Data Analysis of
Air Toxics in Connecticut

Prepared by
NESCAUM

March 2005

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ES-1. Background

Monitoring of ambient air toxics constitutes an emerging area of interest in the environmental community. Accordingly, EPA is currently devising a national strategy for an air toxics monitoring network. Four primary goals have been established for the planned network (EPA, 2004). The first is to establish trends and evaluate the effectiveness of HAP reduction strategies. A second goal, which would be satisfied by the first, is to determine local ambient air toxics concentrations. Additionally, data can be used to evaluate and improve the current modeling tools for air toxics. The final goal is to provide the research community with information that reduces uncertainty in determining the interrelationships among ambient toxics concentrations, human exposure to toxics, and the associated health effects of such exposure.

Many of these same goals have previously been addressed by Connecticut Department of Environmental Protection through the Toxics Air Study in Connecticut, which lasted from 1999 through 2003. This innovative program provides an array of data on air toxics present in the ambient environment, including carbonyls, polycyclic aromatic hydrocarbons (PAHs), metals and volatile organic compounds (VOCs). Beyond the simple goal of providing an estimate of ambient concentrations, the information gathered serves a number of purposes. These include: (1) providing data to assess the fate and transport of toxics in the state, (2) establishing a baseline level to aid in an effectiveness evaluation of HAP reduction strategies, (3) aiding toxic air quality model performance assessments, and (4) determining whether or not additional permit requirements are necessary for Title V or solid waste facilities. Notably, these data are intended to help inform policy development and future air emission reduction efforts for stationary and mobile sources within Connecticut.

ES-2. Report Results

Samples targeting 100 ambient air toxics were collected from seven sites over a five-year period, beginning in 1999 and ending in 2003. Six of the sites were located near Title V permitted or solid waste facilities while the seventh was considered a rural background site. A quality assurance review was conducted and determined the majority of data collected was acceptable for technical analysis. The specific details of those analyses are contained in the main report, while the most important results are excerpted here.[1]

In the absence of air quality standards for air toxics, the TASC data were put into a health context by comparing ambient levels to the available Connecticut Department of Public Health's proposed annual hazard limiting values (HLVs), which are based upon a quantitative risk assessments for cancer and non-cancer health endpoints. For one compound, formaldehyde, it was determined that the ambient concentrations were above its proposed HLV. However, the levels monitored in Connecticut are similar to ambient

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[1] The analyses within provide a detailed technical discussion of ambient air toxics data collected in Connecticut. Some level of comfort with scientific methods may be required to fully benefit from the investigation as presented in the report text.

concentrations reported throughout the United States. Additionally, indoor air levels of this chemical are often observed at concentrations more than 20 times greater than those measured outside.

For other chemicals, such as acetaldehyde and manganese, the ambient levels were close to their associated proposed HLVs. For some years or sites the levels were just above or immediately below the proposed annual HLV. As with formaldehyde, the levels observed in TASC are comparable to ambient levels measured across the United States through EPA's pilot ambient air toxics monitoring network. For many other compounds, including acetone, methyl ethyl ketone, beryllium, nickel, lead, thirteen VOCs and all of the PAHs, the monitored concentrations were below the proposed annual HLVs, often lower by many orders of magnitude.

Evaluation for some compounds was not possible, as the protocols were not sensitive enough to determine concentrations below the proposed HLV. This group included seven VOCs, arsenic, and cadmium. Many of the aldehydes, including acrolein, could not be assessed given limitations in the analytical methods employed. For a few compounds, namely zinc, chromium and benzene, evaluation was not possible due to sample contamination.

ES-3. Conclusions

The TASC program established a baseline concentration level for many air toxics at sites throughout Connecticut. For the majority of the compounds, the levels appear to be low when judged against Connecticut Department of Public Health proposed annual HLVs. For three chemicals, formaldehyde, acetaldehyde and manganese, the ambient levels may be of concern. When compared to other available toxic data, however, the levels determined through TASC are similar to those found in other parts of the United States (Hafner, *et al*., 2004). In the case of formaldehyde, indoor air levels are expected to be more than an order of magnitude greater than ambient levels. These carbonyl concentrations are likely dominated by motor vehicles, and the same may be true of manganese.

The ambient data have been compared to modeling data from the 1996 National Air Toxics Assessment and can be used to help improve the methods used in model application and model formulation. The monitoring data do not support requiring additional permit conditions for Title V or solid waste sources. However, should additional funds become available in the future and the Connecticut Department of Environmental Protection deems it valuable as part of its toxics reduction program, it may be possible to conduct limited sampling to confirm that significant changes in ambient levels have not occurred.

1. INTRODUCTION

1.1. Background

Toxic air pollutants, also known as hazardous air pollutants (HAPs), are those pollutants that are known or suspected to cause cancer or other serious health effects. Under the Clean Air Act (CAA), HAPs are regulated by technology-based controls to limit emissions to the ambient air. The 1990 CAA Amendments identified 174 types of facilities or source categories that emit one or more of the 188 toxic air pollutants identified in the CAA based on their potential to adversely impact public health. For sources that emit or have the potential to emit any of the listed pollutants, the United States Environmental Protection Agency (EPA) must develop maximum achievable control technology (MACT) standards, which are implemented through the Title V Air Operating Permits program. The Title V permit program provides a regulatory vehicle whereby all a facility's air quality requirements are incorporated into a single permit.

While the MACT strategy to reduce HAPs relies on engineering judgment about the amount of reduction in emissions that can be achieved, there remain only a limited number of federal standards and guidelines established as reference points for the evaluation of health risks from HAPs (Kyle *et al.* 2001). The lack of information on ambient concentrations of HAPs across the country has hindered efforts to assess potential health effects and prioritize and evaluate policy initiatives for reduction of ambient levels. In recent years, the EPA developed and ran a model that used information about emissions to predict ambient concentrations of 148 HAPs for census tracts in the contiguous states for 1990. This modeling predicted concentrations of pollutants in many counties that would exceed previously defined health benchmark concentrations for cancer and noncancer health effects (Caldwell *et al.* 1998; Rosenbaum *et al.* 1998; Woodruff *et al.* 1998; Woodruff *et al.* 2000, EPA 2002). Although subject to limitations, these data indicate that millions of persons in the United States live in areas where estimated ambient concentrations of one or more HAPs exceed levels of concern for health effects in humans. Since this study, changes in both population and emissions have occurred that could modify this conclusion. With respect to actual measures of human health outcomes, however, little health information is presently available to assess the impact from air toxics. Many HAPs lack sufficient hazard data for risk assessment, particularly for noncancer effects (Brown 2001; Lunder *et al.* 2004).

Prior to the CAA amendments of 1990, Connecticut passed regulations which list Hazard Limiting Values (HLVs) for approximately 620 out of an identified 850 hazardous chemicals and chemical groups. The Connecticut Department of Environmental Protection (CT DEP) was one of the first state agencies in the U.S. to implement a health-based air toxics control program. This program, established in 1986, created HLVs, which are fenceline concentrations (surrounding a source) not to be exceeded in order to protect public health.[2] The HLV is used as an input for calculations

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[2] Three separate compound classes were established in the regulations: (1) human carcinogens, (2) teratogens/mutagens/suspected carcinogens and (3) other hazardous substances. These compound classes are tabulated (RCSA 22a-174 Section 29: Tables 29-1, -2, -3) in the regulations although HLVs have not

of the Maximum Allowable Stack Concentration (MASC). MASC values are specified as state-only applicable permit requirements in federal Title V permits, which are required of all major point sources. Specifically, the MASC is the maximum allowable concentration of a hazardous air pollutant in the exhaust stream of a discharge point of a stationary source under actual operating conditions.

The CT DEP is currently involved in a number of programs throughout the state intended to characterize the ambient concentrations and deposition of HAPS; better understand the fate and transport of HAPs in the atmosphere; and evaluate the effectiveness of HAP reduction strategies. In 1994, the DEP started measuring toxic air pollutants from a network of Photochemical Assessment Monitoring Stations (PAMS) monitoring sites within the state. The CAA 1990 Amendments provided for the establishment of PAMS sites in all ozone nonattainment areas designated as serious, severe, or extreme. The PAMS network typically monitors fifty-six target hydrocarbons and two carbonyl compounds, ozone, oxides of nitrogen (NO_x and/or NO_y), and meteorological measurements. Additionally, CT DEP implemented the Toxics Air Study in Connecticut (TASC) from 1999-2003, using the University of Connecticut's Environmental Research Institute (ERI) laboratory to characterize air quality in the vicinity of major stationary sources subject to Title V air permit requirements of the Clean Air Act. Monitoring data collected from this project are intended to help inform policy development and future air emission reduction efforts within Connecticut.

CT DEP in conjunction with the Connecticut Department of Public Health (CT DPH) has recognized a need to update the existing air toxics regulation. The current HLVs are based on modified occupational exposure levels, which represented the state of the science at the time they were established in 1986. The values and their form have remained static since their inception; however, the underlying science has progressed sufficiently that revised estimates are feasible. Because traditional potency estimates derived from human data are generally based on occupational cohorts of healthy males, they may not adequately reflect population variability in susceptibility, including sensitive populations such as children, who may have increased exposures and are physiologically different from adults in how they metabolize chemicals in the body. Recognizing the need to update HLVs and incorporate classical risk assessment approaches, CT DPH recently conducted comprehensive toxicological reviews of fifty-four air toxics and proposed new HLVs based on quantitative risk assessments for cancer and non-cancer health endpoints. The toxicological profiles for each air toxic contain toxicological values underlying the proposed HLV, the basis for the toxicological value, and comparison with other regulatory guideline values used by federal and state agencies. The proposed HLVs could be used to replace the 8-hour and 30-minute averaging times with standardized exposure values for annual and 1-hour exposures, respectively. For carcinogenic toxics, the proposed annual HLVs are set to 1 in 100,000 cancer risk levels for 30 years of exposure at the fenceline of the facility. Importantly, the proposed HLVs also incorporate children's toxicokinetics into the risk framework (CT DPH 2002; Ginsberg 2003).

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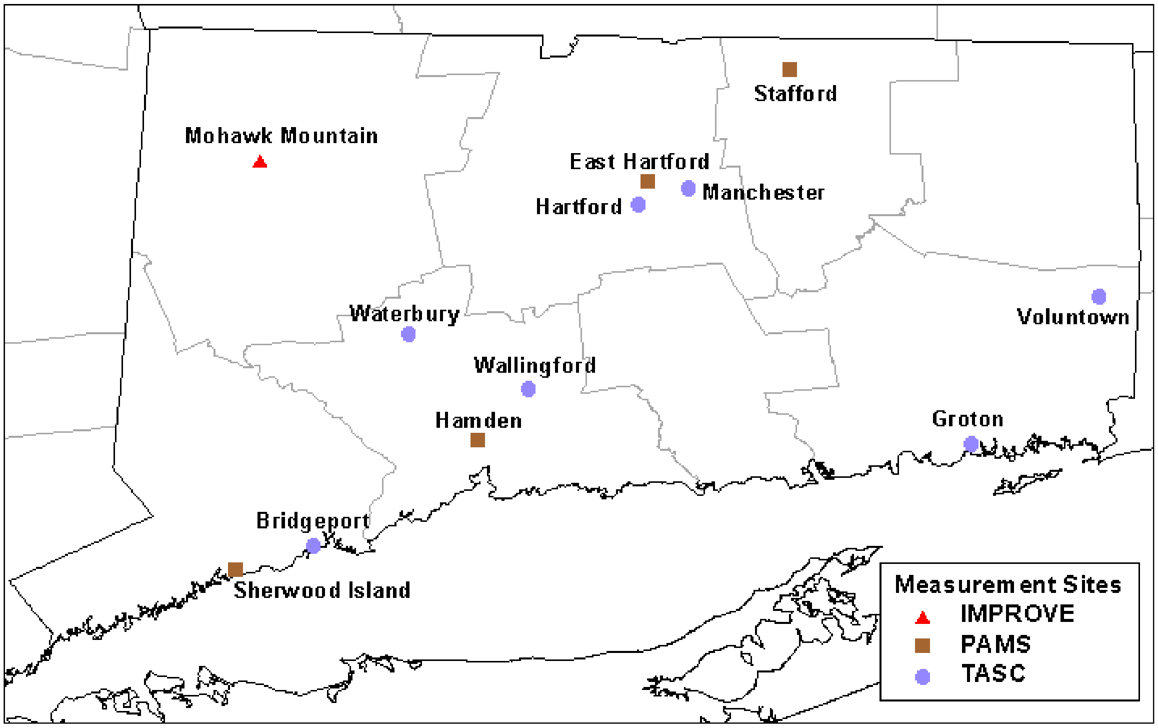
been established for all chemicals. In addition, safety factors of 200, 100 and 50 were built into the values, which were based on occupational health exposure levels.

These updated HLVs, in conjunction with the monitoring conducted by CT DEP over the last decade, provide important information that can be used to evaluate the significance of air toxics to Connecticut.

1.2. Overview of Networks

As shown in Figure 1-1, Connecticut's ambient air PAMS network operated four monitoring sites at East Hartford, Westport (Sherwood Island), Hamden, and Stafford during the course of the TASC study. Currently, three sites are operational: East Hartford, Westport and New Haven (not depicted). The New Haven site at Criscuolo Park began in 2004, at which time the Hamden site was discontinued. Also shown on the map is the TASC network, comprised of six sites situated to monitor along the "fencelines" of Title V and/or solid waste sources and a seventh site representative of the rural background, located in Voluntown, in eastern Connecticut. This network was operational from 1999 to 2003. The final measurement site from which data are analyzed is located at Mohawk Mountain, in northwest Connecticut. This site is part of the IMPROVE particle speciation network and began sampling in 2001 (similar instrumentation was sited at this location previously).

Figure 1-1: Location of Connecticut PAMS and TASC monitoring networks



This report is built around the TASC sampling classes: Carbonyls, Polycyclic Aromatic Hydrocarbons (PAHs), Toxic Metals and Volatile Organic Compounds (VOCs), providing an overview of air toxics data collected from the TASC and PAMS networks (only Carbonyls and VOCs for PAMS[3]). Collection and analysis methods from TASC were evaluated, followed by an analysis of the ambient and blanks data. Comparability between TASC data and EPA's Assessment System for Population Exposure Nationwide (ASPEN) modeling was assessed. In addition, both the monitoring network concentrations and EPA modeling estimates were evaluated with respect to Connecticut HLVs with an eye toward the MASC compliance status of Title V sources and the potential impact of these sources on public health.

1.3. Data Analysis Methodology

In an effort to characterize air toxics in Connecticut, data generated by the TASC network were examined for temporal and geographic trends and levels were compared to applicable health standards and modeled data. Table 1-1 provides an overview of the total number of valid samples that were collected over each year of the study and is further subdivided by location and sample class (Carbonyls, PAHs, Metals and VOCs). Over 1,000 samples were analyzed for each compound class, with the fewest for PAHs (1,049) and the greatest number for carbonyls (1,369).

To the extent possible, all data was included in the analysis. Data quality varied greatly, depending on the specific pollutant of interest. However, in many cases, even data with large uncertainty contains some useful information. For example, if the uncertainty is a factor of five, yet the level of concern is several orders of magnitude above the reported value, a reasonable conclusion can still be drawn regarding the relative hazard of the measured chemical. It is in this spirit that some analyses were conducted, despite misgivings about the absolute reported concentrations, as might be determined from reported blank levels or other quality assurance evaluations.

The first step in assessing the quality of the data was to evaluate the relevant Standard Operating Procedures (SOPs) and Quality Assurance Project Plan (QAPP) followed in the TASC project. In general, these documents are well written and comprehensive. ERI's laboratories were visited to ensure that the proper protocols were being followed for the most recent laboratory analyses. In some instances protocols were not followed explicitly, though deviations in general were not believed to significantly affect data quality. However, these departures should have been better documented, and subsequently incorporated into revisions to reflect actual laboratory practice.

The next step in validating data included the review of field sheets, data report files, and chromatograms. Information from paper files was compared to that contained in the existing database. These examined paper files covered one year's worth of samples (July 2001-July 2002). Sample files were randomly chosen and checked to confirm values in the paper file matched those in the database. For TASC PAH samples, the solution concentrations provided in the files enabled the calculation of an ambient PAH concentration for each compound examined. This analysis showed that the PAH values were entered in the database correctly. The TASC carbonyl samples could not be verified through this field sheet review since only the chromatograms were available for evaluation; the peak area reports required were unavailable. Initial TASC VOC

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[3] The data collection methodologies for PAMS differed from TASC. For VOCs, TASC used 24-hour canister sampling while the PAMS data analyzed are hourly, in situ, auto-GC data. The carbonyl collections for TASC were 24-hours whereas the PAMS carbonyls were collected in 3-hour intervals.

Table 1-1: Number of Valid Samples Collected in TASC

TASC Site	Year	Carbonyls	PAH	Metals	VOC
Bridgeport	1999	27	13	22	31
	2000	54	32	38	56
	2001	51	48	49	51
	2002	57	56	56	58
	2003	8	7	8	6
	Total	197	156	173	202
Groton	1999	37	18	27	36
	2000	58	34	48	45
	2001	54	45	54	42
	2002	58	53	62	50
	2003	7	10	9	9
	Total	214	160	200	182
Hartford	1999	46	20	25	42
	2000	56	31	47	53
	2001	48	39	44	37
	2002	52	50	54	53
	2003	3	2	3	2
	Total	205	142	173	187
Manchester	1999	22	13	18	18
	2000	54	34	48	53
	2001	55	49	53	50
	2002	59	54	61	59
	2003	10	10	9	9
	Total	200	160	189	189
Voluntown	1999	33	10	27	32
	2000	58	30	41	51
	2001	54	46	50	50
	2002	58	52	58	60
	2003	8	9	10	9
	Total	211	147	186	202
Wallingford	1999	12	5	14	0
	2000	53	29	38	39
	2001	51	49	52	51
	2002	58	54	61	58
	2003	10	9	10	8
	Total	184	146	175	156
Waterbury	1999	0	0	0	0
	2000	34	24	24	30
	2001	55	47	53	51
	2002	59	57	61	61
	2003	10	10	9	7
	Total	158	138	147	149
Connecticut Total		1369	1049	1243	1267

spot-checking revealed inconsistencies in converting concentrations between ppb and $\mu g/m^3$. Through conversations with ERI, it was confirmed that incorrect molecular masses had been used for concentration conversion calculations. Moreover, some sample data found in the paper files were not found in our database. After these findings, updated tables were acquired with complete data and correct molecular weight calculations. Finally, spot-checking TASC Metals data showed that the data were entered correctly.

Subsequent analysis began with reported blank concentrations data for the four classes of TASC compounds. Field blank and trip blank sample data were examined to determine percentages of blanks above the detection limit and average blank concentrations. Compounds showing unusually high blank levels were singled out for further analysis and validation. This was also done by comparing blank values to sample values from the same days for certain cases. In a few extreme cases (Total Chromium, Zinc and Benzene), compounds with unusually high blank level were excluded from detailed analysis.

After analyzing blanks concentrations, collocated samplers were compared to determine the level of precision in the measurements. An average relative percent difference between collocated samplers run on the same day was calculated and results were used to assess validity of the methods. Following precision analysis, the detection limits for the various TASC compounds were examined. Method detection limits[4] were provided by ERI along with the corresponding sample data. Average detection limits for the various chemicals were calculated and these values were compared to the HLVs proposed by the CT DPH. This allowed a determination as to whether the method used provided enough sensitivity to detect levels that were harmful to human health.

The detection limits provided by ERI were then used to replace the non-detects in the sample data. Rather than remove all non-detects from the analysis, the detection limit was used to give a conservative measure of pollution values, in effect showing a worst case scenario. The TASC sample data was then used to calculate overall, 4-year, state-wide pollutant averages and confidence intervals as well as site specific 4-year averages which allowed for inter-site comparisons. In the case of metals, a pair of 2-year averages was determined. Temporal trends were examined by looking at seasonal variation of pollutants as well as year to year variation for specific pollutants of concern.

Note that this analysis did not use blank subtraction, since blanks were not necessarily obtained for each individual site and sample time period. Nor does this work attempt to incorporate the field and trip blank levels as the minimum reportable concentration. Incorporation of blank levels for non-detect substitution would likely yield greater upper bound estimates than the approach employed in this report. However, those estimates may not represent an improvement over the MDL substitution approach used in this analysis, especially for those compounds detected in most ambient samples. Regardless, the analysis employed in the report relies on information generated from

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[4] MDLs as reported in the database were determined from a theoretical instrumental detection capability, generally determined as the standard deviation of seven replicate analyses of standard concentrations near the expected detection limit.

measured blank concentrations, the ambient average concentrations, and the detection percentage in ambient samples to assess the reasonableness of calculated ambient levels.[5]

After the quality assurance procedures were completed, the retained pollutant concentrations were compared to the proposed HLVs. This step goes beyond the original intent of the data collection--to determine levels of HAPs in the vicinity of Title V sources. However, the data can reasonably be used to assess which pollutants or compound classes are candidates for more in-depth examination.

Other data analyses in this report include an evaluation of PAMS toxics data, characterizing temporal and geographic trends. Hourly PAMS data were used to describe daily trends and perform inter-site comparisons. Furthermore, PAMS data were compared to TASC data to get a general idea of how the two networks characterized similar geographic areas. Although the networks did not have collocated sites, such comparison is useful as a first order assessment of data quality and confirmation of the expected pollutant behavior.

In addition to monitoring data, 1996 ASPEN modeled air toxics data[6] were investigated and illustrated in this document. County level modeled concentrations were presented to show geographic variability of specific pollutants. Then, modeled levels were compared to TASC monitored pollutant levels to give an indication of how well the model predicted concentrations. Finally, modeled results of pollutant source contributions were examined and presented.

The following four sections review the protocols and associated data generated through the TASC program for the four major compound classes. After these discussions, comparisons are made to the modeled data in Section 6. The final section provides an overall summary of the results and recommends approaches that might be taken based on the information garnered from the sampling campaign.

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[5] Note that comparison of blank and ambient levels *averaged over the entire dataset* (all years and sites) did not always show higher levels for the ambient samples. The result is likely due in part to locational and/or temporal differences in blank levels, as they were not necessarily available for the entire time period of record for this analysis. Additionally, the blank rotation from site to site was often performed in blocks of time, rather than periodically at all sites (i.e. 12 blanks from a site for an entire quarter rather than one blank per month at each site). This explanation is supported by results that showed when date and site specific comparisons were conducted, the ambient levels were greater than blank levels, as would be expected.

[6] Uncertainty in ASPEN modeled data increases as the geographic area or averaging time represented decreases. It may reasonably be expected that modeling results over an annual time frame averaged statewide may better agree with statewide ambient monitoring averages than modeled results for a specific site and day.

2. CARBONYLS

2.1. Introduction

Persons exposed to hazardous air pollutants at sufficient concentrations and durations may have an increased risk of developing certain cancers or experiencing other serious health effects. These effects can include damage to the immune system, as well as neurological, reproductive, developmental, respiratory, and other health problems. Interest in airborne carbonyls (aldehydes and ketones), an important group of HAPs, is growing because either they exist at high levels in motor vehicle emissions or they arise from the atmospheric oxidation of other hydrocarbons emitted from mobile and stationary sources. Carbonyls are also common indoor air pollutants. Sources of carbonyls in indoor air include building materials, furniture, adhesives, and cigarette smoke. Ambient concentrations of formaldehyde and acetaldehyde in urban air have been measured many times and continue to receive scientific attention as toxic air contaminants, mutagens, and carcinogens (Grosjean *et al.* 2002).

The following health information on formaldehyde and acetaldehyde indicate these carbonyl compounds can be both highly reactive and potentially toxic, having adverse chronic and acute health effects.

2.1.1. Formaldehyde

Major primary sources of ambient formaldehyde include automobile exhaust[7] and industrial production. The major sources of formaldehyde in indoor air are cigarette smoke, building materials, furniture, and adhesives. The primary way formaldehyde may enter the body is by inhalation of contaminated air. When inhaled, formaldehyde is quickly absorbed from the nose and the upper part of the lungs and rapidly metabolized at the site of contact. Formaldehyde is primarily metabolized to formate which can be incorporated into other essential molecules or pass from the body in the urine or be further metabolized to carbon dioxide which leaves the body in exhaled air. If metabolism to formate is inhibited or the metabolic mechanism overloaded, internal levels of formaldehyde may increase to the point where it can form bonds between proteins or between proteins and deoxyribonucleic acid (DNA).

The CT DPH's proposed annual average HLV for formaldehyde is 0.45 $\mu g/m^3$ and the proposed 1 hr HLV is 30 $\mu g/m^3$. The underlying toxicological value for this HLV is EPA's inhalation unit risk value from EPA's Agency Integrated Risk Information System (IRIS) (1.3×10^{-5} per ($\mu g/m^3$)). The proposed HLV also incorporates a two-fold extrapolation for children's inhalation exposure and two-fold extrapolation for genotoxic carcinogenic risks to children.[8]

Ambient levels of formaldehyde vapors between 0.4 and 3 ppm (490 $\mu g/m^3$ to 3,700 $\mu g/m^3$), when inhaled even for short periods of time, can irritate the eyes, nose, and

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[7] Formaldehyde emissions from motor vehicles are expected in general, but are worse for vehicles without catalytic converters or ones burning fuel with MTBE.

[8] Typical indoor levels of formaldehyde may be substantially greater than these levels. Homes in California for example reported levels on the order of 60 $\mu g/m^3$ (CARB, 1991).

throat and cause increased tearing and itching. Acute effects include nausea, headaches, and difficulty breathing. Chronic exposure is associated with respiratory symptoms and eye, nose, and throat irritation. EPA has not established a Reference Concentration (RfC) for formaldehyde but the oral Reference Dose (RfD) is 0.2 mg/kg-day based on a decrease in bodyweight gain and effects on the stomach in rats. EPA estimates that consumption of this dose or less, over a lifetime would not result in the occurrence of chronic, non-cancer effects. Some people are known to be more sensitive to formaldehyde than others and repeated exposure, including via inhalation of vapors, is believed to cause an increase in sensitivity in some individuals. Exposure of experimental animals to formaldehyde does not appear to result in reproductive, developmental, or genotoxic effects of significance.

Limited human studies have reported an association between formaldehyde exposure and lung and nasopharyngeal cancer. Formaldehyde is carcinogenic in rodents, producing squamous cell carcinomas in the nasal passages of rats and male mice. EPA has classified formaldehyde in Group B1: Probable human carcinogen, with an inhalation unit risk value of 1.3 x 10^{-5} per ($\mu g/m^3$). EPA estimates that if an individual were to breathe air containing formaldehyde at 8.0 x 10^{-2} ug/m^3over a lifetime, that person would theoretically have no more than a 1 in 1,000,000 increased chance of developing cancer. The International Agency for Research on Cancer (IARC) has classified formaldehyde in Group 2A: Probable human carcinogen based on limited evidence in humans and adequate evidence in animals (IRIS, ATSDR 1999).

2.1.2. Acetaldehyde

Sources of acetaldehyde are similar to those of formaldehyde, including emissions from combustion processes such as mobile source vehicular exhaust and stationary source fuel combustion and industrial processes. Combustion of gasoline containing the oxygenate additives ethanol or ethyl tert-butyl ether (ETBE) may also emit acetaldehyde. In addition, photochemical oxidation is a large source of acetaldehyde concentrations in ambient air. Human exposure to acetaldehyde occurs primarily through inhalation. At low levels of exposure, acetaldehyde is rapidly absorbed and metabolized.

CT DPH also relies on EPA's IRIS value for proposing an annual average HLV for acetaldehyde of 2.7 $\mu g/m^3$ and a 1-hr HLV of 550 $\mu g/m^3$. The proposed HLV also includes the same additional extrapolations as described for formaldehyde to account for children's inhalation and genotoxic exposure to young children.

Acute exposure to acetaldehyde vapor leads to eye, skin and respiratory tract irritation. Long-term or chronic exposure has been shown to damage the respiratory tract in rats. In hamsters, chronic exposure to acetaldehyde has produced changes in the nasal mucosa and trachea, growth retardation, slight anemia, and increased kidney weight. EPA has established a Reference Concentration (RfC) of 9.0 x 10^{-3} mg/m^3 based on degeneration of olfactory epithelium in rats, and has not determined a Reference Dose (RfD).

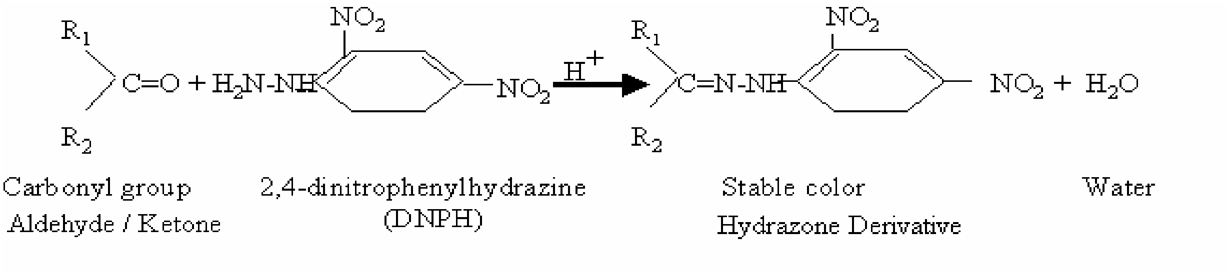
No information is available regarding adverse reproductive or developmental effects of acetaldehyde in humans. In animal studies, acetaldehyde has been shown to cross the placenta. Resorptions, malformation, reduced birth weight and increased postnatal mortality have been reported in rodents given acetaldehyde by injection.

Human data for carcinogenic effects of acetaldehyde are inadequate. An increased incidence of nasal tumors in rats and laryngeal tumors in hamsters has been observed following inhalation exposure to acetaldehyde. EPA classified acetaldehyde in Group B2: Probable human carcinogen on the basis of sufficient evidence for carcinogenicity in animals and inadequate evidence in humans, and determined an inhalation potency value of 2.2 x 10^{-3} mg/m^3. The EPA estimates that if an individual were to breathe air containing acetaldehyde at 5.0 x 10^{-4} mg/m^3 over a lifetime, that person would theoretically have no more than a 1 in 1,000,000 increased chance of developing cancer. IARC classified acetaldehyde in Group 2B: Possible human carcinogen based on sufficient evidence in animals and inadequate evidence in humans (IRIS).

2.2. Description of Carbonyl Sampling and Analytical Method

The method employed by the Environmental Research Institute (ERI) for the determination of aldehydes and ketones in ambient air followed the procedure outlined in EPA Standard Method TO-11a. This same method was employed for PAMS carbonyl sampling. Although this method is specific to sampling formaldehyde, it is commonly used with HPLC modifications to sample other carbonyls. The sampling method used by ERI for samples taken at TASC sites involved drawing ambient air through Sep-PAK (Waters Co., Milford MA.) silica gel cartridges coated with a solution of acidified 2,4-dinitrophenylhydrazine (DNPH). Aldehydes and ketones readily react with this hydrazine reagent in the presence of acid to form stable hydrazones. The reaction follows the equation detailed in Figure 2-1. These hydrazone derivatives are then extracted from the cartridges using acetonitrile and the derivatives are analyzed by High Performance Liquid Chromatography (HPLC).

Figure 2-1: Reaction of carbonyls with 2,4-DNPH in the presence of an acid



Field personnel attached two coated Sep-PAK cartridges in series to a low flow pump. This pump operated at either 0.1 liters per minute (LPM) or 1 LPM for a twenty-four hour sampling period, as discussed in the following paragraph. After sampling was completed, the carbonyl hydrazones were extracted by slowly passing 5 ml acetonitrile through the cartridges. The hydrazones in the extracts were then analyzed by isocratic reverse phase High Performance Liquid Chromatograph (HPLC) with a photo diode array detector operated at 360nm.

During the first year of the program, flow rates of 1 LPM were employed but were reduced in an attempt to minimize breakthrough from the front sampler to the rear. Comparative analyses of the data showed that reducing the flow rate decreased the percentage of tandem samples showing breakthrough. However, when breakthrough did occur under the lower flow rate, the mass captured on the rear cartridge represented a greater percentage of the sum of the mass on front and rear cartridges than found in the high flow rate samplers. It should be noted that monitored averaged atmospheric concentrations on the primary samplers were 30% and 43% higher for acetaldehyde and formaldehyde when breakthrough occurred relative to concentrations when no breakthrough was observed. More significantly, collection of those species with low atmospheric concentrations (e.g. those aldehydes with three or more carbon atoms) suffered after the collection flow rate was decreased since the volume of air sampled decreased by as much as an order of magnitude. Propionaldehyde and butyraldehyde were above detection limits in almost 90% of the samples at the higher flow rate. This collection percentage dropped to 25% and 56% respectively after the flow rate changed.

2.2.1. Interferences[9]

Background Contamination

It has been noted by ERI that pre-coated DNPH cartridges (Waters Corp., Milford, MA) can contain significant levels of formaldehyde, acetaldehyde, and acetone (0.1 to 0.3 µg per cartridge). To address this issue, their SOP recommended desorbing five randomly selected cartridges from each production lot and analyzing the extracts for carbonyl contamination. Accepted levels of background contamination, based on criteria determined by Waters Corporation, was <0.12 µg formaldehyde per cartridge. In this study, the acceptance level was set at 0.15 µg (see Section 2.2.2). Although not used, the SOP described alternative methods for coating the cartridges in-situ, and avoiding problems with pre-coated cartridges. However, when coating samplers in the laboratory, DNPH reagent bottles can become easily contaminated with formaldehyde and acetone since these compounds are common in laboratory air. To resolve this issue, DNPH reagent is commonly recrystallized before its use in the samplers.

Multiple Carbonyl Hydrazones and Rearrangement Products

ERI has utilized method TO-11a to determine environmental levels of 15 carbonyls: formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, crotonaldehyde, butyraldehyde, benzaldehyde, isovaleraldehyde, valeraldehyde, o-tolualdehyde, m-tolualdehydehyde, p-tolualdehyde, hexaldehyde, and 2,5-dimethylbenzaldehyde. To determine levels of these carbonyls, they were allowed to react with 2,4-DNPH on the sampling cartridge and the amount of hydrazone formed was quantified by HPLC. By applying a 1:1 stoichiometric ratio and the total volume of air sampled, the ambient concentration was then determined. Although all carbonyls will

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[9] The technical discussion in this section provides background information related to the current understanding of carbonyl sampling and analysis. The casual reader may wish to proceed to Section 2.2.2.

undergo the reaction highlighted in Figure 2-1, some of the more complex carbonyls will give products that then undergo side reactions, adduct formation, or isomerization, which result in multiple products and therefore multiple peaks appearing in the chromatogram. For these compounds, all the reaction products need to be quantified to give an accurate representation of environmental levels. Although method TO-11a is considered specific to formaldehyde it has been applied to other carbonyls by altering the analysis technique and recognizing its limitations for higher carbonyls. It is generally accepted that a single aldehyde-DNPH peak is not a sufficient measure of aldehyde concentration in carbonyl samples containing acrolein, crotonaldehyde, and acetaldehyde derivatives under acidic conditions (Grosjean *et al*. 1999; Liu *et al*. 2001; Shulte-Ladbeck *et al*. 2001; Huynh *et al*. 2002).

An examination of the chromatograms from the TASC carbonyl samples showed that only one peak was identified for each carbonyl in the sample[10]. This is problematic because the derivative isomers and rearrangement products for acrolein, crotonaldehyde, and acetaldehyde may have been present in ERI's samples, yet not quantified. These compounds' rearrangement products can elute at the same time as other carbonyls being assayed in this study. This would result in an underestimation of the concentrations of certain carbonyls and an overestimation of others. For this reason, adequate separation time and correct peak identification is needed to identify all the isomers and adducts so they may be distinguished from other compounds.

The acid-rearrangement products (other hydrazone products formed in the presence of acid) have been described to a limited extent in the literature with different explanations for the identity of these compounds. Early identification of interferences when using the DNPH method for sampling airborne aldehydes showed the formation of an acrolein rearrangement product, labeled acrolein-x (Tejada 1986). It was initially reported that as the acrolein-DNPH peak disappeared, the acrolein-x peak was formed (eluting after the acrolein peak). The sum of these peak areas remained the same over time. Similar behavior was indicated for crotonaldehyde (Shulte-Ladbeck *et al.* 2001). Others have also described this behavior for unsaturated aldehyde derivatization, identifying these rearrangement peaks as either syn-anti isomers or adducts formed in the presence of acid (Grosjean *et al*. 1999; Huynh *et al*. 2002; Karabatsos *et al*. 1963; Liu *et al*. 2001; Shulte-Ladbeck *et al*. 2001). In addition to the unsaturated aldehydes, acetaldehyde will display an extra chromatogram peak due to the isomerization of acetaldehyde-DNPH (Liu *et al*. 2001; Shulte-Ladbeck *et al*. 2001).

Studies of acid rearrangement product formation on silica gel determined that acrolein and crotonaldehyde form multiple hydrazones (Shulte-Ladbeck *et al*. 2001; Huynh *et al*. 2002, Grosjean *et al*. 2002). The initial peak is from the direct derivatization of these unsaturated aldehydes. The resulting chromatogram peak elutes at the same time as the standard and is identified accordingly. The additional peaks are the result of an adduct forming from the reaction of the aldehyde derivatives with excess 2,4-DNPH on the silica gel adsorbent. This results in chromatogram peaks appearing after

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[10] To properly quantify higher order carbonyls by this method, extra care must be taken. The analyses indicate that ERI may not have fully addressed this complexity in their peak reporting. However, given the very low levels of these compounds detected in the ambient air, this more detailed quantification would probably not have substantially changed the reported results.

the initial peak. It has been found that acrolein can react to form two adducts, commonly referred to as acrolein-x and acrolein-z, while crotonaldehyde forms one adduct referred to as crotonaldehyde-x. In addition to multiple hydrazone formation, isomerization of a hydrazone can result in multiple peaks. Under certain HPLC conditions, an additional acetaldehyde isomer peak is observed and has been referred to as acetaldehyde-x (Liu *et* al. 2001; Shulte-Ladbeck *et al*. 2001). When these rearrangement compounds have been recognized, the total carbonyl concentration is determined by summing the multiple peaks (Shulte-Ladbeck *et al*. 2001; Huynh *et al*. 2002; Grosjean *et al*. 2002).

