

# Air Toxics

<http://www.epa.gov/oar/aqtrnd98/chapter5.pdf>

## Background

Hazardous air pollutants (HAPs), commonly referred to as air toxics or toxic air pollutants are pollutants known to cause or suspected of causing cancer or other serious human health effects or ecosystem damage. Section 112 of the CAA now lists 188 pollutants or chemical groups as HAPs and targets sources emitting them for regulation.<sup>1</sup> Examples of air toxics include heavy metals like mercury and chromium and organic chemicals like benzene, 1,3-butadiene, perchloroethylene (“perc”), dioxins, and polycyclic organic matter (POM).

Hazardous air pollutants (HAPs) are emitted from literally thousands of sources including large stationary industrial facilities or major point sources (such as electric power plants or utilities), smaller area sources (such as neighborhood dry cleaners), and mobile sources (such as automobiles). Adverse effects to human health and the environment due to HAPs can result from exposure to air toxics from individual facilities, exposure to mixtures of pollutants found in urban settings, or exposure to pollutants emitted from distant sources that are transported through the atmosphere over regional, national or even global airsheds. Exposures of concern to HAPs can be

either short-term or long-term in nature. In addition to breathing air contaminated with air toxics, exposure to some HAPs can occur by other means, such as through the ingestion of contaminated food from waters polluted from the deposition of HAPs. Some HAPs can bioaccumulate in body tissues. When a predator feeds on contaminated prey, concentrations of these bioaccumulative HAPs can build up in the predator’s tissues, magnifying the toxic burden. As of December 1998, over 2,506 U.S. water bodies are under fish consumption advisories (for particular species of fish), representing approximately 15.8 percent of the nation’s total lake acreage and 6.8 percent of the nation’s river miles.<sup>2</sup>

## Health and Environmental Effects

Most of the information on potential health effects of HAPs is derived from experimental animal data and studies of exposed workers. The different health effects which may be caused by HAPs include cancer, neurological, cardiovascular, and respiratory effects, effects on the liver, kidney, immune system, and reproductive system, and effects on fetal and child development. The timing of effect and the severity (e.g., minor or reversible vs. serious, irreversible, and life-threatening) may vary

among HAPs and with the exposure circumstances. In some rare cases, effects can be seen immediately. Rare cases involve the catastrophic release of lethal pollutants, such as the 1984 incident in Bhopal, India, where more than 2,000 people were killed by the release of methyl isocyanate into the atmosphere. In other cases, the resulting effects (e.g., liver damage or cancer) are associated with long-term exposures and may not appear until years after exposure. More than half of the 188 HAPs have been classified by EPA as “known,” “probable,” or “possible” human carcinogens. Known human carcinogens are those that have been demonstrated to cause cancer in humans. Examples include benzene, which has caused leukemia in workers exposed over several years to certain amounts of it in their workplace air, and arsenic, which has been associated with elevated lung cancer rates in workers at metal smelters. Probable and possible human carcinogens include chemicals that are less certain to cause cancer in people, yet for which laboratory animal testing or limited human data indicates carcinogenic effects.

Some HAPs pose particular hazards to people of a certain age or stage in life (e.g., young children, adolescents, adults, or elderly people). Available data suggest that

about a third of HAPs, may be developmental or reproductive toxicants in humans. This means that exposure during the development of a fetus or young child may prevent normal development into a healthy adult. Other such critical exposures may affect the ability to conceive or give birth to a healthy child. Ethylene oxide, for example, has been associated with increased miscarriages in exposed workers and has affected reproductive ability in both male and female laboratory animals.

Toxic air pollutants can have a variety of environmental impacts in addition to the threats they pose to human health. Animals, like humans, may experience health problems if they breathe sufficient concentrations of HAPs over time, or ingest HAPs through contaminated food (e.g., fish). Apart from the laboratory testing results on animal species that make up a large portion of the human health effects database, and aquatic toxicity criteria for some HAPs, little quantitative information currently exists to describe the nature and scope of the effects of air toxics on non-human species.

One of the more documented ecological concerns associated with toxic air pollutants is the potential for some HAPs to damage aquatic ecosystems. For example, a number of studies suggest that deposited air toxics contribute to deleterious effects such as reproductive failures, developmental disorders, disease, and premature death in fish and wildlife species native to the Great Lakes. Deposited air pollutants can be significant contributors to overall pollutant loadings entering water bodies (especially for persistent chemicals such as mercury which continue to move among air, water, and sedi-

ments). For the Great Lakes, international programs have examined the importance of deposition of air toxics, relative to other loadings such as direct discharge. While data are presently insufficient for many quantitative estimates comparing air deposition and other loading pathways, deposition of air toxics to the Great Lakes is considered significant and continues to be investigated with a binational monitoring network, the Integrated Atmospheric Deposition Network (IADN).<sup>3</sup>

Persistent air toxics are of particular concern in aquatic ecosystems, as toxics levels can magnify in the food web, resulting in exposures greater than those expected based solely on the levels in water or air. Such "bio-accumulation" and "biomagnification" (where the levels of a toxic substance increase at higher trophic levels of the food web) are seen in New England populations of breeding loons, birds that feed on fish in waters contaminated by airborne mercury. Studies are showing that an estimated 12–31 percent of the breeding loons have mercury levels that put them at risk of behavioral, reproductive and other effects.<sup>4</sup>

### **National Air Toxics Control Program (*The Regulatory Response*)**

In 1990, Congress amended the CAA by adding a new approach to the regulation of HAPs. This new approach is divided into two phases. The first requires the development of technology-based emissions standards for stationary sources of the 188 HAPs. The second phase is to evaluate remaining problems or risks and develop additional regulations to address sources of those problems, as needed.

Phase One is composed of the technology-based standards, known as MACT (Maximum Achievable Control Technology) and GACT (Generally Achievable Control Technology) regulations, under Sections 112(d). All large, or major, sources of the 188 HAPs must be addressed by MACT or GACT regulations, as well as the smaller, area sources found to carry significant risk or identified as important under the Specific Pollutants Strategy [Section 112(c)(6)] or the urban program [Sections 112(c)(3) and 112(k)]. Some combustion sources, such as municipal waste combustors and medical waste incinerators, are regulated under equivalent requirements in Section 129. The purpose of this technology-based approach is to use available control technologies or changes in work practices to get emission reductions for as many of the listed HAPs as possible. It is intended that effective MACT standards will reduce a majority of the HAP emissions and, therefore, reduce potential risks from regulated sources.

Air toxics emission reductions also result from the particulate matter, ozone and carbon monoxide control programs which are directed at both stationary and mobile sources (see emission reductions described in Chapter 2). While the toxic reductions from EPA's mobile source emission standards have been large, prior to 1990, EPA had no specific directions from Congress for a planned program to control toxic emissions from mobile sources. However in 1990, Congress amended the CAA by adding a formal requirement to consider motor vehicle air toxics controls under Section 202(1). Section 202(1), required the Agency to complete a study of motor vehicle-related air

**Table 5-1.** List of 33 Urban Air Toxics Strategy HAPs

VOCs	Metals (Inorganic Compounds)	Aldehydes (Carbonyl Compounds)	SVOCs & Other HAPs
acrylonitrile	arsenic compounds	acetaldehyde	2,3,7,8-tetrachlorodi benzo-p-dioxin (& congeners & TCDF congeners)
benzene	beryllium and compounds	formaldehyde	coke oven emissions
1,3-butadiene	cadmium compounds	acrolein	hexachlorobenzene
carbon tetrachloride	chromium compounds		hydrazine
chloroform	lead compounds		polycyclic organic matter (POM)
1,2 -dibromoethane (ethylene dibromide)	manganese compounds		polychlorinated biphenyls (PCBs)
1,3-dichloropropene	mercury compounds		quinoline
1,2-dichloropropane (propylene dichloride)	nickel compounds		
ethylene dichloride, EDC (1,2-dichloroethane)			
ethylene oxide			
methylene chloride (dichloromethane)			
1,1,2,2,-tetrachloroethane			
tetrachloroethylene (perchloroethylene, PCE)			
trichloroethylene, TCE			
vinyl chloride			

toxics, and to promulgate requirements for the control of air toxics from motor vehicles. EPA completed the required study in 1993, and is presently conducting analyses to update emissions and exposure analyses done for the study as well as working on rulemaking to address the requirements of the section.

After application of the technology-based standards comes Phase Two, which consists of strategies and programs for evaluating remaining risks and ensuring that the overall program has achieved a sufficient reduction in risks to public health

and the environment. This phase will be implemented through such programs as the integrated urban air toxics strategy, and the residual risk program (Section 112(f)). The integrated urban air toxics strategy identifies 33 HAPs which are judged to pose the greatest threat to public health in urban areas.<sup>5</sup> The strategy requires that EPA ensure a 75-percent reduction in cancer incidence from stationary sources; a “substantial” reduction in non-cancer risks from area sources; and to also ensure that disproportionate risks are addressed first by focusing efforts on sensitive

populations or geographic hot spots. In addition, the strategy must assure that area sources accounting for 90 percent of the total emissions of the urban HAPs are subject to MACT or GACT regulations. The list of the 33 urban HAPs are presented in Table 5-1 and are grouped according to their chemical properties [volatile organic compounds (VOCs), metals, aldehydes, and semi-volatile organic compounds (SVOCs)]. This list includes not only those with emissions from area sources, but also includes those posing public health concerns in urban areas regardless of emission source type.

Phase Two also will use information generated through the special studies required in the CAA—the Great Waters program [Section 112(m)], and the Mercury and Utility Studies [Section 112(n)]. The Great Waters program contains an ongoing examination of atmospheric deposition of air toxics to aquatic ecosystems, and the effects of those toxics when concentrated through the food web. The Mercury Study examined the adverse effects of, and possible controls for, mercury from all sources. The Utility Study examined health hazards of, and possible controls for, the numerous toxics from electric utilities.

The CAA recognizes that not all problems are national problems or have a single solution. Authority for national emission standards are complemented by authorities to examine problems on other scales in order to address specific concerns. The CAA also provides mechanisms for increasing partnerships among EPA, states and local programs to address problems specific to these regional and local environments. As we move toward the 21st century, EPA’s National Air Toxics Program is

beginning to progress from the more technologically-based approach for regulating toxics to a more risk-based approach. This shift will require more and better information about all emission sources of HAPs, ambient levels of HAPs, and human and ecosystem exposure to HAPs. The development of an "information infrastructure" to inform the risk-based decisions has been a priority for the EPA over the last few years.

## National Air Toxics Assessment Activities

The success of the National Air Toxics Program critically depends on our ability to quantify the impacts of air toxics emissions on public health and the environment. To that end, EPA has initiated numerous National Air Toxics Assessment (NATA) activities to help identify areas of concern, characterize risks and track progress. These activities include expanded air toxics monitoring, improving and periodically updating emissions inventories, national- and local-scale air quality and exposure modeling, and continued research on effects and assessment tools. NATA activities will lead to improved characterizations of air toxics risk and reductions in risk resulting from ongoing and future implementation of air toxics emissions control standards and initiatives. A major assessment is currently underway at EPA which will address the 188 HAPs. It includes state-by-state updates to emission inventories for the year 1996, known as the National Toxics Inventory (NTI), and nationwide estimation of air quality using the ASPEN (Assessment System for Population Exposure Nationwide) air quality dispersion model. Together with the

Hazardous Air Pollutant Exposure Model (HAPEM4), the NATA national-scale screening assessment will also be used to estimate 1996 population exposures across the nation, and characterize potential public health risks due to inhalation of air toxics, including both cancer and noncancer effects. Although the NTI includes all 188 pollutants, the initial modeling activities focus on the "urban HAP list" (Table 5-1).

