Monitoring Methods for TOXICS in the ATMOSPHERE

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Foreword

This publication, *Monitoring Methods for Toxics in the Atmosphere*, contains papers presented at the Conference on Recent Developments in Monitoring Methods for Toxics in the Atmosphere, which was held on 27–31 July 1987 in Boulder, Colorado. ASTM Committee D-22 on Sampling and Analysis of Atmospheres sponsored the event. Walter L. Zielinski, Jr., National Institute of Standards and Technology, presided as chairman of the conference and also served as editor of this publication. William D. Dorko, National Institute of Standards and Technology, served as coeditor of this publication.

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Introduction

On 27–31 July 1987, a technical conference devoted to monitoring methods for toxics in the atmosphere was held at the University of Colorado in Boulder, Colorado. The conference was sponsored by ASTM Committee D-22 on Sampling and Analysis of Atmospheres.

Numerous types of toxic air pollutants are known to be emitted to the atmosphere. Regulatory standards, instrumentation, and methods have been developed for use in monitoring programs to identify sources of emissions of hazardous air pollutants which pose a risk to health and the environment. Air pollutants of principal concern have typically included air particulate matter and a variety of gaseous pollutants, such as nitrogen and sulfur oxides, ozone, carbon monoxide, and hydrocarbons from both mobile (e.g., motor vehicles) and stationary (e.g., industrial stacks) sources.

More recently, additional pollutants of concern have been identified which pose equal or possibly greater risks to health and the environment. Extensive studies have been under way which involve the development and evaluation of appropriate methodology for ensuring accurate measurements of these pollutants. It is because of these new areas of environmental and public health concern that this conference was developed.

This volume, which is based on that conference, begins with organizational overviews of the status of national and state monitoring programs for toxics in the atmosphere and then proceeds to technical presentations focusing on some of the more important new areas of airborne toxics: namely, volatile organic compounds, acid gases, heavy metals in air particulates, and personal exposures to various toxic air pollutants. Topics such as acid deposition, municipal solid waste and hazardous waste incineration activities, and the growing concerns about toxic volatile organic compounds and indoor air pollutants are included. The technical papers in this volume concentrate on developments and challenges in the areas of instrumentation, monitoring data, sampling, and accurate and stable calibration standards needed to provide data quality assurance in monitoring. Attempts are made to discuss existing capabilities and deficits, and requirements for further needed research to aid the monitoring efforts of industry and federal and state agencies.

The conference on which this publication is based was unique in its design and comprehensive to the extent of the time available. The editors sincerely hope that the material presented herein will be found useful in current research efforts aimed at the improvement of monitoring methods for air toxics and the overall goal of assuring environmental quality for the long term.

This volume is dedicated not only to the conference participants, but also to all investigators who intellectually strive for and doggedly pursue the quantitative assessment of air quality and the improvement thereof.

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Institutional Monitoring Programs

Mark Komp,[1] *Larry Svoboda,*[2] *and Steven Frey*[3]

Air Toxics Monitoring Plan for the Denver Metropolitan Area—Integrated Environmental Management Project

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ABSTRACT: The air toxics monitoring plan for the metropolitan Denver Integrated Environmental Management Project (IEMP) sponsored by the U.S. Environmental Protection Agency (EPA) describes the monitoring program to be used during the project to collect data on ambient levels of toxic compounds in the air. The plan describes the objectives, monitoring approach, and sampling methods and analyses of the program. Aspects of the analyses described in the plan include the determination of the exposure of the population to the toxic concentrations found during the monitoring program and the apportionment of these toxic compounds to sources in the metropolitan area. The data to be collected will be of value not only in Denver, where a comprehensive air toxic database will be completed, but to the ongoing national effort by EPA to assess the magnitude of the air toxics problem in urban areas.