In the carbonyl samples analyzed by ERI, the compounds of most concern are acrolein, crotonaldehyde, propionaldehyde, and butyraldehyde. If acrolein and crotonaldehyde rearrangement products were being formed, inability to quantify their peaks would result in underestimation of their concentrations. Furthermore, acrolein-x and crotonaldehyde-x elute at around the same time as propionaldehyde and butyraldehyde respectively. When this occurs, these compounds' concentrations would be overestimated. Despite having two peaks attributable to acetaldehyde, the isomers commonly elute together. This was the case for TASC samples, with a single peak integrated to represent total acetaldehyde concentration.

Overall, based on the interferences and issues surrounding carbonyl sampling, the methods utilized should give reliable determinations of formaldehyde, acetaldehyde, and acetone. However, as previous research has shown, the method employed here is not as reliable for acrolein and crotonaldehyde. If the analysis does not address the chemistry of these compounds after collection, the levels reported would underestimate true ambient concentrations. Moreover, if multiple peaks are occurring for these carbonyls, other compounds such as propionaldehyde or butyraldehyde concentrations would be over reported (see footnote 10).

2.2.2. Blanks

Two types of blanks were reported for quality assurance in the TASC carbonyl dataset. One field blank and one trip blank per sampling session accompanied the field samples to and from the laboratory. The field blanks were treated in the exact same manner as the field samples, but no air was drawn through the sampler. The trip blanks accompanied the field blanks but differ in that they did not leave their sealed foil pouch. The criteria for both types of blanks, defined by the acceptable background levels listed in TO-11a, were <0.15 μg formaldehyde per cartridge, <0.30 μg acetone per cartridge, and 0.10 μg acetaldehyde and other aldehydes per cartridge. This is equivalent to 0.31 ppbv (0.56 ug/m^3) acetaldehyde, 0.68 ppbv (0.84 ug/m^3) formaldehyde, and 0.70 ppbv (1.66 ug/m^3) acetone for a 180 L sample volume.

Field and trip blank samples were reviewed and showed that only four target compounds were detected with regularity. Acetone and acetaldehyde appeared in more than two-thirds of the blanks and formaldehyde was detected in about a third. The butyraldehyde/methylethyl ketone peak was seen in less than one fifth of the blank analyses. Blank concentrations were compared to the overall mean sample concentrations for the three most prevalent species (Table 2-1). This table demonstrates that the average blank concentrations were well below the ambient concentrations for all three compounds. Ambient formaldehyde values were over ten times greater than blanks, while acetaldehyde was only four times greater. These levels were deemed acceptable.[11]

Table 2-1 Description of Field and Trip Blank Data.

Compound	*Average Sample Concentration (μg/m^3)*	*Average FB Concentration (μg/m^3)*	*Average TB Concentration (μg/m^3)*	*Percent of Sample on FB (%)*	*Percent of Sample on TB (%)*
Acetone	3.11	0.51	0.54	16	17
Acetaldehyde	1.23	0.28	0.25	23	20
Formaldehyde	1.51	0.12	0.12	8	8

2.2.3. Precision

Collocated carbonyl samples were collected throughout the program. The extra collector was rotated throughout the different sites, spending three or four months at any individual location before moving to the next. This allowed for precision measurements at all sites without the requirement that each site have dual collection systems. The composite results for acetone, acetaldehyde and formaldehyde are plotted in Figure 2-2, Figure 2-3 and Figure 2-4, respectively, and summarized in Table 2-2. Excellent agreement is seen between the primary and secondary concentration calculations for all compounds. The best fit linear regression slopes are all nearly one.

Table 2-2: Precision of Collocated Carbonyl Samplers

Carbonyl	*Average RPD (%)*	*Number of Collocated Sets*	*Median RPD (%)*
Formaldehyde	17.13	151	10.95
Acetaldehyde	14.14	147	8.30
Acetone	18.65	152	8.46

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[11] For the TASC data analysis, the practice of blank subtraction was not used since the analyses herein seek to define an upper bound to ambient air toxics data. For this same reason, when making data substitutions for below detection samples, the full minimum detection limit was used, rather than half the detection limit, as is more commonly employed.

Figure 2-2: Scatterplot of Primary and Secondary Collocated Samples

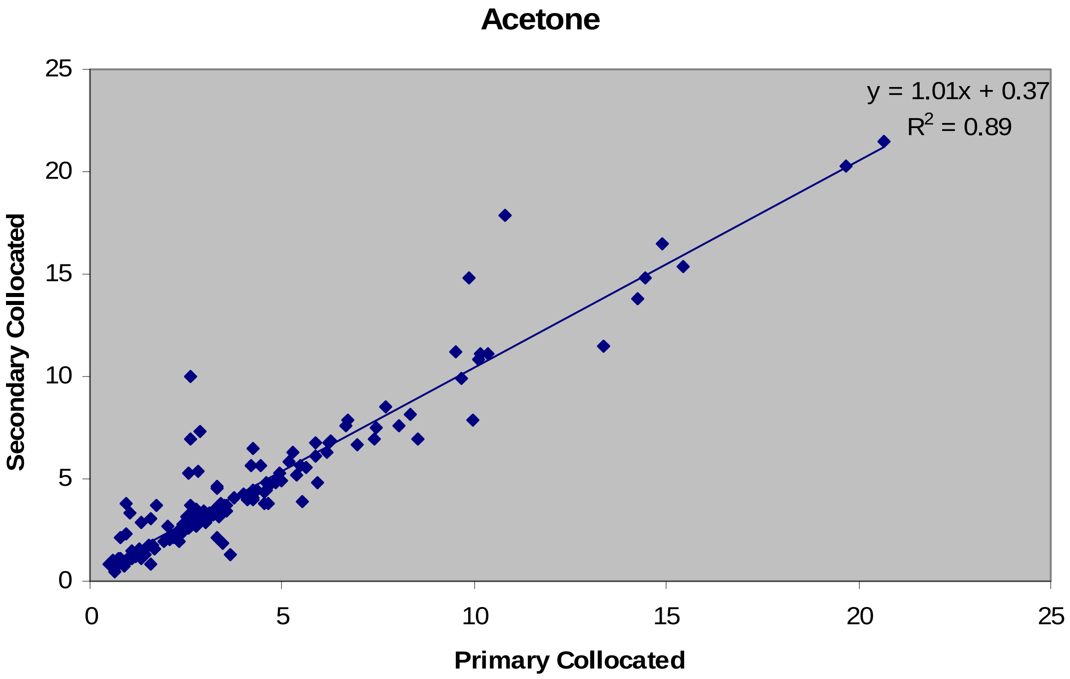


Figure 2-3: Scatterplot of Primary and Secondary Collocated Samples

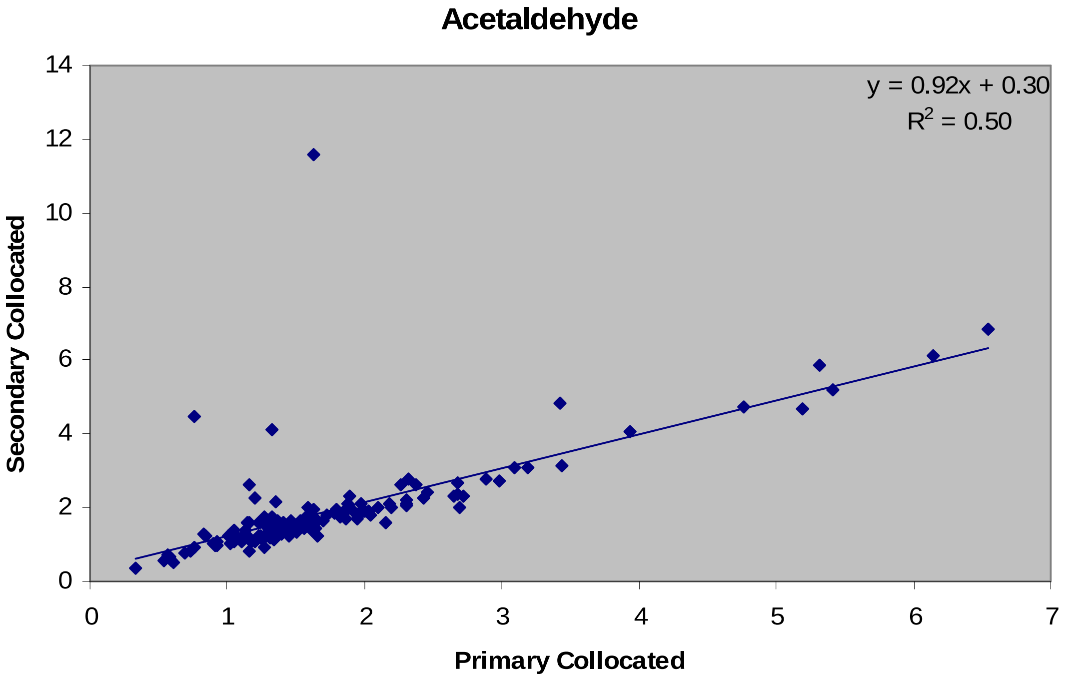
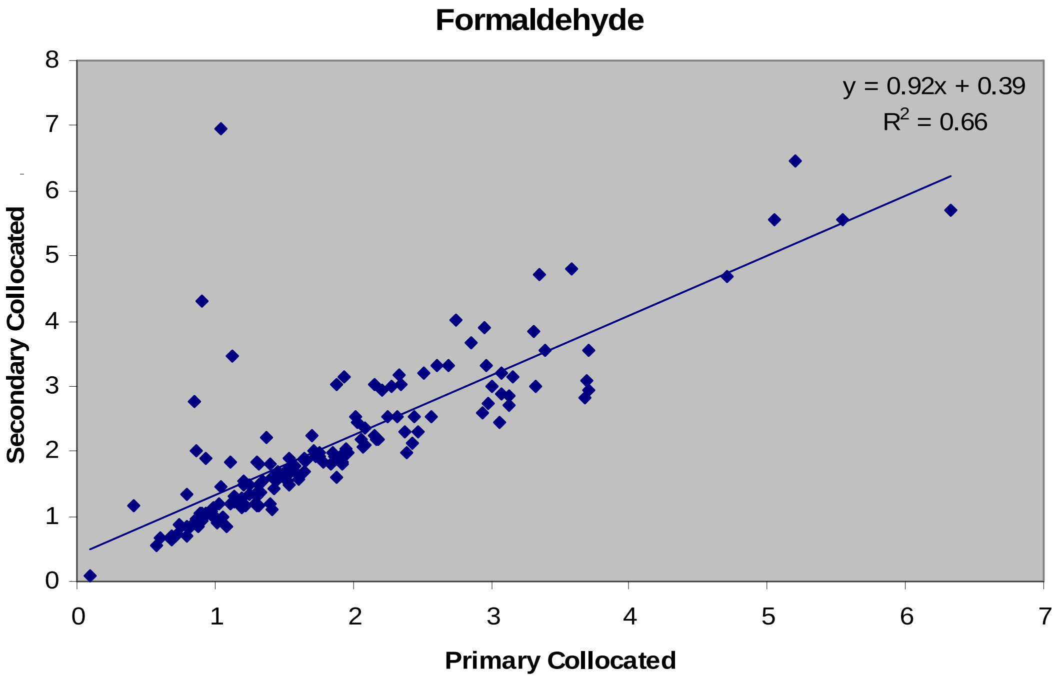


Figure 2-4: Scatterplot of Primary and Secondary Collocated Samples



2.2.4. Detection Limits

The percentage of ambient samples with non-detects for carbonyls across the entire network are summarized in Table 2-3. As can be seen in the table, only acetaldehyde, formaldehyde and acetone are detected in most samples. This implies the reliability discussion due to interferences for compound identification detailed in Section 2.2.1 does not play a significant role in TASC due to the very low levels collected.

The CT DPH has proposed annual HLVs for five carbonyl compounds. These levels are tabulated in

Table 2-4, and are compared to the reported MDLs. Based on this table, one can conclude that the methods employed in TASC are sufficiently sensitive to evaluate acetaldehyde, acetone and methyl ethyl ketone (although this last compound is subject to coelution with butyraldehyde, nonetheless, the low MDL to HLV ratio permits evaluation). The formaldehyde ratio is one-third. Since the precision for this compound is good, comparison of monitored results to the proposed HLV may still be valid, although better resolution would be preferable. The potency of acrolein combined with the identified detection issues/MDL indicates improvements are needed before reliable health assessment can be attained for this compound.

Table 2-3: Percent of Samples Below the Detection Limit for Carbonyls

Carbonyl	*Percent of Samples Below the Detection Limit (%)*
Acetaldehyde	4
Acetone	3
Formaldehyde	1
Propionaldehyde	55
Butyraldehyde/MEK	33
2,5-dimethyl benzaldehyde	94
Benzaldehyde	90
Hexaldehyde	88
m-tolualdehyde	66
o-tolualdehyde	96
p-tolualdehyde	90
Valeraldehyde	93
Acrolein	97
Crotonaldehyde	97

Table 2-4: Comparison of the MDL to the Connecticut Proposed Annual HLV

Carbonyl	*Minimum Detection Limit ($\mu g/m^3$)*	*Proposed Annual HLV ($\mu g/m^3$)*	*Ratio of MDL to HLV (%)*
Acetaldehyde	0.31	2.70	12.0
Acetone	0.53	175.00	0.3
Formaldehyde	0.20	0.45	34.0
Butyraldehyde/MEK	0.51	500.00	0.1
Acrolein	0.24	0.01	2358.0

2.2.5. Summary

Based on ERI's methods for sampling carbonyls at the TASC sites, one can conclude that the method will give reliable estimates for formaldehyde, acetaldehyde, and acetone. Recognized interferences to formaldehyde sampling have been addressed in the SOP and method TO-11a has been determined by the EPA and other organizations as an acceptable method for determining environmental levels. Moreover, this compound is generally found in the highest concentration of all carbonyls and above the detection limit of the method (found above the detection limit in 98.9% of the TASC samples).

Due to the issues outlined previously, there is some uncertainty whether this method is adequate for acrolein, crotonaldehyde, propionaldehyde, and butyraldehyde. It should be noted that greater than 97% of the carbonyl samples showed acrolein and crotonaldehyde levels below the detection limit. This may be due to the issue of multiple hydrazone formation, leading to an underestimation of concentration, or simply due to the low levels of the compounds in the environment. Levels of butyraldehyde and propionaldehyde were below the detection limit in 33% and 55% of samples, respectively for the entire dataset (40% and 72% after the sampling flow rate was decreased). Coelution of acrolein and crotonaldehyde derivative adducts could have led to overestimation of these concentrations.

For the remaining carbonyls, detection occurred in less than 15% of the samples (except for m-tolualdehyde which was detected in 34% of the samples). Therefore, this method of sampling may be inadequate for these carbonyls due to the low levels of these compounds in the environment. Future sampling may explore longer sampling times, improved sampling techniques or different analytical approaches to lower the detection limit.

2.3. Analysis of Monitored Concentrations

2.3.1. TASC Monitored Concentrations

Table 2-5 lists PAMS and TASC network site location characteristics, measurement time periods, and the duration and frequency of carbonyl monitor sampling. The PAMS network sites sampled every three hours, once every three days during summer months, throughout the entire measurement period. The sites started operating between 1994 and 1999 and data analyses in this report extend to August 2002. East Hartford remains the only PAMS site collecting carbonyl samples during the summertime. The current schedule has dropped to four 3-hour samples every third day beginning at 6 AM local time. The TASC network sites sampled once per day every six days throughout the measurement period. Sampling was initiated at two sites in March 1999 and the final site became operational in May 2000. TASC measurements were concluded in March 2003.

Monitoring data for Connecticut were analyzed from the TASC and PAMS networks to better understand the distribution of concentrations of acetaldehyde and formaldehyde. Figure 2-5 shows mean annual concentrations with 95% CIs (confidence intervals) for both compounds for the seven TASC sites. Note that these calculations are based on the entire period of record, which may be different for different sites (Table 2-5)[12]. Year to year acetaldehyde levels indicate there may be a slight upward trend in acetaldehyde levels across the state (not pictured). The highest acetaldehyde values were found at Hartford. Levels found at Groton, Wallingford and Waterbury were slightly lower, but similar to each other. Manchester showed lower levels still with the atmospheric concentrations at Voluntown the least.

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[12] Reported TASC monitored values represent the sum of both front and rear sample tubes.

Table 2-5 Selected characteristics of PAMS and TASC monitoring networks

Network	Site name/town	County	Latitude	Longitude	Start date	End date	Sample duration	Collection frequency
PAMS	Sherwood Island (Westport)	Fairfield	41.1188	73.3369	6/96	6/97	3-hr	every third day (8x's per day)
PAMS	East Hartford	Hartford	41.7844	72.6297	6/94	---	3-hr	every third day (8x's per day)
PAMS	Hamden	New Haven	41.3411	72.9213	6/99	8/02	3-hr	every third day (8x's per day)
TASC	Bridgeport	Fairfield	41.1604	73.2056	6/99	7/02	24-hr	once every six days
TASC	Groton	New London	41.3357	72.0755	3/99	7/02	24-hr	once every six days
TASC	Hartford	Hartford	41.7462	72.648	3/99	7/02	24-hr	once every six days
TASC	Manchester	Hartford	41.7728	72.5608	8/99	7/02	24-hr	once every six days
TASC	Wallingford	New Haven	41.4301	72.8361	10/99	7/02	24-hr	once every six days
TASC	Waterbury	New Haven	41.5229	73.0406	5/00	7/02	24-hr	once every six days
TASC	Voluntown	New London	41.5886	71.8564	5/99	7/02	24-hr	once every six days

For formaldehyde, ambient levels at Wallingford were higher relative to all other Connecticut sites (average annual levels about 3.8 $\mu g/m^3$). Bridgeport, Waterbury, Hartford and Groton had the next highest levels for formaldehyde. The two remaining sites located east of the Connecticut River, Manchester and Voluntown, reported the lowest levels. To place the TASC results in a broader context, Suh *et al*. (2000) report the typical urban range for ambient formaldehyde in the United States as 13.5 to 24.6 $\mu g/m^3$. These results are well above the monitored levels for this study. An EPA sponsored white paper on air toxics data (Hafner *et al.*, 2004) shows urban ranges of formaldehyde of the same order as those monitored here.

In addition to recording the highest formaldehyde levels over the period of record, Wallingford was also the only site to show marked declines in formaldehyde levels from the early years (4.3 $\mu g/m^3$) to the later years (3.3 $\mu g/m^3$)[13]. This observation is consistent with reported process changes at the nearby Title V facility, which resulted in decreased emissions of formaldehyde and its precursors. Despite these measured decreases, formaldehyde concentrations at Wallingford remained the highest of the seven sites in the latter period.

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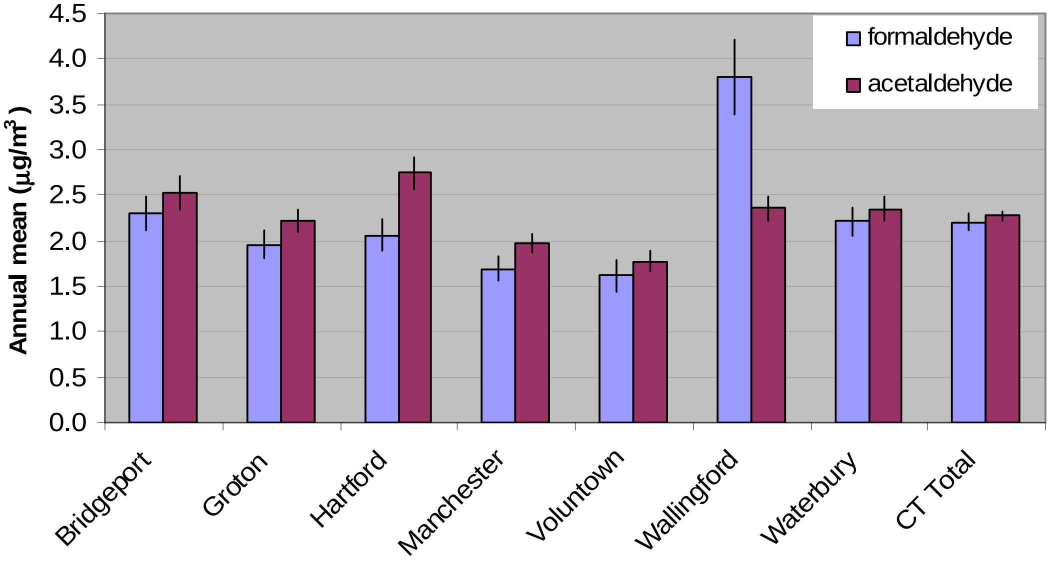
[13] The early years are data through July 2001 while the later years are data from July 2001 to the end of the program in 2003. Summer, fall and winter months had similar number of samples for both periods while spring had fewer for the latter period. Seasonal differences of formaldehyde levels show spring as lower relative to other seasons. But since more spring days were in the early period, and this early period had statistically higher levels at the Wallingford site, it is clear the seasonality difference was overwhelmed by other factors.

TASC site mean concentrations for formaldehyde and acetaldehyde are plotted by season[14] in Figure 2-6 and Figure 2-7, respectively. Averaged over all sites (CT average line in the graphs), concentrations of both compounds were highest during summer. Site specific formaldehyde levels were highest during summer at each site except Wallingford, which had similarly high levels in fall. Fall levels at other sites were lower than summer, with site specific and statewide average lowest levels seen during the winter and spring periods. Site specific acetaldehyde levels were similar to the statewide average behavior. Winter and fall levels were similar, but lower than summer levels for acetaldehyde. The lowest levels were recorded in the spring months.

Figure 2-5: TASC site mean annual concentration of acetaldehyde and formaldehyde (95% CI)



The observed summertime maxima of carbonyls are expected given the role photochemistry plays in atmospheric process of VOCs. Atmospheric oxidation of VOCs serves as a secondary source of carbonyls. Figure 2-8 and Figure 2-9 display seasonal mean annual and 95th percentile CI concentrations for formaldehyde and acetaldehyde, which as discussed suggest a distinct seasonal trend for both compounds. Table 2-6 provides the number of valid measurements by compound for the TASC monitoring network and indicates a fairly balanced distribution of samples across sites and seasons.

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[14] The seasons are defined as Winter (December, January, February); Spring (March, April, May); Summer (June, July, August); and Fall (September, October, November).

Figure 2-6: TASC site seasonal mean concentration of formaldehyde

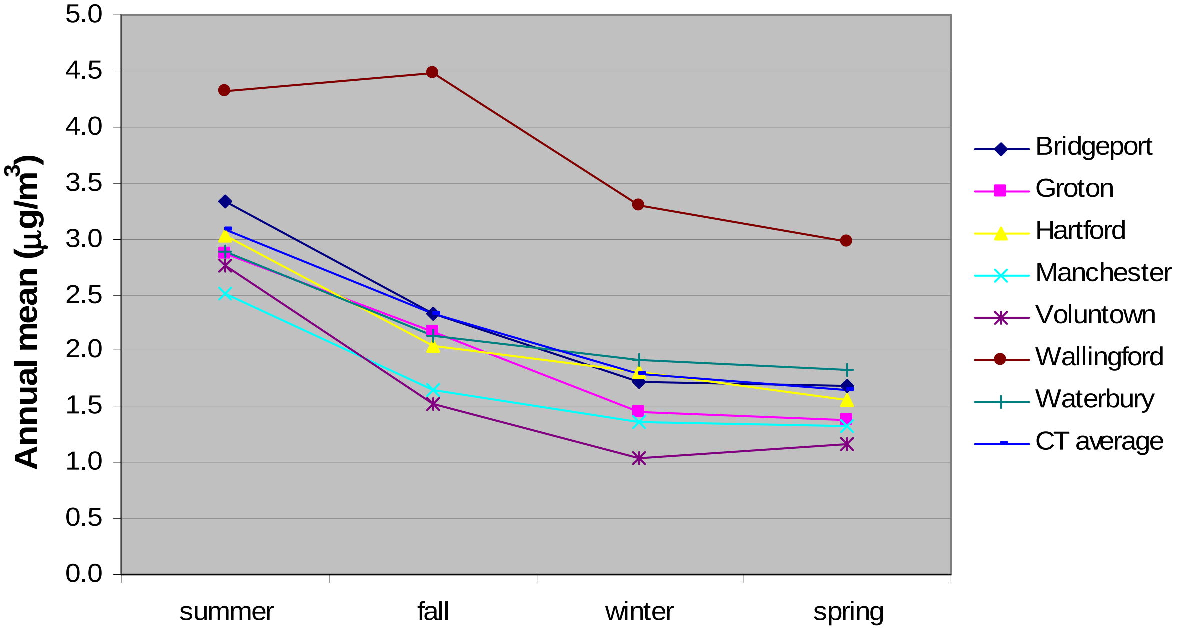


Figure 2-7: TASC site seasonal mean concentration of acetaldehyde

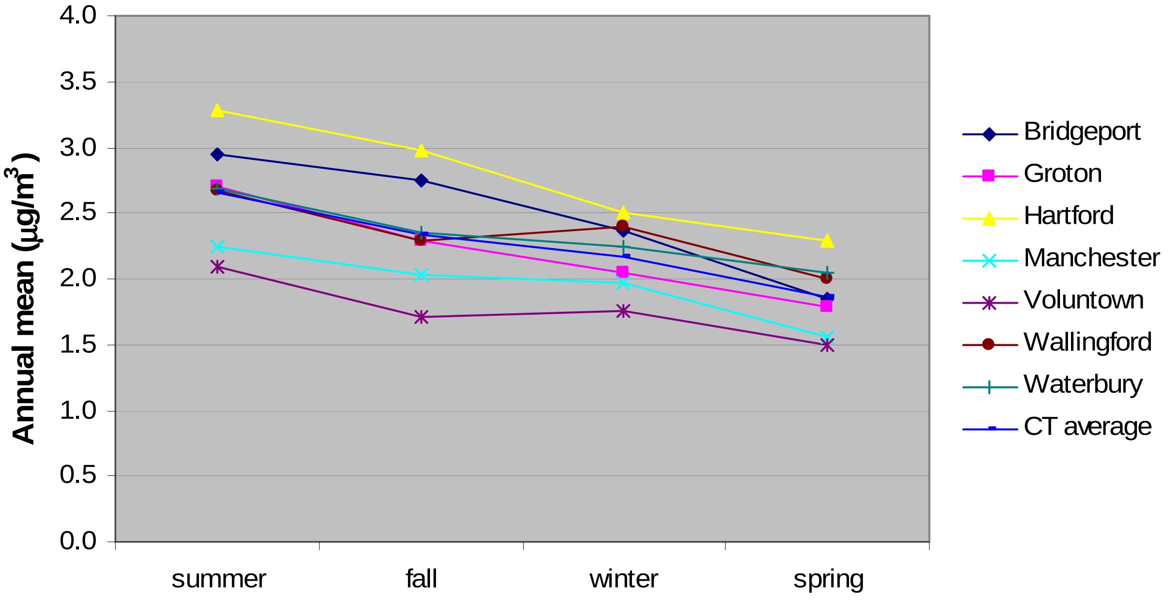


Figure 2-8: TASC site seasonal mean annual and 95th percentile CI concentration of formaldehyde

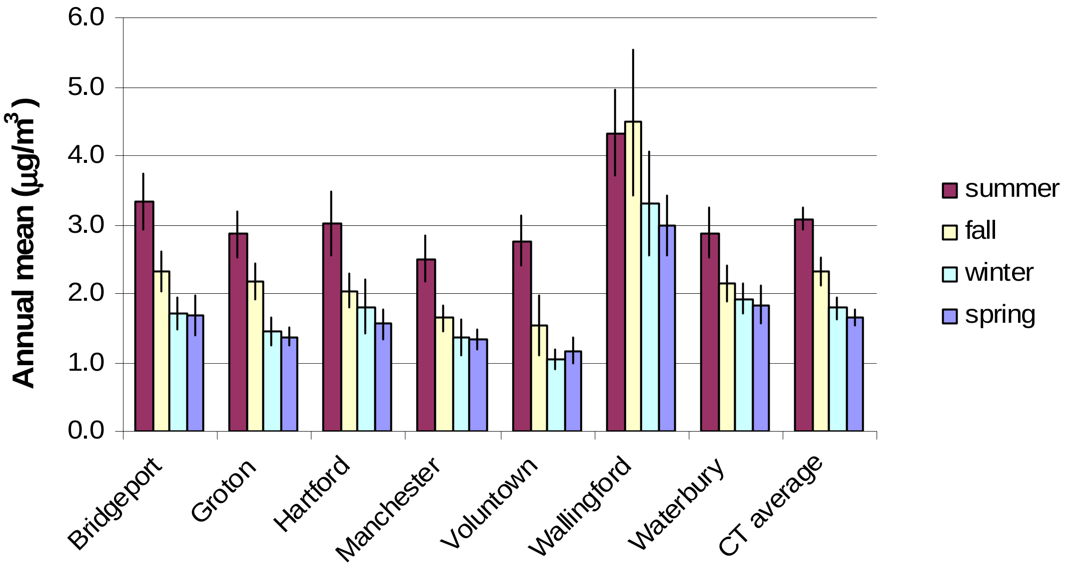


Figure 2-9: TASC site seasonal mean annual and 95th percentile CI concentration of acetaldehyde

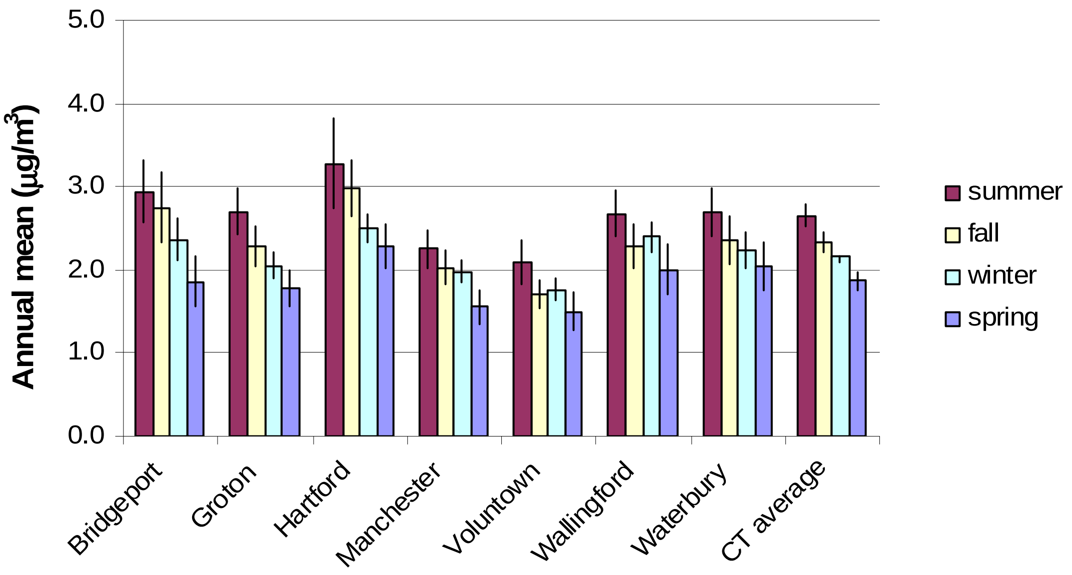


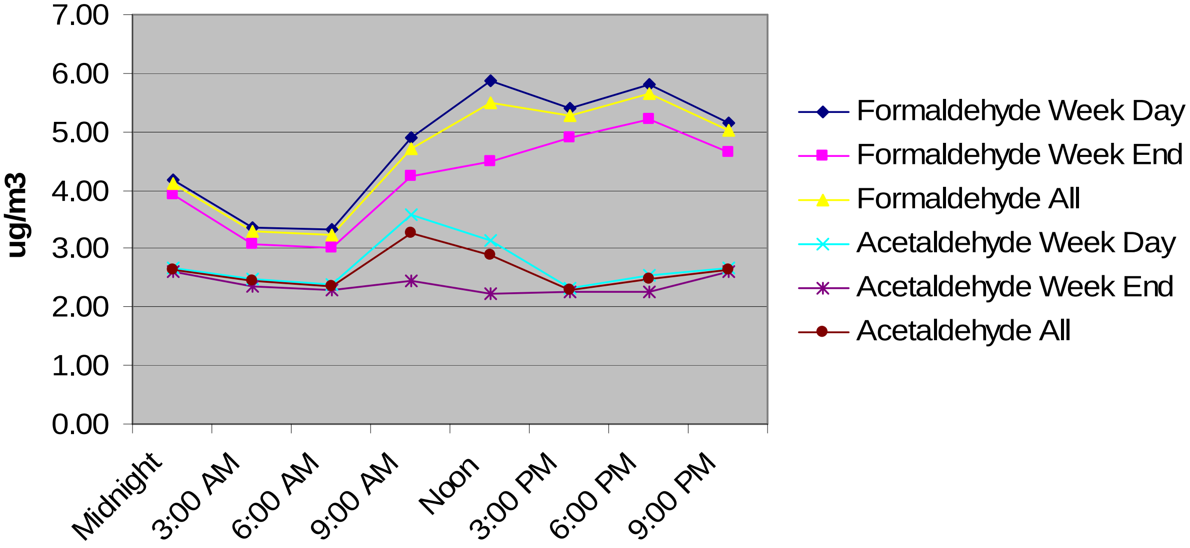
Table 2-6: Number of valid measurements, TASC monitoring network

		Fall	Spring	Summer	Winter	Annual
Bridgeport	Acetaldehyde	52	36	52	49	189
	Formaldehyde	52	40	52	52	196
Groton	Acetaldehyde	50	49	53	51	203
	Formaldehyde	50	53	53	53	209
Hartford	Acetaldehyde	54	53	43	46	196
	Formaldehyde	54	57	43	48	202
Manchester	Acetaldehyde	54	39	45	55	193
	Formaldehyde	54	43	45	57	199
Voluntown	Acetaldehyde	55	42	51	53	201
	Formaldehyde	55	47	49	54	205
Wallingford	Acetaldehyde	52	33	40	51	176
	Formaldehyde	51	37	40	53	181
Waterbury	Acetaldehyde	40	31	41	44	156
	Formaldehyde	39	31	41	44	155
State Total	Acetaldehyde	357	283	325	349	1314
	Formaldehyde	355	308	323	361	1347

2.3.2. PAMS Monitoring Concentrations

PAMS monitoring network 3-hour summertime concentrations (1994 to 2002) are plotted in Figure 2-10.[15] Formaldehyde levels are higher than acetaldehyde levels for all time intervals. Weekend levels are lower than weekdays for both compounds. Formaldehyde weekday values increase throughout the day, peaking in early afternoon. Weekend values track somewhat closely to weekday values. Acetaldehyde weekday values peak during mid-morning. Weekend values are stable throughout the day.

Figure 2-10: PAMS site diurnal 3-hour average summertime concentrations of acetaldehyde and formaldehyde



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[15] At the East Hartford PAMS site, no data were available for 1996. Acetaldehyde data are missing for all sites in 2002. Not all years include midnight, 3 AM, 6 PM, and 9 PM values.

The differences between weekend and weekday behavior is likely driven by mobile source emission differences. The more pronounced diurnal variation of formaldehyde is indicative of the substantial secondary atmospheric formation processes in the atmosphere. These short-term measurements provide more detailed information about the atmospheric behavior of the aldehydes relative to the TASC program.

2.3.3. Comparison of Monitored Data to CT DPH proposed HLVs

A comparison of Connecticut proposed HLVs to monitoring data from the seven Title V related TASC sites indicates that current carbonyl concentrations are either higher than or near the proposed annual formaldehyde and acetaldehyde HLVs, respectively. This could have implications on the public health risk associated with air toxics exposures from stationary and mobile sources at both short- and long-term time scales. Figure 2-11 shows seasonal mean formaldehyde concentrations ranging from about 1.0 $\mu g/m^3$ to 4.6 $\mu g/m^3$, well above CT DPH's proposed 0.45 $\mu g/m^3$ annual HLV. Figure 2-12 shows seasonal mean acetaldehyde concentrations ranging from about 1.5 $\mu g/m^3$ to 3.3 $\mu g/m^3$, with CT DPH's proposed 2.7 $\mu g/m^3$ annual HLV falling in the middle of that range. As has been noted previously, the ambient monitored levels in Connecticut are still below reported levels in some other urban areas in the United States and far below concentrations reported for indoor environments.

