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ENVIRONMENTAL RESEARCH DIVISION

TECHNICAL PROGRESS REPORT

January 1986 - October 1987

T.M. Beasley, Division Director

July 1988

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**ENVIRONMENTAL RESEARCH DIVISION
TECHNICAL PROGRESS REPORT**

January 1986 - October 1987

ABSTRACT

Technical progress in the various research activities of Argonne National Laboratory's Environmental Research Division is reported for the period 1986-1987. Textual, graphic, and tabular information is used to briefly summarize (in separate chapters) the work of the Division's Atmospheric Physics, Environmental Effects Research, Fundamental Molecular Physics and Chemistry, and Organic Geochemistry and Environmental Instrumentation Programs. Information on professional qualifications, awards, and outstanding professional activities of staff members, as well as lists of publications, oral presentations, special events organized, and participants in educational programs, are provided in appendices at the end of each chapter.

1 DIVISION DIRECTOR'S OVERVIEW

In late 1986, the Environmental Impacts and Waste Management Programs of the Environmental Research Division (ERD) were administratively transferred to the Energy and Environmental Systems Division of the Laboratory in an effort to consolidate environmental assessment activities in a single organizational unit. On October 19, 1987, the Environmental Research Division at Argonne National Laboratory was discontinued as an organizational unit. In its place, a Center for Environmental Research was formed within the Division of Biological and Medical Research, which now accommodates both the staff and programs of the former ERD.

As a consequence of these changes, the 1986-1987 technical progress report presented here is not entirely constrained to activities in that time period. Instead, a certain latitude was afforded the staff in reporting their activities under the former ERD structure. In arriving at this decision the substance of the report was considered more important than its strict adherence to editorial form.

The preparation of this final report represents the efforts of Maria Pacholok, Sandra Gotlund, Rebecca Spencer, and Karen Haugen. I am indebted to them for the patience and professionalism they displayed during its preparation.

T.M. Beasley, Director
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2-1/2-2

2 ATMOSPHERIC PHYSICS PROGRAM

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2 ATMOSPHERIC PHYSICS PROGRAM

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**No longer a member of the Division.*

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2.1 PROGRAM OVERVIEW

M.L. Wesely (Program Manager)

The Atmospheric Physics Program conducts research on the transport, chemical transformation, and deposition of trace substances in the fluid environment. In 1986, issues of "acid rain" continued to be the motivation behind most of our research activities. Other sustained activities included studies of atmospheric transport and dispersion over complex terrain and of the physical and chemical behavior of trace substances in the Great Lakes. This chapter summarizes the orientation and some of the progress made in our research projects in 1986. More complete descriptions can be found in the publications listed in Appendix 2-E.

Our research on air-surface exchange not aided directly by precipitation consisted primarily of investigations of dry deposition. Relying heavily on micrometeorological techniques, field experiments were directed toward understanding the physical, chemical, and biological processes at land surfaces that control the uptake of sulfur dioxide, sulfate particles, nitrogen oxides, ozone, and related substances. Parameterizations suitable for evaluating dry deposition rates on the basis of a description of local surface and atmospheric conditions were developed and applied in numerical models for estimating dry deposition on a regional scale. Parameterizations were also designed for application at specific sites where routine measurements of acidic deposition are taken, including one research site operated at Argonne.

Studies of wet deposition of acidifying substances in the atmosphere included a major field experiment on precipitation scavenging mechanisms in cold weather as part of a large multilaboratory program known as PRECP (Processing of Emissions by Clouds and Precipitation). Another major task for PRECP has been theoretical and numerical investigations of cloud physics processes affecting wet deposition. Most recently, we have begun investigations of methods for generalizing results of specific field experiments on wet deposition, to place them in a climatological context.

Transport and diffusion in the atmospheric boundary layer were studied by application of ground-based acoustic sounding systems to probe the wind and thermal structure above complex terrain. Advanced acoustic systems were produced to provide high-resolution measurements of the means and variances of wind components along every few meters of their vertical profiles. Such outputs can be used as direct input to dispersion models on a real-time basis.

Our research on atmospheric numerical modeling included studies of long-range transport and deposition. For example, data bases consisting of precipitation and other meteorological measurements over several years were used to evaluate the averages and trends of sulfur and nitrogen deposition at selected areas in North America.

Projects on the physical and chemical behavior of trace substances in the Great Lakes included experimental studies of sediment transport and resuspension, analysis of water quality surveillance data, and application of systems analysis to environmental problems.

Our newest area of study is atmospheric organic chemistry. This program area is being started with an investigation of the sources of volatile hydrocarbons found in urban Chicago and will expand as needed in studies of air-surface exchange of hydrocarbons and atmospheric photochemical reactions.

2.2 AIR-SURFACE EXCHANGE

2.2.1 Summary

Our research on air-surface exchange included studies of both dry and wet deposition of acidifying substances in the atmosphere. On dry deposition, diverse studies employing micrometeorological techniques were applied to study the physical, chemical, and biological processes that control the removal of SO_2 , sulfate, NO_x , NO_y , and O_3 . The objectives were usually to develop parameterizations of deposition velocities (downward flux divided by concentration at a specified height) in terms of the aerodynamic and surface resistances to uptake. These parameterizations were applied in efforts to obtain long-term estimates of dry deposition amounts at specific routine measurement sites, which supply the necessary observations of local atmospheric and surface conditions. Considerably larger areas, where the necessary atmospheric and surface data are supplied by regional-scale numerical models of transport, chemical transformation, and deposition, are of interest as well. While our studies of dry deposition originated from several small projects supported by U.S. Department of Energy (DOE) and U.S. Environmental Protection Agency (EPA) programs on acid deposition, our wet deposition studies are entirely supported by DOE's PRECP program. In this section, a brief summary is also given of our participation in multilaboratory field experiments on precipitation scavenging of acidifying substances. Other aspects of our contributions to the PRECP program are described under section 2.4 on numerical modeling.

2.2.2 Experimental Studies of Dry Deposition

D.L. Sisterson, R.L. Hart, M.L. Wesely, and D.R. Cook

2.2.2.1 NO Flux Measurements Over Grass

Eddy correlation techniques were used to measure the vertical flux of NO at a height of 8 m over grass at the Argonne deposition site during the period of October 1983 through June 1984 (Wesely et al. 1986b). Surface conditions varied from short brown grass with no snow cover (winter) to lush tall grass (summer), and the soil was usually moist but not waterlogged. Concentrations of NO, NO_2 , and O_3 ; fluxes of momentum and heat; soil temperature; and miscellaneous meteorological variables were also observed. In all, 256 runs (25 min) for all variables were recorded, 79 at night and 177 during the day. Periods of steady meteorological conditions and pollutant concentrations were selected for subsequent analysis, in which data obtained over three to five hours

were averaged in order to decrease the scatter of deposition velocity estimates (Wesely and Hart, 1985). The final working data set, which consists of eight nighttime periods and 19 daytime periods, is shown in Table 2.1.

