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Project Summary

Hazardous Air Pollutants: Wet Removal Rates and Mechanisms

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Fourteen hazardous organic air pollutants were evaluated regarding their potentials for wet deposition by precipitation scavenging. This effort included a survey of solubilities (Henry's Law constants) in the literature, measurement of solubilities of three selected species, development of a general deposition model (MPADD) that includes dry deposition and plume depletion, and performance of scavenging field experiments to provide a data base for testing the model. Solubility parameters (dimensionless ratio of aqueous concentration to air concentration) for ethylene oxide, nitrobenzene, and methyl chloroform were measured in rainwater at two temperatures each; the values obtained agreed generally with previous work except those for methyl chloroform, which were somewhat lower than previous experimental and calculated values. Four field experiments were conducted: three used nitrobenzene and one involved methyl chloroform. Agreement of measured concentrations with model-calculated values was good for nitrobenzene, despite larger-than-desired experimental uncertainties during two of the releases. Analytical difficulties resulted in only a few measurements of methyl chloroform rainwater concentrations; these, however, were in general agreement with model calculations and expectations on the basis of methyl chloroform's much lower solubility than that of nitrobenzene.

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 Report ordering information at back).

Introduction

The U.S. Environmental Protection Agency is evaluating the environmental fate of a number of possibly hazardous organic chemicals that are being considered for regulation. The removal from the atmosphere by precipitation scavenging of a selected list of these chemicals, shown in Table 1, is the focus of the present project. The major objective is to provide a reliable and convenient methodology for evaluating the wet removal of the listed pollutants, which is based on a sound understanding of the pertinent atmospheric interactions.

The research directed toward fulfillment of this objective was divided into three components: deposition modeling, solubility determinations, and field experimentation. The modeling effort resulted in the development of the Multi-Pollutant Atmospheric Deposition and Depletion (MPADD) Model, a versatile computer code for predicting the wet and dry deposition behavior of reactive or non reactive species. The solubility component included a survey of known Henry's Law behavior of the listed hazardous air pollutants (HAPs), and measurements were made on three of them. To provide a data base for evaluating the MPADD model, field experiments employing controlled releases of two HAPs were conducted.

The following sections summarize the results from these components. Conclusions and recommendations are based upon the project as a whole

Modeling

The MPADD model is a complete revision of the former Scavenging Model Incorporating Chemical Kinetics (SMICK), developed for the EPA by Battelle, Pacific Northwest Laboratories in the early 1970's The major change is a completely

Table 1. *Hazardous Air Pollutants of Present Interest*

Acetaldehyde
Acrylonitrile
Carbon Tetrachloride
Chloroform
Cresols
Epichlorohydrin
Ethylene Oxide
Methyl Chloroform
Methylene Chloride
Nitrobenzene
Perchloroethylene
Phenols
Phosgene
Polychlorinated Biphenyls

new numerical integration subroutine, which is more efficient and offers a considerable reduction in computer time. Other advances include the inclusion of dry deposition as well as wet deposition, and an accounting for plume depletion. MPADD is modularized, allowing for a variety of source configurations, plume descriptions, chemical reaction mechanisms, and pollutant physical properties (including gaseous or aerosol).

A schematic of the macroscopic features of MPADD is shown in Figure 1. The plume is subject to diffusion, possible chemical reactions, and dry and wet deposition. The mass transfer between the aqueous phase (raindrop) and gas phase is integrated numerically along the raindrop's trajectory (determined by fall velocity and wind speed), and resulting ground-level concentrations are evaluated at the receptor This process is repeated for a selectable number of raindrop sizes, and the bulk rain concentration at the receptor is computed by weighting over the calculated or measured raindrop size spectrum. The above procedure is done at a selectable number of cross-plume positions, and cross-plume integrated fluxes (wet and dry) are evaluated. At each downwind distance, the process is repeated, and depletion of the plume by wet and dry deposition is accounted for. The result is a deposition pattern and values for removal rates in the downwind area

