AD-779 551

PRECIPITATION SCAVENGING OF ORGANIC CONTAMINANTS

Jeremy M. Hales, et al

Battelle-Pacific Northwest Laboratories

Prepared for:

Army Research Office - Durham

April 1974

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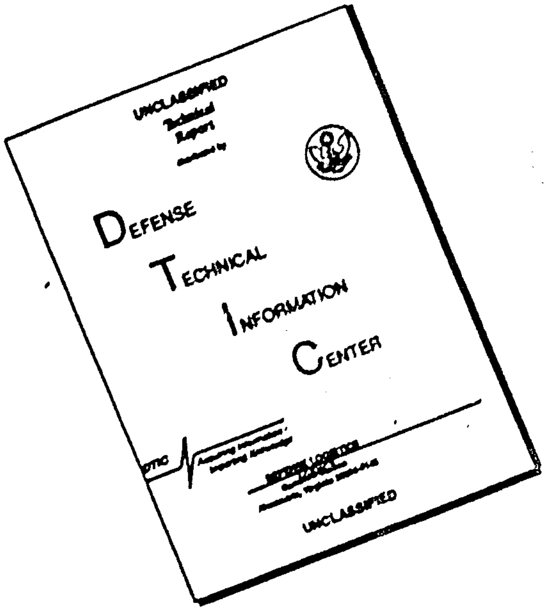

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(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Battelle-Northwest Laboratories Richland, Washington	2a. REPORT SECURITY CLASSIFICATION Unclassified
	2b. GROUP NA

3. REPORT TITLE

PRECIPITATION SCAVENGING OF ORGANIC CONTAMINANTS

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

FINAL REPORT

5. AUTHOR(S) (First name, middle initial, last name)

Jeremy M. Hales and Richard N. Lee

6. REPORT DATE April 1974	7a. TOTAL NO. OF PAGES 105	7b. NO. OF REFS 17

8a. CONTRACT OR GRANT NO. DAHC04-72-C-0035	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO. P-10417-EN	
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d.	

10. DISTRIBUTION STATEMENT

Approved for Public Release; Distribution Unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY U. S. Army Research Office - Durham Box CM, Duke Station Durham, North Carolina 27706

13. ABSTRACT

An investigation of the washout behavior of trace organic vapors has been initiated under sponsorship of the U. S. Army Research Office - Durham. The concentration of the moderately soluble materials ethylacetoacetate and diethylamine was determined for rain samples collected downwind of an elevated point source. This data is compared with concentrations calculated via the EPAEC gas washout model which incorporates meteorological data, source strength, the Gaussian plume model and tracer solubility to predict tracer concentrations along the plume trajectory. Disagreement between the observed and calculated concentrations is attributed primarily to the quality of the tracer solubility data.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Precipitation Scavenging						
Washout of Organic Vapors						

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FINAL REPORT

Richard N. Lee and Jeremy M. Hales

April 1974

U. S. Army Research Office - Durham

Contract No. DAHC04-72-C-0035
Project No. P-10417-EN

Atmospheric Sciences Department
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P. O. Box 999, Richland, Washington 99352

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SUMMARY

The EPAEC gas washout model has been applied to the organic tracers ethylacetoacetate and diethylamine. This model utilizes source strength, vapor solubility and basic meteorological parameters to estimate the tracer concentration in downwind rain samples. Contrary to the study of SO_2 washout, the observed concentrations are in rather poor agreement with predictions derived from the model. A detailed error analysis has identified poorly defined tracer solubility as the major source of this discrepancy. Solubilities expressed in terms of the Henry's Law relationship, $H' = \frac{\text{vapor pressure}}{\text{molar concentration}}$, have been derived from the available literature and are judged to be inappropriate for the low vapor concentrations encountered. Field results have also been used to calculate the fractional washout of the vapor per kilometer from the source. These results together with existing diffusion models may be used to estimate the vapor concentrations of these materials along a plume trajectory.

CONTENTS

FIGURES

FIGURES - Continued

TABLES

TABLES - Continued

ACKNOWLEDGMENTS

This research was conducted by scientific and technical personnel of the Atmospheric Sciences Department of Battelle, Pacific Northwest Laboratories, under contract DAHC04-72-C-0035 for the U. S. Army Research Office - Durham. Project Officer was Dr. Arthur V. Dodd, Director, Environmental Sciences Division, U. S. Army Research Office - Durham, North Carolina.

The principal investigators were Dr. J. M. Hales and Dr. R. N. Lee. The authors wish to recognize the valuable contribution of Mr. D. W. Glover for the design and fabrication of the vapor dispersion system and his leadership during the field study. Other personnel making significant contributions to this study were:

R. E. Erwin
M. C. Miller
J. Mishima
D. J. Newland
J. W. Sloot.

CHAPTER 1.

INTRODUCTION

BACKGROUND AND OBJECTIVES

The primary objective of this research program is to evaluate and model precipitation scavenging as a mechanism for removal of trace organic gases and vapors from the atmosphere. Significant levels of organic vapors in various stages of oxidation exist in both polluted and natural atmospheres, and the existence of measurable amounts of organic materials in natural rainwater has been recognized for some time. Junge (1963), for instance, indicates that about 1 milligram of organic per liter of rain may be expected under average rural pollution-level and rainfall conditions. This would mean that for over a land surface of one square kilometer, each millimeter of rain scavenges, under average rural conditions, about one kilogram of organic material.

Presumably the degree of organic scavenging varies with the concentration and type of material in question, although practically no research has been dedicated to this phenomenon to date insofar as gases and vapors are concerned. Also very little attempt has been made to isolate specific organics within natural rainfall samples, although the limited work that has been done in this area interestingly indicates that along with the simpler organics some surprisingly complex forms exist, including polysaccharides, organochlorine compounds, and Vitamin B_{12} (cf. Semenov, *et al* (1967) (1968), Tarrant and Tatton (1968), and Parker (1968)).

Significant experimental research has been carried out regarding the scavenging of organic particulates. These aerosols, however, which have been confined primarily to dye materials because of their utility as tracers, are not expected to show significantly different behavior from inorganic aerosols having similar physical characteristics. Because of this, the ongoing and past research involving aerosol scavenging can be considered to apply equally well to both organics and inorganics, and at present, a comparatively broad base of scientific information exists in this area.

This same statement cannot be made with regard to organic gases and vapors, however. Past studies of gas scavenging have been limited to inorganic materials, and only recently has their level of effort been advanced to a state comparable with that of aerosol research. During the past ten years, however, significant and encouraging advances in the field of gas scavenging have been made, including the field studies of I_2 and Br_2 washout by Engelmann (1968), the laboratory investigations of SO_2 and NO_2 washout by Georgi and Bielke (1970), the theoretical analysis of tritium washout by Hales (1972a) and the field and theoretical analysis of SO_2 washout by Hales and his coworkers (1972b) (1972) (1973).

These latter workers pointed out and experimentally verified the fact that for gas scavenging, both absorption of the gas into the raindrops and its desorption from the raindrops are important in the overall scavenging process. This "reversible" aspect depends primarily upon the solubility of the gas and contrasts with the behavior of aerosols, which can reasonably be assumed to attach permanently to raindrops in an "irreversible" manner.

Demonstration of the reversible interaction between trace gases and natural rain led to the development of a descriptive model for gas scavenging. Although generalizable to other source configurations, this model envisioned at the outset a plume emitted from a single point source as shown in Figure 1. Rain falling through the plume absorbed gas as it fell into the concentrated regions, and under some conditions desorbed material as it fell through the less concentrated areas below. The theoretical treatment was based on conventional mass-transfer theory; for the set of simplifying conditions including

1. A Gaussian plume with invariant background concentration
2. Vertical rainfall
3. Linear mass transfer and solubility behavior

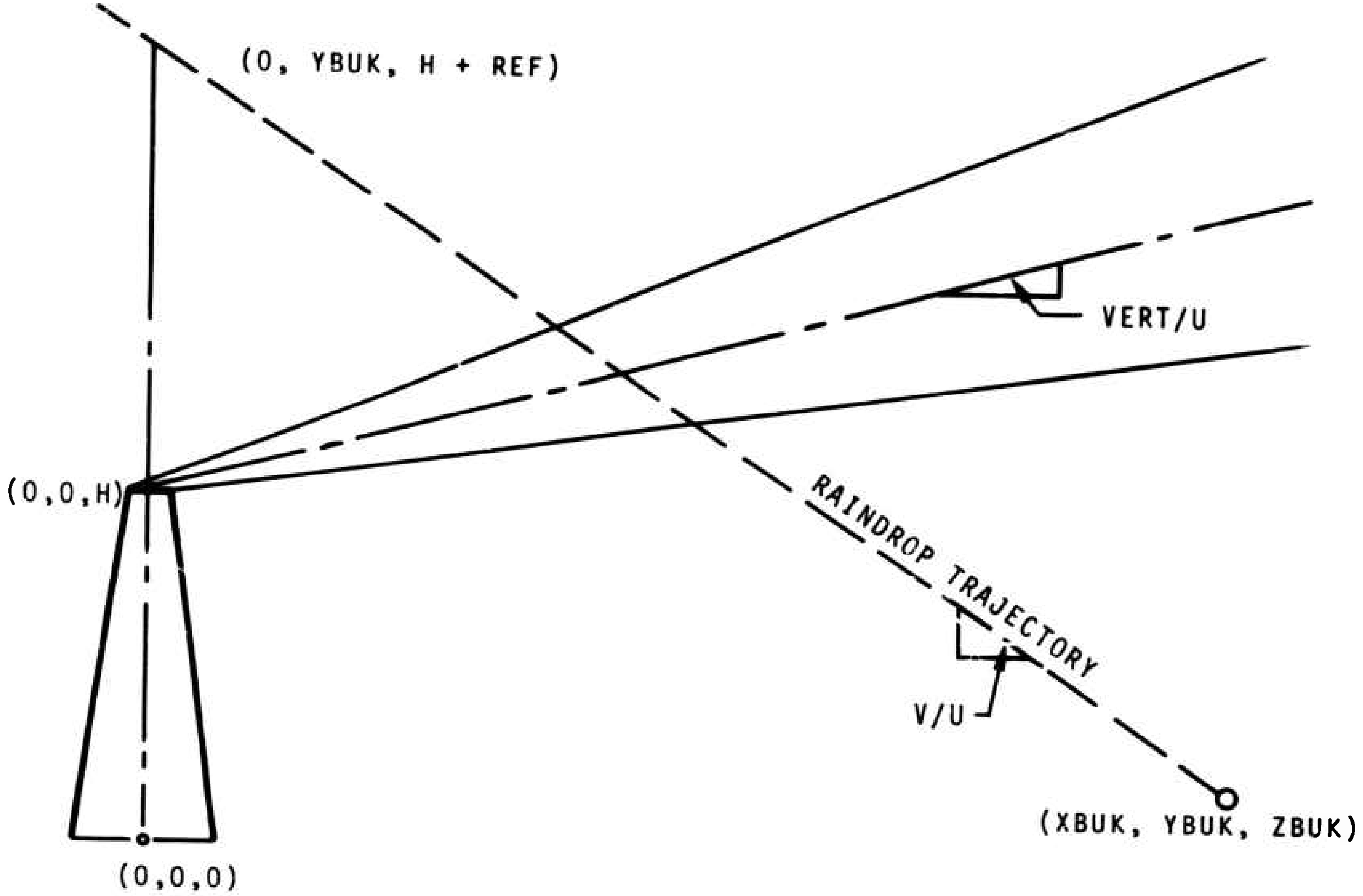

FIGURE 1. PICTORIAL BASES FOR EPAEC MODEL.

4. First-order gas-phase reaction kinetics, this model could be expressed explicitly in terms of the equations

$$c_{Ab}(a) = -\frac{3QK_y r}{2\sqrt{2\pi}\,\sigma_y\,\bar{u}v_z a}\exp\left(-\frac{y^2}{2\sigma_y^2}+\frac{\sigma_z^2\zeta^2}{2}\right)$$

$$\left\{\exp(\zeta h)\left[\left(1-\text{erf}\ \frac{-\sigma_z^2\zeta-h}{\sigma_z\sqrt{2}}\right)\right] \quad +\right.$$

$$\left. +\quad \exp(-\zeta h)\left[\left(1-\text{erf}\ \frac{-\sigma_z^2\zeta+h}{\sigma_z\sqrt{2}}\right)\right]\right\} \quad +$$

$$+\ y_{bkg}/H' \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$\zeta = \frac{3K_y H'}{av_z} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

and

$$r = \exp(-kx/\bar{u}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

where $c_{Ab}(a)$ is the concentration of pollutant in radius-a drops at the ground-level receptor point. Other terms in the equation are defined in the Table of Nomenclature and are summarized here as follows:

h = release height
H' = solubility constant
k = reaction rate constant
K_y = overall mass-transfer coefficient
Q = emission source strength
r = rate of chemical reaction of pollutant
v_z = terminal fall velocity of raindrop
y_{bkg} = background pollutant mixing ratio
σ_y, σ_z = plume dispersion parameters

A more accurate version of this model was subsequently developed, which was not constrained by assumptions 2 and 3 above. This version, which has been named the "EPAEC" scavenging model, cannot be presented in an explicit form similar to that of Equation 1. It can be described superficially, however, in terms of the computer subroutine hierarchy shown in Figure 2. This algorithm computes ground level concentrations numerically comparable to those calculated analytically by Equation 1. It also proceeds further to calculate weighted averages of concentrations in accordance with prescribed raindrop size statistics, and computes cumulative crosswind washout values. A feature of the EPAEC model is its modular construction, which enables rapid modification and maximum utility. Thus, if calculations for a different type of plume (a puff, say) were desired, one would simply replace the plume model module and proceed to execute the program. Similarly a variety of gases can be accommodated by utilization of the appropriate solubility model in the overall program. A detailed description of the EPAEC model has been presented in an earlier report (Dana (1973)) and is included with this document as an appendix.

SCIENTIFIC APPROACH

The EPAEC model is considered to be a rather realistic description of precipitation scavenging of gases from plumes. It has been shown to compare favorably with experimental measurements of SO_2 washout under a variety of conditions, indicating its potential utility as a means of investigating (and subsequently modeling) the washout of organic materials. The scientific approach of this program, therefore, is to perform field experiments of precipitation scavenging of organic gases under well-defined conditions and compare these results with corresponding predictions of the EPAEC model. Deviations between experiment and theory then can be analyzed in view of basic model assumptions and subsequent improvements can be attempted on the basis of this analysis. The following chapter presents a detailed description of these comparisons.

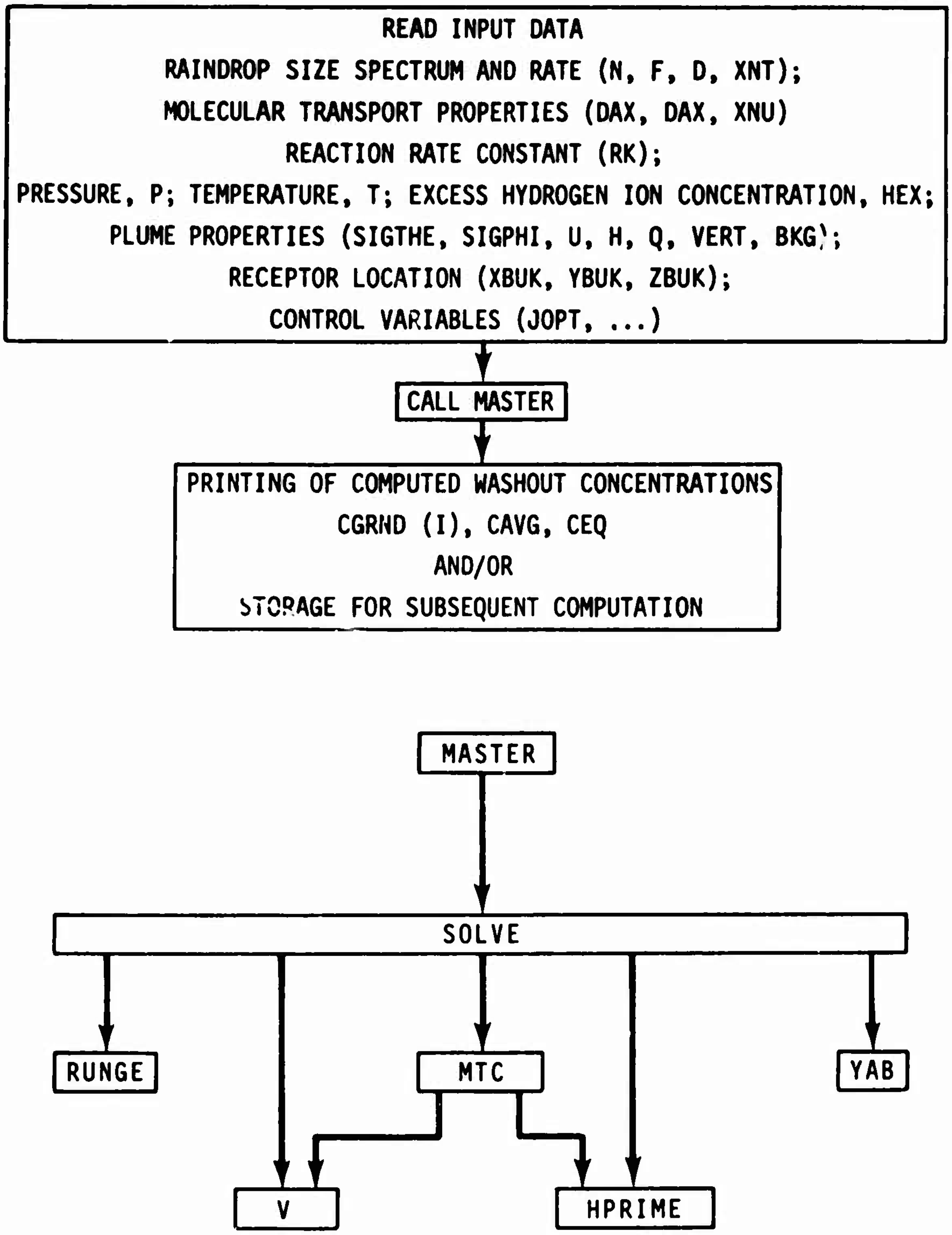

Figure 2. SUBROUTINE HIERARCHY IN EPAEC MODEL.

CHAPTER II.

FIELD EXPERIMENTS

The tests described in this report were conducted at the Quillayute Air field on the Olympic Peninsula of western Washington. This site offered the advantages of ample rainfall, a U. S. Weather Bureau station and isolation from pollution sources which might contribute significant background interference. While much of the terrain in this region is heavily wooded, the airfield provided a sizable area free of structures which would yield irregularities in the air motion over the sampling network. Although hangars located approximately a quarter mile upwind of the tower used to release the tracers may have been the source of turbulence observed during previous tests at this site, meteorological data recorded during this series provided no evidence of such turbulence. The stand-by status of the airfield allowed tests to be conducted without interference during daylight hours. However, its designation as an emergency landing strip required the tower to be lowered during the evening hours in order to eliminate it as a hazard to aircraft requiring use of the airfield during this period of reduced visibility. This stipulation limited the number of tests which could be conducted and extended the time required to put the release equipment into operation.

Figure 3 illustrates the distribution of the rain samplers with respect to the tower. Arc A, at 300 feet, consisted of 17 sampling sites located at 5° intervals within the 80° arc defined by lines drawn NNE(20°) and WNW(300°) from the tower. Arc B consisted of 29 sampling locations encompassing the same angle as arc A and following the geometry of the airfield runways. Although the prevailing winds during each test carried the tracer through the region described by the arcs, additional samplers were set out during experiments 2, 3, 4 and 5 to insure plume enclosure.

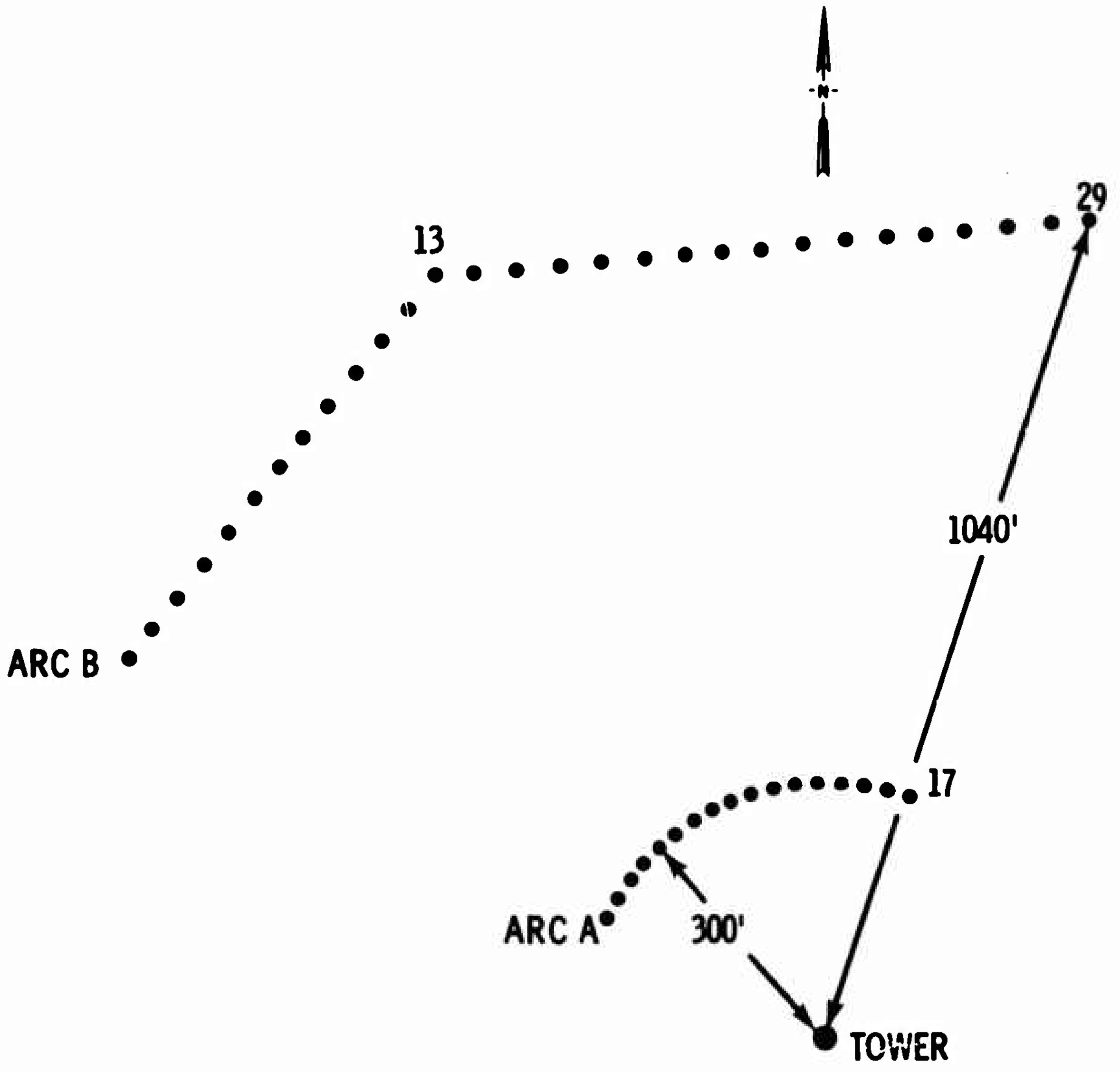

Figure 3. DISTRIBUTION OF SAMPLING SITES WITH RESPECT TO THE SOURCE.

