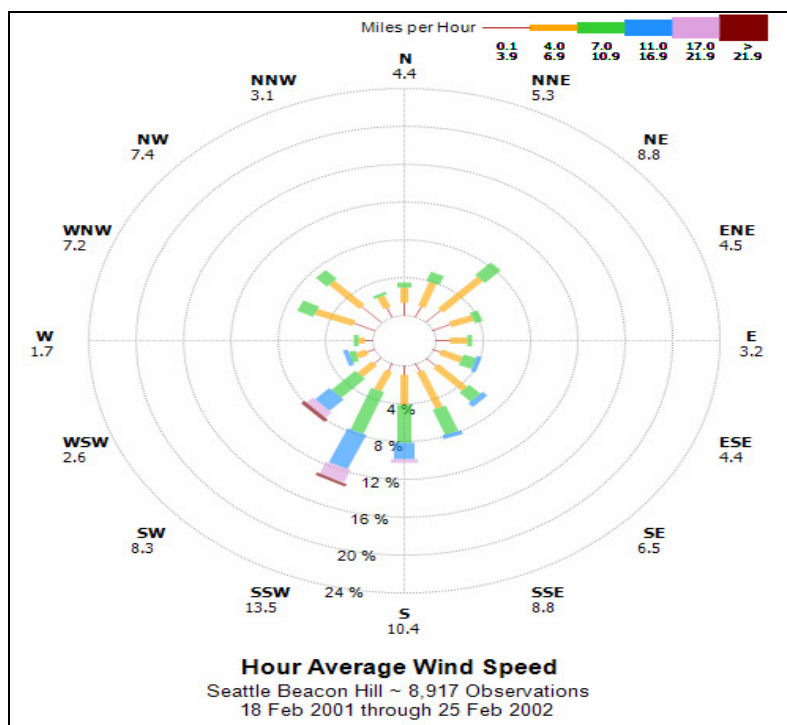
Figure 3. Wind roses of (top) Beacon Hill, and (bottom) Lake Forest Park
(http://www.pscleanair.org/airq/windrose)

SUMMARY AND CONCLUSIONS
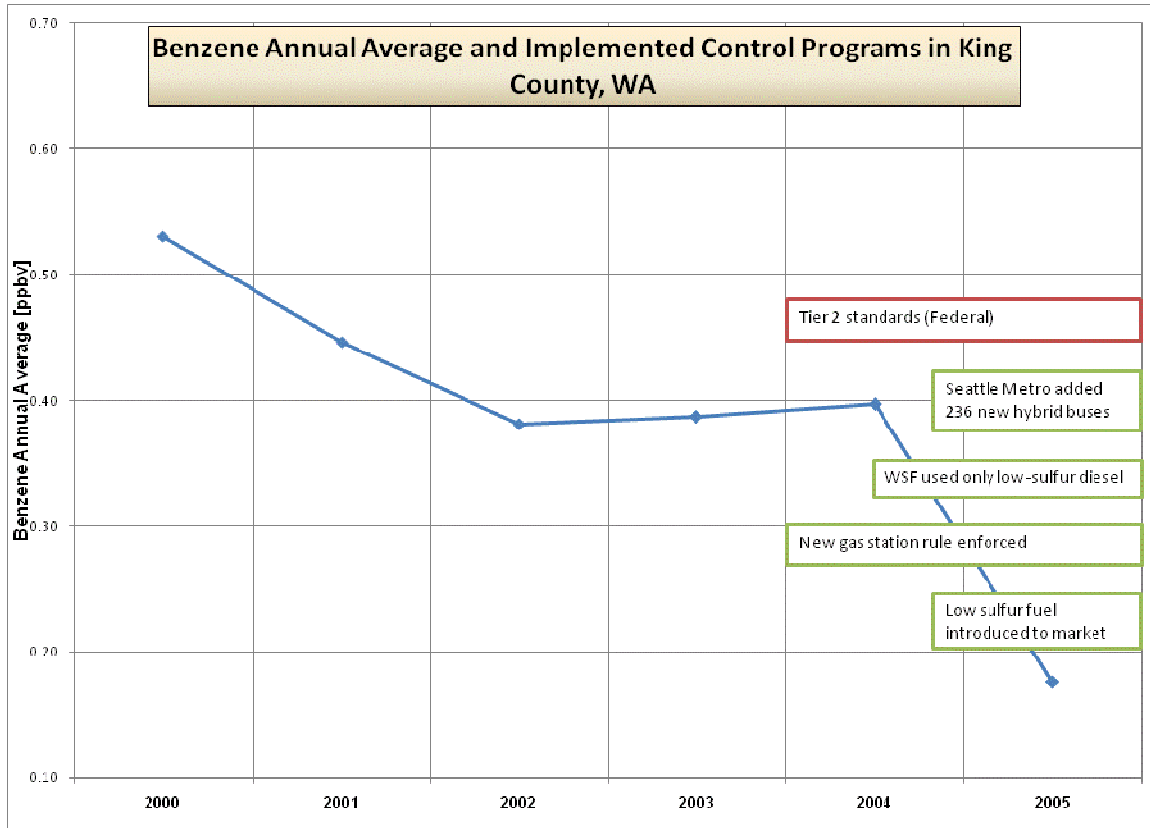
Figure 4. Timeline of benzene annual average and implemented control programs in King County, WA