The vertical flux of NO (F_N) at a height of several meters is probably determined by rates of dry deposition and emission at the surface, the strength of turbulent mixing, and possible rapid in-air chemical reactions that could significantly alter the vertical flux as a function of height. A traditional, engineering approach to describing dry deposition is to express the flux in terms of a deposition velocity ($v_d = -F_N/[NO]$). We have chosen not to use deposition velocity in Table 2.1 and in further discussion of NO fluxes because deposition of NO at the surface does not always appear to be the dominant process affecting the fluxes measured at 8 m. Instead, Table 2.1 lists a normalized flux ($F_N/[NO]$), for which a positive value indicates that the flux is directed upward. The standard errors (S.E.) shown apply to deposition velocities as well as normalized fluxes.

It is known that the vertical flux of NO can be strongly affected by rapid in-air chemical reactions (e.g., Fitzjarrald and Lenschow 1983). The vertical flux of NO was hypothesized to depend upon reactions with O_3 and, especially at night, reactions involving NO_3 . Since the strengths of these and other reactions can vary markedly from day to night, the data from the two portions of the day were analyzed separately.

About 90% of the variation (R^2) in the nighttime NO fluxes could be explained statistically by using multiple regression. At face value, the regression indicates that NO flux at a height of 8 m at night was controlled by a rather small resistance (near 3 s cm^{-1}) to surface uptake and by in-air reactions involving NO_2 and NO_3 . However, these inferences are questionable because of the limited data set and the rather large run-to-run variability of the flux estimates.

Nearly 60% of the variation in the daytime NO fluxes could be accounted for by multiple regression. Results suggest that the average NO flux was small in magnitude and directed upward, that reactions involving NO_3 were not important, and that rapid in-air reactions involving O_3 and NO_2 and surface emissions strongly influenced the eddy fluxes measured at 8 m. The surface emission term suggests only a weak temperature dependence, which may be inaccurate because the number of samples is quite small and the temperature variations were otherwise quite minimal.

2.2.2.2 SO_2 and O_3 Flux Estimates with the Modified Bowen Ratio Technique

The modified Bowen ratio technique is a gradient method based on the assumption that the vertical transfer processes of one scalar are similar to those of another in the surface layer, in this case temperature. This technique has been used with a tram system developed at Argonne that moves a single intake line between two heights every 15 min to determine SO_2 and O_3 concentration differences (Sisterson et al. 1984). During July and September 1986, two "benchmarking" experiments were conducted in which estimates of SO_2 and O_3 fluxes made by the modified Bowen ratio technique were compared to those made by eddy correlation.

TABLE 2.1 Summary of data taken during experiments, where n is the number of 25-min samples averaged and roughly centered on the time shown, G is insolation, T_s is surface temperature, RH is relative humidity, u_* is friction velocity, and z/L indicates atmospheric stability

Date	Time (CST)	n	$\overline{F_N}/[\overline{NO}] \pm \text{S.E.}$ (ppb cm/s)	[NO] (ppb)	[NO ₂] (ppb)	[O ₃] (ppb)	G (W/m ²)	T _s (°C)	RH (%)	u _* (cm/s)	z/L
<u>Night</u>											
28 Oct 83	0300	9	0.00 ±0.14	0.1	7.8	18	0	9.3	55	49	0.04
20 Feb 84	0515	6	-0.07 ±0.16	0.4	12.4	7	0	0.9	76	18	0.08
21 Feb 84	0200	10	0.08 ±0.09	0.2	15.0	6	0	1.4	74	18	0.06
17 May 84	2130	9	0.16 ±0.12	0.2	19.4	48	0	15.0	36	37	0.07
18 May 84	0145	6	-0.28 ±0.14	0.1	7.5	54	0	14.2	44	53	0.03
31 May 84	2130	5	0.04 ±0.09	0.1	9.5	45	0	15.8	43	14	~1
1 Jun 84	2230	8	0.10 ±0.11	0.2	14.6	57	0	17.8	45	17	~1
2 Jun 84	0300	9	-0.15 ±0.10	0.3	12.4	37	0	17.0	51	29	0.08
<u>Day</u>											
14 Oct 83	1315	6	0.49 ±0.20	1.3	4.4	21	508	14.0	55	52	-0.07
25 Oct 83	1215	8	0.13 ±0.10	1.8	2.9	26	571	14.0	40	49	-0.11
19 Feb 84	1015	8	0.12 ±0.38	0.4	6.8	8	30	0.9	91	47	0.00
19 Feb 84	1515	8	0.23 ±0.12	0.5	8.5	10	26	1.0	93	45	0.00
1 Mar 84	1445	6	-0.05 ±0.16	1.7	3.4	28	502	0.4	46	14	-1.18
26 Apr 84	0900	7	0.07 ±0.14	1.4	10.4	77	526	8.2	53	44	-0.09
17 May 84	1200	9	-0.42 ±0.18	1.8	6.8	69	817	13.2	32	41	-0.20
17 May 84	1615	8	-0.06 ±0.19	0.7	5.3	91	503	15.3	34	36	-0.05
18 May 84	1145	8	0.71 ±0.18	0.6	4.0	87	679	15.3	47	48	-0.07
18 May 84	1530	7	0.49 ±0.40	0.5	5.0	88	469	16.8	40	52	0.00
23 May 84	1600	9	0.54 ±0.15	0.8	7.7	54	513	17.6	50	32	-0.19
24 May 84	0800	9	0.06 ±0.07	2.6	8.4	43	505	14.4	66	40	-0.08
24 May 84	1615	8	0.38 ±0.15	0.5	7.4	73	447	17.8	54	58	0.02
31 May 84	1315	8	0.26 ±0.15	0.7	5.5	66	811	15.5	40	44	-0.04
31 May 84	1715	8	0.04 ±0.15	0.8	7.5	65	349	16.6	43	40	0.04
1 Jun 84	1545	6	0.21 ±0.06	0.6	4.8	101	595	18.0	55	41	-0.03
2 Jun 84	0830	7	-0.06 ±0.03	1.5	7.4	51	521	16.7	72	27	-0.25
2 Jun 84	1200	7	0.16 ±0.08	0.8	6.6	86	716	18.4	63	40	-0.06
2 Jun 84	1545	8	-0.01 ±0.07	1.2	7.1	61	315	19.7	68	42	0.05

Application of the modified Bowen ratio technique by sampling pollutant concentrations alternately at two different heights with a single intake line raised or lowered every 15 min requires assumption of steady-state conditions. Since this is not always the case, an interpolation method was developed that looks at trends at one height to assist in determining an estimate of pollutant concentrations at the other height. In this manner, for each 15-min period, a measured pollutant concentration at one height and an estimated value at the other allowed concentration differences to be calculated every 15 min instead of each half hour. Two consecutive 15-min periods were averaged to produce a deposition velocity every half hour. These data were then averaged over periods of two to four hours.