Rain samples were collected in polyethylene bottles fitted with 7 3/8-inch polyethylene funnels as shown in Figure 4. In order to inhibit desorption of the volatile tracer, the rain was frozen as it was collected. This was accomplished by thermally insulating the sample bottles in polystyrene containers and surrounding them with dry ice.

In addition to the collection of rain samples, the integrated vapor phase concentration of tracer at ground level was determined through the use of a limited number of vapor samplers, Figure 4. These units consisted of a battery-operated pump which drew air at 1 lpm through an impinger containing 10 ml of distilled water (ethylacetoacetate release) or 10 ml of 5×10^{-5} N nitic acid (diethylamine release). At the conclusion of an experiment, the impinger solutions were transferred to polyethylene bottles for storage. The impingers were then rinsed with distilled water in preparation for the next test. Addition of fresh distilled water or dilute acid was delayed until the period immediately preceding the next experiment. Analysis of the impinger solution gave the total mass of tracer in the air sampled and provided an indication of the contribution of dry deposition to the tracer concentration of the rainwater. Since only a limited number of the vapor samplers were available, their distribution among the sampling sites was dictated by the observed wind conditions prior to release of the tracer.

Of major concern in determining the success of the washout experiment was the tracer dispersion system. Since one of the tracers was not especially volatile (boiling point 180°), it was essential that complete evaporation be assured while maintaining a rate of release which was sufficient to allow detection of the tracer in the downwind precipitation samples. The tracer dispersion equipment designed and built by Battelle-Northwest to meet the above requirements is shown in Figures 5 and 6. It consists of a 5-gallon storage tank, a compressed air cylinder and vapor gun containing two sonic nozzles mounted inside an 8-inch aluminum tube. Release was made by transferring the tracer under low pressure to the sonic nozzles and injection into the atmosphere by high pressure air from an air compressor. A heat gun was positioned directly behind the

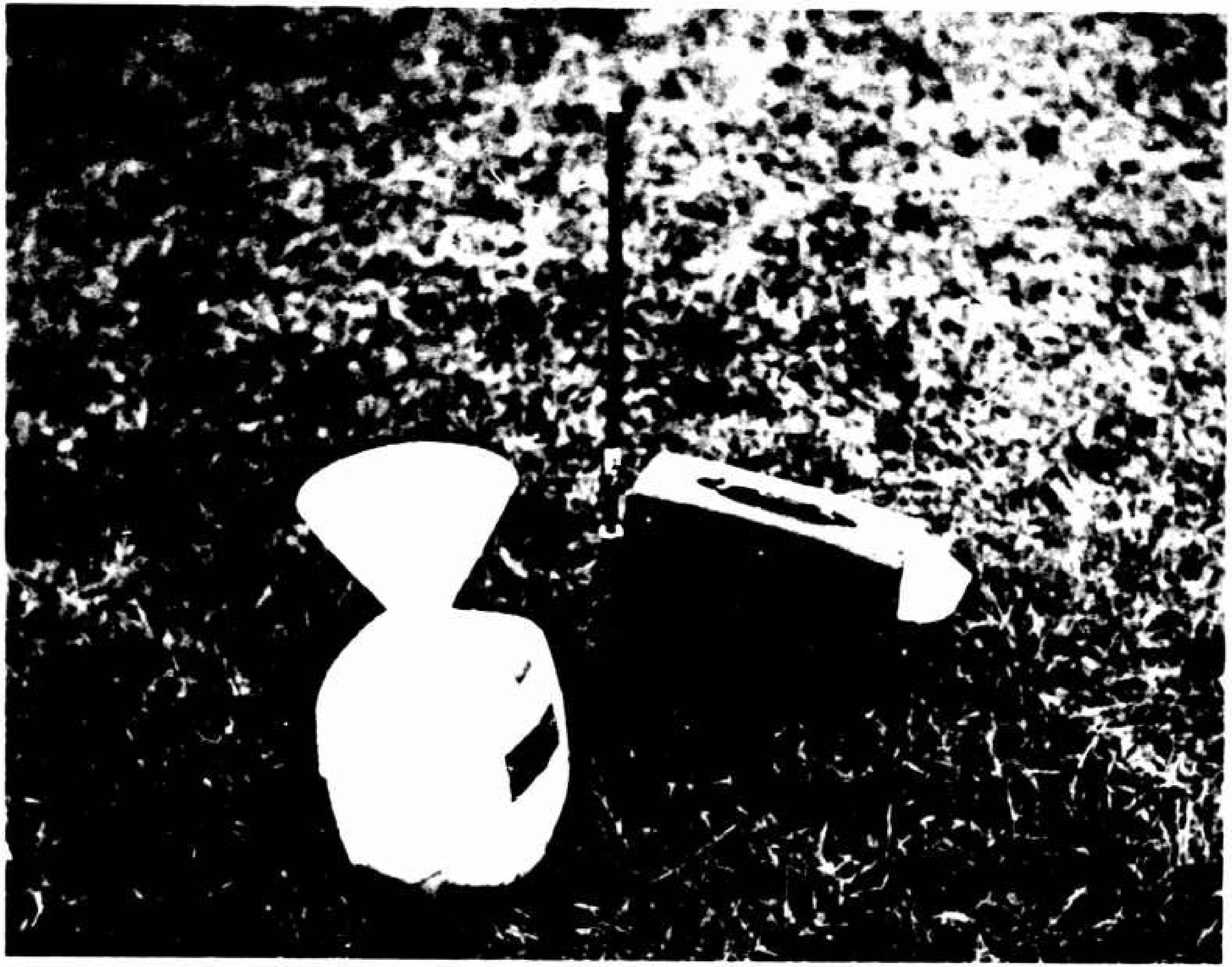

Figure 4. RAINWATER AND VAPOR SAMPLERS.

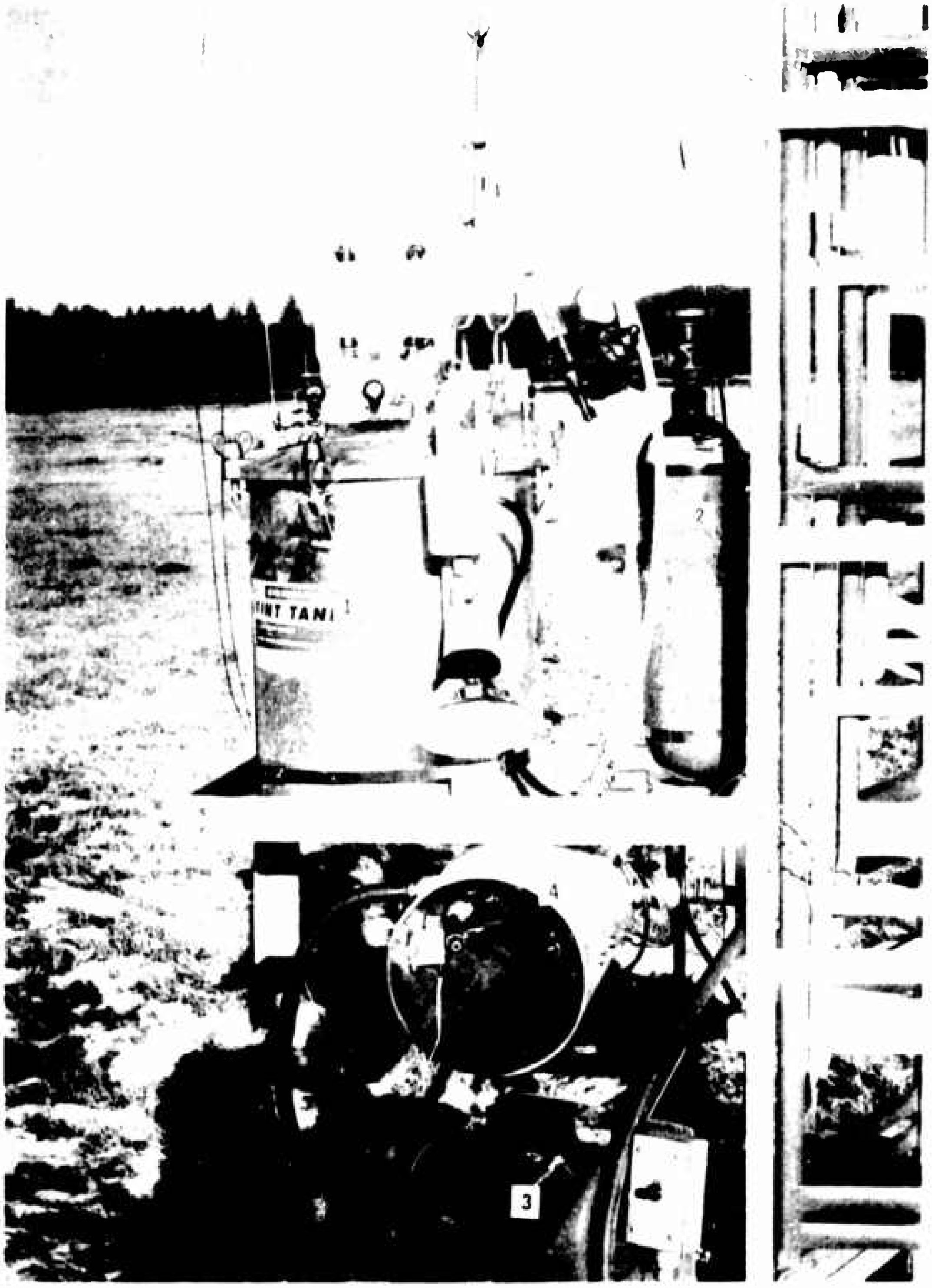

Figure 5. VAPOR DISPERSION ASSEMBLY: 1. TRACER STORAGE TANK; 2. NITROGEN FOR LOW PRESSURE TRANSFER OF TRACER; 3. AIR COMPRESSOR; 4. VAPOR GUN.

Figure 6. VAPOR GUN. 1. HEAT GUN
2. SONIC NOZZLES

sonic nozzles so that the air stream receiving the tracer was slightly above ambient temperature. Ground level testing of this equipment is shown in Figure 7.

When favorable test conditions were observed, the tower was raised, the tracer storage tank filled and the vapor dispersion equipment secured at the top of the tower (100 ft). The configuration of the meteorological sensors and the release equipment is shown in Figure 8. While the tower was being placed in position, the rain and vapor samplers were distributed as illustrated previously. In order to confine sampling as nearly as possible to the period of release, the impingers were turned off and the rain samplers covered until tower preparation was complete. The sampling equipment was then placed in operation before generation of the organic plume. Although some rain was necessarily collected before dispersion of the tracer, the effect of the resulting dilution was at least partially compensated for by the procedure followed in retrieving the samples. Samples were collected in a sequence which was the same as that followed in putting them into service.

In addition to the downwind sampling locations identified in Figure 3, at least one background rain and vapor sample was obtained at a site >100 feet upwind of the source. These samples were handled in the same manner as those located downwind of the tower. The results of the chemical analysis of all field samples are recorded in Appendix D. It will be noted that most background samples appear to indicate the presence of some tracer. The origin of this apparent tracer load is discussed in Chapter 5. It is evident, however, that the magnitude of this background interference is too low to obscure the washout behavior of the tracers.

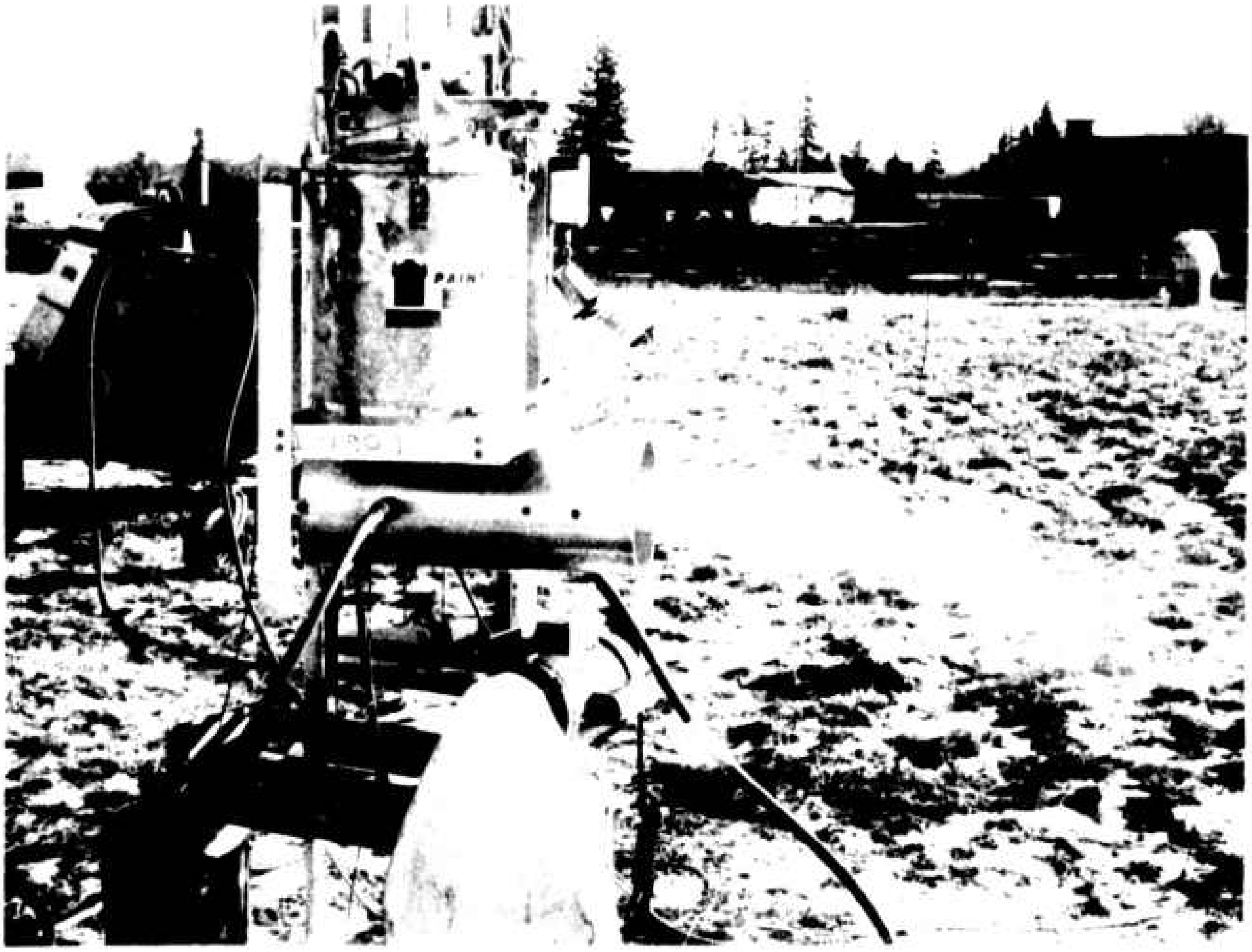

Figure 7. GROUND LEVEL TEST OF VAPOR DISPERSION EQUIPMENT.

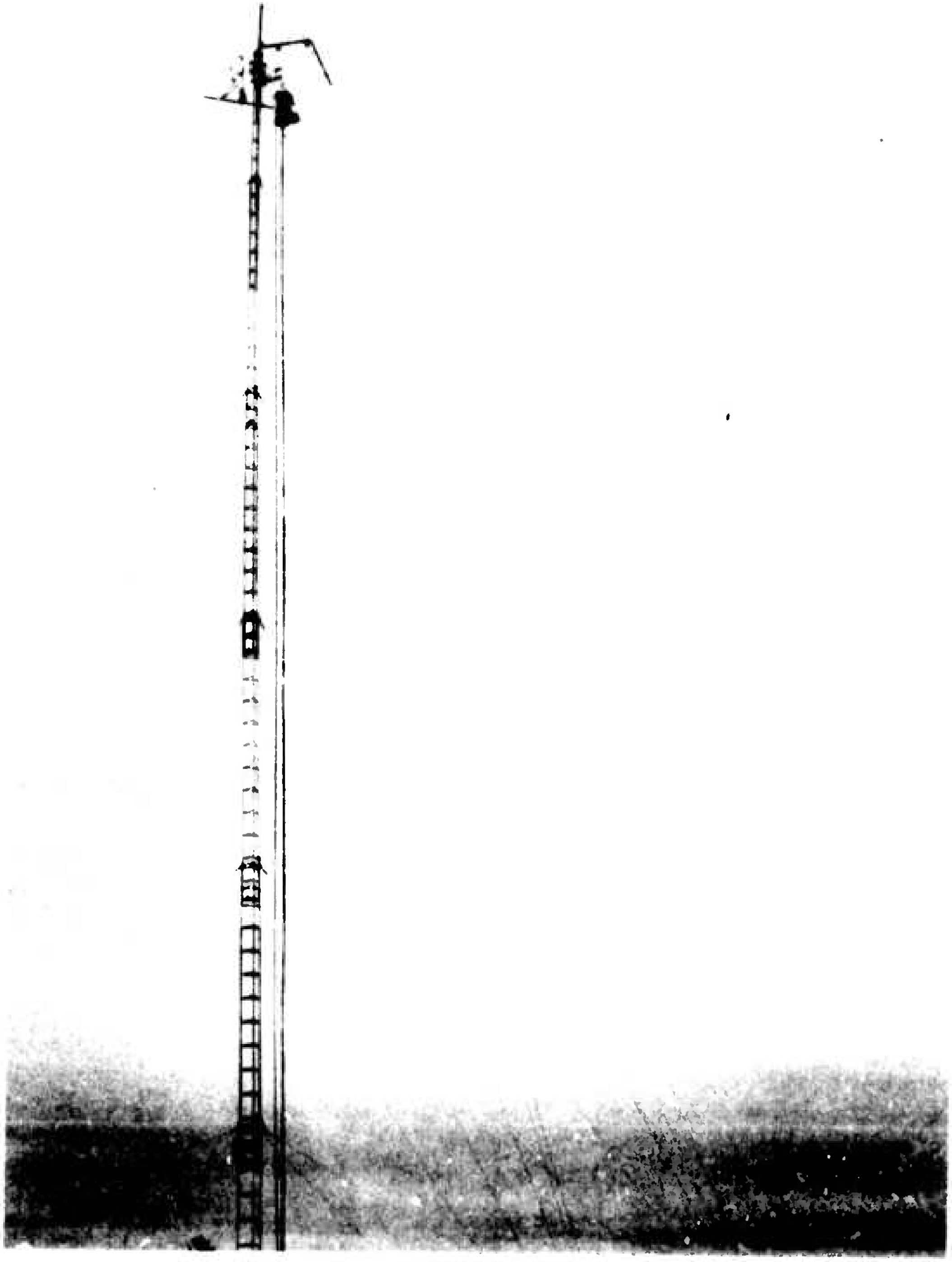

Figure 8. OPERATION OF VAPOR DISPERSION EQUIPMENT DURING FIELD EXPERIMENTS

CHAPTER III.

CHEMICAL ANALYSIS

ANALYTICAL PROCEDURES

Analysis of field samples was accomplished by colorimetric methods which are documented in the chemical literature. The initial phase of this study was directed to the investigation of these procedures in order to determine their respective detection limits and identify problems which might arise from the methods to be used for the collection and storage of the field samples. This preliminary work as well as the subsequent analysis of field samples was done with a Bausch and Lomb Spectronic 20 spectrometer using a 1-inch test tube as the sample cell. A discussion of this preliminary work will provide an indication of the confidence one can place in the results tabulated in Chapter 5 and follows a description of the ethylacetoacetate and diethylamine analysis procedures.

Ethylacetoacetate Analysis--A 25.0 ml aliquot of the ethylacetoacetate solution was pipetted into the spectrometer cell followed by 2.0 ml of chilled diazonium salt solution prepared by mixing equal volumes of 0.5% potassium nitrite and 0.0074 M p-aminoacetophenone (0.1 M in HCl). Addition of 1.0 ml of reagent grade piperidine to the well-mixed solution produced a transient diazonium addition product having an absorption maximum at 435 nm. Observation of the change in transmittance with time confirms the report published in the Operation Procedure Guide (1965) that maximum color development occurs 3 minutes after piperidine introduction, and does not undergo noticeable decay for a period of more than 1 minute. Transmittance readings were therefore taken 3 to 4 minutes after piperidine addition.