## Ambient Monitoring

Ambient air toxics monitoring is another important component of NATA. Ambient measurements are useful to: characterize ambient concentrations and deposition in representative monitoring areas, provide data to support and evaluate dispersion and deposition models, and establish trends and evaluate the effectiveness of HAP reduction strategies. There are approximately 300 monitoring sites currently producing ambient data on hazardous air pollutants. EPA is working together with state and local air monitoring agencies to build upon these monitoring sites to develop a monitoring network which is representative of air toxics problems on a national scale and which provides a means to obtain data on a more localized basis as appropriate and necessary. The network will represent an integration of information from many monitoring programs, including PAMS, which provide information on VOCs and aldehydes, and the new urban PM<sub>2.5</sub> chemical speciation and rural IMPROVE networks which provide information on HAP trace metals. This new national network will be developed over the next several years. Trend data will initially be used to help characterize air quality,

and to support and evaluate models and later to better describe national HAP trends.<sup>6</sup>

Several states have long-standing air toxics monitoring programs which already produce measurements on many HAPs including the important urban HAPs. Some of these state programs are assisted by EPA's contractor-supported Urban Air Toxics Monitoring Program (UATMP), as well as the Non-Methane Organic Compound (NMOC) and Speciated Non-Methane Organic Compound (SNMOC) monitoring programs. The UATMP is dedicated to toxics monitoring which involves measurements of 39 HAP VOCs and 13 carbonyl compounds.<sup>7</sup> The Agency's Photochemical Assessment Monitoring Stations (PAMS) also measure HAPs among the many pollutants that are precursors of ozone.

The PAMS program requires routine year-round measurement of VOCs which include nine HAPs: acetaldehyde, benzene, ethylbenzene, formaldehyde, n-hexane, styrene, toluene, xylenes (m/p-xylene, o-xylene) and 2,2,4-trimethylpentane. Three of these are on the list of urban HAPs (acetaldehyde, benzene and formaldehyde). For a more detailed discussion of the PAMS program, see the ozone section in Chapter 2 of this report. Although the state air toxics and PAMS data are limited in their geographic scope, they do not cover many HAPs for most states, and are not necessarily sited to represent the highest area-wide concentrations, they can still be used to provide useful information on the trends in ambient air toxics at this time.

**Table 5-2.** Comparison of Typical Urban and Rural Concentrations for VOCs and Aldehydes, Based on 1996 Ambient Measurements

HAP	Urban Sites		Rural Sites		Urban to Rural
	Number of sites µg/m <sup>3</sup>	Annual Average Concentration, µg/m <sup>3</sup>	Number of sites	Annual Average Concentration, µg/m <sup>3</sup>	Ratio of average concentrations
1,2-Dibromoethane	60	0.70	1	0.04	17.5
Ethylene dichloride	88	0.40	7	0.04	9.9
Styrene	74	1.75	11	0.18	9.6
Trichloroethylene	84	0.62	8	0.08	8.0
Vinyl chloride	86	0.31	7	0.05	6.6
1,2-Dichloropropane	52	0.30	7	0.05	6.0
Tetrachloroethylene	90	1.17	8	0.21	5.6
1,3-Butadiene	60	0.84	7	0.15	5.5
1,1,2,2-Tetrachloroethane	32	0.09	2	0.02	5.2
trans-1,3-Dichloropropene	10	0.03	1	0.01	3.8
Methylene chloride	95	1.40	8	0.40	3.5
cis-1,3-Dichloropropene	10	0.03	1	0.01	2.9
Chloroform	94	0.47	8	0.21	2.2
Carbon tetrachloride	86	0.89	7	0.52	1.7
Acrolein	24	0.20	2	0.12	1.6
Toluene	101	5.68	9	3.82	1.5
Benzene	121	2.08	11	1.60	1.3
Formaldehyde	38	5.17	4	4.10	1.3
Acetaldehyde	38	2.94	4	3.37	0.9

**Table 5-3.** Comparison of Typical Urban and Rural Concentrations for Trace Metals, Based on 1996 Ambient Measurements

HAP	Urban Sites		Rural Sites		Urban to Rural
	Number of sites ng/m <sup>3</sup>	Annual Average Concentration, ng/m <sup>3</sup>	Number of sites	Annual Average Concentration, ng/m <sup>3</sup>	Ratio of average concentrations
Nickel (fine)	13	1.14	65	0.22	5.2
Cadmium (pm10)	12	1.65	4	0.52	3.2
Arsenic (fine)	13	1.05	65	0.34	3.1
Lead (fine)	13	4.70	65	1.66	2.8
Manganese (fine)	13	3.34	65	1.26	2.7
Lead (coarse)	13	3.15	2	1.22	2.6
Nickel (pm10)	24	3.65	8	1.46	2.5
Nickel (tsp)	88	10.53	18	4.53	2.3
Manganese (pm10)	20	13.67	8	7.30	1.9
Chromium (coarse)	13	2.25	2	1.23	1.8
Chromium (pm10)	25	6.14	8	3.40	1.8
Beryllium (tsp)	31	0.08	7	0.05	1.6
Chromium (tsp)	90	8.03	18	5.05	1.6
Nickel (coarse)	13	1.35	2	0.87	1.6
Chromium (fine)	13	0.93	65	0.71	1.3
Lead (pm10)	40	22.40	11	19.12	1.2
Manganese (coarse)	13	12.57	2	11.35	1.1
Chromium VI	27	0.13	2	0.12	1.0
Arsenic (pm10)	25	3.09	8	3.05	1.0
Arsenic (coarse)	13	1.01	2	1.00	1.0
Beryllium (pm10)	7	0.30	4	0.30	1.0
Mercury (coarse)	13	1.02	2	1.02	1.0
Mercury (fine)	13	1.04	2	1.13	0.9
Manganese (tsp)	71	33.34	17	41.65	0.8
Mercury (pm10)	17	0.84	4	1.10	0.8
Mercury (tsp)	35	0.96	2	1.70	0.6
Arsenic (tsp)	73	7.04	9	33.86	0.2
Lead (tsp)	296	177.02	39	861.31	0.2
Cadmium (tsp)	80	1.95	17	13.33	0.1

## Status of Urban and Rural Ambient Concentrations

Several hundred locations monitor for air toxics year-round and have sufficient data to estimate annual average concentrations for many HAPs. This section focuses on the urban HAP list. Year-round ambient concentrations are available for 25 HAPs on the list. Extensive data for styrene and toluene are also available. Tables 5-2 and 5-3 compare typical urban and rural annual average concentrations for VOCs, aldehydes and trace metals. Some of the HAP data are represented by more than one type of measurement [e.g., chromium (PM<sub>10</sub>) and chromium (TSP)]. The amount of rural data is limited for VOCs and for some of the trace metal HAPs. Nevertheless, tentative observations about urban-

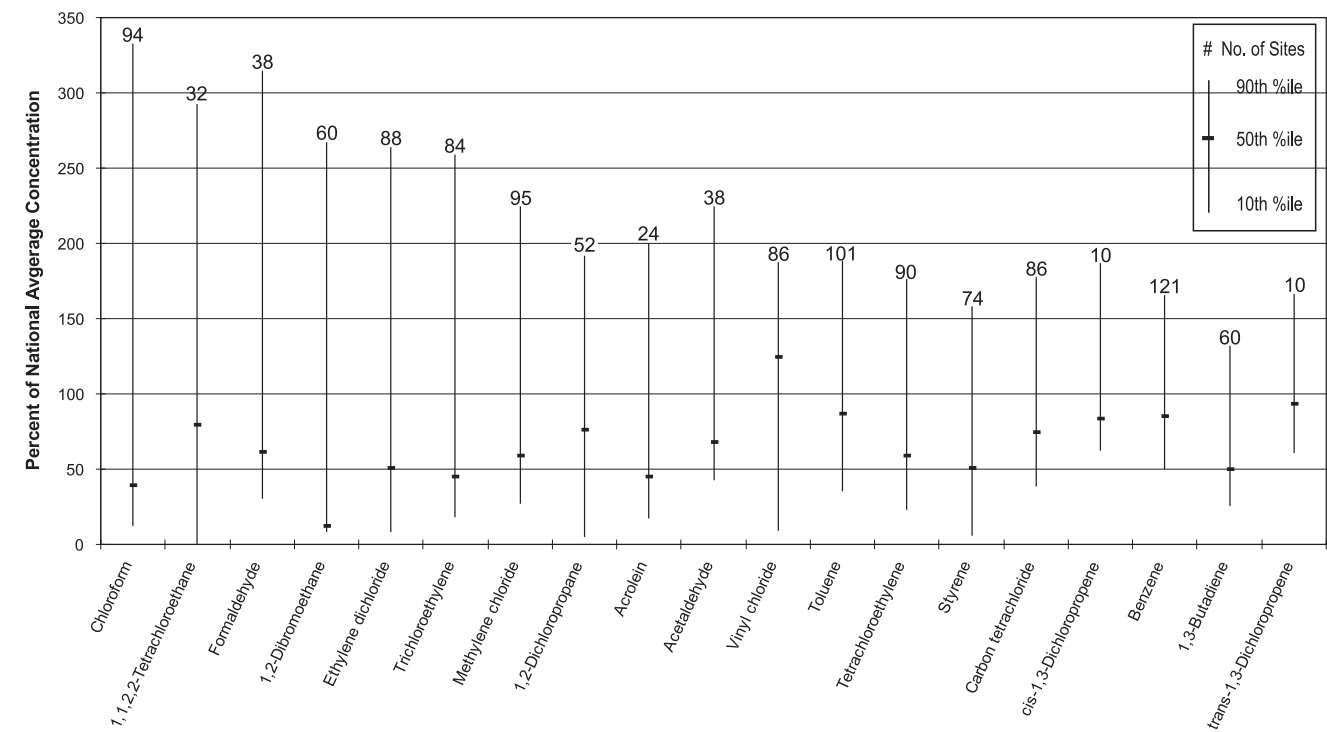
rural differences in ambient levels can be presented. In this chapter, urban air quality is based on monitoring sites located within metropolitan statistical areas. It is noted that this definition is not necessarily the same as the one which will be used in Section 112k rule making.