Figure 2-11: TASC site seasonal mean formaldehyde concentrations compared to CT Proposed HLV

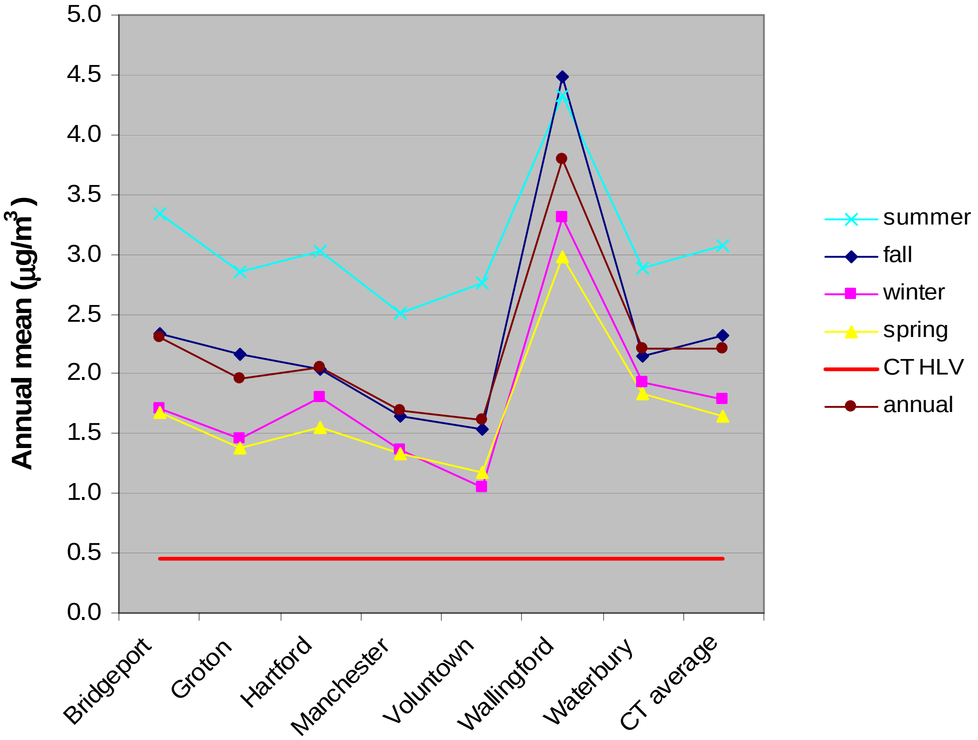
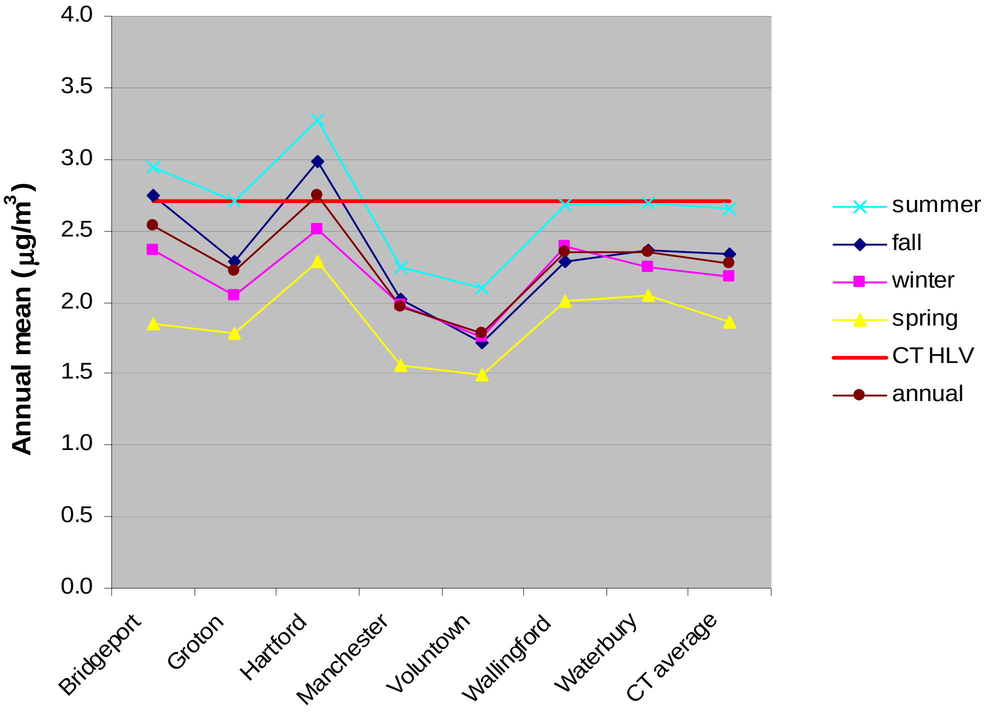


Figure 2-12: TASC site seasonal mean acetaldehyde concentrations compared to CT Proposed HLV



The above data show that long-term carbonyl concentrations are greater than Connecticut's proposed HLVs for formaldehyde and similar to the proposed HLV for acetaldehyde, which indicates these species are candidates for continued evaluation. Acetone levels were far below the proposed HLV for that compound. While the annual concentrations in this assessment do not represent short-term peak concentrations, it might be important to consider the relationship between short-term peak concentrations and longer-term average concentrations. It is possible that longer integration times would deemphasize the importance of temporal variations. To help understand the influence of sample collection time intervals, hourly samples could be collected. The hourly measurements could then be summed over various time periods to provide further insight into the temporal resolution needed to capture short-term peak concentrations. In Spicer *et al.'s* study of air toxics in an urban area (Columbus, Ohio), spatial variability, temporal variability, and inherent measurement variability were compared to determine which element explained the most variability. It was found that the major contribution to HAPs variability was the temporal component. When evaluated using data with 3-hour time resolution, the temporal component contributed over 50% of the total variability for 19 of 38 frequently detected compounds. In contrast, the spatial component contributed less than 20% of the variance for all species except sulfur (Spicer *et al.* 1996).

3. POLYCYCLIC AROMATIC HYDROCARBONS

3.1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of compounds released to the air mainly through combustion of organic substances. These compounds were one of the first atmospheric pollutants to be identified as suspected carcinogens (Harrison *et al*., 1996). This class of compounds, composed of fused benzenoid rings, contains several carcinogenic and mutagenic species of environmental concern. Within this group, compounds vary from volatile to semivolatile, existing in the environment in the vapor state or adsorbed to particles. There are over 100 different PAHs and they generally occur as parts of complex mixtures, not as simple compounds.

The largest attributable source of PAHs in the atmosphere is motor vehicle exhaust, which accounts for about one-third of total PAH emissions in the United States (Marr *et al*., 1999). The primary source of PAHs from motor vehicles is from incomplete combustion of fuel. The remaining PAHs in the atmosphere are released from a variety of other combustion activities. Other sources of PAHs include combustion of coal, oil, gas, and wood. Industry, power generation, and residential heating are the largest contributors of atmospheric PAHs after mobile sources. Natural sources of PAHs include forest fires and volcanic activity while major sources of indoor PAHs include cigarette smoking, cooking, and home heating (Ohura *et al*. 2004).

The toxicity of these compounds varies depending on the PAH being examined. Animal experiments have shown that carcinogenic activity of PAHs is associated mainly with compounds composed of four or more aromatic rings. Moreover, the manner in which the rings are fused can be an indicator of toxicity, with those compounds containing bay or fjord regions generally falling in the mutagenic class (Bostrom *et al*. 2002).

Of the PAHs sampled in the TASC network, six have been classified as probable human carcinogens by the EPA Integrated Risk Information System (IRIS): benzo(a)anthracene, chrysene, benzo(b+j+k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, and dibenzo(ac+ah)anthracene. These compounds have been classified as group B2 probable human carcinogens due to sufficient evidence of carcinogenicity in animals but insufficient data linking them to specific human cancers. These PAHs have been linked to human cancers in mixtures of compounds.

The most carcinogenic PAH in the group examined in this study is benzo(a)pyrene. It has been found to cause respiratory tract tumors in hamsters after exposure by inhalation. In addition, it has been found to cause lung cancer after intratracheal installation as well as cause contact site tumors from oral and dermal exposure (IRIS Profile 1994). The CT DPH has proposed an annual HLV of 0.005 ug/m^3 for benzo(a)pyrene based on the unit risk level developed by California EPA. This level was set at the 1 in 100,000 cancer risk level based on 30 years of exposure. An additional 2-fold extrapolation was applied to account for increased inhalation exposure in children as well as a 2-fold extrapolation to account for increased genotoxicant susceptibility in children.

Hazard limit values for the remaining five carcinogenic PAHs were set based on their potency relative to benzo(a)pyrene. Their carcinogenicity has been established in similar ways as benzo(a)pyrene, all showing mutagenic effects in animals but insufficient studies linking them to specific human cancers. The actual proposed HLVs for these compounds can be found in the next section.

The annual HLV for the non-carcinogenic PAHs (acenaphthene, acenaphthylene, anthracene, benzo(e)pyrene, benzo(ghi)perylene, fluorene, fluoranthene, phenanthrene, and pyrene) was proposed to be 15 $\mu g/m^3$ to correspond to EPA's National Ambient Air Quality Standard (NAAQS) for $PM_{2.5}$. These compounds have been classified by IRIS as Group D, not classifiable as human carcinogens; no data are available to discern a carcinogenic effect based on exposure through inhalation (IRIS Profiles). The CT DPH attempted to extrapolate inhalation risk levels from the oral reference doses developed by IRIS but found them to be higher than the NAAQS $PM_{2.5}$ standard, even when a 2-fold children's extrapolation was taken into account. Since PAHs tend to exist in particle form in ambient air, CT DPH determined that this level would yield adequate protection.

3.2. Description of PAH Sampling and Analysis

The method employed by the ERI for the determination of PAHs in ambient air followed a slightly modified version of EPA test method TO-13a. The method allowed for the quantification of 19 PAHs: acenaphthene, acenaphthylene, anthracene, acenaphthene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, Benzo(e)pyrene, benzo(g,h,i)perylene, chrysene, dibenzo(a,c)anthracene, dibenzo(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene, and pyrene. Benzo(b)fluoranthene, benzo(j)fluoranthene, and benzo(k)fluoranthene were reported as a combined species called benzo(b+j+k)fluoranthene. Similarly, dibenzo(a,c)anthracene and dibenzo(a,h)anthracene were reported as a combined species called dibenzo(a,c+a,h)anthracene.

PAHs were sampled by drawing ambient air through a filter and an adsorbent cartridge using a calibrated General Metal Works Sampler. Due to the volatility of certain PAHs, both a filter and adsorbent cartridge were needed to collect all ambient PAHs. At equilibrium under ambient temperature, the two ring naphthalene exists almost entirely in the vapor phase while PAHs containing five rings or more are almost completely adsorbed onto particles. Intermediate three and four ring PAHs are distributed between the two phases (Zielinska *et al*. 2004).

The filter served to collect particle bound PAHs, while a cartridge containing XAD-2 and PUF collected the volatile PAHs and the component that volatilized after collection. Each adsorbent type has shown different collection efficiencies and storage capabilities for different PAHs, each having its own strengths and weaknesses (EPA Method TO13A). PUF is considered the best method for most PAHs, and therefore EPA Method TO13a recommends this as the primary sorbent. However, naphthalene, acenapthylene, and acenapthene possess relatively high vapor pressures and show poor collection efficiencies on PUF (35% for naphthalene). These smaller compounds are more efficiently collected on an XAD-2 cartridge and therefore both sorbents were used in this sampling process.

TASC sites in Connecticut were sampled for PAHs once a week between mid-1999 and beginning of 2003. During the first two years, the sampling time was seven days while in the last two years samples covered one 24-hour period every sixth day. ERI was able to decrease the sampling time while maintaining detection frequency due to a change in detection technique that lowered the detection limit of the instrument[16].

After ambient air sampling, the filter and sorbent were both extracted in the laboratory by Soxhlet extraction. The samplers were placed in the Soxhlet apparatus and a surrogate standard was added to the extraction solvent. This surrogate standard (P-terphenyl-d14) was used to assess any sample processing errors or matrix effects. The surrogate recovery was evaluated for acceptance by determining whether concentrations fell within the set criteria. The solvent used to extract the cartridges and filters was acetone in hexane (1:1, v/v, 500ml). The total time of extraction of the XAD-2, PUF, and filters was 16 hours.

After extraction, the sample was dried by passing it through a glass funnel containing anhydrous sodium sulfate. The sample was then transferred to a Kuderna-Danish concentrator. The extractor flask and the drying agent (sodium sulfate) were then washed with hexane and added to the concentrator flask. The K-D flask was then placed in a hot water bath and the solvent was allowed to evaporate from the flask, concentrating the sample. When ~5 ml of solvent was left, a dry stream of nitrogen was passed over the solvent, evaporating the sample down to 1 ml.

Following this step, cleanup by solid phase extraction using silica gel was performed by passing the extracts through conditioned Water's silica-gel cartridges. After this step, the samples were evaporated to 1ml using dry nitrogen and then spiked with an internal standard and sent for PAH analysis. Samples were analyzed for the 19 PAHs using an electron impact gas chromatograph/mass spectrometry (EI GC/MS) in the scan or selected ion monitoring mode.

3.2.1. Interferences

The main method interference is caused by contaminants in reagents, glassware, or other components of the analysis procedure. Due to this, reagents are regularly analyzed as laboratory blanks to ensure purity. Furthermore, glassware is cleaned with reagent water and rinsed with acetone and hexane prior to use. Possible matrix interferences can also occur when contaminants are coextracted from the sample.

In addition to laboratory introduced interferences, sample degradation has been shown to occur if samples are exposed to heat, ozone, NO_2, or ultraviolet light. It is therefore recommended that proper steps are taken to minimize exposure to these factors, including sample transport in dry ice and use of incandescent or UV-shielded lights during analysis (EPA-TO13a).

3.2.2. Blanks

Several types of blanks were used in this analysis for quality assurance. A reagent solvent blank was run before processing any of the samples to demonstrate no

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[16] MS Analysis was switched to Select Ion Mode (SIM) from Scan mode. This effectively increases detection of the specific ions by increasing dwell time for select ions while foregoing detection of others.

interferences from the reagents, analytical system, and glassware were present. For each analytical batch the SOP called for a reagent blank and a surrogate sample to be analyzed. These samples were used to assess any interference throughout all stages of the sample preparation and measurement process. In addition, a laboratory method blank and a preparation solvent blank were used to determine whether quality assurance criteria were met. The laboratory method blank consisted of a sampling cartridge (filter, PUF, XAD-2) from each batch being extracted and analyzed in the same way as the samples, without being shipped to the field. Acceptance criteria were less that 5.0 ug of naphthalene and less than 2.0 ug of the sum of all other PAHs. The preparation solvent blank consisted of a solvent sample that had been put through the entire procedure with no cartridge present. Acceptance criteria for the preparation solvent blank were less that 0.5 ug of naphthalene and less than 0.2 ug of the sum of all other PAHs.

To assess background levels in the sampling process, trip blanks and field blanks were processed and analyzed along with the field samples. The field blanks were treated in the exact same manner as the field samples, but no air was drawn through the sampler. Field blanks were used to monitor possible contamination resulting from the handling of samples collected in the field. The trip blanks accompanied the field blanks but differ in that they did not leave their sealed pouch. Trip blanks monitor possible contamination during the transportation of sampling media. Blanks data for PAH samples were examined for all the sites except Hartford[17]. The available blanks data were for Bridgeport (11/02-2/03), Groton (11/01-11/02), Manchester (7/01-2/03), Voluntown (7/01-2/03), Wallingford (12/01-1/03), and Waterbury (7/02-10/02).

An analysis of the field and trip blank samples demonstrated that the majority of the PAHs studied were detected in fewer than 50% of the samples. Four PAHs, naphthalene, pyrene, fluoranthene, and phenanthrene, were detected most frequently in the blank samples. Naphthalene was above the detection limit in 71% of the field blank samples and 72% of the trip blank samples. The concentration reported from trip and field blank samples were 15% of the naphthalene concentration reported by the ambient samples on similar days. Fluoranthene and phenanthrene (detected in 81% and 91% of blanks, respectively) showed a similar ratio of blank concentration to ambient concentration, about 8%. Pyrene was at levels above the detection limit in 49% of the trip blank samples and 64% of the field blank samples. Pyrene showed slightly higher levels on the blanks relative to the sample concentration on similar days (28% for field blank and 11% for trip blank) (Table 3-1).

Table 3-1: Description of Field and Trip Blank Data.

Compound	*Average FB Concentration (ug/m3)*	*Average Sample Concentration on FB Days (ug/m3)*	*Average TB Concentration (ug/m3)*	*Average Sample Concentration on TB Days (ug/m3)*	*Percent of Sample on FB (%)*	*Percent of Sample on TB (%)*
Naphthalene	0.0037	0.0246	0.0036	0.0242	15.1	15.0
Phenanthrene	0.0009	0.0088	0.0008	0.0090	9.8	8.4
Fluoranthene	0.0004	0.0024	0.0003	0.0037	19.1	8.0
Pyrene	0.0004	0.0014	0.0003	0.0022	28.0	11.5

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[17] Results from Hartford blank samples after July 2001 were not available in the database. Also, the available database did not include blank samples for any site taken and analyzed prior to July 2001.

3.2.3. Precision

Collocated sampler data were analyzed for three sites, Bridgeport, Groton and Voluntown, to assess sampling precision. These samplers were run together from 7/2002 to 2/2003 in Bridgeport, 7/2001 to 10/2001 in Groton, and from 11/2001 to 7/2002 in Voluntown. Precision, determined by the average relative percent difference between collocated samples, varied between 19% and 54%, depending on the compound being measured. The best precision was found for the larger, less volatile compounds (chrysene and benzo(a)anthracene) while the worst precision was found in the lighter, more volatile compounds (Naphthalene and acenaphthene). Table 3-2 shows the average and median percent differences in collocated samples for the PAHs measured at TASC sites.

Table 3-2: Precision of Collocated PAH Samplers.

PAH	*Average RPD (%)*	*Number of Collocated Sets*	*Median RPD (%)*
Naphthalene	54.8	80	36.0
Acenaphthylene	41.0	23	36.1
Acenaphthene	36.9	67	27.2
Fluorene	32.6	78	22.0
Phenanthrene	31.9	82	19.7
Anthracene	25.1	21	20.8
Fluoranthene	29.7	82	12.4
Pyrene	30.2	81	13.9
Benzo(a)anthracene	19.8	37	13.2
Chrysene	21.5	57	11.5
Benzo(b+j+k)fluoranthene	24.4	63	12.0
Benzo(e)pyrene	23.6	44	12.7
Benzo(a)pyrene	23.7	33	23.7
Indeno(1,2,3-cd)pyrene	24.8	35	16.8
Dibenz(a,c+a,h)anthracene	21.7	22	18.2
Benzo(g,h,i)perylene	25.6	48	14.9

3.2.4. Detection Limits

The method detection limit is the minimum concentration of a compound that can be reported with 95% confidence that the value is above zero. The number of samples above the detection limit varied slightly by the sampling site. However, a consistent set of PAHs were found above the detection limit across all sites. Table 3-3 shows the percent of all the samples taken from all the sites that showed levels below the detection limit. The data reveal that a wide range of detection occurs across different PAHs, attributed to the abundance of different PAHs in ambient air.

The issue of detection limits becomes a concern when the limit of detection is at or above the levels of health concern. Table 3-4 presents the method detection limits for the 15 PAHs that have HLVs proposed by CT DPH. Based on the comparison of the detection limit to the HLVs it is clear that the method employed by ERI was sufficient to detect levels of PAHs well below the levels of concern. This is especially true of the smaller PAHs, for which the proposed annual HLV is set at 15 μg/m^3.

Table 3-3: Percent of Samples Below the Detection Limit for PAHs.

PAH	*Percent of Samples Below the Detection Limit (%)*
Naphthalene	3
Acenaphthylene	53
Acenaphthene	6
Fluorene	2
Phenanthrene	1
Anthracene	66
Fluoranthene	2
Pyrene	1
Benzo(a)anthracene	40
Chrysene	16
Benzo(b+j+k)fluoranthene	11
Benzo(e)pyrene	30
Benzo(a)pyrene	51
Indeno(1,2,3-cd)pyrene	56
Dibenz(a,c+a,h)anthracene	65
Benzo(g,h,i)perylene	33

Table 3-4: Comparison of the Minimum Detection Limit to the Connecticut Proposed Annual HLV.

PAH	*Minimum Detection Limit (ug/m^3)*	*Proposed Annual HLV (ug/m^3)*	*Ratio of MDL to HLV (%)*
Acenaphthylene	0.000174	15	<0.1
Acenaphthene	0.000174	15	<0.1
Fluorene	0.000174	15	<0.1
Phenanthrene	0.000174	15	<0.1
Anthracene	0.000174	15	<0.1
Fluoranthene	0.000116	15	<0.1
Pyrene	0.000116	15	<0.1
Benzo(a)anthracene	0.000116	0.034	0.3
Chrysene	0.000117	1.14	<0.1
Benzo(b+j+k)fluoranthene	0.000117	0.03	0.4
Benzo(e)pyrene	0.000117	15	<0.1
Benzo(a)pyrene	0.000117	0.005	2.3
Indeno(1,2,3-cd)pyrene	0.000117	0.09	0.1
Dibenz(a,c+a,h)anthracene	0.000117	0.0045	2.6
Benzo(g,h,i)perylene	0.000117	15	<0.1

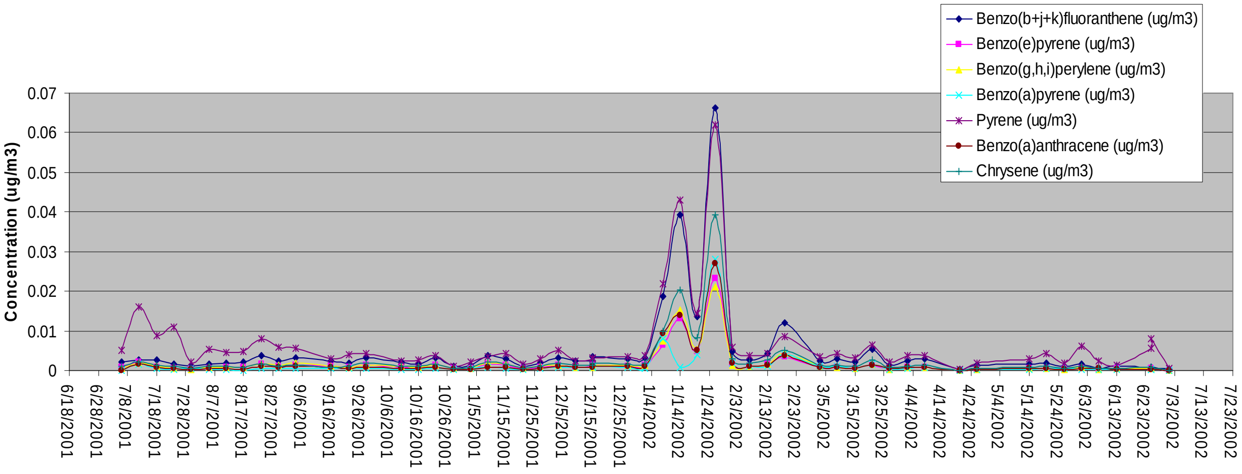
3.3. Analysis of Monitored Concentrations

3.3.1. Overall Connecticut Levels

The first step in analyzing TASC PAH data was to address the issue of samples below the detection limit. Since many of the PAHs were detected in roughly 35% to 65% of the samples, characterizing concentrations using only these samples would not accurately represent the ambient levels. Therefore, it was decided that the non-detect samples would be replaced with the value of the detection limit. All concentrations reported in this chapter will represent a theoretical maximum concentration, since it was assumed that all PAHs not detected were present at a concentration equal to the detection limit. This yields a conservative estimate of the ambient concentration[18].

The next step in summarizing PAH concentrations across Connecticut was to address a spike in PAH concentrations during January of 2002. ERI reported PAH concentrations for pyrene, benzo(a)anthracene, chrysene, benzo(b+j+k)fluoranthene, benzo(e)pyrene, benzo(g,h,i)perylene, and benzo(a)pyrene at daily levels 10 to 20 times higher for four sampling days that month (Figure 3-1). This caused increased average concentrations and variability in Groton as well as the seven-site, statewide average concentrations. Figure 3-1 shows the daily PAH concentrations for the third sampling year in Groton.

Figure 3-1: Daily PAH Concentrations in Groton During Third Sampling Year.



Since this spike in concentration was not seen in any other sites for any other time periods, it was assumed that an episode had occurred in Groton. These four days (1/8/2002, 1/14/2002, 1/20/2002, and 1/26/2002) were not included in the ambient level

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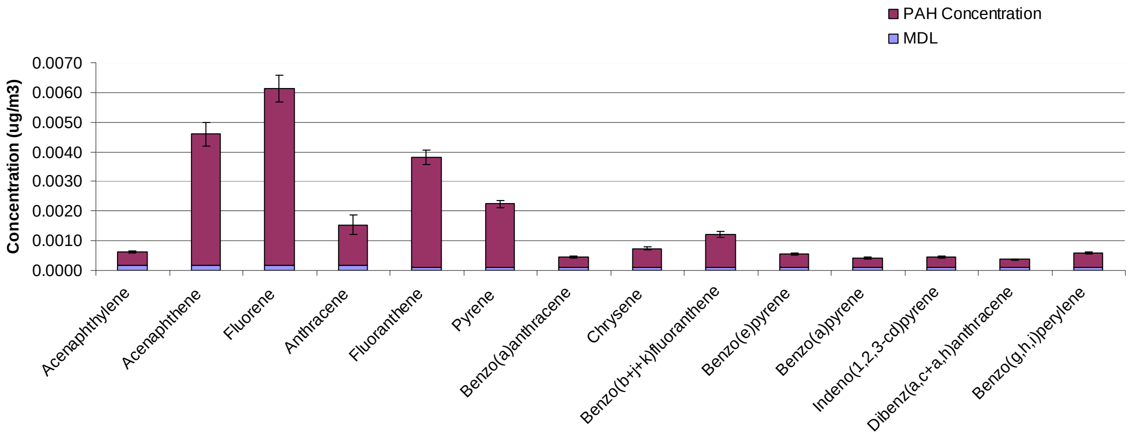
[18] Given that blank concentrations were generally well below (under 30%) levels observed in ambient samples and precision was of the order of 35% or lower, substitution of MDL for non-detect PAH samples provides a reasonable upper bound estimate.

characterization and trend analyses presented here. A limited investigation was conducted but did not provide an explanation for the source of these spikes. Construction or roadwork near the sampling site may have contributed to the observed, uncharacteristic levels. Regardless, the monitored levels for those weeks, although similar to proposed *annual* HLVs, were not sustained and are well below the proposed short-term proposed HLVs.

The average concentrations of PAHs across all six TASC sites for the 4 years sampled are shown in Figure 3-2. The most prevalent PAH, naphthalene, was removed from this figure due to its low toxicity and relatively high concentrations in ambient air. Naphthalene is found at concentrations 10 to 100 times higher than the rest of the PAHs examined in this study. The error bars represent the 95% confidence interval of the data. It can be seen that benzo(b+j+k)fluoranthene exhibits the highest concentration in Connecticut of all the carcinogenic PAHs {benzo(a)anthracene, chrysene, benzo(b+j+k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, and dibenz(a,c+a,h)anthracene}.

Figure 3-2: Connecticut 4-year Average Concentrations of PAHs.



The levels of PAHs in Connecticut were found to be well below the hazardous limiting values proposed by CT DPH. Table 3-5 shows a comparison of the four-year state-wide PAH concentrations and the HLV for each compound. Dibenz(a,c+a,h)-anthracene, Connecticut's most prevalent carcinogenic PAHs, is only at 5.6% of the proposed HLV. The most toxic PAH, benzo(a)pyrene is at 5.4% of the proposed HLV, followed by Benzo(b+j+k)fluoranthene at 3.6%. These ambient levels are an order of magnitude lower than the proposed HLVs. For the less toxic species, ambient levels are three or more orders of magnitude lower than the proposed annual HLVs and should represent no significant health concern.

Table 3-5: Comparison of 4-year Average Connecticut Ambient PAH Concentration to the Proposed HLV

PAH	*4-year Average Concentration (ug/m^3)*	*Proposed Annual HLV (ug/m3)*	*Ratio of Concentration to HLV (%)*
Acenaphthylene	0.00047	15	<0.1
Acenaphthene	0.00501	15	<0.1
Fluorene	0.00653	15	<0.1
Phenanthrene	0.01342	15	0.1
Anthracene	0.00162	15	<0.1
Fluoranthene	0.00379	15	<0.1
Pyrene	0.00217	15	<0.1
Benzo(a)anthracene	0.00034	0.034	1.0
Chrysene	0.00060	1.14	0.1
Benzo(b+j+k)fluoranthene	0.00109	0.03	3.6
Benzo(e)pyrene	0.00041	15	<0.1
Benzo(a)pyrene	0.00027	0.005	5.4
Indeno(1,2,3-cd)pyrene	0.00031	0.09	0.3
Dibenz(a,c+a,h)anthracene	0.00026	0.0045	5.8
Benzo(g,h,i)perylene	0.00046	15	<0.1

3.3.2. Seasonal Variation

An examination of seasonal variability of PAHs in Connecticut showed that the concentrations of the majority of PAHs studied were highest in the winter and fall and lowest in the summer and spring (Figure 3-3 and Figure 3-4). Four PAHs, phenanthrene, fluorene, acenapthene, and fluoranthene showed highest concentrations in the summer months.

The seasonal variability of PAHs in Connecticut follows an expected trend based on the major sources of PAHs. Since traffic, the major source of PAHs, does not follow a seasonal trend, the higher concentrations of the high molecular weight, particle bound PAHs in the winter and fall may be attributed to increased use of heating sources (Sisovic *et al*., 2001; Ohura *et al*., 2004). In contrast, lower molecular weight PAHs like phenanthrene and fluorene exhibit higher concentrations in the summer months. This positive correlation with ambient temperature may suggest that volatilization from surfaces is an appreciable source of gaseous PAHs in the summer (Dimashki *et al*., 2001; Ohura 2004). Another factor that may lead to seasonal variability is chemical degradation of PAHs by atmospheric oxidants like ozone. It has been noted that higher molecular weight PAHs are negatively correlated with ozone concentration while no significant correlation is seen with the smaller PAHs (Schauer *et al*., 2003).

Figure 3-3: Seasonal Variability of High Molecular Weight PAHs

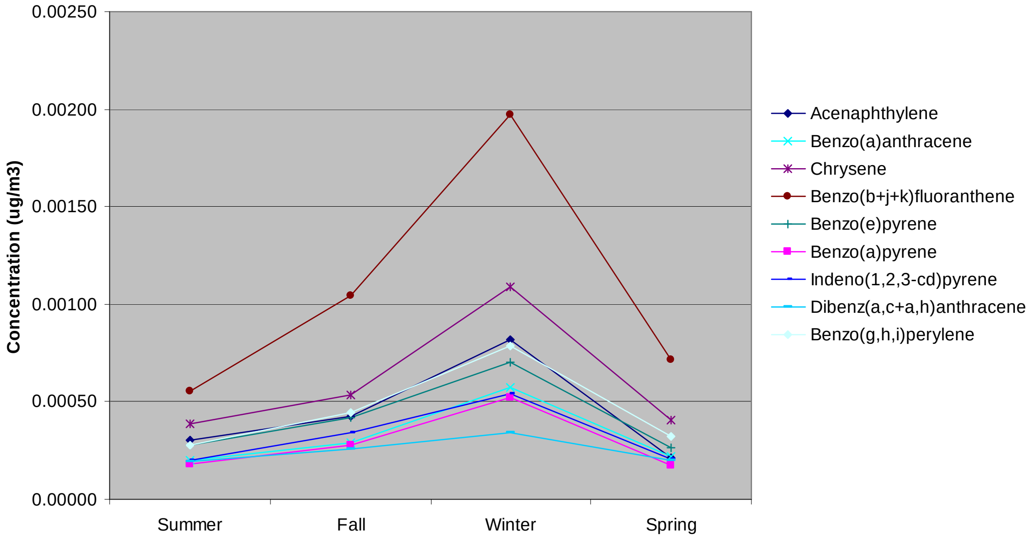
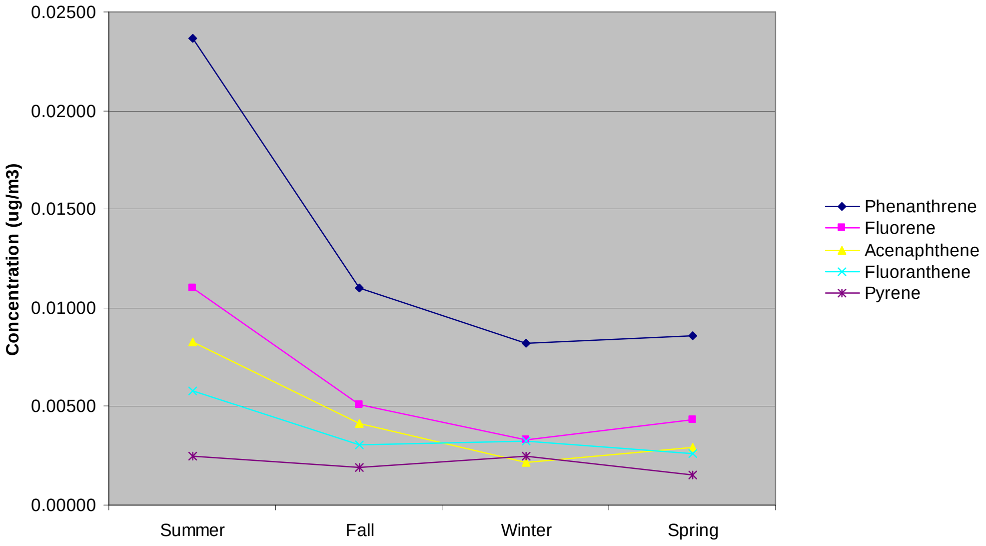


Figure 3-4: Seasonal Variability of Low Molecular Weight PAHs



3.3.3. Site Variation

Nearly all the PAHs measured in the TASC network showed the same site to site trend. The highest concentrations occurred in Groton and Wallingford. The lowest concentrations occurred in Voluntown. Hartford and Manchester had similar concentrations of PAHs, slightly lower than those found in Bridgeport and Waterbury. Concentrations of PAHs at the various TASC sites are shown in Figure 3-5 and Figure 3-6.

Figure 3-5: TASC Site Variability of Higher Concentration PAHs

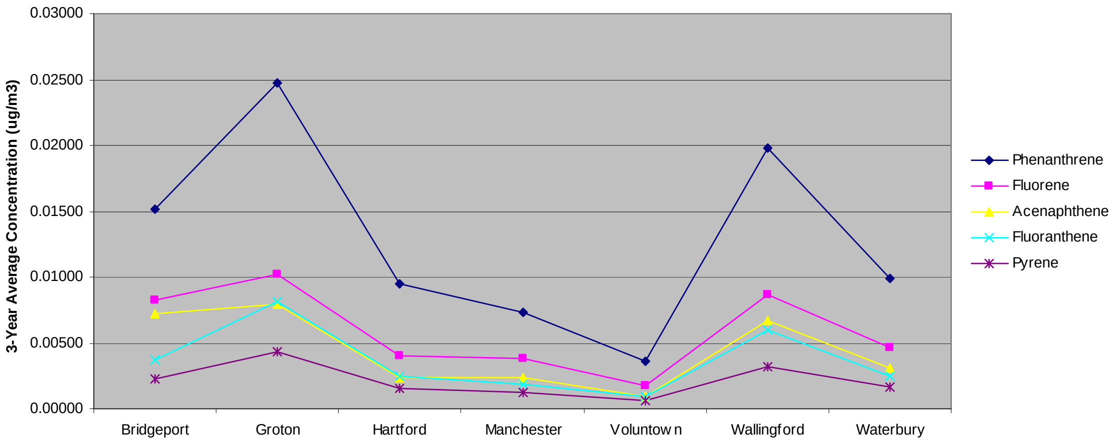
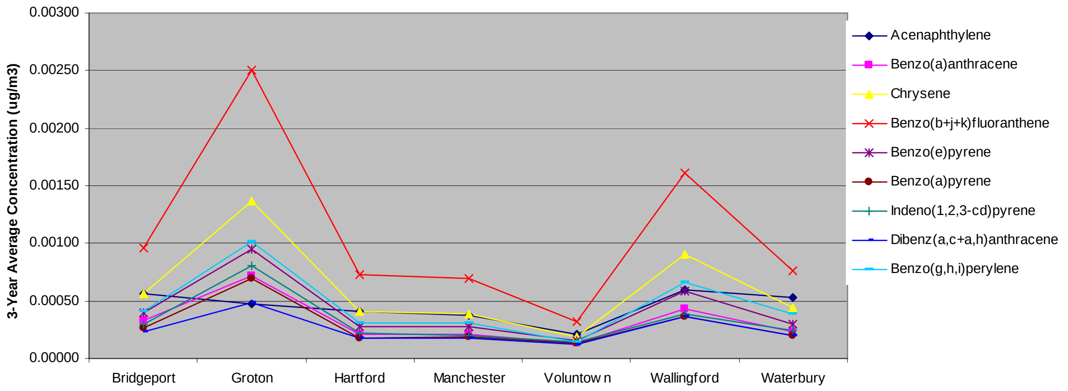
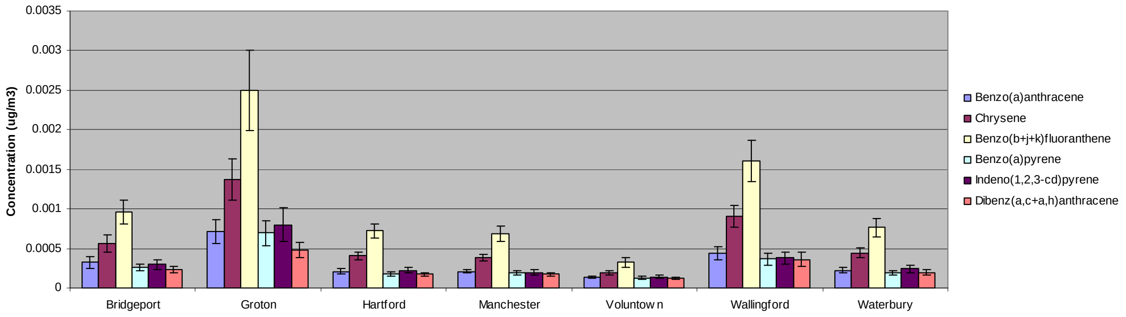


Figure 3-6: TASC Site Variability of Lower Concentration PAHs



In order to further assess the areas of human health concern, Figure 3-7 compares concentrations of the six carcinogenic PAHs at different sites. Again, this figure shows that benzo(b+j+k)fluoranthene is at the highest concentration, likely due to the fact its concentration represents the sum of three PAHs. Of the individual PAHs, indeno(1,2,3-cd)pyrene is at the highest level across all the sites sampled. The CT DPH considers this PAH the third most toxic PAH, after benzo(a)pyrene and dibenzo(a,h)anthracene.

Figure 3-7: Site Variability of 4-year Average Concentrations of Carcinogenic PAHs (error bars indicate 95% confidence).



3.3.4. Comparison of Monitored Data to CT HLVs

To assess the levels of toxic PAHs across Connecticut, we examined the levels of benzo(a)pyrene across all TASC sites. Benzo(a)pyrene is the most toxic PAH and is the main indicator of carcinogenic PAHs (EPA TO13A, Bostrom, *et al.*, 2002). Figure 3-8 displays the annual mean concentrations of benzo(a)pyrene for the four years sampled by TASC. The years represent 12 months spanning summer to summer, except the last year of data which only represents July 2002 until end of February 2003.