The analysis of standard ethylacetoacetate solutions shows the Beer's Law plot to be linear to 24 μg (0.96 ppm) with a detection limit of 1.0 μg (0.04 ppm).* Analysis of those solutions which show concentrations greater than 0.9 ppm were repeated using a smaller sample aliquot, diluting to 25.0 ml and analyzing as before.

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* An estimate of the analytical error was obtained from analysis of standard solutions included with each batch of field samples. These solutions, spanning the linear Beer's Law range, show a standard deviation of less than 25 per cent.

Diethylamine Analysis--The colorimetric procedure reported by Dahrgren (1964) for the analysis of aqueous amine solutions was adopted for this study. A 25.0 ml aliquot of the sample solution was pipetted into the spectrometer cell and the pH adjusted by the addition of 1.0 ml of phosphate buffer (pH 6.6). One milliliter of 10^{-3} M sodium hypochlorite was added allowing 10 minutes for complete conversion of the amine before destroying the excess hypochlorite with 1.0 ml of 0.5% sodium nitrite. Reaction of the chloramine product with 1.0 ml of starch-potassium iodide solution yielded the intense blue color characteristic of the starch-triiodide complex. Fifteen minutes was allowed for maximum color development before measuring the transmittance at 540 nm.

Examination of a series of standard diethylamine solutions shows a linear Beer's Law plot to at least 10.0 μg (0.5 ppm) with a detection limit of approximately 2 μg (0.08 ppm).*

Since all field samples were frozen during collection and stored at subfreezing temperatures, these solutions were allowed to warm slowly to room temperature before proceeding with the analysis as outlined above.

STABILITY OF AQUEOUS TRACER SOLUTIONS

Among the questions which required examination before proceeding with the field tests was the problem of tracer stability. As with all experiments dependent on accurate chemical analysis of environmental samples, it was exceedingly important to consider those mechanisms which might diminish tracer concentration during storage. Since the rain samples were frozen as they were collected, desorption of the volatile organic during the field tests does not appear to be a viable path for tracer loss. However, chemical reaction, such as hydrolysis of ethylacetoacetate, and adsorption to container walls during storage were recognized as

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*As with the ethylacetoacetate samples, solutions containing known amounts of diethylamine were analyzed with the field samples. This served as a means of insuring against possible positive interference by ammonia in the reagent solutions and allowed an estimate of precision. These results, as well as multiple analysis of some field samples, suggest a maximum experimental error of approximately 30 per cent.

potentially significant. Some insight into the role of these processes was gained by preparing dilute solutions of the tracers, and storing them at room temperature in polyethylene bottles of the type used in the field experiments. Analysis performed on aliquots of these solutions were in excellent agreement with those conducted immediately after their preparation. Some of the data acquired during this preliminary study are summarized in Table 1. It is evident from this work that dilute tracer solutions are sufficiently stable to allow them to be stored for several weeks. Storage at sub-freezing temperatures and analysis at the Battelle Hanford laboratory was therefore adopted as the procedure to be followed in handling the field samples.

TABLE 1.

STABILITY OF AQUEOUS TRACER SOLUTIONS

Tracer	Initial Concentration	Concentration (Days of Storage)	
Ethylacetoacetate	0.81 ppm	0.81 (4)	0.83 (24)
Ethylacetoacetate	0.40	0.43 (4)	0.42 (24)
Diethylamine	0.25	0.26 (29)	

The vapor sampling systems used to provide a measure of the integrated plume concentration at ground level, while not essential to the field program, did provide input for accessing the contribution of dry deposition to the tracer load of the collected rain samples. Since the utility of these systems depended on the efficient removal of the tracer from air drawn through a midget impinger, preliminary work included an investigation of these systems. These tests consisted of placing a dilute solution of the tracer in the impinger and drawing clean air through it for a period of approximately two hours. The impinger solutions were analyzed to determine the evaporative loss of tracer during operation of the sampler. As with the field experiments, distilled water was used for the ethylacetoacetate test and dilute nitric acid (5×10^{-5} N) for the diethylamine test. The results recorded in Table 2 illustrate that dilute acid forms an efficient trap for diethylamine capture while distilled water is somewhat less effective in scrubbing ethylacetoacetate from air drawn through the impinger. Samples obtained during Experiments 1 and 4 have been analyzed and the calculated mass of tracer in each sample recorded in Tables 14 and 18.

TABLE 2.

THE RESULTS OF TESTS DESIGNED TO INDICATE THE EFFICIENCY OF THE VAPOR, SAMPLING SYSTEM

	Impinger	µg Tracer		Period of	
Tracer	Solution	Initial	Final	Operation	Per Cent Loss
Ethylacetoacetate	distilled water	20.2	12.3	2 hr. 15 min.	39
Diethylamine	5×10^{-5} N HNO_3	5.0	5.1	2 hr.	0

CHAPTER IV.

DATA PROCESSING

As indicated in Chapter II, a number of support measurements were performed in addition to the assessment of washout concentrations. These included the anemometer measurements, rain-gauge records and raindrop-size spectrum determinations. This section describes the procedures used for processing these data.

The Gill anemometer data were processed in several stages. The first of these steps involved reading the field-generated METRODATA tapes, converting the raw data, and writing on industry-compatible 7-track tapes using a Battelle Atmospheric Sciences Department-owned NOVA computer. This system employed a data culling routine which detected and flagged faulty data entries on the output tapes, so that tape quality could be monitored visually by observing printed listings.

The 7-track tapes were listed using a high speed printer in conjunction with an AEC-owned UNIVAC 1108 computer. These listings, which were in the form of tables giving clock readings and uncalibrated values of the U, V, and W wind components at 0.42 second intervals, were scrutinized for faulty data as detected by the NOVA culling routine. These checks showed that the wind data had been recorded with high quality; the few culled data points that did appear in the records were replaced with the values immediate preceding, resulting in essentially zero distortion of the processed results.

Following the quality-control checks, the 7-track data tapes were resubmitted to the UNIVAC computer where calibrated mean wind velocities, directions, and standard deviations of vertical and azmuthal wind directions were calculated. Computed standard deviations were based on sampling and averaging times of, respectively, the experiment times and one-fourth the source-receptor transit times. Formulae employed for this purpose are listed as follows:

$$\bar{\theta} = 180^\circ - 57.3 \frac{\Sigma(\tan^{-1} \frac{u}{v})}{N} ,$$

$$\sigma_\theta = \{\frac{\Sigma([\tan^{-1} \frac{u}{v}]^2)}{N} - [\frac{\Sigma(\tan^{-1} \frac{u}{v})}{N}]^2\}^{1/2},$$

$$\sigma_w = \{\frac{\Sigma w^2}{N} - [\frac{\Sigma w}{N}]^2\}^{1/2} ,$$

$$\sigma_\phi = \frac{\sigma_w}{\bar{u}}$$

The nomenclature in these equations is consistent with that used throughout the meteorological literature and is defined in the Table of Nomenclature. Results of these calculations for the anemometer data taken from the field experiments of this study are given in Table 3.

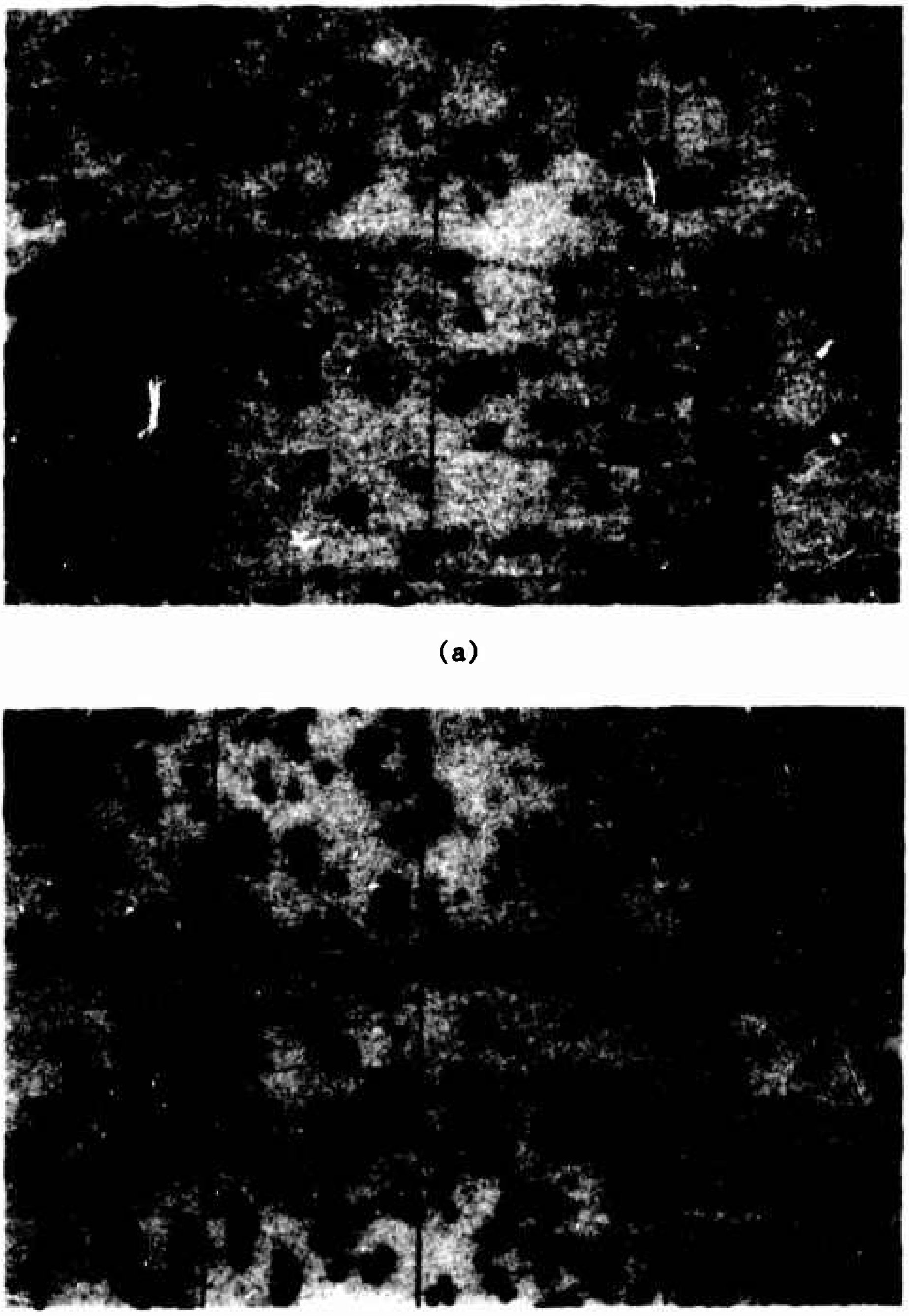
TABLE 3.

METEOROLOGICAL PARAMETERS CALCULATED FROM GILL ANEMOMETER DATA

Run	Sampling Time Sec.	Average Wind Speed cm/sec	Average Heading, (From True North) Radians	σ_θ Radians	σ_ϕ Radians
1A*	300	416.6	2.68	0.159	0.0435
1B	1210	467.2	2.79	0.224	0.0727
2	1490	328.4	2.55	0.233	0.0674
3	2390	376.3	2.93	0.137	0.0757
4	1820	711.2	3.00	0.0942	0.0648
5	1620	711.7	3.00	0.105	0.0676

*Run 1 divided into two components owing to temporary lull in rain and consequential shutdown during mid-experiment.

Operation of the raindrop spectrometer provided ozalid images as shown by the example in Figure 9. The sizes of these raindrop images were related to actual drop sizes by a previous calibration: thus the raindrop spectra



(a)

(b)

Figure 9. REPRESENTATIVE OZALID IMAGES FROM (a) EXPERIMENT 3 AND (b) EXPERIMENT 5.

could be obtained simply by sizing the images and applying the calibration. Image sizing was performed using a Zeiss Spectrometer. Resulting raindrop size spectra determined for each of the five tests are presented in Table 4.

Table 4. MEASURED RAINDROP SIZE SPECTRA AND RAIN RATES.

Size Range (Diameter) mm	Run 1	Run 2	Run 3	Run 4	Run 5
0- .224	0.122	0.305	0.134	0.170	0.237
.224- .349	0.268	0.389	0.230	0.285	0.180
.349- .417	0.069	0.058	0.111	0.090	0.094
.417- .497	0.147	0.033	0.065	0.050	0.075
.497- .594	0.182	0.028	0.054	0.035	0.043
.954- .710	0.081	0.033	0.122	0.065	0.113
.710- .847	0.039	0.051	0.094	0.110	0.075
.847-1.011	0.036	0.045	0.088	0.085	0.056
1.011-1.321	0.042	0.051	0.074	0.070	0.082
1.321-2.117	0.009	0.007	0.028	0.040	0.045
Mass Mean Drop Size mm	0.602	0.590	0.726	0.740	0.772
Rain Rate cm/hr	0.20	0.59	0.25	0.25	1.1

In addition to showing the raindrop spectra, Table 4 presents the mean rainfall rates recorded onsite by the fast-response rain gauge. The data obtained from this unit were intended primarily for the purpose of analyzing the effects caused by the finite time intervals required for deployment of the sampling arcs; actual charts from the rain gauge for each test are reproduced in Appendix C.

Computations with the EPAEC model required, in addition to the data provided in Tables 3 and 4, information pertaining to the molecular transport and solubility properties. Values of the specific properties needed for this purpose are given in Table 5.

Table 5. SOLUBILITY AND MOLECULAR TRANSPORT PROPERTIES.

	Ethylacetoacetate	Diethylamine
Diffusivity in Air cm^2/sec	.074	.096
Solubility in Water* at 10° C $moles/cm^3$	4.0	.091
Kinematic Viscosity of Air cm^2/sec	.14	

* Defined by: Solubility $= \frac{1}{H'} = \frac{c}{y}$, where c is the liquid phase concentration in $moles/cm^3$ and y is the gas-phase mole fraction.

Diffusion coefficients of the test materials were calculated using collision integral theory; associated errors are expected to be of the order of five percent. Solubilities appearing in Table 5 are known with much less certainty, perhaps being in error by factors of five or more. The reason for this uncertainty is the unanticipated lack of solubility data reported for these materials at the low concentrations of present interest. These values are "best estimates" obtained from high-concentration data by assuming the validity of Henry's Law and applying the Clausius Claperyon Equation. A detailed description of the calculations leading to the values in Table 5 is given in Appendix A.

A description of the actual entry of data into the EPAEC model can be facilitated by considering the input segment of the program reproduced below:

```
100   READ   (5,320)    N,J1,J2,J3,J4,JOPT,JP,JEND
      IF    (J1.EQ.1)   GO TO 110
      READ   (5,330)    (D(I),I=1, N)
      READ   (5,330)    (F(I),I=1, N)
110   IF    (J2.EQ.1)   GO TO 120
      READ   (5,340)    DAX,DAY,HEX,XNU,P,T,XNT,RK
120   IF    (J3.EQ.1)   GO TO 130
      READ   (5,350)    SIGTHE, SIGPHI,U,H,Q,VERT,BKG
130   IF    (J4.EQ.1)   GO TO 140
      READ   (5,360)    XBUK,YBUK,ZBUK,DELTAY,DELTAZ
```

The first READ statement reads the number of steps in the discrete raindrop size spectrum (N) in addition to a series of control variables. If these are set as follows:

J1-J4 = 0
JOPT = 1 for gas-phase limited conditions. JOPT = 0 for stagnant-drop conditions.

JP = 1
JEND = 0.

The variables used in this code are described in detail in Appendix E and will only be summarized here, as follows:

D, F - Raindrop Diameter and Frequency

DAX*, DAY - Liquid and Gas Phase Diffusivities

HEX* - Solubility Parameter

P, T, XNT - Pressure, Temperature, Rain Rate

RK* - Reaction Rate Constant

SIGPHI, SIGTHE, U, H, Q - Plume Parameters

VERT* - Plume Loft Velocity

BKG* - Background Concentration

XBUK, YBUK, ZBUK, DELTAY, DELTAZ - Receptor Location and Grid Spacing Parameters

A typical listing of input data is given below:

```
5     0    0     0    0     0    1    1

.01        .02        .03        .04        .05
.05        .10        .25        .45        .15
           .74E-1                1.4E-1     1.0E0     2.90E2    1.3E-4
.062       .056       5.13E2     3.05E3     6.6E-2
 3.0E4
```

---

*Variable not significant to present useage of program.

Solubility data were entered in subroutine form rather than through READ statements. The EPAEC routine was executed several times for each run to test the effects of varying solubilities. These results are presented for each field experiment in the following chapter.

CHAPTER V.

RESULTS

In the preceding chapters we have attempted to place this work with respect to previous investigations of washout and the contribution of this study to the development of a comprehensive washout model. We have also sought to identify and explore questions having a direct bearing on the results of this study and hence the interpretations and conclusions to be drawn from it. In this chapter we will discuss the five field experiments which focus on the washout behavior of ethylacetoacetate and diethylamine vapors. A description of the meso and micro scale meteorology will be followed by descriptive observations taken from the field notes and a graphical presentation of the analytical data. The observed tracer concentrations in rain water will then be compared with those predicted by the washout model. Since the tracer solubilities calculated in Appendix A represent only estimates based on the best available literature data, concentrates are also predicted assuming a range of different solubilities including infinite solubility ($H' = 0$).

EXPERIMENT 1

Experiment 1 was conducted on January 11, 1973. At 0100 an occluded frontal system had passed Quillayute moving eastward. At 1000 a very deep cold, low pressure area was located 630 nautical miles west-northwest of the test site, oscillating and moving slowly northward. The low sloped west-northwest aloft, causing a strong southwesterly flow of cold, moist, unstable air with a series of low-amplitude short waves moving rapidly around the low system and onto the Washington and Oregon coasts. This brought shower activity and orographic precipitation to the test area. A 110-knot jet stream oriented southwest to northeast over Hoquiam, Washington was moving southward keeping the primary storm track south of the test area. The freezing level was at approximately 5200 feet.

All precipitation and vapor samplers were in operation by 1130 PST. Release of ethylacetoacetate commenced at 1150, was interrupted momentarily from 1158 to 1159 when the rain stopped and terminated at 1209. The average rainfall rate was 0.20 cm h^{-1} during the test period. Winds were generally out of the south-southeast (157°) at about 9 mph with occasional gusts up to 20 mph. A total release of 9.8 liters was accomplished over the 18-minute experiment.

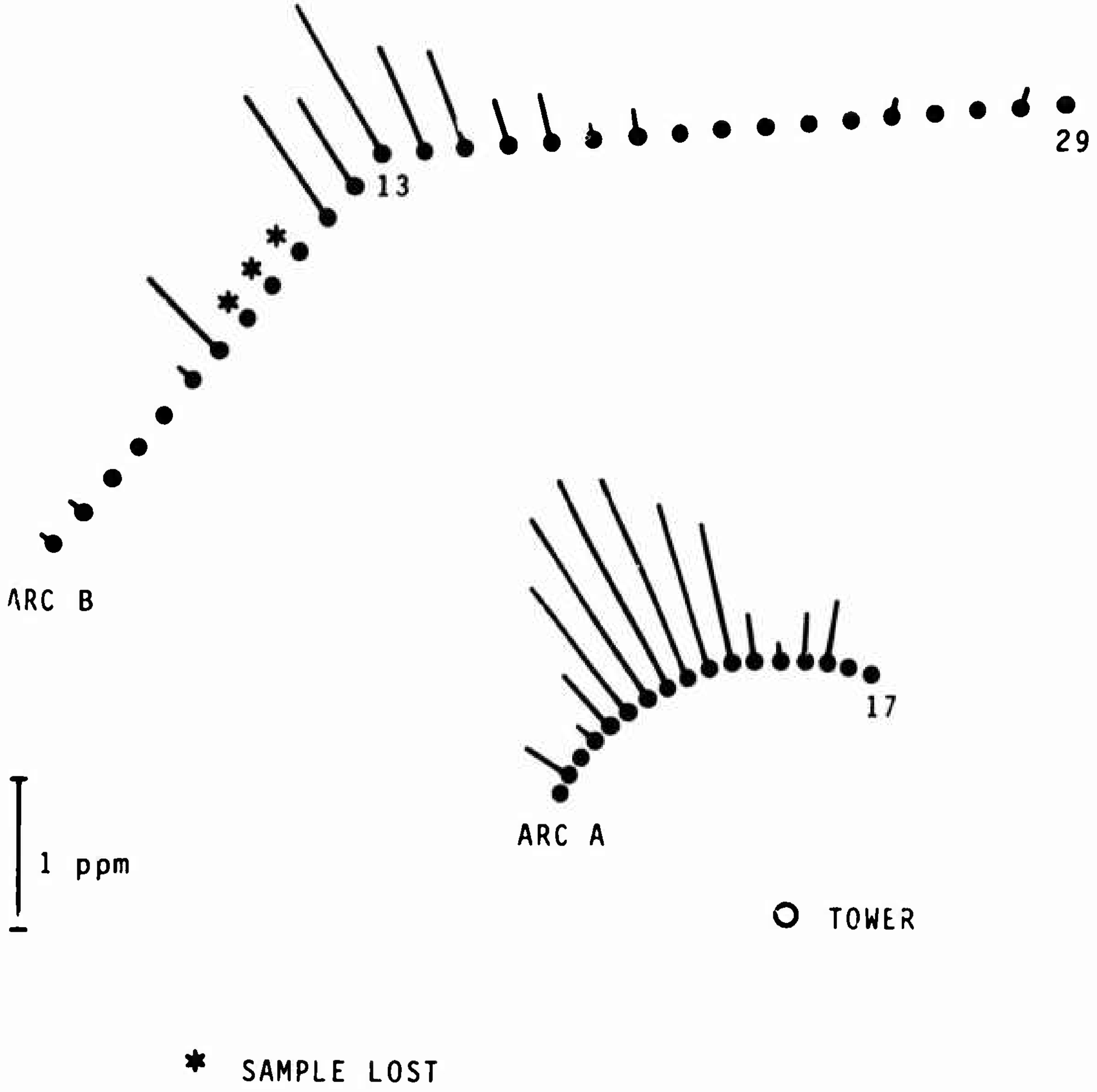


Figure 10. MEASURED CONCENTRATIONS OF EAA IN RAINWATER, RUN 1.