For many VOCs and aldehydes, the concentrations are relatively similar between urban and rural locations (e.g., carbon tetrachloride, formaldehyde and benzene). In particular, pollutants associated with ubiquitous mobile sources appear to be more similar between urban and rural areas. On the other hand, several HAPs show large differences among sampling locations (e.g., styrene and vinyl chloride). This contrast may be attributed to many factors including geographic distribution of emission sources, the limited number of monitoring sites and the proximity of the

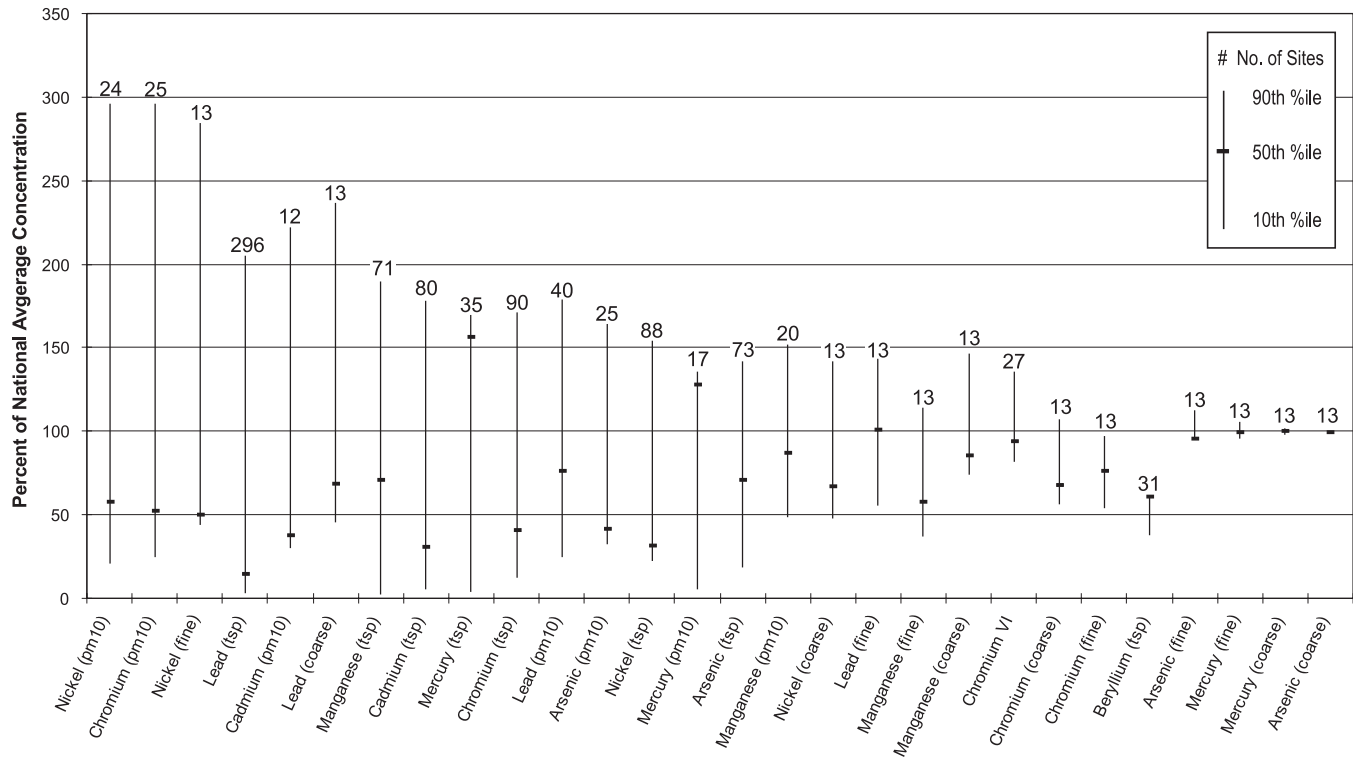
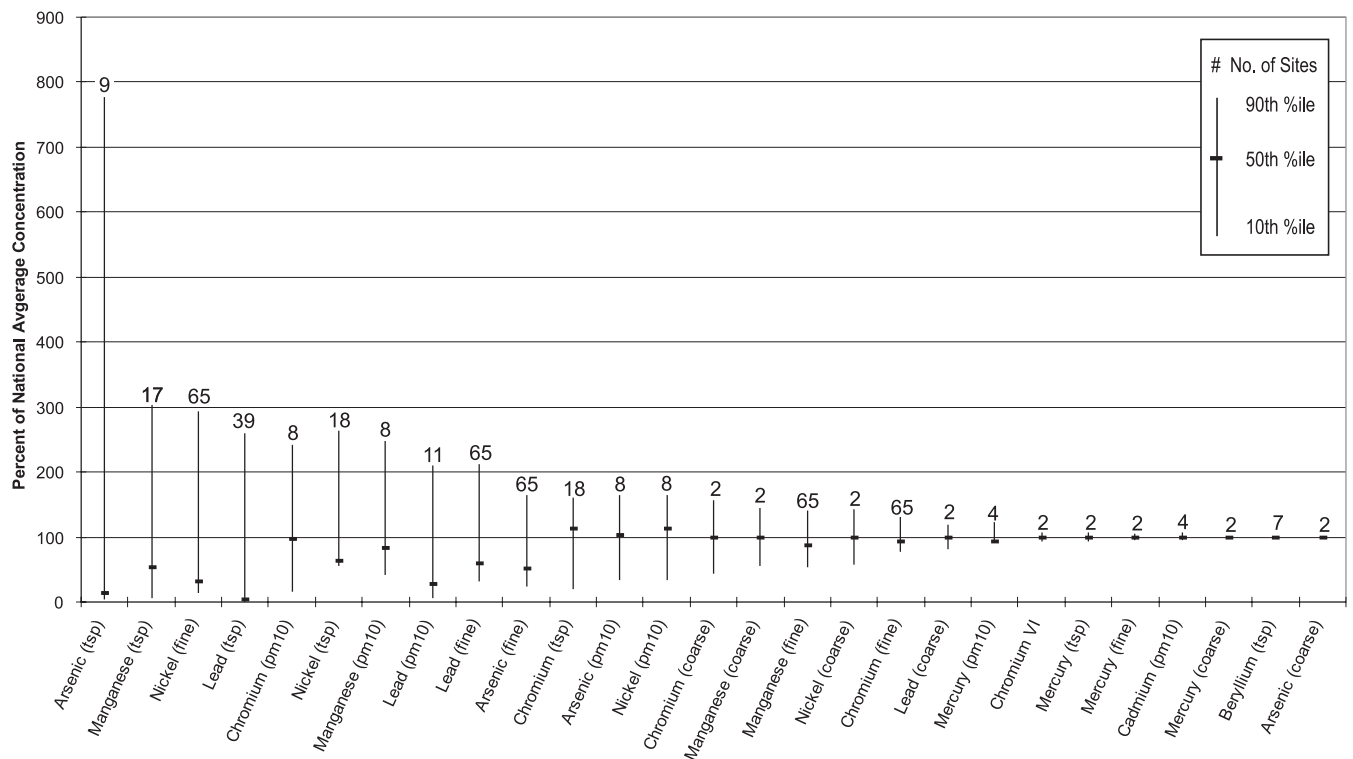
sites to those sources, the lifetime / transport of the pollutant in the atmosphere and uncertainty in the measurements. For some of the metals, average rural concentrations appear higher (e.g., lead and cadmium). The number of monitoring sites are limited, therefore these reported rural concentrations are not necessarily representative of typical rural areas.

To further illustrate the variability in annual average HAP concentrations, site-specific urban data are separately examined for the distribution of annual average concentrations. Figures 5-1a – 5-1c present the 10<sup>th</sup>, 50<sup>th</sup> and 90<sup>th</sup> percentiles of annual average concentrations for urban VOCs and aldehydes as well as urban and rural trace metals. The data are normalized to their respective urban or rural annual averages to show the relative variability for

**Figure 5-1a.** Relative variability in VOC and aldehyde annual average concentrations among urban sites, based on 1996 ambient measurements.



Note: "National Average" represents the average concentration of all included monitoring locations.

**Figure 5-1b.** Relative variability in trace metal concentrations among urban sites, based on 1996 ambient measurements.**Figure 5-1c.** Relative variability in trace metal concentrations among rural sites, based on 1996 ambient measurements.

each HAP. These figures reveal large variations among reporting locations for some VOCs and aldehydes (e.g., chloroform, formaldehyde and trichloroethylene), and also show that others (e.g., benzene and 1,3-butadiene) are relatively similar among monitoring locations. Again, annual average concentrations for HAPs associated with mobile sources tend to be more geographically homogeneous. For trace metals, reported urban and non-urban concentrations display large differences in annual averages for some HAPs (e.g., total suspended nickel and total suspended lead among urban locations, and arsenic among rural sites), while they are relatively similar for others. As stated above, the differences in concentration variability among HAPs may be attributed to many factors.

When examining differences in annual means among individual monitoring locations, the quantity and completeness of the monitoring data may be important. Because air toxics are typically sampled 30–100 days per year, the lack of every day assessments can contribute to imprecision in annual average concentrations. This is particularly true for sites with large day-to-day variations in the concentrations of certain HAPs. These conclusions are tentative and warrant further study.

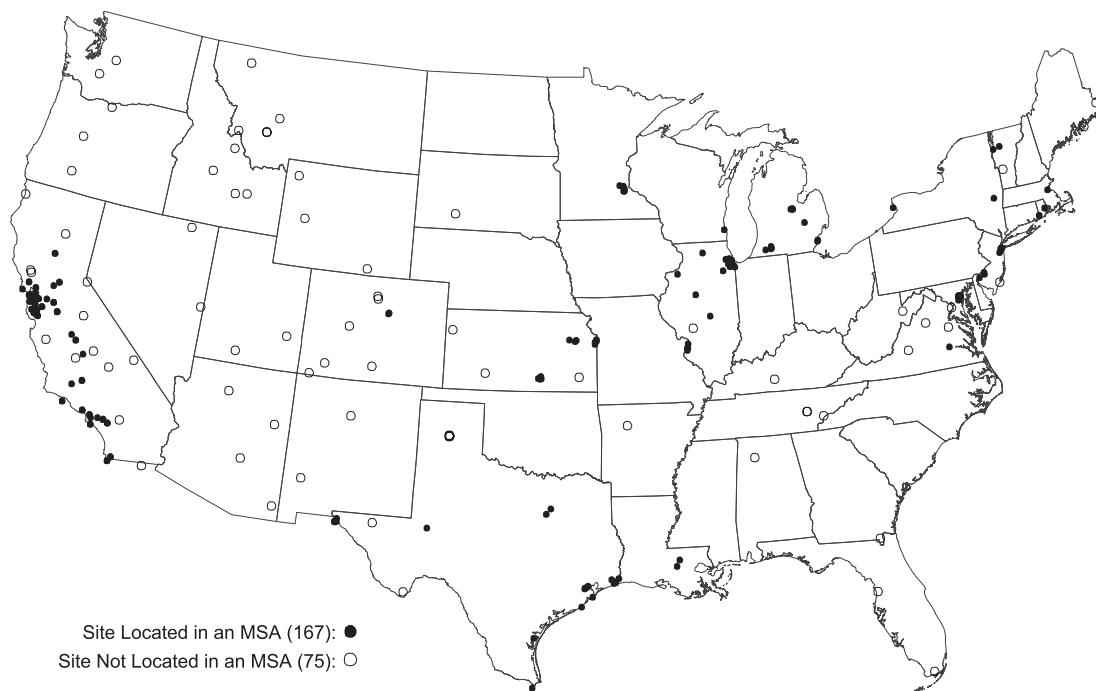
#### Trends In Ambient Concentrations

The most widely measured HAP is lead, which is also a criteria pollutant. It is monitored in most states, both in metropolitan and non-metropolitan areas. Other urban HAPs have been monitored in the metro-

politan areas of 24 states since the mid 1990s. Several VOCs, aldehydes and metals have good data history in metropolitan areas. Most of these monitors, however, are concentrated in a few states, with 40 percent of them in California alone. Nevertheless, these data can be used to provide a preliminary picture of nationwide trends in urban air toxics. Long-term monitoring in rural areas for VOCs and aldehydes has generally been more limited. A good history of several trace metal concentrations in rural areas is derived from the Interagency Monitoring of Protected Visual Environments (IMPROVE) program. The locations for the urban and rural monitors with long-term data are shown in Figure 5-2.

Trends derived from these data are separately presented for metropolitan

**Figure 5-2.** Locations for urban and rural air toxics monitors with long-term data.



*Note:* Sites only monitoring for lead (Pb) are not shown.