The observed reduction trend in Seattle's ambient BTEX levels may be attributed to various mobile emission control strategies at the federal, state, and local levels (Fig. 4). Federal regulations requiring more stringent standards for vehicle emission control systems, fuel sulfur content and use of reformulated gasoline contributed to a reduction in MSATs. The state of Washington mandated vapor recovery at fueling stations and a shift to low sulfur diesel fuel in its fleet of highway vehicles and ferries. In Seattle, the bus fleet was modernized, biodiesel was mixed with the conventional petroleum based diesel,

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and local refineries started the switch to reformulated gasoline in late 2004. All of these

activities contributed to the reduction of BTEX levels in Seattle's atmosphere. Thus, the

implemented control programs appear successful in reducing air toxics from mobile

sources. The lower benzene levels measured in 2005 suggest success but continued

monitoring of BTEX and other air toxics remain critical in the determination of a control

strategy's successful implementation.

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CHAPTER FOUR

Simulation of Chloroform Emissions from a Water Reservoir in Seattle, Washington

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ABSTRACT

Hourly chloroform emissions from water reservoir located in a residential neighborhood near central Seattle, WA, were calculated using a Henry's law approach based on trihalomethane water supply concentrations and hourly temperature and wind speed observations. The calculated emission rate was then used as input to a simple Gaussian plume model to calculate hourly average ambient chloroform concentrations at a receptor corresponding to an air toxics sampling site located within 50 meters of the reservoir. Only days with measured ambient chloroform levels greater than 0.10 ppbv were selected for modeling. Of these days, only those where the predominant wind direction was northeasterly from the reservoir toward the sampling site were selected. The results indicated that the emission rate was sensitive to the chloroform concentration in water and to wind speed, but insensitive to temperature. Simulated 24-hour average chloroform concentrations were in good agreement with ambient measurements when the chloroform water concentration was approximately 20 ug/l. The chloroform emission rate was estimated to range from 2 to 8 mg/sec and the total estimated emission from reservoir was 335 lb/yr.

INTRODUCTION

Many of the volatile chemical species known as halocarbons are classified as

hazardous air pollutants. The di, tri and tetra chloromethanes are on the US EPA list of

"core" air toxics. The trihalomethane, chloroform, is routinely measured at all of the

national Air Toxics Trends (NATTS) sites currently in operation. This includes the

Beacon Hill monitoring station in Seattle,WA. In a companion paper, we reported

ambient chloroform concentrations measured at Beacon Hill plus other sites in the Seattle

area over the period from 2000 to 2005 (*1*). These studies showed that annual average

chloroform concentrations near continental background levels were measured at four

Seattle area sites, but that Beacon Hill and one other site in the Seattle exhibited much

higher concentrations. Both of the sites with elevated chloroform were adjacent to water

treatment reservoirs. In order to better understand the relationship between water

chlorination and ambient chloroform concentrations, we used a mass transfer model to

calculate the rate at which chloroform is released from the water storage reservoir. In

turn, this estimated emission rate was used in a simple dispersion model to simulate

chloroform concentrations at the air toxics sampling site located immediately to the

southwest of the reservoir. These results were then compared to the measured ambient

levels as a way to evaluate the uncertainty in the estimated emission rate. The results of

this analysis are presented in this manuscript.

Chloroform is a clear, volatile, slightly water-soluble liquid, which may volatilize

and be emitted to the atmosphere (*2*). Primary sources of chloroform include the

manufacturer of fluorocarbon 22 refrigerants and fluoropolymers, oxibisphenoxarsine

(OBPA), 1,3-diisocyanate, and pharmaceutical products. The chlorination of water is the

major indirect source of chloroform emissions (*2*). Publicly owned water treatment works (POTWs), cooling towers, pulp and paper mills, air stripping towers, and perchloroethylene production all can produce chloroform as a by-product and release it to the atmosphere. In most localities, water chlorination is normally the dominant emission source of chloroform.

Natural water contains humic acids that when disinfected with chlorine yield chloroform and other trihalomethanes (*3,4*). Temperature and pH were found to be significant factors in trihalomethane formation (*3,5,6*). Volatilization of water contaminants (including chloroform) has been modeled as dependent on air and water concentrations, Henry's law constant, surface area and mass transfer coefficients (*5*). Wind speed, temperature, and molecular size have been reported to affect the magnitude of the mass transfer coefficients (*7*).

