UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
ATMOSPHERIC RESEARCH AND EXPOSURE ASSESSMENT LABORATORY
RESEARCH TRIANGLE PARK
NORTH CAROLINA 27711

September 19, 1990

Memorandum

SUBJECT: Status Report of Research on Population Exposure Methodology for Mobile Source Pollutants

FROM: Gary J. Foley
Director, Atmospheric Research and
Exposure Assessment Laboratory (MD-75)

TO: Richard D. Wilson
Office of Mobile Sources (ANR-455)

I am writing in response to your request for a status report on AREAL's FY89-90 mobile source population exposure research. Attachment 1 summarizes the research that we are conducting with resources provided to support Issue D of the Air and Radiation Research Committee (i.e., A101 D21). Attachment 2 presents a recent example of the research AREAL also conducts to support short-term, high-priority requests for assistance from your office.

As you know, the available resources in A101 D21 (about 5 FTEs and $150K annually) are not adequate to address the broad range of mobile source population exposure research issues of concern to your office. However, AREAL frequently is able to increase our productivity in this area by conducting research with extramural funds from other sources that is directly relevant to mobile source population exposure scientific issues. I have included descriptions of the related research programs in Attachment 1 also.

With the emphasis placed on mobile source pollutants in the draft Clean Air Act Amendment legislation, we hope that population exposure research will receive increased priority during FY92-93 and, ultimately, increased funding. In the interim, I have provided information in Attachment 1 about those research activities which will be continued or initiated during FY91.

Attachments

cc: Rick A. Linthurst, RD-680
John D. Bachmann, MD-11
Charles Gray, Ann Arbor
Mark Joyce, ANR-443
Phil Lorang, Ann Arbor
Dale Pahl, MD-56
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ATTACHMENT 1

STATUS REPORT ON POPULATION EXPOSURE METHODOLOGY

FOR

MOBILE SOURCE POLLUTANTS

ATMOSPHERIC RESEARCH AND EXPOSURE ASSESSMENT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
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INTRODUCTION

This status report covers the major activities conducted during 1989 and 1990 by AREAL/RTP under Issue D (and others) of the Air Research Committee as they relate to population exposure methodology for mobile source pollutants. The report is essentially an update of a December 1988 report on work done in support of Issue D. In addition to exposure modeling activities, descriptions are included of monitoring and methods development programs judged to be relevant to the issue. Finally, information is provided on research activities which are scheduled to be continued or initiated next year.

1989/90 ACTIVITIES

EXPOSURE MODELING

The following summaries contain information on current activities in exposure modeling. The research discussed in these summaries addresses the issue of serial correlation of exposures. Previous modeling approaches have estimated exposures in a deterministic or statistical fashion. Both of which have ignored the effects of serial correlation. The authors recognized that this tends to underestimate maximum exposures and that the effect of serial correlation in exposure estimates cannot be ignored. Specifically, model enhancements have been made to NEM (National Exposure Model) that relate exposures this hour with ambient concentrations that existed the previous hour. Previous versions of NEM used simple linear regression to relate exposure to simultaneous ambient concentrations. The proposed version of the model includes a correlation coefficient to relate concentrations within microenvironments to ambient concentrations this hour and the previous hour. Model development has continued with SHAPE (Simulation of Human Activity and Pollutant Exposure) to statistically characterize the effect of serial correlation in exposure estimates. The third summary describes a preliminary analysis that attempts to quantify the magnitude of the effect of serial correlation.

1. Modification to NEM Model

The NEM modeling methodology was initially developed in 1979 for estimating population exposure to various pollutants. This methodology has evolved over the years to its present form which attempts to account for the variation of exposure throughout urban populations. NEM divides a defined human population into specific groups, simulates their movements through environmental settings of varying air quality, and provides estimates of exposure in these settings. The model achieves this through the use of realistic activity patterns based on actual diary notes.

A critical component of the NEM methodology is the model used to predict exposure from ambient data. Previous versions of NEM used simple linear regression to relate exposure to simultaneous ambient concentration within each microenvironment. However, the correlation coefficient between these variables was found to be very low. New modeling research summarized in the report referenced below attempts to improve the predictive capability of the model by accounting for the influence of previous ambient levels and the dependence of prior exposure levels. This research represents the first attempt to account for these factors in the major microenvironments where people spend most of their time. Personal exposure data collected in the Denver Personal Monitoring Study and ambient fixed site monitoring data in Denver were used to establish the relationships between these two variables.