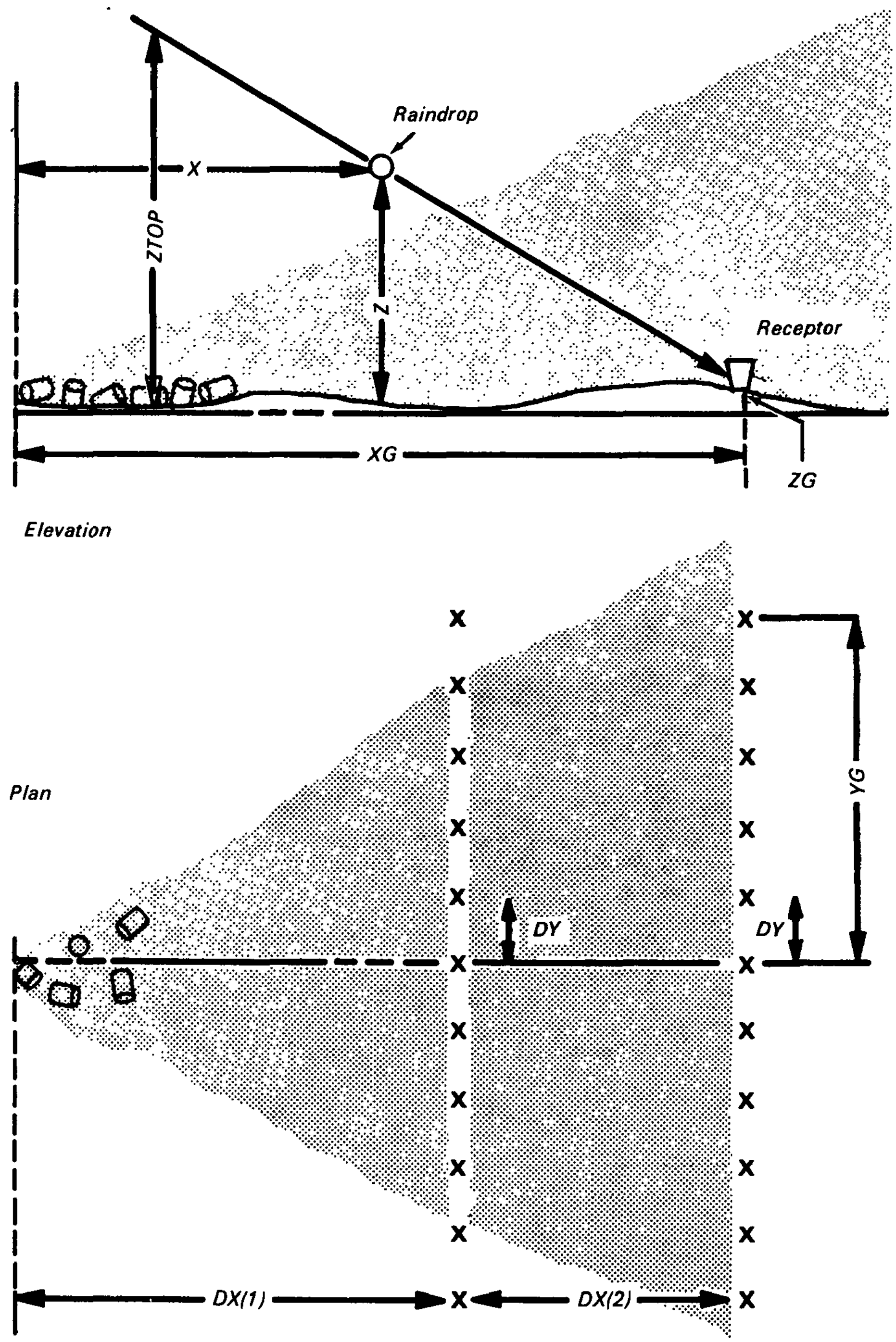

Figure 1. *Schematic elevation and plan views of model layout.*

Solubility

The Henry's Law constant is probably the most important physical property of a gaseous pollutant affecting precipitation scavenging. A literature survey was conducted to assess the knowledge of solubility of HAPs, and to assist in selecting species for measurements during the current project. The results of this survey are shown in Table 2. Additional measurements were performed for ethylene oxide, nitrobenzene and methyl chloroform. Measured results for α, a dimensionless form of the Henry's Law constant, for the three species are also listed in Table 2. Each experimental value entered in Table 2 is the average of three separate runs.

Table 2. *Solubility Parameters α For Hazardous Air Pollutants*

Species	T °K	α, dimensionless[a] Calculated	Measured
Acetaldehyde	298	$\gg 1$	
Acrylonitrile	298	9x10^3	
Carbon tetrachloride	293	1 04	
	298	0.86	0.81,.87
Chloroform	293	8.35	
	298	7.57	7.21
Cresols			
p-cresol	298		2.8x10^3
4-6, dinitro-o-cresol	298		1.7x10^4
Epichlorohydrin	298	760	
Ethylene oxide	278		3.8
	283	5.3	
	288		6.2
	293	7 9	
	303	11.2	
Methyl chloroform	280		4.7
	288		2 4
	293	6.28	
	298	5.99	4.97
Methylene chloride	298	1.5,8.04,9.1	1.4,7 67,10
Nitrobenzene	280		3.8x10^3
	288		1.7x10^3
	293	1.88x10^3	
	298	1.016x10^3	
Perchloroethylene	293	1.18	
	298	0.85,2 4	0.85,2.0
Phenol	293	3.4x10^4	
	298		1.88x10^4
Phosgene	278	4.06	
Polychlorinated biphenyls			
Arochlor 1242	298		42.9
Arochlor 1248	298		6.99
Arochlor 1254	298		8 73
Stovhlot 1260	298		34.4

Table 2 - Continued

[a]*Ratio of aqueous phase concentration to gas-phase concentration*
[b]*Present project*

Field Experiments

A test of the efficacy of MPADD to predict HAP rainwater concentrations under actual field conditions was provided through controlled-release field experiments. The release system provides a fine mist of the liquid pollutant that volatilizes quickly before encountering raindrops over the sampling positions. Samplers were placed in arcs at distances of 200 and 400 m downwind of the release tower. To simplify the plume description employed in MPADD and to minimize dry deposition, the source point was elevated 26 m. Two species with (presumed) widely different solubility parameters were chosen as the materials to be released. Nitrobenzene possesses the desirable characteristics of high aqueous solubility and low volatility. In contrast, methyl chloroform is representative of a large number of industrial halo carbons characterized by low solubility and high volatility.