The mean chloroform levels in marine water sampled from the North Sea was found to be 73 ng/L and the average ambient air chloroform level over the sea was found to be 19.0 pptv (*8*). Mean chloroform concentrations measured at the shower nozzle are much higher ranging from 51 to 64 mg/L at temperatures of about 40°C (*9*). The average ambient chloroform concentration at continental locations was 18.5 pptv during 1985-1996 period, but a few sites reached levels as high as 40 pptv for their annual average (*10*). The background chloroform concentration in King County, WA (Seattle area) was reported to be 0.1375 $\mu g/m^3$ (28 pptv) with an uncertainty of 0.0274 $\mu g/m^3$ (5.6 pptv ppbv) (*11*). McCarthy et. al. reported a much lower chloroform background concentration of 0.045 $\pm$ 0.0015 $\mu g/m^3$ (9 pptv $\pm$ 0.3 pptv ppbv) (*12*).

Figure 1 shows an aerial view of the Beacon Hill sampling station and water treatment reservoirs. The air quality monitoring station is located between the reservoirs (see arrow) and chloroform emissions are only from the North Reservoir since it was the only one used.

Figure 1. Aerial view of Beacon Hill sampling site and the reservoirs

The Cedar River is the source of the water stored in the Beacon Hill Reservoir. The measured trihalomethane (THM) concentration of the water from Cedar River, varies from year to year (Table 1). For the year 2000, data in the table were from the South Fork Tolt River because Cedar River data were unavailable. Tolt River is the source of

water supplied to Seattle areas north of Green Lake. Seattle Public Utilities operates both

water treatment facilities and the various water distribution systems in Seattle. Water

treatment includes screening, fluoridation, corrosion control, pH adjustment, and

chlorination. In 2004, ozonation and UV-disinfection were added to the treatment facility

at Cedar River. A chlorine residual of 4 ppm has been reported at Cedar River.

Table 1. THM Levels at Cedar River (ppm)

YEAR	AVE	MIN	MAX
2000*	76	55	86
2001	38	18	55
2002	27	15	45
2003	32	23	55
2004	24	22	49
2005	33	25	41

* from South Fork Tolt River

METHODOLOGY

Ambient chloroform concentrations were measured as part of the Urban Air

Toxics Monitoring under the US EPA Pilot Cities Study and National Air Toxics

Trends Study (NATTS). Sampling and analyses were previously reported (*13*). THM

concentrations were obtained from annual reports (*15*). Chloroform concentration in

the reservoir was parameterized from the annual THM minimum, average and

maximum concentrations. Since chloroform comprises an average of 82% of the

aqueous THM concentrations (*3*), for the first approximation, C_w used in the

calculation of the emission rate was the THM concentration multiplied by a factor or

0.82 and then converted to mol/m^3. Hourly and 24-hr average chloroform

concentrations at the air toxics sampling site were calculated using a Gaussian plume

model. The modeling was performed by simulating the reservoir as a dense array of

point sources in a code implemented using Igor Pro 6.0 (*14*). Input parameters to the

model are listed in Table 2. Hourly meteorological data for the sampling days were

obtained from the Washington State Department of Ecology (WA DOE) database.

Modeling results were then compared with measured chloroform levels.

Table 2. Input parameters to the model

Parameter	Unit	Source
Q, emission rate	g/s	Calculated from WS,WD, σ_θ, T, P, THM, MWt, Henry's law constant, mass transfer coefficient, surface area of reservoir
WS, wind speed	m/s	WA ECY database
WD, wind direction	degrees	WA ECY database
σ_θ, std dev of wind direction	degrees	WA ECY database

In the model, a simple Gaussian plume equation for point sources was used

(eq. 1):

$$C(x,y,z) = \frac{Q \exp(-0.5(y/\sigma_y)^2)[\exp(-0.5((z+h)/\sigma_z)^2 + \exp(-0.5((z-h)/\sigma_z)^2)]}{2\pi U \sigma_y \sigma_z}$$

where Q is the emission rate in g/s, z is the receptor height set at 2 m, h is the source

height set at 0 m, and U is the wind speed component in the downwind direction at that

hour in m/s. σ_y is calculated from the downwind distance *x* of the receptor from the point

source and the turbulence measure, σ_θ (in radians), at that hour:

$$\sigma_y = x\sigma_\theta, \quad\quad\quad\quad\quad\quad (\text{eq. 2})$$

The vertical diffusion coefficient, σ_z, is a function of stability conditions and calculated

using Pasquill-Gifford correlation curves (*18*). The reservoir was treated as an array of

point sources covering 175 m x 200 m with each point source arranged 1 m apart. The

lower left corner of the reservoir is located 50 m east and 20 m north of the receptor.

