

# **AIR TOXICS MONITORING**

## ***CONCEPT PAPER***

Office of Air Quality Planning and Standards

Revised Draft  
February 29, 2000

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## **AIR TOXICS MONITORING *CONCEPT* PAPER**

### **1 The Air Toxics Program and the Role of Ambient Air Monitoring**

#### **1.1 Background**

There are currently 188 hazardous air pollutants (HAPs), or air toxics, regulated under the Clean Air Act (CAA) that have been associated with a wide variety of adverse ecosystem and health effects, including cancer, neurological effects, reproductive effects and developmental effects. These air toxics are emitted from multiple sources, including major stationary, area, and mobile sources, resulting in population exposure to these air toxics. While in some cases the public may be exposed to an individual HAP, more typically people experience exposures to multiple HAPs and from many sources. Exposures of concern result not only from the inhalation of these HAPs, but also, for some HAPs, from multi-pathway exposures to air emissions. For example, air emissions of mercury can deposit in sediments and water where they are biotransformed into methyl mercury and then bioaccumulate in fish, resulting in exposures to people who eat the fish.

Our current Government Performance Results Act (GPRA) commitments specify a goal of reducing air toxics emissions by 75% from 1993 levels to significantly reduce the risk to Americans of cancer and other serious adverse health effects caused by airborne toxics. Because of our limited tools to assess the impacts of these emissions on public health and the environment, we are focusing on reducing emissions to the extent possible. However, as we develop new assessment tools and begin to address the public health and ecological risks associated with these emissions as required by the CAA, we will be modifying that goal to one that focuses on risk reductions associated with exposure to air toxics. In working toward this risk-based goal, we will first focus on the cumulative effects of air toxics in urban areas, the multi-media effects of air toxics on water bodies whose water quality and aquatic life are affected by the deposition of persistent and bioaccumulating air toxics, and the effects on sensitive populations and on economically disadvantaged communities. Eventually, we have a long-term goal of eliminating unacceptable risks of cancer and other significant health problems from exposures to air toxics emissions and to substantially reduce or eliminate adverse effects on our natural environment.

#### **1.2 National Air Toxics Program**

To address the concerns posed by air toxics emissions and to meet our strategic goals, we have developed a national air toxics program designed to characterize, prioritize, and equitably address the impacts of HAPs on the public health and the environment. The national air toxics

program seeks to address air toxics problems through a strategic combination of several agencies' activities and authorities, including regulatory approaches and voluntary partnerships. We envision four key areas of activities:

- C Source-specific standards and sector-based standards, including Section 112 standards, i.e. Maximum Achievable Control Technology (MACT), Generally Achievable Control Technology (GACT), residual risk standards, and Section 129 standards.
- C National, regional, and community-based initiatives to focus on multi-media and cumulative risks, such as the Integrated Urban Air Toxics Strategy, Great Waters and National Estuary Program, Mercury initiatives, Persistent Bioaccumulative Toxics (PBT) and Total Maximum Daily Load (TMDL) initiatives, and Clean Air Partnerships.
- C National Air Toxics Assessment (NATA) activities which will help EPA identify areas of concern, characterize human health and ecosystem 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. These efforts 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.
- C Public education and outreach.

The NATA activities, as discussed below, will be critical to the success of all the other major areas of activities within the national air toxics program.

### **1.3 National Air Toxics Assessments**

The success of the national air toxics program critically depends on our ability to understand and quantify the impacts of air toxics emissions on public health and the environment. To that end, EPA has initiated numerous NATA activities. All of these activities are aimed at providing the best technical information regarding air toxics emissions, ambient concentrations, and health and environmental impacts to support the development of sound policies in the national air toxics program. These activities include:

- C the measurement of air toxics emission rates from individual pollution sources;
- C the compilation of comprehensive air toxics emission inventories for local, State,

- C and national domains;
- C the measurement of ambient concentrations of air toxics at monitoring sites throughout the nation;
- C the analysis of patterns and trends in ambient air toxics measurements;
- C the estimation of ambient and multimedia air toxics concentrations from emission inventories using dispersion and deposition modeling;
- C the estimation of human and environmental exposures to air toxics, and;
- C the assessment of human and environmental risks due to air toxics;
- C ongoing research in above areas to improve assessments over time.

The wide range of NATA activities listed above illustrates that emissions data, ambient concentration measurements, modeled estimates, and health and environmental impact assessments are all needed to fully characterize air toxics impacts and to determine risk. Specifically, emissions data are needed to quantify the sources of air toxics impacts and aid in the development of control strategies. Ambient monitoring data are then needed to characterize air toxics ambient concentrations and toxics deposition, to better understand the fate and transport of air toxics in the atmosphere and to help evaluate atmospheric dispersion and deposition models. Since ambient measurements cannot practically be made everywhere, modeled estimates are needed to extrapolate our knowledge of air toxics impacts into locations without monitors. A combination of reliable modeling systems along with well designed ambient networks is the best approach for estimating ambient concentrations and population/ecosystem exposure across the nation. Exposure assessment information and health effects information need to be integrated in order to characterize air toxics risks. Ambient measurements provided from routine monitoring programs together with personal exposure measurements which currently can be obtained from ongoing research studies are important to evaluate these air quality and exposure models.

## **1.4 The Role of Ambient Monitoring in NATA**

### **1.4.1 Air quality characterization, model evaluation and trends assessment**

This concept paper focuses on the role of ambient measurement data as one key element of the full air toxics assessment process. The purposes for collecting ambient monitoring data should be kept in mind when designing and implementing the measurement networks.

For the initial role of monitoring to support NATA, we anticipate that ambient air toxics data will be useful to:

- C Characterize ambient concentrations and deposition in representative monitoring areas,

- C Provide data to support and evaluate dispersion and deposition models, and
- C Establish trends and evaluate the effectiveness of HAP reduction strategies.

In addition, initial new monitoring together with data analysis of existing measurements will be needed to provide a sufficient understanding of ambient air toxics concentrations throughout the country in order to decide on the appropriate quantity and quality of needed data.

As part of the overall NATA process, ambient air quality data are important to help assess the national toxics inventory and national air toxics modeling and later long-term HAP trends. Initially, ambient air quality monitoring should focus on characterization (to assess community-wide concentrations in urban areas and ecosystem impact, and to quantify ambient conditions in the vicinity of localized hot spots or specific areas of concern like schools) and to provide data to support or evaluate models. As the monitoring program matures, trend sites can be established to assess the effectiveness of the air toxics program components.

To achieve our purposes, we must 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 appropriateness of a candidate monitoring site with respect to the data uses described above and the timing for needed data will be the key considerations in identifying sites for the initial data collection activities and for the development of a longer-term national network.

A key component for the air toxics monitoring network is the HAPs that should be measured. It is not possible to measure all HAPs at all locations. Recognizing this, the CAA amendments required EPA to develop a subset of the 188 toxics identified in Section 112 which are thought to have the greatest impact on the public and the environment in urban areas. This subset is comprised of the 33 HAPS identified in the Integrated Urban Air Toxics Strategy (UATS)<sup>1</sup> commonly referred to as the “Urban HAP List.” Because this list was developed to reflect a variety of possible exposure periods (acute/chronic), pathways (inhalation, dermal, ingestion), and types of adverse health effect (cancer/noncancer), the toxics monitoring network should attempt to address the full list. However, the near-term monitoring discussed in this paper primarily focuses on ambient air monitoring and does not completely address the pollutants for which ingestion are the principle route for exposure.

Considering the chemical properties of these HAPs, they can be grouped into several general categories (Table 1) which include volatile organic compounds (VOCs), metals, aldehydes, and semi-volatile organic compounds (SVOCs).

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<sup>1</sup>The strategy was finalized on July, 19 1999 (64 FR 38705).

**Table 1 - List of Urban Air Toxics HAPs**

VOCs	Metals (Inorganic Compounds)	Aldehydes (Carbonyl Compounds)	SVOCs and other HAPs
acrylonitrile	arsenic compounds	acetaldehyde	2,3,7,8-tetrachlorodibenzo-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)			
1,1,1,2,2-Tetrachloroethane			
tetrachloroethylene (perchloroethylene, PCE)			
trichloroethylene, TCE			
vinyl chloride			

Given the importance of these pollutants and the impracticality of monitoring for all 188 HAPs on a national basis, we feel that initial monitoring efforts should focus on a subset of HAPs which contains most or all of the HAPs on this list. This is not to say that all UATS HAPs should be measured at all sites and that other HAPs should not be measured in specific situations. This issue is discussed further in Section 3.1.1.

#### 1.4.2 Exposure and Risk Assessment

To understand and properly quantify the health and environmental risks associated with ambient emissions of air toxics, it is important to know to what levels of a pollutant people and ecosystems are actually exposed. In general, ambient air concentrations, produced by fixed station monitors, do not directly estimate long-term human inhalation exposures (although they may be appropriate for ecosystem exposure). Such exposures are either measured with personal monitors,



which follow a human subject through time and space, or are predicted with exposure models, which simulate long-term human activities. However, ambient monitors indirectly provide information that is essential to a proper exposure and health risk characterization.

To date, long-term widespread databases of personal exposure monitoring for many pollutants are limited (and have been developed primarily by organizations outside of the agency). Thus, most inhalation exposure characterizations currently rely on model predictions of inhalation exposure. A key component to these models is to properly characterize the concentration in the different indoor and outdoor places where people spend their time (called microenvironments or MEs). Research has shown that for many pollutants there is a definitive relationship between the outdoor ambient concentration and that found in these MEs (i.e., home, vehicles, workplace, park, ...). Thus, in most exposure models, the outdoor ambient concentration along with ME relationships and human activity pattern data (an accounting of which MEs people spend their time in) are used to predict human inhalation exposure concentrations. With adequate temporal and spatial coverage, ambient monitor data can serve as the required outdoor ambient concentration for these exposure models. Where adequate coverage does not exist, exposure assessments can rely on air dispersion models to provide the air quality data at the required temporal and spatial coverage.