Figure 3-8: Annual Mean Benzo(a)pyrene Concentrations at Six Sites in Connecticut

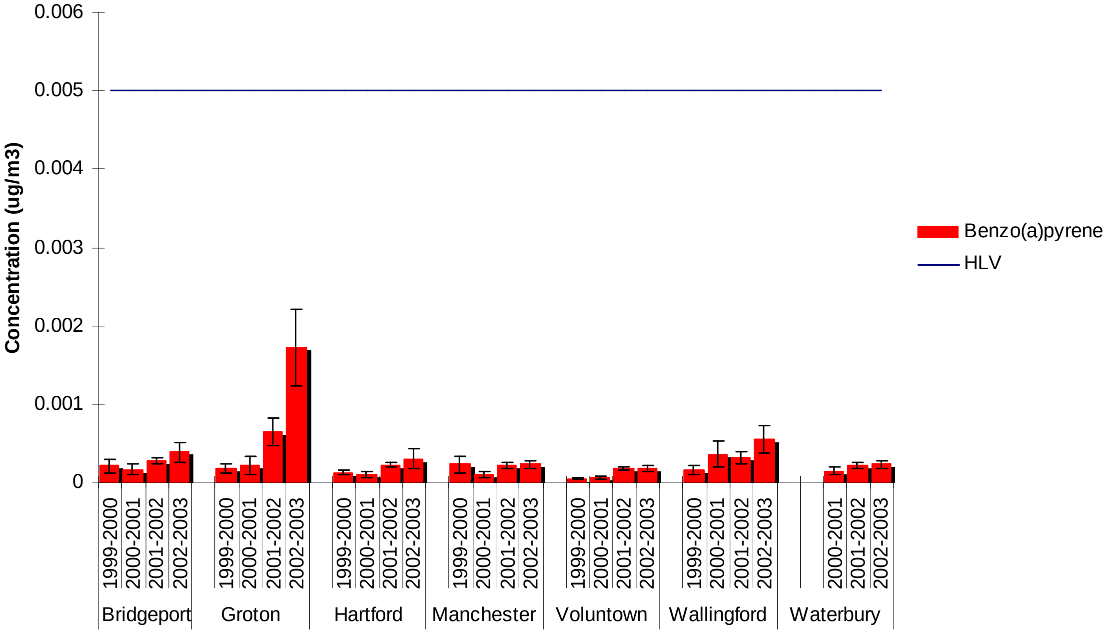


Figure 3-8 shows that the annual mean benzo(a)pyrene concentrations are well below the health standard proposed by CT DPH. Moreover, although the mean from the last year of the Groton data is higher than the rest of the averages, its upper 95% confidence interval is still well below the proposed HLV. This high concentration in most likely due to the fact that the last year's average only represents 8 months of data and those months represented are winter and fall months where benzo(a)pyrene levels have been shown to be highest.

Overall, carcinogenic PAH concentrations at TASC network sites in the state are well below the HLVs proposed by CT DPH. The highest annual average benzo(a)pyrene level found during this four year sampling period was in Groton between the summer of 2002 and winter of 2003. This annual mean of 0.00172 μg/m^3 is 3 times lower than the proposed HLV. The highest annual mean where all 12 months of data were available was also in Groton between summer of 2001 and summer of 2002. This annual mean of 0.00064 μg/m^3 is 8 times lower than the proposed HLV.

4. METALS

4.1. Introduction

Metals pose significant public health risk due to toxicity or carcinogenicity of certain elements in the group or compounds containing these metals. The Clean Air Act Amendments of 1990 list ten metal compounds among the 188 hazardous air pollutants (HAPs). These metals include compounds of arsenic, beryllium, cadmium, chromium, cobalt, lead, manganese, mercury, nickel, and selenium. These metals were added to the list due to their toxic effects from inhalation. Emission of metals into the atmosphere can also cause ecological toxicity and possibly result in oral exposure through the food web (Utsunomiya *et al*. 2004). The Toxics Air Study in Connecticut (TASC) network monitored twelve metals: arsenic, cadmium, chromium (as total Cr), nickel, beryllium, cobalt, manganese, vanadium, lead, zinc, antimony, and selenium. Mercury was not included due to the extra cost and analytical demands for monitoring. The CT DPH has proposed HLVs for eight of these metals: arsenic, beryllium, cadmium, chromium (both Cr^{VI} and total Cr), manganese, nickel, zinc and lead.

Metals are released into the air as a result of activities such as fossil fuel combustion (including vehicles), metal processing industries, and waste incineration. They can exist in both soluble and insoluble elemental states or combined as organometallic compounds. They can be released as a component of particulate matter or as a vapor that then condenses to particles (in high temperature metals smelting). Almost all metals in air are associated with particles (Holgate *et al*. 1999). Specific metals can be generally associated with certain processes. Cadmium is associated with the smelting of non-ferrous metals. Oil fly ash emitted by power plants and industries that burn oil can contain high levels of nickel and vanadium compounds. Fly ash from coal-fired power plants contains high levels of all the metals examined in this study. Incineration of municipal waste is a contributor of atmospheric metals including zinc, lead, arsenic, cadmium, cobalt, copper, manganese, nickel, and antimony. Open-hearth furnaces at steel mills constitute a significant source of zinc, copper, chromium, manganese, nickel, and lead. The major source of lead used to be leaded gasoline but now the primary sources are oil burning, small scale smelting, and resuspended soils (Holgate *et al*. 1999). Sources of arsenic include copper, zinc, and lead smelters, and glass and chemical manufacturers (Klaasen 1996).

Of the eight metals with proposed HLVs, arsenic and chromium (in particular, hexavalent Chromium, Cr^{VI}) are the most toxic. These two compounds have been classified by the Environmental Protection Agency’s Integrated Risk Information System (EPA IRIS) as Group A- known human carcinogens. Arsenic has been shown to cause increased incidences of lung cancer through several occupational studies involving smelter workers exposed to high levels in different areas (WA, UT, MT, Sweden, and Japan) (IRIS 1998). Hexavalent chromium, the carcinogenic form of chromium, has been associated with increased incidences of lung cancer in exposed workers (IRIS 1998). Although workers in these occupational epidemiological studies were exposed to both chromium (VI) and chromium (III), only chromium(VI) was found to cause tumors in laboratory animals.

Cadmium is released into the atmosphere through mining activities, burning of fossil fuels, and incinerators (ATSDR 1999). Cadmium levels in air are generally low but higher levels can occur in urban areas with high air pollution levels from the burning of fossil fuels. IRIS has placed cadmium in group B1- probable human carcinogen. There are a few studies involving workers in cadmium smelters showing workers' increased risk of lung cancer. It has also been found to cause cancers in animals from exposure through inhalation.

The Group A classification was based on several cohort studies showing workers exposed to nickel refinery dust have increased risk and incidences of lung and nasal cancers. Nickel refinery dust is a mixture of many nickel compounds, and it is not certain which of the carcinogenic nickel species is in the refinery dust (IRIS 1991). Animal studies have demonstrated the carcinogenic effect of nickel subsulfide, a known component of nickel refinery dust. Other studies of the elemental form of nickel has shown some carcinogenic potential, but with less risk than other components of the refinery dust (IRIS 1991). The CT DPH has proposed an HLV for nickel based on the levels set by the California EPA and ATSDR.

The remaining carcinogenic metals in this group, beryllium and lead, have been placed in groups B1 and B2 (probable human carcinogens) respectively (EPA IRIS). Beryllium has been linked to increased incidences of lung cancer in exposed populations. There is limited information linking beryllium to incidences of human cancers but sufficient animal evidence to add it to this group. Similar evidence is available for lead. CT DPH has proposed its HLV for lead based on the ATSDR's blood lead to air lead slope factors. The HLV was proposed to minimize the rise in children's blood lead and make a very minor contribution to the background so there is no increase in percent of children with blood leads over 10 ug/dl.

The only metal sampled that has an HLV recommended for non-carcinogenic effects was manganese. Manganese is released into the air from metallurgic and chemical industries and burning of fossil fuels. In humans, its main toxic effect is in the brain where it causes Parkinson-like symptoms when inhaled at moderate concentrations over long periods of time (Gerber *et al*. 2002). This impairment of neuro-behavioral function as well as detrimental lung effects has been seen in workers exposed to manganese fumes (IRIS 1996). CT DPH proposed its HLV based on the inhalation reference dose established by IRIS to protect the general public.

The last five metals, cobalt, copper, antimony, selenium and vanadium have no HLV proposed by the CT DPH, since these were not identified as priority chemicals in their assessment report. Copper, selenium, and zinc have all been classified by EPA IRIS as Group D, non-carcinogenic. Antimony is currently under review by IRIS in regards to its carcinogenic potential. Some of these compounds, like selenium and antimony are found in very low concentrations in air. Furthermore, the level at which these metals will exert a health effect occur is much higher than what is encountered in ambient air. For example, OSHA health standards for levels of antimony in workroom air is approximately 500 times higher than ambient levels seen near antimony mines or processing companies while selenium levels in ambient air are orders of magnitude lower than the occupational health standards (ATSDR 1992, 2003).

4.2. Description of Metals Sampling and Analysis

The Environmental Research Institute (ERI) assessed ambient metals concentrations at TASC sites by sampling the air concentrations of thirteen metals[19]: arsenic, cadmium, chromium, copper, nickel, beryllium, cobalt, manganese, vanadium, lead, zinc, antimony, and selenium. The sampling method involved drawing ambient air through a pre-weighed quartz fiber filter for a known amount of time at a measured flow rate. Using the flow rate and the sampling time, the total air volume was determined. After sampling, the filters were returned to the laboratory for preparation and analysis.

Laboratory preparation of the sample filters began by reweighing the filters to determine the mass collected during sampling. The filters were digested in 50% Aqua-regia solution (consisting of concentrated hydrochloric acid and nitric acid in deionized water). After digesting the filter, nitric acid was added to each sample and sonicated for an hour. This solution was gravity filtered using Whatman #41 filter paper and subsequently washed with a 4M nitric acid. The resulting solution was used for the analysis. Sample analysis was performed by Inductively Coupled Plasma Optical/Atomic Emission Spectroscopy (ICP-OES/AES), Graphite Furnace Atomic Absorption (GFAA), and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). These methods determined the mass of each type of metal sampled, which was then used to determine the ambient concentration by dividing by the total air volume sampled.

TASC sites in Connecticut were sampled for metals in total suspended particles (TSP) once a week between mid-1999 and the beginning of 2003. During the first two years, the sampling time was seven days while in the last two years they sampled one 24-hour period every sixth day. The sample duration change began in July 2001. This change resulted in a decreased sample collection volume (~3100 m^3 to 410 m^3 on average) and corresponding increase in MDL for each metal.

4.2.1. Interferences

The main interferences in this method are those attributed to ICP emission spectroscopy. These include inter-element effects, spectral interferences, and calibration curve interferences. These interferences are addressed by applying correction methods during calibration and analysis.

4.2.2. Blanks

To assess background levels in the sampling process, trip and field blanks were processed and analyzed along with the field samples. The field blanks were treated in the same manner as the field samples, but no air was drawn through the sampler. The trip blanks accompanied the field blanks but did not leave their sealed pouch. Examination of the blanks data showed that blank metals samples were only available for five sites during the third and fourth year of the sampling period, although blanks were performed throughout the program. Trip blanks were analyzed in Groton (11/01-11/02), Manchester (7/01-11/01), Voluntown (7/01-2/03), and Wallingford (8/01-1/03). Field blanks were analyzed in Bridgeport (11/02-2/03), Manchester (7/01-7/02), and Waterbury (7/02-10/02).

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[19] Reported values represent all valences for each metal, i.e. total Cr was measured, not Cr^{III} or Cr^{VI}.

An analysis of the blanks data showed that levels were below the detection limit in over 75% of the samples for arsenic, beryllium, cadmium, cobalt, antimony, selenium, and vanadium. Copper was detected in 90% of the trip blanks and 91% of the field blanks. Copper levels in these samples were on average 2% of the sample concentration on similar days. Total chromium, manganese, nickel, and lead were all detected in 75%-90% of the field and trip blank samples. A comparison of blank chromium concentrations to sample concentrations on similar days showed that the trip blanks levels were 71% of the sample concentration. Moreover, the concentrations on the field blanks were at 77% the level of the sample concentration. Zinc showed similarly high blank levels. The levels shown on the blanks were almost identical to the levels on the samples on similar days (97%). Nickel and lead were present on the field blanks at 39% and 23% the levels on the ambient samples, respectively.

The high levels of zinc and total chromium on the blanks indicate that reported ambient concentrations may be overestimating the true levels. This is of particular concern for total chromium due to its health effects and low proposed HLV. Chromium was detected in 79% of the field blanks and 69% of the trip blanks. Therefore, the sampled values are unreliable as field levels are very similar to the blank values. Since the average field blank and trip blank concentrations of 0.0055 ug/m^3 are three times higher than the proposed HLV, no conclusions can be drawn regarding the health risk from this metal. The remaining metals of concern from a health standpoint—arsenic, beryllium, cadmium, manganese, nickel, and lead—were either rarely detected or detected at levels well below the proposed HLV on blank samples.

4.2.3. Precision

Collocated samplers were deployed by ERI to assess metals sampling precision. Data from three sites, Bridgeport (7/02-2/03), Groton (7/01-10/01), and Voluntown (11/01-7/02) were evaluated for this report. Table 4-1 shows the average relative percent differences between collocated measurements and the number of valid collocated sets. This latter number gives an indication of the prevalence for each metal in the ambient samples. The greater the number of valid collocated pairs, the more frequently the metal is detected. Beryllium, for example, was not detected in any of the collocated samples, while zinc and manganese were detected in all 85 pairs analyzed. The table demonstrates that the best collocated precision was achieved for zinc and vanadium while the highest percent differences were found for copper. The majority of the RPDs ranged between 20% and 35%. It is interesting to note that there is no apparent correlation between the number of valid collocated sets and the average RPD. This implies that when metals like selenium and cobalt *were* detected, they were at appreciable levels. This may also reflect periodic impacts at the sites. For instance, selenium was only present in the colder months (late September through early March). Antimony, on the other hand, was detected at both Bridgeport and Groton, but not Voluntown. Since nearly half of the collocated samples analyzed were from the background Voluntown site, these data yield information about spatial distribution of metals as well.

Table 4-1: Precision of Duplicate Metals Measurements

Metal	*Average RPD (%)*	*Number of Collocated Sets*
As	35.4	22
Be	NA	0
Cd	35.2	13
Co	33.5	23
Cr	24.2	67
Cu	64.0	83
Mn	22.0	85
Ni	20.8	76
Pb	27.8	80
Sb	21.0	32
Se	30.3	20
V	12.5	79
Zn	18.3	85

4.2.4. Detection Limits

The method detection limit is the minimum concentration of a compound that can be reported with 95% confidence that the value is above zero. The number of samples displaying levels above the detection limit varied depending upon the metal of interest. Table 4-2 shows the percent of samples below the detection limit for the various metals examined. Despite the fact that sample volume decreased to 410 m^3 (from 3100 m^3) on average after July 2001, little difference was observed in the percentage of time metals

Table 4-2: Percent of Metals Samples Below the Detection Limit

Metal	**Percent of Samples Below the Detection Limit Before 7/01(%)**	**Percent of Samples Below the Detection Limit After 7/01(%)**
Arsenic	57.6	61.8
Beryllium	96.2	98.7
Cadmium	74.3	73.5
Cobalt	30.6	40.3
Chromium	8.4	12.9
Copper	2.8	1.4
Manganese	0.2	0.2
Nickel	3.1	4.3
Lead	1.5	2.3
Antimony	35.0	42.2
Selenium	47.2	66.8
Vanadium	2.7	4.0
Zinc	0.1	0.2

were detected in the ambient sample. The table indicates the wide range of detection for various metals, due to the wide range of concentrations in ambient air. While zinc and manganese are detected in virtually all of the samples, beryllium is rarely detected.

To assess whether the method employed by ERI to measure ambient metals concentrations was sensitive enough to see the levels of health concern, the detection limits were compared to the HLVs recommended by CT DPH. Table 4-3 shows the proposed annual HLV for the toxic metals compared to the average detection limit for two time periods (before and after July 2001). From the table, it can be concluded that the method's detection limit was sufficiently low for beryllium, manganese, nickel and lead to compare to the proposed annual HLV. Since MDL and proposed HLV levels were of the same order for arsenic and cadmium, especially in the latter period, health assessments of these two metals based on the TASC data would be inappropriate.

Table 4-3: Comparison of the Minimum Detection Limit to the Proposed HLV

Metal	*Mean Detection Limit Before 7/01 (ug/m3)*	*Mean Detection Limit After 7/01 (ug/m3)*	*Proposed HLV (ug/m3)*	*Ratio of Detection Limit to HLV Before 7/01(%)*	*Ratio of Detection Limit to HLV After 7/01(%)*
Arsenic	0.0005	0.0009	0.0014	36.3	66.3
Beryllium	0.0001	0.0003	0.0024	5.4	11.2
Cadmium	0.0005	0.0017	0.0032	15.9	54.6
Manganese	0.0001	0.0011	0.03	0.4	3.6
Nickel	0.0006	0.0013	0.05	1.3	2.6
Lead	0.0007	0.0009	0.5	0.2	0.2

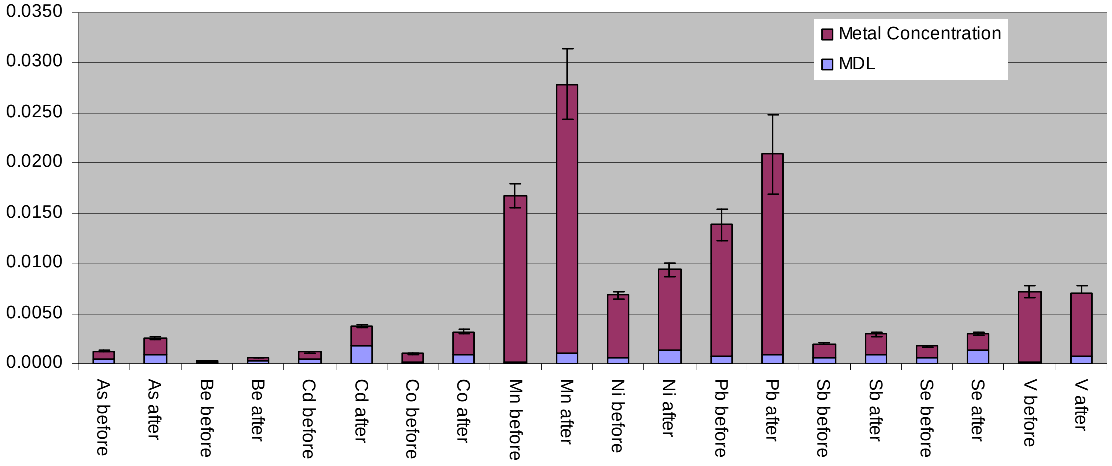
4.3. Analysis of Monitored Concentrations

4.3.1. Overall Connecticut Levels

The issue of non-detect samples was addressed in the same way for metals as for carbonyls, PAHs and VOCs. Samples showing levels below the detection limit were assigned a value of the detection limit. Therefore, all reported average concentrations may represent the maximum likely ambient concentration. This was done to provide a conservative measure of ambient concentration.

The average concentration of various metals across the seven TASC sites in Connecticut over the four years from 1999-2003 is shown in Figure 4-1, with the 95% confidence interval shown with error bars. The level represented for beryllium essentially shows the detection limit since it was detected in fewer than 2% of the samples. Therefore no further analysis was conducted for this metal. Copper and zinc are not graphed in this figure due to scaling issues; their concentrations are much higher than the rest of the metals. Additionally, the zinc values are unreliable given the high blank levels noted, while for copper, no chronic adverse health effect level was proposed by CT DPH.

Figure 4-1: Average Connecticut Ambient Metals Concentrations before and after sample volume change of July 2001



4.3.2. Seasonal Variation

There were no consistent seasonal trends in ambient concentrations for the metals evaluated in Connecticut. Figure 4-2 and Figure 4-3 show the variation of these metals from samples taken prior to July 2001 when samples were a week in duration. The behavior was similar for the period after July 2001 (not pictured). Nickel, selenium and vanadium showed higher average concentrations in the winter than the other three seasons. This could potentially show the influence of increased residential fuel use in wintertime. Lead showed higher average concentrations in the summer.

Figure 4-2: Seasonal Variation of Selected Metals Found at Higher Concentrations

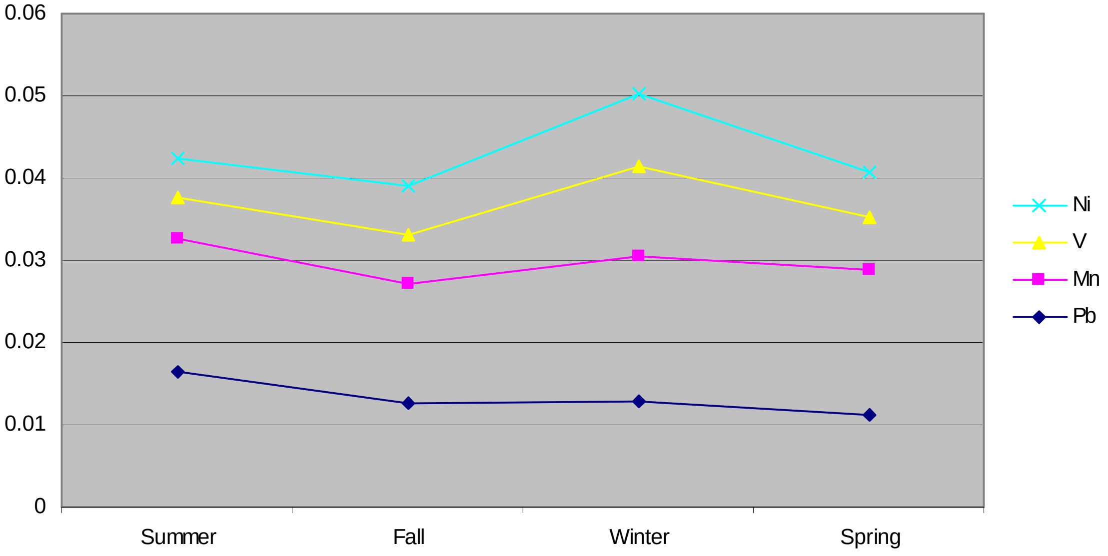
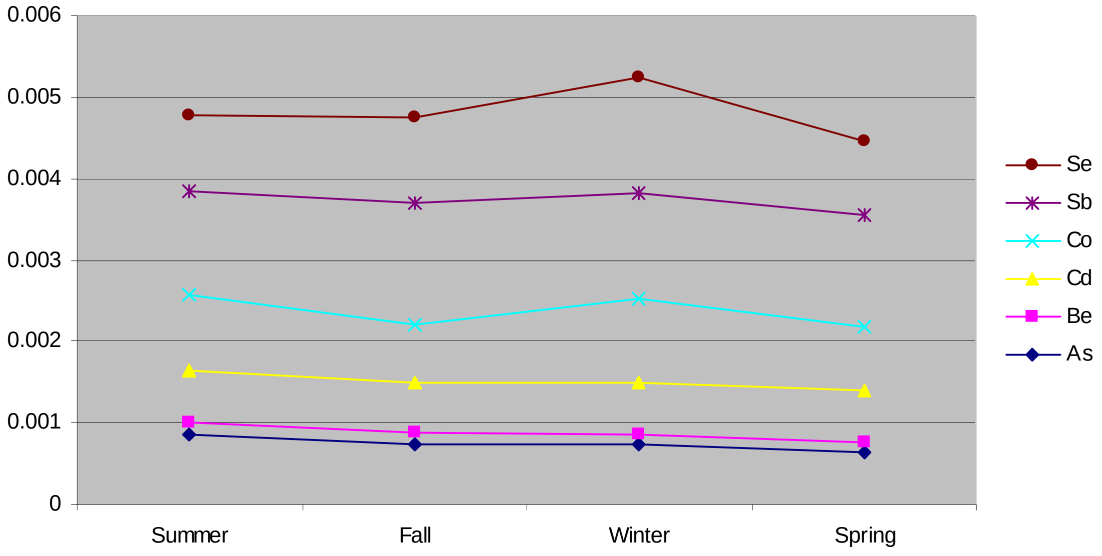


Figure 4-3: Seasonal Variation of Selected Metals Found at Lower Concentrations



4.3.3. Site Variation

There did not seem to be a consistent trend of site variation across all the metals. Figure 4-4a-h show the distribution of TASC metals data by sampling site. The data are divided into two sets at each site, based on sample duration (before and after July 2001). Arsenic, cadmium, and selenium (not graphed) show little site to site variability. This is most likely due to the high percentage (roughly ½ to ¾) of non-detects for these metals and therefore the concentrations are driven by the detection limit. Likewise, beryllium was not pictured because it was rarely detected in the samples. Copper shows the highest mean concentration in Hartford and the lowest in Wallingford in the early period. The concentrations are more uniformly distributed in the later period. Manganese displays the highest means and medians in Groton, Bridgeport and Waterbury with the lowest levels occurring in Voluntown. Nickel and vanadium levels were recorded highest in Groton, Bridgeport and Wallingford and showed the lowest levels in Voluntown. Lead displayed the highest values in Bridgeport and Hartford, showing higher mean and median concentrations than the other five sites sampled. Antimony levels were similar across five of the sampling sites with lower levels in Manchester and Voluntown. Finally, zinc levels show curious behavior in the second period, with substantial increases across all sites. Although the average MDL for zinc increased an order of magnitude, the detection levels were well below the ambient concentrations and non-detects were rare. No conclusions can be drawn from the zinc data given its levels were routinely comparable to ambient measurements.