KEY WORDS: toxics, air toxics, samplers, volatiles, semivolatiles, particulates, exposure assessment

The Denver Integrated Environmental Management Project (IEMP) is an effort to evaluate the human health risks from exposure to ambient pollutant levels in the Denver metropolitan area. The project will investigate the health risk from several environmental sources (e.g., groundwater, radon, and air toxics pollutants). This monitoring plan has been designed to collect data on air toxics pollutants concentrations in Denver for use in determining health risks.

There is very little existing information on current levels of toxic air pollutants in the Denver area. While many previous studies have investigated the composition of air pollution in the Denver area, few efforts have examined the toxic compounds associated with mobile source, wood burning, and power plant emissions. Therefore, to properly evaluate the human health risks associated with toxic compounds in Denver air, it is necessary for the Denver IEMP to estimate annual human exposure through a field monitoring program.

The purpose of the IEMP monitoring program is to quantify concentrations of air toxic compounds at four representative sites in Denver. This information will be used to perform

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a screening level exposure assessment of health risks from a specific number of toxic air pollutants. This analysis will contribute to the overall comparative IEMP assessment of environmental risks in the Denver area. The result will be of value not only to the Denver IEMP and the study of air toxics in Denver, but to the ongoing national effort by EPA to assess the magnitude of the air toxics problem in urban areas.

The Denver IEMP air toxics monitoring effort complements an ongoing study of toxic pollutants in metro Denver's air that is being conducted by EPA Region VIII and the Colorado Department of Health. This study, called the Denver Air Toxics Study (DATS), will develop high-altitude emission factors for key sources (gasoline vehicles, diesel vehicles, wood stoves, and fireplaces) and develop control strategies for toxic air pollutants from these sources. The emission factors will be used in applying a seasonal average dispersion model to project the level and distribution of air toxics across the Denver metro area. The model will be evaluated for its ambient toxic predictive capability using the IEMP ambient data. Air toxic reductions will then be evaluated with the model to project the effectiveness of the control strategies.

The purpose of this paper is to present the objectives of the IEMP monitoring effort and to describe the basic design of the monitoring program to meet those objectives.

Objectives

The air toxics sampling program was designed to meet the requirements for health-related analyses for the Denver IEMP and will have four specific primary objectives.

1. The program will collect ambient data for compounds that will be selected based on a combination of the following factors:

(*a*) Compounds that are known or suspected of being present in the ambient atmosphere in Denver based on previous ambient data collection efforts or knowledge of existing emission sources.

(*b*) Sampling methods and analysis techniques capable of detecting and quantifying the pollutant at anticipated ambient levels.

(*c*) Toxicological or other health-related data available for various health-related analyses. Compounds of interest for the health-related analyses will be based on the following criteria.

- Agency-accepted data for such compounds that either exist or are expected to be available by March 1988 for determining cancer risks.
- Agency-accepted reference doses (RFDs) for such compounds that either exist or are expected to exist by March 1988 for determining noncarcinogenic health effects from exposure levels.
- Compounds for which limited health information (beyond what has been outlined in points 1 and 2 above) exists and which are present at observable concentrations in Denver's air and are suspected of being a potential problem.

2. The program will collect ambient data on these selected pollutants from representative sites and during representative time periods in order to provide spatially and temporally valid estimates of annual exposures experienced by the general population.

3. The program will collect limited data from high-episode periods in order to approximate acute exposures and compare them to annual average exposures.

4. The program will gather ambient data that can be used to identify sources of air toxics for selected pollutant categories, primarily for organic particulates, and estimate the approximate ambient contribution from each source category.

5. Data collected by the program will be subject to a rigorous quality assurance program and will consider data uncertainties, accuracies, and quality controls.

Goals

In addition to examining carcinogenic risk from individual compounds, the cumulative risks from air toxics will be estimated. For carcinogens with no derived unit risk factors, a qualitative evaluation of cancer "risk" will be made using accepted agency procedures and guidelines for making such determinations.

The air toxics monitoring program will also identify some compounds present in Denver's air which are lacking the health information necessary for estimation of risk. The need for further research on these compounds and for development of quantitative risk assessment methods will be emphasized.

