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RESEARCH TRIANGLE PARK, NC 27711

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OFFICE OF
AIR QUALITY PLANNING
AND STANDARDS

MEMORANDUM

SUBJECT: Air Toxics Monitoring Concept Paper

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Attached for your information and distribution to your State and local monitoring agencies is the Office of Air Quality Planning and Standards (OAQPS) draft "Air Toxics Monitoring Concept Paper" and the addendum "Funding and Initial Network Development." This paper has been developed in concert with Regional monitoring staff and also reflects preliminary comments from the State and Territorial Air Pollution Program Administrators/Association of Local Air Pollution Control Officials. The paper describes the air toxics program and the role of ambient monitoring. It also lays out a strategic monitoring approach and our suggestions for establishing an air toxics network over the next 2 years. The Office of Air and Radiation has targeted significant resources in FY 1999, and \$3 million of a \$16.7 million FY 2000 increase in State grant funds, to buy air toxics monitoring equipment in order to help establish this network. The OAQPS has worked with State and local agencies and regions to reach agreement on the criteria for allocating the \$3 million for purchasing air toxics monitors.

As you know, the U. S. Environmental Protection Agency (EPA) and its State and local partners are in the process of developing and implementing a national air toxics program designed to characterize, prioritize, and equitably address the impacts of hazardous air pollutants on the public health and the environment. The program is comprised of four key elements:

(1) source and sector based standards; (2) national, regional and community-based initiatives which focus on multimedia and cumulative risks; (3) ongoing education and outreach; and (4) national air toxics assessments.

Assessment or characterization activities are critical to the success of the other elements and the overall program effort. The assessments are intended to help identify areas of concern, characterize risks, and track progress. Assessment activities include: expanded air toxics monitoring, improving and periodically updating emissions inventories, multilevel air quality and exposure modeling, and continued research on effects and assessment tools.

The Agency has established as one of its objectives the ability to better define residual risks and determine the additional controls that may be needed to address toxic pollutant emissions. This is being addressed through the continued development of the National Toxics Inventory and added emphasis on air toxics monitoring. In FY 1999 we increased our efforts to better characterize *urban* air toxic problems. We have recently drafted, after consultation with State and local representatives, an air toxics concept paper which focuses on the role of ambient monitoring in the *overall* air toxics assessment process. The concept paper addresses the design of a national ambient monitoring network including its objectives, strategic approach, scope, covered pollutants, relationship to ongoing activities, monitoring protocol, other design considerations, and future focus. The concept paper includes an initial allocation of the increased air grant resources for air toxics monitoring.

As we finalize the concept paper over the coming months, we look forward to your continued support. We also look forward to working together in the implementation of the national network. You may direct questions about the concept paper to Neil Frank of the Emissions Monitoring and Analysis Division at (919) 541-5560.

As one of our outreach activities in this area, we are planning an Air Toxics Workshop on June 2 and 3 in Research Triangle Park, North Carolina (see attached flyer) which is open to all interested parties. We invite your participation. Questions about the workshop may be directed to Dave Guinnup (guinnup.dave@epa.gov or 919/ 541-5368).

Attachments

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AIR TOXICS MONITORING *CONCEPT PAPER*

Office of Air Quality Planning and Standards

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AIR TOXICS MONITORING *CONCEPT PAPER*

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AIR TOXICS MONITORING *CONCEPT* PAPER

1. The Air Toxics Program and the Role of Ambient Air Monitoring

a. 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 health effects, including cancer, neurological effects, reproductive effects and developmental effects, as well as ecosystem effects. These air toxics are emitted from multiple sources, including major stationary, area, and mobile sources, resulting in population exposure to these air toxics as they occur in the environment. 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 are deposited in water and people are exposed to mercury through their consumption of contaminated 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 risk 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 focus on the cumulative effects of air toxics in urban areas, the multi-media effects of air toxics on water bodies and on populations whose water and food 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.

b. Air Toxics Program

In order to address the concerns posed by air toxics emissions and to meet our strategic goals, we have developed an air toxics program (ATP) designed to characterize, prioritize, and equitably address the impacts of HAPs on the public health and the environment. The ATP seeks to address air toxics problems through a strategic combination of agencies' activities and authorities, including regulatory approaches and voluntary partnerships. We envision four key areas of activities:

- 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.
- National, regional, and community-based initiatives to focus on multi-media and cumulative risks, such as the Integrated Urban Air Toxics Strategy, Great Waters, Mercury initiatives, Persistent Bioaccumulative Toxics (PBT) and Total Maximum Daily Load (TMDL) initiatives, and Clean Air Partnerships.
- National air toxics assessments (NATA) that will help EPA 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, leading 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.
- 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 ATP.

c. National Air Toxics Assessments and the Role of Ambient Monitoring

The success of the ATP 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. All of these activities are aimed at providing the best technical information regarding air toxics emissions, ambient concentrations, and health impacts to support the development of sound policies in the ATP. These activities include:

- the measurement of air toxics emission rates from individual pollution sources;
- the compilation of comprehensive air toxics emission inventories for local, State, and national domains;
- the measurement of ambient concentrations of air toxics at monitoring sites throughout the nation;
- the analysis of patterns and trends in ambient air toxics measurements;
- the estimation of ambient air toxics concentrations from emission inventories using dispersion modeling;
- the estimation of human and environmental exposures to air toxics, and;
- the assessment of risks due to air toxics.

The wide range of NATA activities listed above illustrates the fact that emissions data, ambient concentration measurements, modeled estimates, and health impact information are all

needed to fully assess air toxics impacts and to characterize risk. Specifically, emissions data are needed to quantify the sources of air toxics impacts and aid in the development of control strategies. Ambient data are then needed to understand the behavior of air toxics in the atmosphere after they are emitted. Since ambient measurements cannot practically be made everywhere, modeled estimates are needed to extrapolate our knowledge of air toxics impacts into locations without monitors. Exposure assessments, together with health effects information, are then needed to integrate all of these data into an understanding of the implications of air toxics impacts and to characterize air toxics risks.

This concept paper focuses on the role of ambient measurement data as one key element of the full air toxics assessment process. The rest of this section describes the specific uses of ambient monitoring data and outlines some key considerations for focusing the spatial, temporal, and measurement aspects of a national air toxics monitoring effort.

The anticipated analytical uses of ambient monitoring data should be kept in mind when designing the measurement network. Specifically, we anticipate that ambient air toxics data will be useful to:

- Directly evaluate public exposure & environmental impacts in the vicinity of monitors,
- Help to establish an ambient baseline for toxics risk characterization,
- Track trends in ambient levels to facilitate tracking progress toward emission and risk reduction goals
- Assess the effectiveness of specific emission reduction activities,
- Evaluate and subsequently improve air toxics emission inventories, and
- Evaluate and subsequently improve model performance.

Since for obvious reasons it is not possible to monitor everywhere, we must develop a monitoring network which is representative of air toxics problems on a national scale and which provide 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 will be the key consideration in identifying sites for the national network.

i. Urban Air Toxics Pollutants

There are 33 HAPS identified in the draft Integrated Urban Air Toxics Strategy (UATS)¹. They are a subset of the 188 toxics identified in Section 112 of the CAA which are thought to have the greatest impact on the public and the environment in urban areas. These chemicals can be grouped into several general categories which include volatile organic compounds (VOCs), metals, aldehydes and semi-volatile organic compounds (SVOCs).

¹EPA proposed the draft UATS in the Federal Register on September 14, 1998. A final strategy is scheduled to be signed by the Administrator on June 18, 1999.

Draft 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	hydrazine
carbon tetrachloride	chromium compounds		polycyclic organic matter (POM)
chloroform	lead compounds		polychlorinated biphenyls (PCBs)
1,2 -dibromoethane (ethylene dibromide)	manganese compounds		quinoline
hexachlorobenzene	mercury compounds		
1,3-dichloropropene	nickel compounds		
1,2-dichloropropane (propylene dichloride)			
ethylene dichloride, EDC (1,2-dichlorethane)			
ethylene oxide			
methylene chloride (dichloromethane)			
1,1,2,2,-Tetrachloroethane			
tetrachloroethylene (perchloroethylene, PCE)			
trichloroethylene, TCE			
vinyl chloride			

Given the importance of these urban pollutants and the impracticality of monitoring for all 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.

ii. Locations of Interest for HAPs

Information on air toxics is needed for both urban and rural areas. Urban-oriented information is needed to address the range of population exposures across and within urban areas, while rural data are needed for characterization of exposures of non-urban populations, to establish background concentrations and to better assess environmental impacts. Among urban environments, it is important to focus on both large metropolitan areas and the smaller cities where there may be significant numbers of air toxics sources, because both types of communities can experience high levels of exposure and risk. Further, characterization of exposures within communities representing various socio-economic groups is also an important part of our national assessments.

iii. Temporal Considerations

A monitoring network for air toxics should primarily emphasize long-term measures of air quality. The major part of the effort to develop air quality and emissions data, therefore, should focus on year-round information. To provide maximum flexibility in data use, however, the data collection should be based on (1) continuous sampling wherever possible, (2) intermittent (e.g., every sixth day) collection of 24-hour samples throughout the year for remaining HAPs, and (3) samples of longer than 24 hours only where analytically necessary. Individual 24-hour data will be stored in EPA and State/local agency databases, but will usually be compiled into statistical summaries to reflect peak concentrations, as well as seasonal, quarterly, annual, or multi-year averages.