Figure 4-4a: Distribution of Cobalt Concentrations at TASC Sites

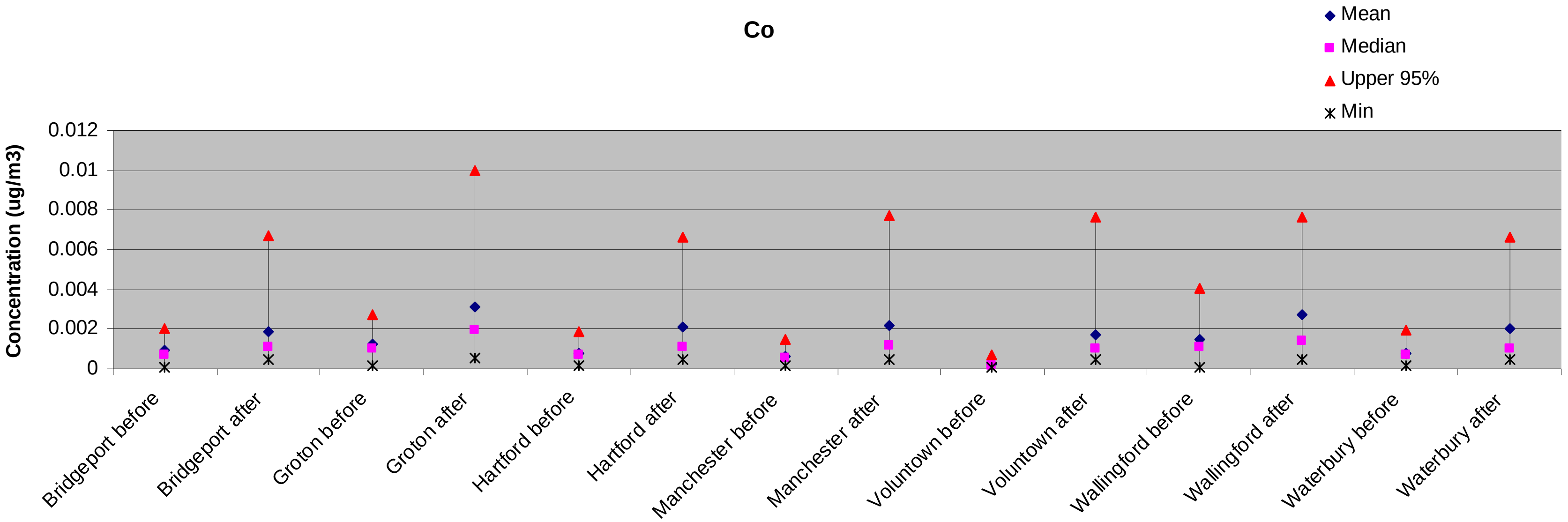


Figure 4-4b: Distribution of Copper Concentrations at TASC Sites

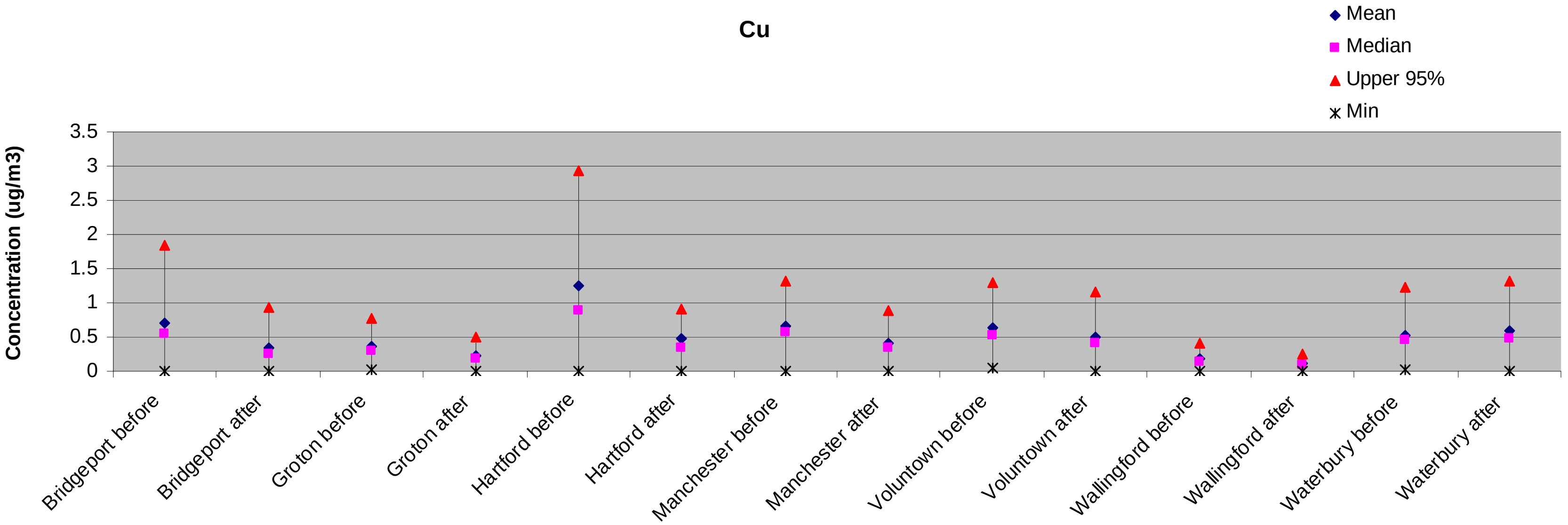


Figure 4-4c: Distribution of Manganese Concentrations at TASC Sites

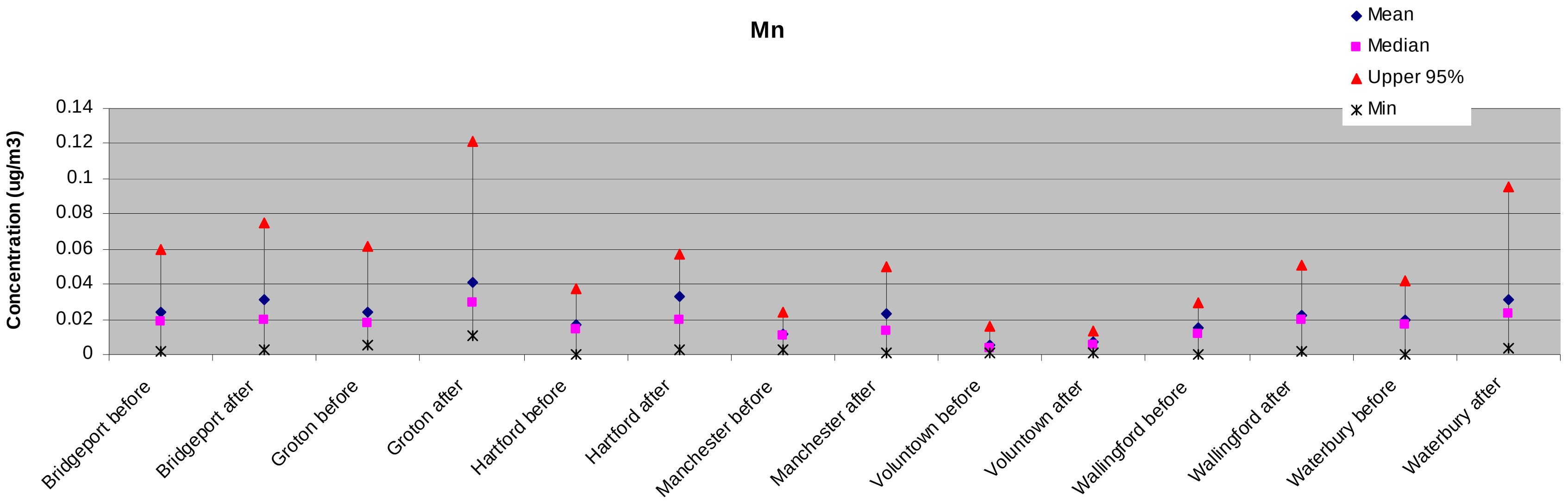


Figure 4-4d: Distribution of Nickel Concentrations at TASC Sites

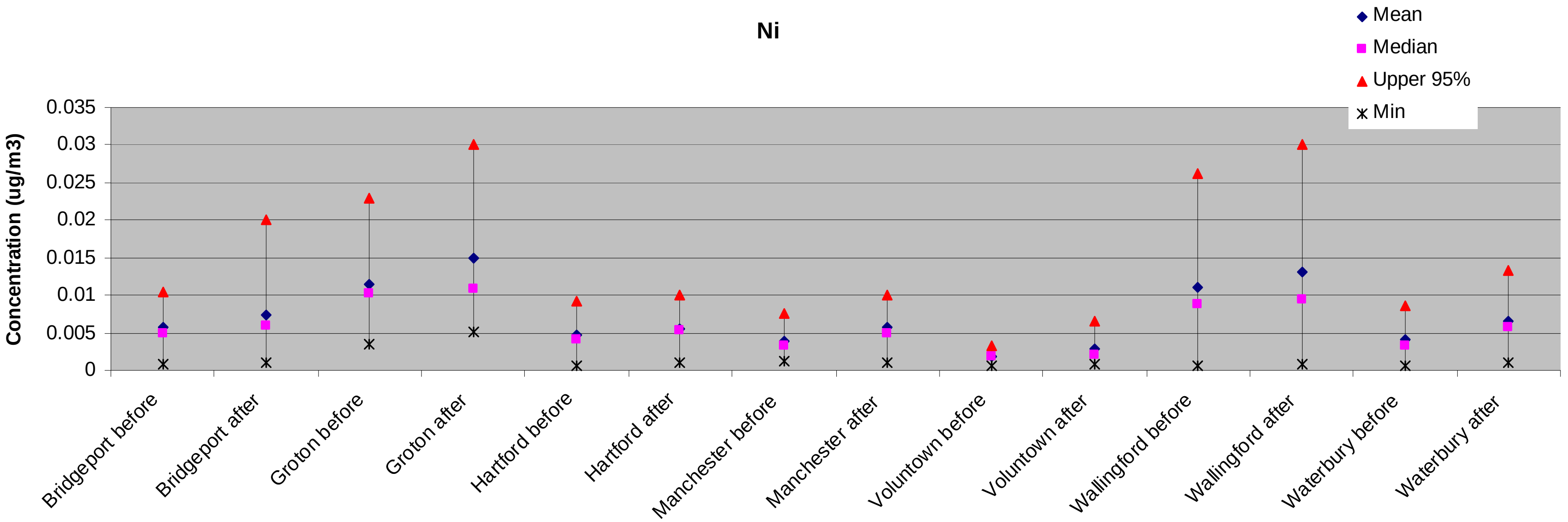


Figure 4-4e: Distribution of Lead Concentrations at TASC Sites

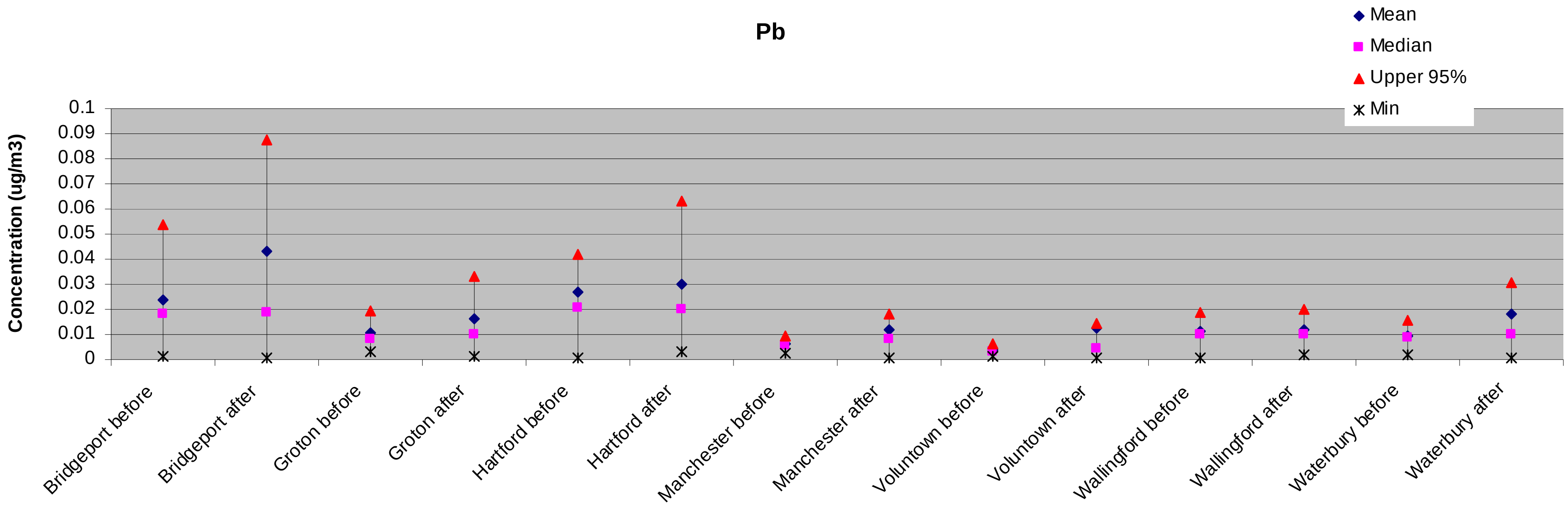


Figure 4-4f: Distribution of Antimony Concentrations at TASC Sites

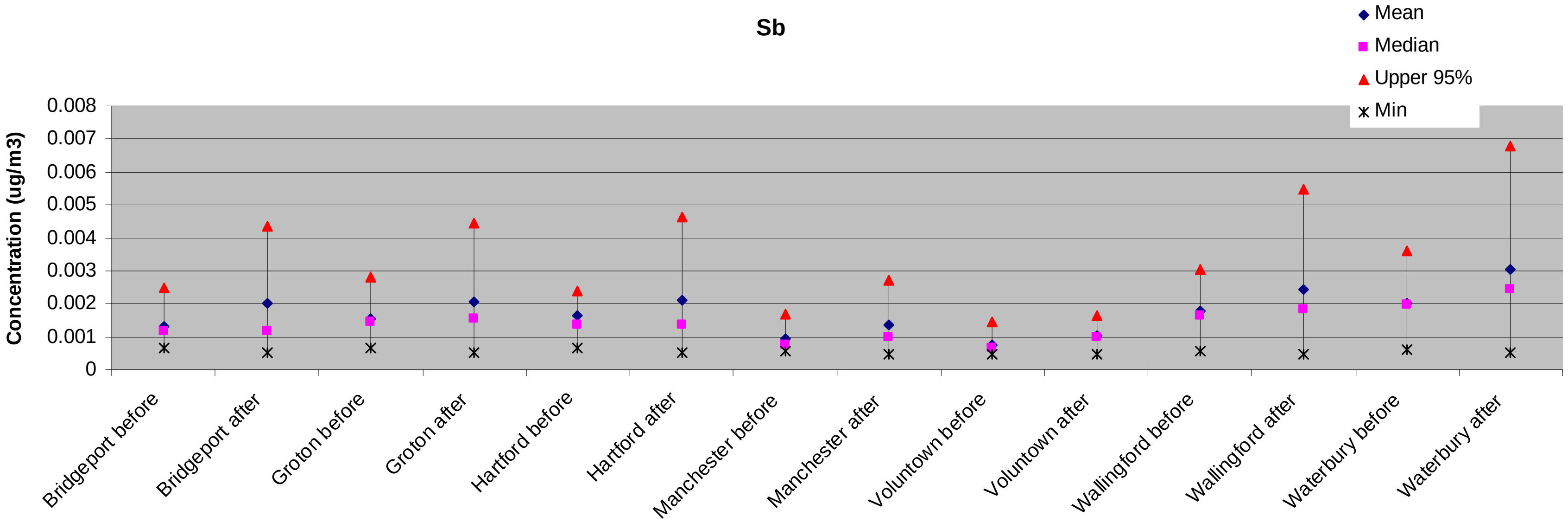


Figure 4-4g: Distribution of Vanadium Concentrations at TASC Sites

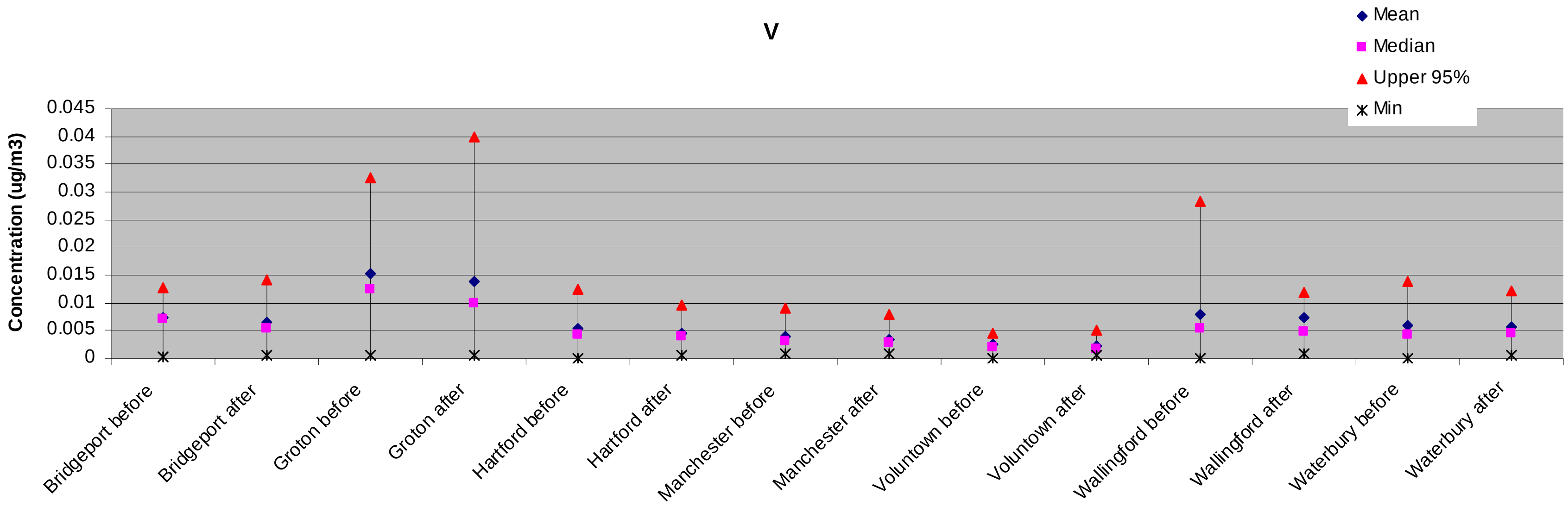
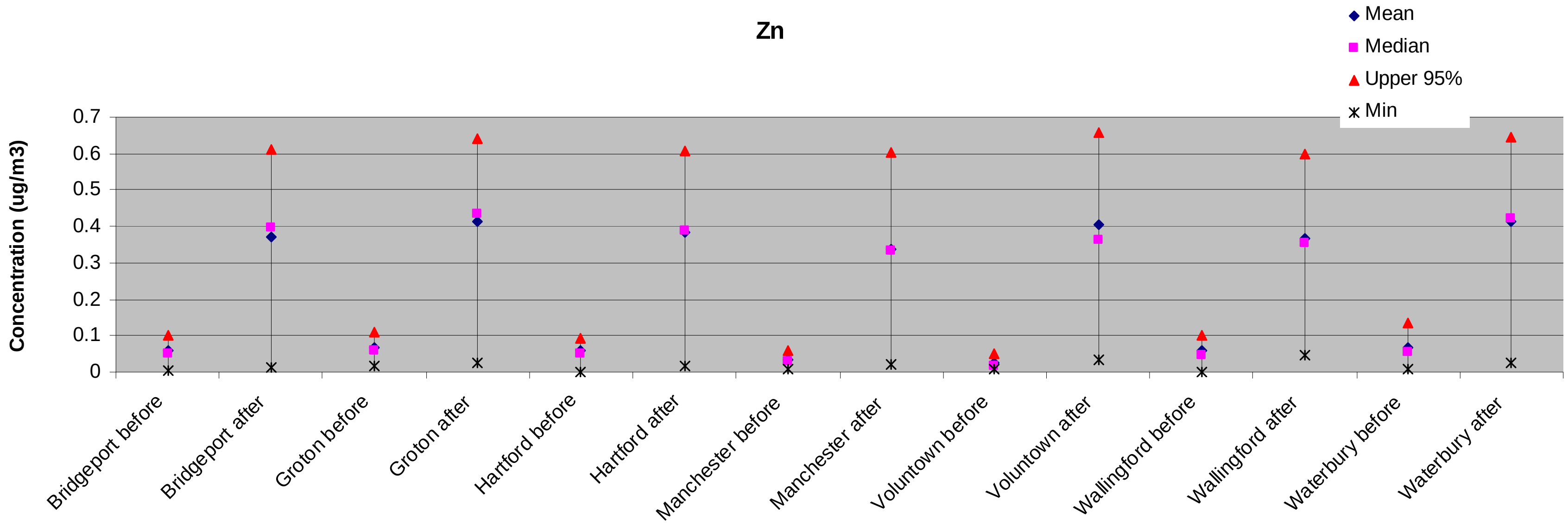


Figure 4-4h: Distribution of Zinc Concentrations at TASC Sites



For most elements, the reported levels increased in the second period relative to the first. This may not truly reflect changes in ambient levels given the noted differences in MDLs and the associated effect of MDL substitution for non-detects. However, Table 4-3 indicates this effect may be small, since the distribution of non-detects before and after is fairly similar. However, the difference between median and mean levels is increased for the 24-hour samples relative to the week-long samples. This implies the observed concentration increases for 24-hour samples may be a result of sample days occurring on higher pollution days. The longer sampling time may smooth out some of the day to day variations in ambient levels. The "before" samples should also more accurately reflect annual levels since their collection period covered virtually all of the days in the monitored years, whereas the 24-hour samples were on a one in six day schedule, representing only one-sixth of the days.

4.3.4. Comparison of Monitored Data to CT HLVs

A comparison of CT DPH's proposed HLVs to statewide average metals' concentrations indicates that levels of manganese are close to its proposed HLV (Table 4-4). For the early period, manganese concentrations were about half its proposed HLVs while measured levels roughly doubled in the later period to concentrations near the proposed annual HLV. Nickel and lead also showed higher concentrations after July 2001. For both metals and periods, however, the ambient concentrations were well below the proposed annual HLV. The blanks for Mn, Ni and Pb were sufficiently low, as were their MDLs, such that a comparison to the annual HLV is reasonable. For As, the case is more difficult given that the MDL approaches the proposed annual HLV. The analyses presented here indicate improved methodologies are required to better assess the levels of arsenic found in Connecticut.

Table 4-4: Comparison of Monitored Data to the Proposed HLV (ND = Detected in fewer than 15% of samples)

Metal	*Connecticut Average Level Before 7/01 (ug/m3)*	*Connecticut Average Level After 7/01 (ug/m3)*	*Proposed Annual HLV (ug/m^3)*	*Ratio of Monitored Concentration to HLV- Before 7/01(%)*	*Ratio of Monitored Concentration to HLV- After 7/01(%)*	*Average Field Blank Concentration (ug/m3)*
Arsenic	0.0007	0.0016	0.0014	52.3	115.5	ND
Manganese	0.0166	0.0268	0.03	55.3	89.3	0.005
Nickel	0.0062	0.0081	0.05	12.3	16.2	0.002
Lead	0.0131	0.0200	0.5	2.6	4.0	0.004

To gain more insight from the existing information, the data were analyzed by site and by sampling year to examine the magnitude and potential spatial trends of the annual arsenic concentrations at the seven TASC sites in Connecticut. Figure 4-5 shows the annual mean arsenic levels at the seven sites and their relation to the CT DPH's proposed HLV. The years span a summer to summer time period (except year 4 which ends in March 2003) and the error bars represent the 95% confidence interval.

Figure 4-5: Annual Means of Arsenic Concentrations at TASC Sites

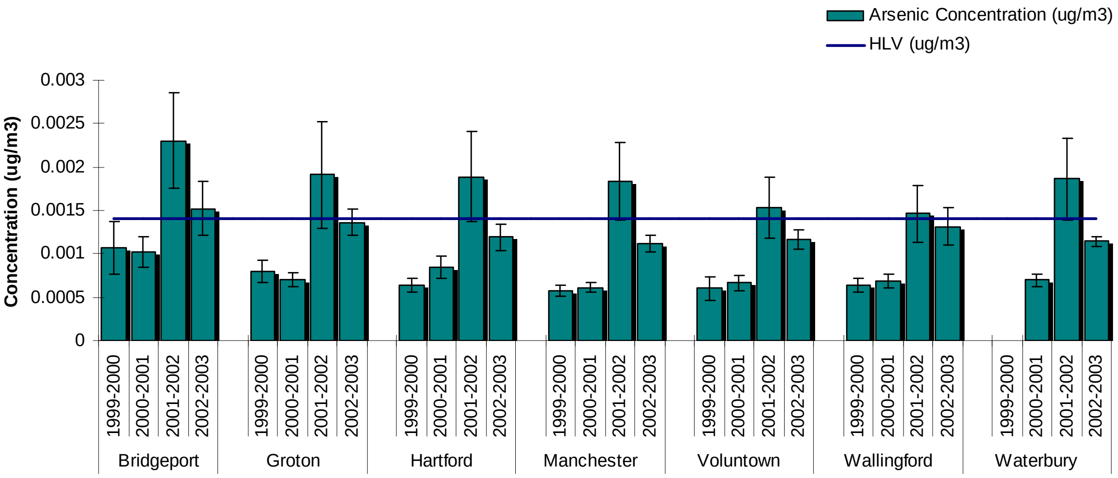
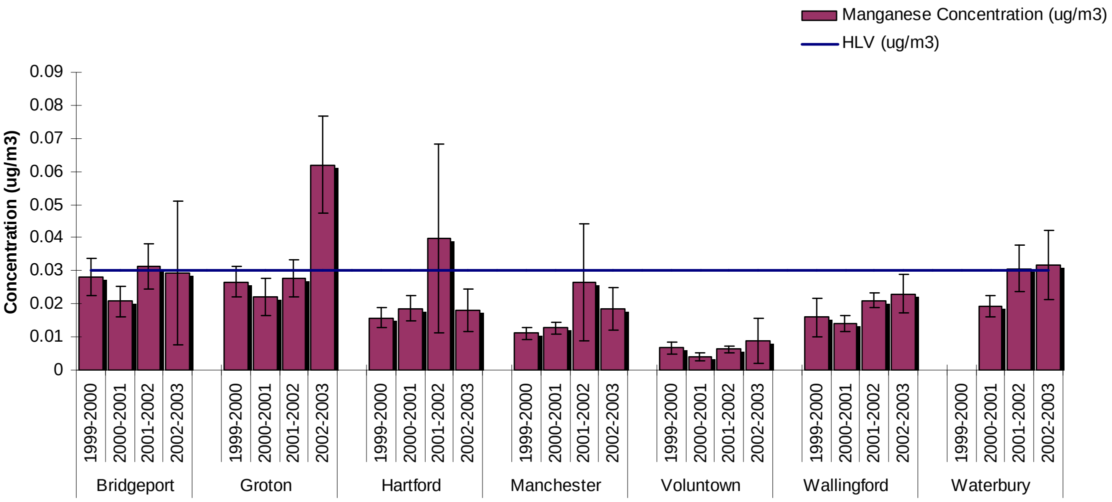


Figure 4-5 indicates that the annual mean arsenic concentration in the first two years of sampling was below the proposed HLV at all seven sites, with reasonably similar concentrations across the state. Levels in Bridgeport appeared the greatest. During the final two years, the arsenic level increased relative to the first two years at all sites. The consistent spatial distribution may imply that the levels of arsenic in Connecticut are more regional than local in nature. To some extent, the uniformity may simply reflect limitations of the analytical method, since about half of the samples were non-detects. The observed difference between the third and final sample periods could result from the absence of data for the period of March through June of 2003. These levels are similar to those reported from pilot sites in EPA's air toxic network (Hafner, *et al.*, 2004).

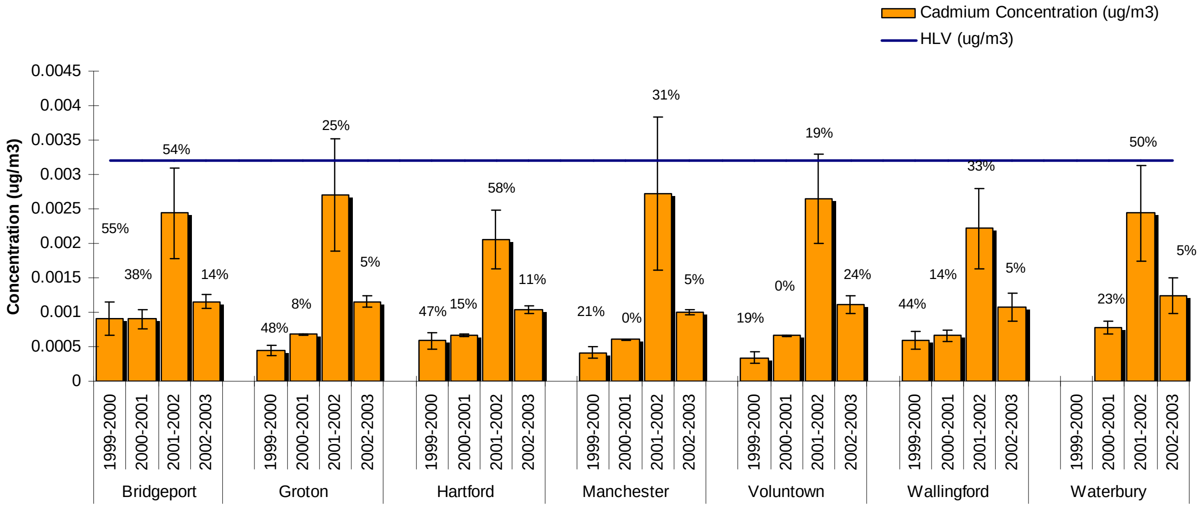
Figure 4-6: Annual Means of Manganese Concentrations at TASC Sites



Much like arsenic, the statewide levels of manganese were close to the proposed HLV, warranting further discussion. Figure 4-6 shows the annual mean manganese concentration for the seven sites for each of the years sampled. The error bars represent the 95% confidence interval while the years represent a summer to summer time period (except year 4 which ends at March 2003). Unlike arsenic, the spatial variation in Figure 4-6 shows that the mean manganese concentrations vary widely from site to site. Bridgeport, Groton and Waterbury have levels consistently near the proposed annual HLV, while ambient concentrations at Voluntown were roughly three times lower. The distribution may reflect local source influences. Some of this variability could result from the level of diesel truck or other traffic near the sampling sites, as manganese complexes may be added to fuels (Poirot *et al.*, 2001; Lewis *et al.*, 2003). The Mn concentrations reported in Connecticut are similar to those observed at pilot sites from EPA's air toxic network (Hafner, *et al.*, 2004).

Average annual cadmium concentrations were generally below the proposed HLV except for the third year of monitoring (summer 2001 to summer 2002) (Figure 4-7). The numbers above each bar represent the percent of samples above the detection limit for that site and year. There does appear to be some spatial variation, with lowest concentrations observed at the background site in Voluntown. Given that cadmium was generally detected in less than half the samples for all but two data groups it is difficult to make a definitive conclusion on whether levels pose a health risk. In fact, the differences between the early and later years are substantially driven by the increased MDL and effects of MDL substitution for non-detects in average calculations. It should be noted that the MDL in the early period is almost an order of magnitude lower than the proposed HLV and therefore may be sensitive enough to indicate levels are truly below the proposed annual HLV for those years.

Figure 4-7: Annual Means of Cadmium Concentrations at TASC Sites. (Numbers indicate percent of samples above the detection limit.)



Overall, due to issues surrounding blanks and detection limits, it is difficult to conclude the potential health concern for all metals monitored by TASC. This is particularly true for Zn and Cr, whose blank levels were comparable to ambient sample concentrations. Lead and nickel levels throughout the state appear to be well below the proposed annual HLV. Manganese and arsenic concentrations are close to the proposed annual HLV throughout the state, although manganese manifests a spatial distribution not observed for arsenic. These two metals may warrant further observation. There is significant uncertainty surrounding cadmium concentrations due to low ambient levels. Nonetheless, this metal may not be of concern, as supported by the first two years of data.

5. VOLATILE ORGANIC COMPOUNDS

5.1. Introduction

Volatile organic compounds (VOCs) are a major class of organic pollutants in air which include alkanes, alkenes, aromatics, aldehydes, ketones, alcohols, and halogenated compounds. VOCs exert two major health impacts in the atmosphere. Several compounds in this group show toxic effects in exposed populations while VOCs are also important precursors to the formation of ground level ozone. VOCs are generated from a wide range of sources including motor vehicles, chemical and food industries and solvent use.

The majority of the 33 priority hazardous air pollutants identified by EPA in 2000 are volatile organic compounds. Exposure to several of these VOCs is associated with adverse health effects including acute health effects as well as chronic effects such as cancer (linked to benzene exposure) or liver and kidney damage (linked to exposures to chlorinated compounds)(Sax *et. al.* 2004). Specific health information for many of these VOCs derived from EPA's Integrated Risk Information System and CT DPH can be found in Appendix A.

The Toxics Air Study in Connecticut sampled for 54 VOCs at six sites in Connecticut: Bridgeport, Groton, Hartford, Manchester, Voluntown, Wallingford, and Waterbury. Of these 54 VOCs, the CT DPH has proposed annual HLVs for 22 compounds due to studies showing health risks resulting from exposure. Of these 22 compounds, acrylonitrile has been proposed the lowest annual HLV of 0.086 ug/m^3. Acrylonitrile is used in the chemical and plastics industry and found in automobile exhaust (Klaassan, 1996). IRIS has been classified this compound in group B1- probable human carcinogen due to occupational studies showing increased risk of lung cancer in exposed workers (IRIS, 1991).

Volatile organic compounds originate from a wide variety of sources including motor vehicle exhaust, paint and solvent use, chemical manufacturing, and many others. Although some compounds in this group originate mainly from certain sources, such as benzene, xylene, and ethylbenzene emissions from industry and mobile sources or chlorinated compound emissions from dry cleaners, human exposures are usually the result of a combination of many sources (Pratt *et al.* 2004). Stationary sources, mobile sources, area sources, and background levels all contribute to the total levels of VOCs in the environment.

VOCs are unique from metals and PAHs as human inhalation exposures do not result mainly from outdoor air. Many studies have reported higher VOC concentrations in indoor air due to emissions from building products, cooking, smoking, and synthetic materials (Serrano-Trespalacios *et al.*, 2004). Regulatory agencies typically maintain emissions data, monitoring results, and modeling results for outdoor levels of VOCs. However, it has been noted that such information does not adequately describe human exposure as there is a scarce amount of data describing indoor levels as well as human exposure resulting from a combination of indoor and outdoor activities (Sexton *et. al.*, 2004; Serrano-Trespalacios *et al.*, 2004; Sax *et. al.* 2004).

5.2. Description of VOC Sampling and Analysis

To determine ambient levels of volatile organic compounds (VOC) in Connecticut, the Environmental Research Institute applied a method based on EPA's standard method TO-15. This method allowed for the quantification of 54 VOCs over 4 years at the seven TASC sites throughout Connecticut. Sampling and analysis involved collecting ambient air in a Summa canister and VOCs were quantified by Gas Chromatograph (GC).

VOCs were sampled at the seven TASC sites by collecting air samples in a stainless steel Summa or Silco canister for 24 hours once every sixth day of the sampling period. A diaphragm pump was used to push air into the canisters at a flow rate of 12.5 ml/min. The acceptable range for the final pressure was set to 10-30 psig.

Concentration of the ambient air sample began by passing the sample through a glass bead packed cryogenic trap, cooled to a temperature of -170°C. The trap was then heated to 20 °C and 40ml of helium was passed through the trap, transferring the sample to a second trap packed with Tenax, cooled to -40°C. The step allows carbon dioxide to pass through the trap, while collecting the compounds of interest. The VOCs were flushed from the trap and transferred to a cryofocus loop at the head of the column before being transferred to the GC for separation.

5.2.1. Interferences

Contamination and interferences can occur with the highly volatile organics like methylene chloride and vinyl chloride. These compounds can diffuse through valves and fittings during shipping and storage and contaminate the sampling system. Furthermore, these volatile compounds are prone to peak broadening and coelution with other species if they are not delivered to the GC column in a small enough volume of carrier gas. These interferences are mitigated by running canister blanks and refocusing the sample before analysis by cooling the head of the chromatographic column, as was performed in the protocol employed in this study.

The majority of contamination problems result from impurities in the carrier gas or VOCs outgassing from the plumbing ahead of the trap. VOC purifiers such as activated carbon are used at the inlet of all carrier gasses to ensure their purity. The system is verified to be pure of contaminants by consistently analyzing calibration blanks and lab method blanks.

Since cross-contamination can occur when high level and low level samples are analyzed sequentially, method blanks are used to check for compound carryover. Whenever a sample above 50 ppb was analyzed, the SOP called for an by analysis of a blank. If contamination of the blank had occurred, the system should have been cleaned.

The stability of all VOCs under all sampling conditions is unknown. However, minimal sample losses during collection can occur due to a few processes. Short-term losses of VOCs can occur due to physical adsorption of VOCs on canister walls or dissolution of certain compounds in water that has condensed in the canisters. Some losses can occur from chemical reactions of VOCs with ozone or other gas-phase species that are cocollected. Finally, gradual decreases in VOC concentrations can occur over time due to chemical reactions between VOCs in the canisters or biological degradation (EPA Method TO-15).

5.2.2. Blanks

Environmental Research Institute has reported two types of blanks in their dataset: field blanks and trip blanks. The field blanks were treated in the exact same manner as the field samples, but no air was drawn through the sampler. The trip blanks accompanied the field blanks but differ in that they were left in the sampling vehicle for the duration of sample collection. Field blanks were analyzed from four sites: Bridgeport (6/1999-2/2003), Manchester (3/2001-9/2002), Wallingford (7/2000-4/2001), and Waterbury (7/2002-11/2002). Trip blanks were analyzed at all seven TASC sites: Bridgeport (6/1999-6/2001), Groton (11/2001-11/2002), Hartford (8/1999-4/2001), Manchester (5/2000-2/2003), Voluntown (6/1999-2/2003), Wallingford (10/1999-1/2003), and Waterbury (5/2000-9/2001).

Analysis of the reported VOC blanks data showed that none of the VOCs measured were detected in over 50% of the blanks. Table 5-1 shows the percent of samples that could be detected in field and trip blanks for select VOCs. Table 5-1 indicates that acetone, benzene, and methylene chloride are the only VOCs that were detected in over 30% of the blank samples. It must be noted that this percent detection represents the entire 4-year sampling period.

Table 5-1: Percent Detects for Field and Trip Blanks

VOC	*Percent of Field Blanks with Levels Above DL (%)*	*Percent of Trip Blanks with Levels Above DL (%)*
Dichlorodifluoromethane	2.1	3.6
Chloromethane	0.7	2.1
1,2-Dichlorotetrafluorethane	0.0	0.0
Chloroethene	0.0	0.0
Bromoethane	0.0	0.0
Chloroethane	0.7	0.0
Acetone	48.6	46.2
Trichlorofluoromethane	0.7	2.6
Acrylonitrile	0.0	0.0
1,1-Dichloroethene	0.0	0.0
Methylene Chloride	27.8	38.5
Carbon Disulfide	0.0	0.0
3-Chloro-1-Propene	0.0	0.0
1,1,2-Trichloro-1,2,2-Trifluoroethane	0.7	1.0
trans-1,2-Dichloroethene	0.0	0.0
1,1-Dichloroethane	0.0	0.5
Methyl Tertiary Butyl Ether (MTBE)	0.7	1.5
2-Butanone (MEK)	11.8	8.7
cis-1,2-Dichloroethene	0.0	0.0
Chloroform	0.0	0.0

VOC	*Percent of Field Blanks with Levels Above DL (%)*	*Percent of Trip Blanks with Levels Above DL (%)*
tert-Butyl formate	0.0	0.0
1,2-Dichloroethane	0.7	0.0
1,1,1-Trichloroethane	0.0	0.5
Benzene	30.6	31.3
Carbon Tetrachloride	0.0	0.0
Tertiary Amyl Methyl Ether (TAME)	0.0	0.0
1,2-Dichloropropane	0.0	0.0
Bromodichloromethane	0.0	0.0
Trichloroethene	0.0	0.5
Methyl Methacrylate	0.7	0.5
cis-1,2-Dichloropropene	0.0	0.0
Methyl isobutyl ketone (MIBK)	0.7	0.0
trans- 1,3-Dichloropropene	0.0	0.0
1,1,2-Trichloroethane	0.0	0.0
Toluene	14.6	11.8
Dibromochloromethane	0.0	0.0
1,2-Dibromoethane	0.0	0.0
Tetrachloroethene	0.7	0.0
Chlorobenzene	0.7	2.1
Ethylbenzene	3.5	4.6
m+/or p-xylene	2.1	3.1
Bromoform	0.0	0.0
Styrene	2.1	3.1
o-Xylene	4.2	5.6
1,1,2,2,-Tetrachloroethane	0.0	0.0
1-Ethyl-4-Methyl-benzene	2.1	2.1
1,3,5-Trimethyl Benzene	0.0	0.5
1,2,4-Trimethyl Benzene	0.7	2.1
Chloromethyll Benzene	0.0	0.0
1,3-Dichlorobenzene	0.0	0.0
1,4-Dichlorobenzene	0.0	0.0
1,2-Dichlorobenzene	0.0	0.0
1,2,4-Trichlorobenzene	0.7	0.5
Hexachloro-1,3-Butadiene	0.0	0.5

Table 5-2 and Table 5-3 display the percents of field blanks and trip blanks with levels above the detection limit for three sampling periods. Assuming the analysts followed the same procedure for blank preparation and analysis throughout the sampling campaign, one would expect similar percent detects for all three periods. However, there is a large difference between the numbers of blanks showing VOC levels above the detection limit in 2001 and 2002. This is most pronounced with benzene, where only 2% of field blanks and no trip blanks showed levels above the detection limit in 2001, while 74% and 85% of trip blanks and field blanks, respectively, displayed concentrations above the detection limit in 2002. This same pattern applied to acetone, methylene chloride, and toluene. Other compounds were so rarely detected, this pattern was not discernible.

Table 5-2: Percent of Field Blanks with Levels Above the Detection Limit

Date	*Acetone*	*Methylene Chloride*	*Benzene*	*Toluene*
6/99-12/00	59.5	30.0	2.5	10.0
1/01-12/01	8.5	4.3	2.1	0.0
1/02-2/03	77.2	45.6	73.7	29.8

Table 5-3: Percent of Trip Blanks with Levels Above the Detection Limit

Date	*Acetone*	*Methylene Chloride*	*Benzene*	*Toluene*
6/99-12/00	87.0	85.8	7.4	11.1
1/01-12/01	8.3	4.2	0	2.1
1/02-2/03	72.7	57.6	84.9	21.2

Based on these two tables, there may have been inconsistencies in how blanks were analyzed or how compound peaks were quantified in sample chromatograms during the third calendar year of the study (2001). Since virtually no benzene, acetone, methylene chloride, or toluene was reported in the blanks for this year, it was speculated that many of the chromatogram peaks were not quantified. Further examination of the chromatograms for this year showed several instances of automatic peak integration results being deleted or manually integrated by the analysts. Moreover, it was noted that many small benzene peaks had been ignored in the integration.

Examining the numbers alone, it is clear that the blank concentrations were not correctly characterized in the third calendar year of the study. In an effort to characterize the quality of the benzene and acetone data, the levels of these compounds in the blanks were compared to ambient levels in 2002. Table 5-4 and Table 5-5 display the percent detects, mean concentration, and median concentrations of the field blanks and trip blanks compared to those levels in ambient samples on the same days. Table 5-4 indicates that in this fourth year of analysis, where it has been assumed that the blanks were correctly quantified, blank levels of benzene were almost identical to ambient levels. Acetone levels in the blanks were on the order of three times lower than ambient levels on these days.

The high levels of benzene in the blanks during this third year of sampling yields some concern for the ambient levels reported. Much like what was noted for total chromium concentrations, since levels in the blanks are very similar to ambient levels, the reported levels could be overestimating actual ambient concentrations. Furthermore, these levels in the blanks are well above the HLV proposed for benzene (0.72 ug/m^3) and thus make it impossible to come to any conclusion regarding the health impacts of the actual ambient levels.

Table 5-4: Comparison of Blanks to Ambient Concentrations of Benzene in 2002

	Field Blanks	Ambient Samples on Field Blank Days	Trip Blanks	Ambient Samples on Trip Blank Days
Percent Detected (%)	73.7	92.9	84.9	91.7
Mean Concentration (ug/m^3)	3.7	3.7	3.7	4.2
Median Concentration (ug/m^3)	3.4	3.8	3.6	4.2

Table 5-5: Comparison of Blanks to Ambient Concentrations of Acetone in 2002

	Field Blanks	Ambient Samples on Field Blank Days	Trip Blanks	Ambient Samples on Trip Blank Days
Percent Detected (%)	77.2	100.0	72.7	98.3
Mean Concentration (ug/m^3)	7.7	18.3	6.3	17.9
Median Concentration (ug/m^3)	5.1	15.5	4.4	14.8

5.2.3. Precision

The analysis of collocated samples was limited to those compounds that could be detected in at least half of the samples. Table 5-6 shows the average relative percent difference (RPD) between the collocated sets for these 9 VOCs. The precision for collocated samplers is best for trichlorofluormethane and worst for acetone, from this table. Most of the compounds fall within 25% average relative percent difference between collocated samplers.

Table 5-6: Precision of Select VOCs

VOC	*Average RPD (%)*	*Number of Collocated Sets*
Dichlorodifluoromethane	10.2	149
Chloromethane	15.0	98
Acetone	44.3	162
Trichlorofluoromethane	10.1	104
Methylene Chloride	26.6	85
Methyl Tertiary Butyl Ether	15.1	62
2-Butanone	38.8	109
Benzene	24.2	146
Toluene	35.0	147

5.2.4. Detection Limits

Although 54 VOCs were measured, the majority of these compounds were below the detection limit in a large percentage of the samples reported. Table 5-7 displays the percent of samples collected showing levels above the detection limit for the VOCs measured in the TASC network. This table also shows the average detection limit for these compounds and the proposed annual HLV set by the CT DPH. Those percents in bold red text indicate the organics that were detected in at nearly half or more of the samples. The rows that have been shaded indicate those compounds whose proposed HLVs are near or below the average detection limit of the method and thus not sensitive enough to detect these levels.

Table 5-7: Percent of Samples not Detecting Different VOCs

VOC	*Percent Of Samples Non Detects (%)*	*Average Detection Limit (ug/m3)*	*Proposed Annual HLV (ug/m3)*	*Synonym*
Dichlorodifluormethane	**12.6**	0.835	NA	
Chloromethane	**36.9**	0.615	15	Methyl chloride
1,2-Dichlorotetrafluorethane	99.9	1.394	NA	
Chloroethene	100.0	0.573	1.33	Vinyl chloride
Bromoethane	100.0	0.938	NA	
Chloroethane	92.5	0.525	500	
Acetone	**6.3**	1.307	175	
Trichlorofluoromethane	**32.2**	1.117	NA	
Acrylonitrile	98.9	0.759	0.086	
1,1-Dichloroethene	99.9	0.887	NA	
Methylene Chloride	**50.5**	0.608	12.5	Dichloromethane
Carbon Disulfide	98.7	0.779	350	
3-Chloro-1-Propene	99.2	0.702	NA	
1,1,2-Trichloro-1,2,2-Trifluoroethane	99.1	2.099	NA	
trans-1,2-Dichloroethene	100.0	0.986	NA	
1,1-Dichloroethane	99.8	1.011	NA	
Methyl Tertiary Butyl Ether	**51.7**	1.081	NA	
2-Butanone (MEK)	**35.9**	0.933	500	
cis-1,2-Dichloroethene	99.9	0.986	NA	
Chloroform	99.3	1.464	0.51	
tert-Butyl formate	100.0	1.670	NA	
1,2-Dichloroethane	99.1	1.011	0.23	
1,1,1-Trichloroethane	97.4	1.228	500	Methyl chloroform
Benzene	**10.7**	0.72	0.75	
Carbon Tetrachloride	100.0	1.571	0.78	
Tertiary Amyl Methyl Ether	98.8	0.940	NA	
1,2-Dichloropropane	100.0	1.039	NA	
Bromodichloromethane	100.0	2.009	NA	
Trichloroethene	94.2	1.611	3	Trichlorethylene
Methyl Methacrylate	99.0	0.717	120	
cis-1,2-Dichloropropene	100.0	1.128	NA	

VOC	Percent Of Samples Non Detects (%)	Average Detection Limit (ug/m3)	Proposed Annual HLV (ug/m3)	Synonym
Methyl isobutyl ketone	95.7	1.229	NA	
trans- 1,3-Dichloropropene	100.0	0.904	NA	
1,1,2-Trichloroethane	97.6	1.628	NA	
Toluene	**11.4**	0.659	200	
Dibromochloromethane	100.0	3.407	NA	
1,2-Dibromoethane	100.0	2.293	NA	
Tetrachloroethene	97.3	2.542	2	Perchloroethylene
Chlorobenzene	98.0	1.037	35	
Ethylbenzene	76.6	0.978	50	
m+/or p-xylene	65.9	1.952	215	
Bromoform	99.9	4.391	NA	
Styrene	82.1	0.427	50	
o-Xylene	67.6	0.760	215	
1,1,2,2,-Tetrachloroethane	99.7	1.366	NA	
1-Ethyl-4-Methyl-benzene	92.1	0.738	NA	
1,3,5-Trimethyl Benzene	97.4	1.107	NA	
1,2,4-Trimethyl Benzene	79.7	1.107	NA	
Chloromethyll Benzene	100.0	1.162	NA	
1,3-Dichlorobenzene	99.5	1.347	NA	
1,4-Dichlorobenzene	98.0	0.900	NA	
1,2-Dichlorobenzene	99.3	1.197	NA	
1,2,4-Trichlorobenzene	98.3	2.588	NA	
Hexachloro-1,3-Butadiene	98.6	4.507	NA	

Table 5-7 indicates that the detection limits for acrylonitrile, chloroform, carbon tetrachloride, tetrachlorothene, and 1,2-dichloroethane are above the levels deemed hazardous by the CT DPH. The benzene detection limit is essentially at the proposed HLV while chloroethene and trichloroethene MDLs are within a factor of three of their proposed HLVs. Therefore, levels of these compounds could be at or above the HLV, but not detected due to lack of sensitivity of the method. Newer methods including longer sampling times or more sensitive detection techniques should be explored so the detection limit can be lowered to a level well below the proposed HLVs.

Table 5-7 shows that the majority of VOCs measured could not be detected across the state. Due to this, the eight most prevalent (in ~50% or more of the total number of samples): VOCs detected were examined dichlorodifluoromethane, chloromethane, acetone, trichlorofluoromethane, methylene chloride, methyl tertiary butyl ether (MTBE), 2-butanone (MEK), and toluene.