A detailed explanation of the risk assessment methodology to be used in the IEMP analysis will be prepared by IEMP staff after collection of the data. This will include a discussion of available options for quantification of risk estimates based on the type and quantity of data collected.

Monitoring Approach

In developing the plan, the key pollutants of interest were identified and priorities were assigned based on past studies by Lewis et al. [*1*], local air pollution sources, and potential known health risks. Methods to monitor and analyze for these pollutants were assessed, taking into account agency guideline methods or the accurate sampling and analysis methods available. Some of the methods proposed for use in this study involve instruments which are considered to be in the developmental stages. The program has been designed with the assistance of the Office of Research and Development (ORD) within EPA to utilize the best expertise on these developing technologies, methods, and procedures.

The monitoring design considered various sampling frequencies and monitoring periods that influenced the scope and cost of the program. Alternative sampling frequencies were evaluated which would maintain statistically significant results and represent a cost-effective program. Seasonal variation of criteria pollutants in the Denver area was also analyzed to determine the viability of seasonal monitoring to cover Denver's worst air pollution seasons while still allowing for reasonable estimates of annual exposures.

Finally, the staff identified appropriate sites for monitoring based on visual inspection of current sites and an analysis of the spatial and temporal variability of criteria pollutant data from these sites. This process determined the suitability of selected monitoring stations to provide representative values indicative of the expected area-wide nature of air toxic emissions in Denver.

All of this information was assembled to systemically develop a monitoring program that considered these concerns within the constraints of a budget of $400 000. Presented in the following sections are the rationale and basis for the selected approach.

Design Rationale

To support the health assessments that will be conducted under the IEMP, ambient concentration data on toxic air pollutants with known health effects are needed which can be used to estimate annual averages. In addition, ambient data that represent short-term exposures are desirable since they may be used to estimate acute exposures and potential acute effects.

Although modeling could have been used to estimate approximate concentrations, a monitoring approach was selected based on the lack of emissions data for toxic pollutants and the interest in secondary pollutants, especially formaldehydes.

The key elements of the approach to the air toxics monitoring are the sampling equipment at each site, sampling period and frequency, number of samples per season, and the number of samples to be analyzed. Each element was defined based on a series of analyses which support the following technical objectives without exceeding the program budget. Specifically, this program was designed to include the following features:

1. Collect ambient concentration data on toxic air pollutants that are likely to be present in metro Denver using the best available sampling and analysis techniques.
2. Maintain a minimum of three and a maximum of four sampling sites for adequate geographical representation based on previous work of an EPA consultant.
3. Produce ambient measurements that are spatially and temporally representative of annual and acute exposures experienced by the general population.
4. Collect at least 40 separate day and night samples at one selected site per season so that it will be possible to use a linear regression to apportion the pollutants to the principal sources. The priority for the pollutant apportionment will be dictated by the cost of analysis and the technical feasibility of differentiating the source.

Pollutant Coverage

Pollutant coverage for ambient air toxics monitoring includes four pollutant classes:

1. volatile and semivolatile organics,
2. aldehydes/ketones,
3. organic and inorganic inhalible particulates, and
4. acidic gas and particulate deposition.

In determining the list of compounds to analyze, a comprehensive list of compounds was reviewed and selections made on the basis of four factors.

The factors considered in selecting pollutant classes and compounds include:

1. Is the pollutant known or suspected of being present in the ambient atmosphere in Denver based on previous ambient data or knowledge of existing emissions sources?
2. Are existing monitoring techniques and analytical methods capable of detecting and quantifying the pollutant at likely ambient levels?
3. Can health-related analyses be performed based on available toxicological information?
4. Are the pollutants necessary for the identification of the source in linear regression modeling analysis.

Together, the pollutant classes selected for coverage include emissions from mobile sources and residential wood burning, which are likely to be key contributors to air toxics in Denver. These sources, along with power plants, are major contributors to visibility problems and violations of criteria pollutant standards in the metro area.