When evaluating exposures from criteria air pollutants (ozone, carbon monoxide, etc.), past regulatory exposure assessments have relied on ambient measurements from fixed-site monitors for use in exposure models. This could be accomplished because routine long-term ambient monitoring data for such pollutants were available to a high degree of spatial resolution in many metropolitan areas. For exposure assessments in support of the ozone national ambient air quality standard development, 6-16 monitoring sites in 9-10 areas around the country have been used to help estimate concentrations in MEs. For most air toxics pollutants, a comparable spatial monitoring resolution is generally not available. As a result, exposure assessment for air toxics are typically driven by ambient concentration estimates from dispersion models. In addition to filling the void of assuring adequate spatial coverage, dispersion models also have the ability to predict future concentrations or evaluate the past effects of various emissions scenarios on ambient concentrations. For example, EPA is currently performing a national screening assessment which will calculate human exposures based on modeled ambient levels from a nationwide dispersion model (the Assessment System for Population Exposure Nationwide, or ASPEN). The ASPEN system calculates these ambient levels based on a knowledge of meteorology, chemistry, and rates at which air toxics pollutants are emitted into the atmosphere from all man-made sources in the nation (this information is compiled in EPA's 1996 National Toxics Inventory, NTI). The ambient concentration outputs from ASPEN are then used to calculate human exposures using the Hazardous Air Pollutant Exposure Model (HAPEM4). Estimated exposures from HAPEM4 will then be combined with quantitative health impact information to estimate population health risks estimates. Thus, as noted in Section 1.4.1, the role of ambient monitoring data in the ASPEN model evaluation process will be an essential step in assuring the appropriateness of the predicted exposure and health risk estimates.

## **2. Current Federal, State and Local Air Toxics Monitoring Activities**

Through a combination of Federal, State, local and tribal monitoring activities, there are approximately 300 sites currently collecting ambient data on hazardous air pollutants.

To support some States with the measurement of air toxics in ambient air, OAQPS initiated the Urban Air Toxics Monitoring Program (UATMP) in 1988. Since its inception, this voluntary contractual support program has been used by many State and local agencies to assess the nature and magnitude of various air toxics problems. The current UATMP supports the collection and analysis of VOCs, aldehydes and other HAPs (See attachments 4-7). For this program, one 24-hour integrated sample is collected every 12 days; the sample is sent to a laboratory for analysis and the resultant concentration values are reported to EPA's Aerometric Information Retrieval System (AIRS) database. To participate in the program, States commit funds to the OAQPS contract and receive a year's worth of monitoring support from the contractor.

Other air quality monitoring programs also provide information on HAPs. The Photochemical Assessment Monitoring Stations (PAMS) program has been collecting air toxics data for 9 volatile organic compound (VOC) HAPs since 1993 in more than 20 major urban areas. The HAPs on the PAMS list are:

- Formaldehyde
- Toluene
- Benzene
- Ethylbenzene
- Xylenes (m,p-xylene and o-xylene separated on PAMS list)
- Hexane
- Styrene
- 2,2,4-Trimethylpentane
- Acetaldehyde

These data are stored in the AIRS database, along with all criteria pollutant monitoring data. In the near future, PM<sub>2.5</sub> speciation monitors will provide measurements of 10 HAP metals at over 50 urban locations in the country. Rural and remote monitoring of these HAP metals takes place as part of EPA's efforts to assess regional haze. These data are produced by the IMPROVE and CASTNET networks. The current network of IMPROVE sites will be expanded to 110 Class I monitoring areas (national parks and wilderness areas) for calendar year (CY) 2000 data collection. CASTNET has eight rural sites in the eastern US. In addition to these networks, the Mercury Deposition Network (MDN), a sub-network of the National Atmospheric Deposition Program (NADP), provides regional measurements of mercury deposition in precipitation at 37 sites, while the Great Lakes and National Estuary Program networks measure a variety of HAPs at more than a dozen sites. Details about a new dioxin monitoring network are provided at the end of this section.

A recent STAPPA/ALAPCO survey identified 252 sites which currently monitor for air toxics and another 150 sites which plan to monitor in CY-2000. At least 32 States will be involved. The number of current and planned monitors by State, and the type of HAPs monitored are shown in Attachments 1-3. Through a voluntary effort of States, local agencies and private entities to report air toxics monitoring data, EPA has also inventoried air toxics monitoring data. A summary of the number of States who have monitored a specific HAP in 1997 and reported the data to EPA is shown in the table on the following page. Work is underway to integrate the results from the recent STAPPA/ALAPCO survey with the combined AIRS and archive data bases. As soon as this has been completed, the summary table will be updated to reflect the expanded air toxics informational data base<sup>2</sup>.

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<sup>2</sup>Note that some HAPs do not appear in the current inventory of monitoring information because there are no demonstrated or routine monitoring methods. (Refer to the discussion in Section 3.2.8). For other pollutants, the methods can be very expensive (e.g. dioxin and congeners).

**Table 1. Ambient Measurements of Urban Air Toxics HAPs (States in 1997)\***

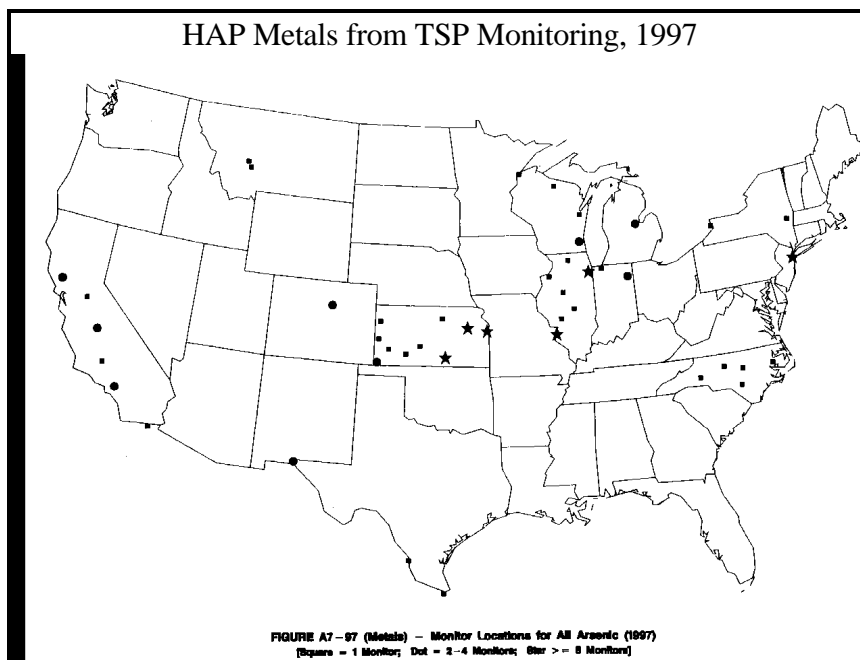
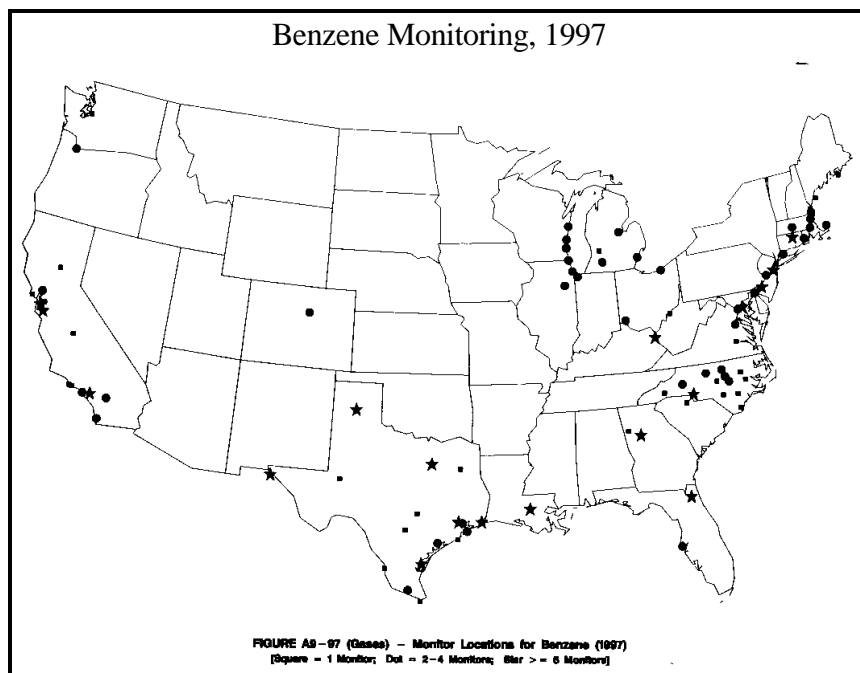
VOCs	#States	Metals**	#States	Aldehydes	#States	SVOCs and other HAPs	#States
acrylonitrile	0	arsenic compounds	11	acetaldehyde	16	2,3,7,8-tetrachlorodibenzo-p-dioxin (& congeners & TCDF congeners)	0
benzene	28	beryllium and compounds	5	formaldehyde	16	coke oven emissions	0
1,3-butadiene	8	cadmium compounds	11	acrolein	8	hexachlorobenzene	1
carbon tetrachloride (tetrachloromethane)	8	chromium compounds	10			hydrazine	0
chloroform (trichloromethane)	11	chromium VI	1			polycyclic organic matter (POM) 112(k)	4
1,2 -dibromoethane (ethylene dibromide)	9	lead compounds	33			polychlorinated biphenyls (PCBs)	0
1,3-dichloropropene	0	manganese compounds	7			quinoline	0
1,2-dichloropropane (propylene dichloride)	8	mercury compounds	2				
ethylene dichloride, EDC (1,2-Dichlorethane)	10	nickel compounds	9				
ethylene oxide	0						
methylene chloride (dichloromethane)	14						
1,1,2,2,-tetrachloroethane	8						
tetrachloroethylene (perchloroethylene, PCE)	13						
trichloroethylene, TCE	12						
vinyl chloride (chloroethylene)	10						

\* States reporting data to AIRS or captured in the OAQPS Air Toxics Archive Data Base

\*\* Most metal analyses are from TSP. A fewer number are from PM<sub>10</sub> or fine particles.

Note: More States reported some specific HAPs in 1996 at the time of this survey. MDN network information has not been included.

As examples of the extent of current State and local agency monitoring coverage for urban HAPs, three maps are presented. First is a map of the 1997 monitoring sites measuring and reporting benzene (the most commonly measured HAP). The second map shows arsenic data, exemplifying the lesser coverage for ambient concentrations of HAP metals.