A complete monitoring program also should include a temporary capability to measure short-term air quality indicators (e.g., hourly ambient concentrations) for certain HAPs that may present acute threats at specific locations and times. Times, locations, and analytes for this type of short-term monitoring may be selected by criteria such as model predictions, citizen requests, etc. The capability may be provided by mobile monitors or by temporary stationary sample sites.

2. Current Federal and State Air Toxics Monitoring Activities

Some air toxics data are currently available on a national level. The Photochemical Assessment Monitoring Stations (PAMS) program has been collecting air toxics data for 8 volatile organic compound (VOC) HAPs since 1993 in more than 20 major urban areas. These data are stored in EPA's Aerometric Information Retrieval System (AIRS) database, along with all criteria pollutant monitoring data. In the near future, PM_{2.5} speciation monitors will provide measurements of 10 HAP metals at over 50 locations in the country.

Several States have long standing air toxics monitoring programs. These include California, Texas and New Jersey. To support other states with the collection 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. This annual UATMP supports the collection and analysis of VOCs, aldehydes and other HAPs. 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 the AIRS database. To participate in the program, States commit their own funds to the OAQPS contract and receive a year's worth of monitoring support from the contractor.

There are at least 28 States which are currently involved in ambient monitoring for some of the urban HAPs. A summary of the number of States who have monitored a specific HAP in 1997 and reported the data to EPA (either through AIRS or as a result of EPA's Air Toxics Archive effort) is shown in the table on the following page.