TABLE 6.

OBSERVED TRACER CONCENTRATION VERSUS CONCENTRATIONS PREDICTED FOR VARIOUS SOLUBILITIES - EXPERIMENT 1 (EAA).

Station	$C_{obs.}$	$C_{H'=0}$	$C_{H'=0.25}$	$C_{H'=4}$
A 3	<0.10 ppm	0.04 ppm	0.04 ppm	0.02 ppm
4	0.16	0.19	0.18	0.10
5	0.50	0.35	0.71	0.34
6	1.1	2.61	2.41	0.94
7	1.5	9.10	7.96	1.96
8	1.6	36.2	27.7	2.97
9	1.5	16.6	13.9	2.63
10	1.2	4.98	4.48	1.44
11	1.0	0.79	1.12	0.52
12	0.32	0.26	0.25	0.14
13	0.10	0.05	0.05	0.02
B 8	--	0.06	0.05	0.02
9	--	0.24	0.21	0.07
10	--	0.80	0.67	0.20
11	1.0	2.11	1.68	0.43
12	0.70	4.32	3.18	0.71
13	1.2	6.39	4.43	0.91
14	0.78	5.90	4.21	0.87
15	0.73	3.29	2.54	0.58
16	0.33	1.48	0.97	0.27
17	0.35	0.31	0.27	0.09
18	0.12	0.07	0.06	0.02

EXPERIMENT 2

Experiment 2 was performed on the afternoon of January 11, 1973. The synoptic pattern and upper air flow was therefore the same as described for Experiment 1. A weak frontal system was developing approximately 240 nautical miles off the Washington coast and most stations in western Washington were reporting rain or rain shower activity. The freezing level at the time of release had fallen to 4200 feet.

Anemometers at the test site showed light southeasterly winds at the release height and ground level winds with a more easterly orientation. In response to this observation three additional rain samplers were added to the western edge of both arc A and B to insure plume enclosure. Release of ethylacetoacetate was initiated at 1519 and terminated at 1543 after a discharge of 11.4 liters of the tracer. The rainfall rate averaged approximately 0.59 cm hour^{-1}. Winds were generally out of the southeast (146°) at 7 mph and gusting to a maximum of 22 mph.

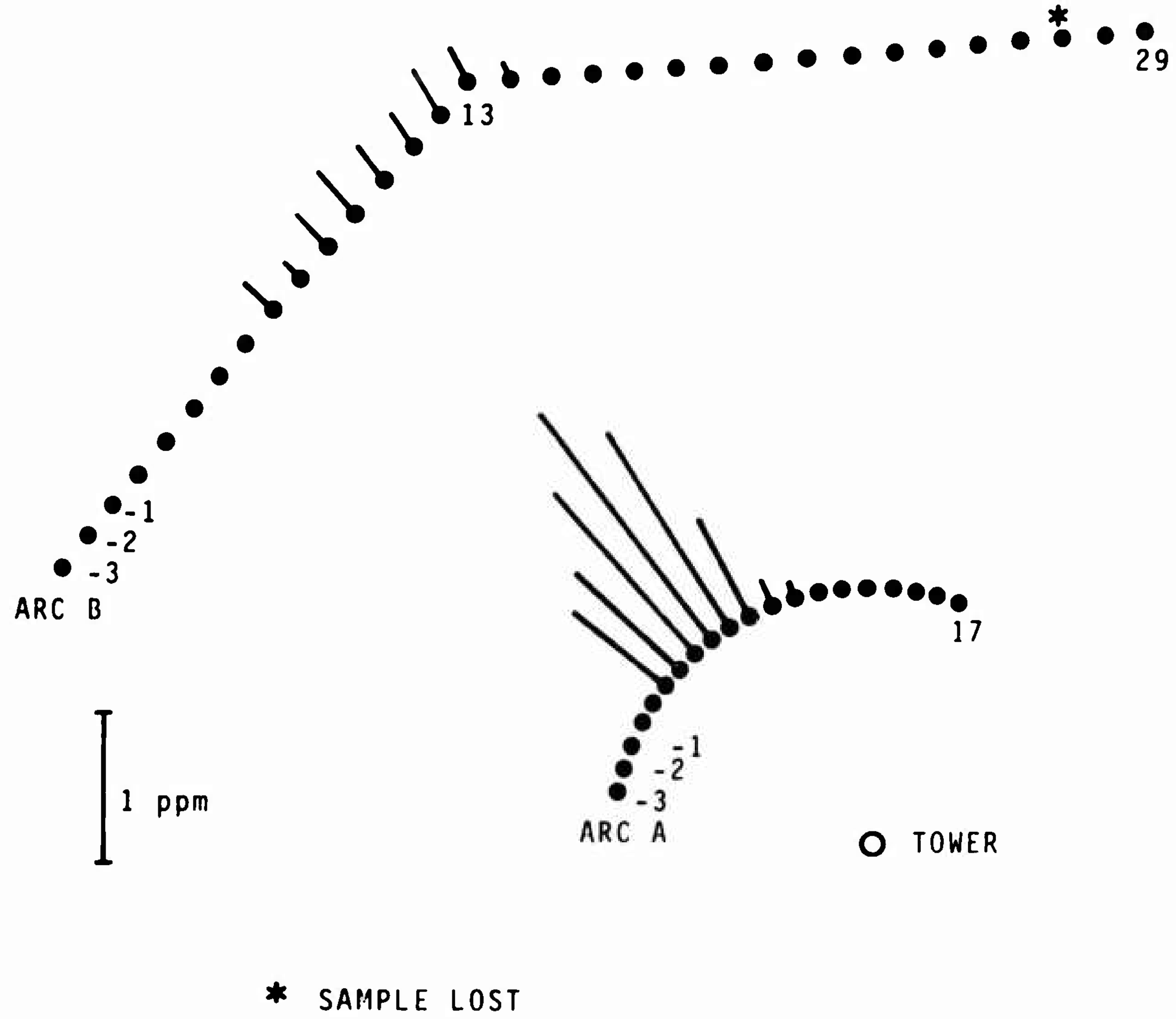


Figure 11. MEASURED CONCENTRATIONS OF EAA IN RAINWATER, RUN 2.

TABLE 7.

OBSERVED TRACER CONCENTRATION VERSUS CONCENTRATIONS PREDICTED FOR VARIOUS SOLUBILITIES - EXPERIMENT 2 (EAA).

Station	$C_{obs.}$	$C_{H'=0}$	$C_{H'=0.25}$	$C_{H'=4}$
A 1	<0.10 ppm	0.29 ppm	0.27 ppm	0.14 ppm
2	<0.10	0.94	0.89	0.43
3	0.80	2.6	2.38	1.03
4	1.0	5.8	5.23	1.97
5	1.5	12.0	9.99	2.94
6	2.0	50.3	28.7	3.39
7	1.6	12.0	9.99	2.94
8	0.77	5.8	5.23	1.97
9	0.20	2.6	2.38	1.03
10	0.11	0.94	0.89	0.43
11	<0.10	0.29	0.27	0.14
12	<0.10	0.07		
13	<0.10	0.02		
B 5	<0.10	0.01		
6	0.26	0.05		
7	0.16	0.19	0.16	0.06
8	0.31	0.62	0.49	0.17
9	0.36	1.7	1.23	0.38
10	0.31	3.7	2.44	0.68
11	0.27	6.2	3.73	0.97
12	0.37	7.5	4.31	1.09
13	0.28	6.2	3.73	0.97
14	0.12	3.7	2.44	0.68
15	<0.10	1.7	1.23	0.38
16	<0.10	0.62	0.49	0.17
17	<0.10	0.19	0.16	0.06
18	<0.10	0.05		

EXPERIMENT 3

This experiment was conducted on January 12, 1973. At 1400 PST a primary low pressure system had moved northward into the southwestern Gulf of Alaska. A broad surface trough line extended southward from the low with a developing wave in this trough line located approximately 480 nautical miles southwest of the test site and moving to the northeast. A weak warm front from this wave intersected the Oregon coast between Newport and Astoria moving northward at 27 knots and causing light overrunning precipitation to the north. The upper-air low pressure area had moved eastward to about 700 nautical miles off the coast of Vancouver Island causing a lower-atmosphere flow of cold, moist, unstable air from the southwest (230°). Light shower activity and orographic precipitation combined with the overrunning to give continuous precipitation of variable intensity. The early morning freezing level was at 6300 feet and dropped to about 2200 feet by 1600 PST. The main storm track was kept to the south of the test site by a 90-knot jet stream oriented at 260° and passing over Newport, Oregon.

Prior to release of diethylamine, winds at the 100 foot level were observed to be out of the south (175°) at 10 mph. Surface winds were light and slightly variable. In order to be assured of total plume enclosure, two rain samplers were added to the eastern edge of arc A and three to the edge of arc B. Tracer release was initiated at 1440 and terminated at 1520. Rainfall was variable throughout the test period becoming very light at 1455 but increasing significantly by 1512. The average rainfall rate was 0.25 cm hour^{-1}. Winds were generally from the south-southeast (168°) at an average speed of 8 mph and gusting to 26 mph. A total volume of 16.6 liters of diethylamine was dispersed during the 40 minute test period.

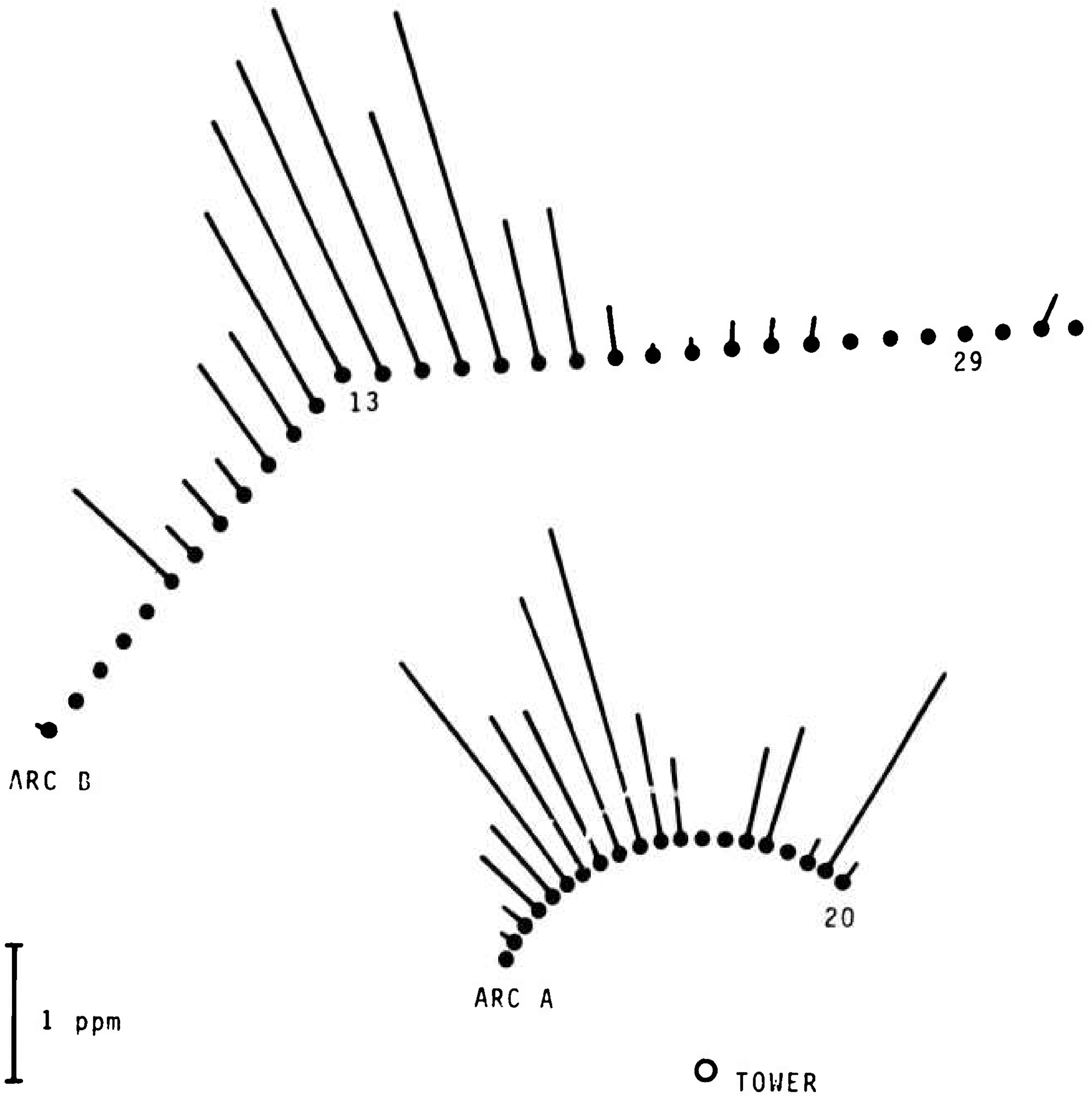


Figure 12. MEASURED CONCENTRATIONS OF DEA IN RAINWATER, RUN 3.

TABLE 8.

OBSERVED TRACER CONCENTRATION VERSUS CONCENTRATIONS PREDICTED FOR VARIOUS SOLUBILITIES -- EXPERIMENT 3 (DEA).

Station	$C_{obs.}$	$C_{H'=0}$	$C_{H'=11}$	$C_{H'=21}$
A 4	0.6 ppm			
5	0.7			
6	2.1		0.005 ppm	
7	1.4	0.1 ppm	0.042	0.018 ppm
8	1.3	1.5	0.225	0.084
9	2.1	6.9	0.628	0.221
10	2.5	2.2	0.898	0.304
11	1.0	6.9	0.628	0.221
12	0.6	1.5	0.225	0.084
13	<0.1	0.1	0.042	0.018
14	<0.1		0.005	
B 11	0.9	0.01	0.002	0.001
12	1.7	0.12	0.021	0.012
13	2.2	0.81	0.112	0.058
14	2.7	2.9	0.304	0.154
15	3.0	4.8	0.425	0.212
16	2.1	2.9	0.304	0.154
17	2.8	0.81	0.112	0.058
18	1.1	0.12	0.021	0.012
19	1.2	0.01	0.002	0.001

EXPERIMENT 4

The second experiment incorporating the use of diethylamine was conducted on January 16, 1973. A deep low pressure system was centered 400 nautical miles northwest of the test site moving eastward at about 25 knots. A trough extended south-southeast from the low to 200 miles off the Washington coast and a small frontal wave over northcentral Oregon was filling and moving northeastward. The flow of cold, moist, unstable air aloft was southwesterly bringing a series of fast moving, low-amplitude, short waves to the Washington coast and causing showers. A 130-knot jet stream from the southwest was located between Salem and Eugene, Oregon. The freezing level was at 3800 feet.

Release of diethylamine was initiated at 1129 and terminated at 1159. The 30-minute test was characterized by southerly winds (172°) at about 16 mph and gusting to 25 mph. The rainfall rate was fairly uniform averaging 0.25 cm hour^{-1}. Seventeen liters of the tracer were vaporized during the test.

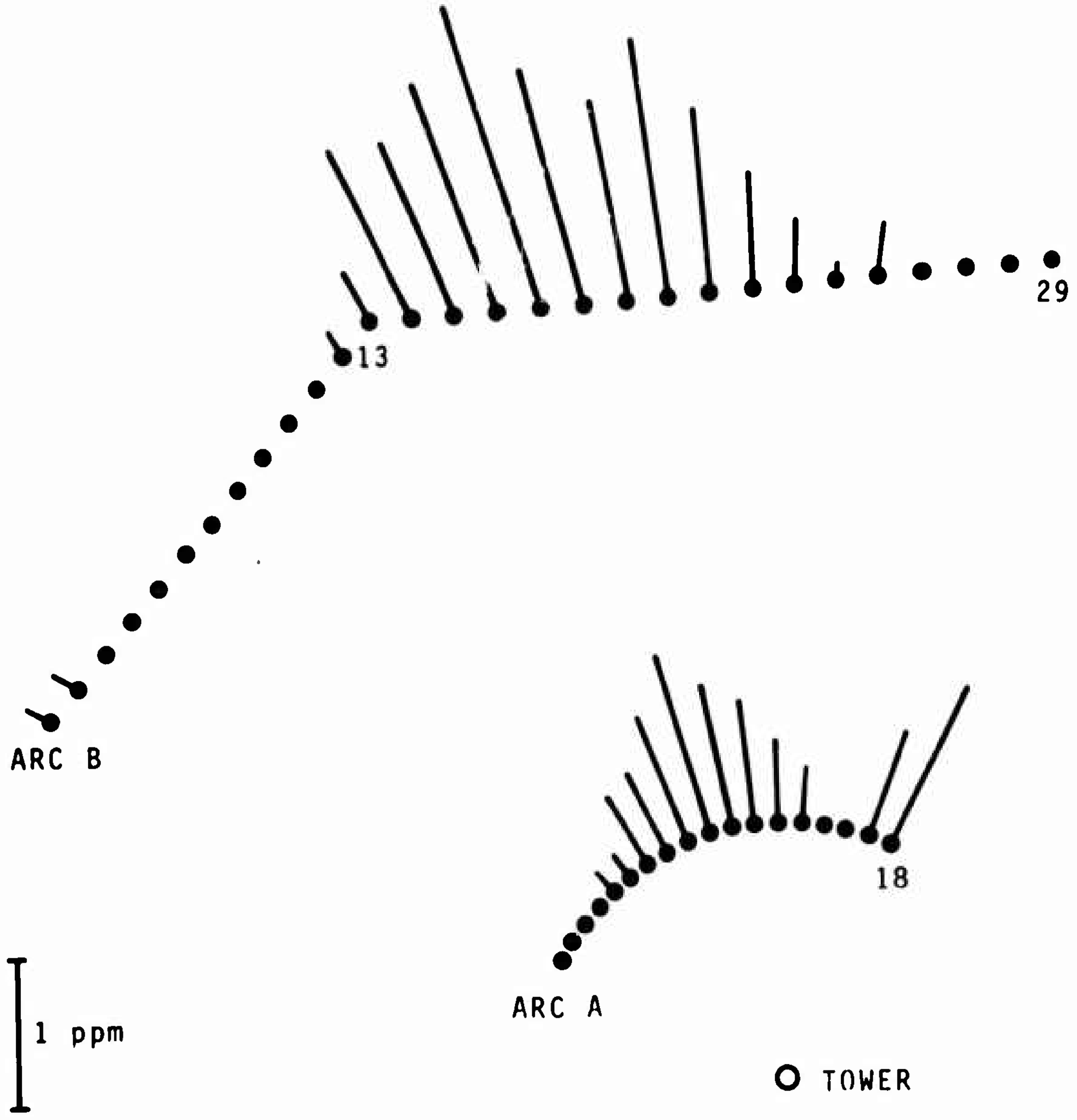


Figure 13. MEASURED CONCENTRATIONS OF DEA IN RAINWATER, RUN 4.

TABLE 9.

OBSERVED TRACER CONCENTRATION VERSUS CONCENTRATIONS PREDICTED FOR VARIOUS SOLUBILITIES - EXPERIMENT 4 (DEA).

Station	$C_{obs.}$	$C_{H'=0}$	$C_{H'=11}$	$C_{H'=21}$
A 6	0.19 ppm			
7	0.55			
8	0.62	0.03 ppm	0.014 ppm	0.006 ppm
9	0.96	1.2	0.357	0.153
10	1.3	20.7	1.4	0.478
11	1.0	1.2	0.357	0.153
12	0.85	0.03	0.014	0.006
13	0.56			
14	0.39			
B 12	0.21			
13	0.42			
14	1.3			
15	1.3	0.04	0.013	0.007
16	1.7	1.2	0.19	0.095
17	2.2	10.4	0.48	0.228
18	1.7	1.2	0.19	0.095
19	1.4	0.04	0.013	0.007
20	1.8			
21	1.3			
22	0.80			
23	0.45			

EXPERIMENT 5

This experiment was also conducted on January 16, 1973. The surface low pressure system noted before (Experiment 4) had moved to 150 nautical miles off Vancouver Island. The surface trough line had filled and broadened and the frontal wave located over north central Oregon was dissipating over extreme southeast Washington. Other features remained virtually unchanged.

The generation of diethylamine vapor was begun at 1309. At this time heavy rain was falling which for the first 3-4 minutes was mixed with sleet or hail. Winds at the release height were southerly while those at the surface were from the south-southwest (∿210°). The rainfall rate remained fairly constant throughout most of the release period (1309-1336) decreasing to a light shower at 1332. The average rainfall rate over the course of the experiment was 1.1 cm hour^{-1} and winds were generally observed to be from the south (173°) at about 16 mph. The total volume of tracer released during this period was 7.7 liters.