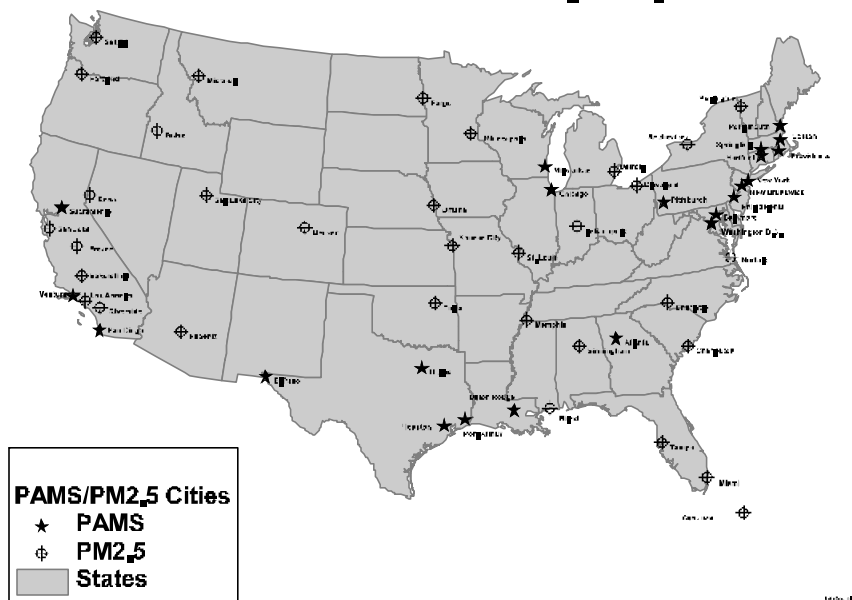


The third map, presented below provides the most recent information on the Mercury Monitoring Network for 1999.



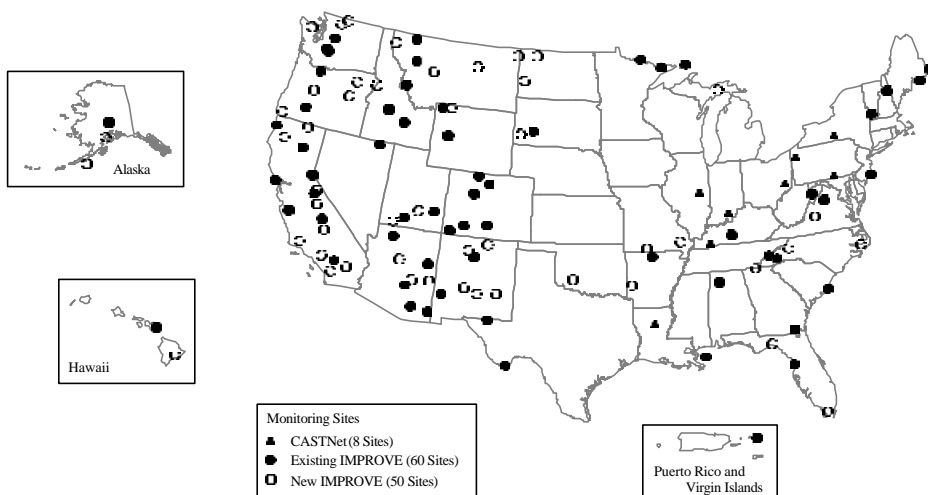
The map below shows the locations of all PAMS areas (which currently provide some daily monitoring of VOC and aldehyde HAPs) and the locations of all proposed PM<sub>2.5</sub> speciation trend sites which will provide information on HAP metals. Some of these sites will be good platforms for expanded air toxics monitoring.

## Cities with PAMS & PM<sub>2.5</sub> Platforms



The rural IMPROVE and CASTNet Networks currently produce data on trace metal HAPs and may be useful platforms for other HAP monitoring.

IMPROVE and CASTNet Monitoring Networks  
(as of February 2000)





As seen in Table 1, dioxin is not routinely monitored by State and local agencies. A new Dioxin Exposure Initiative has identified the need for establishing a nationally-based, long-term, ambient air monitoring network. Known as the National Dioxin Air Monitoring Network (NDAMN), it is designed to serve some of the same objectives mentioned earlier:

- S      Provide ambient air data useful for calibrating regional-scale long-range transport models used in estimating air concentrations of dioxin as a function of dioxin source emissions;
- S      Provide air monitoring capability for the occurrences and levels of dioxin-like compounds in areas where animal feeds (used to feed domestic livestock) are primarily grown;
- S      Provide for the long-term monitoring of dioxin-like compounds in different regions of the United States, and over different seasons.
- S      Provide data on potential transboundary import of CDDs/CDFs into the United States.

Details about data quality objectives and analytical methods for NDAMN are available elsewhere (ref: [www.epa.gov/nceawww1/1page.htm](http://www.epa.gov/nceawww1/1page.htm) ) Phase 1 is a limited deployment of the network in areas that are west of the Continental Divide where deposition is occurring downwind of source activities, and in regions where agricultural activity dominates (approximately 10 to 20 air monitoring stations). Phase 2 will consist of approximately 30 to 40 air monitoring sampling stations throughout the U.S.

The aforementioned air toxics monitoring stations and related ambient air monitoring networks can support the development of a new national network. An adequate geographic distribution of locations and HAP measurements is desired to satisfy the needs of the public health and environmental components of the air toxics program. The next section will identify the short-term and long-term objectives and outline a strategic air toxics monitoring approach. This process will identify how to best utilize the current monitoring stations and networks, what changes or enhancements are needed, and what activities should be undertaken to satisfy the monitoring objectives and to develop a national network.

### **3 Design of National Ambient Monitoring Network to Support Air Toxics Program**

#### **3.1 Air Toxics Monitoring Objectives and Principles**

The monitoring network should be incrementally designed to first address the highest priority needs of the air toxics program: to focus on pollutants and sources which pose the greatest risk to the largest number of people and the greatest risk to the environment. Over time, the network will evolve to satisfy the following monitoring objectives:

##### **3.1.1 Measure pollutants of concern to the air toxics program.**

Because of our limited knowledge in measuring many of the 188 HAPs, the program should initially focus on those pollutants that EPA, State and local agencies have identified as having the most significant potential health impacts and routine measurement methods. The list of HAPs in the UATS is a logical starting point. Several UATS pollutants are also important from an ecosystem risk assessment perspective (POMs and toxic trace elements). As additional priority air toxics are identified and as monitoring capabilities improve, additional HAPs can be added to the monitoring program.

This is not to say that all UATS HAPs must be measured at all locations and that non-UATS HAPs should not currently be measured at some locations. To permit comparisons among HAPs and to facilitate dispersion and deposition model evaluation, however, some number of “core” UATS HAPs should be initially measured at a number of locations nationwide. These HAPs should reflect the practicality of their measurement and include those associated with highest toxicity-weighted emissions or those that are judged responsible for a large percentage of the risk associated with exposures to ambient air toxics. Similarly, as many UATS HAPs as possible should be measured at an agreed upon, albeit initially small, number of “comprehensive” monitoring locations. Such comprehensive platforms should be selected to reflect a broad representative mix of UATS HAP emissions. As monitoring capabilities improve and available resources increase, the list of compounds and locations can change.

For those States and jurisdictions where it can be shown that ambient concentrations are consistently below the minimum detectable concentrations of current monitoring methods or are below established health based exposure levels, the target list of HAPs may be modified to exclude these compounds. As noted later in this paper, the target list of HAPs should be periodically reviewed and modified accordingly as monitoring methods or health based levels are revised.

### **3.1.2 Use scientifically sound monitoring protocols to ensure nationally consistent data of high quality.**

Appropriate sampling and analytical methods should be followed. Emphasis should first be placed on standardized methods and analysis and then on supporting quality assurance efforts between laboratories. Regional or national laboratories could also be helpful to ensure consistent analysis. The methods must consider risk-based concentrations and must be sufficiently sensitive to provide an adequate limit of detection. The monitoring protocol must provide for adequate quality assurance and data management. A Quality Assurance Project Plan (QAPP) is currently under development by EPA.

### **3.1.3. Collect a sufficient amount of data to estimate annual average concentrations at each monitoring site.**

The required frequency of sampling is guided by a variety of factors which include the day-to-day variability in HAP concentrations, the measurement precision of the sampling and analysis methods, cost, and the intended purpose of the data. Air toxics measurements which are collected for making comparisons to dispersion and deposition model predictions will require lower precision and, possibly, less frequent sampling than data needed to detect trends in ambient concentrations. Sampling frequencies can vary seasonally with more frequent sampling needed in seasons or time periods with higher source and meteorological variability.

The selection of sampling frequencies will be guided by the data quality objective (DQO) process. DQOs are currently under development and will provide recommendations on the need to sample according to the typical UATMP sampling frequency of once every 12 days, the frequency for VOCs collected at PAMS sites of one in six days or the frequency to be used at PM<sub>2.5</sub> speciation trend sites and IMPROVE sites of once in three days. Because of different data collection objectives, the sampling frequencies may differ during the first few years of the nationwide air toxics monitoring effort than the frequencies used for the longer-term program.

Sampling frequencies and sampling time periods may also be HAP specific especially in the case of existing national networks. Consideration of what defines “sufficient data” for a particular pollutant depends on the day-to-day concentration variability, as well as estimated precision and accuracy of the monitoring method. While 24-hour samples may be the goal from a health risk assessment perspective, there should also be flexibility to use alternate frequencies and sampling times to accommodate different needs. In particular, compounds requiring lower detection limits may require sampling times greater than 24 hours. Composite samples collected for stable compounds may offer a better and a more cost effective screening technique. Finally, staggered sampling schedules across a network (i.e. sites sampling on the same frequency but on different days) can possibly provide better information on day-to-day or pollutant event behavior.

### **3.1.4 Reflect “community-oriented” (i.e. neighborhood-scale ) monitoring locations.**

Fixed-site air toxics monitors to support model evaluation and health-based trends assessments should be sited to be representative of average concentrations within a 0.5 to 4 km area. In EPA monitoring regulations, this geographic imprint of a monitoring site is termed “neighborhood scale.” Such measurements are intended to be representative of area-wide, average model predictions. In fact, locations representative of larger areas and populations are preferred for this purpose. Separate State, local or tribal toxics monitoring efforts may focus on smaller scale (i.e middle or micro-scale) monitoring sites. All spatial scales of monitoring may be conducted using fixed-site, or movable monitoring platforms.

### **3.1.5 Comply with uniform siting guidelines.**

Monitoring locations should comply with established siting guidelines to permit unbiased comparisons among metropolitan areas and geographic regions of the country. General siting criteria for PAMS site Type-2 and PM<sub>2.5</sub> core monitoring stations can be followed when establishing the desired neighborhood-scale air toxics monitoring sites. These guidelines provide specifications on set back distances from major roads and stationary sources, inlet heights, and other siting considerations.