The emission rate was the volatilization rate calculated from the chloroform water

concentration (C_w), reservoir surface area (A), Henry's law constant for chloroform (H),

mass transfer coefficients in the gas and liquid phases (K_G, K_L), absolute temperature (T),

background concentration (P_B) and gas constant (R):

$$Q = \frac{(K_G K_L)(HC_W - P_B)(MW)(A)}{(HK_G + RTK_L)}$$ (eq. 3)

This equation was derived from the mass flux equation (6):

$$N = K_{OL}(C_w - P_B / H)$$ (eq. 4)

where K_{OL} is the overall mass transfer coefficient which can be calculated from K_L and

K_G. The magnitudes of K_L and K_G are 10^{-6} and 10^{-3} m/s respectively. Since the Henry's

law constant for chloroform is temperature-dependent, it was calculated for each hour

using the equation:

$$H = \exp((\ln H_{ref}) + b((1/T) - (1/T_{ref})))$$ (eq. 5)

where $H_{ref} = 3.7 \times 10^{-3}$ atm-m^3/mol, $b = 4100$, and $T_{ref} = 298.15$ K (15).

A background mixing ratio of 9 pptv was included in the model. This background

mixing ratio was converted from the background concentration 0.045 µg/m^3(11) at a

temperature of 298.15K (25°C, 77°F). The background mixing ratio is normalized to the

ambient temperature in the model.

RESULTS AND DISCUSSION

Figure 2 shows the ambient chloroform levels measured at the Beacon Hill site in

Seattle, Washington from 2000 to 2005. This graph shows chloroform levels varying

from a low of about 10 pptv to a maximum value of 265 pptv. This site was chosen to be

representative of air toxic levels in Seattle and currently serves as a National Air Toxics

Trends Station (NATTS). The selection of Beacon Hill for the NATTS network was

based on an air toxic monitoring study in 2001 that included six Seattle area sites.

However, as we have reported previously (*13*), ambient chloroform levels were higher at

the Beacon Hill site than in most other Seattle area neighborhoods due to its close

proximity to a water treatment reservoir. As shown by the data in Table 3, there is a

statistically significant spatial variation ($p < 0.0001$) of chloroform levels in Seattle. A

higher average annual chloroform concentration was measured at Beacon Hill (BH) and

Maple Leaf (ML) both of which were located near water treatment reservoirs.
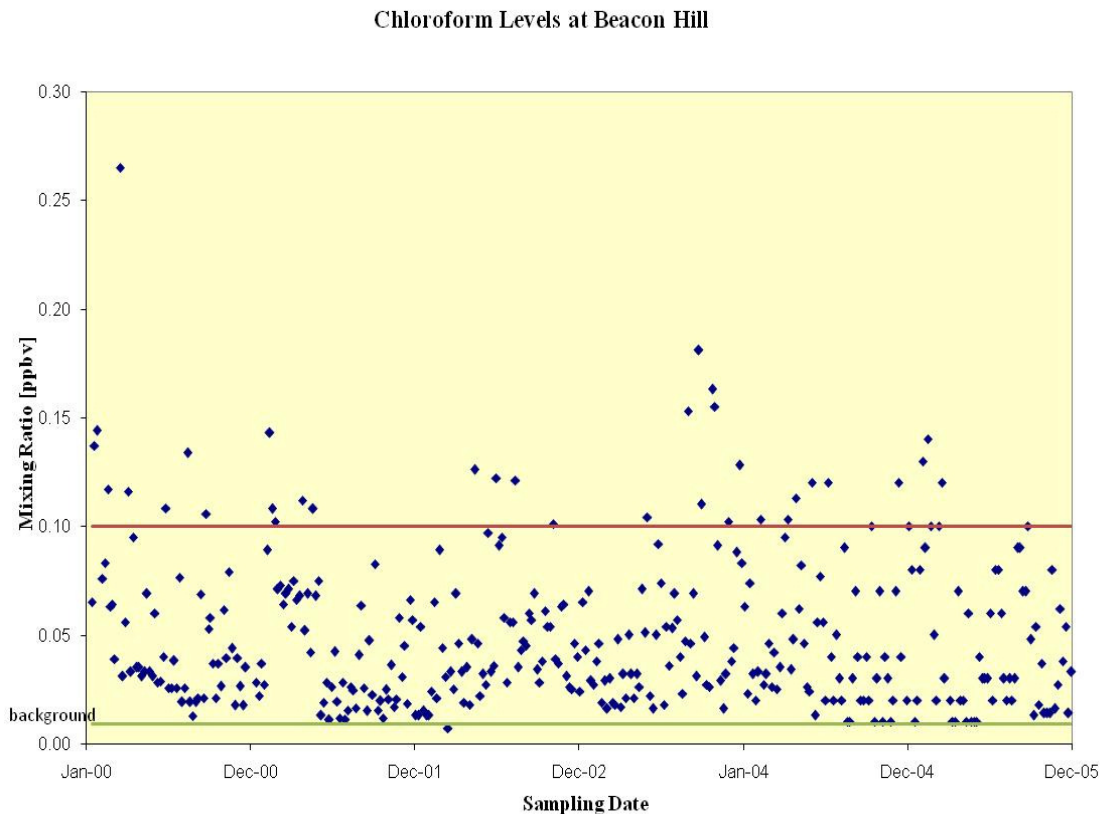
Figure 2. Time series plot of chloroform levels measured at Beacon Hill from 2000 to
2005