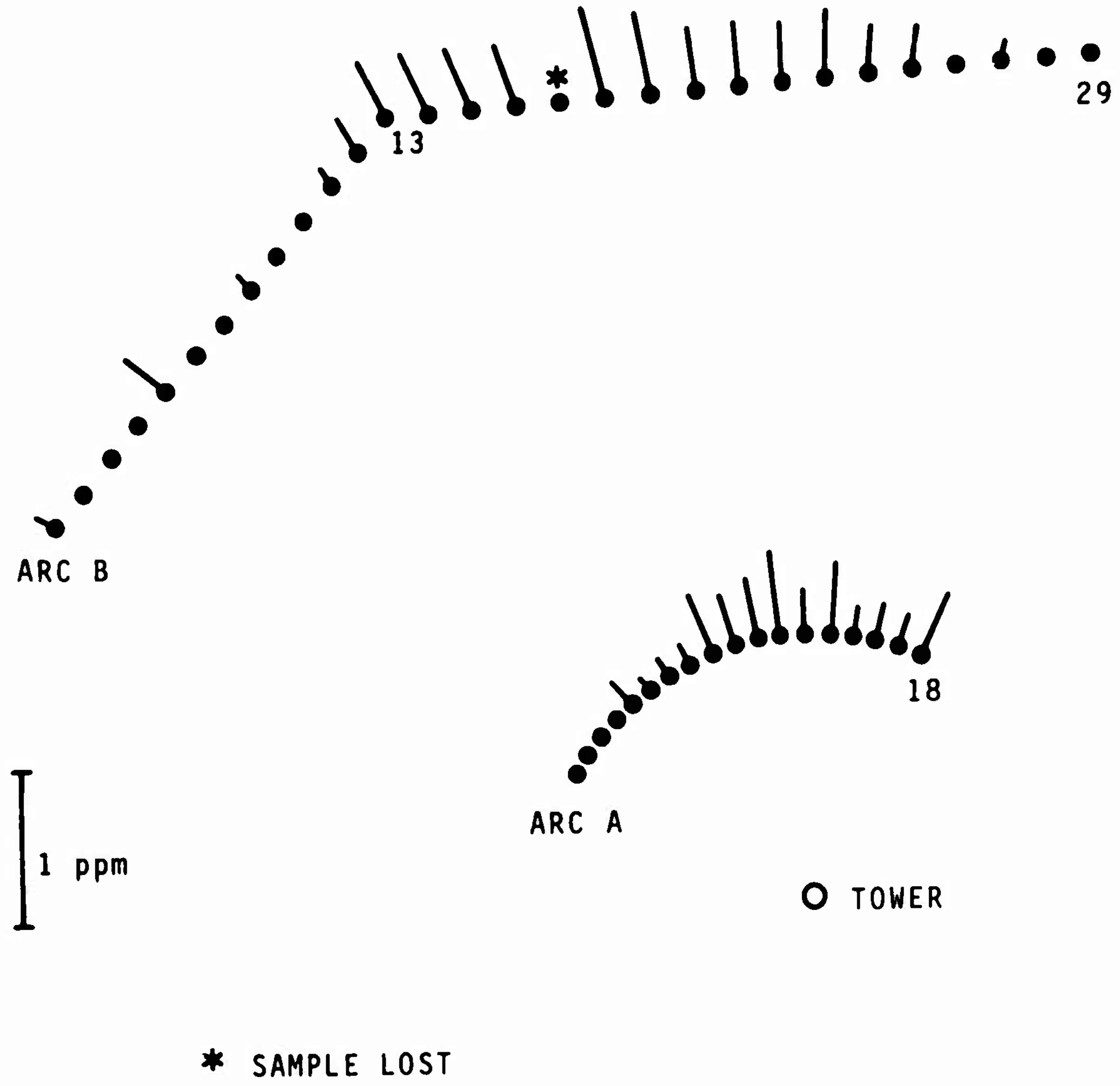


Figure 14. MEASURED CONCENTRATIONS OF DEA IN RAINWATER, RUN 5.

TABLE 10.

OBSERVED TRACER CONCENTRATION VERSUS CONCENTRATIONS PREDICTED FOR VARIOUS SOLUBILITIES - EXPERIMENT 5 (DEA).

Station	$C_{obs.}$	$C_{H'=0}$	$C_{H'=11}$	$C_{H'=21}$
A 8	0.17 ppm			
9	0.47			
10	0.37	0.04 ppm	0.02 ppm	0.01 ppm
11	0.43	0.80	0.24	0.10
12	0.57	10.7	0.70	0.25
13	0.32	0.80	0.24	0.10
14	0.48	0.04	0.02	0.01
15	0.17			
B 12	0.28			
13	0.41			
14	0.47			
15	0.47		0.001	0.001
16	0.47	0.08	0.01	0.019
17	--	0.76	0.054	0.112
18	0.63	5.03	0.097	0.207
19	0.56	0.76	0.054	0.112
20	0.43	0.08	0.010	0.019
21	0.43		0.001	0.001
22	0.42			

CHAPTER VI.

DISCUSSION OF RESULTS

As indicated by the data in Tables 6 through 10, the EPAEC model predicts, for the best available estimates of solubility, results higher than those measured for the case of ethylacetoacetate and lower for that of diethylamine. Furthermore, the magnitudes of the deviations are such that the EPAEC model, with the input parameters employed, provides a rather unsatisfactory quantitative description of observed behavior. We attribute this lack of agreement primarily to the previously noted uncertainties in the solubility parameters; the present chapter presents an analysis of the various errors associated with this experiment in support of this conclusion.

The possible sources of disagreement between predicted and experimental washout concentrations can be divided into three categories. These are

- Experimental errors
- Inadequacies of the washout model
- Inappropriate values of model input parameters

Several of these features can be analyzed by noting behavior observed during the EPA's SO_2 studies conducted previously at the same location using the same techniques. These categories will be addressed individually in the following text.

EXPERIMENTAL ERRORS

The primary sources of possible experimental error are itemized as follows:

- Rain sampling and analysis,
- Wind measurement,
- Raindrop size measurement,
- Release rate measurement,
- Release state of material

and • Desorption and dry deposition of material on collectors

The errors associated with these measurements were all small compared to the deviations exhibited in the previous chapter. As indicated previously the sampling and chemical analysis involves estimated errors of ∿30 percent for diethylamine and <25 percent for ethylacetoacetate. Wind measurement using the precisely leveled and calibrated Gill Anemometer was not expected to exceed 5% error, even under adverse conditions; measurements of organic release rates were valid to within one or two percent, Measured raindrop size spectra were open to some question because of fluctuations in rain characteristics during the course of the experiments. Attempts to compensate this effect were made by choosing representative spectra obtained from several measurements made during each run. Although there was a fair degree of uncertainty in the "representative" spectra chosen in this manner, this was rendered of lesser importance owing to the rather weak dependence of washout on drop size expected under these test conditions. Associated deviations between experimental and predicted concentrations are expected to be less than ten percent.

Finally, the release state of the organic material is of some concern in that the plume was assumed (by the EPAEC model) to be in the vapor state at all times. This condition was satisfied well in most cases by the vapor generator. For ethylacetoacetate, however, a visible plume of fine (probably submicron) droplets was observed to exist for a short distance downwind of the generator. Because of the short length of the visible plume prior to complete droplet evaporation we estimate that any resulting deviation was less than ten percent for the inner arc and negligible for the outer arc.

An aspect of sampling not included with the above estimates of sampling and analysis errors involves the possibility of tracer desorption from the rainwater during its time of residence on the sampler funnel surface. This effect was studied during the previous SO_2 tests, and it was concluded that associated errors decrease with increasing rain rate, and the potential error resulting from desorption increases with decreasing solubility. For SO_2 (solubility comparable to that of ethylacetoacetate) at Quillayute, this error is within twenty percent under the most adverse conditions. For lower solubility substances such as diethylamine, however, the associated error is expected to be larger. Rather paradoxically, however, the observed deviations between experiment and theory occur in a direction opposite to that expected from the desorption effect. This being the case, one must conclude that desorption effects were not the primary source of disagreement.

Two aspects of the chemical analysis of field samples are also worthy of mention at this point. The apparent tracer concentration of the background samplers has been alluded to previously in this report. It is the feeling of the authors that particulate matter within the background rain samples is responsible for transmittance values which are generally less than 100%. Thus light scattering rather than absorption may account for a fraction of the decrease in transmittance registered for the field samples. Although experimental support for this conclusion is lacking, the tracer concentrations suggested by the analysis of background samples is considerably less than those observed for samples taken from beneath the plume. Error introduced by this background material is thus of such a magnitude as to offer only a minor influence of the discrepancy between the observed and predicted sample concentrations. Examination of the data contained in Tables 13, 15, 16, 17, and 19 (Appendix D) confirms that the apparent tracer concentration of the background samples rarely exceeds 20% of the level found in samples from beneath the plume.

In addition to vapor capture by raindrops passing through the plume (washout) dry deposition of the organic vapor at ground level may offer a second mechanism for tracer accumulation. Some estimate of the importance of this process may be ventured by an examination of the results obtained from the vapor samplers. For example, if the concentrations of vapor in the gas phase adjacent to the surface are demonstrated to be much lower than those aloft, it is permissible (under the present test conditions) to neglect the contribution of dry deposition relative to that of scavenging. Data acquired from the analysis of the samples taken during Experiment 4 suggests that this is indeed the case. These data are tabulated in Table 11.

TABLE 11.

RELATIVE MASS OF DIETHYLAMINE IN RAIN AND VAPOR SAMPLES ACQUIRED DURING EXPERIMENT 4.

Station	Mass of DEA in Rain	Mass of DEA in Vapor Sampler	Integrated Vapor Concentration
A-7	21 μg	1.0 μg	0.033 μg/l
8	22	1.5	0.050
9	33	1.7	0.057
10	29	1.0	0.033
11	28	<0.8	<0.027
12	20	<0.8	<0.027
13	19	<0.8	<0.027
14	11	<0.8	<0.027
B-12	7.1	1.3	0.043
13	15	<0.8	<0.027
14	30	1.5	0.050
15	44	2.6	0.087
16	39	3.6	0.12
17	57	2.6	0.087
18	58	2.7	0.090
19	49	2.4	0.080
20	34	1.0	0.033

In view of the above considerations we conclude that experimental errors are not responsible for a significant portion of the observed discrepancies between experimental and predicted washout concentrations. Subsequent sections of this chapter will deal with additional aspects of this disagreement.

INADEQUACIES OF THE WASHOUT MODEL

The assumptions employed during the formulation of the EPAEC model are numerous and have been described in detail elsewhere (Dana, et al 1973). These include the following:

- A steady state exists
- The plume is gaseous and is described by the bivariate-normal equation
- The rain is composed of spherical droplets, which fall vertically with known terminal velocities, and move laterally with the mean wind velocity.

Our previous work for the Environmental Protection Agency on SO_2 washout (Dana 1972, 1973) has included a rather extensive analysis of these assumptions. Part of this analysis has involved comparisons of model-predicted washout concentrations with those observed experimentally under a large variety of circumstances. In general these comparisons exhibit good agreement; washout distributions such as those shown in Figure 15 which pertain to an SO_2 experiment conducted during the EPA SO_2 series, are obtained. This evidence suggests strongly that the tests and basic model described in the present report, which are in most aspects identical to those applied during the previous SO_2 study, should be valid well within the margins of disagreement exhibited in Tables 6 through 10.

One can argue that effects such as fluctuating-plume behavior and short-term variations in rain rate should combine to produce anomalies not considered here by the model assessment, and thereby cause deviations between experiment and theory. While this is certainly true, the fact remains that markedly superior agreement has been obtained for the SO_2 calculations <u>using essentially the same modeling approach as that employed</u> here. In view of this finding we conclude that the primary source of error in the present study does not involve the basic structure of the washout model.

INAPPROPRIATE VALUES OF MODEL INPUT PARAMETERS

The validity of many of the model input parameters has been discussed previously in the Experimental Errors Section, above. Molecular properties (solubility, diffusivity, and viscosity data), however, were determined from literature values or by calculation and deserve additional consideration here. The kinematic viscosity of air, used in mass-transfer calculations, is known with high accuracy, and therefore can be disregarded from further consideration in this context. Diffusivity estimates, obtained from collision integral theory as shown in Appendix B are expected to be in error by no more than ten percent (Reid and Sherwood (1958)). These values are thus sufficiently accurate to eliminate any concern for high associated errors in the washout calculations.

As indicated previously, solubility estimates were not nearly as high in quality as those of the other parameters. These values, calculated as shown in Appendix A, are open to question on several counts. In the case of ethylacetoacetate, the solubility recorded in the Handbook of Chemistry (Lange, 1956) is not documented and the conditions under which it was determined are thus unknown. The maximum concentration of tracer within the plume at 300 feet is estimated by the Gaussian plume diffusion model to be $\sim 10^{-6}$ g/liter for the conditions observed during Experiments 1 and 2. Since early gas solubility work was generally directed to much higher concentration levels, the handbook value is probably not valid for the test conditions. Indeed the washout model is only able to predict rain concentrations approaching those observed if one assumes a Henry's Law constant, H', nearly twenty times larger than the estimated value of $0.25 \frac{(\text{atm})\text{cc}}{\text{mole}}$.

Contrary to ethylacetoacetate, a Henry's Law constant has been reported for diethylamine although this value is also the product of a study at rather high vapor concentrations. There is also some question regarding the vapor pressures used to adjust H' to the experimental conditions. The vapor pressure data of Stull (1947) are in conflict with that used in the calculations in Appendix A. Stull's data would give an H' value of

8.5 $\frac{(atm)cc}{mole}$ and therefore predict rain concentrations closer to those observed.

While the absence of high quality solubility data does not permit an assessment of the EPAEC model's ability to predict the washout of sparingly soluble organics, the data acquired from this test series may be used to estimate the fractional washout per unit distance from the source. The mass of contaminant captured per kilometer per minute, w, is calculated from the equation

$$w = \frac{V \Delta Y \Sigma C}{A \Delta t} \times 10^5$$

where Σ C = sum of tracer concentrations across the sampling arc in ppm

V = average volume of rainwater samples in cm^3

A = cross-sectional area of funnel in cm^2

and t = length of experiment in minutes

In order to complete calculations from the data accumulated for each sampling arc, estimates of the concentrations of missing samples were made from the tracer loads observed in neighboring samples. The percent of tracer washed out per kilometer is calculated from w and a knowledge of the source strength, Q. A summary of pertinent field data and the estimated fractional washout per kilometer are contained in Table 12.

It is interesting to note the more efficient capture of diethylamine by rainwater although its solubility, as estimated from available data, is somewhat lower than that of ethylacetoacetate. One is thus led to suspect the efficiency of ethylacetoacetate vapor generation. The low volatility of this material and the greater release rates calculated from the field notes lend support to this contention. The lack of a correlation between the fractional washout calculated for arcs A and B is however surprising since one might expect some capture of the liquid tracer by samplers in Arc A under conditions of incomplete vaporization and therefore a much larger fractional washout from Arc A data as opposed to that from Arc B.

TABLE 12.

SUMMARY OF FIELD DATA AND ESTIMATED FRACTIONAL WASHOUT OF TRACERS

						w		
Q, gm/min	Run/Arc	[illegible], μg/cm^3	Volume, cm^3	Time, min	Δy, cm	μg/cm min	gm/km min	% Loss/km
556	1/A	10.1	45	18	793	64	6.4	1.2
556	1/B	9.25	45	18	1524	112	11.2	2.0
486	2/A	7.98	125	24	793	105	10.5	2.2
488	2/B	2.44	125	24	1524	62	6.2	1.3
275	3/A	16.2	41	40	793	42	4.2	1.5
275	3/B	22.3	41	40	1524	111	11.1	4.0
403	4/A	8.55	32	30	793	23	2.3	0.6
403	4/B	15.4	32	30	1524	80	8.0	2.0
220	5/A	4.28	95	25	793	41	4.1	1.9
220	5/B	7.13	95	25	1524	132	13.2	6.0

CHAPTER VII.

CONCLUSIONS

Rain scavenging of organic vapors of intermediate solubility has been investigated. Comparison of rainwater concentrations predicted by the EPAEC model with those observed shows generally poor agreement. This comparison and an assessment of the errors contributed by various input parameters and the experimental design permit the following conclusions to be drawn;

1. The assumption of infinite solubility is unjustified for the organic materials ethylacetoacetate and diethylamine. Concentrations which are decidedly below those predicted on the basis of this assumption signal reversible rainwater-organic vapor interaction in which pickup of the contaminant is impeded or even reversed under some circumstances.

2. The errors associated with tracer solubilities prevent an adequate appraisal of the predictive power of the washout model. Solubilities, which have been estimated from the available literature, must be determined for the low vapor concentrations encountered in the field experiments before any conclusions may be reached regarding the adequacy of the model.

3. The data derived from the field study is judged to be of high quality. Errors contributed by the analytical technique, vapor generation, meteorological data acquisition and rainwater collection system have all been appraised. In view of these considerations, it appears that a thorough evaluation of the EPAEC model is contingent primarily on the attainment of improved solubility data.

REFERENCES

1. Dahrgen, G. Spectrophotometric Determination of Ethyl-, Diethyl-, and Triethylamine in Aqueous Solution, *Anal. Chem.*, vol. 36, no. 596, 1964.

2. Dana, M. T., J. M. Hales and M. A. Wolf. Natural Precipitation Washout of Sulfur Dioxide Final Report to Environmental Protection Agency, BNW 389 (1972).

3. Dana, M. T., J. M. Hales, W.G.N. Slinn, and M. A. Wolf. Natural Precipitation Washout of Sulfur Compounds From Plumes, Final Report to Environmental Protection Agency EPA-R3-73-047 (1973).

4. Dailey, B. P. and W. A. Felsing. Partial Vapor Pressures of Aqueous Ethylamine Solutions, *J. Am. Chem. Soc.* vol. 61, 2808, 1939.

5. Engelmann, R. J., R. W. Perkins, D. I. Hagen, and W. A. Haller. Washout Coefficients for Selected Gases and Particulates, Proc. 59th Annual Meeting Air Pollution Control Assoc.; also USAEC Report BNWL-SA-657, Battelle-Northwest, June 1966.

6. Georgii, H. and S. Beilke. Investigation of the Incorporation of Sulfur Dioxide into Fog and Rain Droplets, *Tellus* 20, 435-441 (1967).

7. Hales, J. M. Scavenging of Gaseous Tritium Compounds by Rain, AEC Report BNWL 1659 (1972).

8. Hales, J. M., M. A. Wolf, and M. T. Dana. A Linear Model for Predicting the Washout of Pollutant Gases from Industrial Plumes, *AIChE Journal* 19, 292-297 (1973).

9. Junge, C. E. Air Chemistry and Radioactivity, *Academic Press*, New York (1963).

10. Lange, W. A. (ed.) Handbook of Chemistry, Handbook Publishers, Inc., Sandusky, Ohio, p. 538 (1956).

11. Parker, B. C. Rain as a Source of Vitamin B-12, *Nature*, 219, 617-18 (1968).

12. Perry, J. H. Chemical Engineers' Handbook, *McGraw-Hill*, New York (1963).

13. Reid, R. C. and T. K. Sherwood. The Properties of Gases and Liquids: Their Estimation and Correlation, *McGraw-Hill*, New York (1966).

14. Semenov, A. D., L. I. Nemtseva, T. S. Kishkinova, and A. P. Pashanova. Organic Substances of Atmospheric Precipitation, *Doki Akad. Nauk.* SSSR 173 (5), 1185 (1967).

15. Semenov, A. D. and T. S. Kishkinova. Carbonyl Compounds in Natural Waters, *Gidrokhim. Mater.* 44, 83, 1968.

16. Stull, D. R. Vapor Pressure of Pure Substances: Organic Compounds, *Ind. Eng. Chem.* 39, 517, 1947.

17. Tarrant, K. R. and J. O'G. Tatton. Organochlorine Pesticides in Rainwater in the British Isles, *Nature* 219, 725, 1968.

NOMENCLATURE

a	drop radius, 1
c	concentration in liquid phase moles/1^3
h	plume release height, 1
H'	solubility parameter, 1^3/mole, cf. Table 5
k	mass transfer coefficient moles/1^2t
N	number of observations in a wind sample
Q	emission release rate (volumetric) at source exit conditions 1^3/t
u,v,w	wind speeds in x,y,z directions 1/t
v_z	raindrop velocity in z-direction 1/t
x,y,z	distance coordinates in downwind, crosswind, and vertical directions, 1
y	gas-phase mole fraction
ζ	mass transfer parameter defined by equation (2)
ϕ,θ	polar coordinates of wind direction, radians

subscripts

A	"pollutant A"
b	bulk
x	liquid phase, x-direction
y	gas-phase, y-direction
z	vertical direction
θ,ϕ	θ,ϕ directions

APPENDIX A

SOLUBILITY ESTIMATES

DIETHYLAMINE

Solubility of diethylamine was estimated from the high-concentration data of Dailey and Felsing (1939), who give

$$P/c = H' = 16.25\ \frac{\text{mm Hg liter}}{\text{mole}} = 21.38\ \frac{(\text{Atm})\ \text{cc}}{\text{mole}}\quad \text{at } 25^\circ\ \text{C. By}$$

assuming applicability of the Clausius-Claperyon Equation and applying the vapor pressure data of Perry (1966), one can interpolate to estimate solubility at other temperatures. At 5° C

$$H'_{5^\circ} = H'_{25}\left(\frac{P_5}{P_{25}}\right) = 21.38\left(\frac{35.2}{66.7}\right) = 11.28\ \frac{(\text{Atm})\text{cc}}{\text{mole}}\ .$$

ETHYLACETOACETATE

Lange (1956) gives $C = 13$ gm EAA/100 gm water at 17° C.

$$\simeq 8.85 \times 10^{-4}\ \frac{\text{moles}}{\text{cc}}$$

From Perry (1963) the vapor pressure of EAA at 17° $P = .440$ mm Hg.

$$= 5.79 \times 10^{-4}\ \text{Atm}$$

$$H' = \frac{P}{C} = .65\ \frac{(\text{Atm})\text{cc}}{\text{mole}}\quad \text{at } 17^\circ\ \text{C}$$

Using the Clausius Claperyon Equation as before

$$H'_5 = H'_{17}\left(\frac{P_5}{P_{17}}\right) = .65\left(\frac{.168}{.440}\right) = .25\ \frac{(\text{Atm})\text{cc}}{\text{mole}}$$

APPENDIX B

GAS DIFFUSION COEFFICIENT CALCULATIONS

Diffusion coefficients were estimated by applying collision integral theory as described by the Wilke-Lee modification of Hirschfelder's relationship (cf. Reid and Sherwood (1958)). The basic equation is given by

$$\text{Day} = \frac{a_o\, T^{3/2}\, [(M_1 + M_2)/M_1 M_2]^{1/2}}{P\, \sigma_{12}^2\, \Omega_d} \quad \text{where}$$

a_o $= 0.00214-0.000492\left(\frac{M_1 + M_2}{M_1 M_2}\right)^{1/2}$

M_1, M_2 = molecular weights of air and vapor

T = absolute temperature

P = pressure

σ_{12} = intermolecular force constant

and Ω_d = collision integral.