With respect to the specific compounds for which quantitative data will be generated, Appendix presents a preliminary list of specific compounds within each pollutant class for which data are desired with some additional justification for compound selection. Appendix also includes preliminary information on sources, whether validated sampling and analysis techniques exist, and the existence of quantitative health scores for the chemical. The only pollutant of concern that has not been included in the sampling program is peroxyacetyl nitrate (PAN). We do not believe that sampling techniques have sufficiently demonstrated the ability to obtain reliable data for PAN.

Although the most useful data for the IEMP are ambient concentrations for compounds for which health-related data are available, the capabilities of the available sampling and analytical techniques will permit collection of concentration data for additional pollutants for which there is little or no health-effects data. The concentration data for these pollutants will be collected for future reference. Similarly, lack of appropriate analytical methods may preclude collecting data for specific compounds of interest. The specific details of the analytical procedures are defined in the quality assurance project plan (QAPP) prepared by PEI Associates, Inc. [2].

Sampling Equipment and Laboratory Analysis

A strong effort was made to select sampling equipment and general analytical methods that represent the state-of-the-art techniques or are part of EPA's recommended guidelines for sampling. For particulates and semivolatiles, a PUF sampler (polyurethane foam) is preferred over XAD-2 for cost and operational considerations when biological testing is not being conducted. With respect to aldehydes, dinitrophenylhydrazine (DNPH) cartridges with high-performance liquid chromatography (HPLC) analysis were selected for operational conditions. For volatiles, Summa canisters with analysis by gas chromatography/electron capture detection (GC/ECD) and gas chromatography/mass spectrometry (GC/MS) were selected as the most practical and cost effective methods currently available.

Using the validated analytical methods, at least 83 specific organic pollutants can be covered. Specifically, these will include a minimum of 41 volatile organics, 18 particulate and semivolatile compounds, and a minimum of 10 aldehydes/ketones. For the source receptor modeling, it will be necessary to conduct an elemental analysis with X-ray fluorescence (XRF), sulfate and nitrate analysis with ion chromatography, and an analysis of the elemental carbon and volatile carbon using a high-temperature volatilization and combustion technique. The source receptor modeling needs will be met by obtaining separate day and night samples of the PM-2.5 particulate fraction on a teflon filter for the XRF, a quartz filter will be used for the carbon analysis, and an annular denuder followed by teflon and nylon filters will be used for the sulfate and nitrate analysis. The monitoring methods selected are presented in Table 1.

Sampler Location and Frequency

Location

To support exposure assessments, ambient concentrations measured at the selected monitoring sites should be representative of a relatively broad area. Consequently, appropriate sites should be located where air is well mixed and unaffected by specific local sources of emissions.

A series of analyses were conducted to identify the number and location of sites needed to create a geographically representative ambient air toxics monitoring network. The results showed that three sites, with a fourth site for comparison, would reasonably represent the region. An evaluation of monitoring sites for this study gave preference to the existing State Air Quality Monitoring Network in order to minimize site preparation costs and to take advantage of historical data.

The number and location of monitoring sites were selected on the basis of the following considerations:

1. A series of statistical analyses of criteria pollutant data from 1982 through 1985 was performed by Versar [3] to determine the representativeness of the existing network for

TABLE 1—*Goal of sample collection strategy.*

SAMPLER	DETECTION POLLUTANT	LEVEL	ANALYSIS METHOD
Stainless Steel Canister	Low molecular weight Halocarbons, Benzene, Tolune, Xylenes, (others)	ppt to ppm	GC/EC/ FID/MS
DPNH	Formaldehyde other Aldehydes	ppt to ppm	HPLC
Puf /High Samplers Volume	Light, volatile aromatics and polynuclears, pesticides high molecular weight hydrocarbons extractable organics.	ppt to ppm and ug/m^3	GC/MS
Annular denuder	HNO_3, HCL, SO_2, SO_4, acidic particulates	ppt to ppm	Ion chro tograph
PM-2.5 Sampler	Mass of fine particles, elemental composition, carbon (elemental and volatile)	ug/m^3	XRF & Combustion for carbon