### **3.1.6 Represent geographic variability in annual average ambient concentrations.**

A national network should represent a variety of conditions and environments that will permit characterization of different emission sources and climatological/meteorological conditions. Such a network would support dispersion model evaluation, understanding of the relationships between emissions and air quality under different circumstances and allow for the tracking of changes in emissions. National assessments should reflect the differences among cities and between urban and rural areas for selected HAPs. Accordingly, the network should reflect the following network design goals:

- C Include some areas with potentially high anticipated concentration,
- C Distinguish differences within and between geographic regions (to describe characteristics of different climatic areas,
- C Determine background concentrations, and
- C Reflect relative variability and the spatial patterns of HAPs across communities.

For model evaluation, trends assessments and other data uses, the national network of ambient air toxics monitoring should reflect the diversity of mobile, area and stationary sources across the country as well as providing important information about upwind or regional background locations (in rural areas), and intra- and inter-regional transport of HAPS. National emission inventories and dispersion and deposition model output can be used to help characterize

data needs and to help identify inadequacies, important gaps or redundancies among the existing monitoring sites and data. With the measured concentrations from the monitoring network, the national emission inventories and dispersion and deposition model output can be evaluated. In particular, it will help assess the incongruities between singular measurement locations with grid based modeled outputs. This is an iterative process.

### **3.1.7 Build upon existing national and State/local monitoring programs.**

By building the Nation's air toxics monitoring network upon existing monitoring programs (adding new sites where necessary), large scale efficiencies of resources can occur. For this reason, the program should maximize use of appropriate existing platforms (where there is consistency with air toxics monitoring objectives) and take advantage of mobile monitoring and saturation monitoring resources. State and local agencies and tribal organizations can use the NATA ASPEN modeling results to help site new monitors.

## **3.2 Strategic Air Toxics Monitoring Approach**

The national ambient air toxics network will take several years to implement. Two to three years are needed to collect and analyze available air toxics monitoring data in order to better understand the sources of spatial and temporal variability of ambient air toxics and to establish the basis for the long-term monitoring program. These activities include: developing an accurate inventory of current air toxics monitoring activities (*i.e.* integrating results of STAPPA/ALAPCO survey and private monitoring activities with the EPA archive of air toxics monitoring data); enhancing existing monitoring efforts and initiating new monitoring where needed to cost-effectively fill initial data gaps and to address network design issues; performing new monitoring and analyzing new and existing air quality data to better understand air quality patterns (spatial and temporal relationships); and utilizing dispersion and deposition modeling and other NATA outputs to assess existing air toxic networks and to better characterize air toxic concentrations. At the end of the initial network development period, long term monitoring objectives can be set and then more permanent monitoring stations can be selected to address these objectives. To facilitate an effective long-term monitoring program, an air toxics network review process will be conducted periodically.

### **3.2.1 Make use of existing monitoring sites**

To initiate the national air toxics monitoring program, the extent and adequacy of current and historical HAP measurements among the existing networks must be analyzed before significant new monitoring is initiated. New air toxics monitoring sites established during FY-00/01 should be established to address future network design issues and to build upon and fill obvious data gaps among existing air toxics monitoring sites (State/local/tribal air toxics monitoring sites, PAMS sites, planned PM chemical speciation sites, the MDN monitoring program, the Great Lakes and NEP monitoring networks, NDAMN, and the IMPROVE and CASTNET monitoring networks).

There is a wealth of existing air toxics monitoring data which should be thoroughly analyzed to address a variety of public health and ecosystem related questions and issues which are discussed in Section 3.2.2 of this document.

Although State, local and tribal air toxics monitoring sites will be the principal components of a national air toxics monitoring program, integrations with existing criteria pollutant monitoring programs will permit the leveraging of data collected for the ozone, PM and regional haze programs. Regarding the PAMS network, the Type-2 sites are sophisticated monitoring platforms which already collect information on several urban HAPs. For 8 HAPs, they produce year-round 24-hr measurements and hourly summer-time data. The latter is important to understand temporal patterns of ambient air toxics. While they are reflective of neighborhood or urban scale monitoring, Type-2 PAMS are sited within or immediately downwind of the urban core in accordance with the summer-time wind flows. In many of these large metropolitan areas, these sites are also reflective of typical year-round urban concentrations and will be appropriate platforms for air toxics monitoring. Enhancement of these platforms, when appropriate, will be very cost effective. Specific suggestions for enhancement of the PAMS for monitoring toxic VOCs are discussed in Section 3.2.9 of this document. There are 24 PAMS monitoring areas, most of which have two Type-2 sites.

PM<sub>2.5</sub> speciation trend sites, which are being established in CY-2000, will also reflect community-oriented monitoring sites; they will provide for fine particle measurement of 10 of the 11 HAP metals (including 7 of the 8 metals in the UATS) and often will contain other air toxics pollutant-related sampling equipment such as PM<sub>10</sub> and TSP samplers. The latter will provide opportunity for additional analyses for lead and other HAPs associated with larger particles. The mature PM<sub>2.5</sub> network will have approximately 54 special trend sites. There are also expected to be up to 250 additional PM<sub>2.5</sub> speciation sites which will provide HAP metals and should be considered, in part, for broader regional air toxics monitoring. Another excellent choice for air toxics monitoring platforms will be sites in the PM<sub>2.5</sub> “supersite” network. This network will evolve over the next 1-2 years and will provide monitoring stations which will include a variety of routine and research grade gaseous and PM analyzers, many of which will be directly related to measurement of HAPs. Additional continuous and integrated 24-hr measurements of VOCs together with aerosols, semi-volatiles and meteorological data throughout these intensive monitoring areas will be very useful for more rigorous and scientific model evaluation.

The IMPROVE and CASTNET networks consist of rural or remote monitoring platforms which provide information on the chemical constituents of particulate matter. As such, they provide information on trace metals and can serve as platforms for future monitoring of other HAPs. The national mercury monitoring network (MDN) and the toxics monitoring networks of the Great Lakes and NEP programs provide important information on the ecosystem risk assessment of HAPs.

The development of the national monitoring network should allow for flexibility in the selection of monitoring locations and cities and rural environments that satisfy the stated monitoring objectives. If existing platforms are not suitable for initial monitoring objectives (model evaluation and characterization of air toxics), new community-oriented monitoring stations should be considered. Although PAMS and PM<sub>2.5</sub> sites would permit cost-effective use of existing equipment, they may not be properly sited to meet the needs of the air toxics program. For example, some Type-2 PAMS sites may not be the most representative locations for characterizing annual average air toxics concentrations, because of the relative mix and spatial distribution of point, area and mobile emission sources in these areas. In addition, the Type-2 sites are located for summertime meteorological conditions and this may not ideally represent annual average concentrations. On the other hand, the data from existing monitors must be evaluated to determine the value added or potential redundancy among currently operated sites. For example, monitors in areas influenced by similar emissions or climatology may produce similar concentrations and thereby provide similar information.

As discussed in Section 3.1.6 of this document, data analysis of monitoring data, emission inventories and model predictions will identify the most useful and the least useful data, and ultimately guide the design of the national monitoring program. When appropriate, current monitoring activities across cities and geographic regions should be streamlined to take advantage of information derived from dispersion model predictions and to eliminate redundant information derived from existing monitoring systems. Equipment can be redeployed and resources utilized in other areas or to sample different HAPs in order to make better use of limited monitoring resources.

### **3.2.2 Perform data analysis/assessment.**

Data analysis is an important component of every air monitoring program. Air toxics data do not have value unless they are quality assured and then analyzed in the context of the overall NATA. Adequate resources must be allocated for data analysis, implementation of statistical quality assurance procedures, data management, data assessment and data reporting. This approach will make best use of previously collected data which can conserve new monitoring resources. It will also enhance data quality and ensure an effective air toxics monitoring system. Data analysis and assessment protocols should be developed to define the process by which conclusions may be developed from the ambient air toxics data. These may include model evaluation, trends analysis, and source attribution, among other typical purposes of data analysis. The development of data analysis protocols should be tied to the data quality objectives mentioned earlier.

### 3.2.3 Initial Focus on Model Evaluation

In the initial phases of this effort, one of the primary purposes of data analysis is to evaluate the NTI and ASPEN modeling of ambient concentrations of air toxics. Comparisons between the observed concentrations collected through the monitoring network and the predicted concentrations from the model will be developed to better understand both the NTI and ASPEN outputs. As initial comparison studies will focus on the national-scale ASPEN modeling efforts, long term model-monitoring comparison efforts may focus on smaller scale studies (*e.g.*, urban, local and hot-spot studies) or special monitoring programs (*e.g.*, multimedia concerns).

Applicable monitoring data will be used as a “reality check” on model output. These data should represent sufficient geographic and emission source diversity to determine if the entire modeling system (model, emissions, meteorology) provides appropriate estimates of ambient concentrations to assist in assessment of the goals and objectives of the air toxic program. A broad selection of locations are needed for the model evaluation. These stations must provide good geographic coverage, represent different climatological regimes and reflect background concentrations in rural areas as discussed in Section 3.1.6 of this document.

In populated areas, well sited community-oriented locations should be utilized. These locations should follow established siting protocols and may be selected from the current State and local monitoring program locations or should be new sites to fill gaps in the model evaluation data base. This neighborhood-oriented monitoring approach will be analogous to the core network for PM<sub>2.5</sub>. Such monitoring sites should not be located in areas with large concentration gradients, and, as such, should not be very close to large sources. As discussed in Section 3.1.4 of this document, they should typically have a spatial scale of representativeness of 0.5 to 4 km which is ideally suited for comparison to county-wide average predictions from a national dispersion model like ASPEN. Ideally, the network should place a small number of sites in each monitoring area to assess spatial variability in HAP concentrations. This may be accomplished with fixed sites, movable platforms or portable monitors. However, the availability of limited monitoring resources and the need for good geographic coverage will only allow multiple monitors in some areas.

The monitoring should also be standardized in other ways: The sites must monitor throughout the year and on the same days/ sampling schedule (*e.g.* 24-hr averages every 6<sup>th</sup> day or other appropriate intervals); use consistent sampling, analytical methods and laboratory procedures; and follow established quality assurance protocols.