Ambient Measurements of Urban Air Toxics HAPs (States in 1997)*

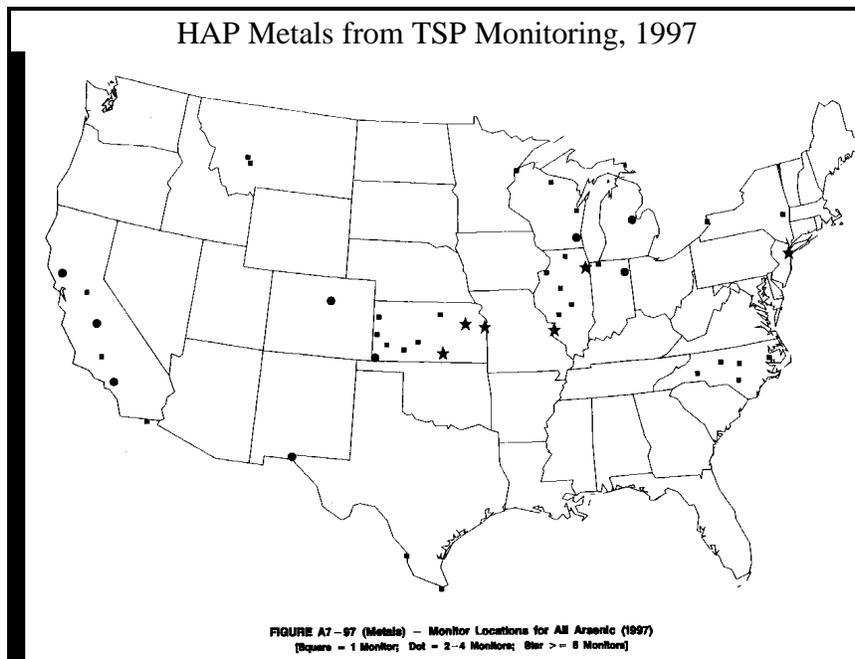
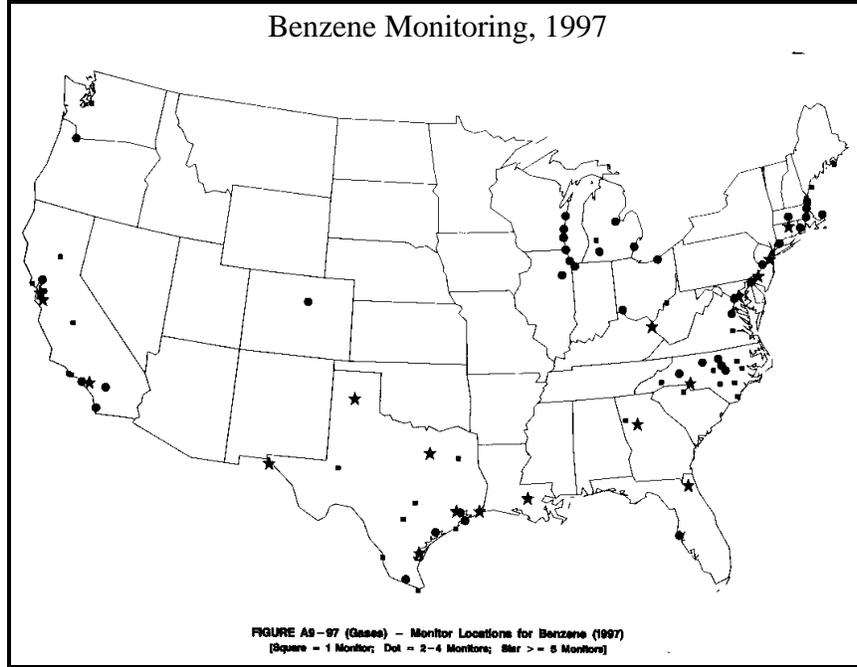
VOCs	#States	Metals**	#States	Aldehydes	#States	SVOCs and other HAPs	#States
1,3-butadiene	8	arsenic	11	acetaldehyde	16	2,3,7,8-tetrachlorodibenzo-p-dioxin (& congeners & TCDF congeners)	0
1,3-dichloropropene	0	beryllium	5	formaldehyde	16	coke oven emissions	0
ethylene dibromide (1,2-dibromoethane)	9	cadmium	11	acrolein	8	hydrazine	0
acrylonitrile	0	chromium	10			polycyclic organic matter (POM) 112(k)	4
benzene	28	Chromium VI	1			Polychlorinated biphenyls (PCBs)	0
Hexachlorobenzene	1	lead	33			quinoline	0
1,1,2,2,-Tetrachloroethane	8	manganese	7				
chloroform (trichloromethane)	11	mercury	2				
carbon tetrachloride (tetrachloromethane)	8	nickel	9				
ethylene dichloride, EDC (1,2-Dichloroethane)	10						
ethylene oxide	0						
methylene chloride (dichloromethane)	14						
propylene dichloride (1,2-dichloropropane)	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 PM₁₀ or fine particles.

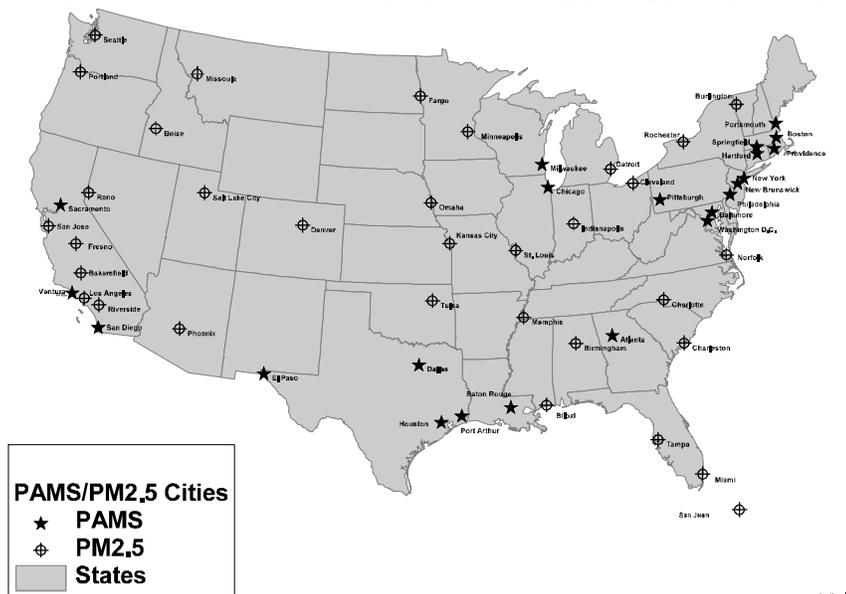
Note: More States reported some specific HAPs in 1996 at the time of this survey.