criteria pollutants. The results of statistical analyses of the means and standard deviations for data on carbon monoxide (CO) and total suspended particulates (TSP) from 1982 through 1985 show that monitoring sites can be clustered into three relatively independent groups representing ambient concentrations for three geographic areas. This distinction can be attributed to differences in topographical and meteorological characteristics of the three areas, as well as to differences in the distribution of sources. Consequently, inclusion of one monitoring site per area is considered to be a reasonable approach for screening exposures to regional air pollution in the metro Denver area.

2. The determination was made to assume that the meteorological and topographical conditions which affect regional mixing for the criteria pollutants would also apply to toxic pollutants.

3. A field survey of the candidate sites was conducted to identify interference from localized sources or other problems that would affect the set up and operation of monitoring equipment.

The primary site (intensive sampling frequency) will be located at the Auraria Campus site near Speer Boulevard and Larimer. The site represents the urbanized area characteristic of the South Platte Valley region. The Auraria location will require the establishment of a new monitoring site. The Auraria site was chosen over other existing stations in the region

based on the need to select a site representing average exposure to community/daytime workers and a permanent residential population. The two existing state monitoring sites in the downtown area did not meet the basic criteria for exposure assessment and logistics. The CAMP station was found to be too highly influenced by local traffic, and the other existing station located at 414 14th Street was found to have significant operational and siting problems.

The second and third sites are located at Arvada and the National Jewish Hospital (NJH), respectively. The Arvada site represents the western metropolitan area, which consists of medium-density suburban residential neighborhoods. Based on historical air quality data, the western metropolitan area is more heavily influenced by residential wood burning than the other two previously mentioned monitoring areas. The NJH site will represent the eastern most metropolitan area. The site is located adjacent to a major arterial street. Land use for the area indicates that a significant portion of Denver's population is exposed to these conditions.

A fourth site will be added to the monitoring program. Some concern was raised regarding whether the NJH would be truly representative of air toxics concentrations in the eastern metro area. This question was raised due to a major arterial street intersection (Colorado Boulevard and Colfax Avenue) in the area. Thus, a supplemental monitoring site is located at the Palmer Elementary School (995 Grape Street, Denver), which is located in a residential area that experiences less vehicular traffic. A 2.5 μm particulate sampler and a CO analyzer will provide data to correlate the site with NJH. Both the NJH and Arvada sites are currently part of the state-operated air quality monitoring network.

The locations of the four monitoring sites within the metropolitan area are given in Fig. 1.

Determination of Sampling Frequency

In determining an encompassing sampling program, the frequency at which the sampling would take place was based on two priority considerations. The development of high-quality annual average exposure data for risk assessment and a statistically valid database for subsequent source apportionment analysis. Sampling frequency also considered the budget constraints of the project ($400 000) and the instrument configuration at each site.

The sampling frequency considered the establishment of one of the sites as a primary station site where samples are to be collected more frequently than the other sites. For IEMP it was determined that the Auraria site would collect samples every third day, while the three remaining sites would collect samples on a less frequent basis or once every sixth day. A one in three day sampling schedule is considered to be sufficient in collecting an extensive amount of data without taxing the limitations of the site technician to perform maintenance on the equipment. At the same time, a one-in-six-day sampling schedule is considered the maximum time that should be allowed to elapse between samples in order for the samples to be representative of the time period in which you are sampling.

The Auraria site was chosen for the more frequent sampling because of its downtown location. Twelve-hour sampling was initiated in order to assess any difference in ambient air quality concentration from day versus nighttime activities in the Auraria area. The three additional monitoring stations were used to establish background levels for the area, and the less frequent sampling was deemed suitable for the establishment of background concentrations. Table 2 depicts the equipment configuration for the sites and their respective sampling frequencies.