It is this initial ambient data set along with the ASPEN national modeling effort that will help define the spatial locations for future monitor efforts. The development of the network will therefore be an iterative process, with a continuing assessment of the appropriateness of specific monitoring locations.



### **3.2.4 Longer-term trends network.**

The longer-term monitoring network will include permanently sited monitoring stations which will be used to establish trends and evaluate air toxics program goals. Although the next few years of data collection and analysis will focus on air toxics characterization and model evaluation, these formative years will also be important to better define network requirements for the long-term trends network for specific air toxics. Any new characterization sites should be selected to also potentially serve as long-term trend sites. Network managers may consider traditional monitoring and network design principles in choosing new gap filling locations so that they reflect stable monitoring environments, with potential for long-term monitoring. Similar to the requirements for model evaluation, the sites selected for trends analysis should:

- be neighborhood-oriented and reflective of general population exposure;
- comply with established physical siting protocols;
- provide good geographic coverage and represent different climatological regimes;
- include appropriate numbers of sites with influences by specific emission sources (mobile and stationary);
- represent regional background and transport concentrations (rural areas);
- include common sets of HAPs at sufficient numbers of sites;
- monitor throughout the year and on the same days/ sampling schedule ;  
(e.g. 24-hr averages every 6<sup>th</sup> day);
- ensure sufficient data capture; and
- use consistent sampling, analytical methods, laboratory procedures and quality assurance protocols

### **3.2.5 Incorporate long-term and short-term monitoring elements where possible**

The network may incorporate fixed-station long-term monitoring as well as short-term monitoring elements. Where possible, this will enable the network to address the multiple objectives of the air toxics program. The network can be modeled after the existing State and Local Air Monitoring Station (SLAMS). Such a network includes long-term National Air Monitoring Stations (NAMS) designed to study trends and pollutant impacts in major metropolitan areas. It also includes other SLAMS monitoring stations to address State level characterizations and assessments on a 3-5 year time frame.

### **3.2.6 Allow for temporary air toxics monitoring activities.**

The national air toxics monitoring program should allow for short-term, local studies. Such monitoring is desired by many State and local areas. It may utilize temporary or mobile monitoring stations and be an adjunct to the network of fixed site monitoring locations. These activities can be useful to facilitate proper assessments of geographic variability, both between and within metropolitan areas and permit development of hourly ambient concentrations for certain HAPs that may present health risks from acute exposure. Such short-term data collection activities can also assist with developing source receptor relationships, identifying contributing sources and understanding atmospheric processes. The collection of on-site meteorological data would be useful to assist with these assessments. The aforementioned activities will be particularly useful during the formative years of national network implementation.

Examples of temporary air quality monitoring activities may also include: characterization of environmental justice concerns, assessment of ambient concentrations representative of small geographic areas like schools which may be potentially impacted by specific sources (“hot spots”) or specialized augmentation of routine monitoring to meet State or local needs.

### **3.2.7 Integrate air toxics and other monitoring.**

Collectively, a national toxics network consists of many existing programs including the sites operated by State and local agencies, the HAPs measured in the PAMS program, metals measured in particulate matter programs (particularly the PM<sub>2.5</sub> speciation and IMPROVE programs), the NADP/MDN program, the Great Lakes and NEP monitoring programs, MDAMN, and new initiatives currently under discussion. The new air toxics monitoring program is an integration across many separate monitoring activities which are envisioned to form a comprehensive air monitoring network. The long-term goal for a national monitoring program should also include monitoring of sensitive ecosystems such as the deposition monitoring efforts for the Great Lakes and coastal waters and support future environmental assessment programs such as the EPA-ORD Mercury Research Strategy, North American Free Trade Agreement (NAFTA) related environmental initiatives, and other trans-boundary pollutant assessment programs.

### **3.2.8 Utilize standard monitoring methods.**

Standardized monitoring methods should be used. Currently, there are standard methods that cover 27 of the 33 UATS HAPs. Methods for the five HAPs not covered are either not generally considered to be practical or have not been demonstrated and require additional methods development. The methods are as follows:

- Toxic Compendium Method TO-15, “Determination of Volatile Organic

Compounds in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)” or TO-14A, “Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography” are standard EPA methods to be used. These methods provides for collection of volatile organic compound (VOC) HAPs, including most of the 14 VOCs on the 33 UATS HAPs list<sup>3</sup>. See attachment 4.

Compendium Method TO-15 is an extension of the Method TO-14 description in the following ways:

TO-15 incorporates a multisorbent/dry purge technique for water management, thereby addressing a more extensive set of compounds (oxygenated).

TO-15 using the GC/MS technique versus multiple-detectors as the **only** means to identify and quantitate target compounds. The GC/MS approach allows for specific detection of the target analytes and reduces the chance for misidentification or the effects of coeluting compounds. The use of non-specific detectors (e.g., FID, ECD) or a combination of these detectors, used in TO-14 is determined by the required specificity and sensitivity of the application. While non-specific detectors are in some cases more sensitive than specific detectors, they vary in specificity and sensitivity for a specific class of compounds. Trade-offs in sensitivity between non-selective multiple detectors and GC/MS can be somewhat mitigated by the use of ion trap technology versus full scan quadrupole MS.

- Chemical speciation of filter-based mass collected at particulate matter sites can provide data on several elements using Compendium Method IO-3, “Chemical Species Analysis of Filter-collected Suspended Particulate Matter.” This analysis includes as many as 11 HAP metals and as many as 8 UATS metals. See Attachment 5. Particle sampling can include PM<sub>2.5</sub> to focus on the fine fraction of suspended particles, or total suspended particulate (TSP) for using a high-volume (hi-vol) sampling system to permit analysis of metals among all suspended particulate matter. This is consistent with the intended analytical approaches and services available through EPA contracts. Some valence-specific metals, like chromium VI (hexavalent chromium) have been identified as having high toxicity and would require separate chemical analyses. These chemicals would be collected with the same particulate matter samplers but would be analyzed with more specific analytical techniques.
- The analysis of mercury and speciated forms of mercury (if desired) will require

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<sup>3</sup>Monitoring agencies have reported difficulties with recoverability of acrylonitrile with this method

the use of technology outside of Compendium Method IO-3. Consideration should be given to the use of continuous gas-phase total and speciated mercury monitors for future, long-term monitoring efforts. Continuous monitoring instrumentation is currently commercially available and somewhat expensive for both total and speciated mercury monitoring. More methods research is needed to provide a standardized, routine monitoring method for mercury.

- Toxic Compendium Method TO-11A, “Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography” provides for the collection of three aldehyde HAPs including two UATS aldehydes belong to the family of chemicals known as carbonyls. See Attachment 6.
- Toxic Compendium Method TO-13A, “Determination of benzo(a)pyrene and other Polynuclear Aromatic Hydrocarbons in Ambient Air Using Gas Chromatography with Mass Spectrometry” provides for the collection and analysis of PAHs. This method covers one urban HAP, polycyclic organic matter (POM) (a group of compounds). With this method, this HAP is being represented by seven polynuclear aromatic hydrocarbons (PAHs), including (benz(a)anthracene, chrysene, benzo(b)fluorathene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene and dibenz(a,h)anthracene). See Attachment 7.
- Toxic Compendium Method TO-4A, “Determination of Pesticides and Polychlorinated Biphenyls in Ambient Air Using High Volume Polyurethane Foam (PUF) Sampling Followed by Gas Chromatographic/Multi-Detector (MD)”, provides for the analysis of hexachlorobenzene. See Attachment 7.
- Toxic Compendium Method TO-9A, “Determination of Polychlorinated, Polybrominated and Brominated/Chlorinated Dibenzo-p-Dioxins and Dibenzofurans in Ambient Air” provides for the analysis of 2,3,7,8-tetrachlorodibenzo-p-dioxin & congeners & TCDF congeners. Note that this method is reported to be resource-intensive/expensive.
- The urban HAPs currently without practical or demonstrated methods are acrolein, acrylonitrile, ethylene oxide, hydrazine, coke oven emissions, and quinoline.

### **3.2.9 Enhancement of the PAMS for monitoring toxic VOCs**

An opportunity to leverage the installed instrument base of the PAMS for monitoring of toxic VOCs should be considered. The PAMS networks utilize gas chromatography either for on-site ambient air monitoring at the PAMS monitoring site (auto-GCs) or for

monitoring of sample air taken from canisters filled at the site and analyzed in a central laboratory (laboratory GC). These systems consist of a gas chromatograph and a detector (typically a flame ionization detector or FID at the monitoring stations) and provide concentration data for the PAMS target list of hydrocarbons. The PAMS list includes the compounds benzene, toluene, and other aromatic hydrocarbons (for a total of 9 HAPs) that are on the list of 188 toxics identified in Section 112 of the CAA. Hence there is a historical database available for these compounds. However, these systems may have the capability for providing essentially all of the air toxic VOCs. To do this the auto-GCs would need to be augmented by: (1) adding a supplemental list of target compounds, e.g. subsets of the TO-15 target list, to the target compound list detected by the FID and (2) adding an electron capture detector (ECD) for detection of many of the chlorinated VOCs. The first change can be accomplished by implementing data processing and calibration procedures which are similar to those used for the PAMS target list. The second change is possible because the auto-GCs are usually designed to allow for at least one additional detector system. Another dimension of the auto-GCs is their configuration to allow analysis of samples taken in canisters and also samples taken in solid sorbent tubes. Thus, samples taken at various locations could be taken to a centrally-located GC or auto-GC for analysis so that VOC spatial variability can be determined.

Note that since the PAMS sites have been chosen based primarily on the need to gather ozone and ozone precursor data, they may not be ideal for the monitoring of Urban HAPs. In addition, States have noted that changes to the PAMS system such as described above, may add more complexity and variability to the already complicated PAMS measurement process. Accordingly, in coordination with the States, the EPA is investigating the practicality of adding the additional detector to the GCs in the PAMS program before including recommendations for these changes as part of the air toxics monitoring program.

### **3.2.10 Incorporate measurements for other HAPs when possible (Support research and development efforts to permit new and better analyses).**

The network should allow for measurements of additional HAPs. For example, there are a number of urban HAPs without demonstrated routine sampling and analytical methods associated with them. Examples are acrolein, ethylene oxide, hydrazine, quinoline, and coke oven emissions. In addition there are other methods which are costly to implement. For example, dioxin (i.e. 2,3,7,8-tetrachlorodibenzo-p-dioxin & congeners & TCDF congeners) and speciated mercury. Research is needed to develop new or more cost-effective monitoring methods to permit the measurement for these HAPs on a routine basis. It is also important to modify current measurement capabilities to improve and streamline the operational aspects of monitoring and make it less labor intensive. These efforts become important adjunct activities to the overall ambient air toxics monitoring strategy.

