

# Measurements of VOCs from the TAMS Network

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Target volatile organic compounds (VOCs) were measured at a network of urban air monitoring locations in Boston, Chicago, Houston, and the Seattle/Tacoma area. Following a pilot-scale field evaluation of available techniques for determining concentrations of VOCs in ambient air, a technique based on evacuated stainless steel canisters was selected to collect whole air samples. Twenty-four-hour integrated samples were collected every twelfth day at ten sites over a 2-year study period. Battelle Columbus Laboratory (BCL) analyzed the samples for 25 target VOCs using cryogenic focusing, gas chromatographic separation and mass selective detection with flame ionization detection as backup. Duplicate canister samplers were operated each sampling period at one of the ten sites in the Toxic Air Monitoring System (TAMS) network to estimate overall method precision. In addition, every 10th analysis was repeated by BCL to obtain a measure of analytical precision. Finally, each sampling period a clean evacuated canister was sent to Research Triangle Park to be filled with an audit gas mixture of known concentrations. The audit canisters were analyzed along with the routine field samples to estimate method accuracy. The target compounds found most ubiquitously were benzene, toluene, xylene and ethylbenzene. These aromatic compounds were highly correlated and proportionally related in a manner suggesting that the primary contributors were mobile sources in all the urban locations studied. Annual median concentrations for target compounds ranged from 0.1 to 4.0 part per billion volume (ppbv) range, while individual 24-h concentrations occasionally reached as high as 20 ppbv.

In June 1984, a document entitled "Strategy for Monitoring Ambient Air Toxic Pollutants,"<sup>1</sup> was issued by the U.S. Environmental Protection Agency (EPA) proposing a multi-year research and development program in the area of toxic air pollutant assessment. As

part of the overall strategy, the document called for the development and operation of a pilot-scale monitoring network consisting of one air toxics sampling site in each of three cities in the first year, with subsequent expansion to 10-15 sites possible in future

years. EPA's Atmospheric Research and Exposure Assessment Laboratory in Research Triangle Park, North Carolina (AREAL/RTP) was given the responsibility for implementing this pilot program, known as the Toxic Air Monitoring System (TAMS) network. The objectives established for this program were to evaluate methods of sample collection and analysis for toxic air pollutants, begin to characterize ambient concentrations in selected urban atmospheres, and transfer monitoring technology and results to regional offices, state and local agencies.

## Experimental Methods

The TAMS monitoring program was initiated in 1985 with the establishment of one air monitoring station each in Boston, Chicago and Houston. These three cities were selected for this program by the Office of Air Quality Planning and Standards (OAQPS) from a list of urban areas with populations greater than one million persons. An effort was made to include in the study a diversity of emission and climate types, while not duplicating air toxics research already underway by other programs. The selection of specific monitoring locations within each city was made in consultation with OAQPS and the appropriate regional, state and local authorities. Siting criteria included population density, area emission types and rates, site accessibility, electric power availability, and site security. In most cases, an existing state or local agency monitoring station was found to meet the requirements of the TAMS program. For each site, a local person was recruited, hired, and trained specifically for the opera-

## Implications

Title III of the 1990 Clean Air Act Amendments requires that ambient monitoring be conducted in urban areas for a broad range of hazardous air pollutants, including volatile organic compounds. This paper describes an approach to sampling and analysis for VOCs which was used successfully by U.S. EPA in a network application over a two-year period. The data quality achieved is summarized, along with a discussion of observations from ten urban monitoring locations. The monitoring system, based on whole air collection in a stainless steel canister, generally performed well in the field and produced data of high quality.

tion of the TAMS air toxics sampling equipment.

The initial sampling methodology employed for the collection of VOCs at the TAMS sites consisted of a distributed air volume (DAV) sampling system (four air volumes and a field blank per sampling period) with Tenax-GC as the solid adsorbent. Twenty-four-hour integrated samples were collected every sixth day. Identification and quantitation of target compounds was accomplished at AREAL/RTP by using thermal desorption of the sample followed by gas chromatographic separation and mass spectrometric (GC/MS) analysis for 96 target compounds. Sample validation was based on the degree of consistency in blank-corrected concentration across the four samples for each compound.