Preliminary results indicate that about two hours of data averaging were required to produce reliable O_3 deposition velocities within 15 to 20% of the eddy correlation values. However, four to six hours of averaging were often required to produce SO_2 deposition velocities of comparable precision because of the low signal-to-noise ratio produced by the SO_2 sensor when ambient concentrations were small. Currently, the tram system is being modified with the tram acting as a reference, traveling between continuous samplings at the two heights.

2.2.2.3 Routine Pollutant Concentration and Flux Measurements at the Argonne Deposition Monitoring Site

The deposition research site at Argonne is one of three core (CORE) sites that have been established in the United States to develop and test the concentration monitoring method as well as other approaches to estimating dry deposition. Routine measurements of NO , NO_2 , NO_x , O_3 , and SO_2 concentrations and meteorological measurements are made at this site (e.g., Sisterson et al. 1986a) to provide air quality information to test the accuracy of the CORE filterpack system. Besides this activity, eddy correlation and other methods are used to evaluate and parameterize deposition velocities of SO_2 and O_3 (Wesely et al. 1986a; Sisterson et al. 1984). Negotiations are currently underway to set up an EPA dry deposition site at the Argonne deposition monitoring site as part of the National Dry Deposition Network (NDDN). Argonne would provide air quality information to test the accuracy of the NDDN filterpack system.

The CORE filterpack SO_2 concentrations have been compared to weekly averaged real-time SO_2 concentrations measured from November 1984 through October 1985, for the weeks when both systems were fully operational. Table 2.2 shows that agreement was usually rather poor (only within 25%) during the initial start-up period of the sampling, with the filterpacks apparently giving low values. Preliminary investigation indicated no obvious single meteorological parameter that could explain the observed differences. Precipitation periods perhaps served as the best indicator because periods of no rain usually had better agreement between the filterpack and averaged real-time data than periods with rain. Since this study period, modifications have been made to the filterpack system to improve flow rate stability, decrease potential filterpack "leaking," and obtain more weekly systems checks of the filterpack system. Further comparisons will be made as the filterpack data become available. On the basis of a limited initial data set, these modifications appear to have improved the agreement between filterpack and averaged real-time SO_2 concentrations for the Argonne site.

TABLE 2.2 Comparison of Argonne mean and weekly filterpack SO₂ data, where n is the number of half-hour averages used

Dates	n	$\mu\text{g}/\text{m}^3$			Precip. (in.)							
		ANL	ATDD	%dif.	Tue	Wed	Thu	Fri	Sat	Sun	Mon	Tue
11/27-12/04	333	11.39	7.4	-35	0.43	0.00	0.00	0.00	0.15	0.00	0.00	0.00
12/04-12/11	332	33.89	22.9	-32	0.00	0.03	0.02	0.00	0.00	0.15	0.00	0.00
12/19-12/26	669	37.36	29.0	-22	--	0.00	0.00	0.75	0.00	0.00	0.06	0.00
12/26-01/02	--	--	--	--	0.10	0.10	0.05	0.30	0.00	0.50	1.2	0.00
01/08-01/15	334	22.67	33.6	+48	0.00	0.00	0.08	0.03	0.00	0.00	0.01	0.00
01/22-01/29	335	19.63	13.6	-31	0.00	T	0.05	0.03	0.00	0.00	0.00	0.00
01/29-02/05	345	36.89	18.8	-49	0.00	0.10	0.02	0.00	0.00	0.00	0.10	0.10
02/05-02/12	311	41.96	26.1	-38	0.00	0.00	0.00	0.00	0.07	0.20	0.25	T
03/12-03/19	332	18.24	15.5	-15	0.00	0.23	0.00	0.00	0.00	0.00	0.00	0.00
03/26-04/02	331	21.72	23.3	+7	0.00	0.45	0.86	0.07	0.15	0.35	0.00	0.00
04/23-04/30	326	18.32	10.8	-41	0.76	0.01	0.00	0.00	T	0.00	0.00	0.00
04/30-05/07	338	38.54	37.2	-3	0.03	0.00	0.00	0.00	0.00	0.16	0.08	0.00
05/07-05/14	336	44.68	23.9	-47	0.05	0.00	0.00	0.00	0.00	0.02	0.00	0.02
05/14-05/21	334	18.93	8.7	-54	0.42	0.14	0.54	0.00	0.01	0.00	0.27	0.00
05/21-05/28	336	26.46	16.0	-40	0.00	0.00	0.00	0.00	0.00	0.00	0.42	0.34
05/28-06/04	342	18.52	7.3	-61	0.00	0.00	0.02	0.00	0.00	0.03	0.00	T
06/04-06/11	337	34.70	19.5	-44	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.50
06/11-06/18	213	7.57	5.4	-29	0.00	0.00	T	0.52	0.50	0.03	T	0.00
06/25-07/02	331	29.27	17.4	-41	0.00	0.00	0.12	0.01	0.00	0.00	0.00	T
07/02-07/09	332	20.12	11.3	-44	0.27	0.00	0.25	0.00	0.00	0.00	0.00	0.00
07/16-07/23	331	21.82	19.6	-10	0.00	0.00	0.00	T	0.00	0.00	0.00	0.00
08/13-08/20	330	20.60	14.8	-28	0.00	0.25	0.44	0.00	0.00	0.00	0.00	0.00
08/20-08/27	316	17.20	15.9	-8	0.00	0.00	0.00	T	0.00	0.01	T	0.00
08/27-09/03	338	20.06	17.0	-15	0.00	0.00	0.55	0.02	0.00	0.00	0.00	0.00
09/03-09/10	336	35.95	26.2	-27	0.00	0.00	0.00	0.35	0.00	0.80	0.09	0.00
09/10-09/17	336	18.30	18.2	-1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
09/17-09/24	335	22.25	25.3	+13	0.00	0.00	0.00	0.02	0.04	0.71	0.17	0.00
09/24-10/01	333	18.33	15.8	-14	0.00	0.02	0.02	0.00	0.00	0.00	0.25	0.00
10/01-10/08	335	18.54	13.6	-26	0.00	0.00	0.00	0.90	0.00	0.00	T	0.39
10/08-10/15	335	34.25	16.0	-53	0.16	0.08	0.18	0.03	0.07	0.02	0.06	0.02
10/15-10/22	334	30.73	25.7	-16	0.00	0.00	0.00	2.5	0.01	0.00	0.00	T
10/22-10/29	336	41.68	38.3	-8	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.00
Average:		25.82	19.16	-25								
RMS difference:		9.2										

2.2.3 Estimates of Regional-Scale Dry Deposition

M.L. Wesely

Parameterizations of dry deposition velocities for SO_2 , particulate SO_4^{2-} , O_3 , NO plus NO_2 , and HNO_3 have been derived for application in regional-scale models, specifically for the Regional Acid Deposition Model (RADM). The parameterizations were derived on the basis of numerous field and laboratory studies and are applied to eleven landuse types and five seasonal categories in North America (Sheih and Wesely 1986). An earlier version of the computer subroutine, or module, supplied for this purpose (Sheih et al. 1986) was adapted for use in RADM and applied to compute deposition velocity fields for SO_2 , sulfate, and HNO_3 over eastern United States and southeastern Canada (Walcek et al. 1986). For a three-day springtime simulation, Walcek et al. (1986) found the domain-averaged deposition velocities at a height of approximately 40 m during midday for SO_2 , sulfate, and HNO_3 to be 0.8 cm s^{-1} , 0.2 cm s^{-1} , and 2.5 cm s^{-1} , respectively. These and corresponding nighttime values are larger than values frequently found in regional-scale simulations. For example, preliminary testing of the module at Argonne with synthesized typical wind speeds and stability conditions indicates that typical monthly averages in the Northeast during summer are near 0.5 cm s^{-1} for SO_2 , 0.17 for sulfate, and 1.5 for HNO_3 . These differences are reasonable, however, because typical day-to-day variability of deposition velocities as large as $\pm 50\%$ can be caused by normal variability of local atmospheric conditions, and the RADM run was for only a three-day period.