**Table 5-4.** National Summary of Ambient HAP Concentration Trends in Metropolitan Areas, 1993–1998

Hazardous Air Pollutant	Number of Urban Sites					
	Total	Significant* UP Trend	Non-Significant UP Trend	No Trend	Non-Significant DOWN Trend	Significant* DOWN Trend
Acrylonitrile	4		2	1	1	
Benzene	84	3	6		48	27
1,3-Butadiene	62	6	17	3	16	20
Carbon tetrachloride	65	1	25	3	23	13
Chloroform	74	9	28	3	23	11
1,2-Dibromoethane	38		5	16	15	2
1,2-Dichloropropane	27		5	5	9	8
Ethylene dichloride	55		11	17	16	11
Methylene chloride	73	4	13	2	37	17
1,1,2,2-Tetrachloroethane	12		6	2	4	
Tetrachloroethylene	74	2	13		43	16
Trichloroethylene	59	5	19	3	24	8
Vinyl chloride	50		10	22	13	5
Arsenic (coarse)	10			9	1	
Arsenic (fine)	10		1	3	6	
Arsenic (PM <sub>10</sub> )	14		1	1	7	5
Arsenic (tsp)	70	1	8	37	17	7
Beryllium (PM <sub>10</sub> )	7			7		
Beryllium (tsp)	28		6	20	2	
Cadmium (PM <sub>10</sub> )	8		3	2	1	2
Cadmium (tsp)	52	1	9	7	31	4
Chromium (coarse)	10				5	5
Chromium (fine)	10		2	1	6	1
Chromium (PM <sub>10</sub> )	14		7		6	1
Chromium (tsp)	63	4	21	2	30	6
Chromium VI	26		1		19	6
Lead (coarse)	10				4	6
Lead (fine)	10				7	3
Lead (PM <sub>10</sub> )	28	1	2	14	10	1
Lead (tsp)	266	9	47	6	147	57
Manganese (coarse)	10				6	4
Manganese (fine)	10		4		5	1
Manganese (PM <sub>10</sub> )	13		3		8	2
Manganese (tsp)	54	1	12	2	31	8
Mercury (coarse)	10		3	5	2	
Mercury (fine)	10		2	8		
Mercury (PM <sub>10</sub> )	6		4		2	
Mercury (tsp)	26		19	2	4	1
Nickel (coarse)	10				6	4
Nickel (fine)	10		2	1	4	3
Nickel (PM <sub>10</sub> )	13		3	1	6	3
Nickel (tsp)	63	1	13	2	27	20
Acetaldehyde	10		6		3	1
Formaldehyde	16	2	12		2	
Acrolein	7	1	4	1	1	
Benzo(a)pyrene (total PM <sub>10</sub> & vapor)	18		1		16	1
Dibenz(a,h)anthracene (total PM <sub>10</sub> & vapor)	18		5		13	
Indeno(1,2,3-cd)pyrene (total PM <sub>10</sub> & vapor)	18				16	2
Benzo(b)fluoranthene (total PM <sub>10</sub> & vapor)	18		1		15	2
Benzo(k)fluoranthene (total PM <sub>10</sub> & vapor)	18				17	1
Styrene	60	2	14		35	9
Toluene	78	1	9		42	26

\*Statistically significant at the 10-percent level (See Appendix B: Methodology, Air Toxics Methodology section).

(urban) and non-metropolitan (rural) sites. Table 5-4 present a national summary of these 6-year trends in ambient air toxics concentrations in metropolitan statistical areas.

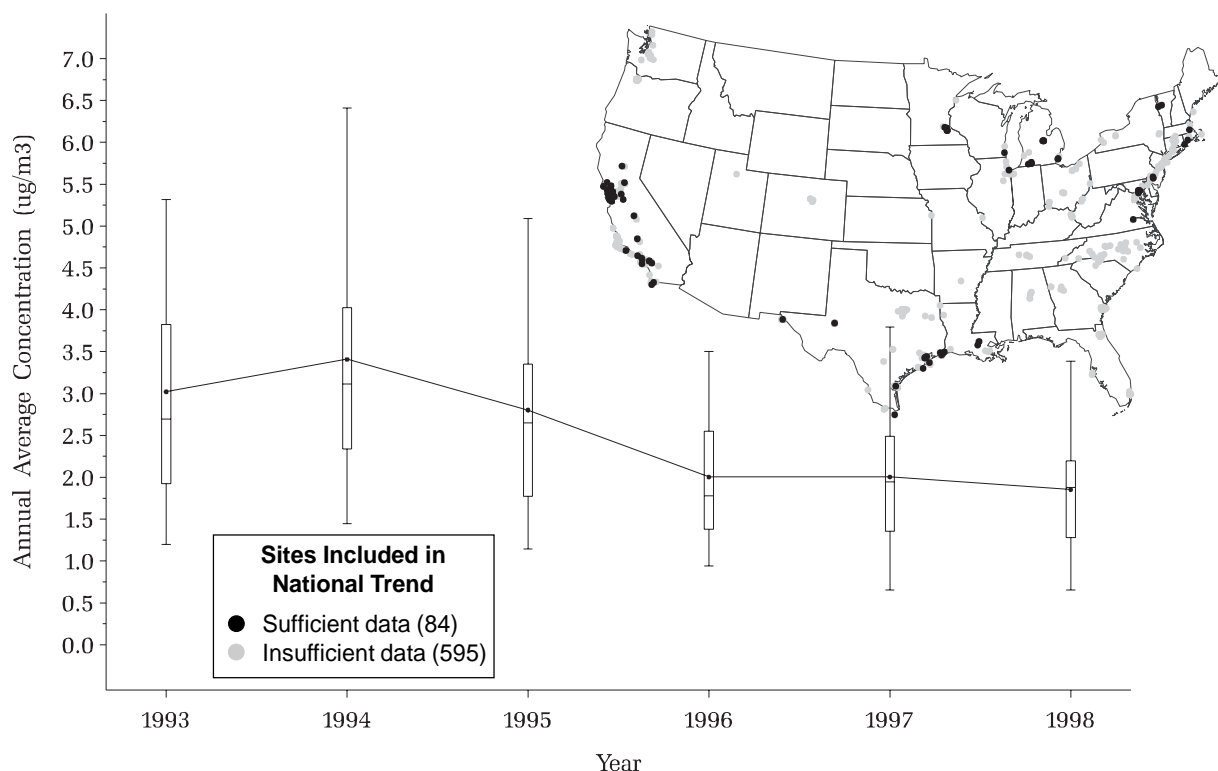
Among the 33 HAPs on the urban strategy list, 25 pollutants have sufficient historical data for this 6-year trends assessment. These air contaminants include 13 of the 15 urban VOCs, all eight urban HAP trace metals, the three aldehydes and several specific polycyclic aromatic hydrocarbons (PAHs). Also included are styrene and toluene, which are two additional pervasive air toxics whose monitoring sites have good nationwide coverage. The table presents the number of sites with increases and decreases in measured ambient concentrations from 1993–1998. For trace metals, results repre-

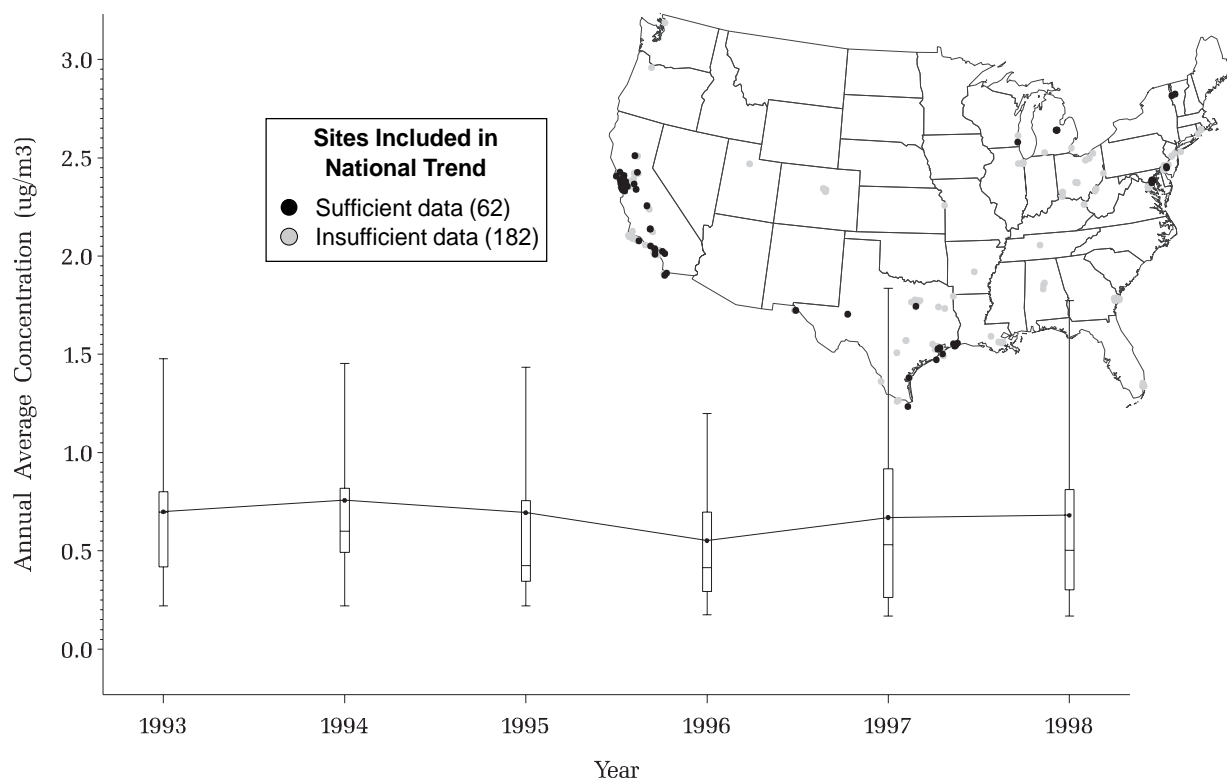
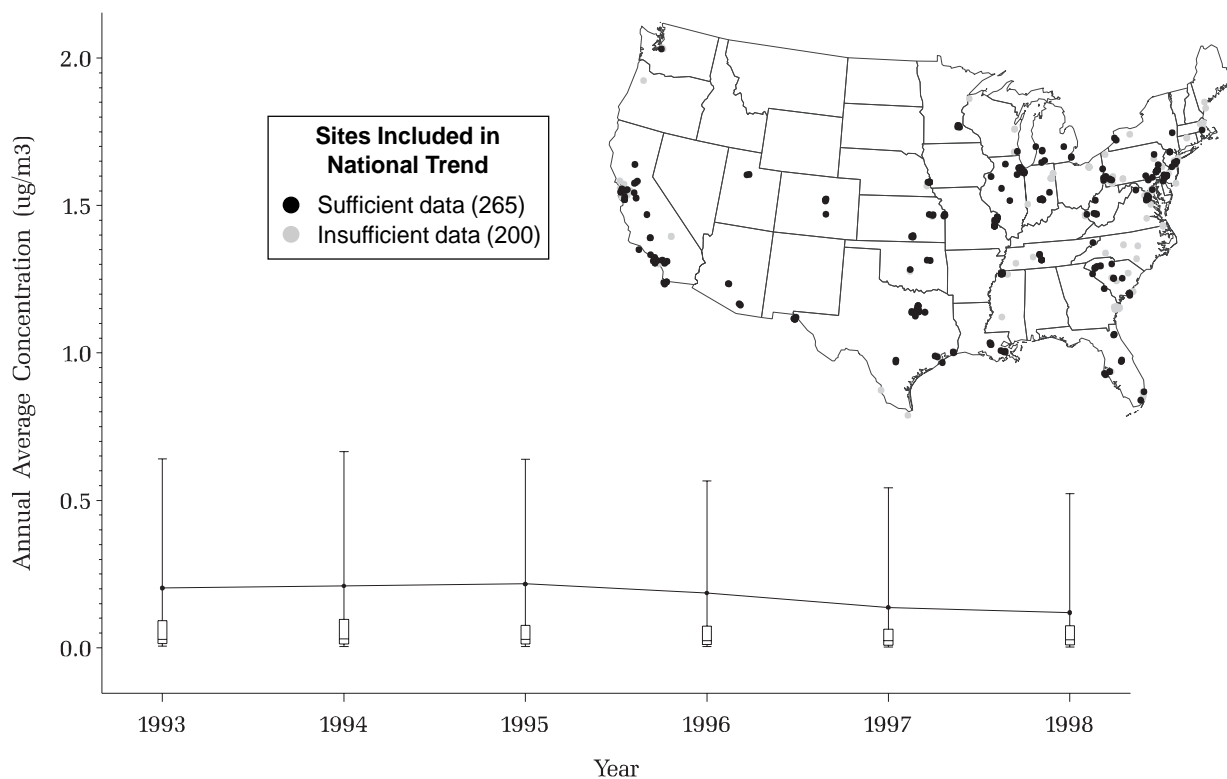
senting more than one particulate size fraction are included. Similarly, trends are shown separately for several individual PAHs which are constituents of POM. For each of these hazardous air pollutants with sufficient historical data, the number of sites with statistically significant changes are highlighted in **bold**. When many individual locations reveal a significant change, this is more characteristic of a national trend.