In August 1986, a methods comparison study was begun at a second site established in the Houston area. Houston Site #2 is situated in suburban Deer Park, about midway between the Houston Ship Channel and the Bayport industrial complex. For a 10-month study period, two polished stainless steel canister samples were collected concurrently with the DAV-Tenax samples and returned to RTP for analysis. A comparative analysis of the results<sup>2</sup> demonstrated that while the two methods yielded substantially equivalent mean concentrations, method precision was superior for the canister collection technique. In light of these results, it was decided in August 1987 to replace the Tenax-based samplers at existing TAMS sites with canister-based systems and to deploy the canister-based systems at new TAMS sites called for in fiscal year 1988 (FY-88) program plans. Also, because of the projected increase in sample load, a decision was made to reduce the sampling frequency to every twelfth day and to seek a contract laboratory for provision of clean canisters and analytical services to the expanded network.

#### Field Operations

During FY-88, the TAMS network was expanded to include a total of ten urban air monitoring stations. Three

sites were located in each of the original cities: Boston, Chicago and Houston. In each city, the first two sites were selected to represent the primary industrial sectors of the urban area, and the third site was located in a more residential area for purposes of contrast. Midway through the fiscal year, a single station became operational in the Seattle/Tacoma metropolitan area. This site was located in an industrial complex on land controlled by the Port of Tacoma. Descriptive information for each TAMS site appears in Table I.

The canister samplers deployed in the network were similar in design to the K-type samplers built by EPA for use in the Kanawha Valley Study,<sup>3</sup> two of which were used in the TAMS methods comparison study. Prior to deployment, the samplers were cleaned and certified according to procedures which have since been codified in Method TO-14 of EPA's Compendium of Methods.<sup>4</sup> It was decided to operate the TAMS samplers in a passive (i.e., vacuum-filling) mode to eliminate the pump as a potential source of sample contamination, mechanical failure, or air leaks.

Every twelfth day, a whole-air sample was collected at each TAMS site in a clean, evacuated canister with initial vacuum equal to ~30 in. Hg. Sampling commenced at 6 a.m. and continued for a 24-h period. Flow of air into the canister was regulated by a mass flow controller set to a rate of ~3.5 cc/min. A certified mass flow meter was used to verify correct sample flow before and after each sample collection period. If properly followed, this procedure resulted in a sample under a slight vacuum (~2-3 in. Hg.) at the conclusion of the 24-h sampling cycle. Beginning and ending sampling times, canister pressures, and flow rates were recorded by the field operator.

#### Laboratory Operations

All canister samples collected at the TAMS sites in FY-88 and FY-89 were prepared and analyzed by Battelle Columbus Laboratory (BCL). The cryogenic GC/MSD system used to analyze these samples was identical to the system that had been used at AREAL/

RTP for processing earlier TAMS samples. Canisters were cleaned with a vacuum and oven system<sup>4</sup> and sent to the field sites in time for each sampling date. Returned canisters were checked in and the final pressure was recorded. Sample analysis was achieved with a Hewlett-Packard (HP) model 5880 A (level 4) GC equipped with a flame ionization and a mass selective detection system (HP 5970). A 50-m by 0.32-mm-i.d., HP-1 fused-silica column was used to resolve the target compounds. The column exit flow was split by a low dead-volume tee (Alltech, Inc.). One-third of the flow was directed to the mass selective detector (MSD); the remaining flow passed through the flame ionization detector (FID).

A Perma Pure dryer (model MD-125-48F) with a tubular hygroscopic ion-exchange membrane (Nafion) was used to remove water vapor selectively from the sampled gas stream. Use of the drier permitted collection of larger volumes of sample air (350 cc), thereby lowering the limit of detection. The MSD was operated in the selective ion monitoring (SIM) mode of operation for canister analyses. In this mode, the MSD monitored only preselected ions, rather than scanning all masses continuously between two mass limits. As a result, increased sensitivity and improved quantitative analysis were achieved. For the canister samples, two characteristic ions were monitored for each target compound and quantitation was based upon peak areas. The minimum quantitation limit (MQL) used for all compounds was 0.1 part per billion by volume (ppbv).

#### Quality Assurance

In the field, duplicate canister samplers were operated each sampling period at Houston Site #2 to obtain information for estimating the overall precision of the measurement system. In the laboratory, one canister was reanalyzed each sample period to provide information on analytical precision. During the second year of the program, a clean evacuated canister was sent each sampling period to EPA to be filled with a mixture of known NIST-traceable concentrations of VOCs from an audit gas cylinder. The canister was then returned to BCL for analysis with the routine field samples. These data were collected to obtain estimates of analytical bias.