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Table 3. Descriptive Statistics of Chloroform Levels in Seattle, WA

Site	Mean (ppbv)	95% CI (ppbv)	Max (ppbv)	Min (ppbv)	n
Lake Forest Park	0.030	0.004	0.080	0.011	61
Maple Leaf	0.047	0.009	0.185	0.008	62
Beacon Hill	0.044	0.007	0.143	0.011	69
Georgetown	0.029	0.005	0.110	0.010	65
Sea-Tac	0.026	0.004	0.062	0.007	63
Lake Sammamish	0.026	0.004	0.093	0.001	55

Chloroform emissions from drinking water in California was estimated to be 190 tons per year in the South Coast air basin, and accounted for 51% of total chloroform emissions in 1988 (*14*). Because we are unaware of any previous reports of the impact of reservoir emissions on air in Seattle, it was of interest to estimate the emission rate of chloroform from the Beacon Hill Reservoir. We first calculated chloroform volatilization rates based on water concentration and other parameters and then estimated ambient chloroform concentrations at the BH monitoring site using a Gaussian plume model. The predicted ambient concentrations could then be compared with the actual measurements made at the site as a way to evaluate the accuracy of the emission estimates.

Days when the ambient 24-hr average chloroform concentration exceeded 0.10 ppbv were selected for modeling purposes (Table 4). This level is about 10 times the background concentration measured in Seattle and indicates a definite impact from the nearby water treatment impoundment. Because of the geographic relationship between the monitoring site and reservoir, the highest concentrations were always recorded when winds for much of the 24-hr period were from the northeasterly quadrant.

Table 4. Ranked 24-hour Average Ambient Chloroform Concentration and
Meteorological Conditions at Beacon Hill, Seattle, WA

Date	chloroform (ppbv)	No. of hours $0 \leq WD \leq 90$	WS (m/s)	Temperature (°F)
03/16/2000	0.265	5	5.7	45
09/24/2003	0.181	15	2.1	62
10/24/2003	0.163	18	2.7	50
10/30/2003	0.155	23	3.3	44
08/31/2003	0.153	11	3.1	64
01/25/2000	0.144	2	3.4	43
02/12/2001	0.143	19	2.3	39
02/15/2005	0.140	23	3.2	36
01/19/2000	0.137	12	4.4	38
08/13/2000	0.134	3	2.8	61
02/03/2005	0.130	1	2.2	48
12/23/2003	0.128	2	2.5	49
05/14/2002	0.126	16	4.1	48
07/01/2002	0.122	20	3.2	57
08/12/2002	0.121	14	3.3	69
06/02/2004	0.120	12	3.3	59
07/08/2004	0.120	10	2.5	60
12/11/2004	0.120	22	3.9	44
03/17/2005	0.120	0	3.0	47
02/18/2000	0.117	16	1.6	40
04/03/2000	0.116	6	2.2	54
04/27/2004	0.113	3	no data	52
04/25/2001	0.112	9	2.5	58
01/31/2000	0.110	1	2.6	43
09/30/2003	0.110	5	1.7	61
06/26/2000	0.108	14	2.8	71
02/18/2001	0.108	7	2.3	44
05/19/2001	0.108	13	3.4	51
09/24/2000	0.106	12	3.9	59
06/02/2003	0.104	12	3.4	57
02/09/2004	0.103	19	2.0	38
04/09/2004	0.103	13	2.6	54
02/24/2001	0.102	no data	0.0	42
11/29/2003	0.102	19	2.3	45
11/04/2002	0.101	13	1.4	43

A sensitivity analysis with the air quality model indicated that the ambient chloroform concentration was most sensitive to trihalomethane (THM) water levels and wind speed. The hourly wind speeds during model periods were well known because they were measured at Beacon Hill. Chloroform levels in the water reservoir were not measured on the modeling days so we had to estimate the water concentration based on the reported annual THM data (Table 1). As a first estimate we utilized the yearly average THM and multiplied by 0.82 to get the chloroform concentration. In most cases, applying this chloroform water concentration yielded an ambient chloroform level that was in reasonable agreement with the measured value. However, by adjusting the water concentration we could obtain a best-fit volatilization rate that allowed nearly perfect agreement between modeled and measured ambient chloroform concentrations (Table 5). The best-fit chloroform water concentrations are typically lower than the 41 ug/l average chloroform generated in finished water that EPA estimated in 1984 (*15*).