Rainwater samples were collected in Teflon and amber glass funnel/bottle collectors. Before experiments, the bottles were charged with volumes of pentane sufficient to cover the collected rainwater and thus minimize gas-liquid phase transfer prior to collection. This was particularly important for the experiment employing the highly volatile methyl chloroform.

Four release plume experiments were conducted during the early months of 1983, three involving nitrobenzene, and one with methyl chloroform. Figure 2 shows the comparison of the calculated and experimental results for the first of the four releases.

Conclusions and Recommendations

The Multi-Pollutant Atmospheric Deposition and Depletion (MPADD) code is a significant advance in the area of modeling precipitation scavenging and dry deposition of hazardous and other types of pollutants. It contains a new timesaving integration scheme and is versatile in that it produces both dry and wet fluxes, describes depletion of the pollutant plume, and can accept a variety of plume model and chemical reaction mechanisms. Applications during the present project were to gaseous species with physical properties and chemical reaction behaviors that could be described relatively simply. As knowledge of the properties of hazardous air pollutants increases, MPADD should be tested and the relevant subroutines refined accordingly.

The literature of the solubility behavior of hazardous air pollutants is not extensive and measurements of Henry's Law constants do not involve so wide a range of temperatures as one would like for atmospheric assessments Experimental values for acetaldehyde and acrylonitrile apparently do not exist. Measurements of solubility during the present project were

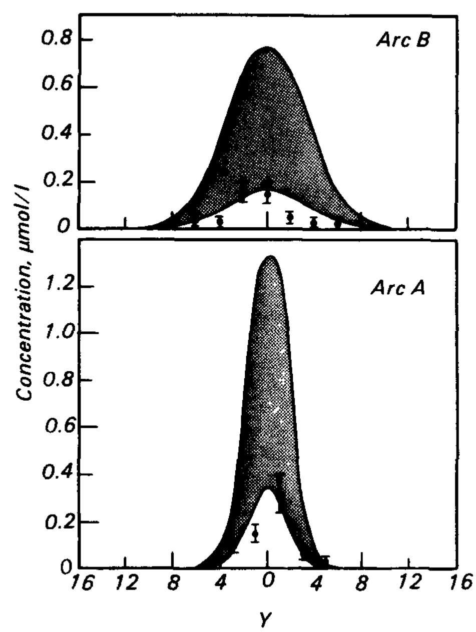

Figure 2. *Observed and calculated rainwater concentrations, run H1-A. The shaded area represents the uncertainty in source term input to MPADD.*

made for three species: ethylene oxide, nitrobenzene, and methyl chloroform. These measurements were performed in rainwater, and they filled temperature gaps in the Henry's Law constant record for these species. The results generally agreed with previous work except for methyl chloroform, for which the magnitudes were somewhat lower than previous results.

Solubility is a very important property influencing precipitation scavenging behavior. It is therefore important that more measurements be made on species of particular interest. In particular, data at more temperatures are needed, and dependence on pH and other chemical variables should be investigated for species for which for this could be chemically significant.

Four controlled-release experiments employing nitrobenzene and methyl chloroform were conducted during the early months of 1983. The results were valuable in providing data under realistic atmospheric conditions for testing the MPADD model and solubility information. Although a difficulty with the release solution led to above-normal uncertainty in released mass during two of the three nitrobenzene experiments, agreement with MPADD predictions was good (generally within a factor of two) for this species. However, the calculated rainwater concentrations were generally higher than those observed. This result could be due to the mass-transfer description in the model or to uncertainty in nitrobenzene solubility, which is apparently a strong function of temperature. Analytical problems led to a loss of many of the concentration measurements from the methyl chloroform release. The surviving values, though not sufficient to provide a measure of cross-plume integrated flux, do show that the scavenging follows the predicted behavior in being much less efficient than nitrobenzene, due to much lower solubility.

The results of the field study provided strong support for the validity of the MPADD model, but additional experiments should be performed using particular species of environmental concern and/or species with chemical properties different from those previously tested.

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The complete report, entitled "Hazardous Air Pollutants: Wet Removal Rates and Mechanisms," (Order No. PB 85-138 626; Cost: $13.00, subject to change) will be available only from:
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