Ω_d was obtained from tabulated values upon applying the relationships:

$\sigma_{12} = 1/2(\sigma_1 + \sigma_2)$

$\sigma_2 = 1.18\ \vartheta^{1/3}$

$\sigma_1 = 3.617$ Å (For Air)

$$\frac{\varepsilon_{12}}{k} = \frac{\sqrt{\varepsilon_1 \varepsilon_2}}{k}$$

$\frac{\varepsilon_1}{k} = 97°$ K (For Air)

$\frac{\varepsilon_2}{k} = 1.21\ T_b$

where ϑ is the molar volume of material at its normal boiling point T_b.

$$T_b = 453^\circ \text{ K} \quad \text{for EAA.}$$

$$T_b = 329^\circ \text{ K} \quad \text{for DEA.}$$

Molar volumes were estimated using group contributions (Reid and Sherwood (1958)). The result is

$$\vartheta = 151.6 \ \frac{\text{cm}^3}{\text{mole}} \ \text{for EAA.}$$

$$\vartheta = 82.3 \ \frac{\text{cm}^3}{\text{mole}} \ \text{for DEA.}$$

Combining the above and applying the tables gives

$$\sigma_{12} = 4.96 \ \text{Å} \quad \text{for EAA,}$$

$$\sigma_{12} = 4.39 \ \text{Å} \quad \text{for DEA,}$$

$$\varepsilon_{12}/k = 230^\circ \text{ K} \quad \text{for EAA,}$$

$$\varepsilon_{12}/k = 197^\circ \text{ K} \quad \text{for DEA,}$$

$$\Omega_d = 1.29 \quad \text{for EAA,}$$

$$\Omega_d = 1.22 \quad \text{for DEA,}$$

$$\text{Day}_{10^\circ \text{ C}} = .0741 \ \frac{\text{cm}^2}{\text{sec}} \ \text{for EAA}$$

$$\text{Day}_{10^\circ \text{ C}} = .0956 \ \frac{\text{cm}^2}{\text{sec}} \ \text{for DEA.}$$

APPENDIX C

A tipping bracket rain gauge was among the instruments employed to furnish a description of the test conditions. This unit was modified to record rainfall in 0.06 mm increments. Recordings made during each of the tracer releases are reproduced on the following pages.

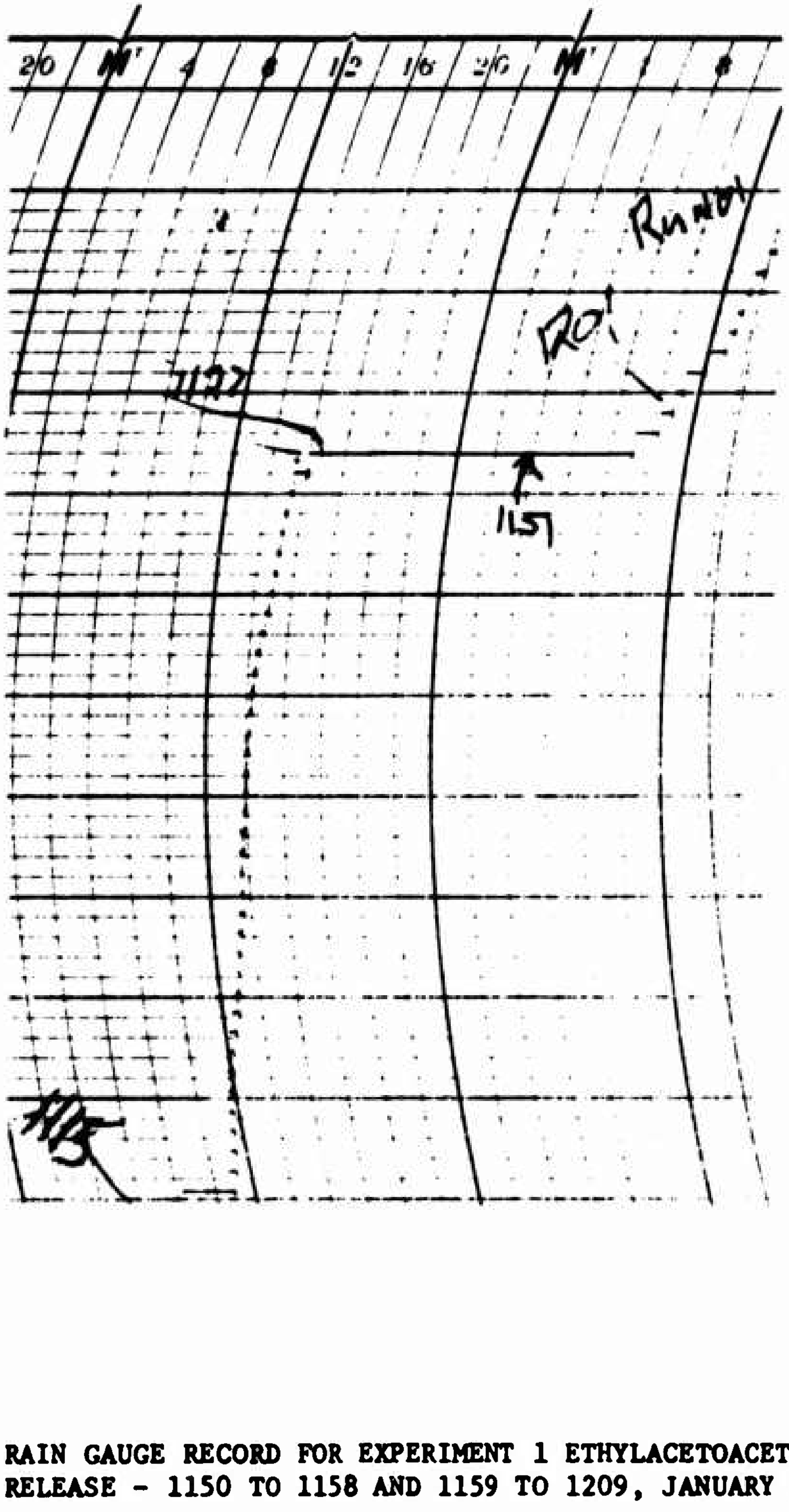


Figure 15. RAIN GAUGE RECORD FOR EXPERIMENT 1 ETHYLACETOACETATE RELEASE - 1150 TO 1158 AND 1159 TO 1209, JANUARY 11, 1973.

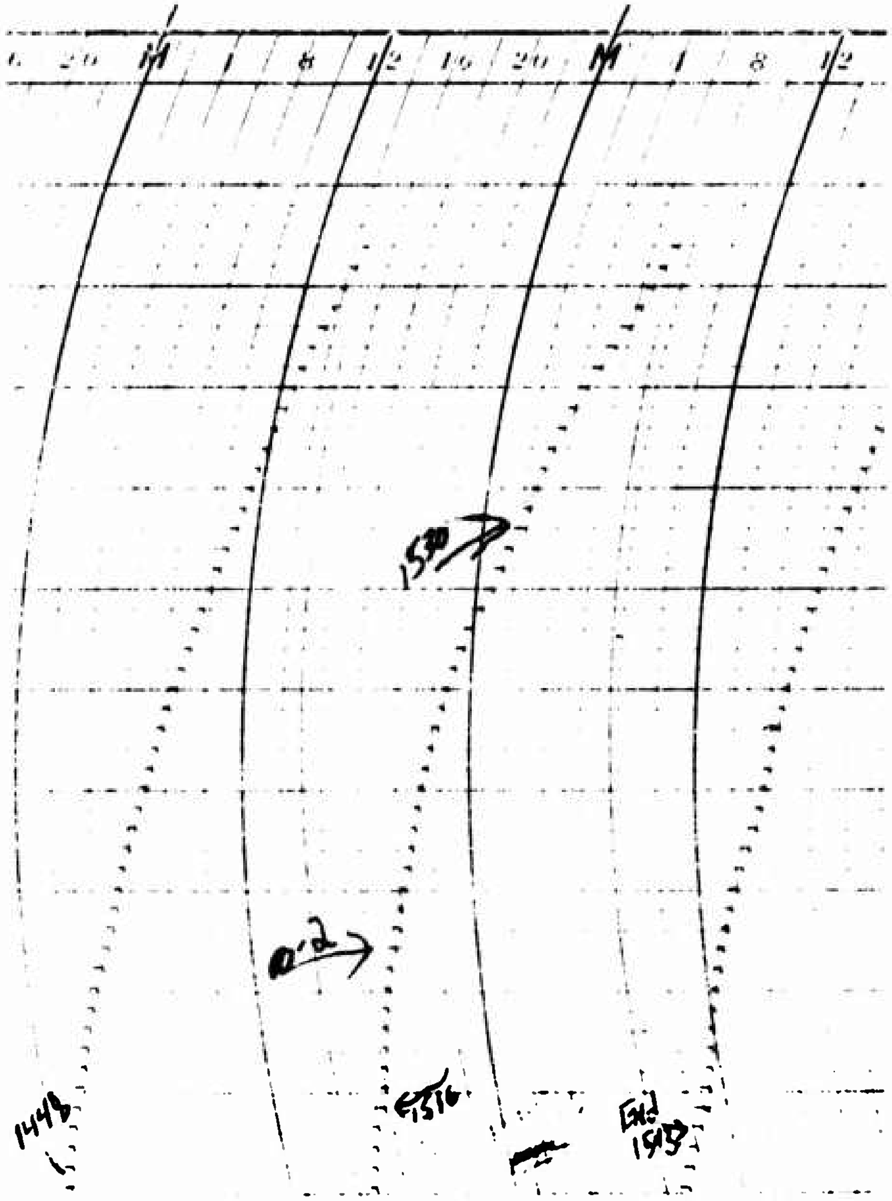


Figure 16. RAIN GAUGE RECORD FOR EXPERIMENT 2 ETHYLACETATE RELEASE - 1519 TO 1543, JANUARY 11, 1973.

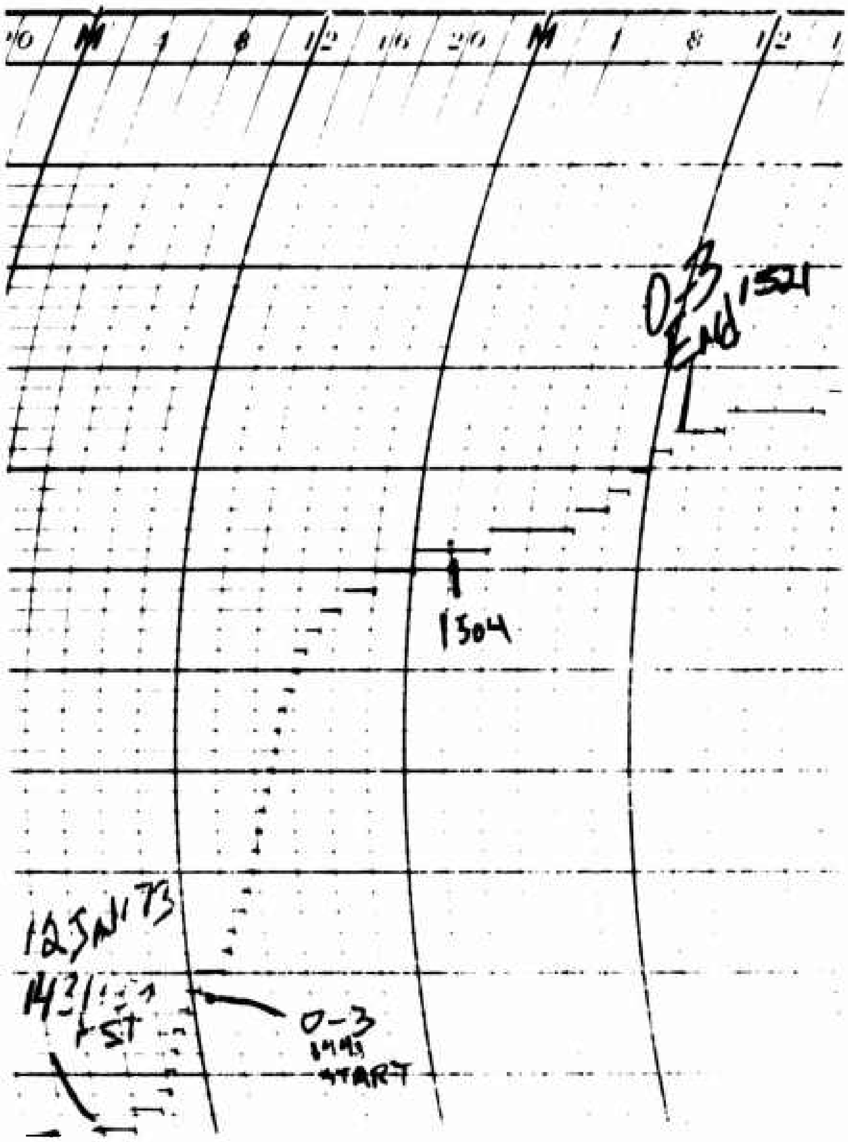


Figure 17. RAIN GAUGE RECORD FOR EXPERIMENT 3 DIETHYLAMINE RELEASE - 1440 TO 1520, JANUARY 12, 1973.

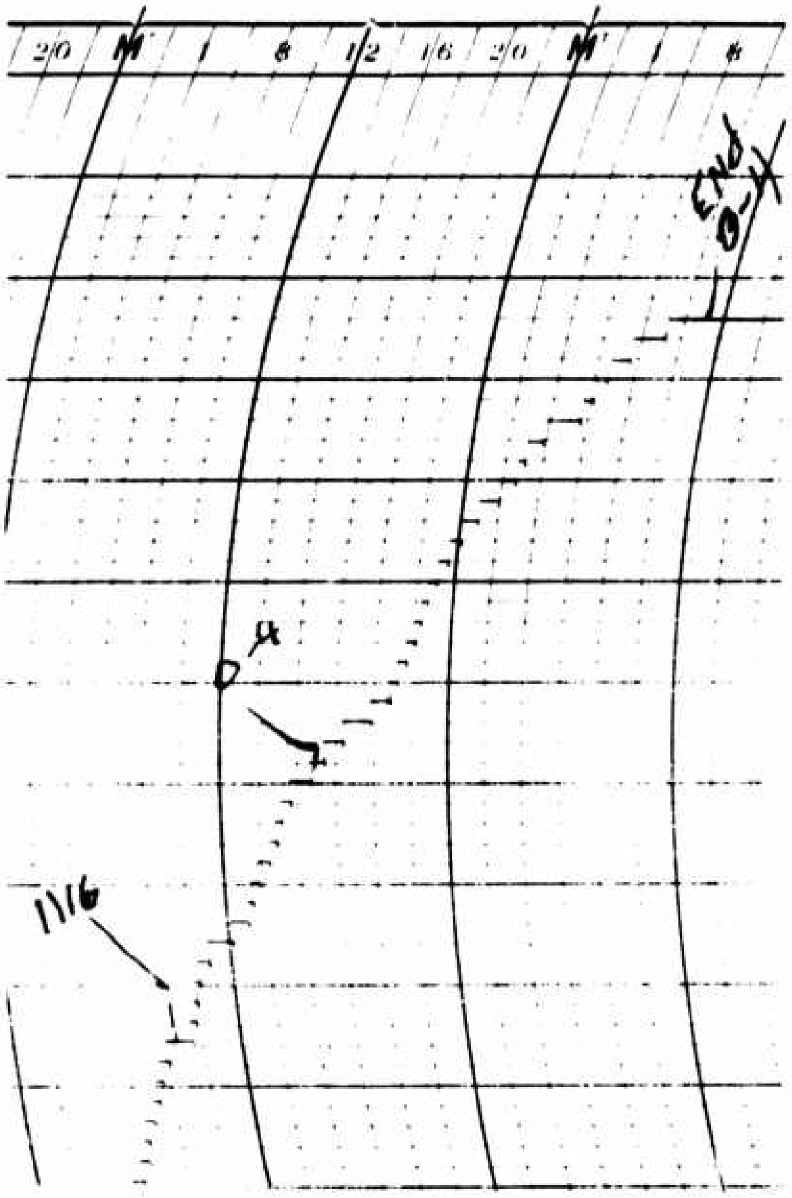


Figure 18. RAIN GAUGE RECORD FOR EXPERIMENT 4 DIETHYLAMINE RELEASE - 1129 TO 1159, JANUARY 16, 1973.

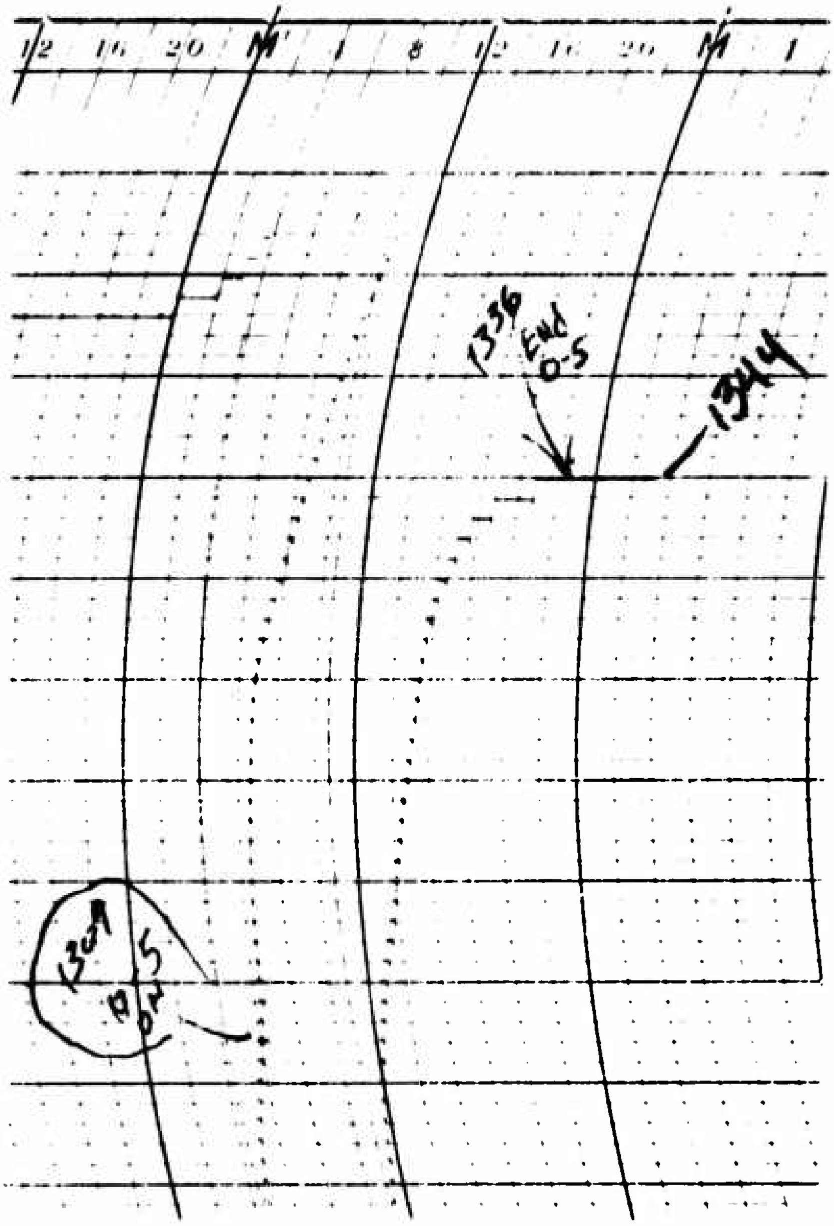


Figure 19. RAIN GAUGE RECORD FOR EXPERIMENT 5 DIETHYLAMINE RELEASE - 1309 to 1336, JANUARY 16, 1973.

APPENDIX D

The following pages contain tabulations of the tracer concentrations in rain samples collected during this test series. The impinger solutions taken from the vapor samplers operated during Experiments 1 and 4 have been analyzed and are also included. These results gave an indication of the significance of dry deposition and further analysis of impinger solutions was not undertaken.

TABLE 13.

EXPERIMENT 1.

Tracer-Ethylacetoacetate
Time of Release - 18 minutes
Source Strength - 4.6 x 10^{-2} mole $sec.^{-1}$
Rainfall Rate
0.20 cm hr^{-1}

Station	Sample Vol.	EAA Conc.	EAA Conc. - Less Background
BKG	88 ml	0.11 ppm	
BKG	95	0.09	
A-1	108	0.08	<0.1 ppm
A-2	100	0.45	0.35
A-3	91	0.12	<0.1
A-4	79	0.26	0.16
A-5	78	0.60	0.50
A-6	64	1.2	1.1
A-7	61	1.6	1.5
A-8	57	1.7	1.6
A-9	56	1.6	1.5
A-10	55	1.3	1.2
A-11	52	1.1	1.0
A-12	51	0.42	0.32
A-13	52	0.20	0.10
A-14	57	0.43	0.33
A-15	61	0.52	0.42
A-16	56	0.15	<0.1
A-17	61	0.19	<0.1
B-1	50	0.23	0.13
B-2	47	0.22	0.12
B-3	44	0.11	<0.1
B-4	47	0.17	<0.1
B-5	45	0.15	<0.1

TABLE 13. (Continued)

EXPERIMENT 1.