### **3.2.11 Review network periodically.**

Air toxics data collection activities and a future national network should be reasonably dynamic and modified as needed. The program should include the following:

- Annual or biannual reviews of the network should be designed to eliminate redundancy of measurement within and across cities, to modify sampling frequencies and to adjust measurement protocols to ensure that data quality objectives are achieved.
- The number of toxics to be monitored also needs to be evaluated periodically and may need to be increased or decreased as appropriate
- The target list of pollutants should be modified to make cost-effective use of available resources while still satisfying the multiple goals of the air toxics program. If a particular analyte requires its own discrete monitoring method and it is not detectable, then it should be considered for elimination from routine sampling and laboratory analysis. This does not necessarily apply to compounds that are part of a suite of compounds that are generated with a particular monitoring method (like TO-15 or XRF). PCBs or Dioxin might be method specific examples. While air toxics monitoring efforts may initially include a large set of HAPs, the target list may be reduced as information about ambient concentrations or predicted concentrations become available. However, the analysis of once non-detectable compounds in key monitoring areas should be periodically revisited to ensure that new emission sources (or better monitoring technologies) have not emerged. It is suggested that this occur once every 3-5 years.
- More sensitive monitoring methods should also be developed and monitoring re-initiated when the risk based benchmarks and observed concentrations are both less than current method detection limits.
- The network planning process should also make use of surrogate measures whenever appropriate to help identify areas where more specific monitoring is needed (e.g. nickel or zinc as a predictor for mercury; and carbon monoxide as a predictor of mobile source pollutants such as benzene and 1-3 butadiene).

## **4 Initial Network Development**

The national air toxics monitoring network will be established over a several year period through a cooperative Federal, State, local and tribal effort. To obtain guidance from EPA's State and local partners and to take advantage of their air toxics monitoring expertise, EPA has convened a steering committee which consists of EPA, State and local monitoring agency representatives. Over the past 6 months, this committee has contributed to the development of this document and has helped define near-term activities to assist the design and implementation of a national air toxics network.

The following sections address the activities and protocols anticipated during the initial rollout and subsequent years. A more detailed, but still tentative approach, for FY-00/01 air toxic monitoring activities is also presented. Many details must still be developed and will be described in addendums to this document.

### **4.1 Preliminary schedule of monitoring and data analysis activities**

#### **4.1.1 Activities during 3-year rollout:**

(FY-00 )	Select core HAPs
(FY-00 )	Develop QAPP
(FY-00 )	Develop DQO's
(FY-00 )	Develop initial monitoring plan with stated objectives
(FY-00)	Select FY-00 Pilot Project Areas
(FY-00)	Distribute FY-00 grants and guidance
(FY-00)	Identify existing sites for continued monitoring
(FY-00 )	Procure equipment
(FY-00/01)	Establish new sites and begin monitoring
(FY-00/01)	Determine laboratory support process
(FY-00)	Utilize Model Predictions to guide selection of FY-01 monitoring sites
(FY-00/02)	Analyze data from current State/local toxic monitoring sites
(FY-02)	Analyze Data from New Pilot Project Monitors
(FY-02)	Utilize Model Predictions
(FY-02)	Develop long-term network monitoring plan based on model results/data analyses/network objectives and insights gained from FY-00 Pilot Projects
(FY-01/02)	Determine resource availability and funding status
(Ongoing)	Conduct local monitoring projects as needed

#### **4.1.2 Post Rollout Activities**

(FY-03)	Begin implementation of national network
(FY-03/05)	Complete full network deployment

- |               |   |
|---------------|---|
| (Ongoing)     | Conduct data analyses   |
| (Every 2 yrs) | Conduct network reviews/recommend network modifications as necessary<br>Consider current state-of-knowledge; current state of monitoring technologies; need to add/delete HAPs; need to add/delete sites; allocation of resources; etc. |
| (Ongoing)     | Conduct local monitoring projects as needed   |

## **4.2 FY-00/01 activities**

The initial focus should be on meeting the objectives of the initial 3-year rollout of the new monitoring network.

The principle focus during these formative years will be to:

- characterize pollution gradients reflecting diverse areas and a variety of emission sources,
- provide information on concentration levels and pollutant variability to compare with ASPEN model outputs,
- obtain data to determine if a small number of monitors operating at minimum sampling frequencies can adequately characterize the toxics in urban areas,
- depict the range of concentrations which may be expected in differing urban/rural environs and source influences (mobile sources, industrial activity, background, etc.), and
- provide a data base sufficient to optimize the eventual implementation of a national air toxics monitoring effort.

To accomplish these goals, the steering committee has recommended that pilot sampling programs should be conducted in several urban areas and non-urban rural areas. Two to four urban areas influenced by diverse emission sources and different climatological conditions would be selected to produce air toxics measurements for one to two years at multiple neighborhood scale monitoring sites using the same monitoring protocols. Fewer monitoring sites would be required in the non-urban areas. These data will be subsequently assessed to better understand the sources and magnitudes of variability associated with ambient air toxics concentrations within and between monitoring locations across the U.S.

Where there is consistency between these objectives and existing monitoring sites, efforts should be directed toward the enhancement of existing State and local air toxic sites (including PAMS sites where appropriate), enhancement of new PM<sub>2.5</sub> chemical special sites (a total of 54 urban PM<sub>2.5</sub> monitoring areas have been proposed) and possible enhancement of existing rural monitoring networks (IMPROVE/CASTNET/MDN/NEP/Great Lakes).

For consistency with long-term air toxics program objectives, it is essential that a number of long-standing State and local air toxic sites are also maintained. This requires resources to



refurbish these sites as needed to ensure high data quality and continuation of good data capture. Resources permitting, new community-oriented ambient air toxics monitoring platforms could also be established to fill gaps in existing State, local and tribal networks (e.g. currently unmonitored urban areas with high toxicity weighted HAP emissions). Similarly, new rural monitors where current background data is lacking or is uncertain could be established. In all cases, the platforms should be equipped or upgraded to enable an appropriate suite of required urban HAPs.

To maximize the use of resources in gaining new air toxics data, movable or mobile platforms and portable samplers, may be utilized in addition to fixed sites to help define temporal and spatial patterns within urban areas. This will help to assess existing monitoring locations, to identify representative locations for model evaluation or for long-term monitoring. Such activities will help to characterize air toxics, to evaluate model predictions, to facilitate the derivation of network design requirements, to reduce the need to relocate established monitors and to address community concerns. Movable platforms will be particularly useful during the formative years when the aforementioned pilot studies are conducted. The monitoring activities during the first years should also reflect appropriate quality assurance, data management, data analysis and data submission to AIRS.

#### **4.3 Initial Monitoring Protocols.**

The first few years should utilize established monitoring protocols. This will include analysis for VOCs (using TO-14A or TO-15) from year-round 24-hr canister samples collected intermittently. The TO-14A/15 compounds include benzene, 1,3-butadiene, 1,4-dichlorobenzene, carbon tetrachloride, trichloroethylene, vinyl chloride, etc. A complete list of these analytes is attached (Attachment 4). The TO-14/15 compounds were selected as the first priority because the analysis method has been proven, is cost-effective, and provides data on most of the urban air toxic VOCs of interest.

Additional 24-hr samples and analyses could include IO-3 for HAP metals (using XRF analysis on TSP filter media), POMs using the TO-13A method and aldehydes (including formaldehyde and acetaldehyde) using TO-11A. Many of the PM<sub>2.5</sub> platforms will also include measurements for PM<sub>10</sub> and/or TSP, so comparison of fine to coarse particle urban HAP metals is also possible. PM<sub>2.5</sub> sampling is planned for a 1-in-3-day schedule; for other pollutants (including TSP), sampling will be likely scheduled once in 6 to 12 days depending on the results of the data quality objectives process.

As technology develops, continuous and less labor intensive monitoring equipment may become available. A new continuous formaldehyde analyzer is currently undergoing field evaluation and may be ready for limited deployment during FY-2000. Continuous total and speciated mercury monitors are currently commercially available.

Some other measurements are relatively more expensive, but are very important and worth including in the initial network. In particular, specific analysis for mercury using new continuous speciation analyzers could possibly be included at selected sites for comparison to XRF measurements for particulate mercury and mercury surrogates (particulate zinc and nickel) and wet deposition measurements. However, because of limited resources, these mercury analyzers may be utilized on a limited basis. Dioxin measurements are even more expensive, so the NDAMN network can be used to provide useful information on dioxin. However, monitoring may be considered by the States on a case-by-case basis for selected sites.

#### **4.4 Detailed FY-00/01 Monitoring Plan**

To support the initial data collection goals (model evaluation, air toxics characterization and network design), a detailed monitoring plan is needed. This plan will identify urban and rural areas selected for the pilot monitoring programs and other geographic regions or metropolitan areas for continued, new or expanded monitoring activities. It will also specify the initial core HAPs<sup>4</sup> to be monitored at appropriate number of sites in specific source/population/climatological regimes; monitoring methods; recommendations for the use of existing PAMS continuous monitors and deployment of other continuous analyzers; recommendations for sampling frequencies for the integrated 24-hour sampling methods; and quality assurance protocols. The need for additional monitoring during the initial phases of data collection and for long-term monitoring will be addressed. As new priority air toxics are identified, future monitoring activities should address other pollutants of concern in the air toxics program. The longer term plan will therefore address the need to produce measurements of additional compounds from the larger set of 188 CAA HAPs .

The detailed monitoring plan will be developed over the next several months. At this point, we cannot precisely project the size of the national monitoring network. It is noted that monitoring sites which participate in the FY-00/01 pilot networks or other short-term gap-filling sites may not be part of a final long term national network. The number of sites for the final network will be developed from the initial data assessments, revised iteratively as additional monitoring and modeling information becomes available and also modified as the objectives of the national air toxics program evolve.

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<sup>4</sup>Recommendations for these core/target HAPs have been developed by a committee of State/local agency and EPA. technical staff. These pollutants are identified as a part of Attachments 4, 5, 6 and 7 to this document. The pollutants were chosen based on the availability of standard gas mixtures, available and practical sampling/analysis methods, and the sensitivities of the available methods.