It is appropriate at this time to examine some of the shortcomings of the RADM dry deposition module and suggest improvements. An example is the means by which the module assumes that surface wetness affects the surface resistance for SO_2 . Walcek et al. (1986) used the assumption that wetting by rainfall tends to decrease surface resistance to zero and thus to increase deposition velocity to the maximum value allowed by gas phase resistances. This procedure has been criticized and in fact has not been found to be valid in some preliminary experiments conducted at Argonne. It appears that surface wetness due to rainfall can increase surface resistance, probably because the rain may already be near saturation with dissolved SO_2 . In addition, one would not expect much oxidation of SO_2 in rain that has reached the ground because of its low pH and the scarcity of oxidants such as gas phase H_2O_2 . For the future, we recommend assuming that surface wetness due to rainfall does not reduce surface resistance, and in some cases will increase resistance if the rainfall chemistry indicates that to be the case.

Surface wetness caused by dew is condensed water that may initially decrease surface resistance to SO_2 substantially. However, with some dry deposition of SO_2 and possibly sulfates, it is known that the surface resistance will increase markedly, especially if some evaporation occurs later and causes some concentration of substances in the dew droplets (e.g., Fowler 1978). Handling this in a regional-scale dry deposition simulation requires several types of information that are difficult to gather, especially rate of dewfall and subsequent evaporation. At best, some typical time sequences of varying surface resistances, modulated by duration of dewfall (indicated by a relative humidity of near 100% at the surface); computed dry deposition rates of SO_2 ; and rate of evaporation, might be applied with the module. Another complicating factor is that

substances released or leached from vegetation might alter the chemistry of the dewfall substantially, and the amount of alteration might vary with plant species.

Another deficiency in the current dry deposition module is the limited number of chemical species for which dry deposition velocities can be computed with some confidence. Hydrogen peroxide, formaldehyde, other aldehydes, organic peroxides, peroxyacetic acid, organic acids, and ammonia are the major substances or groupings of substances that are considered for dry deposition in RADM but for which limited information is available (NCAR 1986).

Other problems should be addressed with future research. One is that rapid in-air reactions can change markedly the fluxes and deposition velocities of certain substances with height. This is known to be true for ozone, nitrogen oxides, and perhaps nitrates. For the present, the dry deposition module uses the fact that the sum of NO and NO₂ tends to act as a conservative quantity above the surface. The variation of ozone flux with height has been ignored, although Fitzjarrald and Lenschow (1983) have shown that the variation can be substantial above a height of 10 m.

2.2.4 Air-Sea Exchange of CO₂

M.L. Wesely

[Adapted from the abstract of a paper published in *Journal of Geophysical Research* 91:10,533-10,535 (1986)]

Measurements of short-term, local air-sea exchange of CO₂ by eddy correlation from surface towers have shown that the transfer (piston) velocities in coastal areas are very large in comparison to long-term oceanic estimates from radioisotope studies. The latter agree with radon evasion and laboratory investigations involving nonreactive gases. Horizontal atmospheric advection seems to be the most likely source of significant error in the eddy correlation estimates but is probably not the cause of the large transfer velocities because they were measured in a wide range of conditions by independent investigators. Furthermore, extrapolation of the large transfer velocities measured by eddy correlation to world average air-sea exchange rates does not provide a realistic basis on which to evaluate the validity of the local eddy flux measurements in coastal areas. Important chemical and physical phenomena affecting CO₂ exchange rates may be quite different in coastal as opposed to open-ocean conditions, and further research is needed in both cases.

2.2.5 Experimental Wet Deposition Studies

D.L. Sisterson, R.L. Hart, D.R. Cook, M.L. Wesely, and J.D. Shannon

The PRECP program (Sisterson et al. 1986b) had its third experiment (PRECP-III) in an ongoing series during the period of January 13 to February 5, 1986, near Syracuse, New York. This wintertime study was focused on the scavenging of pollutants by snow. Observations documented inflow, in-cloud (cloud water and interstitial), and outflow pollutant concentrations in a region centered around Boonville, New York, on the western

slopes of the Adirondack Mountains. Relative scavenging rates were investigated for different pollutant species by obtaining both event and sequential precipitation samples at the surface and aloft by airborne snow collection. Figure 2.1 shows the surface event and sequential precipitation sampling sites used during the experiment.

Argonne provided the field program co-manager for PRECP-III. We helped plan the scientific goals of the field experiments and oversee the day-to-day field operations. Argonne was responsible for site selection for the surface precipitation collection network and assisted in its operation. At the Boonville surface site, Argonne collected air quality and meteorological data and later analyzed and interpreted the data.

New and innovative snow collection and preservation techniques were developed for PRECP-III. Samples were fixed for peroxide and sulfur IV by melting a known amount of snow into a known amount of fixative solution, with the remainder of the uncontaminated sample saved for the standard suite of inorganic and trace metal chemistry analyses. The special plastic bag liner and 30 gallon "trash can" collector used for PRECP-III were compared to a variety of other collectors for uniformity of data during the Snow Collector Intercomparison Test (SCIT) that was conducted during the

FIGURE 2.1 Precipitation sampling sites used in western New York during PRECP-III.

experiment. Preliminary analysis has been completed, and a manuscript is being prepared.

The Argonne mobile research facility (Sisterson et al. 1986b) was located at the Boonville site and provided measurements of NO, NO₂, O₃, NO_x, SO₂, and sulfate, in addition to standard meteorological measurements. Analysis of this data has been completed and sent to the PRECP-III data bank. Figure 2.2 shows selected pollutant concentration roses determined from the air quality and meteorological data collected during the experimental period.

The PRECP-I field study data summary and data index report was completed this year (Tanner et al. 1986). This report provides a summary of the activities during the April 1985 acid rain studies, an index and reporting of all measurements made and data obtained, and descriptions of the aircraft and surface sampling platforms and apparatus. In addition, the PRECP-II limited air quality and meteorological data obtained by Argonne were completed and sent to Battelle Pacific Northwest Laboratory for inclusion in the data base. Pollutant concentration roses are not shown here because measurements of all parameters except O₃ were at the detection limit for nearly all of the experimental period.