#### Results and Discussion

Results by TAMS site ranged from 73.9 to 97.5 percent data completeness. These values were computed as the percentage of scheduled sampling periods for which valid aerometric re-

Table I. Location of TAMS monitoring stations.

City	No.	Location	Classification	Code
Boston	1	1 Summit Dr	Industrial	BOS1
	2	115 Southampton St	Industrial	BOS2
	3	Orchard & Common St	Residential	BOS3
Chicago	1	727 E. 111th St	Industrial	CHI1
	2	7800 W 65th St	Industrial	CHI2
	3	O'Hare International	Airport Property	CHI3
Houston	1	1262 Mae Drive	Industrial	HOU1
	2	1050 W Pasadena Dr	Industrial	HOU2
	3	4510 Aldine Mail Rd	Residential	HOU3
Tacoma	1	2301 Alexander Ave	Port/Industrial	SEAT

sults were actually obtained. Reasons for missing samples included mechanical or personnel problems in the field, missed shipment dates and laboratory malfunction. Overall, the results were judged to be acceptable in light of the original data quality objective (DQO) for data completeness (i.e.,  $\geq 75$  percent).

In Figure 1, the percentage of TAMS data reported as discriminant values (i.e.,  $>0.10$  ppbv) is shown by compound averaged across all sites. Although the target compound list was limited to VOCs which might be expected in urban air, many of the targeted compounds were often not found in measurable quantities at several of the TAMS monitoring sites. Further quantitative analysis was therefore limited to compounds found at concentrations above the MQL at least 75 percent of the time. Thirteen of the 25 target compounds met this criterion, ten having 95 percent or more discriminant values (see Figure 1).

#### Data Quality

The replicate values provided by BCL for every tenth sample were used to calculate analytical precision estimates for the 13 compounds of interest. Also, the results from the duplicate samplers operated at Houston site #2 were

used to estimate overall method precision for each compound. These estimates were computed in each case as the pooled standard deviation expressed as a percentage of the overall mean for the paired data sets. Concentration values below the MQL were set to one-half that level for computation. The resulting coefficients of variation (%CVs) for replicates and duplicates appear in Figure 2.

The 13 compounds of interest fall into three classifications, as shown in Figure 2: freons, aromatics, and chlorinated alkanes. Although the freons exhibit relatively high %CVs for duplicate samples, the %CVs for replicate analyses are quite comparable with those for other compounds. This suggests that problems may have been encountered in obtaining representative ambient air samples for the freons. For example, the duplicate samplers were located on the roof of an air-conditioned trailer from which freons may have been emitted. Also, freon-113 may have been used as a solvent to clean components in the mass flow controllers. Because of the relatively high %CV for duplicates, freon data were excluded from further analyses. The other compounds exhibited overall method precision in accordance with the project DQOs (i.e.,  $\leq \pm 25$  percent). For carbon tetrachloride, the

%CV for replicate analyses exceeded the %CV for duplicate samples. This anomaly probably is due to the consistently low concentrations of carbon tetrachloride reported (i.e., just slightly above the quantitation limit).

A comparison of the analytical results from BCL with the known or spike values from EPA for audit gas samples showed that analytical bias was generally within  $\pm 25$  percent for the compounds in the mixture. An explanation was found for each occasion when excursions beyond these DQO bounds did occur. Appropriate corrective measures were then instituted, such as obtaining a calibration gas of improved purity for one compound and correcting the humidification process for audit sample preparation at one point in the program.

#### Monitoring Data

The median and maximum 24-h VOC concentration values for the two-year study period are shown by site in Table II. For the aromatic compounds, concentration levels and their relationships are very similar from site to site and even across cities. The median concentrations for chlorinated alkanes are comparatively low (i.e., less than 1.0 ppbv in most cases). However, maximum 24-h values for the solvents