As examples of the extent of current monitoring coverage for urban HAPs, two maps are presented. First is a map of the 1997 monitoring sites measuring and reporting benzene (the most commonly measured HAP) and next is one for arsenic to show the lesser extent of current coverage for the HAP metals.



The map below shows the locations of all PAMS areas which currently provide some VOC and aldehyde HAPs and the locations of all proposed PM_{2.5} 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_{2.5} Platforms



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

a. Air Toxics Monitoring Objectives

The monitoring network should be designed to address all of the needs of the air toxics program. The network shall be designed to satisfy the following objectives:

i. 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 that EPA has identified as having the most significant potential health impacts. The list of HAPs in the UATS is a logical starting point.

ii. Use scientifically sound monitoring protocols to ensure nationally consistent data of high quality.

Appropriate sampling and analytical methods should be followed. The methods must consider the threshold concentrations at which effects have been documented 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.

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

A general guideline to estimate annual average concentrations at each monitoring site is to collect a minimum of one 24-hour sample every six days. Following the national particulate matter sampling schedule, one in six day sampling will result in as many as 61 samples per year . This is the same uniform sampling frequency for VOCs collected at PAMS sites and twice the typical UATMP sampling frequency of once every 12 days for measurement of air toxics. It should be recognized for a particular pollutant, however, that sufficient data depends on the estimated precision and accuracy of the monitoring method. If the precision and accuracy are within XX %, this will permit estimation of annual averages within +/- 10 percent and allow trends to be detectable within 5 years with a probability of YY%. A more complete description of data quality objectives (DQOs) is currently under development by EPA.

iv. Complement existing national and State/local monitoring programs.

By integrating a new toxics network with existing programs, large scale efficiencies of resources can occur. For this reason, the program should maximize use of existing platforms where appropriate and take advantage of mobile monitoring and saturation monitoring resources, where appropriate.

v. Reflect “community-oriented” (i.e. neighborhood-scale) population exposure.

Fixed-site (stationary) monitors 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 more reflective of typical population exposure, can be used to estimate long-term population risk and should be the primary component of the new monitoring network. A separate toxics monitoring effort may focus on smaller scale (i.e middle or micro-scale) monitoring sites. For all scales of measurement, the monitors should represent typical population exposure as well as exposure in communities nearby air toxics emission sources that may be disproportionately impacted.

vi. 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 meteorological conditions. Such a network would support population risk characterization, 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:

- (1) include cities with high population risk (both major metropolitan areas and other cities with potentially high anticipated concentrations),
- (2) distinguish differences within and between geographic regions (to describe characteristics of areas affected by high concentrations vs. low concentrations), and
- (3) reflect variability among pollutant patterns across communities.

b. Strategic Air Toxics Monitoring Approach

i. Community-oriented focus.

The initial focus of the network should be on community-oriented locations. This population-oriented approach will be analogous to the core network for PM_{2.5} and the basis for the National Air Monitoring Station (NAMS) trend network for the criteria pollutants. Initially, the network should place a minimum of 2 sites in a variety of metropolitan areas. With 2 sites, one site should reflect maximum population-oriented concentration for at least a subset of the target HAPS. This site could be in urban/industrial areas where populations live near major sources. The second site should be reflective of “typical” high concentrations in areas with high population density. Accordingly, this will reflect relatively high exposure and population risk. These “typical” sites should be several miles away from major point sources and may represent the average-case scenario. Both types of sites can be used for emission tracking, emission inventory corroboration and model validation. When an area only has one site, it should be more representative of average exposure.

ii. Incorporate long-term and short-term monitoring elements.

The network should emphasize fixed station long-term monitoring, but also contain short-term monitoring elements. This will enable the network to assess the multiple objectives of the 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) 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.

The initial network can focus on long-term monitoring sites. The mature network could have approximately 100 trend sites (in at least 50 areas) among a total of 200 to 300 air toxics monitoring sites.

iii. Make use of existing State/local platforms for first 2 years of monitoring.

To initiate the national air toxics monitoring program, the new air toxics monitoring sites established during FY-99 and FY-00 should build upon existing State/local air toxics monitoring sites, PAMS sites or planned PM chemical speciation sites. In general, PAMS sites will be appropriate platforms for air toxics monitoring because they reside in most of the largest metropolitan areas and the "site type 2" is sited in the area of maximum ozone precursor concentrations (which already include measurement of 8 HAP VOCs and usually 2 aldehydes). The type-2 PAMS sites are on the downwind edge of an urban area, and are reflective of a neighborhood monitoring scale. There are approximately 25 PAMS monitoring areas, most of which have two type-2 sites.