2.3 TRANSPORT AND DIFFUSION IN THE ATMOSPHERIC BOUNDARY LAYER

2.3.1 Summary

Research on vertical and horizontal transport and diffusion of trace substances in the lower atmosphere continued during 1986. A principal part of this effort was investigation of the physics of transport and diffusion in drainage flows that occur above complex terrain during stable nocturnal conditions. This work was carried out under DOE's Atmospheric Studies over Complex Terrain (ASCOT) project, a multiyear program that has included two large multilaboratory investigations. In 1980, the flows on the slopes and outflow region of a large (approximately 5-km-wide) basin were studied near Anderson Creek in northern California. This was followed in 1984 by a study of flows down a long (15-km), well-defined valley that included several tributaries. In each of these efforts, the Atmospheric Physics Program made measurements with both remote and in-situ sensing systems to gather information on the physics of such flows. The information is being used by ASCOT to develop models capable of describing atmospheric dispersion of trace substances above such terrain.

Additional studies of flow over complex terrain were undertaken with support of White Sands Missile Range Atmospheric Sciences Laboratory. Studies of the wind field over a large (ca. 100 X 100 km) area in the Sacramento Valley and foothills of the Sierra Nevada in northern California are being documented to support model development for the Department of Defense. Argonne participated with the minisodar and sodar during January and February 1986 and April and May 1986 at two locations in the Sierra Nevada foothills.

FIGURE 2.2 Concentration roses constructed from air quality and meteorological data collected during PRECP-II, in Oklahoma.

A significant amount of effort was devoted to the development of the minisodar, a high-frequency sodar, for measurement of wind profiles with increased accuracy and spatial resolution. This instrument has demonstrated potential for dependable, accurate results in all types of weather, which makes it desirable for use in emergency response situations dealing with toxic chemical releases.

2.3.2 Studies of Flow over Complex Terrain

R.L. Coulter and T.J. Martin

Analysis of the data amassed during the 1984 field campaign of ASCOT by Argonne and other national laboratories has resulted in a detailed description of the down-canyon flow field in Brush Creek Valley (BCV) with excellent detail. The mass flux as a function of time and position along the Canyon is well defined, principally because of data from the Doppler lidar, Doppler sodars, and tethersondes.

The sources for the mass flux along this canyon are less well known, however. The down-valley mass flux must, of course, be replaced. Is this flux concentrated in flow from tributaries to the main canyon or from sidewalls along the main canyon, or does a uniform subsidence above the entire canyon continually replace the flow out of the main canyon? This study focused on the role of the tributaries in the overall drainage pattern within Brush Creek Canyon (Orgill et al. 1985; Coulter and Martin 1986).

Estimates of the mass flux within Pack Canyon (PC), a tributary to BCV, were made by using data from the Argonne minisodar and tethersonde located in the center of PC, roughly 100 m above the BCV floor (Orgill et al. 1985). A second set of measurements located approximately 150 m down PC from the Argonne site toward BCV was made by Lawrence Livermore Laboratory by using laser anemometers at three elevations above the floor of PC. The two sets of measurements provide the data required for estimating the mass convergence within the tributary.

The highly periodic nature of the flow within the tributary (Coulter and Martin 1986) precludes the use of tethersonde profiles for mean flux estimates because of the length of time needed to obtain a single velocity profile (ca. 45 min). Thus, the main data set used for these estimates at the Argonne site is that of the minisodar. These data consist of estimates of the flow along the axis of the minisodar, i.e., along an axis parallel to the center of the tributary but at an angle to the surface of the tributary (Fig. 2.3). It was assumed that the flow from PC was parallel to the surface of the canyon. Obviously this is not always the case, as is shown by the periodic nature of the flow; however, over time periods of one hour or more this assumption may be reasonable.

In order to estimate the flux, one must make some additional assumption as to the distribution of flux across the tributary. We have assumed that the flow is constant across the middle half of the canyon, decreasing linearly to zero at the canyon sidewalls. The calculation of mass flux (F) can be written

$$F = 0.75\rho/\cos(\theta) \int v(z)l(z)dz, \quad (2-1)$$

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PACK CANYON TOPOGRAPHY
CROSS SECTION

FIGURE 2.3 Topographic cross section of Pack Canyon at the Argonne minisodar and tethersonde site as seen from the SW (cross section) and from the NW (longitudinal section)

where ρ is the density of air, $v(z)$ is the along-canyon velocity component at height z , and θ is the elevation angle of the minisodar above the terrain. The width $l(z)$ of the canyon as a function of height above the Argonne site was determined from topographic maps of the area, the velocity estimates were adjusted for pointing angle of the minisodar, and equation (2-1) was integrated numerically to provide estimates of flux at one-hour intervals for each of the experimental nights. In some instances the minisodar data did not cover the entire depth of the drainage layer within PC. In these instances, the profile was extended to the top of the drainage layer by using tethersonde profiles to delineate the top of the layer and by extrapolating minisodar profiles to zero downslope velocity at that height.

Table 2.3 shows the results of these calculations as well as estimates made at the Lawrence Livermore site. It also shows the prevailing direction of the mesoscale wind immediately above the ridge enclosing BCV. The magnitude of the flux from PC is largest at the Argonne site when the mesoscale wind is along PC toward BCV (45 deg); this indicates that scavenging of the northeast upper ridges of BCV lessens the flow in the tributary on the northeast side, as one should expect. What is more surprising is the significant increase in the flux between the Argonne and Lawrence Livermore sites when the mesoscale wind is opposite the drainage flow from PC.

One explanation for the increased convergence with opposing wind direction is that the elevated, cross-canyon (across BCV) flow entrains some of the BCV drainage flow and is then itself entrained into the flow of PC. In order for this to occur,

TABLE 2.3 Mean values of fluxes past the Argonne (ANL) and Lawrence Livermore (LLL) sites in Pack Canyon and other pertinent parameters for the five experiments in 1984

Experiment	Time (MST)	Flux (10^6 kg/s)		Wind Direction	Brush Canyon Drainage Depth (m)
		ANL	LLL		
0	18-24	--	--	45	200->600
	00-06	0.016	--	45->90	550
1	18-24	0.028	0.037	90	200->400
	00-06	0.011	0.027	135->180	450
2	18-24	0.010	0.058	225	150->325
	00-06	0.010	0.044	225	325
4	18-24	0.017	0.059	225	200->350
	00-06	--	0.066	225	390
5	18-24	--	0.063	290	150->280
	00-06	0.020	0.052	315->360	400

downward motion is necessary above the drainage layer of PC. Direct measurements of the vertical velocity were made with the minisodar on only one night. Fortunately, on this night (September 29-30, 1984) conditions were relatively steady. During the first part of the night the downslope winds were monitored in the usual manner. Vertical velocity measurements were made later in the night. Assuming steady conditions in the mean, two sets of measurements can be combined to form a picture of the two-dimensional flow field in the vertical plane along the center of PC (Fig. 2.4). This figure shows a descending flow near the top of the measurement area with some slight evidence of return flow from BCV Canyon, as was suggested above. At lower levels, the flow turns down PC and aligns itself parallel to the surface.

