



Project Summary

Ambient Air/Source Transport and Transformation Relationships for Selected Hazardous Air Pollutants

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The study was undertaken with the goal of obtaining information that might improve modelling techniques for hazardous organic vapors in the atmosphere. It was proposed that both source-receptor and dispersion models be applied. Detailed examination of alternative choices for pollutant, emission site and method of determination was made. This resulted in the selection of the benzene/toluene/xylene class as pollutants, a waste disposal site near Taft, California (in the San Joaquin Valley) as source, and adsorption on Tenax cartridges from the air, followed by thermal desorption and gas chromatography as method of determination. Cleanup procedures for Tenax were developed that allowed generally quite good agreement with comparison measurements with reference mixtures supplied in canisters by the Atmospheric Sciences Research Laboratory. Co-located canisters and Tenax tubes were sometimes in agreement and sometimes not. These disagreements may be due in part to interferences from other organic compounds that are separated differently on the packed GC column used for the Tenax analyses and the capillary GC column used for the canister analyses. Collections of Tenax were made on several occasions by means of a remotely controlled system of samplers developed in this project. Poor meteorological conditions and a sampling array now seen to be too small prevented obtaining satisfactory data for modelling

purposes in 1985. In 1986 an expanded network, better meteorology, and use of an integrating anemometer greatly improved data collection. It was found, however, that the unexpected presence of unidentified strong and irregular sources of the target compounds prevented consistent interpretation. Both receptor and Gaussian dispersion models were examined in various forms, but could not be applied to the collected data.

Analyses of canister gases by capillary GC at the ASRL showed a remarkably complex mixture of pollutants in most of the samples. Over 200 compounds were seen in some cases, and non-methane hydrocarbons totalled as much as 9.5 ppm carbon.

This Project Summary was developed by EPA's Atmospheric Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Summary Report ordering information at back).

Introduction

Atmospheric modelling of volatile substances is usually done from the source forward, by means of dispersion models. If the concentration of pollutants of interest decreases from causes in addition to dispersion, the modelling predictions of course are inaccurate. Source-receptor modelling, in which the ambient air composition is related

to specific sources or source types by means of its composition, is another approach of interest. The approach is particularly useful for certain hazardous substances that are not found in the atmosphere except through emissions from specific sources; also fingerprint compositions identified at specific sources are useful for this type of modelling. The study was undertaken with the aim of carrying out air sample collections of one or more hazardous substances in such a way as to be applicable to both types of modelling.

Phase I included the selection of pollutants to be studied, the selection of the study site, and the selection of the sampling and analytical methodology. Phase II included the actual sampling, analysis, and data interpretation. Engineering Science (ES), Berkeley, California, participated as subcontractor in both phases; in site selection and development of sampling strategy in Phase I, and in meteorological forecasts and measurements as well as data interpretation in Phase II. The Atmospheric Sciences and Research Laboratory (ASRL) of the U.S. Environmental Protection Agency (EPA) at Research Triangle Park (RTP), North Carolina (NC), participated by providing standard reference gas mixtures, loans of canisters and pumps for parallel gas sample collection, and independent analyses of canister samples for quality assurance purposes. The ASRL sample analyses were made with capillary gas chromatography and provided a very detailed hydrocarbon breakdown for the canister samples.

Procedure

Phase I: Selection of Pollutant, Site and Methods

The hazardous pollutant or pollutant group was selected from the list of "Chemicals Under Assessment" (as of 1983) in Section 112 of NATION EMISSION STANDARDS FOR HAZARDOUS AIR POLLUTANTS (NESHAPS). Ten of these with very low volatility, or without well-defined chemical composition, were deleted. Ten others were added in the process of selection, making a total list of 48 compounds for consideration. This list was screened on the criteria of usage or occurrence in California, emission potential and volatility. The additional criteria of estimated ambient half-life and estimated toxicity or carcinogenicity were also considered. A further requirement was a suitable

methodology for collection and analysis. The final selection of the benzene group (benzene, toluene, and *o*-, *m*- and *p*-xylenes) was based upon both site availability and suitable methodology for collection and analysis.

An early decision was made to confine the study to the California area, because of the greatly increased cost of sampling elsewhere in the country, and the risk of sample deterioration during shipping long distances back to the Global Geochemistry Corporation (GGC) laboratory. Potential emissions from the chemical industry in the state were examined, but the use of a landfill source appeared more promising. Moreover there was interest on the part of both EPA and local agencies for information on landfill emissions. The characteristics of active landfills in the state were examined. A class II-1 landfill able to accept all but the most toxic wastes was found in the southern San Joaquin Valley within a hundred miles of the GGC laboratory. This facility has good terrain and, based on historical records, suitable meteorological conditions. Small-scale pilot trials indicated the site released suitable organic compound levels for sampling.

The choice of sampling method was narrowed down to either canisters or Tenax tubes. The Tenax tubes were chosen both because of their lower cost and because they are more readily deployed in sampling arrays, due to their light weight and operation with battery-powered pumps. Canisters provided by ASRL were also used, and served as valuable means of checking on quality control. Some development was required to determine how to clean and prepare Tenax traps for sample collection, storage and analysis. It was found effective to seal off the ends of the glass cartridges containing the Tenax, after initial conditioning and again after sampling, in order to minimize contamination. Contents of the tubes were thermally desorbed directly onto a packed GC column combined with a photoionization detector sensitive to C₆ to C₈ aromatics. Aliquots from the ASRL sample canisters were passed onto Tenax tubes for analysis, and the canisters were then shipped to ASRL for a more detailed analysis by capillary column GC with flame ionization detection. Interlaboratory comparisons were also made by means of EPA reference mixtures of benzenoid hydrocarbons provided by ASRL and analyzed by both laboratories.