Modeling results from this analysis suggest that the use of the concurrent and previous hourly ambient concentration provides a slight improvement in the estimation of exposure levels. The percent variation explained with this model was approximately 10-15% greater than earlier values, depending upon the microenvironment. A large percentage of variation remains unexplained, 50-75% for most environmental settings. The component of exposure not explained by ambient level is incorporated into the residual term. By accounting for the observed dependence of the residuals, the model is conceptually closer to the structure of the observed data and the frequency distribution of predicted CO exposures is much closer to the distribution of the actual exposures. This result is particularly important to OAQPS for the assessment of the number of people exposed to levels exceeding alternative ambient air quality standards.

Research Products - The Incorporation of Serial Correlation into a Version of NEM Applicable to Carbon Monoxide by T. Johnson et. al., PEI.

EPA Contact - Tom McCurdy (Mail Drop: 56 FTS: 629-5658).

2. Refinements of Averaging Time Exposure Models

Additional investigation has been performed on the incorporation of auto correlation into averaging time models. When profiles of activity patterns are used to generate time series of simulated exposure, one typically samples from exposure distributions which are microenvironment-specific to each activity. If the simulation time step is short, then independent sampling at each time step, ignoring autocorrelation, will result in aggregates with too little variability from one simulation to another. Autocorrelation can often be modeled with one or two extra parameters and then used in the simulation. Furthermore, one may substantially reduce computation by generating a single averaged exposure for each activity segment whose distribution depends in

a simple way on the activity duration and the modeled autocorrelation. The process has been illustrated using the El Camino Real commuting exposure study data of Ott, Switzer, and Willits. These results will appear soon in a published report (Toxicology and Industrial Health).

The microenvironmental approach to total human exposure modeling requires the development of submodels that realistically describe the concentrations experienced in the microenvironments that the population occupies. These submodels should be based on experimental data from pollutant exposures found in the microenvironments, reflecting both the appropriate expected values and the appropriate variability of concentrations. For some applications, the nature of the time series also may be important. This report deals primarily with the variability of the time series of concentrations.

A two-step method of analyzing the variability was applied to one-minute average CO exposures measured on 88 trips on El Camino Real over a one-year period in California. The two-step method decomposed the variability in two parts: between-trip variability and within-trip variability. To deal with the between-trip variability, the one-minute average CO concentrations on each trip were normalized by dividing them by the overall mean concentration for each trip. This step appeared justified by the observed proportionality between the trip standard deviations and trip means. The similarity of the frequency distributions of the resulting normalized CO concentrations for the different trips was exploited to obtain pooled variogram estimates needed for the averaging time model.

When different averaging times were considered, the same approximate lognormal distributional form emerged, with variability expressible via the averaging time model. A fitted parametric averaging time model, based on an exponential variogram, gave estimates of variability very close to the empirically calculated variability for a wide range of averaging times.

The resulting parametric averaging time model can be used in microenvironmental probability models to simulate time-averaged exposures for microenvironmental segments (trips) when the segment average is selected from an appropriately described distribution.

Research Products - Averaging Time Modeling of Exposure Simulation with Application to the El Camino Vehicle Data by W.R. Ott, P. Switzer, and N. Willits, January 1990.

EPA Contact - Wayne Ott (Stanford University 415/367-8158).

3. A Sensitivity Analysis on the Effect of Serial Correlation on Exposure Estimates

Statistical methods of estimating concentration values for use in human exposure estimates have become increasingly more popular because of the complexities in correlating the temporal and spatial concentration variations within microenvironments with the location of people. The number of variables and their associated uncertainty make deterministic models difficult to use. SHAPE and NEM which include statistical methods for characterization of the concentration values for different microenvironments, are examples of human exposure models that are a combination of deterministic and statistical methodologies. In SHAPE, concentrations are estimated by sampling from a concentration distribution for a given microenvironment in a Monte-Carlo fashion. In the simulations conducted thus far, the SHAPE model has ignored serial correlation effects. The authors recognized that this tends to underestimate maximum exposures since the concentration in a given microenvironment is related to source terms and atmospheric processes. This method tends to underestimate for another reason. If an individual is in a "dirty" microenvironment, for example a commute that exposes him to particularly high CO levels, he tends to be exposed to that level every commute. Monte-Carlo simulations conducted thus far have made no provision for this effect, and therefore tend to underestimate the highest exposures and overestimate the lowest exposures. The purpose of this sensitivity study is to quantify the factors affecting serial correlation in indoor microenvironments. Further, we investigate in a very preliminary way use of personal exposure monitoring data to infer the value of variables needed to estimate indoor concentrations such as the rates of air exchange, pollutant removal, and pollutant generation.