This type of flow at the Argonne site suggests that a rising motion occurs at some point closer to the junction of PC and BCV, some of which is entrained into the mesoscale flow above. This rising motion is a natural result of the pooling of several flows (PC and BCV, in this case) as they converge (Coulter and Martin 1983). If this type of flow is combined with the main Brush Creek drainage, and if tributaries on both sides of BCV are considered, a double-helix-type structure with centers aligned parallel to BCV results. The existence of this type of cross-valley circulation pattern is extremely difficult to verify because of the very small magnitudes involved. Only a small amount of recirculated mass from the BCV drainage air is required to explain the relatively large percentage of BCV flow attributable to PC.

FIGURE 2.4 Resultant wind vector within Pack Canyon on Sept. 30, 1984, assuming the wind vector to be along the axis of the canyon. Vertical components were derived from minisodar data and horizontal components from mean tether-sonde data.

This analysis gives insight into the flow pattern associated with draining valleys and the complexities that can arise in complex terrain. Verification of this type of flow pattern is badly needed. With the completed version of the minisodar available, the vertical velocity field above PC as a function of position is within our grasp, and a more fundamental understanding of drainage flows in complex terrain is attainable.

2.3.3 Development and Application of a Minisodar

R.L. Coulter and T.J. Martin

Techniques for measuring wind profiles with remote sensors have improved rapidly during the past two decades, principally in accuracy and data acquisition to greater heights. Presently, conventional sodar typically gives results from 50 to 800 m, while lidar and radar operate from somewhat higher minimum altitudes to 10 km or more. A data gap thus exists in the lowest 50 - 100 m where, in some cases, conditions are changing most rapidly with height. The development of high-frequency, so-called minisodar techniques (Mousley and Cole 1979; Weill 1983; Coulter and Martin 1985) and the use of multiple frequencies provide instrumentation capable of investigating this region on fine temporal and spatial scales.

Most conventional sodars use parabolic antennas and a single large transducer to provide the acoustic energy transmitted into the atmosphere. The use of frequencies near 1500 Hz permits operation to heights near 1 km without exceedingly large antennas and noise-shielding structures. The minisodar replaces the parabolic antenna and transducer with a phased array of small piezoceramic speakers that operate at frequencies from 4 to 12 kHz. This results in a significant reduction in physical size of antenna and noise shield (hence the term "mini"). Because there is no transducer-antenna coupling, data can be obtained within 10 m of the surface.

Higher frequencies result in increased resolution in estimates of wind speed. The Doppler shift is determined from analysis of the range-gated signal. Because the length of the time series within a range gate is finite, the increased resolution provided by higher frequencies allows the vertical resolution to be increased. However, because atmospheric absorption of sound increases rapidly with frequency (Harris 1966), the maximum altitude attainable is usually limited to 400 m or less for manageable array sizes.

The minisodar developed at Argonne uses a bistatic configuration with a central, vertically pointed transmitter-receiver array and two fan beam transmitter arrays separated from the receiver, usually by about 30 to 50 m. The arrays transmit nearly simultaneously at different frequencies. As a result, the signal detected at the receiver contains information along all three axes. The use of simultaneous pulses from transmitters separated horizontally means that the three components of air motion are derived from the same volume in space as well as the same (almost) point in time. Thus, estimates of the variance of the horizontal components of motion can be made without the problems of combining three measurements from different points to calculate statistics that require horizontal homogeneity for validity (Kristensen and Gaynor 1986).

The Argonne minisodar operates over frequencies between 3 and 12 kHz, with range capability limited primarily by antenna transducer characteristics and atmospheric absorption. Signal amplitude and velocity information are displayed during operation on a portable graphics computer terminal. Statistics for selected parameters over a selectable interval are also displayed. Signal amplitude, wind speed, and signal quality information for each axis are stored on a high-capacity cartridge tape drive when desired.

2.3.3.1 Measurement of High-Resolution Wind Profiles

Three situations are especially suitable for use of the minisodar. Flow in complex terrain, particularly during nighttime, often follows restricted pathways and changes character rapidly with height as different horizontal scales of topography become important. Thus, measurements near the surface are especially important. In addition, small, rugged devices are necessary to make measurements in difficult terrain such as that encountered during ASCOT 1984 in Brush Creek Canyon (Orgill et al. 1985; Coulter and Martin 1985). Secondly, the stable nocturnal boundary layer in more simple terrain may be less than 100 m deep with strong temperature and wind gradients. Again, the ability to sample lower minimum heights is important, as is the ability to measure variances of vertical velocity at lower levels of turbulence (Coulter and Martin 1985). Finally, the instrument can be used when precipitation is falling. Because of the higher frequency of transmitted sound, the spectrum of falling rain or snow is usually well separated from that of atmospheric motion. Thus, through spectral analysis techniques outlined below, the two can be separated, and both the wind profiles and the raindrop fall velocity and size spectrum can be analyzed as a function of height.

Nocturnal Boundary Layer - Complex Terrain. The complete three-dimensional system was first operated during the Winds In Nonuniform Domains (WIND) program during January-February and April-May 1986 (section 2.3.4 of this volume). Figure 2.5 shows an example of wind profiles from one nighttime period. Note the development of the wind speed maximum near 15 m above the surface and the variation of wind direction with height that is evident within 50 m of the surface. The maximum in wind speed is characteristic of simple slope flow (Horst and Doran 1986) under well-defined drainage conditions. The nearest collaborating measurements were from an eight-level tower (to 30 m) located about 500 m north and about 25 m higher. Although data are not yet available from the tower, observations made from the tower during this time agree qualitatively as to magnitude and location of the wind maximum. A conventional sodar could have detected little of the atmospheric structure near the surface in this location.

FIGURE 2.5 Wind speed, direction, and vertical velocity profiles from consecutive one-hour periods on May 3, 1986, during project WIND. The horizontal lines represent the typical heights of measurement of conventional sodars in the lowest three range gates.

Precipitation. The WIND project also provided the opportunity to operate the system during precipitation, principally rain. As was detailed above, the spectral selection processes available with the system allowed the signal due to scattering from raindrops to be eliminated from the signal processing. Broad-band noise created from raindrops striking the reflector was eliminated by erecting a rain shield upwind and above the enclosure. Figure 2.6 illustrates the wind profiles taken during a period of moderate rainfall. The vertical velocity associated with raindrops was eliminated from the spectrum during operation. This is necessary for both vertical velocity and horizontal velocity data because the bistatic information is influenced by both the horizontal and vertical velocities. Increased scatter in the derived vertical velocity profile is due to some overlap of the wings of the precipitation spectrum with the vertical wind velocity spectrum; however, in general, the profiles were not significantly affected by the precipitation. Variances, on the other hand, were significantly increased. Figure 2.7 is an example of the profile of rain terminal velocities obtained by reversing the signal acceptance criteria to ignore the atmospheric component. This can be related directly to the droplet size spectrum through Stokes law. Although it is not possible at present

FIGURE 2.6 Wind speed, direction, and vertical velocity profiles from consecutive one-hour periods on February 12, 1986, during moderate to heavy rainfall. Values were estimated by eliminating that part of the vertical velocity spectrum less than -2.5 m/s.