Tracer-Ethylacetoacetate
Time of Release - 18 minutes
Source Strength - 4.6 x 10^{-2} mole sec.$^{-1}$
Rainfall Rate
0.20 cm hr^{-1}

Station	Sample Vol.	EAA Conc.	EAA Conc. - Less Background
B-6	41	0.24 ppm	0.14 ppm
B-7	40	0.76	0.66
B-8	Lost	--	--
B-9	Lost	--	--
B-10	Lost	--	--
B-11	37	1.1	1.0
B-12	41	0.80	0.70
B-13	45	1.3	1.2
B-14	44	0.88	0.78
B-15	43	0.83	0.73
B-16	36	0.43	0.33
B-17	42	0.45	0.35
B-18	5	0.22	0.12
B-19	46	0.28	0.18
B-20	46	0.18	<0.1
B-21	43	0.17	<0.1
B-22	50	0.18	<0.1
B-23	46	0.19	<0.1
B-24	46	0.15	<0.1
B-25	46	0.22	0.12
B-26	57	0.08	<0.1
B-27	53	0.07	<0.1
B-28	59	0.24	0.14
B-29	53	0.15	<0.1

TABLE 14.

EXPERIMENT 1.

Impinger Solutions

Station	Mass of Ethylacetoacetate
BKG	0.8 μg
A-3	0.8
4	0.0
5	1.6
6	1.2
7	0.8
8	0.8
9	1.9
10	0.4
11	0.4
12	0.2
13	0.0
14	0.0
B-10	2.6
11	1.3
12	1.6
14	2.6
15	2.1
16	2.1
17	1.0
18	2.4
19	0.8
20	1.6

TABLE 15.

EXPERIMENT 2.

Tracer-Ethylacetoacetate
Time of Release - 24 minutes
Source Strength - 6.3 x 10^{-2} mole $sec.^{-1}$
Rainfall Rate
0.59 cm hr^{-1}

Sampling Station	Sample Vol.	EAA Conc.	EAA Conc. - Less Background
BKG	105 ml	0.08 ppm	
A(-3)	~100	0.08	<0.1 ppm
A(-2)	87	0.17	<0.1
A(-1)	~100	0.08	<0.1
A-1	141	0.10	<0.1
A-2	127	0.05	<0.1
A-3	137	0.88	0.80
A-4	127	1.1	1.0
A-5	138	1.6	1.5
A-6	132	2.1	2.0
A-7	135	1.7	1.6
A-8	133	0.85	0.77
A-9	133	0.28	0.20
A-10	126	0.19	0.11
A-11	133	0.14	<0.1
A-12	128	0.07	<0.1
A-13	~100	0.13	<0.1
A-14	~ 70	0.10	<0.1
A-15	121	0.06	<0.1
A-16	123	0.06	<0.1
A-17	134	0.05	<0.1
B(-3)	85	0.18	<0.1
B(-2)	130	0.07	<0.1
B(-1)	81	0.18	<0.1
B-1	127	0.06	<0.1
B-2	139	0.15	<0.1

TABLE 15. (continued)

EXPERIMENT 2.

Tracer-Ethylacetoacetate
Time of Release - 24 minutes
Source Strength - 6.3 x 10^{-2} mole sec.$^{-1}$
Rainfall Rate
0.59 cm hr^{-1}

Sampling Station	Sample Vol.	EAA Conc.	EAA Conc. - Less Background
B-3	131	0.06 ppm	<0.1 ppm
B-4	138	0.16	<0.1
B-5	130	0.16	<0.1
B-6	142	0.34	0.26
B-7	126	0.24	0.16
B-8	127	0.39	0.31
B-9	137	0.44	0.36
B-10	139	0.39	0.31
B-11	126	0.35	0.27
B-12	140	0.45	0.37
B-13	133	0.36	0.28
B-14	114	0.20	0.12
B-15	129	0.13	<0.1
B-16	125	0.04	<0.1
B-17	117	0.10	<0.1
B-18	108	0.06	<0.1
B-19	133	0.04	<0.1
B-20	128	0.04	<0.1
B-21	111	0.06	<0.1
B-22	113	0.06	<0.1
B-23	128	0.05	<0.1
B-24	130	0.05	<0.1
B-25	125	0.05	<0.1
B-26	114	0.07	<0.1
B-27	--	--	--
B-28	133	0.04	<0.1
B-29	130	0.04	<0.1

TABLE 16.

EXPERIMENT 3.

Tracer-Diethylamine
Time of Release - 40 minutes
Source Strength - 1.7×10^{-1} mole $sec.^{-1}$
Rainfall Rate
0.25 cm hr^{-1}

Sampling Station	Sample Vol.	DEA Conc.	Less Background DEA Conc.
BKG	67 ml	0.0 ppm	
BKG	36	0.3	
A-1	43	0.2	<0.1 ppm
A-2	43	0.3	0.1
A-3	43	0.4	0.2
A-4	43	0.8	0.6
A-5	39	0.9	0.7
A-6	38	2.3	2.1
A-7	42	1.6	1.4
A-8	41	1.5	1.3
A-9	43	2.3	2.1
A-10	45	2.7	2.5
A-11	39	1.2	1.0
A-12	44	0.8	0.6
A-13	38	0.2	<0.1
A-14	39	0.1	<0.1
A-15	34	0.9	0.7
A-16	40	1.1	0.9
A-17	41	0.2	<0.1
A-18	44	0.4	0.2
A-19	30	1.9	1.7
A-20	~40	0.3	0.1
B-1	41	0.3	0.1
B-2	41	0.2	<0.1

TABLE 16. (continued)

EXPERIMENT 3.

Tracer-Diethylamine
Time of Release - 40 minutes
Source Strength - 1.7 x 10^{-1} mole sec.^{-1}
Rainfall Rate
0.25 cm hr^{-1}

Sampling Station	Sample Vol.	DEA Conc.	Less Background DEA Conc.
B-3	39	0.1 ppm	<0.1 ppm
B-4	44	0.3	0.1
B-5	42	0.2	<0.1
B-6	41	1.2	1.0
B-7	44	0.5	0.3
B-8	37	0.6	0.4
B-9	42	0.5	0.3
B-10	39	1.1	0.9
B-11	41	1.1	0.9
B-12	40	1.9	1.7
B-13	40	2.4	2.2
B-14	36	2.9	2.7
B-15	34	3.2	3.0
B-16	39	2.3	2.1
B-17	38	3.0	2.8
B-18	40	1.3	1.1
B-19	43	1.4	1.2
B-20	43	0.6	0.4
B-21	37	0.3	0.1
B-22	43	0.3	0.1
B-23	38	0.4	0.2
B-24	45	0.4	0.2
B-25	41	0.4	0.2
B-26	42	0.1	<0.1
B-27	39	0.1	<0.1
B-28	42	0.2	<0.1

TABLE 16. (continued)

EXPERIMENT 3.

Tracer-Diethylamine
Time of Release - 40 minutes
Source Strength - 1.7×10^{-1} mole sec.^{-1}
Rainfall Rate
0.25 cm hr^{-1}

Sampling Station	Sample Vol.	DEA Conc.	Less Background DEA Conc.
B-29	34	0.2 ppm	<0.1 ppm
B-30	37	0.2	<0.1
B-31	34	0.5	0.3
B-32	32	0.0	<0.1

TABLE 17.

EXPERIMENT 4.

Tracer-Diethylamine
Time of Release - 30 minutes
Source Strength - 3.05 x 10^{-1} mole $sec.^{-1}$
Rainfall Rate
0.25 cm hr^{-1}

Sampling Station	Sample Vol.	DEA Conc.	-Less Background DEA Conc.
BKG	29 ml	0.29 ppm	
BKG	29	0.36	
A-1	24	0.29	<0.10 ppm
A-2	31	0.25	<0.10
A-3	32	0.17	<0.10
A-4	23	0.07	<0.10
A-5	17	0.52	0.19
A-6	33	0.52	0.19
A-7	38	0.88	0.55
A-8	36	0.95	0.62
A-9	34	1.29	0.96
A-10	22	1.64	1.3
A-11	28	1.30	1.0
A-12	23	1.18	0.85
A-13	33	0.89	0.56
A-14	28	0.72	0.39
A-15	30	0.20	<0.10
A-16	36	0.11	<0.10
A-17	36	1.07	0.74
A-18	30	1.49	1.2
B-1	34	0.52	0.19
B-2	31	0.51	0.18
B-3	41	0.[illegible]	<0.10
B-4	32	0.13	<0.10
B-5	40	0.14	<0.10

TABLE 17. (continued)

EXPERIMENT 4.

Tracer-Diethylamine
Time of Release - 30 minutes
Source Strength - 3.05 x 10^{-1} mole $sec.^{-1}$
Rainfall Rate
0.25 cm hr^{-1}

Sampling Station	Sample Vol.	DEA Conc.	-Less Background DEA Conc.
B-6	36	0.22 ppm	<0.10 ppm
B-7	38	0.21	<0.10
B-8	37	0.22	<0.10
B-9	27	0.36	<0.10
B-10	32	0.12	<0.10
B-11	33	0.28	<0.10
B-12	34	0.54	0.21
B-13	35	0.75	0.42
B-14	23	1.6	1.3
B-15	34	1.6	1.3
B-16	23	2.0	1.7
B-17	26	2.5	2.2
B-18	34	2.0	1.7
B-19	35	1.7	1.4
B-20	19	2.1	1.8
B-21	28	1.6	1.3
B-22	32	1.1	0.80
B-23	27	0.78	0.45
B-24	~35	0.43	0.10
B-25	35	0.72	0.39
B-26	~35	0.25	<0.10
B-27	32	0.24	<0.10
B-28	34	0.27	<0.10
B-29	32	0.05	<0.10

TABLE 18.

EXPERIMENT 4.

Impinger Solutions

Station	Mass of Diethylamine
BKG	<0.8 μg
A-3	2.0
4	<0.8
5	<0.8
6	1.7
7	1.0
8	1.5
9	1.7
10	1.0
11	<0.8
12	<0.8
13	<0.8
14	<0.8
B-9	<0.8
10	<0.8
11	<0.8
12	1.3
13	<0.8
14	1.5
15	2.6
16	3.6
17	2.6
18	2.7
19	2.4
20	1.0

TABLE 19.

EXPERIMENT 5.

Tracer-Diethylamine
Time of Release - 25 minutes
Source Strength - 2.6 x 10^{-1} mole $sec.^{-1}$
Rainfall Rate
1.1 cm hr^{-1}

Sampling Station	Sample Vol.	DEA Conc.	Less Background DEA Conc.
BKG	106 ml	0.15 ppm	
BKG	107	0.07	
A-1	108	0.13	<0.10 ppm
A-2	94	0.04	<0.10
A-3	84	0.13	<0.10
A-4	63	0.20	<0.10
A-5	101	0.31	0.20
A-6	109	0.21	0.10
A-7	125	0.25	0.14
A-8	123	0.28	0.17
A-9	120	0.58	0.47
A-10	52	0.48	0.37
A-11	95	0.54	0.43
A-12	48	0.68	0.57
A-13	51	0.43	0.32
A-14	85	0.59	0.48
A-15	99	0.28	0.17
A-16	76	0.34	0.23
A-17	96	0.33	0.22
A-18	79	0.52	0.41
B-1	80	0.27	0.16
B-2	86	0.19	<0.10
B-3	104	0.21	0.10
B-4	90	0.16	<0.10
B-5	81	0.44	0.33

TABLE 19. (continued)

EXPERIMENT 5.

Tracer-Diethylamine
Time of Release - 25 minutes
Source Strength - 2.6 x 10^{-1} mole $sec.^{-1}$
Rainfall Rate
1.1 cm hr^{-1}

Sampling Station	Sample Vol.	DEA Conc.	Less Background DEA Conc.
B-6	87	0.05 ppm	<0.10 ppm
B-7	81	0.06	<0.10
B-8	84	0.25	0.14
B-9	97	0.18	<0.10
B-10	98	0.11	<0.10
B-11	98	0.21	0.10
B-12	92	0.39	0.28
B-13	79	0.52	0.41
B-14	71	0.58	0.47
B-15	86	0.58	0.47
B-16	89	0.58	0.47
B-17	--	--	--
B-18	87	0.74	0.63
B-19	98	0.67	0.56
B-20	99	0.54	0.43
B-21	87	0.54	0.43
B-22	116	0.53	0.42
B-23	92	0.56	0.45
B-24	96	0.43	0.32
B-25	83	0.44	0.33
B-26	90	0.17	<0.10
B-27	88	0.24	0.13
B-28	89	0.17	<0.10
B-29	94	0.18	<0.10

APPENDIX E

DESCRIPTION OF COMPUTER CODE FOR THE EPAEC NONLINEAR NONFEEDBACK WASHOUT MODEL

The computer code can be described, in a somewhat superficial sense, in terms of the flow chart shown in Figure 2. This figure demonstrates that washout calculations may be performed using the code simply by employing a main program that performs the following functions: 1) reading of appropriate input data; 2) execution of algorithm by the statement CALL MASTER; 3) printing of resulting computed values. MASTER is a master coordinating subroutine which employs all of the program functions to calculate washout as indicated in Figure 2.

The utility of the above arrangement is that it allows the code to be applied generally for a variety of specific purposes; one simply writes a main program designed to fulfill his particular requirements, and employs the statement CALL MASTER to execute the basic algorithms required. The Centralia power plant computations described in our previous report (Dana, et al (1973)), for example, were executed using a main program that memorized the topography of the surrounding area, computed relative distances based on the plume location, and then calculated corresponding washout concentrations by the statement CALL MASTER.

A generalized main program can be employed to perform the above functions, if desired. Use of such a program will provide results identical to those computed using customized main programs, the major disadvantages being probable increased inconvenience in data input and less control over output formats. An example of such a generalized program is shown on the pages immediately following, which define the computer nomenclature. Named EPAEC, this program employs a common statement to facilitate exchange of information with the subroutine MASTER. The following EXTERNAL statement designates the function subroutines V, HPRIME, and YAB to be used internally; this statement is essential to the operation of any main program for this purpose.

Reading of input data proceeds, governed by the control variables J1-J4 which allow the bypass of designated READ statements if desired. Finally, an optional, internally-generated receptor spacing (DYDUM) is calculated. This provides for performance of subsequent calculations at 5-degree increasing cross-plume distances.

Upon printing the input data, MASTER is called. Execution of this subroutine pertains to a single receptor location. Upon completion of the calculations controlled by MASTER, appropriate printing is performed, including that of REF, which is the variable denoting height above the source passed by individual raindrops at x = 0.

At this point, depending upon the current value of the control variable JEND, the program has two options. It can either proceed to the adjoining cross-plume location, perform subsequent computations, and integrate to provide (ultimately) a downwind washout rate (WORATE) or it can read new input data and proceed to calculations for other conditions. In the event that cross-plume integrations are performed, the program terminates when relatively low concentrations are encountered on the edges of the plume, and the downwind washout rate is printed.

The program is terminated completely whenever no additional data cards are found, or when the control variable JEND is set equal to 1. An example data set for use with EPAEC has been given previously in Chapter 4.

DESCRIPTION OF BASIC COMPUTATIONAL ALGORITHM

Exclusive of the input-output functions governed by the main program, the basic computational algorithm can be described by the hierarchy of subroutines shown in Figure 2. The primary function of this algorithm is to solve the drop-response equation

$$\frac{dc_{Ab}}{dz} = \frac{3K_y}{v_t a}(y_{Ab} - H'c_{Ab}) \quad , \qquad \text{(E1)}$$

which was given previously (Hales, *et al* (1972)). The calculations performed by the computer listing given here envision a rain-plume situation as shown in Figure 1.

In this visualization a single raindrop of radius R falls through the plume to a receptor over a linear trajectory determined by the wind speed U and the terminal fall velocity V. A computational grid is set up along the trajectory, and Equation E1 is solved numerically using a Runge-Kutta finite-difference approximation to obtain the value of c_{Ab} (CGRND in the computer code) at the receptor location. This procedure is repeated for all drop sizes in the discretized spectrum and the results are averaged to obtain a final mixed-mean concentration (CAVG) for that location.

y_{Ab} values along the trajectory are furnished by a plume model in the form of a subroutine (YAB). At present this subroutine is written to accomodate the Gifford-Pasquill Bivariate-Normal plume model, modified to account for quasifirst-order chemical reaction, plume loft, and ambient background. Descriptions of the subroutines shown in Figure 2 are given individually in the following text. Listings of these subroutines are provided at the end of this Appendix.

Subroutine V provides the terminal fall velocity dz/dt, as a function of raindrop radius R. This internal function is simply an empirical polynomial fit to measured terminal velocity data.

Subroutine HPRIME utilizes appropriate computations thereof, to determine values of the apparent Henry's-law constant appropriate to the current value of either c_{Ab} or y_{Ab}, depending on the value of the control variable LGOPT. If LGOPT is set equal to 1 in the calling sequence, calculation is based on the value of y_{Ab}; otherwise the current value of c_{Ab} is employed.

Subroutine MTC computes the overall mass-transfer coefficient K_y. It begins by calculating the gas-phase coefficient. Then, if the control variable JOPT has been set equal to 1, (gas-phase limiting), the overall coefficient is returned as the gas-phase value. Otherwise, a liquid coefficient is calculated, and the gas and liquid coefficients are combined to obtain the corresponding stagnant-drop values.

Subroutine RUNGE, in conjunction with subroutine SOLVE performs the numerical integration of Equation E1, SOLVE supplying RUNGE values of the derivative dc_{Ab}/dz (F in the computer code) and RUNGE returning values of

c_{Ab}. RUNGE is a fourth-order Runge-Kutta algorithm which has been adapted from a previous work. This algorithm is rather complex and will not be discussed in detail here, except to state that its expected errors are of the order of the fractional grid spacing to the fourth power. For a complete discussion of this method the reader is referred to the work of Carnahan, *et al* (1969).

Subroutine YAB, as mentioned previously, provides values of the gas-phase mole fraction of pollutant as a function of spatial location x, y, and z. The Gifford-Pasquill Bivariate-Normal equation, modified for quasifirst-order gas-phase chemical reaction, is employed for this purpose. The subroutine computes values of the dispersion parameters, and proceeds directly with a solution of the bivariate-normal equation to provide the return value YAB. H in this subroutine is a virtual value, and depends upon the value of emission height supplied by the calling program.

Subroutine SOLVE performs the function of establishing the computational grid and implementing RUNGE to obtain the solutions to Equation E1 The routine begins by initializing variables and then testing for the occurrence of equilibrium scavenging. This is accomplished by calculating a virtual emission height (HSTAR) and an appropriate dispersion parameter (SIGMAZ). This is followed by determination of an effective Henry's-law constant, which is employed in conjunction with the criterion (GROUP < 15) to determine whether or not equilibrium scavenging occurs. If equilibrium conditions are indeed predicted, the scheme bypasses the solution of Equation E1, and simply returns the equilibrium washout concentration value.

In the event that equilibrium conditions are not predicted, the routine initializes the concentration of pollutant in the drop, C(1), to its appropriate above-plume value, and proceeds to establish a computation grid. In performing this function it first tests for plume undercut by the raindrop (REF < 0). In the event that undercutting occurs, the grid network is established by dividing the vertical distance between the sampler and the height at which the drop crosses X = 0 into thirty equally-spaced measurements.

If plume undercutting does not occur, a "normal" grid spacing is established. This is accomplished by finding an appropriate vertical spread parameter (SIGMA) for early stages of the drop-plume encounter and (rather arbitrarily) beginning numerical computations at an elevation equal to the effective release heights plus three times the computed spread (HSTAR + 3 * SIGMA). Grid spacing is set at one-sixtieth of the vertical distance between the receptor and the point where calculations are initiated.

A final modification of the computation grid structure is performed if the raindrop encounters a plume having a low degree of spread ("compact plume"). This is done simply by testing for whether the current spacing is less than one-fourth the computed spread parameter SIGMA. If not, a top grid spacing (TDZ) is set equal to SIGMA/4 (SIGMA/8 if SIGPHI is greater than 0.5). If "compact" plumes are encountered, this finer grid spacing is employed for 25 increments, and the original grid spacing, DELTAZ, is employed thereafter. The choices of grid spacings described above were arrived at after experimentation with various arrangements. This system provides for general stability and accuracy of the algorithm, with reasonable economy in execution time.

As described earlier, numerical solution of the object equation is accomplished using subroutine RUNGE. This subroutine is called repeatedly, and control is transferred between it and the calling subroutine SOLVE, which updates the downwind distance (x) and effective release height HSTAR. SOLVE also updates the derivative function F(1) and supplies this value to RUNGE, which in turn provides calculated values of the concentration C(1).

Calculations continue until the receptor location is encountered. Then the value of the ground-level rain concentration (COBJ) is calculated and returned with other pertinent variables in the calling sequence.

Subroutine MASTER coordinates calculations for the ensemble of drops in the discretized spectrum, and combines the resulting concentration values to obtain mixed-mean levels. MASTER simply calls subroutine SOLVE for each raindrop size in the spectrum, saves the individual concentrations in the array CGRND(I), and averages according to the equation

$$\mathrm{CAVG} = \frac{\sum_{1}^{N} F(I)D(I)^{3}CGND(I)}{\sum_{1}^{N} F(I)D(I)^{3}} \ .$$

Control is then transferred to the main program for subsequent printing operations.

MODIFICATION OF THE COMPUTER CODE

The modular form of the general computer code enables it to be modified easily for use in other applications. Such modifications can be categorized into two types, depending on whether they are meant to improve the accuracy of the calculations or to adapt the algorithm for use with substances other than those originally intended.

The first type of modification--an incorporation of an improved plume model for instance--can usually be accomplished by modular replacement of one or more subroutines in a straight-forward manner. The second type of modification usually can be accomplished easily, depending on the materials of interest. If this material is a nonreactive gas, one simply must replace the solubility function HPRIME with one appropriate to the gas in question. Other routines are generally applicable, and corresponding modifications are accomplished automatically by changes in the physical-properties input data. Scavenging of a totally soluble gas, for instance, can be calculated simply by modifying the function HPRIME to return a zero value whenever it is called.