5.3. Analysis of Monitored Concentrations

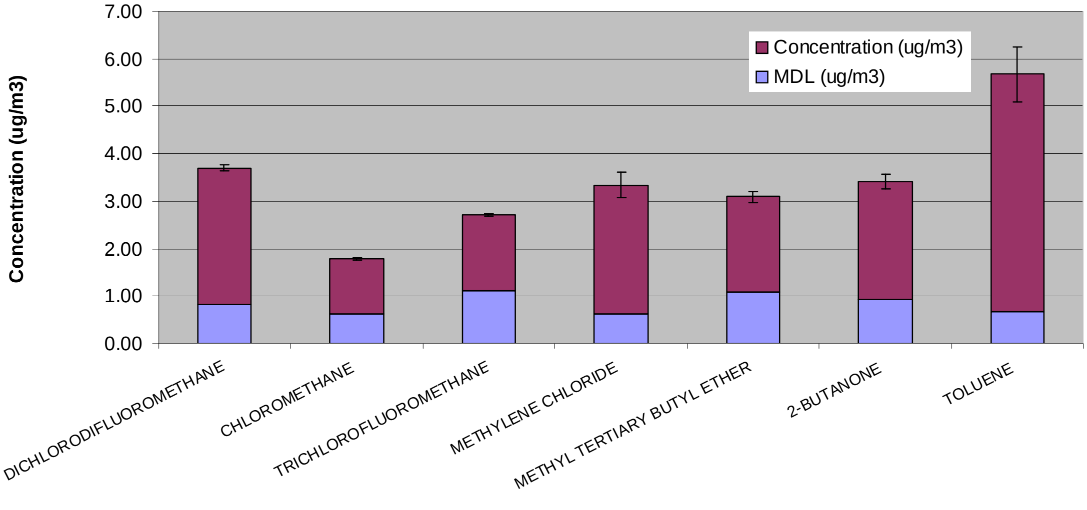
5.3.1. TASC Monitored Concentrations

Overall Connecticut Levels

The issue of non-detect samples for VOCs was addressed consistently with the other compound classes in the report. Samples showing levels below the detection limit were assigned a value of the detection limit. Therefore, all concentrations may represent the maximum possible ambient concentration. This was done to provide a conservative measure of ambient concentration.

Figure 5-1 shows the overall Connecticut concentrations of seven VOCs that were detected in over half of the samples. As Figure 5-1 indicates toluene is at the highest concentration across the state, followed by dichlorodifluoromethane and benzene. The majority of the compounds sampled were left out of analysis since they were not detected in most of the samples. Acetone was left off of this table since its concentration level was higher than the rest of the VOCs (4-year average- 19.68+/-0.76 μg/m^3 (95%CI))[20].

Figure 5-1: Overall 4-Year Connecticut Mean Based on TASC Monitoring



Seasonal Variation

There was no consistent seasonal trend for the various VOCs measured in Connecticut (Figure 5-2). In general the majority of VOCs showed no appreciable variation across the different seasons. Toluene showed a slightly higher mean concentration in the fall while acetone (not pictured) showed higher concentrations in the summer and spring. Chloromethane, dichlorodifluoromethane, methylene chloride, chloromethane, and 2-butanone all showed slightly higher levels in the summer and spring than in the fall and winter.

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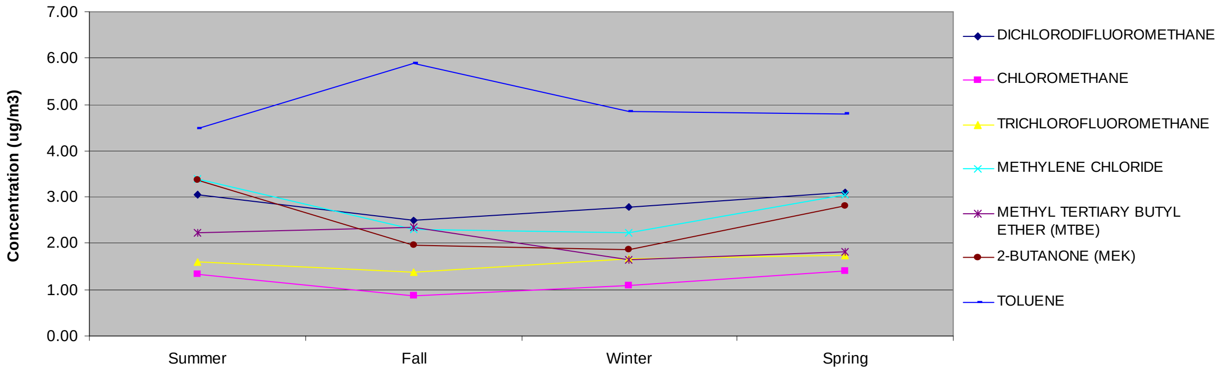
[20] Inclusion would have changed the y-axis scale, making the other bars appear small. Note the ambient monitored level reported here is low when compared to the proposed HLV for acetone (175 μg/m^3). In addition, acetone blank levels were substantial, as shown in Table 5-5.

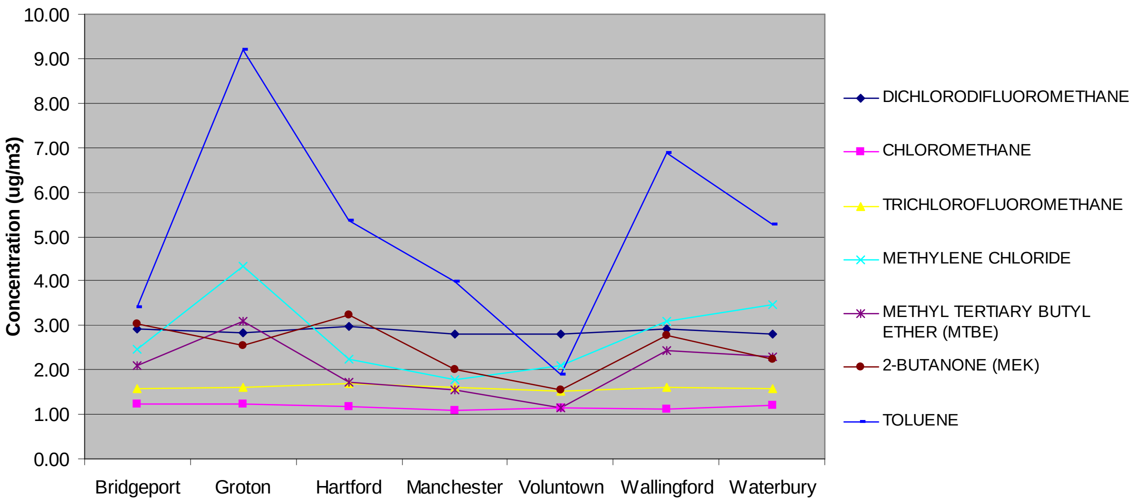
Figure 5-2: Seasonal Variation of Various VOCs



Site Variation

Of the VOCs detected in over half of the TASC samples, toluene showed the most site to site variability (Figure 5-3). Its levels were highest in Groton and Wallingford, while levels were lowest at the background site in Voluntown. This same site to site trend was seen for 2-butanone and MTBE. The remaining VOCs analyzed did not show appreciable inter-site variability.

Figure 5-3: Site Variation of Various VOCs



Monitored Data Compared to Connecticut's HLVs

The 4-year averaged concentrations for four compounds showed overall monitored levels to be below the HLVs proposed by the CT DPH. Chloromethane and methylene chloride levels were roughly 5-10 times lower than their proposed HLVs while ambient levels of toluene and 2-butanone were two orders of magnitude lower than their proposed HLVs. Significant uncertainty in benzene levels due to blanks contamination indicates that further sampling may be required to properly assess the levels of benzene at these monitoring sites. Since the MDL of the method used here was similar to the proposed annual HLV, improved methods of sampling and analysis should be explored to give better determinations of actual benzene levels and public health impacts.

5.3.2. PAMS Monitored Concentrations

VOC concentrations were monitored hourly by the Photochemical Assessment Monitoring Stations (PAMS) at four sites in Connecticut: East Hartford, Hamden, Sherwood Island, and Stafford. Appendix B displays a table with all of the VOCs measured at these sites from 1999 until 2001. Hourly measurements were only made from May 1st until September 30th every year and the percent of samples above the detection limit are tabulated. This table indicates that contrary to TASC sampling efforts, most compounds could be detected in over 50% of the samples. However, the suite of target compounds is quite different.

The annual summertime mean concentrations for the VOCs measured at PAMS sites in Connecticut are found in Figure 5-4, Figure 5-5, Figure 5-6 and Figure 5-7. These averages were obtained from an analysis of PAMS data performed by Sonoma Technology Inc. (Petaluma, CA). In general, earlier sampling years tended to show higher concentrations of VOCs than later years. The data indicates that in East Hartford, propane, isopentane, toluene, and the xylenes were at higher concentrations than the other VOCs measured. Hamden, Sherwood Island, and Stafford also showed higher concentrations of these compounds, while showing much higher levels of isoprene. Note that the concentrations shown in Figures 5.5 to 5.8 are in ppbC, not ug/m^3.

Figure 5-4: Annual Summertime Means of VOCs in East Hartford

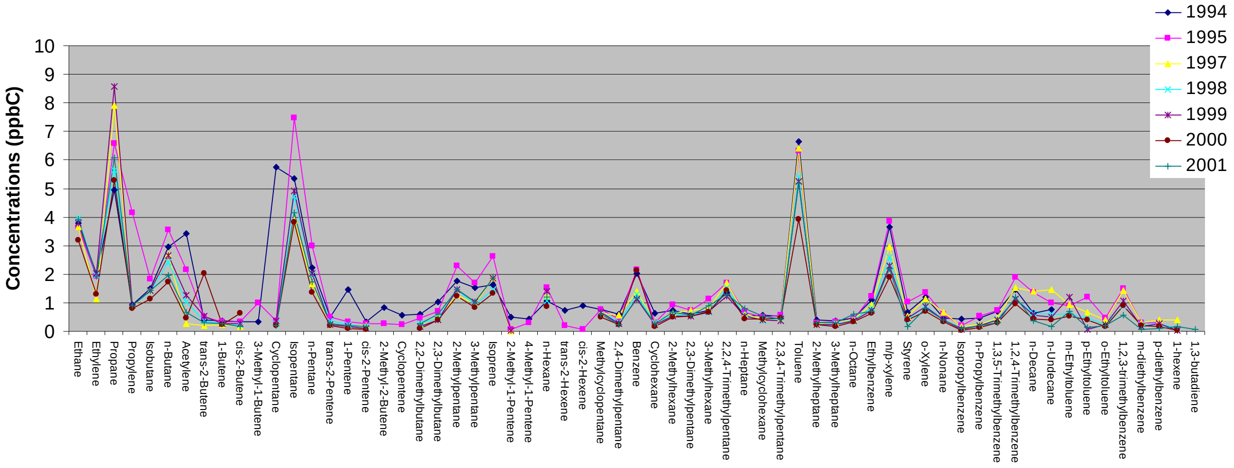


Figure 5-5: Annual Summertime Means of VOCs in Hamden

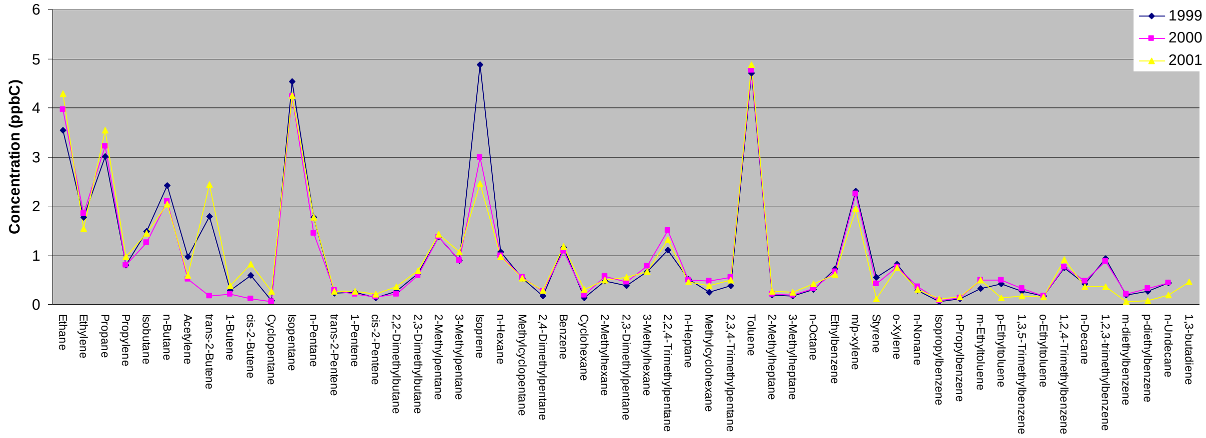


Figure 5-6: Annual Summertime Means of VOCs in Sherwood Island

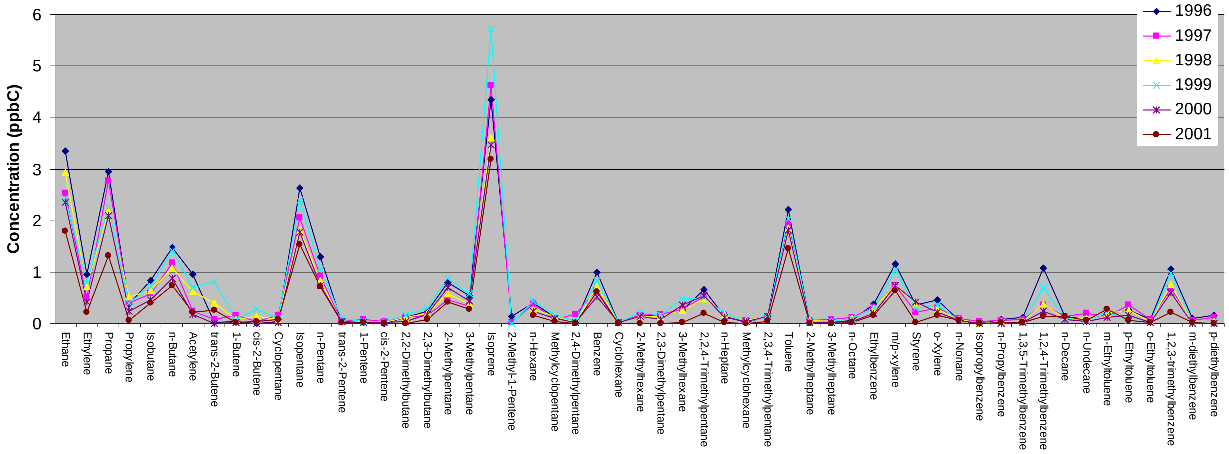


Figure 5-7: Annual Summertime Means of VOCs in Stafford

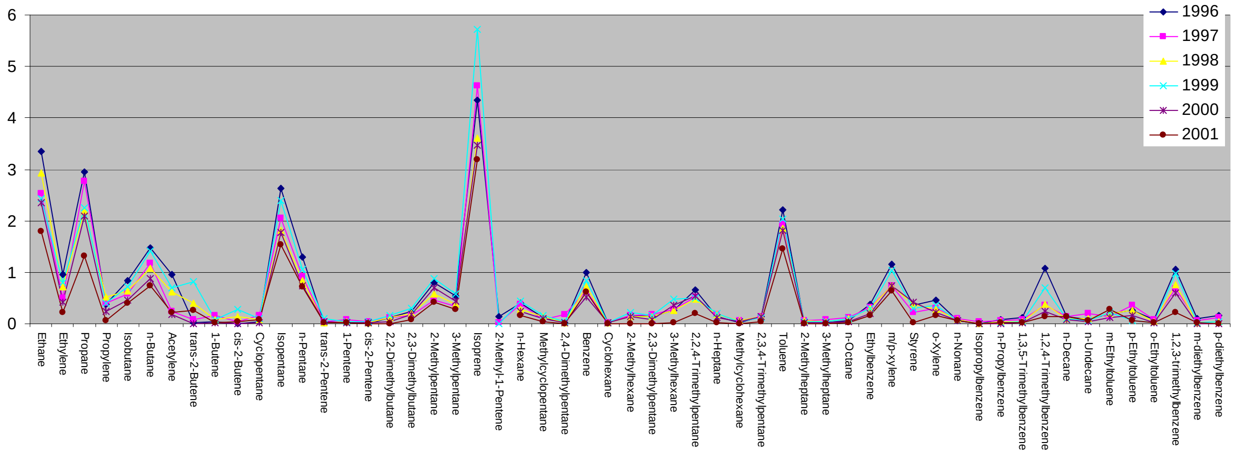


Figure 5-8, Figure 5-9, Figure 5-10 and Figure 5-11 display the mean hourly concentrations for the four PAMS sites in Connecticut. These values were obtained by calculating the average concentration at each hour across every day in the summers of 1998-2001. At all the sites, for the majority of compounds, peak concentrations occurred at around 6am while the lowest concentrations occurred between 2 PM and 4 PM. In East Hartford, Hamden, and Sherwood Island concentrations of virtually all the VOCs began to rise after 7pm. The high levels in the morning may be attributed to overnight buildup in the boundary layer. Concentrations are expected to decrease into the afternoon due to decreased emissions, higher rate of chemical removal due to increased sunlight, and more dilution due to the increasing height of the boundary layer. In the evening one would expect concentrations to increase again due to increased emissions from afternoon rush hour traffic and decreased chemical removal and oxidation with decreased sunlight.

Figure 5-8: Hourly Mean Concentrations of VOCs in East Hartford

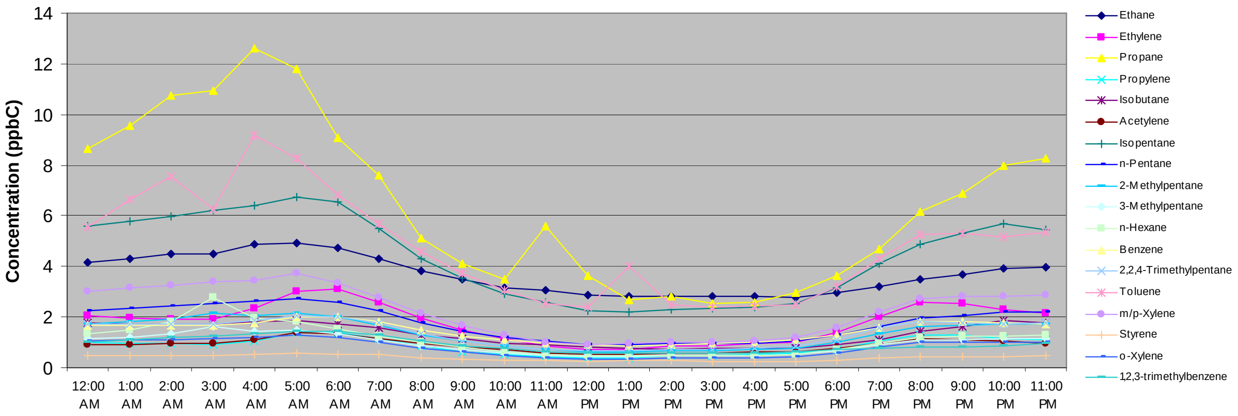


Figure 5-9: Hourly Mean Concentrations of VOCs in Hamden

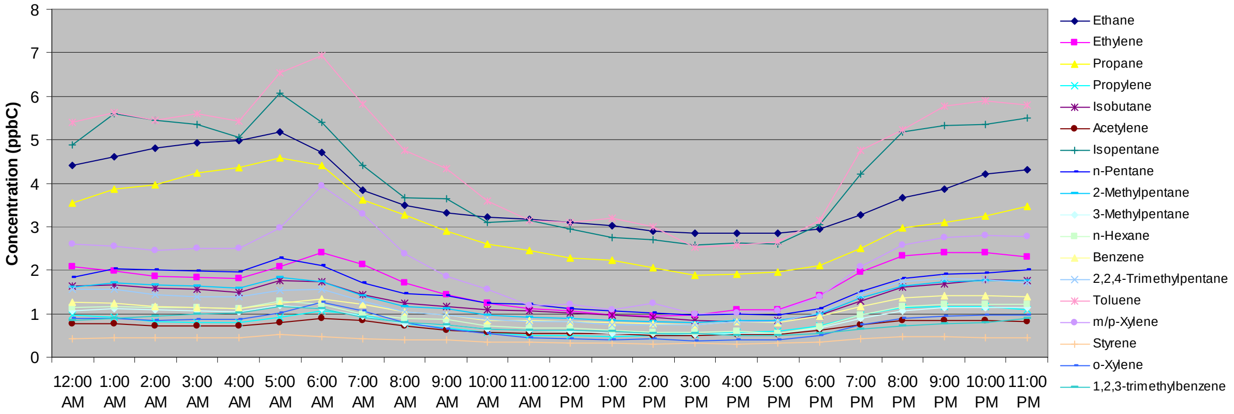


Figure 5-10: Hourly Mean Concentrations of VOCs in Sherwood Island

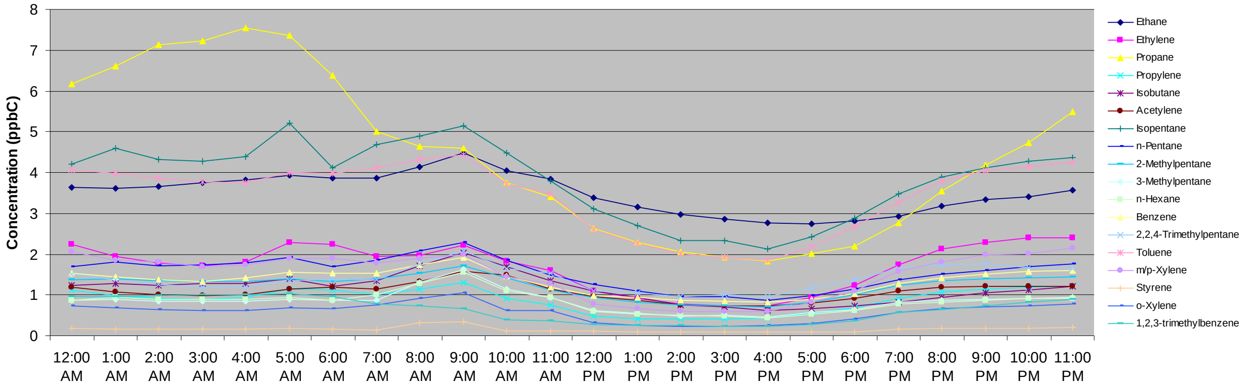
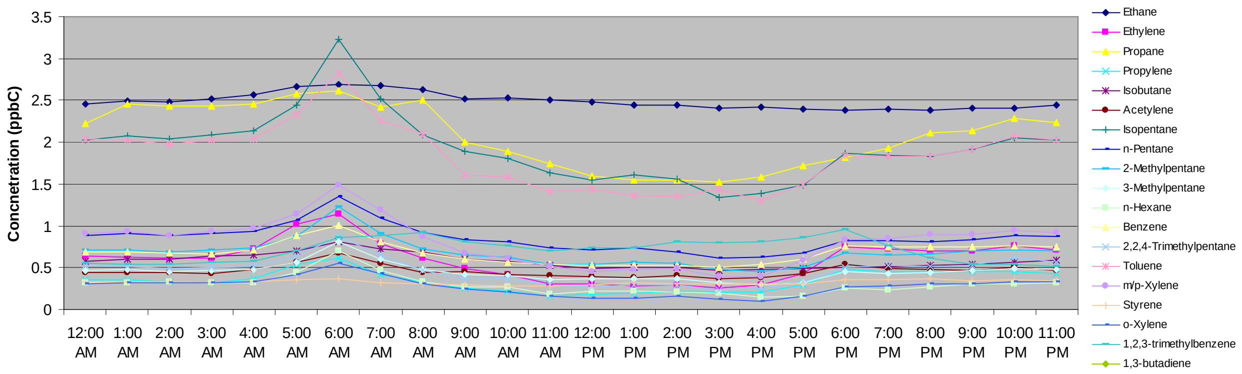


Figure 5-11: Hourly Mean Concentrations of VOCs in Stafford



5.3.3. Comparison of TASC Data to PAMS Data

Levels of toluene were compared between TASC and PAMS sites in the same counties. Therefore, Hartford and Manchester TASC concentrations were compared to East Hartford PAMS concentrations, Bridgeport TASC was compared to Sherwood Island PAMS, and Wallingford TASC was compared to Hamden PAMS concentrations. The comparison of the median concentrations for each year is seen in Table 5-8.

Since PAMS samples were only taken in the summer, there were a very limited number of TASC samples available for the comparison as samples were only taken weekly at these sites. For TASC sites, there were between 8 and 20 samples taken each summer depending on the year and the site analyzed. In contrast, there were between 1200 and 2200 hourly samples taken at the PAMS sites for the same time periods. This large difference in sample size should be kept in mind when comparing TASC and PAMS summertime concentrations. Additionally, inherent differences exist between the in-situ sampling of the PAMS program and the canister sampling employed by TASC. To mitigate the effect of outliers in the TASC data, median concentrations were reported and compared.

Table 5-8: Comparison of Summertime Median Concentrations of Toluene for Sites in the Same County. (concentrations in ug/m^3)

Year	Hartford TASC	East Hartford PAMS	TASC/PAMS
1999	3.58	1.66	2.15
2000	8.59	2.10	4.08
2001	NA	1.29	NA
2002	2.73	1.55	1.76
Year	Bridgeport TASC	Sherwood Island PAMS	TASC/PAMS
1999	2.79	1.19	2.35
2000	2.33	1.28	1.83
2001	3.01	1.18	2.55
2002	3.03	1.13	2.68
Year	Manchester TASC	East Hartford PAMS	TASC/PAMS
1999	6.01	1.66	3.61
2000	2.11	1.45	1.46
2001	3.15	1.29	2.44
2002	3.19	1.55	2.06
Year	Wallingford TASC	Hamden PAMS	TASC/PAMS
1999	NA	1.74	NA
2000	5.37	1.72	3.13
2001	4.33	1.52	2.85
2002	3.35	1.69	1.98

TASC concentrations of toluene were between 1.5 and 4 times higher than PAMS sites in the same county. The level of agreement between sites seemed to differ depending on the summer sampled. There are several possible explanations for the differences between TASC and PAMS concentrations. First, as mentioned before, only 8 to 20 samples were used to characterize median concentrations at TASC sites as opposed to the thousand or more used in PAMS site characterization. The low sample size would increase the level of uncertainty in characterizing the entire summer. Second, the position of the samplers in relation to stationary sources or roads and highways would have a significant effect on the concentrations reported. TASC sites were chosen to characterize areas around Title V sources and therefore may be subject to different source mix of VOCs than the PAMS sites. Finally, differences could be due to the different sampling protocols, with PAMS samples being collected *in situ* and directly analyzed in the field; TASC used canister sampling.

To better constrain these observed differences, a second comparison of the PAMS and TASC networks was performed using reported concentrations from identical days. Table 5-9 shows median values from days where both TASC and PAMS sampling occurred. Comparing values from the same day shows substantially better agreement between the two networks. The ratios of this approach are in most instances half of those using all PAMS data and are much closer to one to one. However, it is not expected that the two networks would show the same levels for reasons previously stated. In general, the PAMS samplers are further removed from both point and mobile sources and should exhibit lower ambient concentrations, consistent with this analysis.

Table 5-9: Comparison of TASC and PAMS concentrations on the same day

Year	*Hartford TASC*	*East Hartford PAMS*	*TASC/PAMS*
1999	3.48	3.04	1.14
2000	5.3	2.63	2.02
Year	*Bridgeport TASC*	*Sherwood Island PAMS*	*TASC/PAMS*
1999	2.62	2.58	1.01
2000	2.33	3.21	0.73
2001	3.30	2.42	1.36
Year	*Manchester TASC*	*East Hartford PAMS*	*TASC/PAMS*
1999	12.29	2.82	4.36
2000	2.00	2.80	0.71
Year	*Wallingford TASC*	*Hamden PAMS*	*TASC/PAMS*
2000	5.46	2.93	1.86
2001	4.52	2.85	1.59

The TASC VOC data set is the least certain of the four compound classes sampled. During 2001, quality assurance issues were identified by looking at blank samples. This seemed to impact benzene more than other VOCs. The data comparison between TASC and PAMS for toluene shows reasonably agreement, which provides some confirmation that data quality for this compound may be acceptable. Since very few species were observed on blank samples, and reported toluene concentrations are reasonable, the results for the few other VOCs detected should be considered satisfactory.

The levels for chloromethane, methylene chloride, toluene, acetone and 2-butanone appear to be below the proposed HLVs for those chemicals. A number of other compounds were not detected and are therefore also not expected to cause concern. However, the sampling and analytical protocols used in TASC lack the sensitivity to characterize eight other VOCs on the target list. These are the compounds with the most stringent proposed HLVs, including benzene. Therefore, planning for future efforts should take the limitations of the current study into consideration.

6. COMPARISON OF CONNECTICUT DATA WITH EPA MODELED PREDICTIONS

6.1. Introduction

Monitoring data from the TASC network were compared to predicted county-level hazardous air pollutant (HAP) concentrations generated by EPA's 1996 national assessment. EPA used the Assessment System for Population Exposure Nationwide (ASPEN) model, a Gaussian dispersion model based on EPA's Human Exposure model, a tool used to model long term concentrations over large spatial scales. Gaussian models are used by EPA and others as the standard approach for estimating outdoor concentrations of air pollutants within 50 kilometers of an emissions source. Long-term average concentrations of HAPs were calculated at the census tract level based on frequencies of various meteorological conditions and emissions rates of HAPs for all major source categories for 1990 (for 148 air toxics), and subsequently for 1996 (for 32 air toxics). The distribution of total modeled HAP concentrations across the country revealed top quartile concentrations occurring in the industrialized areas of the West and East Coasts, around the Great Lakes, and along the Gulf of Mexico. Emissions and estimated concentrations are generally higher in urban than in rural areas. Some pollutants are more evenly distributed around the country while others are linked to areas of industrial activity. Considerable variability of source type contributions was found between national, state, and county levels (Woodruff *et al.* 1998; Rosenbaum *et al.* 1999; EPA 2002).

The 1996 National Toxics Inventory (NTI) is the basis for the emissions used in the national assessment. The NTI consists of emission estimates for four source types: major, area and other, on-road mobile, and non-road mobile. Major sources are defined as stationary facilities with the potential to emit over 10 tons of a single air toxic or over 25 tons of more than one toxic air pollutant per year. Area sources were defined as smaller emitting facilities that emit below the major source threshold. Other modeled emissions include non-specific sources such as wildfires. On-road mobile sources refer to vehicles found on roads or highways while non-road mobile sources refer to those not found on roads and highways.

The EPA compiled the 1996 NTI using five primary data sources including EPA's Toxic Release Inventory, state and local toxic air pollutant inventories, emissions estimates generated from emission factors and activity data, and existing EPA air toxics databases. Mobile source emissions estimates were developed using mobile source emission models including MOBTOX5b and NONROAD as well as a speciation approach based on fuel types and emission factors.

In general, ASPEN's modeled concentrations using the 1996 National Toxics Inventory (NTI) emission estimates and estimates for background concentrations were lower than measured ambient annual average concentrations when evaluated at the exact location of the monitors. However, when the maximum modeled estimate for distances up to 10-20 km from the monitoring location were compared to the measured concentrations, the modeled estimates were closer to the monitored concentrations. This result can be attributed, in part, to spatial uncertainty of the underlying emissions and meteorological data, and the tendency of current air toxics monitoring networks to typically characterize the higher if not highest air pollution impact areas in the ambient air. It also shows that the model estimates are more uncertain at the census tract level but are more reliable for larger geographic scales. Nevertheless, modeled estimates at numerous locations were significantly lower than the measured concentrations even at distances up to 50 km. For these instances, the difference between modeled and monitored concentrations may be attributed to underestimated or missing emissions data and uncertainty in chemical transformation of reactive species (e.g. aldehydes) (EPA 2002).

Because ASPEN results are designed to represent spatial and temporal averages over each tract, peak values that might occur very near sources are not captured by the model. Such higher ambient levels might be expected when monitoring near local point sources or in more densely populated urban areas (Rosenbaum *et al.* 1999; Bortnick and Stetzer 2002). Other limitations to ASPEN likely contribute to underestimations of pollutant concentrations. These include a neglect of calm wind conditions, poor representation of stable atmospheric conditions that occur at night, and a 50 km downwind distance. Increased model uncertainty is also attributed to incomplete emissions inventories. Consistent underestimations of hazardous air pollutants indicate many emission sources may be absent from the inventory (Rosenbaum *et al.* 1999).

This analysis focuses on compounds within the four categories sampled by the TASC network: carbonyls, PAHs, metals, and VOCs. Monitored levels of formaldehyde and acetaldehyde were chosen for comparison from the carbonyls category due to their high ambient levels. PAH levels are described by ASPEN as a sum of the seven carcinogenic PAH compounds (7-PAH). TASC levels were therefore summed in this manner for the analysis. Of the metals, manganese, nickel, lead, and arsenic levels were compared to modeled concentrations. The other metals modeled by ASPEN, cadmium and beryllium, were found at monitored levels that were too low to draw a meaningful comparison. Benzene was the only VOC modeled by ASPEN. Given the uncertainty in its measured TASC concentrations, no comparison to modeled data was conducted.

6.2. Carbonyls

With respect to formaldehyde and acetaldehyde, ASPEN estimates across the United States tended to be lower than monitor averages, although typical values agreed within a factor of 2. Overall, a large fraction of aldehyde monitors could not be associated with larger modeled values (even within 50 km), suggesting systematic underestimation by the modeling system for the aldehydes, at least for some areas (EPA 2002).

Comparison of the 4-year overall Connecticut concentrations of formaldehyde and acetaldehyde to those modeled by ASPEN for 1996 shows that modeled values were lower than monitored values (Figure 6-1 and Figure 6-2). The overall Connecticut median modeled value was 1.4 times lower than the monitored level for formaldehyde and 1.9 times lower for acetaldehyde.

Figure 6-1 Comparison of 4-year average monitored Connecticut formaldehyde concentrations to the 1996 ASPEN modeled concentrations (percent distribution).

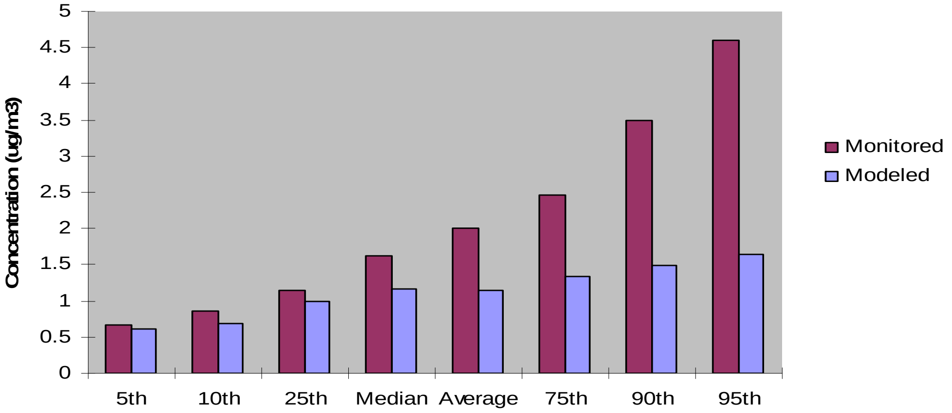


Figure 6-2 Comparison of 4-year average monitored Connecticut acetaldehyde concentrations to the 1996 ASPEN modeled concentrations (percent distribution)

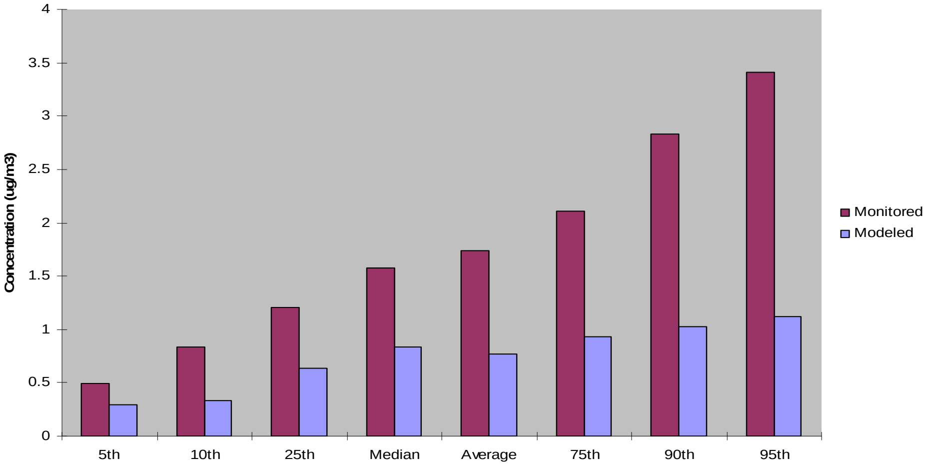


Figure 6-3 and Figure 6-4 display TASC mean annual (covering the entire available data collection period) concentrations of formaldehyde and acetaldehyde to EPA ASPEN modeled mean annual (1996) and 95th percentile concentration (by county). TASC average levels are substantially higher than EPA mean annual and 95th percentile levels at each of the seven sites. TASC monitored concentrations and EPA's predicted concentrations display some degree of variability, although Wallingford and Manchester formaldehyde levels, and Hartford and Manchester acetaldehyde levels are exceptions. Both of these paired sites show different behavior between TASC and EPA. For example, TASC formaldehyde concentrations in Wallingford are considerably higher relative to other sites, while EPA predicted concentrations for Wallingford are not. The opposite pattern occurs at Manchester. Voluntown formaldehyde concentrations are lowest for both EPA and TASC.