PM_{2.5} speciation trend sites which will be established in 1999 and 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 PM₁₀ and TSP samplers. The latter will provide opportunity for additional analyses for lead and other HAPs associated with larger particles. The mature PM_{2.5} network will have approximately 54 special trend sites. There are also expected to be up to 250 additional PM_{2.5} speciation sites which will provide HAP metals and should be considered for broader air toxics monitoring. Another excellent choice for air toxics monitoring platforms will be sites in the PM_{2.5} 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.

The development of the national monitoring network should allow for flexibility in the selection of monitoring locations and cities that satisfy the stated monitoring objectives. If existing platforms are not suitable for characterization of population exposure to air toxics, new community-oriented monitoring stations should be established. For example, some type 2 PAMS sites may not be the best locations for measuring air toxics, because of the relative mix and spatial distribution of point 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 maximum annual average concentrations or year-round exposure. Nevertheless, general siting criteria for PAMS site-type 2 and PM_{2.5} core monitoring stations can be followed when establishing the desired neighborhood-scale air toxics monitoring sites. These guidelines provide specifications on set back distances, inlet heights and other siting considerations.

iv. Allow for short-term or special air toxics monitoring activities.

The national air toxics monitoring program should include monitoring to support short-term, area-specific studies. Such monitoring 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 acute threats at specific locations and times. The collection of on-site meteorological data would be useful to assist with these assessments.

Examples of short-term monitoring is characterization of “hot spot” communities potentially impacted by specific sources or specialized long-term monitoring to meet State needs.

v. Utilize standard monitoring methods.

Standardized monitoring methods should be used. Currently, there are standard methods that cover 29 of the 33 UATS HAPs. The 4 HAPs not covered are either not generally considered to be practical or do not have demonstrated or applicable methods available and require additional methods development. The demonstrated or applicable methods are:

1. Toxic Compendium Method TO-15, “Determination of Volatile Organic Compounds in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry”. This method provides for collection of 51 volatile organic compound (VOC) HAPs, including all 16 of VOCs on the 33 UATS HAPs list. See attachment 1.
2. Chemical speciation of filter-based mass collected at particulate matter sites will provide data on 58 elements, which includes 11 HAP metals and all 8 UATS metals. See Attachment 2. Particle sampling can include PM_{2.5} 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. For PM_{2.5}, X-ray Fluorescence (XRF) is the suggested analytical technique chosen for the PM_{2.5} chemical speciation program. (However, XRF cannot detect one HAP metal: beryllium). For TSP, it can be XRF or ICP/MS. This is consistent with the intended analytical approaches and services available through EPA contracts. Some valence specific metals, like chromium VI (also known as hexavalent chromium) have been identified as having high toxicity and would require separate chemical analysis. These chemicals would be collected with the same particulate matter samplers but would be analyzed with more specific analytical techniques.
3. 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 4 aldehyde HAPs, including all 3 of the UATS aldehyde compounds. It is noted that aldehydes are also known as carbonyls.
4. The HAP category of polycyclic organic matter (POM) is being represented by 18 polynuclear aromatic hydrocarbons (PAHs). 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; therefore, this method covers 1 urban HAP. See Attachment 4.
5. 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 the HAPs category polychlorinated biphenyls (PCBs); therefore, this method covers 1 HAP. See Attachment 4.

vi. Incorporate measurements for other HAPs when possible (Push research and development efforts to permit new and better analyses).

The network should allow for measurements of additional HAPs. For example, there are 4 urban HAPs which are not generally considered practicable (because of high analytical cost) or have no demonstrated sampling and analytical methods associated with them. These are dioxin (i.e. 2,3,7,8-tetrachlorodibenzo-p-dioxin & congeners & TCDF congeners), which has high associated sampling and analytical costs; and hydrazine, quinoline, and coke oven emissions which have no demonstrated or applicable methods. Research is needed to develop new or more cost-effective monitoring methods to permit the measurement for more HAPs. This becomes an important adjunct activity to the overall ambient air toxics monitoring strategy.

vii. Provide resources for data analysis.

Adequate resources must be allocated for data analysis, implementation of statistical quality assurance procedures, data management and data reporting. This will enhance data quality and ensure an effective air toxics monitoring system. Data analysis protocols should be developed to define the process by which conclusions may be developed from the ambient air toxics data. These may include risk assessments, source attribution, trends analysis, etc. The development of data analysis protocols should be tied to the DQOs mentioned earlier.

viii. Review network periodically.