TABLE 20.

COMPUTER NOMENCLATURE

Symbol	Units	Definition
AA	cm^2	Summing variable for calculation of average concentration
B	gm moles/liter	Dummy variable in subroutine HPRIME used for storage of sum of the equilibrium constant and the excess hydrogen ion concentration
BKG	dimensionless	Mixing ratio of pollutant in gas phase background (moles/mole)
C	gm moles/cm^3	Mixed-mean concentration of pollutant in a specific raindrop
CAVG	gm moles/cm^3	Mixed-mean concentration of pollutant in a collected rain sample
CAVGCL	gm moles/cm^3	Mixed-mean concentration of pollutant in rain sample collected beneath plume centerline
CCUM	gm moles/cm^3	Cumulative concentration used for integration across the plume to calculate washout rate
CDUM	gm moles/$(liter)^2$	Dummy variable used in HPRIME
CEQ	gm moles/cm^3	Concentration of pollutant in rain in equilibrium with ground-level gas-phase concentration
CGRND	gm moles/cm^3	Mixed-mean concentration of pollutant in a specific raindrop at receptor
CLAST	gm moles/cm^3	Dummy variable used for performing cross-plume integration
COBJ	gm moles/cm^3	Mixed-mean concentration of pollutant in a specific raindrop at receptor
CSET	gm moles/cm^3	Mixed-mean concentration of pollutant in a specific raindrop used for calculation of mass-transfer coefficient in subroutine TKY
CTEST	gm moles/cm^3	Dummy variable used to test for cross-plume integration termination conditions; also used to establish compact plume characteristics in SOLVE

TABLE 20. (Contd.)

Symbol	Units	Definition
D	cm	Raindrop diameter
DAX	cm^2/sec	Molecular diffusivity of pollutant in air
DAY	cm^2/sec	Molecular diffusivity of pollutant in water
DELTAY	cm	Cross-plume spacing of calculation points
DELTAZ	cm	Vertical grid spacing employed under non-compact plume conditions
DYDUM	cm	Cross-plume spacing of calculation points generated by computer if no value is entered as data
DZ	cm	Vertical grid spacing
DZTST	cm	Test variable for assessing compact plume conditions
EQCON	gm moles/liter	Equilibrium constant for first dissociation of SO_2 (cf. Equation (40))
F	cm^{-3}	Probability-density function for raindrops of size R in a distributed system; also denotes derivative used in subroutines SOLVE and RUNGE (gm-moles/cm^4)
GR	dimensionless	Dummy variable used in subroutine SOLVE
GROUP	dimensionless	Dimensionless group used to evaluate equilibrium scavenging conditions (cf. Equation (1))
H	cm	Effective emission release height
HANK	liters/gm mole	Henry's-law constant for undissociated SO_2 in water (cf. Equation (39))
HEX	gm moles/liter	Hydrogen ion in rain other than that contributed by dissolved SO_2
HPRIME	cm^3/gm mole	Effective Henry's-law constant for total dissolved SO_2 in water
HSTAR	cm	Plume height, or effective release height

TABLE 20. (Contd.)

Symbol	Units	Definition
HTEST	cm^3/gm mole	Effective Henry's-law constant used for evaluation of equilibrium scavenging conditions
I		Index integer
ICP		Internal control variable in subroutine SOLVE providing for grid spacing modifications in the case of a compact plume
IGRND		Internal control variable in subroutine SOLVE providing for termination of the algorithm as the raindrop encounters the receptor
IS		Internal control variable communicating status of solution between subroutines SOLVE and RUNGE
IY		Internal control variable providing a runaway trap on cross-plume integration sequence
J		Index integer
J1		Read control variable providing for optional reading of raindrop size distribution data
J2		Read control variable providing for optional reading of physical properties data
J3		Read control variable providing for optional reading of plume data
J4		Read control variable providing for optional reading of grid data
JEND		Program termination control variable
JOPT		Mass-transfer coefficient option control variable (JOPT = 1 gives gas-phase controlled coefficient; JOPT = 0 gives stagnant-drop contribution)
JP		Print control variable (JP set equal to 1 suppresses printing of individual raindrop data
LGOPT		Control variable for gas (= 1; or liquid (= 2) based solubility calculations

TABLE 20. (Contd.)

Symbol	Units	Definition
M		Internal/external control
N		Integer for RUNGE and SOLVE Number of discreet drop sizes in descretized spectrum; also number of simultaneous equations in RUNGE
P	atm	Ambient pressure
PHI		Internal computation variable in RUNGE
Q	gm moles/sec	Source strength of plume
R	cm	Raindrop radius
RE	dimensionless	Reynolds number for falling drop
REF	cm	Height above release point where raindrop passes $x = 0$
RK	sec^{-1}	First-order reaction constant for decay of pollutant in plume
S		(Integer) status variable used in subroutine RUNGE--counterpart of variable IS in subroutine SOLVE
SAVEY	dimensionless	Mixing ratio of pollutant in gas phase at receptor
SC	dimensionless	Schmidt number for falling drop
SIGMA	cm	Internal estimate of plume spread in z-direction--utilized when compact plumes are encountered
SIGMAY	cm	Plume spread in y-direction
SIGMAZ	cm	Plume spread in z-direction
SIGPHI	radians	Plume spread in ψ-direction
SIGTHE	radians	Plume spread in θ-direction
SIGY	cm	Plume spread in y-direction at receptor

TABLE 20. (Contd.)

Symbol	Units	Definition
SIGZ	cm	Plume spread in z-direction at receptor
T	° K	Ambient temperature
TDZ	cm	Compact plume grid spacing
TEST1	liter/gm mole	Test variable for asymptotic dilution conditions
TKY	gm moles/cm^2 sec	Overall mass-transfer coefficient (cf. Eq. (41))
TDZ	cm	Grid spacing for compact plume
U	cm/sec	Mean wind velocity
V	cm/sec	Terminal fall velocity of raindrop (fall in +z direction)
VERT	cm/sec	Plume loft velocity
WORATE	gm moles/cm	Downwind washout rate
X	cm	Downwind distance from source
XBUK	cm	Downwind distance of receptor from source
XCL	cm	X position where drop falls across release elevation
XK	gm moles/cm^2 sec	Liquid-phase mass-transfer coefficient
XNT	cm/sec	Rainfall rate
Y	cm	Crosswind distance from source
YAB	dimensionless	Mixing ratio of pollutant in air (moles/mole)
YBUK	cm	Crosswind distance of receptor from source
YK	gm moles/cm^2 sec	Gas-phase mass-transfer coefficient
Z	cm	Distance above stack base
ZBUK	cm	Distance of receptor above stack base

```
      PROGRAM EPAEC(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
C     PROGRAM **EPAEC** TO SOLVE NONLINEAR-NONFEEDBACK MODEL FOR GAS
C     SCAVENGING.  PROGRAMMED IN FINAL FORM MARCH, 1973 BY
C     J. M. HALES UNDER CONTRACT TO THE DIVISION OF METEOROLOGY,
C     ENVIRONMENTAL PROTECTION AGENCY.
C
C     PROGRAM READS IN THE NUMBER OF DISCRETE DROP SIZES IN THE RAIN
C     SPECTRUM AND THE VARIOUS DECISION VARIABLES. IT THEN READS THE
C     RAIN DISTRIBUTION DATA AND (OPTIONALLY) THE LIQUID-PHASE MASS-
C     TRANSFER COEFFICIENTS.  SUBSEQUENTLY IT READS IN THE PHYSICAL
C     PROPERTIES, THE WIND VELOCITY AND SOURCE STRENGTH, AND THE
C     LOCATION OF THE RECEPTOR.  CALCULATION THEN PROCEEDS AS DOCUMENTED
C     THROUGHOUT THE PROGRAM.  THIS CODE USES THE CGS SYSTEM OF UNITS,
C     EXCEPT FOR PRESSURE, WHICH IS IN ATMOSPHERES, AND FOR SOME
C     CONCENTRATIONS EMPLOYED IN THE SOLUBILITY CALCULATIONS,
C     WHICH ARE GIVEN IN MOLES PER LITER.  CONVENTIONAL CONCENTRATION
C     UNITS ARE MOLES PER CUBIC CENTIMETER.
      COMMON D(20),F(20),CGRND(20), SAVEY,N,J1,J2,J3,J4,JOPT,JP,JEND,
     1DAX,DAY,HEX,XNU,P,T,XNT,SIGTHE,SIGPHI,U,H,Q,XBUK,YBUK,ZBUK,
     2DELTAZ,SIGY,SIGZ,CEQ,CAVG,RK,BKG,VERT
      EXTERNAL V,HPRIME,YAB
100   READ (5,320) N,J1,J2,J3,J4,JOPT,JP,JEND
      IF (J1.EQ.1) GO TO 110
      READ (5,330) (D(I),I=1,10)
      READ (5,330) (F(I),I=1,10)
110   IF (J2.EQ.1) GO TO 120
      READ (5,340) DAX,DAY,HEX,XNU,P,T,XNT,RK
120   IF (J3.EQ.1) GO TO 130
      READ (5,350) SIGTHE,SIGPHI,U,H,Q,VERT,BKG
130   IF (J4.EQ.1) GO TO 140
      READ (5,360) XBUK,YBUK,ZBUK,DELTAY,DELTAZ
      DYDUM=.087266*XBUK
      IF (DELTAY.LT.1.) DELTAY=DYDUM
140   IF (J4.EQ.1) YBUK=0.
      WRITE (6,230)
      WRITE (6,240) DAX,DAY,XNU,HEX,P,T
      WRITE (6,250) SIGTHE,SIGPHI,U,H,Q
      WRITE (6,260) XBUK,YBUK,ZBUK
      CCUM=0.
      IY=0
150   CALL MASTER
C     TESTING FOR INITIAL COMPUTATION
      IF (IY.GT.0) GO TO 160
      WRITE (6,270)
C     PRINTING OF BULK RESULTS
160   WRITE (6,280) SIGY,SIGZ,CEQ,CAVG
      WRITE (6,310) SAVEY
      IF (JP.EQ.1) GO TO 180
      DO 170 I=1,N
      R=D(I)/2.
      REF=ZBUK-XBUK*V(R)/U-H
C     PRINTING OF INDIVIDUAL RESULTS
170   WRITE (6,290) D(I),CGRND(I),REF
      IF(JEND.EQ.3) GO TO 100
C     TESTING FOR WHETHER RECEPTOR IS ON CENTERLINE
```

```
      SUBROUTINE MASTER
C     SUBROUTINE FOR CALCULATION OF WASHOUT CONCENTRATIONS IN RAIN
C     AT GROUND LEVEL USING GENERALIZED NONLINEAR MODEL.  IT ACCEPTS
C     INPUT DATA FROM MAIN PROGRAM THROUGH THE COMMON STATEMENT AND
C     THEN PROCEEDS TO CALCULATE RAINDROP CONCENTRATIONS BY CALLING THE
C     REQUIRED SUBROUTINES.  IT THEN CALCULATES THE AVERAGE
C     CONCENTRATION IN THE RAIN SAMPLE AND RETURNS CONTROL TO THE
C     CALLING PROGRAM
      COMMON D(20),F(20),CGRND(20), SAVEY,N,J1,J2,J3,J4,JOPT,JP,JEND,
     1DAX,DAY,HEX,XNU,P,T,XNT,SIGTHE,SIGPHI,U,H,Q,XBUK,YBUK,ZBUK,
     2DELTAZ,SIGY,SIGZ,CEQ,CAVG,RK,BKG,VERT
C     CALCULATION OF STANDARD DEVIATIONS
      SIGY=XBUK*SIGTHE
      SIGZ=XBUK*SIGPHI
      DO 100 I=1,N
      R=D(I)/2.
C     CALCULATION OF INDIVIDUAL CONCENTRATIONS FOR RADIUS R RAINDROPS
      CALL SOLVE (R,COBJ,JOPT,DAX,DAY,HEX,XNU,P,T,SIGTHE,SIGPHI,U,H,Q,XB
     1UK,YBUK,ZBUK,SAVEY,RK,BKG,VERT,CEQ)
      CGRND(I)=COBJ
100   CONTINUE
      CAVG=0.
      AA=0.
C     COMPUTATION OF AVERAGE CONCENTRATION BY DISTRIBUTION OVER DROP SIZES
      DO 110 I=1,N
110   AA=AA+F(I)*D(I)**3
      DO 120 I=1,N
120   CAVG=CAVG+F(I)*CGRND(I)*D(I)**3
      CAVG=CAVG/AA
      RETURN
      END
```

```
      FUNCTION HPRIME(C,HEX,T,P,LGOPT)
C     SUBROUTINE FOR CALCULATING APPARANT HENRY"S-LAW CONSTANT USING
C     JOHNSTONE-LEPPLA PARAMETERS.

      HANK=EXP(9.94-3040./T)/P
      EQCON=EXP(-10.3+1780./T)
C     TRANSFER POINT FOR LIQUID- OR GAS-PHASE BASED CALCULATIONS
      IF(LGOPT.EQ.1) GO TO 100
      B=EQCON*HEX
      CDUM=EQCON*1000.*C
C     TEST FOR LOW-CONCENTRATION CONDITIONS
      TEST1=4.*CDUM/B**2
C     ASYMPTOTIC EXPRESSION FOR LOW-CONCENTRATION CONDITIONS
      HPRIME=1000.*(HANK-HANK*EQCON/B)
      IF(TEST1.LT..001) GO TO 110
C     SOLUTION OF TOTAL SOLUBILITY EQUATION
      HPRIME=HANK*(1.-(-B+SQRT(B**2+4.*CDUM))/(2000.*C))*1000.
      GO TO 110
C     TEST FOR LOW-CONCENTRATION CONDITIONS
100   DUMMY=HEX*HEX*HANK/(4*EQCON*C)
      IF(DUMMY.LT.1000.) GO TO 105
C     ASYMPTOTIC EXPRESSION FOR LOW-CONCENTRATION CONDITIONS
      HPRIME=1000.*HANK*HEX/(HEX+EQCON)
      GO TO 110
C     SOLUTION OF TOTAL SOLUBILITY EQUATION
105   CTEST=(C/HANK+(-HEX+SQRT(HEX**2+4*C*EQCON/HANK))/2)/1000.
      HPRIME=C/CTEST
C     RETURN VALUE OF HPRIME HAS UNITS OF CENTIMETERS CUBED PER MOLE
110   RETURN
      END
```

The above subroutine is that employed for the prediction of SO_2 washout from power plant plumes. The sensitivity of SO_2 solubility to pH required the incorporation of pH data and the SO_2-H_2O equilibrium constant to the calculation of Henry's Law constant, HPRIME. Application of the EPAEC model to the scavenging of ethylacetoacetate and diethylamine involved input of H' values calculated in Appendix A.

```
      SUBROUTINE SOLVE (R,COBJ,JOPT,DAX,DAY,HEX,XNU,P,T,SIGTHE,SIGPHI,U,
     1H,Q,XBUK,Y,ZBUK,SAVEY,RK,BKG,VERT,CEQ)
C     SUBROUTINE FOR CALCULATION OF INDIVIDUAL RAINDROP CONCENTRATIONS.
C     PROGRAM SETS UP APPROPRIATE COMPUTATION GRID FOR NUMERICAL
C     SOLUTION OF THE FIRST-ORDER, ORDINARY DIFFERENTIAL EQUATION
C     DESCRIBING DROP RESPONSE.  IT THEN CALLS THE RUNGE-KUTTA
C     ALGORITHM REPEATEDLY, PROGRESSING FROM THE TOP OF THE
C     COMPUTATION GRID TO GROUND LEVEL.
      DIMENSION C(1),F(1)
C     INITIALIZATION OF VARIABLES
      ICP=0
      M=0
      IGRND=0
      C(1)=0
      I=1
C     BYPASS TEST FOR EQUILIBRIUM SCAVENGING CONDITIONS
      HSTAR=H+VERT*XBUK/U
      SIGMAY=SIGTHE*XBUK
      SIGMAZ=SIGPHI*XBUK
      SAVEY=YAB(T,P,U,HSTAR,Q,XBUK,Y,ZBUK,SIGTHE,SIGPHI,RK,BKG)
      HTEST=HPRIME(SAVEY,HEX,T,P,1)
      IF(HTEST.LE.0.) GO TO 100
      CTEST=SAVEY/HTEST
      CALL MTC(R,DAX,DAY,XNU,T,P,JOPT,CTEST,HTEST,TKY)
      GR=18.9*TKY*HTEST*U*SIGMAY*SIGMAZ**2*EXP(.5*.5*Y*Y/SIGMAY**2)
      GR=-GR/(V(R)*R)
      GROUP=GR*SAVEY/(82.*Q*T/P)
      CORJ=CTEST
      CEQ=CTEST
      IF(GROUP.GT.15.) GO TO 190
C     CALCULATION OF INITIAL RAINDROP CONCENTRATION
      C(1)=BKG/HPRIME(BKG,HEX,T,P,1)
C     TEST FOR PLUME UNDERCUT
100   REF=-XBUK*V(R)/U+ZRUK-H
      Z=REF+H
      IF (REF.GT.0.) GO TO 120
C     SPACING FOR UNDERCUT GRID
      DELTAZ=-XBUK*V(R)/(U*30.)
      GO TO 130
C     SETTING OF NORMAL GRID SPACING
120   XCL=XBUK+U*(H-ZBUK)/V(R)
      SIGMA=SIGPHI*XCL
      HSTAR=H+VERT*XCL/U
      Z1=HSTAR+3.*SIGMA
      IF (Z1.LT.Z) Z=Z1
      DELTAZ=Z/60.
C     TEST FOR COMPACT PLUME
      DZTST=SIGMA/4.
      IF(SIGPHI.GT..5) DZTST=DZTST/2.
      IF(DZTST.GT.DELTAZ) GO TO 130
C     SETTING OF COMPACT GRID SPACING
      TDZ=DZTST
      ICP=1
C     START OF NUMERICAL INTEGRATION LOOP
130   IF (ICP.NE.1.OR.I.GT.25) GO TO 140
      DZ=-TDZ
```

```
      GO TO 150
140   DZ=-DELTAZ
C     INITIATION OF RUNGE-KUTTA ALGORITHM
150   CALL RUNGE (1,C,F,Z,DZ,IS,M)
      IF(C(1).LT.0.) C(1)=0.
      IF (IS.NE.1) GO TO 160
      X=XBUK+U*(Z-ZBUK)/V(R)
      HSTAR=H+VERT*X/U
C     CALCULATION OF MASS-TRANSFER COEFFICIENT
      CALL MTC (R,DAX,DAY,XNU,T,P,JOPT,C(1),HEX,TKY)
C     DETERMINATION OF FIRST DERIVATIVE FOR R-K ALGORITHM
      F(1)=(3.*TKY/(R*V(R)))*(YAW(T,P,U,HSTAR,Q,X,Y,Z,SIGTHE,SIGPHI,RK,H
     1KB)-HPRIME(C(1),HEX,T,P,2)*C(1))
      GO TO 150
C     TEST FOR APPROACH TO GROUND
160   ZTEST=Z+DZ-ZBUK
      IF(ZTEST.LT.100.) GO TO 170
      I=I+1
      GO TO 130
170   IF (IGRND.EQ.1) GO TO 180
      IGRND=1
      DZ=ZBUK-Z
      GO TO 150
180   CORJ=C(1)
190   RETURN
      END
```

```
      SUBROUTINE MTC (R,DAX,DAY,XNU,T,P,JOPT,CSET,HEX,TKY)
C     SUBROUTINE FOR MASS-TRANSFER COEFFICIENT CALCULATION.
C     GAS COEFFICIENT BASED ON FROESSLING EQUATION.  LIQUID
C     COEFFICIENT IS BASED ON CONTINUITY EQUATION SOLUTION FOR
C     RESPONSE TO RAMP CONCENTRATION FORCING FUNCTION.
C
C     CALCULATION OF GAS-PHASE COEFFICIENT
      RE=-2.*R*V(R)/XNU
      SC=XNU/DAY
      YK=(1.+.3*RE**.5*SC**.333)*DAY*P/(R*T*82.057)
      TKY=YK
      IF (JOPT.EQ.1) GO TO 100
C     CALCULATION OF LIQUID-PHASE  COEFFICIENT
      XK=.2778*DAX/R
      TKY=1/(HPRIME(CSET,HEX,T,P,2)/XK+1/YK)
100   RETURN
      END
```

```
      SUBROUTINE RUNGE (N,Y,F,X,H,S,M)
C     SUBROUTINE TO SOLVE DIFFERENTIAL EQUATION DESCRIBING CONCENTRATION
C     RESPONSE OF A FALLING DROP.  RUNGE-KUTTA ALGORITHM IS ADAPTED FROM
C     GENERAL VERSION GIVEN BY CARNAHAN, LUTHER, AND WILKES.
      DIMENSION SAVEY(1),PHI(1),F(1),Y(1)
      INTEGER S
      M=M+1
      GO TO (100,110,130,150,170), M
100   S=1
      GO TO 190
110   DO 120 J=1,N
      SAVEY(J)=Y(J)
      PHI(J)=F(J)
120   Y(J)=SAVEY(J)+.5*H*F(J)
      X=X+.5*H
      S=1
      GO TO 190
130   DO 140 J=1,N
      PHI(J)=PHI(J)+2.*F(J)
140   Y(J)=SAVEY(J)+.5*H*F(J)
      S=1
      GO TO 190
150   DO 160 J=1,N
      PHI(J)=PHI(J)+2.*F(J)
160   Y(J)=SAVEY(J)+H*F(J)
      X=X+.5*H
      S=1
      GO TO 190
170   DO 180 J=1,N
180   Y(J)=SAVEY(J)+(PHI(J)+F(J))*H/6.
      M=0
      S=2
190   CONTINUE
      RETURN
      END
```