Indoor concentration values were simulated by using a mass consistent box model driven by a 48-hour SO_2 data set collected during the RAPS study. One thousand 8-hour averages were generated for three different scenarios. The Monte-carlo simulations underestimated the highest exposures by about 20% and overestimated the lower concentrations by about 30%. The difference between using the actual air exchange rate each hour and an average air exchange rate for each microenvironment during the 48-hour period was slight. This suggest that a model like NEM could be updated to include the affects of serial correlation since a mass consistent box model could be included rather easily.

We conclude that the use of personal exposure monitoring data to derive rate constants may be useful for order of magnitude estimates. More study is needed to ascertain whether the positive correlations and relative magnitudes of the time-averaged cross-

products terms would behave as seen in our analysis if real-world data were used. Our finding suggest that the use of PEM data would underestimate air exchange rates, underestimate emission rates, and overestimate removal rates where only one, or at the most, two processes are in effect.

EPA contact - Bill Petersen (Mail Drop:80 FTS: 629-1376).

EXPOSURE MONITORING

Several monitoring programs have been conducted by AREAL/RTP during the last two years which have shed light on the concentration ranges for mobile source pollutants which are typically encountered in the urban environment. The research goals established for these programs generally included field evaluation of methods, as well as collecting a database for interpretative purposes. The first activity describes the results of monitoring in-vehicle concentrations for a number of mobile source pollutants under a variety of driving conditions. A key finding of this study was that in-vehicle levels of VOCs can be predicted by a simple linear regression model based on the fixed-site measurements obtained from the vicinity of the traffic routes. The next program discussed describes a two-year database collected at a 10-site pilot network for urban VOC measurements (including formaldehyde) known as the TAMS network. The third summary describes a joint EPA/State program to monitor many of the same compounds at sites selected and maintained by State agency personnel.

1. Exposure to VOCs, CO, O3, and NO2 Under Different Conditions

Personal exposure to volatile organic compounds (VOCs) has become of increasing concern as various regulatory options are being considered. Data from several studies including the California TEAM Study suggest that exposure to VOCs such as benzene, m-p-xylene, and ethylbenzene is associated with automotive vehicle use.

The in-vehicle concentrations of 24 gasoline-related volatile organic compounds (VOCs) and three criteria air pollutants, ozone, carbon monoxide, and nitrogen dioxide, were measured in the summer of 1988, in Raleigh, North Carolina. Two, four-door sedans of different ages were used to evaluate in-vehicle concentrations of these compounds under different ventilation conditions on different roads with different traffic patterns. Isopentane was the most abundant aliphatic hydrocarbon (median 1-h concentration was 52.6 $\mu g/m^3$) and toluene was the most abundant aromatic VOC (median 1-h concentration was 43.1 $\mu g/m^3$) measured inside the vehicles. The median concentrations of CO, NO_2, and O_3 were 11 ppm, 81 ppb, and 11 ppb, respectively. No differences were found in the in-vehicle concentrations of 24 VOCs, CO, NO_2, and O_3 between the two experimental cars. In-vehicle VOC and CO concentrations were highest for the urban roadway, second highest for the interstate

highway, and lowest for the rural road. The median concentration ratio of urban/interstate/rural for each VOC was about 10/6/1. No differences in in-vehicle VOC concentrations were found between morning and afternoon rush hour driving, but higher in-vehicle ozone and NO_2 concentrations were found during afternoon driving. The ventilation condition that gave the highest in-vehicle VOC levels was the one in which the windows were closed, the vent was on and the fan was on. The ventilation condition that gave the lowest VOC levels was the one in which the air conditioning was used. The in-vehicle/car exterior concentration ratio for VOCs, CO, and NO_2 was slightly higher than 1. The VOC concentration measured by a pedestrian on the sidewalk was lower than the in-vehicle measurements but higher than the fixed-site measurements on urban roadways 50 m from streets. All 24 VOC concentrations were positively correlated with each other. The VOC measurements were positively correlated with the CO measurement and negatively correlated with the ozone measurement. For the data in this study, in-vehicle VOC levels can be predicted by a simple linear regression model based on the fixed-site measurements obtained from the vicinity of the traffic routes.

Research Products - Driver's Exposure to Volatile Organic Compounds, CO, Ozone, NO_2 under Different Driving Conditions by C. Chan et. al.

EPA Contact - Bill Nelson (Mail Drop:56 FTS: 629-3184).