FIGURE 2.7 Raindrop terminal velocity as a function of height during a convective rainfall period. Data are averaged over 10 minutes. Velocities correspond to 0.1-cm-diameter raindrops.

to record the rain velocity (size) spectrum itself, it would be relatively straightforward to modify the present software. Assuming Rayleigh scattering, the scattered power (S) is

$$S = (A/L^4)(\pi D^6), \quad (2-2)$$

where L is the wavelength of the acoustic energy, D is the diameter of the raindrops, and A is a constant. The intensity of signal return can thus be related to the density of raindrops and rainfall rate.

The minisodar developed at Argonne has proven to be a valuable tool in surface and boundary layer investigations, particularly in complex terrain, nocturnal boundary layers, and precipitation conditions. Data from low heights and fine resolution have proven to be accurate and dependable. An increased sampling rate by a factor of about ten over conventional sodars has been realized. However, due to the minisodar's limited maximum range, operation with other remote sensors is often desirable. For example, with the computational power presently available, a combination of mini- and conventional sodars could be operated simultaneously with the same operating system with relative ease.

2.3.3.2 A Minisodar System for Real-Time, Near-Field Dispersion Modeling

The minisodar routinely measures vertical profiles of wind speed components and can provide inputs directly to an atmospheric dispersion model. A prototype system has been built at Argonne to demonstrate its capabilities. The calculations of dispersion are more specific to local conditions than are modeling estimates whose input data are obtained from distant weather stations. In addition, the system is mobile and has the potential of being rapidly transported to a problem area.

Most emergency responses to atmospheric releases of toxic substances require rapid actions, such as evacuations, in the immediate vicinity (tens of kilometers or less). Because emergencies can occur at night and on weekends when the most highly trained personnel might not be on station, an emergency response system must be automated to the greatest extent possible to take meteorological observations and integrate them with dispersion modeling. The meteorological parameters necessary to compute dispersion should be available immediately with frequent, regular updating, and suitable modeling software should be in place for on-line, real-time analysis of the data.

Data on the wind field in the lower atmosphere are the most critical atmospheric data for predicting the effects of dispersion on ambient concentrations or deposition patterns. In situations where the vertical shear of horizontal wind is large and low-level atmospheric structure is complex, a tower instrumented at only one or a few levels may recover neither a sufficiently deep profile nor adequate detail on the structure of the atmosphere. The minisodar, a high-frequency Doppler acoustic sounding system recently developed at Argonne, provides many of the necessary observations. It can monitor the wind and stability structure of the atmosphere from 10 m to several hundred meters and can operate in all but extreme weather conditions. It has several advantages over conventional commercially available sodars, such as the ability to operate effectively during precipitation, less susceptibility to degradation in performance due to ambient acoustic noise, better resolution and accuracy, and smaller, more portable components.

A significant advantage of the minisodar as compared to instrumented towers is portability. A tall tower that reaches the necessary altitude is not easily relocated, while an easily moved and reassembled tower suitable to support the necessary meteorological instrumentation is not sufficiently high. For sites scattered over a large area, particularly one with nonuniform terrain, portability might be an important asset in establishing emergency response capabilities for temporary hazardous activities in the area. In addition, the minisodar is not limited to the discrete fixed levels of an instrumented tower, but can describe the existing atmospheric structure, subject to the minimum resolution of the system.

An important component for rapid, informed response to emergencies involving atmospheric releases is modeling software that is "hardwired" to a system to collect the meteorological data. Because at many installations a variety of accidental hazardous releases could occur, the dispersion model software should be capable of treating a range of problems. For example, a slow, neutrally buoyant, continuous leakage not discovered immediately might call for modeling over a time period in which meteorological conditions change markedly. In the other extreme, an instantaneous, buoyant release that might result from equipment failure or an explosion calls for the most accurate initial information possible.

To demonstrate the feasibility of using a dispersion model that obtains data directly from the minisodar, we have implemented Argonne's six-particle puff model (Sheih, 1978; 1985) on a personal computer. The model can treat buoyant puffs or plumes and wind and turbulence fields varying in time and space and thus can be used for a variety of emergency scenarios. At Argonne, the result of integrating such software with the minisodar is a system called the ADER (atmospheric dispersion emergency response) system, which is a prototype at an early stage of research and development.

A key to making the modeling software most useful lies in selection of default parameters, because specific data such as source characteristics might not be available in a timely fashion. The suite of potential emergency response problems varies from site to site; thus, it is desirable to tailor the modeling software to each location, even if the same basic model or models are used. The six-particle puff model is used in the prototype ADER system for purposes of demonstration and can be replaced with other models if they can be modified to accept the output of the minisodar.

Some modeling estimates need be retrospective only (i.e., not carried out in real time), while others might be called for within seconds or minutes of an accident or incident. In many of the latter cases, only a normalized concentration or deposition could be estimated, since postanalysis of the accident may well be necessary for estimation of the emission.

Graphics capabilities are a key part of the modeling software because of their importance as an aid in rapid, correct decision making. The graphics software must have a wide range of capabilities and must be in part tailored to the site, so that key terrain features or population centers can be shown. Proper temporary or archival storage of the near-source modeling results would allow efficient meshing with larger-scale models for emergency responses beyond the local area. Development of graphics and archival information is now in a preliminary stage with the ADER system.

While the ADER system developed to date is quite modest and should be considered preliminary, the concept of using a minisodar to collect meteorological data and couple the outputs directly to a dispersion model run in real time has been shown to be feasible.

2.3.4 Project WIND

R.L. Coulter and T.J. Martin

The Atmospheric Physics Program participated in Phase II and III of Project WIND. The project, operated by the White Sands Missile Range, was located along the eastern edge of the Sacramento Valley, north of Chico, California. Argonne operated from two of several sites located in contrasting terrain conditions from within the valley proper to well into the foothills of the Sierra Nevada. The intent of the study is to establish a high-quality data base to be used for model development for the prediction of transport and dispersion at many scales of motion.

During winter investigations (Phase II) Argonne worked at the so-called "Forest" site, located well into the foothills next to a Christmas tree farm. The overall terrain sloped upward to the east, with small-scale terrain variations of approximately 30 m. A high-frequency minisodar was operated at this site.

During spring investigations (Phase III) Argonne participated at two locations. The Forest location was used in practically the same manner as during Phase II, and a second sodar operating at conventional frequencies was located at the "Hogsback" site, approximately 8 km east of Redbluff, California. This second site was at the edge of the foothills to the east and the Sacramento Valley to the west. The terrain around this site was dominated by vertical relief of more than 100 m.