Figure 6-3 Comparison of TASC mean annual concentration of formaldehyde (by site) to EPA ASPEN modeled mean annual and 95th percentile concentration (by county)

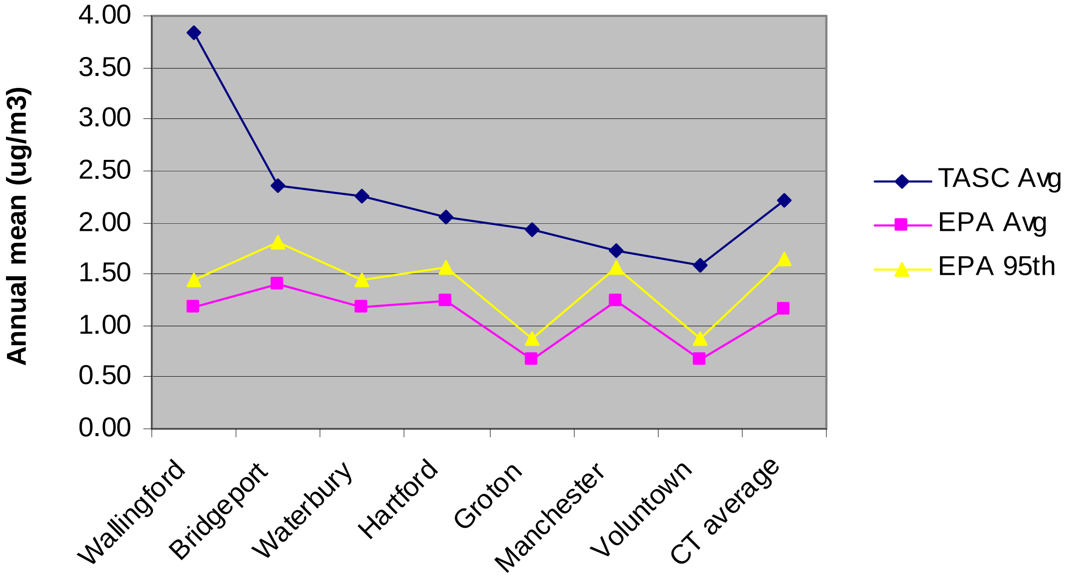
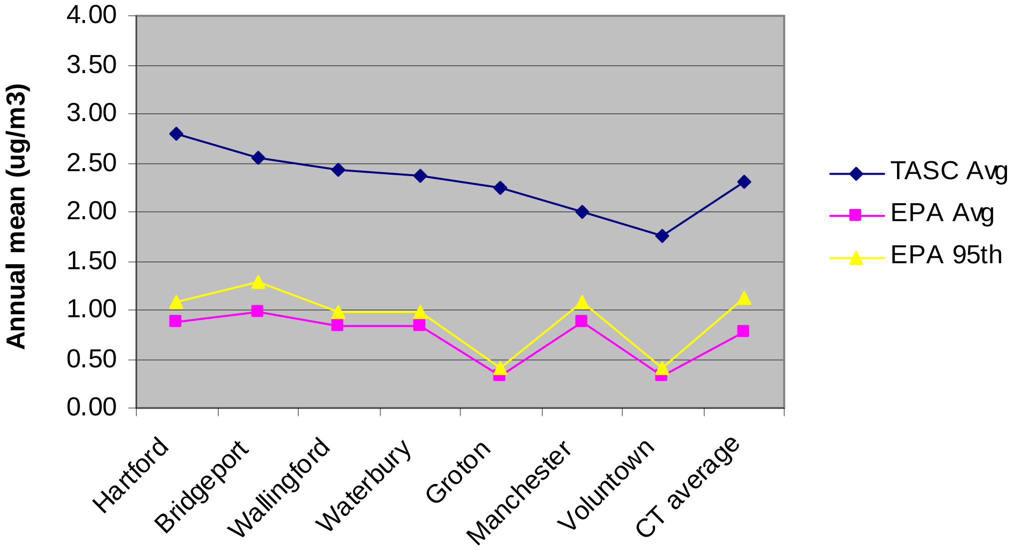


Figure 6-4 Comparison of TASC mean annual concentration of acetaldehyde (by site) to EPA ASPEN modeled mean annual and 95th percentile concentration (by county)



Given that carbonyls are both primary and secondary pollutants, the consideration of background ubiquity must be taken into account when comparing TASC and ASPEN formaldehyde and acetaldehyde values for selected counties in Connecticut. EPA considers background concentrations to consist of contributions to outdoor concentrations resulting from natural sources, persistence in the environment, and long-range transport (EPA 2002).

Figure 6-5 and Figure 6-6 provide estimated source contributions to EPA's modeled mean annual average concentrations of formaldehyde and acetaldehyde, respectively. Figure 6-5 shows that estimated background levels of formaldehyde uniformly contribute 0.25 µg/m3 of the total mean annual average across sites, which represents a range across sites of 18% to 37% of the total modeled concentrations. Onroad and nonroad mobile sources comprise from 34% to 43% and 20% to 42% of the average source contribution, respectively. Other area sources contribute only 4% to 9%. Major source contributions are negligible. Comparing EPA New Haven County formaldehyde estimated source contributions to TASC monitored concentrations (as shown in Figure 6-3) suggests the possibility of a large industrial source influence not represented by EPA estimates. This reflects the earlier observation that these are countywide modeled estimates, whereas TASC is more fenceline impact. Figure 6-6 shows no background contribution to acetaldehyde average levels. Onroad and nonroad mobile sources make up from 60% to 67% and 24% to 35%, respectively; area sources comprise 5% to 9%. No major source contributions for acetaldehyde were modeled.

Figure 6-5 EPA estimated source contribution to modeled mean annual concentrations of formaldehyde in Connecticut (1996)

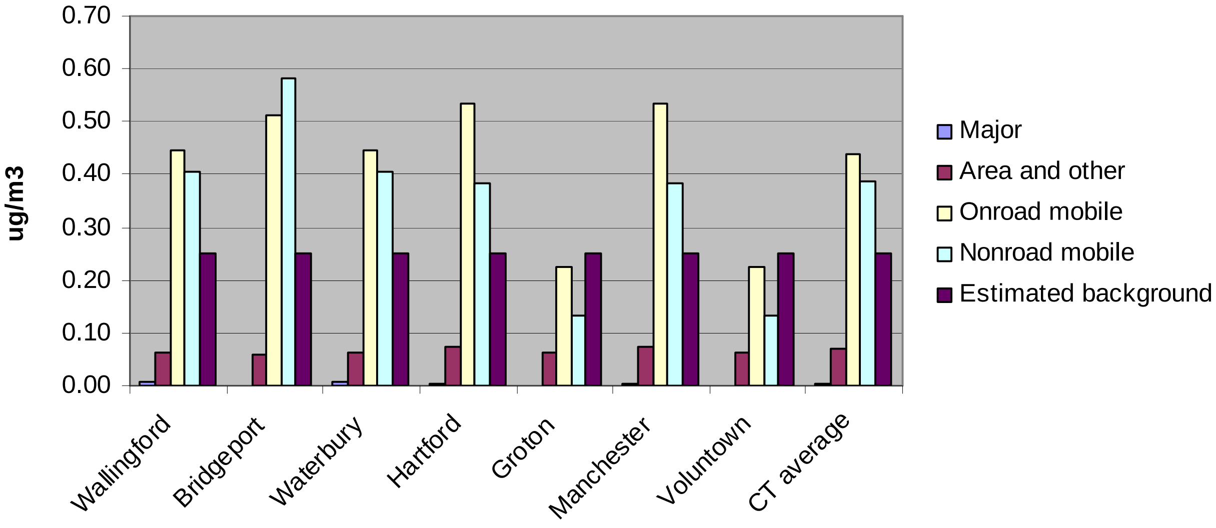
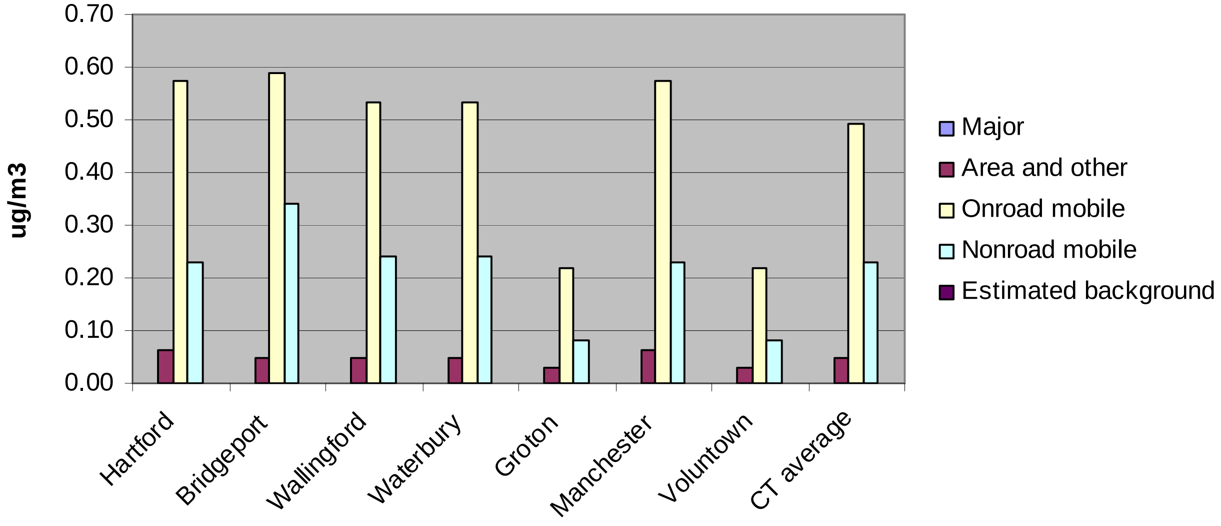


Figure 6-6 EPA estimated source contribution to modeled mean annual average concentrations of acetaldehyde in Connecticut (1996)



6.3. Metals

6.3.1. Manganese

Comparison of the 4-year overall Connecticut concentrations of manganese to those modeled by ASPEN for 1996 shows that modeled values were much lower than monitored values (Figure 6-7). The overall Connecticut median modeled value is about 9 times lower than the monitored level.

Figure 6-7 Comparison of 4-year average monitored Connecticut manganese concentrations to the 1996 ASPEN modeled concentrations (percent distribution).

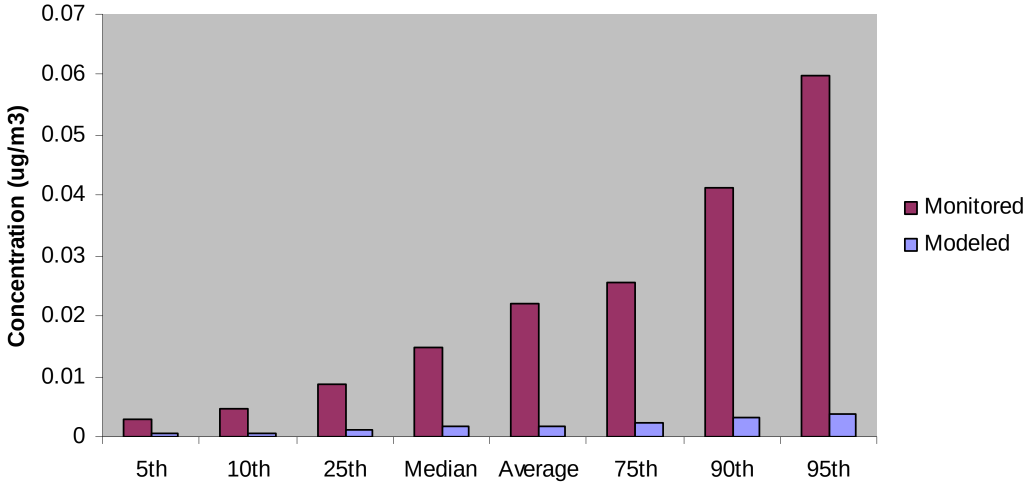


Figure 6-8 and Figure 6-9 display the mean annual (4-year TASC, 2002 IMPROVE) concentrations of manganese at the seven TASC sites and one IMPROVE site (Mohawk Mountain) in comparison to the 1996 ASPEN modeled means and 95th percentile. These figures show that the mean monitored manganese concentrations at all the sites are higher than the upper 95th percentile of the 1996 ASPEN modeled concentrations. The TASC monitored values indicate the highest manganese concentrations occur in Groton, while the lowest occur in Voluntown. No model difference is indicated between these two sites since the modeled data are presented on a county by county basis and both towns are in New London County. According to the 1996 ASPEN modeled results, Litchfield County shows the lowest values (Mohawk Mountain), while New Haven County (Wallingford and Waterbury) shows the highest modeled concentrations.

Figure 6-8 Comparison of CT monitored manganese concentrations to ASPEN modeled levels for seven TASC sites and one IMPROVE site.

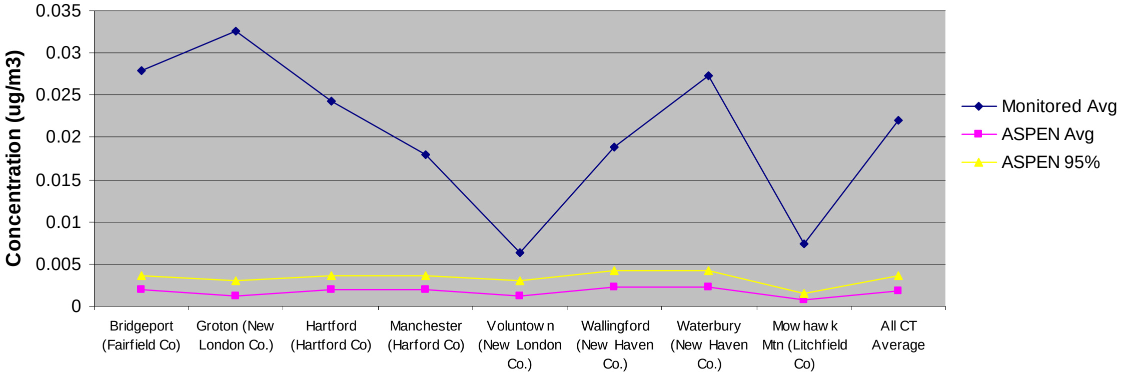


Figure 6-9 1996 ASPEN modeled manganese levels for CT counties

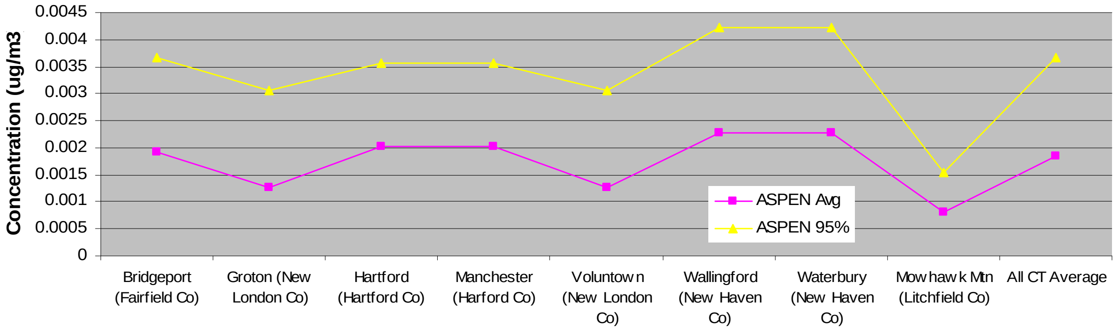
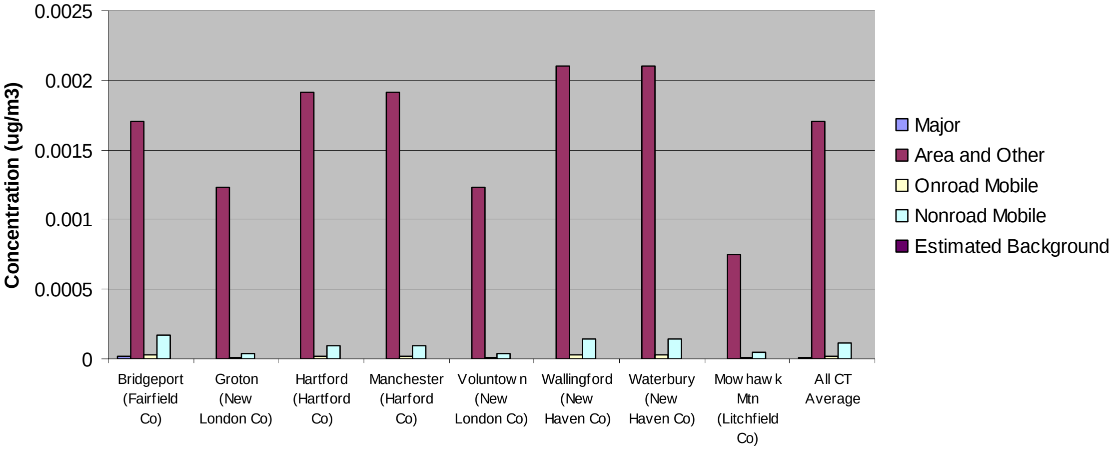


Figure 6-10 shows estimated source contributions to EPA's modeled annual mean concentration of manganese. Area sources are expected to dominate with lesser contributions from nonroad mobile.

Figure 6-10 EPA estimated source contribution to modeled mean annual concentration of manganese in Connecticut.



6.3.2. Nickel

Comparison of the 4-year overall Connecticut concentrations of nickel to those modeled by ASPEN for 1996 showed that modeled values were lower than monitored values (Figure 6-11). The difference was not as pronounced as that seen for manganese as the overall Connecticut median modeled value was about 2.4 times lower than the monitored level.

Figure 6-11 Comparison of 4-year average monitored Connecticut nickel concentrations to the 1996 ASPEN modeled concentrations (percent distribution).

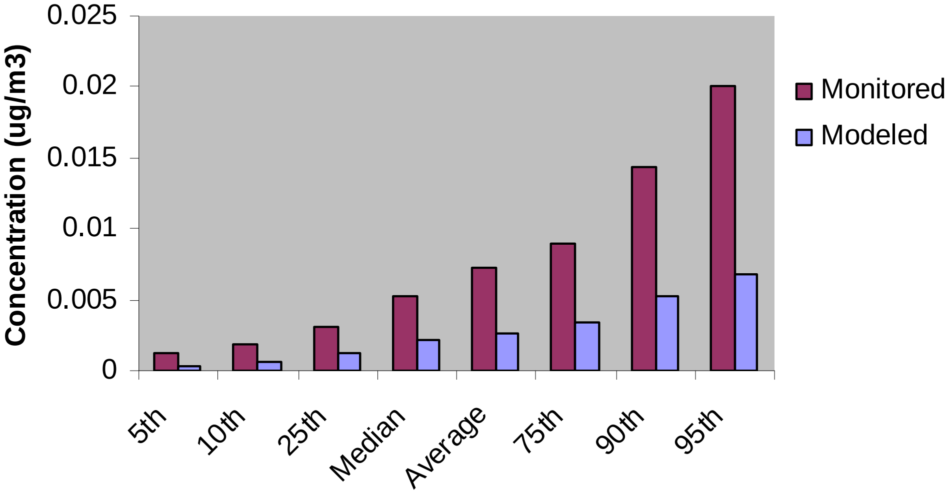
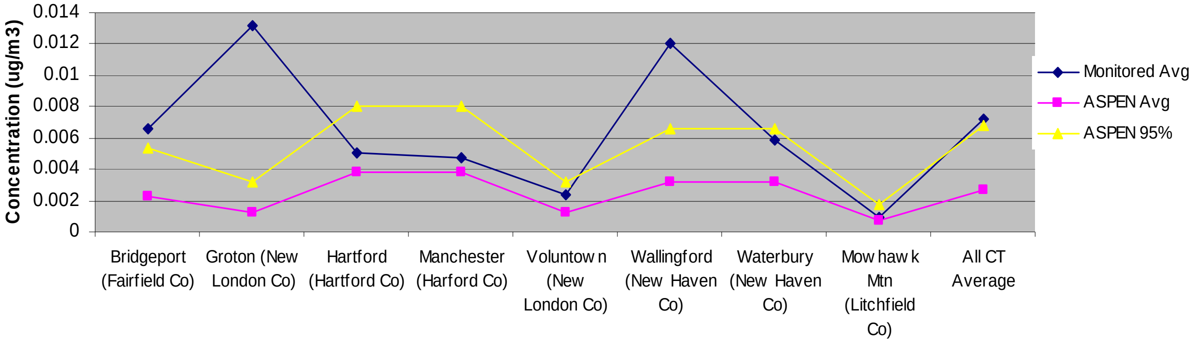


Figure 6-12 displays the mean annual (4-year TASC, 2002 IMPROVE) concentrations of nickel at the seven TASC sites and one IMPROVE site in comparison to the 1996 ASPEN modeled means and 95th percentile. Unlike manganese, nickel levels are higher than the ASPEN modeled 95th percentile at only three TASC sites: Bridgeport, Groton, and Wallingford. The TASC monitored levels show the highest 4-year mean at Groton and Wallingford with the lowest mean in Voluntown. The 1996 ASPEN modeled results show the highest values in Hartford County (Hartford and Manchester) followed closely by New Haven County (Walllingford and Waterbury). Since the ASPEN analysis gave estimates by county, the highest and lowest concentrations from TASC sites (Groton and Voluntown) could not be differentiated since they are both in New London County.

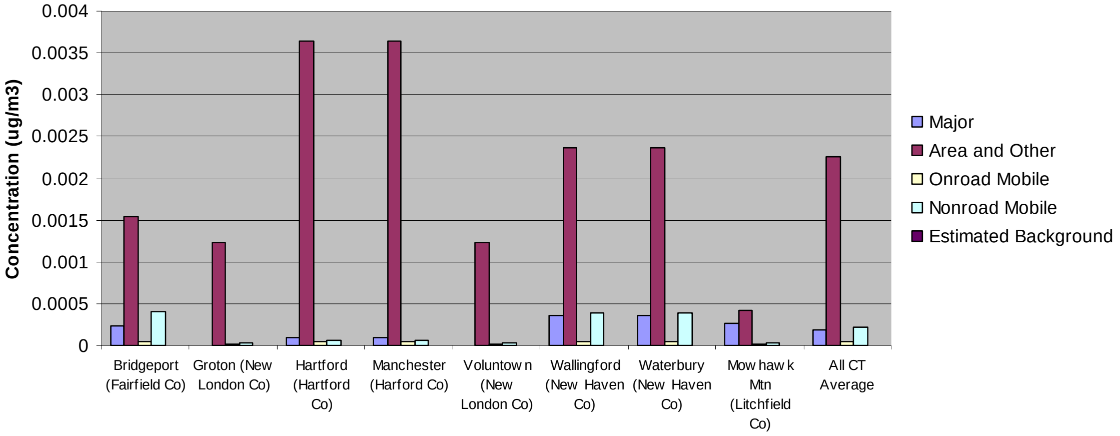
Figure 6-12 Comparison of monitored nickel concentrations to ASPEN modeled levels for seven TASC sites and one IMPROVE site.



The agreement between the modeled levels and TASC monitored levels was best in Hartford County (Hartford and Manchester) and Voluntown. The ratio of the two measurements was between 1.2 and 1.8 for these three sites. The largest ratio between the modeled and monitored means was found in Groton where the monitored levels were ten times higher than the modeled levels for that county. This is most likely attributed to the proximity of the monitoring site to sources in that town. These higher levels would not be as apparent when modeling levels throughout the entire county. The IMPROVE monitored concentrations showed good agreement (ratio of 1.2) with the modeled values provided by ASPEN.

Figure 6-13 shows estimated source contributions to EPA's modeled annual mean concentrations of nickel. According to the 1996 ASPEN estimates, area sources dominate nickel contributions for all sites, ranging from 69% to 96%. Major sources contributed up to 11% of the modeled annual mean, with the highest major source contributions occurring in Wallingford, Waterbury, and Bridgeport. Non-road mobile sources also showed significant contributions in Bridgeport and New Haven County (Wallingford and Waterbury), contributing 18% and 12% to the annual mean, respectively. This modeled data suggests than large stationary sources and mobile sources have little input into total nickel concentrations in New London County and Hartford County. Like manganese, the modeled data indicate no background sources of nickel in the state.

Figure 6-13 EPA estimated source contribution to modeled mean annual concentration of nickel in Connecticut.



6.3.3. Arsenic

Arsenic levels determined by TASC monitoring showed much higher levels than predicted by the 1996 ASPEN model. Figure 6-14 shows the comparison between monitored and modeled arsenic in Connecticut. The median modeled arsenic level for 1996 was about 15 times lower than the 4-year annual statewide monitored median for all TASC sites combined. It should be noted that the detection limit for Arsenic was greater than the modeled values and went undetected in just over half the samples. Based on this, the monitored values in the figure are likely overestimates of the true ambient levels with the exception of the three rightmost bars (75th, 90th and 95th).

Figure 6-14 Comparison of 4-year average monitored Connecticut arsenic concentrations to the 1996 ASPEN modeled concentrations (percentile distribution).

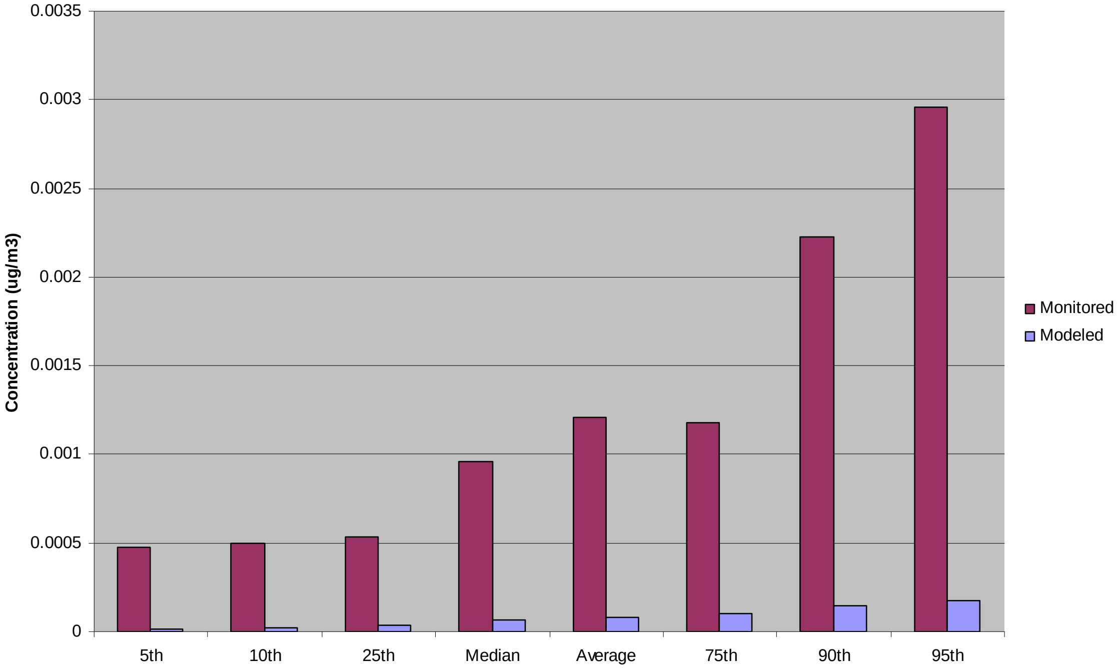
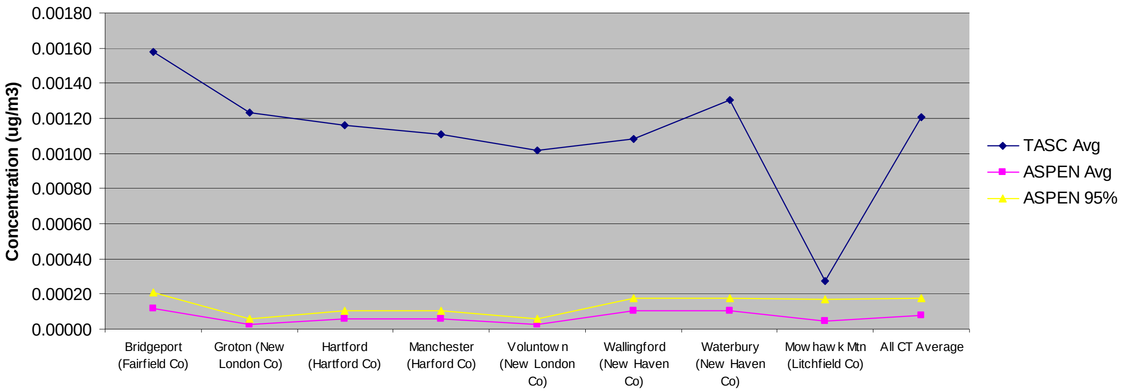


Figure 6-15 displays the mean annual (4-year TASC, 2002 IMPROVE) concentrations of arsenic at the seven TASC sites and one IMPROVE site in comparison to the 1996 ASPEN modeled means and 95th percentile. The TASC monitored levels and modeled estimates agreed in that the both showed the highest values of arsenic in Bridgeport and Waterbury with the lowest levels in Voluntown. However, the modeled levels of arsenic ranged from being 10 times lower than monitored levels in Wallingford to 50 times lower than the monitored levels in Groton. The agreement was better for the IMPROVE site where the monitored value at Mohawk mountain was 5 times higher than the modeled value. The limits of detection for the IMPROVE monitor were 4-5 times lower than TASC, and in part explains the closer agreement with the modeled numbers.

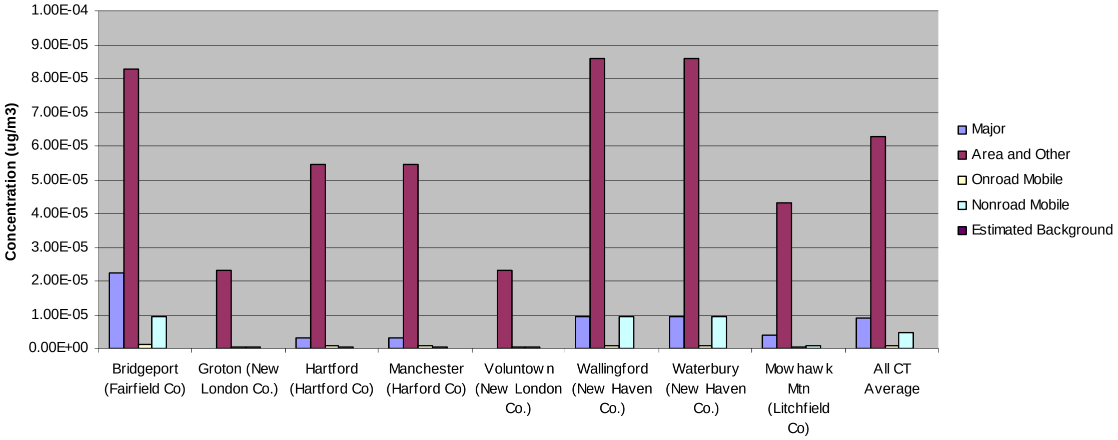
Figure 6-15 Comparison of TASC monitored arsenic concentrations to ASPEN modeled levels for seven TASC sites.



As noted, the large difference in ASPEN modeled and TASC monitored arsenic concentrations is driven by the relatively high detection limit for TASC relative to the modeled levels (in some cases an order of magnitude greater). Additionally, arsenic was detected in just under half of the samples. Another factor could be incomplete or incorrect arsenic emissions inventories, which might lead to an underestimation in the modeled predictions. In addition, deposited arsenic that has been resuspended would be sampled by the monitors but not taken into account by ASPEN modeling.

Figure 6-16 shows estimated source contributions to EPA's modeled annual mean concentrations of arsenic. Across all counties in Connecticut, area sources provide the largest contribution to airborne arsenic, accounting for 70%-95% of emissions. Major sources account for 20% of arsenic emissions in Fairfield County, 5% in Harford County, and 9% in New Haven County. Non-road mobile sources account for 8% of emissions in Fairfield and New Haven counties and 6% of emissions in all of Connecticut.

Figure 6-16 EPA estimated source contribution to modeled mean annual concentration of arsenic in Connecticut.



6.3.4. Lead

Lead levels determined by TASC monitoring tended to be higher than the levels predicted by the 1996 ASPEN model. Figure 6-17 shows the comparison between monitored and modeled lead in Connecticut. The median modeled lead level for 1996 was about eight times lower than the 4-year annual statewide monitored median for all TASC sites combined. The figure shows that although there is poor agreement between the monitored and modeled lead values, both show levels well below the quarterly NAAQS standard of 1.5 ug/m^3.

Figure 6-17 Comparison of 4-year average monitored Connecticut lead concentrations to the 1996 ASPEN modeled concentrations (percent distribution).

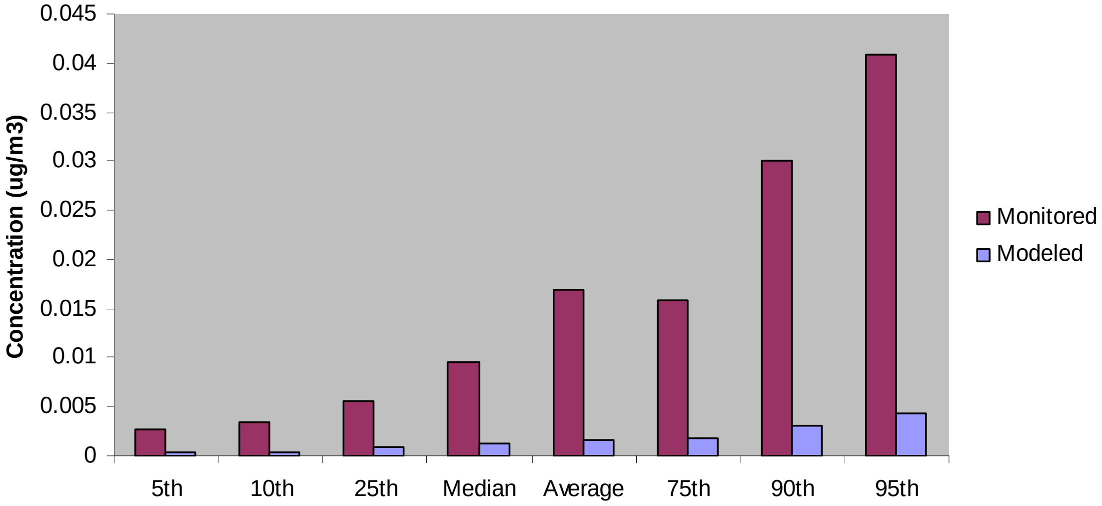


Figure 6-18 displays the mean annual (4-year TASC, 2002 IMPROVE) concentrations of lead at the seven TASC sites and one IMPROVE site in comparison to the 1996 ASPEN modeled means and 95th percentile. The monitored levels and modeled estimates agreed in that they both showed the highest values of lead in Bridgeport and Hartford with the lowest levels in Voluntown. The modeled levels of lead were nine to sixteen times lower than the average values determined from TASC sampling for all the sites except Manchester, which was four times lower. The best *absolute* agreement between monitored and modeled values occurred at Mohawk Mountain, the IMPROVE site. Nonetheless, ASPEN's predicted concentration was a factor of five times lower than the monitored concentration.

Figure 6-18 Comparison of TASC monitored lead concentrations to ASPEN modeled levels for seven TASC sites

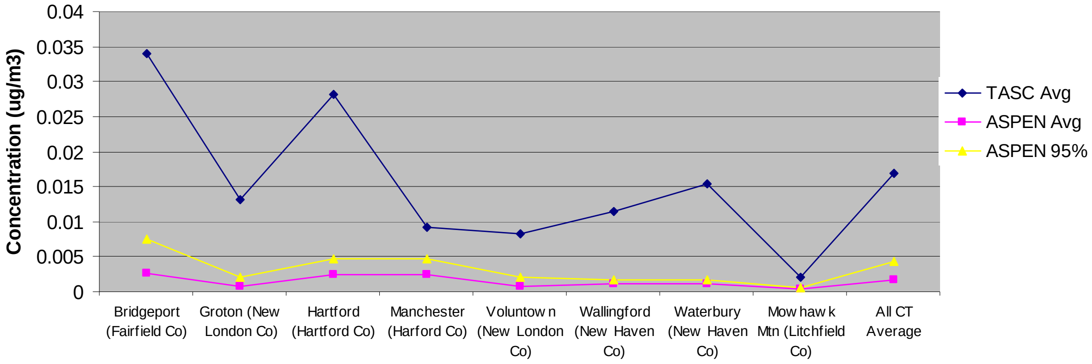
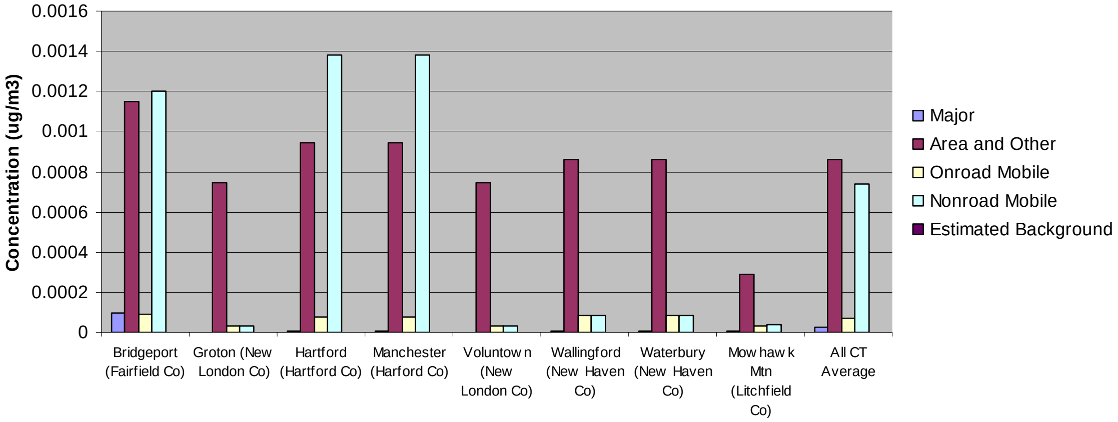


Figure 6-19 shows estimated source contributions to EPA's modeled annual mean concentrations of lead. EPA's ASPEN analysis indicates that area and other sources are significant contributors to mean lead concentrations at all sites. Area source contributions ranged from 40% in Hartford County to 92% in New London County. Non-road mobile sources provided significant contributions to the overall mean in Fairfield County (Bridgeport) and Hartford County (Hartford and Manchester). These sources accounted for 47% of the annual mean in Bridgeport and 57% of the annual mean in Hartford and Manchester. Less of a contribution was seen in the remaining sites, with 8% contribution in New Haven County and 3% in New London County. On-road mobile sources contributed between 3%-4% of the annual mean in all the sites except the two in New Haven County where its contribution was 8%. The only site with a significant major source contribution was Bridgeport, where EPA estimated about 4% of the annual mean lead concentration was attributed to these sources

Figure 6-19 EPA estimated source contribution to modeled mean annual concentration of lead in Connecticut.



ASPEN modeled concentrations of metals have been shown to be consistently lower than those determined by TASC monitoring. This conclusion was also made by EPA's National Air Toxics Assessment when assessing the validity of the ASPEN model (EPA NATA). Based on the lead median ratio, it was determined that the modeled values underestimated monitored levels by a factor of 7.5- consistent with the ratio found in Connecticut. This underestimation is most pronounced when comparing modeled estimates to source oriented monitors.

EPA describes the discrepancy between modeled and monitored lead (and other metals) as due to a combination of several factors. Missing emissions from the inventory would lead to underestimation of concentrations in the modeled results. Spatial uncertainties in emission locations would also lead to uncertainties in the results. Since many lead sources are isolated facilities in rural areas, the area of high concentration may be very small. Errors in emissions locations or release heights could cause the model to miss the peak. This would result in underestimation when compared to a monitor at the emission location (EPA 2002). Furthermore, ASPEN was designed to represent spatial and temporal averages over an entire census tract and peak values very near sources will not be captured (Rosenbaum *et. al.* 1999).