Table 5 lists the chloroform emission rates for 15 days when winds advected reservoir emissions over the monitoring site. Shown in this table are the best-fit chloroform water concentrations that were applied to maximize agreement between measured and modeled ambient chloroform levels. Chloroform emissions varied from a low of 1.7 mg/s on Nov. 29, 2003 to a high of 8.49 mg/s in July 8, 2004. In general, it appears that the volatilization rate of chloroform from the water treatment reservoir is higher in the summer and fall than winter, but there are clearly some exceptions to this pattern.

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Table 5. Modeled 24-hour Average Chloroform Mixing Ratio (ppbv) and Emission (mg/s)

Date	Best-fit Q (mg/s)	No. of hours $0 \leq WD \leq 90$	Best-fit C_W (ug/l)	Modeled (ppbv)	Measured (ppbv)
09/24/2003	6.62	15	30	0.183	0.181
10/24/2003	6.62	18	14	0.162	0.163
10/30/2003	6.21	23	17	0.155	0.155
02/12/2001	2.80	19	12	0.143	0.143
02/15/2005	4.09	23	12	0.140	0.140
01/19/2000	4.19	12	20	0.138	0.137
07/01/2002	7.32	20	12	0.123	0.122
08/12/2002	4.62	14	21	0.121	0.121
07/08/2004	8.39	10	48	0.120	0.120
12/11/2004	2.58	22	19	0.120	0.120
02/18/2000	5.48	16	17	0.118	0.117
06/26/2000	2.31	14	19	0.108	0.108
02/09/2004	2.61	19	12	0.102	0.103
11/29/2003	1.74	13	11	0.102	0.102
11/04/2002	6.62	13	22	0.101	0.101

A detailed picture of emission determination results are provided for September 24, 2003. The prevailing wind direction was northeasterly on this day. The average Cw value for 2003, 32 ug/l, was used to calculate the chloroform emission rate 5.92 mg/s. When this value was applied in the air quality model, hourly average ambient concentrations were obtained as illustrated in the pollutant rose plot shown in Figure 3. A 24-hr average chloroform concentration of 0.15 ppbv was obtained when the individual hourly average values were combined. This is 17% lower than the measured 24-hour concentration of 0.18 ppbv (Table 5). Increasing the chloroform fraction from 0.82 to 0.94 of the THM concentration to a best-fit Cw of 30 ug/l resulted in a chloroform emission rate of 6.62 mg/s and a corresponding 24-hour average modeled concentration of 0.18 that matched the measured value. The time series plot of simulated hourly concentrations for

September 24 is shown in Figure 4. The zero values seen in this figure occur when winds were from a non-northeasterly direction during the midday hours. The zero values are balanced by hourly average chloroform concentrations as high as 0.57 ppbv leading to the predicted concentration of 0.18 ppbv.
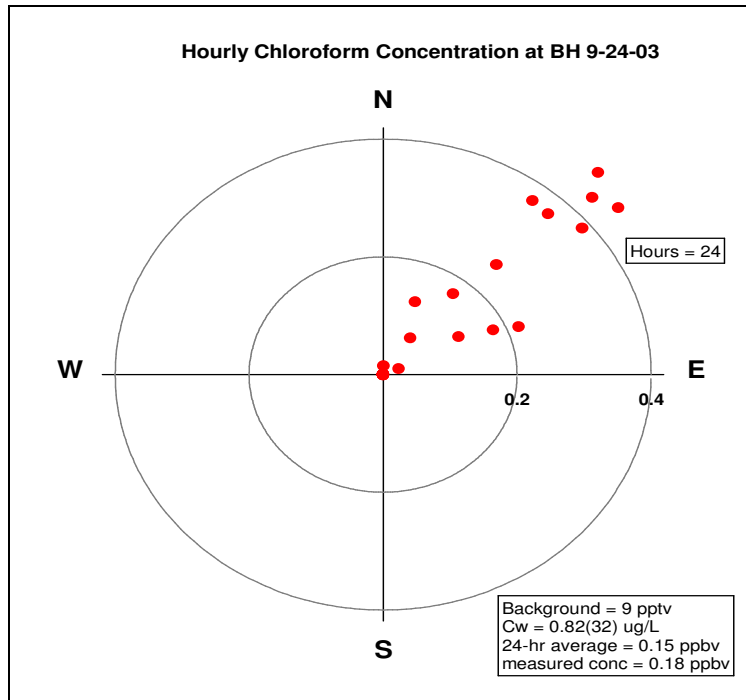
**Figure 3**. Pollutant rose plot for 9-24-03