GGC also developed a remote radio-controlled system for operating as many as sixteen Tenax tube samplers individually from one transmitter point, to allow either simultaneous or sequential sampling as desired.

Phase II: Sampling and Analysis

The project subcontractor, Engineering Science, advised on the meteorological conditions required and the sampling layout needed for the modelling studies. Both source-receptor and Gaussian dispersion models were to be utilized. Consequently, it was intended that data collection serve both purposes. Ten samplers were deployed at an array of seven to eight downwind sites, on site near one to two source ponds and at one upwind site. The samplers were operated using the remote control radio network switching system. The dimensions of the array were adjusted according to the windspeed and estimated atmospheric stability class for adequate coverage of assumed Gaussian dispersion.

Sampling efforts were performed on July 9-11 and September 4-5, 1985, based on favorable meteorological forecasts. However, on both occasions the winds were quite variable during the sampling periods. Good conditions were experienced for only one sampling period and that during the September sampling effort. None of the data sets obtained from these runs was adequate for Gaussian or receptor modelling purposes. During both episodes, canisters obtained from ASRL were used for parallel sampling. These canisters were used both at co-located and independent sites. After sample aliquots were taken for analysis by GGC, the canisters were sent to RTP for more detailed analyses by capillary GC. Only limited opportunities occurred in the fall and winter of 1985-86 for additional sampling at the site. Better conditions were expected in May, 1986. Further sampling with the array enlarged to sixteen tubes was carried out from the 21st to the 25th of May. Three canister runs with five canisters each and eight runs with 16 Tenax tubes were carried out. For these runs an integrating anemometer was used to give much better definition of wind conditions.

Results and Discussion

GC analysis by thermal desorption from Tenax tubes used to sample canisters

ters of EPA reference mixtures agreed well with the ASRL analyses and the known concentrations. Blanks and replicate samples showed low background levels and good reproducibility. The use of a photoionization detector permitted highly specific sensitivity for the benzene group despite the presence of large amounts of other hydrocarbons shown by ASRL's capillary GC-FID analyses of the same canister samples. There were at times large discrepancies between the analyses of field samples in canisters and the co-located Tenax tubes. These discrepancies were probably due to sampling rather than analytical differences. At times however, large amounts of other organic compounds co-eluted with the benzene class compounds and interfered with accurate analysis comparisons. A further striking finding from the canisters was the large number of compounds and the high concentrations present in many of the samples.

The highly variable atmospheric conditions which prevailed during the 1985 sampling appeared in retrospect to have made the sampler number and placement less than optimal. Sample locations were either inadequate in downwind and crosswind directions, or were inadequate in total number to provide a clear picture of plume behavior from the waste ponds. Although there is a consistency in sampling results, there are insufficient data from these runs from which to draw any but the most general conclusions. Overall, the limited quantity and somewhat inconsistent nature of the 1985 sampling results do not support either receptor or Gaussian dispersion models. Additional sampler locations and a reconfiguration of the downwind network were implemented in 1986 to improve sampling results and possibly provide an improved basis for model analysis. The data quality appeared to be better, but it became apparent that there were present large sources of the benzenoid compounds (and many other substances) which were obviously not the known disposal ponds, based on the wind patterns. These again made it impossible to apply either receptor or Gaussian dispersion models to the data in any meaningful way.

Results from the Tenax cartridge samples collected the sampling during July and September of 1985 indicate a reasonable internal consistency in data; the relative magnitudes of the various

chemical species in a sample were consistent, and downwind and crosswind variations followed similar patterns. The data, however are not sufficiently detailed to permit substantive conclusions. The measured concentrations are not statistically significant enough to allow estimation of sensitivity and verification of models. Small sampling size and irreproducibility of results will probably lead to unacceptably low levels of confidence in data interpretation, such that the statistical significance of the data set is insufficient to adequately define a fit with either Gaussian or receptor model hypotheses. The data set obtained in 1986 was larger, both in samples per run and numbers of runs, but nevertheless was still not usable. In some of the runs there were one or more maxima in concentration that could not have originated from the disposal ponds, based on wind patterns, and successive runs did not always resemble one another even when winds were similar. It seemed apparent that either there were bursts of emissions of short duration from the ponds, or there were other intermittent strong sources in the area. Although the disposal site planned for study is in an area of oilfield activity, it was not realized beforehand that there were other local emission sources of the magnitude indicated by the data.

Recommendations

1. For attempts to improve receptor models, it appears that waste disposal sites are not desirable sources, because of the wide variety of substances emitted, unless high resolution analytical techniques (e.g. capillary gas chromatography) are used to discriminate among the many pollutants. Moreover, for this purpose it is also important to have the study source isolated from other sources with similar emissions.
2. Mounting samplers on short poles along the downwind centerline will determine that the plume is indeed a ground-level source, and is not behaving as an elevated source because of ground heating or some other external factor. Sampler elevations of approximately 5 to 10 meters will permit a more definitive vertical profile of the plume and a better grasp on atmospheric conditions through a fit of vertical dispersion (sigma-z) parameters.
3. A better definition of source emissions will be obtained through improved sampler locations and use of tracer, or non-reactive, emissions.
4. The remote control switching system proved to function well and make the operation of a network of at least 16 battery operated samplers over distances of about one kilometer quite practical.

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William Lonneman is the EPA Project Officer (see below).

The complete report, entitled "Ambient Air/Source Transport and Transformation Relationships for Selected Hazardous Air Pollutants," (Order No. PB 87-129 730/AS; Cost: \$30.95, subject to change) will be available only from:

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