Although these ambient air toxics data are only available for a limited number of metropolitan areas, the results generally reveal downward trends for most monitored HAPs on the urban air toxics strategy list. The most consistent improvements are apparent for benzene which is predominantly emitted by mobile

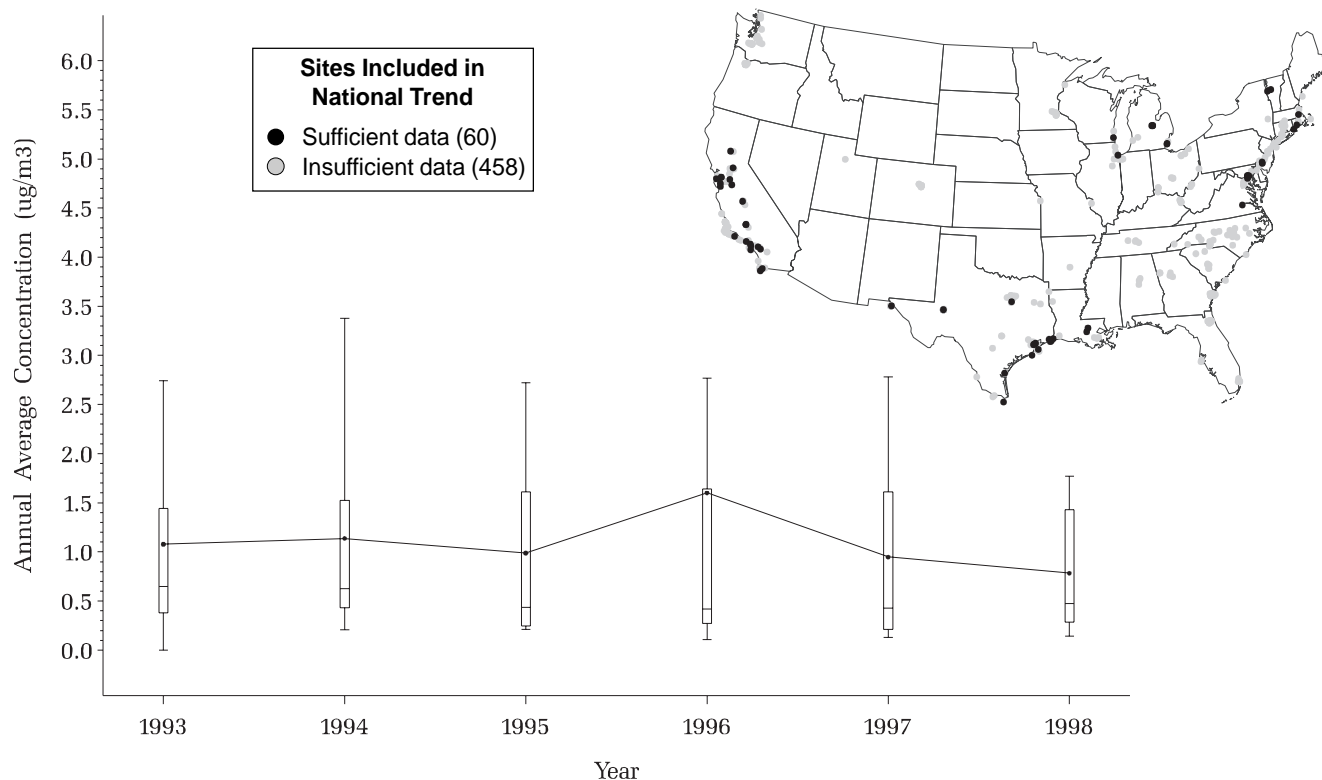
sources; and for total suspended lead. From 1993–1998, annual average concentrations for these two HAPs declined 37 and 41 percent respectively. The majority of ambient concentrations of lead once came from the tail pipe of cars. Since the mid-90s, however, lead has been largely removed from gasoline and almost all of these trace elements now typically emanate from major point sources. More information about particulate lead can be found in the criteria pollutant section in Chapter 2 of this report. Ambient concentrations of toluene (emitted primarily from mobile sources) also show a consistent decrease over most reporting locations. Similar to benzene, annual average toluene concentrations dropped 44 percent. The reduction in benzene and toluene is

**Figure 5-3a.** National trend in annual/average benzene concentrations in metropolitan areas, 1993–1998.

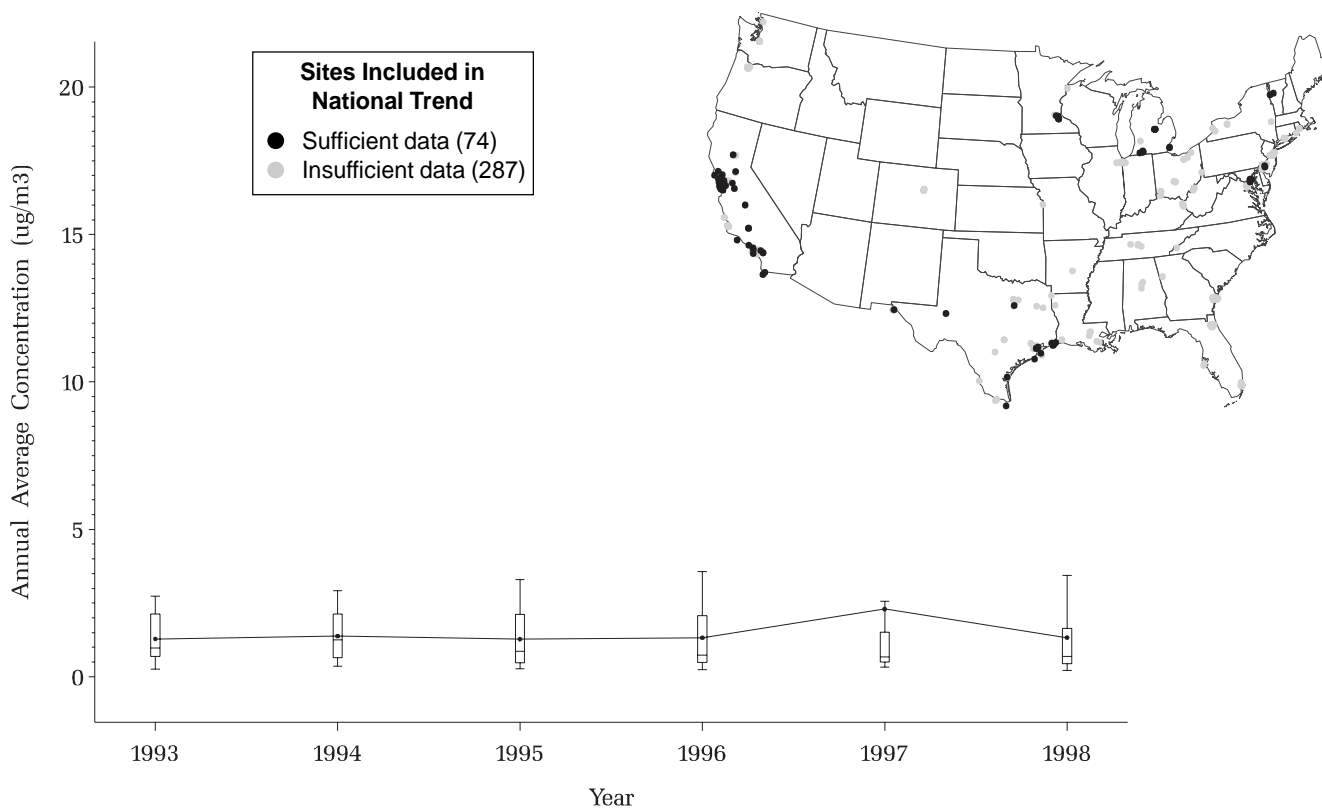


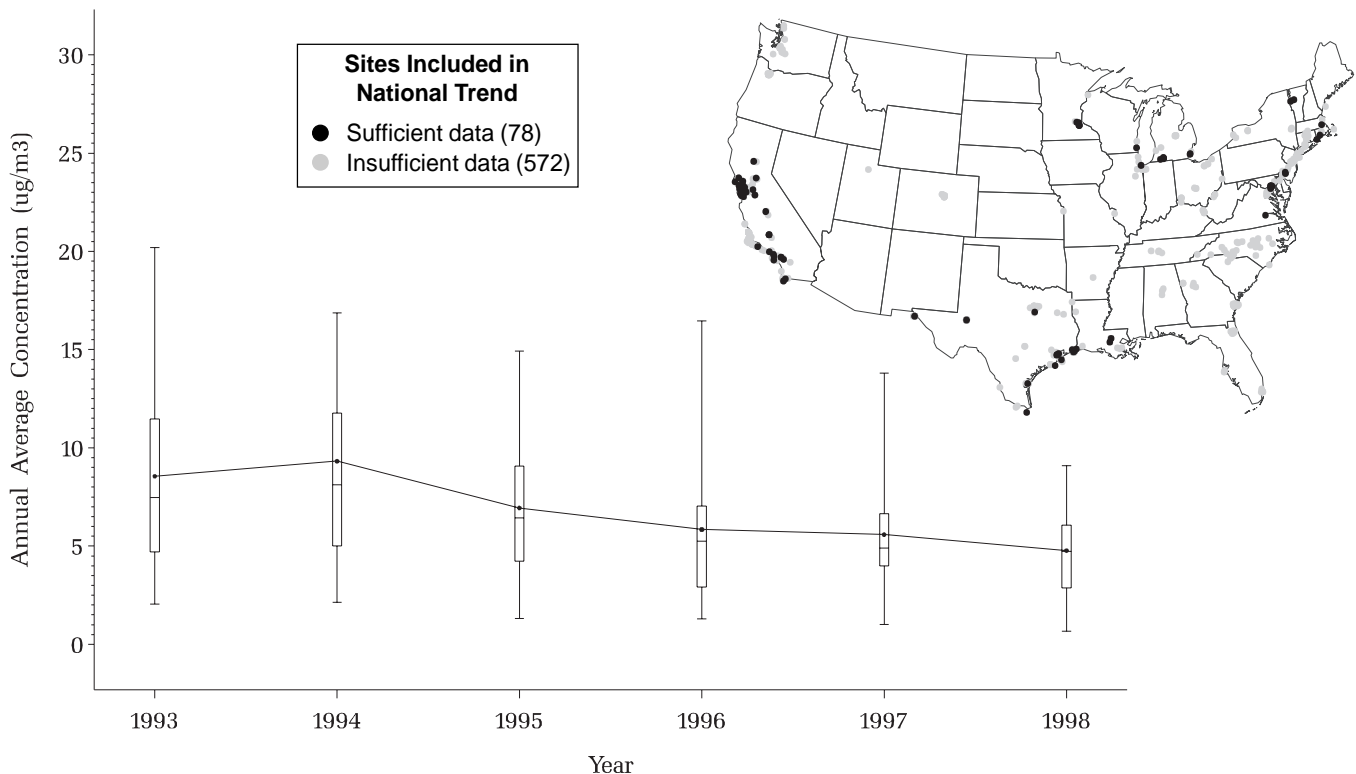
**Figure 5-3b.** National trend in annual/average 1,3-butadiene concentrations in metropolitan areas, 1993–1998.**Figure 5-3c.** National trend in annual/average total suspended lead concentrations in metropolitan areas, 1993–1998.