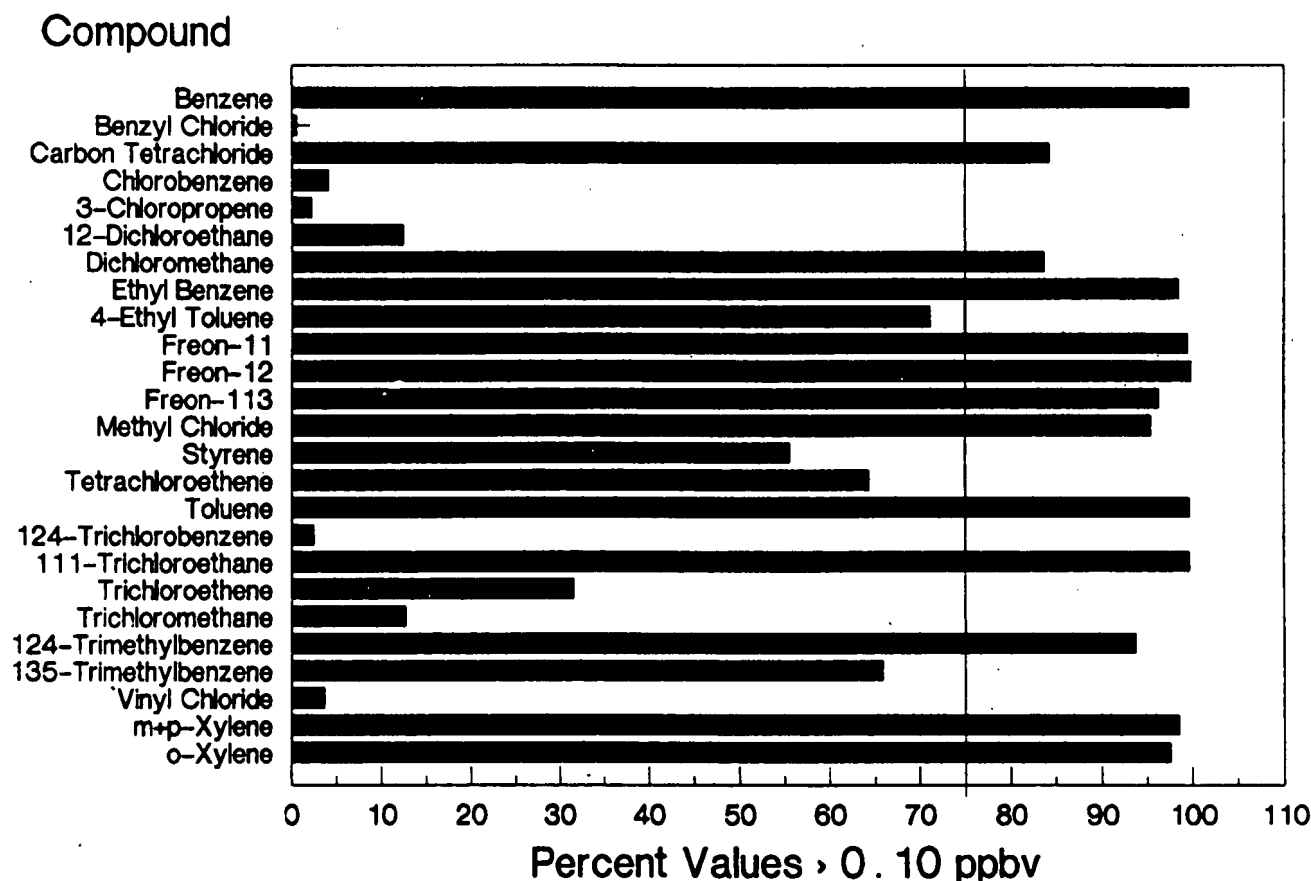


Figure 1. Percent values above quantitation limit.