If it is assumed that the chloroform emission rate data shown in Table 5 is representative of Beacon Hill water treatment reservoir, the annual tonnage of emissions from this source can be calculated. The average Q from Table 5 is 4.81 mg/s. This corresponds to 335 lb/year in chloroform emissions. The 2002 and 2005 King County Emission Inventories estimate total chloroform emissions of 1753 and 1786 lb/yr, respectively. Typically, area sources far outweigh point source chloroform emissions

with water treatment facilities being the dominant area source emitters in King County. If it is assumed that 80% of the total 2002 and 2005 chloroform emissions in King County are released by water treatment reservoirs, the emission estimate for this source category is about 1770 lb/yr (average of 2002 and 2005). Our calculated value of 335 lb/yr for the Beacon Hill reservoir seems to be in reasonable agreement as there are several such facilities in the county.
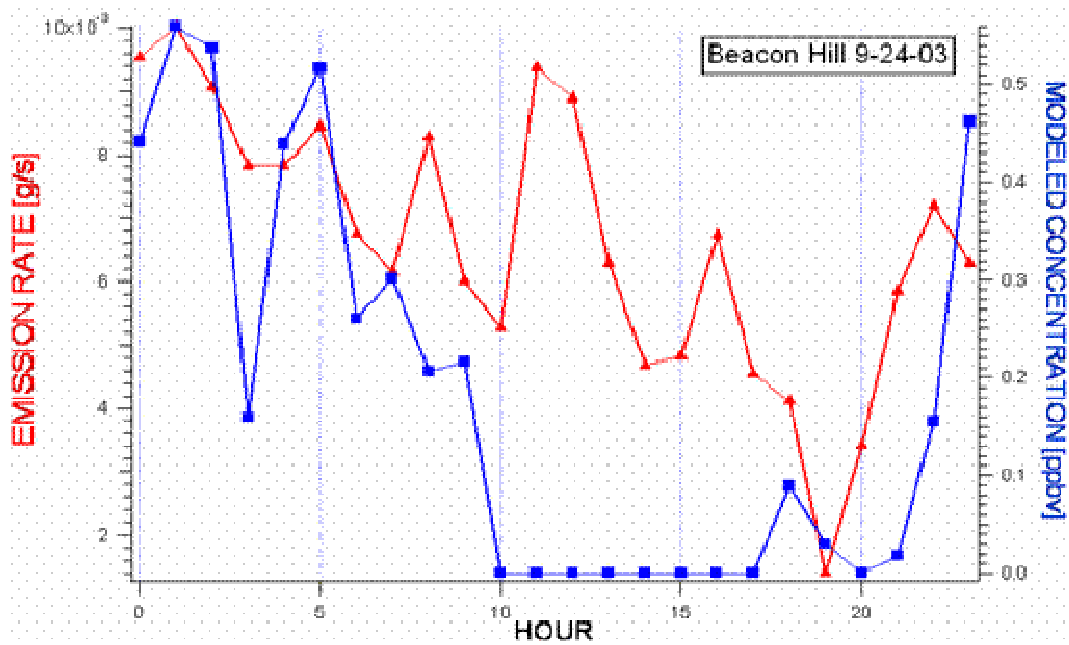
Figure 4. Hourly average modeled chloroform emissions and concentrations assuming only background and reservoir emissions

For the selected day (Sept. 24, 2003), the concentration was determined at various downwind distances up to about 500 meters. The measured ambient chloroform concentration is 0.183 ppbv. Downwind, at a distance of 200 meters, ambient concentration is estimated to be about 0.04 ppbv (Fig. 5).
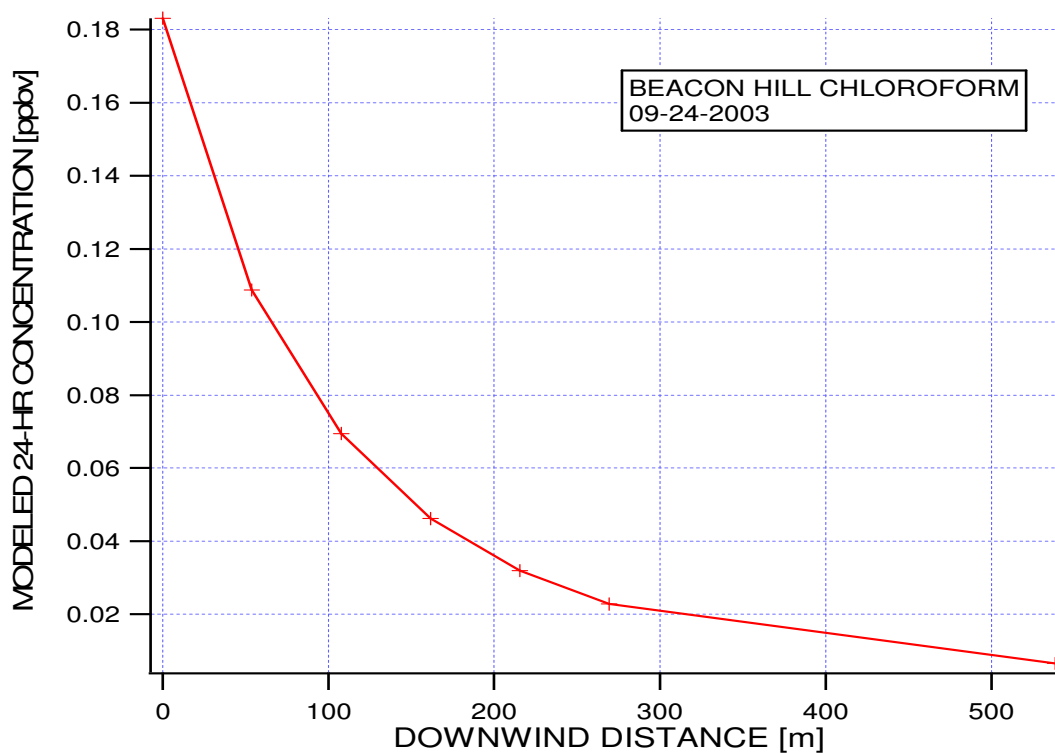
Figure 5. Modeled 24-hr concentration as a function of downwind distance from source