**Figure 5-3d.** National trend in annual/average styrene concentrations in metropolitan areas, 1993–1998.



**Figure 5-3e.** National trend in annual/average tetrachloroethylene concentrations in metropolitan areas, 1993–1998.



**Figure 5-3f.** National trend in annual/average toluene concentrations in metropolitan areas, 1993–1998.

attributed to the use of reformulated gas in many areas of the country. Other HAPs (including styrene) also reveal air quality improvement, but the downward trends are not significant across large numbers of monitoring locations. Some HAPs like 1,3-butadiene and tetrachloroethylene have trends that are more varied across the nation and result in a relatively flat national composite trend.

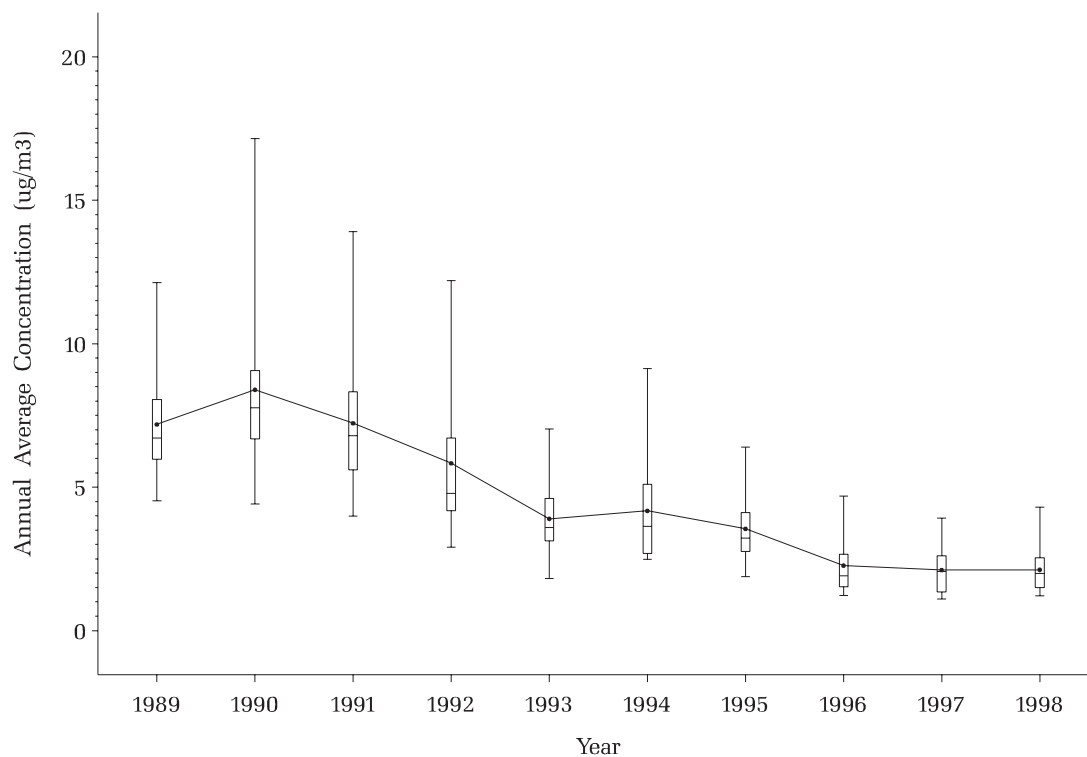
The composite urban trends for six HAPs are graphically presented. Boxplots of the annual average concentrations are shown for benzene, 1,3-butadiene, lead, styrene, tetrachloroethylene, and toluene in Figures 5-3a–f. The number and location of the monitoring sites are also displayed. For comparison, the maps also show the number of sites that produced any measurement data

during the 6-year period. These figures depict the concentration distributions among annual averages in metropolitan areas from 1993–1998. The average trend line for benzene, lead, and toluene shows a steady 6-year air quality improvement, reflecting the consistent behavior among most monitoring locations. This represents a national pattern. Average concentrations decreased 39, 40 and 44 percent respectively.

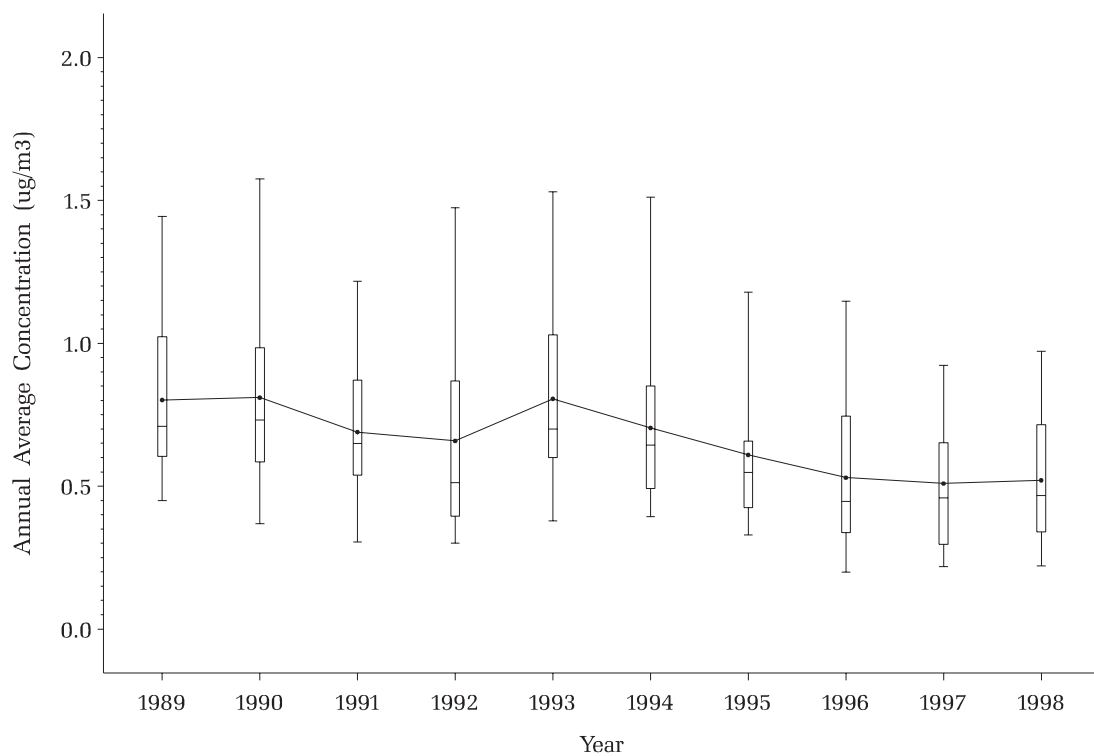
For other HAPs, most urban locations do not reveal predominant or consistent trends among all monitoring areas. In addition, most observed trends for these 21 HAPs are not statistically significant. This is attributed in part to few states with long-term HAP monitoring, to the large year-to-year variability in computed annual average concentrations for

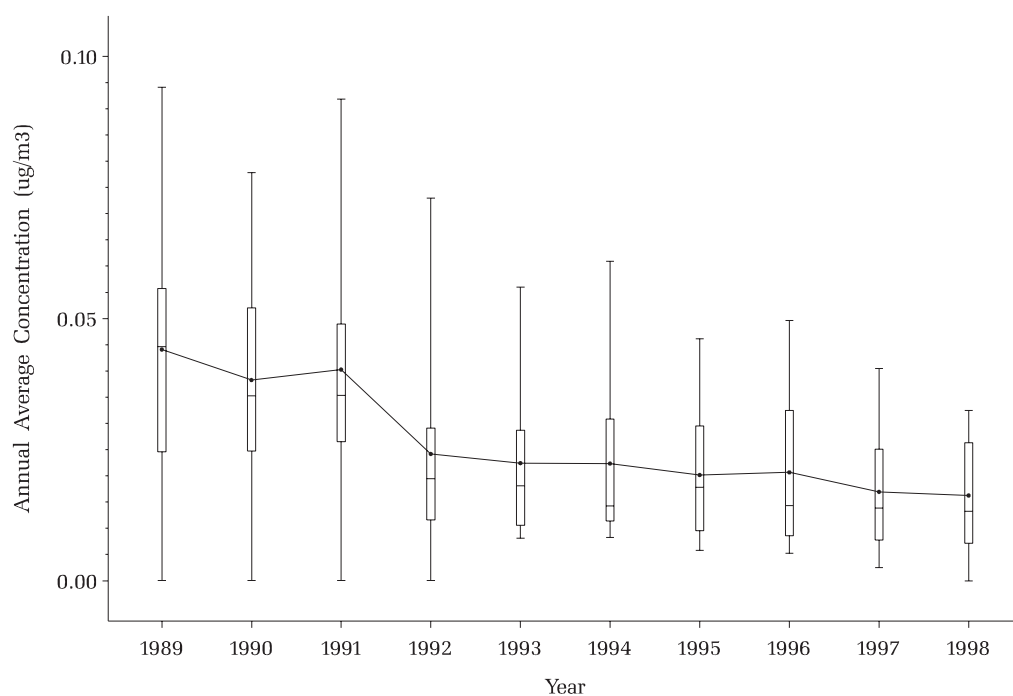
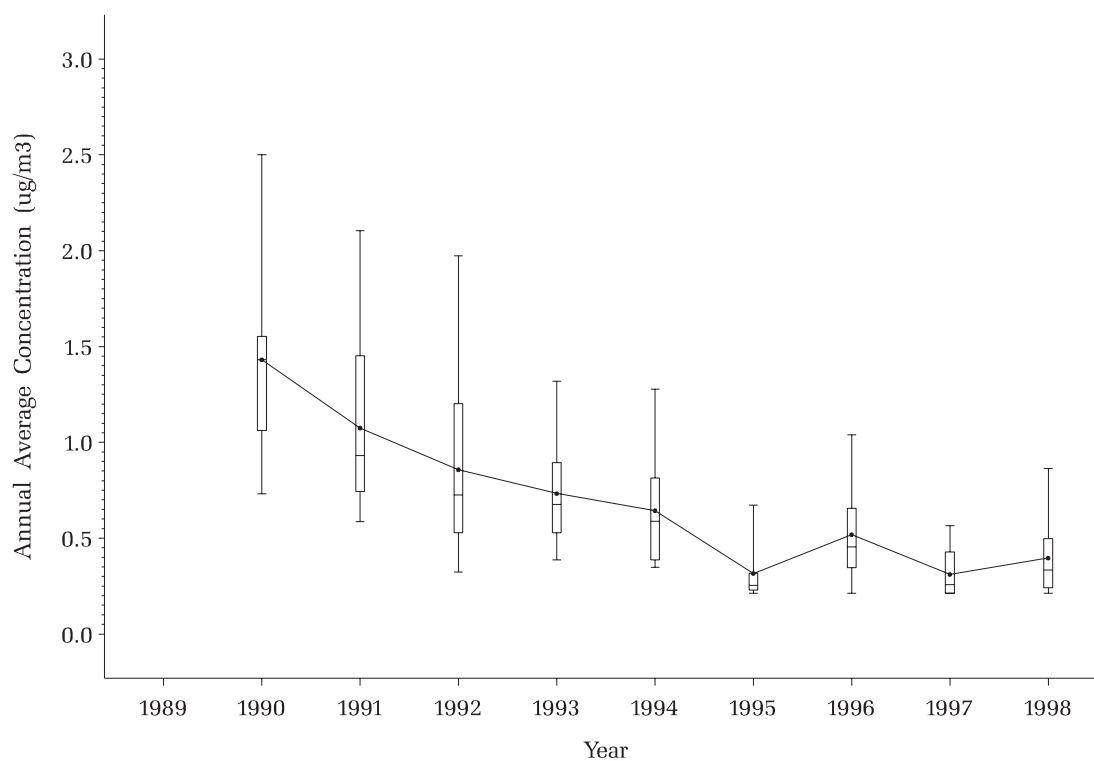
some HAPs and the large variety of contributing emission sources for many of the air toxics. For these pollutants, a national composite trend may not be meaningful at this time. Although the general direction of change is down for most HAPs on the urban list, several states reveal significant 6-year increases at a few locations. These HAPs include 1,3-butadiene, carbon tetrachloride, chloroform, ethylene dichloride, methylene chloride, tetrachloroethylene (also known as perchloroethylene or “perc”) and trichloroethylene. Except for 1,3-butadiene, all of the above mentioned HAPs are generally associated with major stationary sources or a combination of major and area sources. The majority of emissions of 1,3-butadiene come from mobile sources with the remain-