Another possibility for underestimation of lead (or other metal) concentrations is from re-suspension of lead particles. Sources that have a history of lead emissions may be surrounded by soil containing deposited lead which can reenter the air because of wind or human activities. These concentrations would show up on the monitor but are not accounted for in the emissions inventory.

6.4. Polycyclic Aromatic Hydrocarbons

The 1996 National-Scale Air Toxics Assessment used the ASPEN model to predict PAH concentrations by modeling the sum of the seven carcinogenic members of the group- benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, chrysene, dibenz[a,h]anthracene, and indeno[1,2,3-cd]pyrene. The resulting composite species, called 7-PAH, was compared to the TASC monitored concentrations by examining the sum of the monitored concentrations for these 7 PAHs. Unlike metals, ASPEN tended to slightly overestimate the total concentration of the 7-PAHs modeled. This is true despite the fact all the non-detect samples were replaced with a value of the detection limit when representing the monitored concentrations. The median ratio of monitored to modeled 7-PAH concentration was 0.44. The agreement was much better for the upper 95th percentile, with a ratio of 0.95. The ratio of the overall Connecticut monitored mean to the modeled mean was 0.67 (Figure 6-20).

Figure 6-20 Comparison of 4-year average monitored Connecticut 7-PAH concentrations to the 1996 ASPEN modeled concentrations (percent distribution)

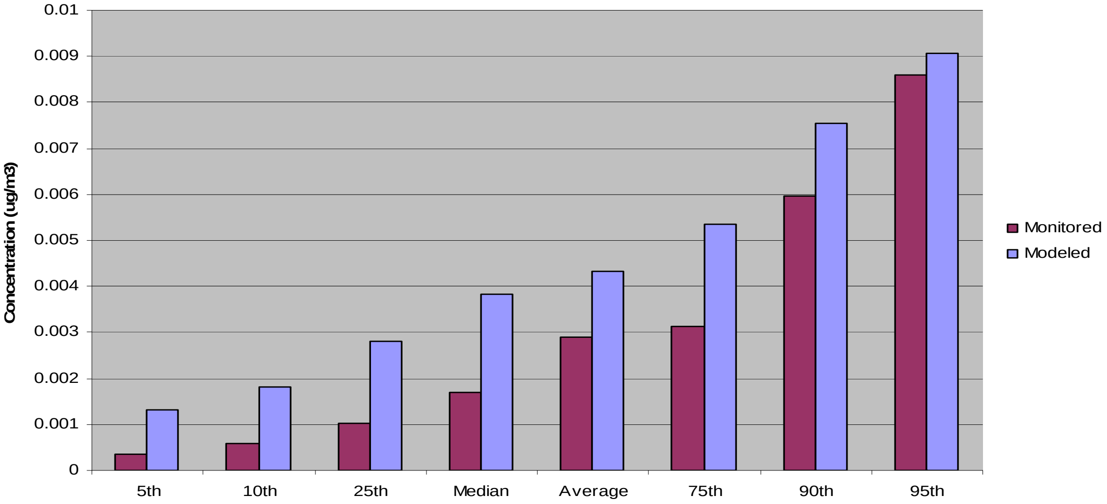


Figure 6-21 displays the TASC mean annual (4-year) concentrations of 7-PAH at the seven sites in comparison to the 1996 ASPEN modeled means and 95th percentile. The highest monitored values occurred in Groton while the highest modeled values were in Bridgeport. The only site underestimated by the ASPEN model was in Groton. This could be explained by the proximity of the monitor to sources of PAHs, where the county's peak concentrations could have been missed by the model. The best agreement between modeled and monitored values occurred in Voluntown and Wallingford where the ratio of monitored to modeled values were 0.48 and 0.87, respectively.

Figure 6-21 Comparison of TASC monitored total concentrations of seven carcinogenic PAHs to ASPEN modeled levels for seven TASC sites.

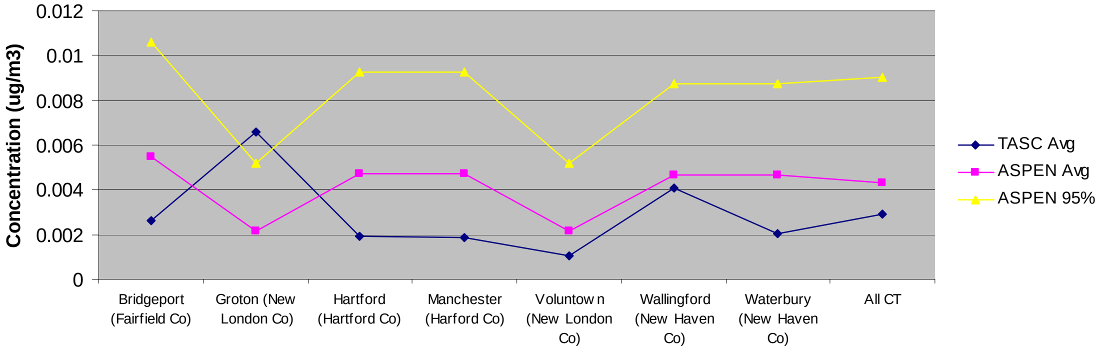
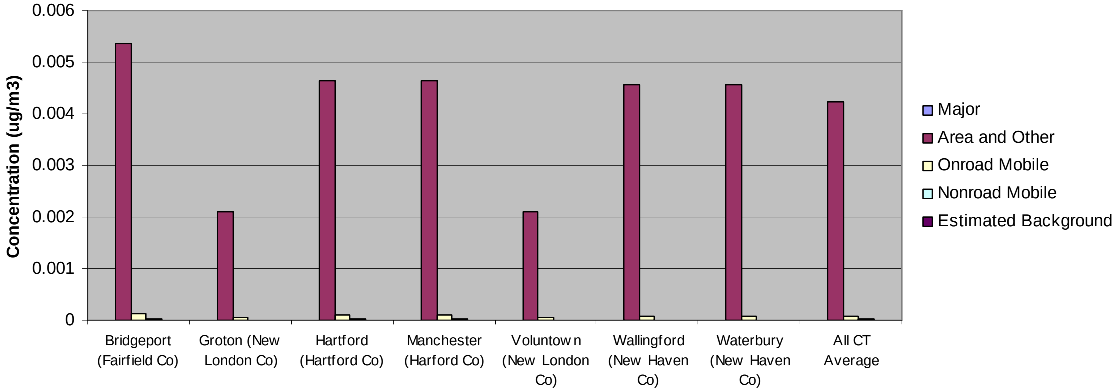


Figure 6-22 shows estimated source contributions to EPA's modeled annual mean of total PAH concentrations for the seven carcinogenic PAHs. The source contributions of PAHs in Connecticut show that area and other sources account for 98% of emissions at all sites while on-road mobile emissions only account for 2%. This is in contrast to previous studies that have reported mobile sources as being the major source of PAHs (Schauer *et al* 2003, Naumova *et al*, 2002, Dimashki *et al* 2001, Marr *et al* 1999, Harrison *et al*, 1996). Non-road mobile sources accounted for less than one percent of the contribution to the mean while major sources and background did not contribute.

Figure 6-22 EPA estimated source contribution to modeled mean annual concentration of total carcinogenic PAHs in Connecticut.



6.5. Discussion

While the difference between ASPEN and TASC monitored values is generally sizeable, the extent to which the TASC network is representative of a broader region may influence the ability to draw meaningful conclusions from the comparison. This is partly because ASPEN modeling was not intended to account for large point sources at scales of spatial resolution below the census tract level. Because uncertainty increases from the county to the census tract level, EPA did not provide tract-level concentrations on their website. Additionally, any comparison must also consider the emissions profile of counties modeled by ASPEN as well as the emissions of large point sources situated near TASC monitoring sites. These factors suggest the potential challenge of distinguishing Title V source emissions located near TASC sites from emissions associated with other sources or background concentrations.

In addition to the uncertainties surrounding the ability of TASC sites to represent entire counties, ASPEN modeling has considerable limitations. The issue of gaps in the emissions data has been previously discussed and constitutes a major limitation to the assessment. Furthermore, a limitation to all Gaussian models is the poor representation of stable air conditions that typically occur at night. The model also does not account for sources that have episodic emissions where high concentrations are released for a short period of time.

Although the model tends to under predict concentrations it is a useful tool in comparing geographic areas and identifying pollutants of greatest concern. It can therefore be used to prioritize data collection and allow for informed decision making on sampling strategy. It also lends information on source contributions of various pollutants.

According to EPA, on a national level, of the four main source types (area and other, major, on-road, non-road) about half of the 32 toxic air pollutants modeled in 1996 have area and other sources as the dominant contributing source type. However, Morello-Frosch *et al*.'s analysis of ASPEN 1990 modeling in California (2000) showed that these numbers vary by location. In California, on average, HAP concentrations and health risks originate mostly from area and mobile source emissions—although in several locations point sources accounted for a large portion of estimated concentrations and health risks. Notwithstanding California's findings, Woodruff *et al*. (1998) found relatively high background concentrations across the U.S. for several HAPs indicating a pervasive presence of these pollutants

An additional consideration is changes in air toxics concentrations that may have occurred since EPA modeling was conducted. Since 1996, EPA has expected a reduction in air toxics emissions from subsequently issued standards that affect industry categories. While estimated on-road mobile source emissions of VOCs declined from 1990 to 1995 (suggesting corresponding reductions in HAPs), these decreases may have been offset to some extent by increases in VOCs emitted by several other source categories, including industrial and non-road mobile sources (Woodruff *et al*. 1998). TASC monitored values represent emissions from 1999-2003. Since the model underpredicts measured levels (using 1996 emissions estimates), one might reasonably expect the differences between ASPEN modeling using updated (lower) emission levels consistent with the TASC monitoring period to be even greater than shown here.

Since HAPs may be of concern for toxicity from acute as well as chronic exposures, both short-term and long-term concentrations are important to consider. Thus, for the ASPEN program to be most effective on a state level, local monitoring data is needed to validate modeled predictions in order to achieve the goals of integrated assessment of the potential health risks from exposures to HAPs. The CT DEP's TASC monitoring data are therefore an important validation tool, although subject to certain limitations of interpretation given the objectives of the TASC network

7. CONCLUSIONS

7.1. Overview

This report reviews hazardous air pollutant (HAP) data collected by the Connecticut Department of Environmental Protection (CT DEP), focused on the monitoring effort undertaken through the Toxics Air Study in Connecticut (TASC). The study provides an array of data on air toxics present in the ambient environment, including carbonyls, polycyclic aromatic hydrocarbons (PAHs), metals and volatile organic compounds (VOCs). Beyond the simple goal of providing an estimate of ambient concentrations, the information gathered serves a number of purposes. These include: (1) providing data to assess the fate and transport of toxics in the state, (2) establishing a baseline level to aid in an effectiveness evaluation of HAP reduction strategies, (3) aiding toxic air quality model performance assessments, and (4) determining whether or not additional permit requirements are necessary for Title V or solid waste facilities. Notably, these data are intended to help inform policy development and future air emission reduction efforts for stationary and mobile sources within Connecticut.

Samples were collected for the selected air toxic chemicals from seven sites over a five year period, beginning in 1999 and ending in 2003. A quality assurance review was conducted that evaluated field and laboratory operating practices. Considerable information regarding data quality was acquired through an assessment of field and trip blanks. Additionally, information from collocated samples provided precision estimates. Overall, the majority of data collected was deemed acceptable for detailed analysis, although several individual compounds were not (including chromium and benzene).

In addition to the data from TASC, ambient toxic pollutant data collected from the Photochemical Assessment Monitoring Stations (PAMS) were reviewed and compared to TASC results. Further comparisons were made with modeled data from the EPA's 1996 National Ambient Toxics Assessment (NATA) and IMPROVE data from northwest Connecticut. These comparisons provide an alternative approach to judge the data quality from TASC.

Quality assured data were then analyzed to illustrate the spatial and temporal behavior of the various species. When levels were below detection, a value equal to the method detection limit was substituted to provide a concentration estimate for those samples. This approach provides a conservative estimate of the ambient concentration for the non-detect days. Review of this adjusted dataset yielded insights into potential regions of interest based on observed differences in ambient concentrations. Other analyses included comparison of ambient levels to the available Connecticut Department of Public Health proposed annual hazard limiting values (HLVs). Several different conclusions could be made based on this analysis[21]. For some species, like formaldehyde, it was determined that the ambient concentrations were above their proposed HLVs. For others, like manganese, ambient levels were deemed to be within

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[21] Importantly, these proposed HLVs are meant to address fenceline concentrations. TASC monitors were sited accordingly, to provide ambient fenceline concentration estimates.

the range of their associated proposed HLVs. Evaluation for some compounds was not possible, as the protocols were not sensitive enough to determine concentrations below the proposed HLV. Many compounds fell into a fourth category, in which ambient levels were substantially below the proposed HLVs. The entire PAH class of compounds fell into this last category.

The TASC program generated a wide array of data, providing valuable details regarding the ambient levels of air toxics in Connecticut. The data analysis highlights are outlined and summarized in the following section.

7.2. Summary of Results

7.2.1. Carbonyls

Carbonyl data from both TASC and PAMS were evaluated. The focus was placed on formaldehyde and acetaldehyde, as these two carbonyls are ubiquitous and at quantifiable levels. Although acetone data were deemed reliable from TASC, little emphasis was placed on the results since its ambient levels were two orders of magnitude below the proposed HLV. Measurements of larger carbonyl species (with greater than two carbons) were not of sufficient quality for in depth investigation. This is no doubt in part due to their scarcity in the environment, and the inability of the methods employed here to measure such low concentrations.

Data quality for formaldehyde and acetaldehyde was high, with ambient levels well over levels detected on blank samples. Precision estimated from collocated samples also indicated the method was able to yield consistent results. Despite the decrease in sample volume collected that occurred early in the program to address breakthrough for these light species, the method detection limit was sufficiently sensitive to measure ambient levels below the proposed annual HLV. This permits a reasonable health assessment to be conducted for these carbonyls.

Both spatial and temporal behavior was investigated for these compounds. Spatial variation was apparent, with the highest formaldehyde levels identified in Wallingford. Manchester and Voluntown exhibited the lowest concentrations of formaldehyde in the State. The levels observed at Wallingford, which were nearly 70% greater than those observed at the next highest monitoring site in Bridgeport, may show the impact of a nearby point source. Emissions inventory information for the facility near which this monitor was sited indicated it was a substantial source for formaldehyde and its precursors. Further investigation showed that a statistically significant decline in ambient concentrations was seen between the first half of the monitoring period and the second. Comparative analysis of these two periods at the other monitoring sites did not show any statistical differences. The decline at Wallingford is likely directly attributable to process changes that occurred at the nearby facility. Acetaldehyde was also spatially variable, with greatest levels found at Hartford and Bridgeport. As previously mentioned, the lowest levels were observed and Manchester and Voluntown.

Temporal variability was investigated with both the TASC and PAMS datasets. First, seasonal behavior was observed using the TASC data. For both acetaldehyde and formaldehyde, significantly higher concentrations were observed in the summertime.

The lowest concentrations were seen during the springtime. This overall statewide pattern was reasonably consistent across all sites. High summertime levels are expected given the substantial role photochemistry plays in the atmosphere for these compounds.

A more in-depth look at summertime levels was conducted using PAMS data, which were collected in 3-hour increments. This analysis revealed potential mobile source influence given the observed weekend/weekday differences. Higher levels were apparent on the weekdays. This result is corroborated by EPA's estimated source contributions for its ASPEN modeling, which indicated mobile source dominated influence for these compounds. In addition, the greater observed diurnal variations in formaldehyde indicate that secondary atmospheric processes are much more important for formaldehyde than they are for acetaldehyde.

The ambient carbonyl levels were also evaluated against the proposed HLVs. Based on this analysis, one can conclude that formaldehyde levels are greater than the level of concern, while acetaldehyde levels are near the level of concern. This conclusion is consistent with monitored results from across the country. In addition, EPA's ASPEN model predicted levels in Connecticut near the proposed HLVs, although they were generally below the monitored results discussed here. The differences are reasonable given the limitations of the model and its prediction of county average concentrations.

7.2.2. Polycyclic Aromatic Hydrocarbons

PAHs are the second compound class discussed in the report. The PAH target list included nineteen different PAHs, although results were reported as sixteen distinct concentrations due to several coeluting species. No data quality issues were identified for this compound class.

For the most prevalent compounds, blank levels were low enough to permit reliable ambient level determination. About half of the species were routinely identified in the ambient samples. Precision analysis conducted with collocated sampler data showed reasonable agreement, although variation was observed. This variation appeared related to compound volatility, with the most volatile compounds showing the greatest relative percent difference between collocated samples. The data analysis also determined that results were not substantially influenced by the sampling and analytical protocol changes that occurred in July 2001.[22]

Statewide ambient levels for the various PAHs were calculated. MDL values were substituted for non-detect samples, consistent with the approach employed for carbonyls. Spatial variability was observed for all PAHs, with similar behavior across sites and species. Groton and Wallingford displayed the highest levels of PAHs with the lowest concentrations monitored at Voluntown, as expected.

Seasonal differences were also observed. Most species fell into one of two categories, showing either a summertime maximum or a wintertime maximum. The general behavior is consistent with that noted in the literature. The most volatile species seem to peak in summertime, which may indicate volatilization is important emission

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[22] The sample schedule was changed from a weeklong sample to a 24-hour sample taken every sixth day. To offset the decreased sensitivity due to lower sample collection volume, the analytical protocol shifted to SIM from scan mode.

mechanism for these species. In contrast, high molecular weight PAHs were observed in the winter months. This could be attributed to increased use of heating sources that operated in the cold months but not the summer ones. One notable, unexplained event occurred in Groton during January 2001. For that month, PAH levels were well above their average conditions, but only in Groton. Although no explanation could be derived from the data, it may be due to local construction or roadwork.

To assess the potential health implications of monitored PAH levels, a comparison between ambient concentrations and proposed annual HLVs was conducted. The methods employed in TASC were sensitive enough to assess all of the PAHs with proposed HLVs. The comparison showed that ambient levels of PAHs range from one to four orders of magnitude lower than the proposed HLVs, implying no significant risk is associated with individual species at the monitored locations. The long-term ambient levels were below the HLVs, even during the event experienced at Groton.

The final analysis of PAH levels in the State contrasted the ambient results to modeled results. A comparison was conducted by summing the concentrations of the seven carcinogenic PAHs monitored, as these were lumped together in the model. There was quite reasonable agreement between the model and monitor results, unlike most of the model to ambient data comparisons. This may indicate good model performance for PAHs. Literature studies point to mobile sources as a substantial contributor to environmental PAH levels, while EPA modeling showed virtually no mobile source emissions for this category. Instead, EPA’s inventory identifies area sources dominating.

7.2.3. Metals

The third major compound class monitored by TASC is metals. Varying levels of success were experienced in the determination of ambient concentrations of the twelve different targeted metals. Many metals were rarely detected in the blank samples. However, blank levels of both chromium and zinc were comparable to detected ambient levels. Precision estimates were made and generally showed relative percent differences in the range of 20 to 35 percent.

Although the data were deemed reliable for most of the metals detected, changes in the sampling protocol in July 2001 did affect detection limits. Before that date, weeklong samples were obtained, whereas after then, a 24-hour sample was collected once every sixth day. This change in MDL made it more difficult to evaluate arsenic and cadmium with respect to proposed HLVs, as the detection limits after the sampling change were at the same levels as the proposed HLVs.

Ambient metals concentrations were summarized statewide for two periods, before and after the July 2001 sample protocol change. In general, the levels after the change for all metals were higher. This may simply be a reflection of the influence that MDL substitution for non-detects has on average results. The differences are most pronounced for metals that had substantially different percent non-detects between the before and after period.

The ambient results did show spatial variation across the State, although it was not consistent from metal to metal. In general, the background site in Voluntown showed the lowest levels, followed by Manchester. Seasonal differences were also plotted on a statewide basis. There did not seem to be any substantial variation from season to season, although nickel, vanadium and selenium all showed their highest levels in the winter. This may reflect increased heating use of fuels in the wintertime, as all three of these metals are present in fuel oil.

Further analysis evaluated the ambient concentrations against the proposed annual HLVs. The methods employed by TASC were sensitive enough for some of the metals, like manganese, nickel and lead. However, detection limits for arsenic and cadmium may not be capable of adequate evaluation against the proposed HLVs. In the case of zinc and chromium, the high levels on the blank meant the monitored ambient concentrations were unreliable, preventing a comparison to proposed HLVs. Lead and nickel levels throughout the State appear to be well below the proposed annual HLV. Manganese and arsenic concentrations are close to the proposed annual HLV throughout the State, although manganese manifests a spatial distribution not observed for arsenic. These two metals may warrant further observation. There is significant uncertainty surrounding cadmium concentrations due to low ambient levels. Nonetheless, this metal may not be of concern, as supported by the first two years of data.

In addition to the comparison with proposed HLVs, data from four metals were compared to modeled predictions. Additional data was incorporated from the IMPROVE monitoring site located in northwestern Connecticut at Mohawk Mountain. As observed previously, ambient levels were consistently greater than modeled levels for manganese, nickel, arsenic and lead. The best agreement was generally observed between the modeled data and the ambient background sites, Voluntown and Mohawk Mountain. Of the four metals, nickel showed the closest correlation. According to the emission inventory modeled, metal emissions are dominated by the area source category, although lead also had substantial non-road mobile sources for some counties in the state. The most substantial ambient concentrations were observed in the same counties where this non-road contribution was predicted to be most substantial.

7.2.4. Volatile Organic Compounds

The final compound class evaluated is volatile organic compounds. TASC monitored for 54 different VOCs. The results of this analysis varied, depending on the specific compound. Overall, there were few useful ambient values derived from the dataset, primarily due to the apparent very low ambient concentrations for most of the species.

The VOC analysis is focused on a collection of the eight most prevalent species. Precision estimates for these compounds were reasonable, with most relative percent differences reported within 25%. Although detected, the group did not include benzene since data quality for this compound was poor. There were seven other VOCs which were primarily below the MDL, whose MDL was also not sensitive enough for evaluation against their proposed HLVs. However, sensitivity for fourteen other species was adequate for comparison.

Variability from site to site was examined. Toluene and methylene chloride showed the most differences, while chloromethane and trichlorofluoromethane showed little variation. Seasonal variation was not appreciable. However, temporal variation was observed on a diurnal scale as evidenced by summertime PAMS data. That variation revealed maximum concentrations for most species in the evening, in some cases, building into the early morning hours. Atmospheric mixing of clean air aloft after sunrise appears to drive concentrations lower during the afternoons.

Hourly PAMS toluene data was compared to 24-hour averaged, every sixth day TASC data as an alternative mechanism for data validation. Although the two networks did not have collocated sites, qualitative agreement was observed when ambient levels of nearby locations were compared. The analysis demonstrated how average ambient concentrations are influenced by the underlying data collection frequency. When averaged over available data from an entire summer, the comparisons between PAMS and TASC was poor. When the comparison was restricted to measurements from the same days, however, the comparison was substantially improved. One can infer that the best longer term average is derived from the dataset which represents the greatest number of days.

The final analysis for VOCs reviewed ambient concentrations in relation to the proposed HLVs. The levels for chloromethane, methylene chloride, toluene, acetone and 2-butanone appear to be below the proposed HLVs for those chemicals. A number of other compounds were not detected and are, therefore, also not expected to cause concern (the MDL is far lower than the proposed HLV). However, the sampling and analytical protocols used in TASC lack the sensitivity to characterize eight other VOCs on the target list. These are the compounds with the most stringent proposed HLVs, including benzene. Therefore, planning for future efforts should take the limitations of the current study into consideration.

7.3. Recommendations

When compared to other available data, the levels of air toxics established through TASC are similar to those found in other parts of the United States (Hafner, e*t al.,* 2004). For the majority of the compounds, the ambient concentrations appear to be low when judged against CT DPH proposed annual HLVs. It should be noted that siting criteria for the network may not adequately reflect the entire range of air toxics concentrations across the State. However, the geographic distribution may adequately establish this range. As future strategies for air toxic reduction continues, one planning tool that could help to evaluate the potential spatial variability of air toxics in Connecticut is an emissions inventory database developed through reported emissions from permitted sources. The database could serve other purposes as well, informing decisions regarding potential revisions of the air toxics regulations and allow tracking of changes in emissions that should be directly reflected in ambient levels.

Although most of the monitored chemicals were found below levels of concern, formaldehyde, acetaldehyde and manganese were not. The carbonyl concentrations are likely dominated by motor vehicles, and the same may be true of manganese. These species deserve continued attention. Carbonyl monitoring continues under the PAMS program. Based on the review here comparing 24-hour TASC measurements and 3-hour PAMS measurements, one can conclude greater value is gained by shorter-term measurements. These avoid sample issues of breakthrough for these light carbonyls and also provide evidence for the impact of local (primarily mobile) sources, with rush-hour increases. The carbonyl samples also serve the dual purpose of aiding the understanding of local ozone chemistry, which is the rationale through the PAMS program.

Acrolein and other carbonyls were not well-characterized by TASC. However, these air toxics are important. EPA is currently pursuing methods development for analysis of acrolein in ambient air. Progress for these analytical techniques should be followed and evaluated. It is likely that measurements of this compound will become routine in EPA's air toxics monitoring program and could be considered for inclusion in Connecticut's network in the future. Although this is true in general, to the extent any additional monitoring is performed, consistency with other monitoring efforts in the country would permit the direct comparison of results in Connecticut to those in other areas of the United States.

Other compounds, such as arsenic and cadmium, require more refined sampling to properly assess their ambient levels against the proposed HLVs. As these are both reasonably toxic components in ambient air, improved quantification is a priority. The early period of TASC sampled for a week. The analytical techniques employed may be sensitive enough providing sample time is extended to a week or more. Continued sampling at a single site could demonstrate the ability to characterize atmospheric concentrations of these two metals, and also provide more data for manganese. However, the current analytical methods will not provide ambient levels of hexavalent chromium, although they are capable of yielding total chromium levels assuming the contamination problem is identified and addressed[23].

Many VOCs fall into this same category as metals, where detection limitations prevented their evaluation. Most of those species could be suitably characterized if the injected sample volume was increased by a factor of 5, which would lower the detection limits below the proposed HLVs by several multiples. However, adequate water vapor and carbon dioxide removal from the sample injection stream would be required.[24] Alternatively, the analysis could be conducted in SIM mode for the compounds of interest. Given the dilute atmospheric levels, it may be important to characterize these low concentration VOCs at one of the sites showing highest concentrations of related VOCs to maximize the chance of detection. Although benzene was not successfully monitored through TASC, the PAMS program does routinely track this compound and other lighter toxic hydrocarbons like toluene and xylenes. All of these species, in addition to 1,3-butadiene, which could be reported through PAMS analyses, share mobile vehicles as a dominant anthropogenic source.

Unlike the other compound classes monitored under TASC, PAHs were found to be below levels of concern across the board. Therefore the least emphasis needs to be placed on this group. Despite the current knowledge of ambient concentrations, periodic evaluation may be warranted to assure levels remain low. Use of the NEI or a locally available emission inventory could be used to track changes in emissions. At first order,

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[23] It appears likely that the contamination issue for Cr and Zn are related to changes in the filter used for sampling. Filter contamination is commonplace. The analytical lab ordered a new set of filters in mid-2001, after which substantial contamination was observed for Cr and Zn.

[24] Documentation for EPA method TO-15 states volumes of 1 L can be collected via this method, which represents a 2.5 times increase in detection capability. Careful evaluation of trapping methodology could permit collection of volumes greater than 1 L.

if no major increases are recorded in the database, no substantial increases in ambient concentrations would be anticipated. Alternatively, continued evaluation of EPA's modeled air toxics results could be used to track potential areas of concern. This approach seems most reasonable for PAHs given the reasonable agreement observed between the NATA 1996 results and the recorded TASC ambient levels.

Although modeling could be used for other compound classes, the results are still very uncertain for long-term localized impact assessment. HAPs may be of concern for toxicity from acute as well as chronic exposures. Thus, for the ASPEN program to be most effective on a state and local level, monitoring data are needed to validate modeled predictions in order to achieve the goals of integrated assessment of the potential health risks from exposures to HAPs. The CT DEP's TASC monitoring data are therefore an important validation tool, although subject to certain limitations of interpretation given the objectives of the TASC network. If future monitoring efforts are considered, they may want to take into account how such measurement data could aid model evaluation. As the modeling tools become more refined and accurate, the need for ambient monitoring may decline.

One piece of information that was not available through TASC, that would prove helpful in data evaluation, is local wind data. Given the week-long sample times for many of the air toxics, local winds may be of limited use. However, for samples of shorter duration, local transport information could be an important means to identify nearby sources impacting a monitoring site.

Other important considerations with regard to the potential future monitoring efforts for air toxics include the consideration of whether monitoring sites are representative of population exposures and the existence of any hot spots associated with particular sources (of any type) or conditions. The TASC network was sited specifically to monitor for property-line concentrations and is likely not the most effective way to evaluate the risks of ambient air toxics. Moreover, cumulative exposures to many pollutants from multiple sources, even if none exceeds HLVs individually, could also be a concern. In that context, however, the integrated risk from air toxics may be overwhelmed by risks from other air pollutants (like fine particles).

Overall, ambient air toxics monitoring data from Connecticut sites reveal that most species' concentrations are below levels of concern. For those which are not, mobile sources appear to be a dominant influence. Continued monitoring may be warranted for certain compounds, with much dependent upon the emergence of new analytical techniques and/or sampling protocols. Other planning tools may prove useful to aid in the continued evaluation of air toxics in the State. These include (1) the development of an air toxics emission inventory for permitted sources and other source categories and (2) modeling performed by EPA, which may yield additional insights. These two alternative approaches should complement the monitoring that has already taken place and help to inform any decisions on future monitoring efforts.

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Appendix A: Health Information for Select VOCs

Table A-1: Health Information for Select VOCs

Compound	IRIS Information	Annual HLV (ug/m^3)	Connecticut Health Information[25]
Chloromethane (*syn: methyl chloride)*	Non carcinogenic effects include CNS toxicity and cellular necrosis. Classified as group D- Not classified as a carcinogen.	15	HLV set to protect against nuerological damage seen in short term and continuous inhalation studies. Based on IRIS RfC. Not enough evidence to consider it a carcinogen.
Chloroethene (*syn: Vinyl Chloride*	Non carcinogenc RfC established due to chloroethene's toxic effects in the liver. Classified as Group A- Human Carcinogen due to sufficient studies establishing its carcinogenicity in humans (liver cancer and brain and nervous system cancers.	1.33	HLV set to 1 in 100000 cancer risk level for 30yr exposure. Based on evidence of an association between inhalation exposure to vinyl chloride and development of angiosarcoma, a rare tumor.
Chloroethane	NA	500	HLV based on the IRIS RfC divided by a 10-fold factor for possible carcinogenicity and a 2 fold factor for exposure to children.
Acetone	Inhalation RfCs based on respiratory irritantion and some CNS and peripheral nervous system effects.	175	
Acrylonitrile	Inhalation RfCs based on degeneration and inflammation of nasal respiratory epithelium and other respiratory system effects. Classified as Group B1- probable human carcinogen based on occupational studies showing higher incidence of lung cancer in exposed workers.	0.086	Based on IRIS risk level set at a 1 to 100000 increased risk level. From occupational studies showing increased incidences of lung cancer.
Methylene Chloride (*syn: Dichloromethane)*	Classified as Group B2- probable human carcinogen based on sufficiend evidence of carcinogenicity in animals.	12.5	Based on IRIS risk level set at a 1 to 100000 increased risk level. From animal studies showing combined liver and lung adenomas and carcinomas.

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[25] From CT DPH (2002)

Compound	***IRIS Information***	***Annual HLV (ug/m^3)***	***Connecticut Health Information***[25]
Carbon Disulfide	Inhalation RfC based on peripheral nervouls system dysfunction.	350	HLV based on IRIS RfC. Substance has not undergone complete evaluation to determine carcinogenic potential.
2-Butanone (*syn: methyl ethyl ketone)*	Inhalation RfC based on developmental toxicity effects	500	HLV based upon the the RfC from IRIS. Based on studies showing developmental toxicity in mice.
Chloroform	Classified as group B2- pobable human carcinogen based on the formation of hepatocellular carcinomas in mice.	0.5	HLV based on 1 in 100000 cancer risk unit from IRIS.
1,2-Dichloroethane	Classified as group B2- probable human carcinogen based on theormation of several tumor types in mice.	0.23	HLV based developed by human extrapolation method from IRIS value that was based on animal studies.
1,1,1-Trichloroethane (*methyl chloroform)*	No Inhalation RfC. Classified in group D- not classifiable as to human carcinogeniciyt.	500	HLV based on the CalEPA chronic Reference Exposure Level baset on a neuropathologic effect shown in a study using gerbils.
Benzene	Inhalation RfC based on an occupational study showing decreased lympocyte count. Benzene is classified as a Group A- Known human carcinogen. Epi. Studies and case studies show evidence of a causal association between benzene exposure and acute nonlymphocytic leukemia. Human data is supported by animal data.	0.75	HLV set to the 1 in 100000 IRIS carcinogenic risk factor. Based on studies used by IRIS linking benzene to leukemia.
Carbon Tetrachloride	Classified as group B2- probable human carcinogen. Based on inadequate human data but sufficient evidence showing formation of hapatocellular carcinomas in rats, mice, and hamsters.	0.8	HLV is based on the cancer slope factor obtained from IRIS. Based on the 1 in 100000 risk level.

Compound	IRIS Information	Annual HLV (ug/m^3)	Connecticut Health Information[25]
Trichloroethene	Carcinogenic assessment withdrawn for further review.	3	Based on the CalEPA unit risk value. Carcinogenic risk determined from 4 inhalation bioassays in mice showing carcinogenic effects in the lung and liver as well as lymphoma
Methyl Methacrylate	Inhalation RfC set from chronic rat inhaltion studies showing degeneration of olfactory epithelium. No evidence of carcinogenicity.	120	Based on IRIS RfC value with extra factors applied for inter-individual effects and children's increased inhalation exposure.
Toluene	Inhalation RfC set due to nuerologic effects shown in occupational studies. Chronic rat studies have shown degeneration of nasal epithelium.	200	Based on the IRIS RfC value with a 2x children's inhalation exposure factor.
Tetrachloroethene (*syn: perchloroethylene)*	NA	2	HLV set for a 1 in 100000 risk based on the PERC inhalation unit risk set by the CalEPA. This was based on studies in mice showing liver carcinoma and leukemia after chronic exposure.
Chlorobenzene	Only oral RfD available. Not classifiable as a human carcinogen	35	HLV is based on an oral to inhalation extrapolation of the IRIS RfD. Oral RfD set due to histopathologic changes in the liver in dogs.
Ethylbenzene	Inhalation RfC set based on developmental toxicity shown in rat and rabbit studies. IRIS most recent information classifies ethylbenzene as group D-not classifiable as human carcinogen.	50	HLV based on the RfC proposed by IRIS. An extra factor was added to the RfC due to recent evidence (1999) showing some carcinogenicity in rats and mice. An extra extrapolation was added to account for higher inhalation exposures per body wt in young children.

Compound	***IRIS Information***	***Annual HLV (ug/m^3)***	***Connecticut Health Information[25]***
Xylenes	IRIS sets an inhalation RfC due to impaired motor coordination observed in rats after subchronic inhalation. Not classifiable as a human carcinoge.	215	HLV derived from the ATSDR's chronic MRL. MRL relies on a worker study in China showing increased symptoms after exposure to mixtures of xylenes. Symptoms range from irritation to nuerologic effects.
Styrene	Inhalation RfC set based on an occupational study showing CNS effects in exposed workers.	50	HLV set developed by looking at the IRIS RfC, ATSDR's MRL, and CalEPA's NOAEL and LOAEL. All looked at occupational studies in exposed workers. An extra factor was added due to more recent studies showing some tumor formation in rats. An extra extrapolation was also added to account for higher inhalation exposures per body wt in young children.

Appendix B: PAMS VOCs

Table B-1: Characterization of PAMS sampling of VOCs in Connecticut[26]

VOC	% of Sample Detected
1,2,3-trimethylbenzene	84.8
1,2,4-Trimethylbenzene	87.9
1,3,5-Trimethylbenzene	43.8
1,3-butadiene	58.0
1-Butene	73.4
1-hexene	20.9
1-Pentene	52.5
2,2,4-Trimethylpentane	83.8
2,2-Dimethylbutane	56.8
2,3,4-Trimethylpentane	65.4
2,3-Dimethylbutane	82.2
2,3-Dimethylpentane	50.3
2,4-Dimethylpentane	28.9
2-Methyl-1-Pentene	14.4
2-Methyl-2-Butene	0.0
2-Methylheptane	46.4
2-Methylhexane	60.8
2-Methylpentane	98.2
3-Methyl-1-Butene	0.0
3-Methylheptane	44.4
3-Methylhexane	75.6
3-Methylpentane	94.0
4-Methyl-1-Pentene	0.0
Acetylene	89.2
alpha-Pinene	0.0
Aromatics	96.0
Benzene to Toluene ratio	94.1
Benzene	93.9
beta-Pinene	0.0
cis-2-Butene	77.8
cis-2-Hexene	0.0
cis-2-Pentene	32.4
Carbonyls	0.0
Cyclohexane	30.0
Cyclopentane	55.5
Cyclopentene	0.0
Dew Point	99.6
Ethane	99.9
Ethylbenzene	81.1
Ethylene	89.2
Isobutane	94.8
Isopentane	99.8

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[26] Red text indicates compounds that were detected in over 50% of the samples.

VOC	*% of Sample Detected*
Isoprene	92.8
Isopropylbenzene	18.2
m/p-Xylene	93.1
m-diethylbenzene	31.3
Methylcyclohexane	50.0
Methylcyclopentane	56.8
m-Ethyltoluene	68.1
n-Butane	99.0
n-Decane	63.4
n-Dodecane	8.4
n-Heptane	64.2
n-Hexane	75.0
n-Nonane	59.7
n-Octane	61.4
n-Pentane	99.1
n-Propylbenzene	39.0
n-Undecane	59.8
o-Ethyltoluene	41.9
Olefins	92.6
o-Xylene	82.7
Paraffins	96.0
p-diethylbenzene	42.1
p-Ethyltoluene	33.5
Propane	99.6
Propylene	84.3
xylenes to benzene	96.1
total xylenes	93.3