## **ATTACHMENTS**

Attachment 1: Existing Air Toxics Monitoring Stations by State (1999)

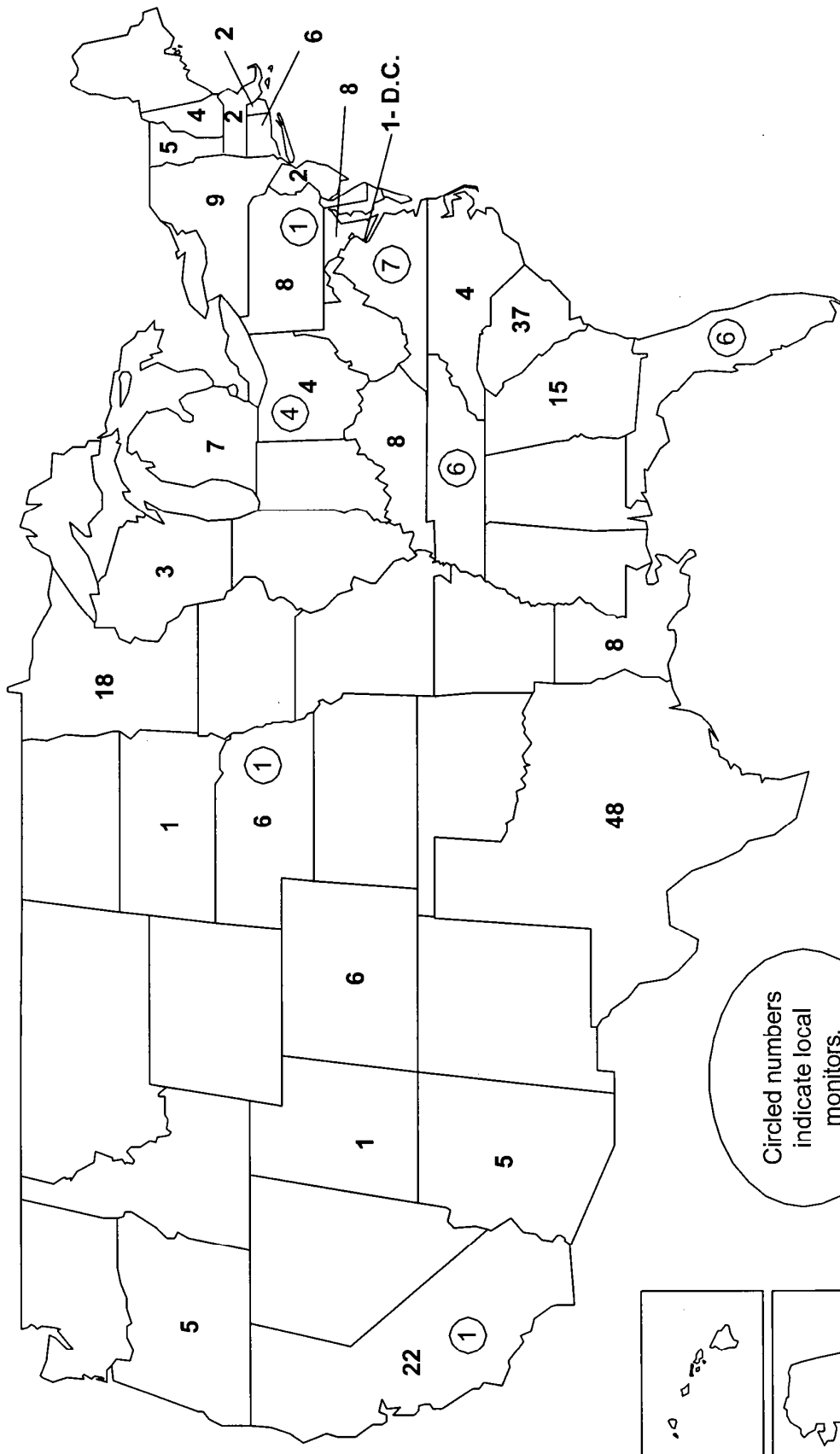
Attachment 2: New Air Toxics Monitoring Stations Planned for Year 2000

Attachment 3: Types of Air Toxics Monitored

# Existing Air Toxic Monitoring Stations by State

(Or planned to be operating by 12/99)

TOTAL - 252

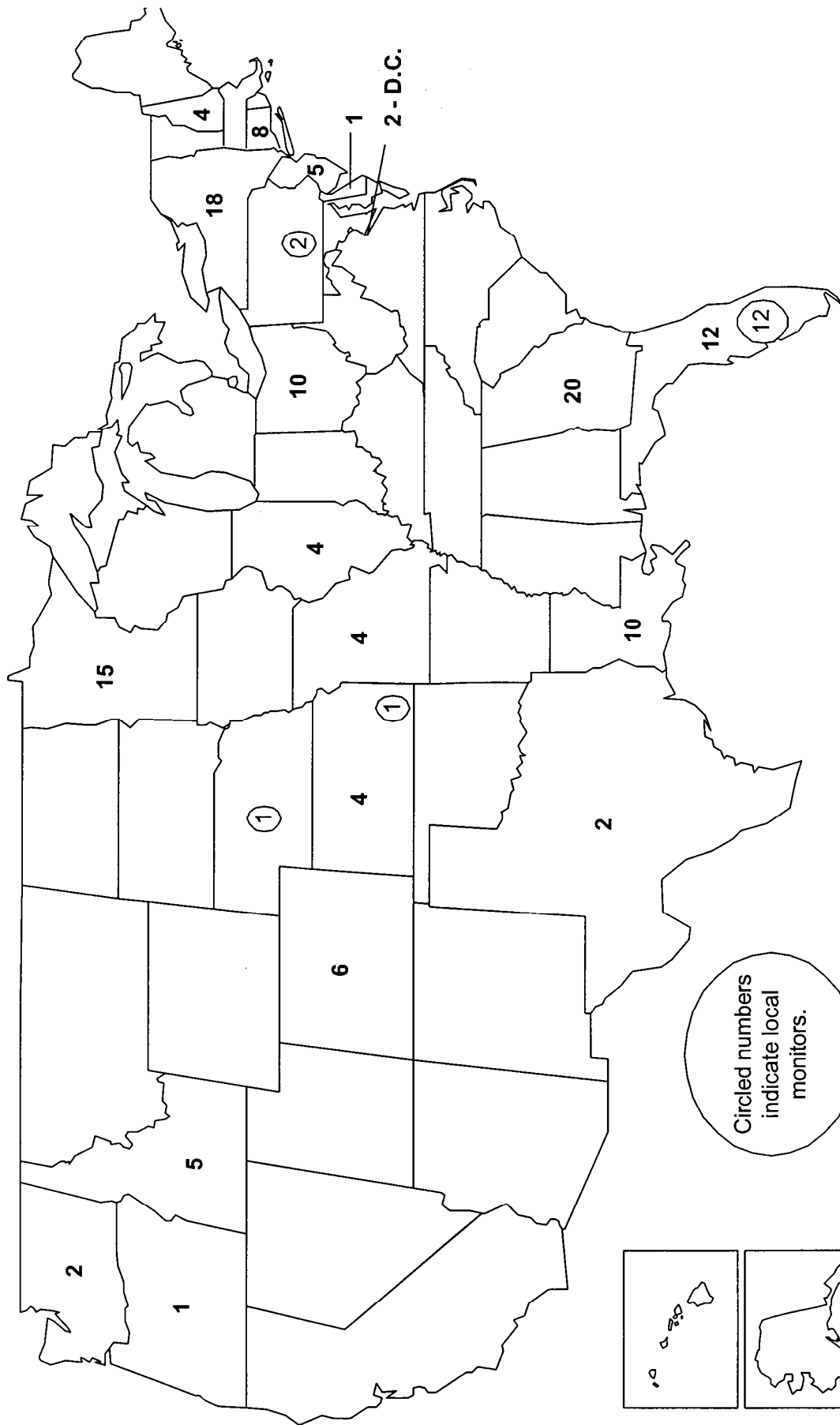


Circled numbers indicate local monitors.

# New Air Toxic Monitoring Stations Planned for Year 2000

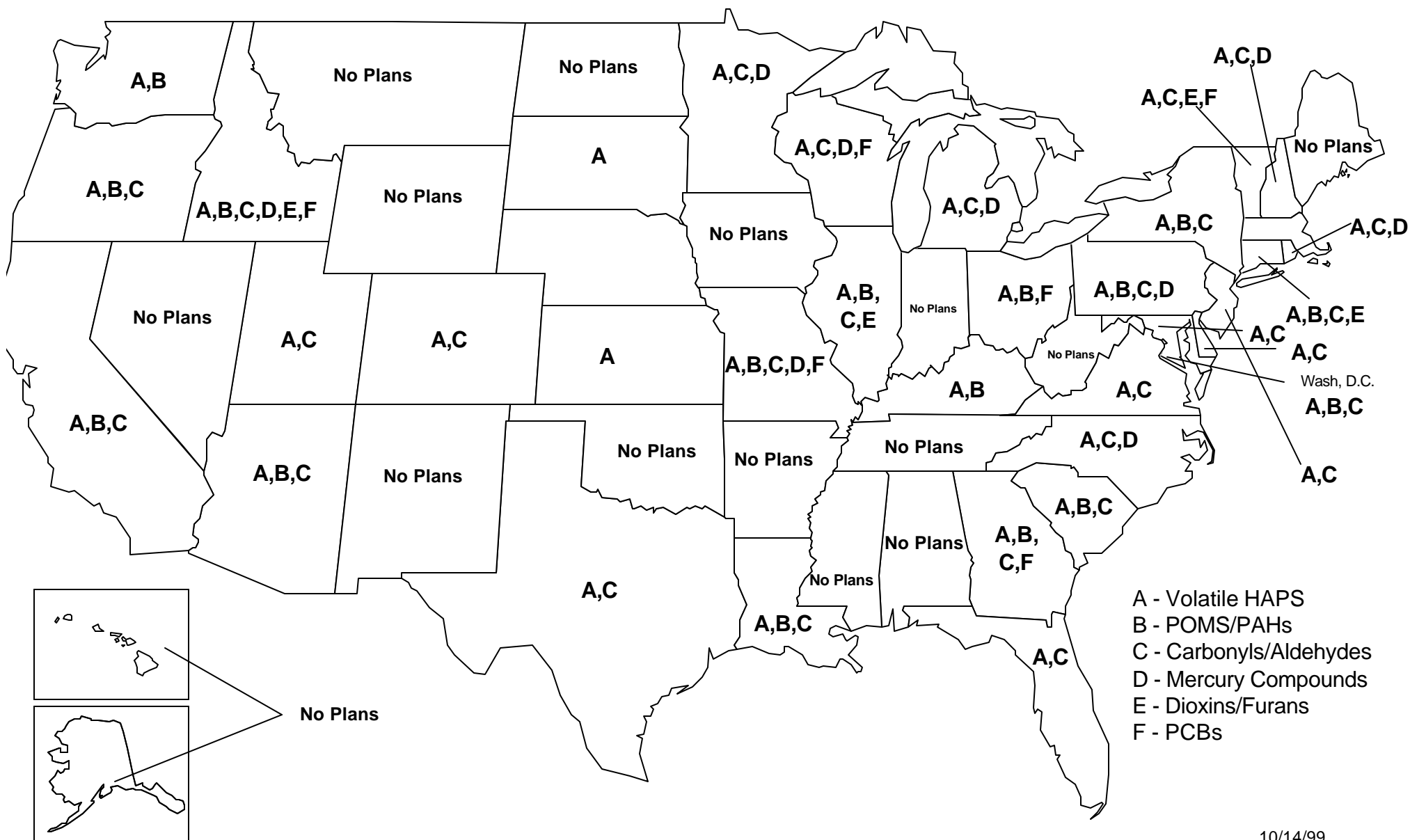
TOTAL - 150

These stations are in addition to existing monitoring stations.