2. Toxics Air Monitoring System (TAMS)

During FY-88 and FY-89, ambient air samples were routinely collected in stainless steel canisters at 10 urban sites as part of the TAMS monitoring network. The sites were selected to represent typical industrial and commercial areas in Boston, Chicago, Houston, and the Seattle/Tacoma metropolitan region. Flow-controlled air samples were drawn over a 24-hr period beginning at 6:00 a.m. every 12th day. These whole-air samples were analyzed by GC/MSD for selected VOCs including benzene, toluene and other aromatic compounds. The MSD was operated in the selective ion monitoring (SIM) mode in order to optimize resolution for the compounds of interest. Concentrations were reported quantitatively if they exceeded 0.10 ppbv. In addition, cartridges coated with 2,4-DNPH were collected concurrently and analyzed by HPLC for formaldehyde.

Quality assurance procedures were incorporated into the program in order to provide measures of the accuracy and precision of the methods used. The QA data revealed that the original DQOs established for TAMS were being achieved in terms of data completeness (>85%), precision (<20%), and accuracy (<20%). Ambient VOC concentrations ranged from below detection (<0.10 ppbv) to 20.0 ppbv. Compound ratios and correlations indicated that motor vehicle emissions accounted for most compounds with mean

concentrations greater than 1.0 ppbv. An intensive study was conducted at one Houston TAMS site from August 15 - 25, 1989 during which sequential 3-hr samples were collected and analyzed to provide information on diurnal VOC concentration patterns. Routine sampling continued through August 20 and all samples were analyzed by September 30, 1989.

Research Products - Final Report on the Operations and Findings of TAMS by G. F. Evans, June 1990.

Database available on EPA's Aerometric Information Retrieval System (AIRS).

Design and Implementation Plan for the Restructured TAMS by G. F. Evans and J. D. Pleil, September 1990.

EPA Contact - G. F. Evans (Mail Drop: 56 FTS: 629-3124).

3. Urban Air Toxics Monitoring Program (UATMP)

The UATMP is a joint undertaking by U.S. EPA and several participating State environmental agencies to determine ambient air toxics concentrations and assess the risk they may pose to human health. The network is aimed at three major groups of pollutants including: the volatile organic compounds (VOCs), airborne particulates (trace metals and benzo[a]pyrene), and aldehydes (as a separate class of organics). Each is monitored in a different way - the VOCs using evacuated canisters, the particulates using a high volume sampler to collect samples on glass fiber filters, and the aldehydes using cartridges containing a 2,4-DNPH substrate. In all cases, field sampling is conducted by State agency personnel and samples are sent to a contract laboratory (Radian Corporation) for analysis.

A report has been prepared to present data summaries and other analyses of the fiscal year 1988 aldehyde data from the UATMP network. The aldehydes quantified in this report are acetaldehyde, formaldehyde, and acrolein. Some aspects of the data presented include seasonal patterns, weekday versus weekend patterns, correlations among the pollutants, and comparison of UATMP data with data from other monitoring programs. It is not possible to productively compare results from one city with another due to siting differences. The VOC and particulate data collected in the UATMP program will be reported on in a future report.

Research Products - UATMP Results of Aldehyde Monitoring for FY88

EPA Contact - Robert Faoro (Mail Drop:14 FTS: 629-5459).

METHODS DEVELOPMENT

The Atmospheric Research and Exposure Assessment Laboratory (AREAL/RTP) is responsible for the assessment of environmental monitoring technology and systems for air and for supplying technical support to other groups in the agency including the Office of Air and Radiation (OAR), the Office of Toxic Substances (OTS), and the Office of Mobile Sources (OMS). In this regard, the determination of exposure to formaldehyde vapor is an area of continuing importance. The continuous real-time monitors described in the first summary provide capability for measurements over the range of concentrations expected in indoor and outdoor air, and can thus help define the extent of personal exposure to formaldehyde. The passive sampling device discussed in the second summary offers a relatively inexpensive, portable, and accurate method for determining integrated exposures to a wide variety of mobile source pollutants including VOCs, ozone, and formaldehyde.

1. Real-Time Monitors for Gaseous Formaldehyde

Two new methods for real-time measurement of gaseous formaldehyde have been developed, one based on a direct spectroscopic approach and the other on continuous scrubbing of gaseous formaldehyde into aqueous solution for subsequent analysis. Both monitors are portable, but the latter method does require occasional replenishment of simple aqueous reagent solutions. This method, however, provides a detection limit of 0.20 ppbv which is about two orders of magnitude below that currently achievable with the direct approach.