# Compound

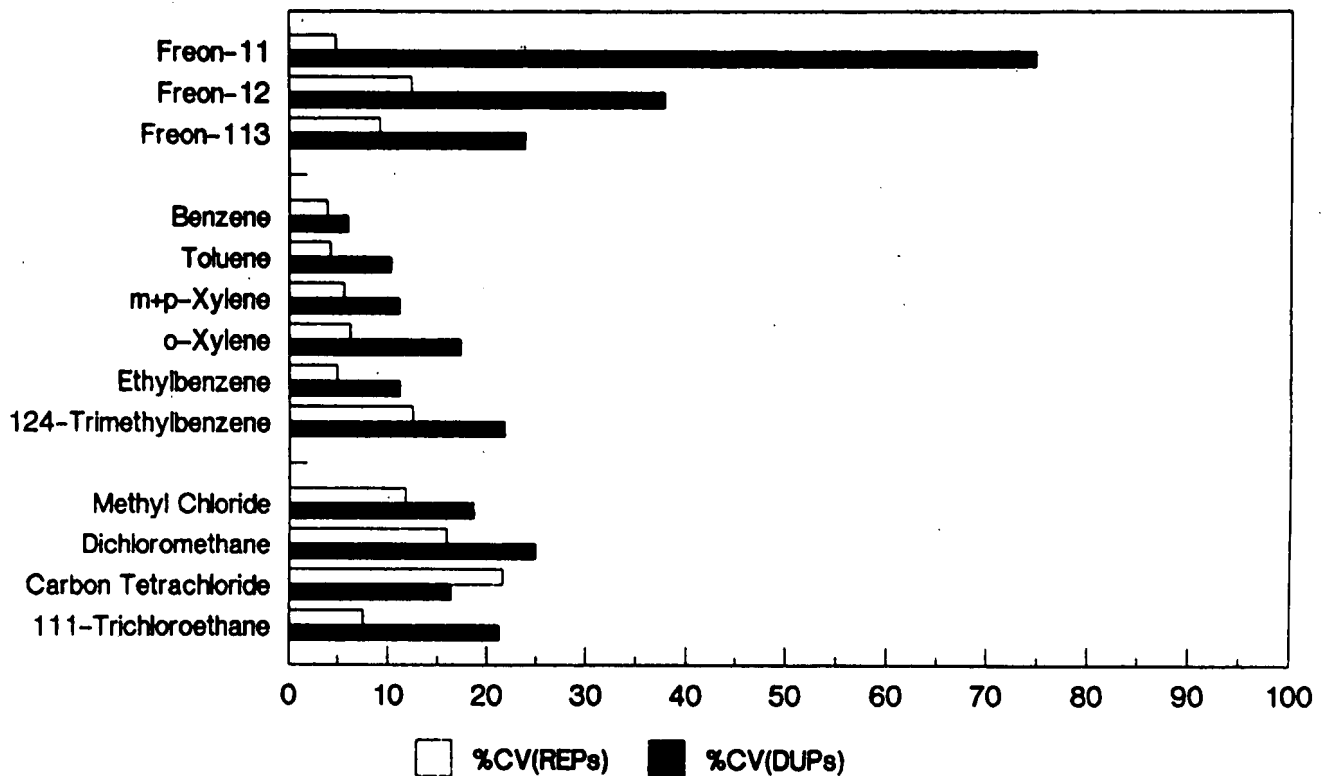


Figure 2. Coefficients of variation for replicates and duplicates.

dichloromethane and 1,1,1-trichloroethane did occasionally approach or even exceed 20 ppbv at industrial sites in Houston and Tacoma.

Review of data plots suggested that some strong associations existed both between and within sites. To explore these relationships further, Pearson product-moment correlations<sup>5</sup> were computed between sites within each city. The highest inter-site correlations were found to exist between Boston sites 1 and 2 and Houston sites 1 and 3 for dichloromethane and the

aromatic compounds ( $r > 0.60$  in all cases). The lowest spatial correlations ( $r < 0.33$ ) were observed for carbon tetrachloride. This compound exhibited little concentration range at most of the sites, remaining very close to the global background level of 0.12 ppbv. Friedman's test<sup>5</sup> (a nonparametric procedure) was computed by city to determine whether consistent differences existed between sites within each city. Generally, in the cases where significant differences were found, the more industrialized areas (sites #1 and #2)

exhibited higher concentrations than the corresponding residential area (site #3).

Correlations were also computed between compounds measured at each TAMS site to estimate the degree of linear relationship between pollutants at the same location. This procedure revealed that o-xylene, m+p-xylene, and ethylbenzene were highly ( $r > 0.90$ ) and mutually correlated at every TAMS site. Also, at most sites, benzene and toluene were positively correlated with one another and with o-x-

Table II. 24-H VOC median and maximum by site (ppbv).