Circled numbers indicate local monitors.

## Types of Air Toxics Monitored (Existing or Planned)



# ATTACHMENT 4

## METHOD TO-14A/15 (VOCs)

No.	POLLUTANT	CAS#	UATS <sup>a</sup>	UATMP <sub>b</sub>	Core <sup>d</sup>	Max <sup>e</sup>
1	1,2- Dibromoethane	106934	X	X		T <sup>f</sup>
2	1,2- Dichloroethane (EDC)	107062	X	X		T
3	1,3-Butadiene	106990	X	X	X	X
4	1,1-Dichloroethane	75343		X		
5	1,1,2,2-Tetrachloroethane	79345	X	X		T
6	1,2,4-Trichlorobenzene	120821		X		
7	1,1,2-Trichloroethane	79005		X		
8	1,2-Dichloropropane (propylene dichloride)	78875	X	X	X	X
9	1,3-Dichloropropene	542756	X	X		X
10	1,1,1-Trichloroethane	71556		X		
11	1,1-Dichloroethylene	75354		X		
12	1,4-Dichlorobenzene	106467		X		
13	2,2,4-Trimethylpentane	540841				
14	2-Chloro-1,3-butadiene (chloroprene)	126998		X		
15	Acetonitrile	75058		X		
16	Acrylonitrile (Monitoring agencies have reported difficulties with recovery using this method)	107131	X	X		
17	Allyl chloride	1070501				
18	Benzene	71432	X	X	X	X
19	Benzyl chloride <sup>c</sup>	100447				
20	Bromoform (tribromomethane)	75252		X		
21	Bromomethane (methyl bromide)	74839		X		
22	Carbon Tetrachloride	56235	X	X	X	X
23	Chlorobenzene	108907		X		
24	Chloroethane (ethyl chloride)	75003		X		
25	Chloroform	67663	X	X	X	X
26	Chloromethane (methyl chloride)	74873		X		

27	Cumene	98828				
28	Ethyl acrylate	140885		X		
29	Ethylbenzene	100414		X		
30	Hexachlorobutadiene	87683		X		
31	Hexachlorocyclopentadiene	77474				
32	Hexachloroethane	67721				
33	m-Xylene	108383		X		
34	Methyl ethyl ketone	78933		X		
35	Methyl isobutyl ketone	108101		X		
36	Methyl tert-butyl ether (MTBE)	1634044		X		
37	Methyl methacrylate	80626		X		
38	Methylene Chloride	75092	X	X	X	X
39	n-Hexane	110543				
40	o-Xylene	95476		X		
41	p-Xylene	106423		X		
42	Styrene	100425		X		
43	Tetrachloroethylene (PCE)	127184	X	X	X	X
44	Toluene	108883		X		
45	Trichloroethylene (TCE)	79016	X	X	X	X
46	Vinyl chloride	75014	X	X	X	X
47	Vinyl acetate	108054				
48	Vinyl bromide	593602				
49	Xylene (mixed)	1330207				

a UATS = Urban Air Toxics Strategy compound

b UATMP = Urban Air Toxics Monitoring Program target list for 1999 and later years.

c May have stability issues over time in cylinders or canisters

d A small subset of HAPs which should be measured at virtually every monitoring site designated as a part of the national HAPs monitoring network.

e A set of pollutants which includes as many of the Urban Air Toxics Strategy pollutants as possible, measured at selected sites.

f Pollutant temporarily listed.

[**Note:** The above list of VOCs are those that can be measured by TO-14a or TO-15. However, some of these are not yet appropriate for routine monitoring because calibration standards are not readily available.]



## ATTACHMENT 5

### METHOD IO-3 (ELEMENTS AND METALS BY XRF AND ICP/MS)

POLLUTANT	CAS# <sup>a</sup>	UATS <sup>b</sup>	UATMP <sup>d</sup>	Core <sup>e</sup>	Max <sup>f</sup>
Antimony	7440360		X		
Arsenic compounds	7440382	X	X	T <sup>g</sup>	T
Beryllium and compounds	7440417	X <sup>c</sup>	X	X	X
Cadmium compounds	7440439	X	X	X	X
Chromium compounds	7440473	X	X	X (total Cr)	X (Cr VI)
Cobalt	7440484				
Lead compounds	7439921	X	X	X	X
Manganese compounds	7439965	X	X	X	X
Mercury compounds	7439976	X	X		T
Nickel compounds	7440020	X	X	X	X
Selenium	7782492				

a Other CAS numbers are defined for the compounds of these metals.

b UATS = Urban Air Toxics Strategy compound

c Beryllium cannot be detected by XRF

d UATMP = Urban Air Toxics Monitoring Program target list for 1999 and later years.

e A small subset of HAPs which should be measured at virtually every monitoring site designated as a part of the national HAPs monitoring network.

f A set of pollutants which includes as many of the Urban Air Toxics Strategy pollutants as possible, measured at selected sites.

g Pollutant temporarily listed.

## ATTACHMENT 6

### METHOD TO-11A (CARBONYL COMPOUNDS) <sup>a</sup>

POLLUTANT	CAS#	UATS <sup>b</sup>	UATMP <sup>c</sup>	Core <sup>d</sup>	Max <sup>e</sup>
Acetaldehyde	75070	X	X	X	X
Formaldehyde	50000	X	X	X	X
Propionaldehyde	123386		X		

a These three carbonyl compounds are also known as aldehydes.

b UATS = Urban Air Toxics Strategy compound

c UATMP = Urban Air Toxic Monitoring Program target list for several years

d A small subset of HAPs which should be measured at virtually every monitoring site designated as a part of the national HAPs monitoring network.

e A set of pollutants which includes as many of the Urban Air Toxics Strategy pollutants as possible, measured at selected sites.

ATTACHMENT 7

**SEMI-VOLATILE ORGANIC COMPOUNDS AND OTHER UATS HAPS**

POLLUTANT	CAS#	UATS <sup>a</sup>	UATMP <sup>b</sup>	Core <sup>f</sup>	Max <sup>g</sup>
Polycyclic organic matter (POM) <sup>c</sup>	NA	X	X		X
Polychlorinated biphenyls (PCBs) <sup>d</sup>	NA	X			X
bis (2-chloromethyl) ether	542-88-1		X		
bis (2-ethylhexyl) phthalate	117-81-7		X		
Hexachlorobenzene <sup>d</sup>	118741	X			X
Dioxin [2,3,7,8-tetrachlorodibenzo-p-dioxin (& congeners & TCDF congeners)]	1746016	X	X		
Hydrazine	302012	X			
Coke oven emissions <sup>e</sup>	NA	X			
Quinoline	91225	X			

a UATS = Urban Air Toxics Strategy compound

b UATMP = Urban Air Toxics Monitoring Program target list for 1999 and later years.

c Method TO-13A; POM represented by 7 PAHs which include:

Benz[a]anthracene

Chrysene

Benzo[b]fluorathene

Benzo[k]fluoranthene

Benzo[a]pyrene

Indeno[1,2,3-cd]pyrene

Dibenz[a,h]anthracene

d Method TO-4A

e Coke oven emissions are a mixture of benzene, toluene, xylenes, cyanide, naphthalene, phenol and POM.

f A small subset of HAPs which should be measured at virtually every monitoring site designated as a part of the national HAPs monitoring network.

g A set of pollutants which includes as many of the Urban Air Toxics Strategy pollutants as possible, measured at selected sites.

## **References**

Toxic Compendium Method TO-4A, "Determination of Pesticides and Polychlorinated Biphenyls in Ambient Air Using High Volume Polyurethane Foam (PUF) Sampling Followed by Gas Chromatographic/Multi-Detector (MD)".

Toxic Compendium Method TO-11A, "A Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography".

Toxic Compendium Method TO-13A, "A Determination of benzo(a)pyrene and other Polynuclear Aromatic Hydrocarbons in Ambient Air Using Gas Chromatography with Mass Spectrometry".

Toxic Compendium Method TO-15, "A Determination of Volatile Organic Compounds in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry"

All of the above are available at: <http://www.epa.gov/ttn/amtic/airtox.html>

Inorganic Compendium Method IO-3.3, "Determination of Metals in Ambient Particulate Matter Using X-Ray Fluorescence (XRF) Spectroscopy".

Inorganic Compendium Method IO-3.5, "Determination of Metals in Ambient Particulate Matter Using Inductively Coupled Plasma/Mass Spectrometry (ICP/MS)".

Inorganic Compendium Method IO-2.1, "Sampling of Ambient Air for Total Suspended Particulate Matter (SPM) and PM10 Using High Volume (HV) Sampler".

"Technical Assistance Document (TAD) for Sampling and Analysis of Ozone Precursors; EPA/600-R-98/161; September 1998." posted at <http://www.epa.gov/ttn/amtic/pams.html>

"PAMS Implementation Manual"; <<http://www.epa.gov/ttn/amtic/pams.html>>

Particulate Matter (PM2.5) Speciation Guidance, Final Draft, Edition 1. October 7, 1999. <<http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/specfinl.pdf>>