The aqueous scrubbing/analysis method was field-tested by continuous operation over a 10-day period during which outdoor and indoor air samples were taken for alternating half-hour periods. Concentrations observed in the field study ranged from 0.2 to 7.0 ppbv and from 10 to >50 ppbv in outdoor and indoor air, respectively. Also, a comparison of real-time (aqueous scrubbing/analysis) with integrated (DNPH/HPLC) measurements showed close agreement even at the 1.0 ppbv concentration level.

Research Products - Final Report on the Development of Real-Time Monitors for Gaseous Formaldehyde by T. J. Kelly and R. H. Barnes, September 1989.

EPA Contact - William McClenny (Mail Drop: 44 FTS: 629-3158).

2. Thermally Desorbable Passive Sampling Devices (PSDs)

A passive sampler was developed for short-term, low-level ambient air monitoring applications. This small, stainless steel device is simply designed and inexpensive. It has a high equivalent sampling rate, is reusable and rechargeable, and is

designed for thermal desorption. Laboratory and field tests with Tenax GC as the sorbent have shown that the device compares very favorably with active (pump-based) samplers and has much better sensitivity than commercial passive samplers which utilize activated charcoal.

Performance was examined under controlled test chamber atmospheres and in actual outdoor and indoor situations. Sampling rates were calculated for several volatile organic compounds. An extensive evaluation of the effects of air velocity on performance also was undertaken. Also, a modification has been made by replacing the granular sorbent with filter paper treated with appropriate reagents to trap nitrogen dioxide or formaldehyde. Effective sampling rates for these compounds have also been computed.

Research Products - Modifications of a High-Efficiency Passive Sampler to Determine Nitrogen Dioxide or Formaldehyde in Air, J.D. Mulik et. al., January 1989.

EPA Contact - James Mulik (Mail Drop: 44 FTS: 629-3067).

FUTURE ACTIVITIES

Plans within AREAL for next year include the development of the design of a hybrid model, that will attempt to strike a balance between deterministic and statistical models. Current design criteria for the hybrid model call for the capability to use empirical data values, and simulated values of concentration within the microenvironments. Wayne Ott will continue his research at Stanford on the effect of serial correlation on exposure estimates. Both of these projects will be primarily in-house efforts because of little or no extramural funding. Therefore both will proceed slowly. At the current funding level the development of the hybrid exposure model is scheduled to be completed in FY-97. Scheduled work with NEM next year include the incorporation of a mass balance approach for the simulation of microenvironmental concentration values.

The driving habits of individuals and the general population lead to the observation that Americans spend many hours during a week in their cars for the purposes of commuting to and from work, pleasure, and family support activities. Within the Denver and Washington CO exposure studies there were examples of individuals who had significant CO exposure while driving to work. For many individuals studied the total amount of time spent in their automobile was equivalent to or exceeded the time spent outdoors during the day. Based upon typical U.S. adult time-activity patterns, similar results could be expected for the general

population. Considering the preceding, it is important to examine the intensity of exposures that result from the complex mixture of chemicals than can enter or be emitted from the vehicle cabin. The major automobile source would be the exhaust from an internal combustion engine that used gasoline, or methanol fuel.

The emissions from the different types of fuels used could be quite different, therefore, key compounds such as benzene and toluene from the gasoline powered automobiles and formaldehyde from methanol powered automobiles will be selected for analysis. Further, as shown by compounds such as CO, there will be penetration of emissions into the cabin. Depending upon the driving conditions, emissions entering the cabin could be a combination of emissions from other automobiles on a road or highway and the vehicle being driven, or primarily the emissions from the vehicle being driven.

An investigation is now in progress with the following two primary objectives:

1. To characterize the types and intensity of human exposures to compounds than can penetrate into or are emitted within the cabin of an automobile for different types of driving conditions.

2. To compare and contrast the intensity and types of exposures that can occur for methanol powered automobiles with those associated with the standard non-leaded gasoline powered vehicles.

An individual can spend many hours each day in an automobile, thus it is possible to have exposures to single or multiple compounds which are emitted within or penetrate into the vehicle cabin. Therefore, it is valuable to determine if exposures to specific chemicals or chemical classes are significant for time scales that might produce health outcomes. Further, if methanol powered or other alternative fuel powered automobiles are introduced to the U.S. automobile fleet, it is important to evaluate potential exposures relative to exposures associated with unleaded gasoline powered automobiles.