The national network should be modified as needed. Annual or biannual reviews of the network should be designed to eliminate redundancy of measurement within and across cities, to modify sampling frequency and to adjust measurement protocols to ensure that data quality objectives are achieved. The target list of pollutants should be modified to make cost-effective use of available resources while still satisfying the goals of the air toxics program. In some cases, an analysis of subsets of the list of urban air toxics may be more appropriate. In particular, if a particular analyte requires its own discrete monitoring method and it is not detectable, then it can be eliminated from routine sampling and analysis. This does not 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. However, the analysis of these compounds (once initiated and not detected) should be periodically revisited to ensure that new emission sources (or better monitoring technologies) have not developed. It is suggested that this occur once every 3-5 years. The network planning process should also make use of surrogate measures whenever appropriate (e.g. nickel or zinc as a predictor for mercury) to help identify areas where more specific monitoring is needed.

4. Initial Network Development

Based on preliminary discussions, the following sections address the activities and protocols anticipated in FY-99 and FY-00 for air toxics monitoring.

a. FY-99 and FY-00 activities

The initial focus should be on population-oriented urban sites. The development of a national network should first focus on enhancement of the additional PAMS areas and enhancement of new PM_{2.5} chemical special sites (a total of 54 urban PM_{2.5} monitoring areas have been proposed.) The PAMS and PM_{2.5} are both community-oriented urban trend sites. An additional focus should be on establishing ambient air toxics monitoring platforms in smaller cities with high toxicity weighted HAP emissions. When appropriate, existing State or local air toxics monitoring sites maybe be utilized instead of the PAMS or PM_{2.5} sites. In either scenario, the platforms should be upgraded to enable the suite of urban HAP analyses described elsewhere in this paper. This approach will make efficient use of existing air toxics-related monitoring activities. The activities during the first 2 years should also reflect appropriate quality assurance, data management, data analysis and data submission to AIRS.

b. Initial Monitoring Protocols.

The first 2 years should utilize established monitoring protocols. This will include analysis for VOCs (using TO-15) from year- round 24-hr canister samples collected once every six days. The TO-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 1). The TO-15 compounds were selected as the first priority because the analysis method has been proven, is cost-effective, and provides about half (16) of urban air toxics of interest.

Additional 24-hr samples and analyses would include HAP metals (using XRF analysis on PM_{2.5} filter media), POMs using the TO13 method and aldehydes (including formaldehyde) using TO11A. Many of the PM_{2.5} platforms will also include measurements for PM₁₀ and/or TSP, so analyses of coarse particle urban HAP metals is also possible. PM_{2.5} sampling is planned for a 1 in 3 day schedule; for other pollutants (including TSP), sampling can occur once in six days.

A new continuous formaldehyde analyzer is currently undergoing field evaluation and will be ready for limited deployment during FY-2000.

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 analyzers should also be included at selected sites in FY-00 for comparison to XRF measurements for particulate mercury and mercury surrogates (particulate zinc and nickel). However, because of limited resources, these mercury analyzers are not intended for the entire initial network. Dioxin measurements are even more expensive and should be considered by the States on a case-by-case basis for selected sites.

c. Proposed Network

Selection of new monitoring locations in the national air toxics monitoring network should be primarily based on potential for population at risk from air toxics and to represent a variety of exposure situations. Therefore a criteria based on total area population, industrial/commercial activity and geographic distribution in the U.S. have been utilized to prepare a candidate list of metropolitan and other locations. This is presented elsewhere. In selection of metropolitan areas, strong consideration was given to areas which are already part of the PAMS network or are proposed for PM_{2.5} Speciation Trends sites. These criteria provide for monitoring in major population centers, achieving a mix of cities with varying industrial base, efficiencies achieved in building upon existing monitoring infrastructure, and providing for a geographic distribution within the U.S. Each candidate monitoring area will have two separate monitoring locations to help establish within city differences.

d. Future Network Focus

After the year 2000, the air toxics monitoring network should continue to grow. An expanded air toxics monitoring network should cover more urban areas (both major cities and smaller areas with high emissions) and have monitors in rural areas (away from primary sources) to permit estimates of background concentrations. Other fixed site monitors should be place in urban hot spots and environment justice areas that may be subjected to localized high concentrations of air toxics. In some cases, temporary or mobile monitors may be utilized in these areas of concern. As new priority air toxics are identified, the network should address other pollutants of concern in the air toxics program.