**Figure 5-4a.** Trend in annual average benzene concentrations for metropolitan sites in California, 1989–1998.

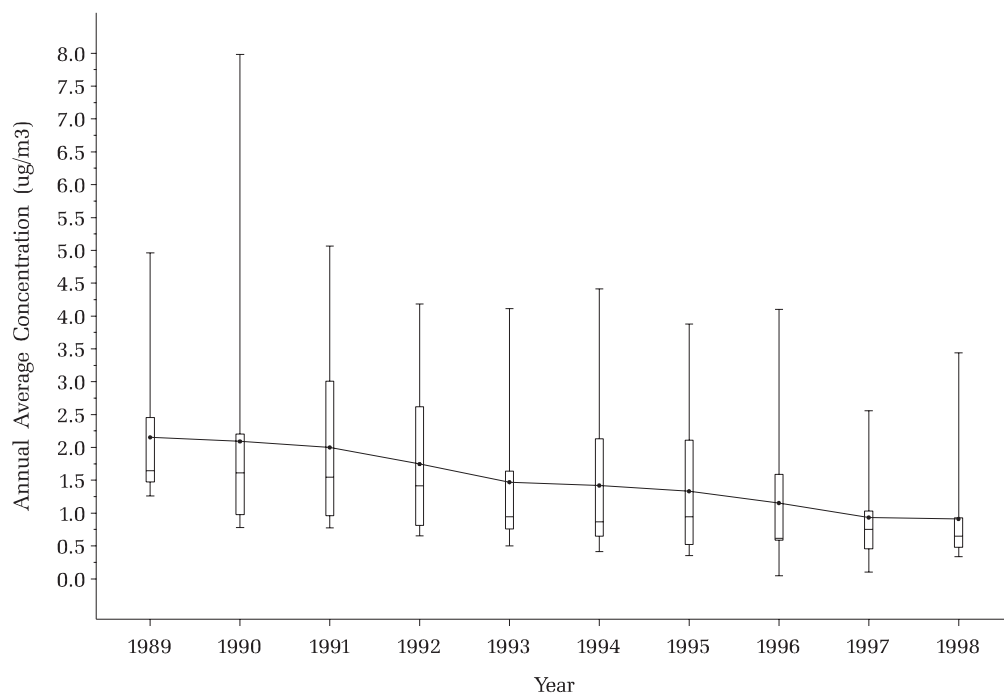


**Figure 5-4b.** Trend in annual average tetrachloroethylene concentrations for metropolitan sites in California, 1989–1998.

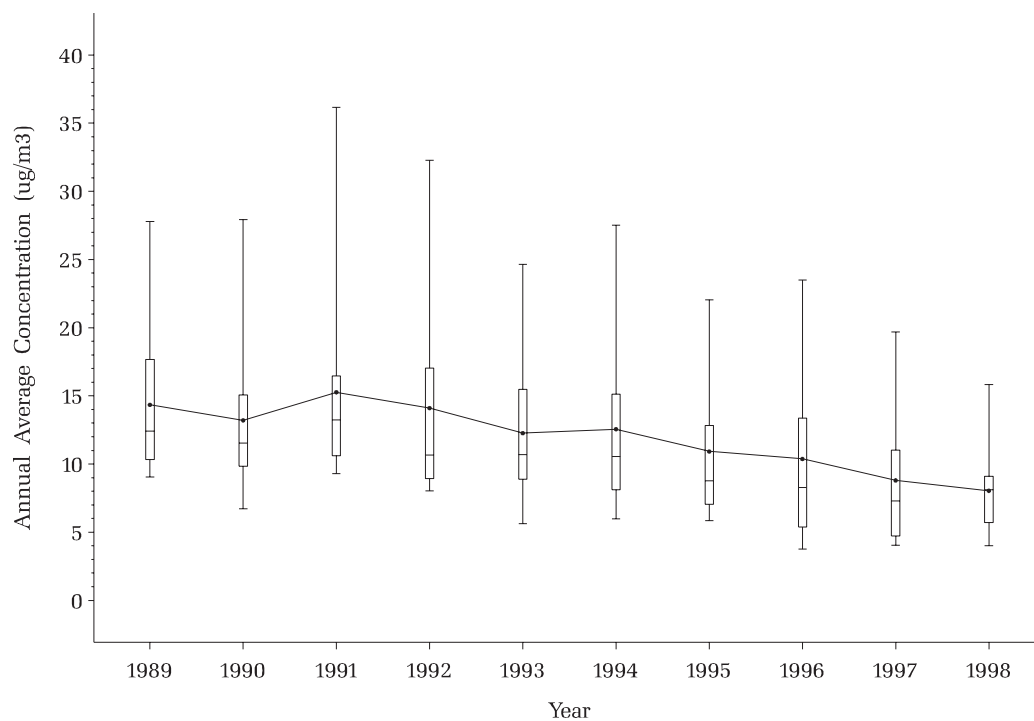


**Figure 5-4c.** Trend in annual average lead concentrations for metropolitan sites in California, 1989–1998.**Figure 5-4d.** Trend in annual average styrene concentrations for metropolitan sites in California, 1989–1998.

**Figure 5-4e.** Trend in annual average tetrachloroethylene concentrations for metropolitan sites in California, 1989–1998.



**Figure 5-4f.** Trend in annual average toluene concentrations for metropolitan sites in California, 1989–1998.





der mostly from area sources. To illustrate a few of the HAPs without consistent trends among reporting stations, boxplots for 1993–1998 are presented for 1,3-butadiene, styrene and tetrachloroethylene. The national trends for these HAPs appear to be flat for the six years, except for average concentration of styrene which shows a drop in 1998. To illustrate the behavior of these compounds in a particular region of the country, trends of monitoring sites in California are presented on the following page.

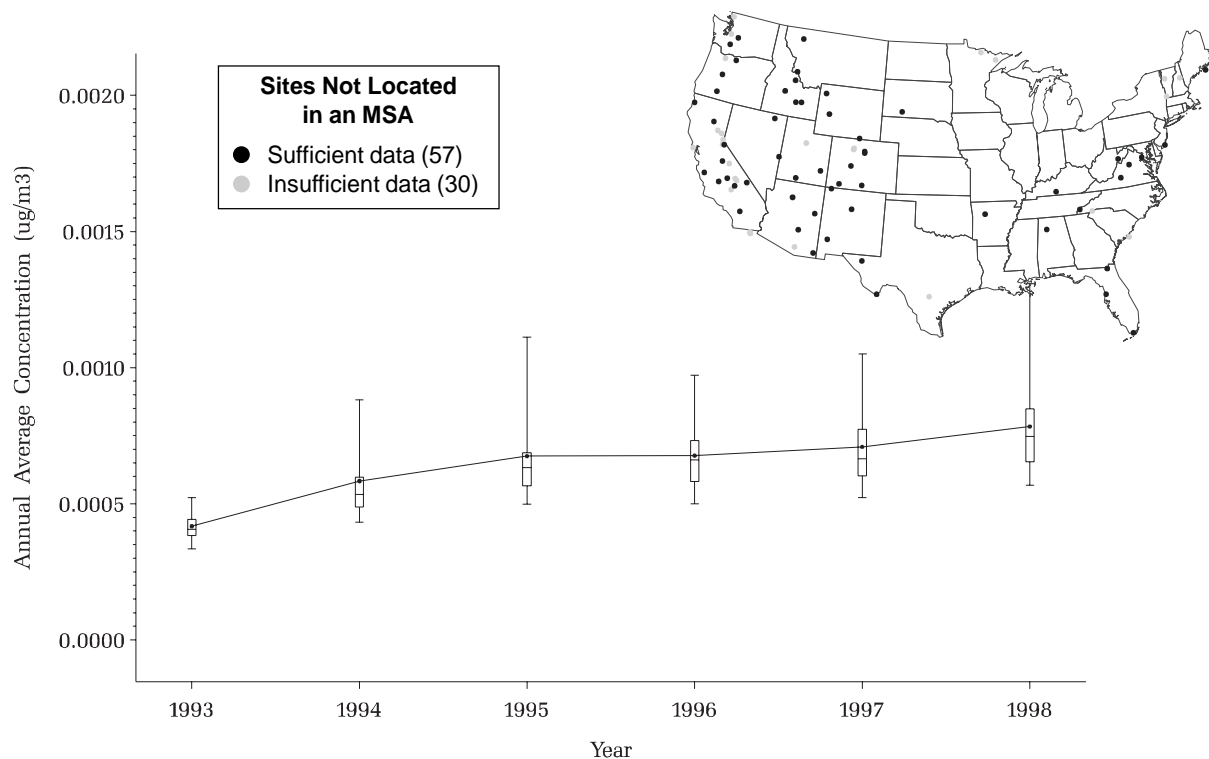
The State of California has the largest and longest running air toxics monitoring network. They have over 30 sites with a 10-year history for several VOCs and almost as many for several trace metals. These data allow us to take a look at a longer time trend

in air toxics. Among the HAPs discussed in this section, notable improvements are seen for benzene, 1,3-butadiene, tetrachloroethylene and toluene. The impressive air quality improvement for urban benzene in California is shown in Figure 5-4a. This figure illustrates the large decrease in ambient concentrations which occurred during the early 1990s. Annual average concentrations declined 70 percent over the 10-year period. Ambient concentrations of tetrachloroethylene associated with dry cleaners is down 58 percent (Figure 5-4e). Toluene associated with mobile sources also showed consistent declines which averaged 44 percent across the state (Figure 5-4f). Another HAP which predominantly comes from mobile sources is 1,3-butadiene. Although site-specific

trends for this pollutant were mixed, the composite trend in Figure 5-4d shows an overall 35-percent decline in ambient concentrations. The reductions in ambient concentrations of tetrachloroethylene are due to better controls on the use of solvents, while the improvements in benzene, 1,3-butadiene and toluene is attributed to the reformulation of gasoline. (For more information about trends in these emissions, see the ozone section in Chapter 2.) For additional detail on the derivation of Figures 5-3a to 5-4f, see Appendix B: Methodology.