Compound	Stat	BOS1	BOS2	BOS3	CHI1	CHI2	CHI3	HOU1	HOU2	HOU3	SEAT
Benzene	Med	0.87	1.15	0.70	1.03	1.17	0.85	1.82	1.09	1.34	0.95
	Max	2.73	1.95	3.18	4.25	7.28	2.02	8.65	6.51	8.96	8.21
Toluene	Med	2.07	3.01	1.85	3.36	2.60	1.83	3.00	1.77	3.16	2.22
	Max	5.60	5.48	11.8	15.2	12.8	9.49	18.6	9.86	19.4	16.3
m + p-Xylene	Med	0.92	1.42	0.73	1.36	1.05	0.81	1.51	0.87	1.44	1.16
	Max	3.03	2.96	3.15	7.79	4.70	2.41	7.83	3.24	9.00	8.33
o-Xylene	Med	0.37	0.53	0.31	0.43	0.35	0.40	0.54	0.34	0.55	0.44
	Max	0.93	1.12	1.13	1.64	1.62	1.16	2.78	1.01	3.31	3.00
Ethylbenzene	Med	0.31	0.44	0.23	0.49	0.35	0.26	0.50	0.29	0.47	0.37
	Max	0.81	0.84	0.92	2.71	1.49	0.81	2.41	1.06	2.46	2.30
Methyl Chloride	Med	0.54	0.57	0.58	0.57	0.56	0.58	0.79	0.72	0.73	0.56
	Max	1.18	1.01	1.02	0.82	4.76	1.34	2.09	2.42	2.23	2.99
Dichloromethane	Med	0.29	0.39	0.42	0.42	0.37	0.38	0.34	0.31	0.31	0.35
	Max	3.10	3.89	1.80	3.97	3.21	3.40	20.6	5.71	3.29	14.1
Carbon Tetrachloride	Med	0.12	0.13	0.13	0.12	0.12	0.13	0.15	0.13	0.12	0.12
	Max	0.16	0.17	0.21	0.44	0.15	0.19	0.88	1.14	0.34	0.17
111-Trichloroethane	Med	0.58	0.71	0.68	0.59	0.68	0.66	0.53	0.41	0.79	0.53
	Max	3.34	2.72	2.61	3.89	4.50	1.84	17.4	7.08	16.9	13.7
124-Tri-Methyl Benzene	Med	0.35	0.59	0.35	0.41	0.37	0.36	0.63	0.37	0.62	0.46
	Max	1.02	1.43	1.33	1.32	1.86	0.87	3.20	1.19	4.48	2.82

**Table III. Ratios of toluene: benzene: xylene: ethylbenzene.**

Site	City			
	Boston	Chicago	Houston	Tacoma
1	7:3:4:1	7:2:4:1	6:4:4:1	6:3:4:1
2	7:3:4:1	7:3:4:1	6:4:4:1	
3	8:3:5:1	7:3:5:1	7:3:4:1	

lene, m+p-xylene, and ethylbenzene. These strong linear associations suggest that a common source category is predominantly responsible for the concentrations of aromatic compounds observed at all the TAMS monitoring locations. The ratios of the median concentrations for aromatic compounds at the TAMS sites are shown in Table III. These ratios, expressed as toluene: benzene: total xylene: ethylbenzene, are quite similar from site to site and closely approximate published ratios among these compounds for motor vehicle emissions (7:3:5:1).<sup>6</sup> Clearly, mobile sources are most likely responsible for the major portion of aromatic VOC concentrations observed at these sites. Comparison of the TAMS database with other results reported and summarized in the literature<sup>7-10</sup> show that the VOC concentrations observed at the TAMS locations are typical of the atmospheric levels of these compounds generally found in U.S. urban areas.

### Conclusions

EPA canister method TO-14 proved fieldworthy in an urban network application over a two-year period of operation. Coupled with GC/MSD analysis, it produced data of acceptable quality in terms of completeness (90 percent overall), precision (within  $\pm 25\%$ ), and accuracy (within  $\pm 25\%$ ) for most VOCs of interest. The 24-h ambient levels of targeted VOCs ranged from less than 0.1 ppbv to slightly greater than 20 ppbv. Measured concentrations were comparable in all urban areas monitored, although the more heavily industrialized areas tended to exhibit higher

concentrations than corresponding residential areas. Toluene was the compound generally found at highest concentrations, with individual 24-h concentrations occasionally approaching 20 ppbv. Mobile sources were most likely the dominant contributors of the aromatic compounds (i.e., benzene, toluene, xylene, and ethylbenzene) observed at all sites in each of the four cities. Annual median concentrations for these compounds ranged from 0.2 to 4.0 ppbv. Annual median concentrations of chlorinated aliphatic compounds were typically less than 1.0 ppbv, although individual 24-h concentrations ranged to 20 ppbv suggesting the need for finer time-scale resolution for applications where peak VOC concentrations are of interest.

### Disclaimer

This paper has been reviewed in accordance with the U. S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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