The long-term goal for a national network should also include monitoring of sensitive ecosystems and other environmental concerns. To meet this end, the national network should incorporate the separately funded deposition monitoring activities associated with the Great Waters Program.

Results from the NATA use of 1996 emission inventories to develop ASPEN model predictions nationwide will provide significant information which can assist in the identification of additional areas and sites which might benefit from additional ambient air toxics monitoring. For now, we project the tentative size of the national network to be 200 sites. This number will be revised iteratively as additional information becomes available and as the air toxics monitoring network expands.

ATTACHMENTS

ATTACHMENT 1

METHOD TO-15 (VOCS)*

No.	CONTAMINANT	CAS#	UATS**
1	1,2- Dibromoethane	106934	X
2	1,2- Dichloroethane (EDC)	107062	X
3	1,3-Butadiene	106990	X
4	1,1-Dichloroethane	75343	
5	1,1,2,2-Tetrachloroethane	79345	X
6	1,2,4-Trichlorobenzene	120821	
7	1,1,2-Trichloroethane	79005	
8	1,2-Dichloropropane (propylene dichloride)	78875	X
9	1,3-Dichloropropene	542756	X
10	1,1,1-Trichloroethane	71556	
11	1,1-Dichloroethylene	75354	
12	1,4-Dichlorobenzene	106467	
13	2,2,4-Trimethylpentane	540841	
14	2-Chloro-1,3-butadiene (chloroprene)	126998	
15	Acetonitrile	75058	
16	Acrylonitrile	107131	X
17	Allyl chloride	1070501	
18	Benzene	71432	X
19	Benzyl chloride+	100447	
20	Bromoform (tribromomethane)	75252	
21	Bromomethane (methyl bromide)	74839	
22	Carbon Tetrachloride	56235	X
23	Chlorobenzene	108907	
24	Chloroethane (ethyl chloride)	75003	
25	Chloroform	67663	X
26	Chloromethane (methyl chloride)	74873	X
27	Cumene	98828	
28	Ethyl acrylate	140885	
29	Ethylbenzene	100414	
30	Ethylene Oxide ***	75218	X
31	Hexachlorobenzene	118741	X

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

- * To be initiated in FY99
- ** UATS = Urban Air Toxics Strategy compound
- *** Method TO-15 is documented as an applicable method for ethylene oxide
- + May have stability issues over time in cylinders or canisters

ATTACHMENT 2

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

CONTAMINANT	CAS# *	UATS**
Antimony	7440360	
Arsenic compounds	7440382	X
Beryllium and compounds	7440417	X
Cadmium compounds	7440439	X
Chromium compounds	7440473	X
Cobalt	7440484	
Lead compounds	7439921	X
Manganese compounds	7439965	X
Mercury compounds	7439976	X
Nickel compounds	7440020	X
Selenium	7782492	

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

** UATS = Urban Air Toxics Strategy compound (Beryllium cannot be detected by XRF)

ATTACHMENT 3

METHOD TO-11A (CARBONYL COMPOUNDS)**

No.	CONTAMINANT	CAS#	UATS**
1	Acetaldehyde	75070	X
2	Formaldehyde	50000	X
3	Acrolein	107028	X
4	Propionaldehyde	123386	

** UATS = Urban Air Toxics Strategy compound. These four carbonyl compounds are also known as aldehydes.

ATTACHMENT 4

SEMI-VOLATILE ORGANIC COMPOUNDS AND OTHER UATS HAPS

CONTAMINANT	CAS#	UATS**
Polycyclic organic matter (POM)*	NA	X
Polychlorinated biphenyls (PCBs)**	NA	X
Dioxin [2,3,7,8-tetrachlorodibenzo-p-dioxin (& congeners & TCDF congeners)]	1746016	X
Hydrazine	302012	X
Coke oven emissions	NA	X
Quinoline	91225	X

* Method TO-13A; POM represented by 18 PAHs which include:

- Naphthalene
- Acenaphthylene
- Acenaphthene
- Fluorene
- Phenanthrene
- Anthracene
- Fluoranthene
- Pyrene
- Benz(a)anthracene
- Chrysene
- Benzo(b)fluorathene
- Benzo(k)fluoranthene
- Benzo(a)pyrene
- Indeno(1,2,3-cd)pyrene
- Dibenz(a,h)anthracene
- Benzo(g,h,i)perylene
- Perylene
- Coronene

** Method TO-4A

ATTACHMENT 5

REFERENCE LIST

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" <<http://www.epa.gov/ttn/amtic/pmspec.html>>