SUMMARY AND CONCLUSIONS

In this paper, an air/water mass transfer model was used to estimate chloroform emissions

from a water reservoir and these emissions were used in a simple Gaussian dispersion

model to simulated24-hour average mixing ratios at the Beacon Hill air toxics site which

is located within 50 m of the reservoir. Comparison of the modeled chloroform levels

and observations provided a basis for correcting the initial emission estimates. With this

approach, chloroform emissions from the water reservoir were estimated to be

approximately 335 lb/yr. In addition, modeled 24-hr concentrations further downwind in

the nearby residential area were more representative of ambient chloroform levels in

Seattle (based on similar sampling at other sites) than measured concentrations sampled

immediately next to the reservoir.

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CHAPTER FIVE

SUMMARY AND CONCLUSIONS

The observed trends in ambient air toxic concentrations measured at Seattle, Washington neighborhoods and their relationship to control programs is the primary goal of this research. Selected volatile organic compounds in the "core" air toxics list were the focus of the results presented in this dissertation.

The results of our six-year monitoring of selected air toxics in Seattle, Washington may be summarized as follows:

Spatial variation. Benzene, chloroform, perchloroethylene, trichloroethylene, and acetaldehyde exhibited spatial variation among the six sites. Chloroform was found to be elevated at Beacon Hill and Maple Leaf, where the sites are located near water reservoirs. Perchloroethylene and trichloroethylene were found to be higher at Georgetown, which is in Seattle's industrial area. Benzene and acetaldehyde are both primarily from mobile sources but also have secondary sources. The proportion of primary and secondary sources may account for the spatial variability of these HAPs.

Temporal variation. Benzene, 1,3-butadiene and formaldehyde showed some seasonal variability. Benzene and 1,3-butadiene were highest in winter while formaldehyde levels may be the highest during any of the seasons. Year-to-year variability was found to be

statistically significant for benzene and 1,3-butadiene which may be attributed to emission changes in the transportation sector. The annual variability in perchloroethylene levels was also found to be statistically significant due to the higher level in 2000 which has remained fairly constant since then. A decreasing trend was observed in ambient levels of HAPs which corresponds with the decreasing trend also observed in the emissions inventory.

Mobile source emissions. The various control programs at the federal, state, and local levels aimed at reducing mobile source emissions were linked to the observed decrease in BTEX levels. Mobile source air toxics were reduced because of federal regulations requiring more stringent standards for vehicle emission control systems, fuel sulfur content and use of reformulated gasoline with lower benzene content. Mandated vapor recovery at fueling stations and a shift to low sulfur diesel fuel in state-owned fleet of highway vehicles and ferries also contributed to the reduction. In Seattle, the bus fleet was modernized and used biodiesel mixed with the conventional petroleum based diesel, and local refineries started the switch to reformulated gasoline.

Chloroform emissions. Chloroform emissions rate from water reservoir was estimated to be 2 to 8 mg/sec. The calculated value of 335 lb/yr for the Beacon Hill reservoir seems to be in reasonable agreement with emissions inventory. Because of the localized source, the measured ambient chloroform level at Beacon Hill may not be representative of Seattle in general.

Conclusions and recommendations for future work. The six-year monitoring in Seattle, Washington enabled the characterization of the spatial and temporal variation of ambient concentrations of hazardous volatile organic compounds. In 2005, a 67% reduction relative to the 2000 level was observed in ambient benzene levels. In order to determine whether this was truly a reduction or merely a periodicity in ambient levels, continued monitoring is recommended. Six years may not be a sufficiently long period to determine trends. A more accurate water chloroform concentration measured at the reservoir may be determined to get a more accurate estimate of chloroform emissions from a water reservoir. Chloroform scavenging by rainfall should also be included in the emissions model as this might be a significant factor in the partitioning of chloroform in the gas and liquid phases.