Results from California's total suspended particulate lead network are consistent with the national trends. Annual average concentrations declined 63 percent and 27 percent over the 10-year and 6-year periods respectively. California has

**Figure 5-5.** Trends in Annual Average Fine Particle Chromium Concentrations in Rural Areas, 1993–1998.



**Table 5-5.** National Summary of Ambient HAP Concentration Trends in Rural Areas, 1993–1998

Hazardous Air Pollutant	Number of Rural Sites					
	Total	Significant* UP Trend	Non-Significant UP Trend	No Trend	Non-Significant DOWN Trend	Significant* DOWN Trend
Benzene	5				4	1
1,3-Butadiene	4				1	3
Carbon tetrachloride	3		2		1	
Chloroform	4				3	1
1,2-Dichloropropane	4			1	3	
Ethylene dichloride	4				3	1
Methylene chloride	4				4	
Tetrachloroethylene	4				2	2
Trichloroethylene	4				3	1
Vinyl chloride	4		3		1	
Arsenic (coarse)	2		1	1		
Arsenic (fine)	61	3	40	1	17	
Arsenic (PM <sub>10</sub> )	6		1	1	3	1
Arsenic (tsp)	5		1	1	1	2
Beryllium (PM <sub>10</sub> )	2		1	1		
Beryllium (tsp)	3			3		
Cadmium (PM <sub>10</sub> )	2				2	
Cadmium (tsp)	6			3	1	2
Chromium (coarse)	2		1		1	
Chromium (fine)	61	28	29	1	3	
Chromium (PM <sub>10</sub> )	6	1	2		3	
Chromium (tsp)	7	1	2	1	2	1
Chromium VI	1					1
Lead (coarse)	2			1	1	
Lead (fine)	61	1	45		15	
Lead (PM <sub>10</sub> )	8	1	1	2	3	1
Lead (tsp)	31		5		15	11
Manganese (coarse)	2		1		1	
Manganese (fine)	61		25		35	1
Manganese (PM <sub>10</sub> )	6		3		2	1
Manganese (tsp)	6			1	5	
Mercury (coarse)	2		1	1		
Mercury (fine)	2			1	1	
Mercury (PM <sub>10</sub> )	4		2	1	1	
Mercury (tsp)	1		1			
Nickel (coarse)	2		1		1	
Nickel (fine)	61	1	12	1	39	8
Nickel (PM <sub>10</sub> )	6		1	1	3	1
Nickel (tsp)	7		1	1	4	1
Acetaldehyde	1				1	
Formaldehyde	1				1	
Acrolein	1				1	
Styrene	5		2		3	
Toluene	5		3		2	

\*Statistically significant at the 10-percent level (See Appendix B: Methodology, Air Toxics Methodology section).

also been measuring fine particle lead (from  $PM_{2.5}$ ) and coarse particle lead (from  $PM_{10-2.5}$ ) in its urban areas. Although concentrations are a small fraction of the total suspended lead, these data also show 6-year declines of 26 and 54 percent, respectively. California's trace metal data also shows declines in total suspended chromium (-29 percent) and the particularly hazardous hexavalent chromium (-52 percent).

Ambient air toxics data in rural areas are much more limited, but the results in Table 5-5 and Table A-20 also indicate widespread air quality improvement for many monitored urban strategy HAPs. Significant downward trends are noted among the few rural sites for benzene and several other VOCs. Lead concentrations in rural areas are also down. In contrast, a notable steady increase in fine particle chromium concentrations is observed in the rural data set. This is illustrated in Figure 5-5. Almost all rural monitoring sites show a 6-year increase in ambient chromium concentrations and most of them are statistically significant. Average concentrations increased 88 percent. The reason for this increase in rural chromium concentrations is not known at this time. The result also needs to be viewed with caution because the reported concentrations are close to the detection limits of the monitoring method ( $0.57 \text{ ng/m}^3$ ).<sup>8</sup> Nevertheless, there is a strong trend in the concentrations above this level. Future trend reports will present more detailed trends in chromium and other HAP trace metals derived from the IMPROVE network and other rural monitoring locations.

## Atmospheric Deposition

### National Atmospheric Deposition Program/National Trends Network

The National Atmospheric Deposition Program (NADP) began in 1978 as a cooperative program between federal and state agencies, universities, electrical utilities, and other industries to determine geographical patterns and trends in wet deposition of sulfate, nitrate, hydrogen ion, ammonium, chloride, calcium, magnesium, and potassium. The NADP was renamed as NADP/NTN (National Trends Network) in the mid-1980s when the program had grown to almost 200 monitoring sites. The monitoring sites are located in rural areas, and data are collected on a weekly basis. The collected data provide insight into natural background levels of pollutants. The network of NADP/NTN monitoring sites allows for the development of concentration and wet deposition maps to describe the trends and spatial patterns in the constituents of acid precipitation. The Mercury Deposition Network (MDN), which is another component of the NADP, measures mercury levels in wet deposition at over 40 NADP sites located in 16 states and two Canadian provinces.

Mercury's adverse effects on ecological and public health have raised the level of awareness regarding its persistence in the environment. As a result, there has been a concerted effort by local, state, and national environmental agencies to accurately measure the annual progress of regulations and technologies aimed at reducing mercury. The MDN is a key element of these efforts by monitoring the presence of mercury and methyl mercury in precipitation.

This has enabled scientists to compile a national database of weekly precipitation concentrations. As a result, state and federal air regulators can monitor progress in reducing mercury concentrations and amend policy decisions accordingly. There are plans to expand the network in the near future, pending availability of new funds. Additional information about the network is available on the Internet at <http://nadp.sws.uiuc.edu/mdn/>.

Data from 1996 and 1997 indicate that the volume-weighted mean concentration of total mercury in precipitation from 22 sites ranged from 6.0–18.9 ng/L and annual deposition of mercury ranged from 2.1–25.3  $\mu\text{g/m}^2$ . In 1997, average mercury concentrations in rain ranged from 6.2–18.3 ng/L at the 21 sites that had a full year of monitoring data and the average concentration for all sites was 10.6 ng/L. In 1996, average mercury concentrations at nine sites with a full year of data ranged from 6.0–14.1 ng/L with an average for all sites of 10.2 ng/L. In 1997, the annual average wet deposition of mercury for 21 sites ranged from 4.3–25.3  $\mu\text{g/m}^2$ , whereas in 1996, the annual average wet deposition of mercury for nine sites ranged from 6.3–19.7  $\mu\text{g/m}^2$ . In the eastern United States, average summer mercury concentrations are more than double winter concentrations and average summer deposition values are more than three times winter values. This can be explained by higher concentrations of mercury in the rain and higher rainfall amounts during the summer.<sup>9</sup>

### Integrated Atmospheric Deposition Network

The Integrated Atmospheric Deposition Network (IADN) is a joint United States-Canada program begun in

1990 under a formal 6-year implementation.<sup>10</sup> The IADN collects data that can be useful in assessing the relative importance of atmospheric deposition. IADN measures concentrations of target chemicals in rain and snow (wet deposition), airborne particles (dry deposition), and airborne organic vapors.<sup>11</sup> Under IADN, trends in pollutant concentrations in air and precipitation are assessed and loading estimates of atmospheric deposition and volatilization of pollutants are made every two years. The IADN network currently consists of one master station per Great Lake and 14 satellite stations. Stations are located in remote areas and do not assess urban sources of pollution.

General conclusions based on IADN data include the following:

- Levels in air and precipitation appear stable for current-use pesticides such as endosulphan, but levels for most other pesticides, PCBs, and lead are decreasing.
- Gas absorption appears to be the dominant deposition process for delivering SVOCs, including PCBs and PAHs, to lake surfaces, while wet and dry deposition dominate for the trace elements and higher molecular weight PAHs.
- For some IADN substances, like dieldrin and PCBs, the surface waters are behaving like a source since the amount that is volatilizing from the water is greater than the amount being deposited to the water.
- The lakes are sensitive to the atmospheric concentration of IADN chemicals, and this highlights the fragility of these resources given that long-range transport from other regions may be a significant source of toxic pollutants.

- Air trajectory analyses indicate that many SVOCs are potentially originating from outside the Great Lakes basin, whereas trace metals and PAHs may be associated with local sources.<sup>12</sup>

In 1998, the Second Implementation Plan for 1998–2004 was developed based on a review of the program from 1990–1996. No major changes are anticipated under the Second Implementation Plan. The IADN will continue surveillance and monitoring activities, related research, and to provide information for intergovernmental commitments and agreements. Additional work to be completed under the Second Implementation Plan is the development of a database for all U.S. and Canadian data. Potential modifications will be discussed in relation to the placement of satellite stations to assess urban inputs and air-water gas exchange, criteria for changes to the IADN chemical list, coordination with other research activities, quality assurance and control of IADN operations, and communication of IADN results.<sup>12</sup>

## References

1. This list originally included 189 chemicals. The CAA allows EPA to modify this list if new scientific information becomes available that indicates a change should be made. Using this authority, the Agency modified the list to remove caprolactam in 1996, reducing the list to 188 pollutants (*Hazardous Air Pollutant List; Modification*, 61 FR 30816, June 18, 1996).
2. "Update: National Listing of Fish and Wildlife Advisories," announcing the availability of the 1998 update for the database: National Listing of Fish and Wildlife Advisories (NLFWA); U.S. EPA Fact Sheet, EPA-823-F-99-005, July 1999. Available on the Internet at: <http://www.epa.gov/ost/fish>.
3. Hillery, B.R., Hoff, R.M., and Hites, R.A. 1997. "Atmospheric contaminant deposition to the Great Lakes determined from the Integrated Atmospheric Deposition Network." Chapter 15 in *Atmospheric Deposition of Contaminants to the Great Lakes and Coastal Waters*. 1997, Joel E. Baker, Editor. SETAC Press. (Society of Environmental Toxicology and Chemistry.)
4. Evers, D. 1998. Assessing availability and risk of methylmercury to the common loon in New Hampshire and Vermont. A preliminary report. Submitted to U.S. EPA, Office of Air Quality Planning and Standards, December 3, 1998.
5. "National Air Toxics Program: The Integrated Urban Strategy," *Federal Register*, 64 FR 38705, Washington, D.C., July 19, 1999. Available on the Internet at: <http://www.epa.gov/ttnuatw1/urbanpg.html>.
6. "Air Toxics Monitoring Concept Paper," U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC. February 29, 2000. Peer Review Draft. Available on the Internet at: <http://www.epa.gov/ttn/amtic/airtxfil.html>.
7. "1997 Urban Air Toxics Monitoring Program (UTAMP)," EPA-454/R-99-036. January 1999. Available on the Internet at <http://www.epa.gov/ttn/amtic/airtxfil.html>.
8. Visibility Monitoring Guidance 1999, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC 27711, June 1999, EPA-454/R-99-003.
9. Sweet, C.W., E. Prestbo, B. Brunette. 1999. Atmospheric wet deposition of mercury in North America. Proceedings of the 92<sup>nd</sup> Annual Meeting of the Air and Waste Management Association. June 21-23, 1999, St. Louis, MO.
10. The IADN fulfills legislative mandates in Canada and the United States that address the monitoring of air toxics. An international Great Lakes deposition network is mandated by Annex 15 of the Great Lakes Water Quality Agreement between the United States and Canada. In the United States, the CAA requires a Great Lakes deposition network.
11. The target chemicals include PCBs, pesticides, PAHs and metals. The compounds included as "target chemicals" were selected based on the following criteria: presence on List 1 of Annex 1 of the Great Lakes Water Quality Agreement (substances believed to be toxic and present in the Great Lakes); established or perceived water quality problem; presence on the International Joint Commission's Water Quality Board's list of criteria pollutants; evidence of presence in the atmosphere and an important deposition pathway; and feasibility of measurement in a routine monitoring network.
12. U.S./Canada IADN Scientific Steering Committee. 1998. Technical summary of progress under the integrated atmospheric depositions program 1990-1996.