Because of the differences in terrain and equipment, operation at the two sites (separated by nearly 50 km) was different, and the data were quite dissimilar. The Hogsback data are heavily influenced by terrain variations close to the measurement site, while the Forest site data reflect the larger-scale terrain features.

2.3.4.1 WIND Phase II

The minisodar was located at the Forest site. The overall terrain in the immediate vicinity sloped about 2 deg upward to the east and nearly 5 deg downward to the west. Vegetation in the immediate vicinity was, for the most part, less than 2 m in height. However, tall, densely planted pines (30 m) were located approximately 300 m to the east and 200 m to the south. Within the generally sloping terrain, a sudden large depression of about 30 m was located approximately 250 m to the northeast.

Over certain periods, principally during precipitation, special handling of the data during retrieval was necessary. In these conditions it was possible to separate the reflection of acoustic energy due to precipitation from the atmospheric echo in frequency space. By limiting the computer's search to certain frequency domains, the atmospheric echo could be isolated. Ambient noise due to precipitation striking the reflector panel was greatly reduced by erecting a foam panel upwind and above the enclosure. This combination, while of some discomfort to the operator(s), proved highly successful.

Table 2.4 shows the times of operation of the sodar. The operators were in a learning curve, particularly with respect to operation in precipitation conditions. Thus, during transition periods (with and without precipitation) and recovery from generator failures, etc., data recovery was smaller than might otherwise be expected. Overall, the system operated successfully for greater than 90% of the project period.

Although extensive meteorological analysis of the data has not been performed other than for quality assurance, a few observations can be made at this time. A well-defined, strongly stable surface layer developed in only a few (relative to flat terrain) situations, even at night. As a result, laminar layering with waves embedded, e.g., were rarely evident, at least at lower elevations. This may be due to the combination of the overall slope from east to west encountering prevailing winds from the south and southwest, which results in large wind shear aloft and resultant destabilization of the

TABLE 2.4 Argonne minisodar operation times and conditions at Forest site

Date	<u>Local Time</u>		Comments, Conditions
	Start	End	
PHASE II			
Jan 27, 1986	1000	1700	Clear, sunny
Jan 29, 1986	1000	1600	Moderate to heavy rainfall throughout; turbulent, windy
Jan 30, 1986	2200	0500	Light to moderate rainfall throughout
Feb 01, 1986	1005	1055	Generator fail (0440-0500); light rain in evening, increasing; gusty, turbulent
Feb 05, 1986	1330	2055	Generator fail (1930); transition to drainage flow; snow shower (1800)
Feb 06, 1986	0910	1515	Light winds; clear
Feb 07, 1986	1210	1100	Bad timing chip, no data until 1200; cold evening, drainage flow
Feb 10, 1986	2125	0500	Clear, drainage flow
Feb 12, 1986	0345	1100	Snow, rain mix changing to steady rain
PHASE III			
Apr 21, 1986	0900	1645	Clear, hot; system runs unattended
Apr 23, 1986	0900	1650	Overcast, cool, light winds
Apr 24, 1986	2300	0455	Occasional light rain, variable clouds
Apr 26, 1986	1815	1100	Hardware problems; fluorescent light interference; no data written until 1800
Apr 30, 1986	1500	2100	Daylight time; clear, stratus deck at 1100
May 01, 1986	0900	1655	Partly cloudy; very light rain near end
May 02, 1986	0900	1055	Heavy clouds, occasional rain
May 05, 1986	2100	0455	Clear, cold; slope flow
May 07, 1986	0300	1055	Clear, cold; slope flow

layer. In addition, with prevailing winds from southwest (upslope), the maximum in the wind speed profile was quite often between 100 and 150 m, even during daytime. Further investigation into the specifics of this occurrence are needed, but the low-level wind speed maximum probably results from the influence of terrain on the mean wind field.

2.3.4.2 WIND Phase III

Phase III took place between April 21, 1986, and May 7, 1986. As was noted above, two sites were operated during this period.

Forest. The operation at the Forest site was very similar to that during Phase II except that the baselines were held constant at 40 m throughout the period and were oriented along true north and true east.

There was much less precipitation during this phase of operations, although it was not entirely absent. Thus special handling of data retrieval was rarely necessary. The data periods are listed in Table 2.4. The missing data on April 26, 1986, were due to the absence of any data written to tape. The reason for this is as yet unexplained. Most other data periods were successful.

Again during this phase, little laminar flow was evident at nighttime. In spite of this, however, the wind speed maximum at very low levels characteristic of slope flow was observed on May 5 and May 7, 1986. Observations at the tower located to the north of this measurement site confirmed the low-level maximum between 10 and 20 m.

Hogsback. The location of the sodar at the Hogsback site forced us to limit the baselines to 160 m because of the severity of the terrain within cable distance of the generator supplying power. Placement of the receiver was on the eastern edge of a precipice that fell sharply about 250 m to Antelope Creek, with one baseline at 167 deg relative to the transmitter and the other at 257 deg. Many considerations go into location of a bistatic system. Although it may have been possible, with great difficulty, to increase the baselines, the height difference between transmitter and receiver would have severely limited the accuracy of the estimates.

Table 2.5 shows project time periods and data intervals for the Hogsback data. No data are reported for April 21, 1986, the trial run day, because it was necessary to change the position of the generator in order to limit the ambient noise to the sodar. Upon data analysis, it became apparent that no amplitude data were written to the data files, although all other pertinent data were available and the amplitude data were available for gray-scale display. Thus the raw backup data were analyzed whenever available to provide this information.

Observations of the Hogsback data show a marked domination of the wind field by terrain influences. In general, wind speeds were considerably higher at Hogsback than at the Forest site and were considerably more turbulent. The mean vertical velocities observed at the Hogsback site were very much dependent upon wind direction and

TABLE 2.5 Argonne sodar operation times and conditions at Hogsback site

Date	<u>Local Time</u>		Comments, Conditions
	Start	End	
PHASE III			
Apr 23, 1986	0905	1700	Sunny, windy, cool
Apr 24, 1986	2100	0500	Generator fail (0100); occasional light rain; cloudy, humid; deep layer with gravity wave early
Apr 26, 1986	0920	1100	Clear, cool night; much structure aloft; drainage winds
Apr 30, 1986	1505	2300	Daylight time
May 01, 1986	0855	1700	Sunny, few stratus; light winds; some rain to west, late
May 02, 1986	0930	1050	Cloudy, windy; some wind noise; intermittent light rain after 1500
May 05, 1986	2100	0500	Clear; descending layers aloft
May 07, 1986	0300	1100	Clear, stable night; slow inversion rise

stability and were often different from zero. This implies that corrections to the measured frequencies must be used for data from this site, regardless of the type of sodar employed. Furthermore, the vertical velocities must be highly dependent upon position with respect to terrain. For this reason one might speculate that all wind components should be measured from the same point in space at such a site. With winds from the southwest through southeast, the sharp rise in the terrain usually caused strong vertical velocities. However, in conditions of sufficient stability, the terrain influences were reduced above the lowest 100 m or so. A probability distribution of vertical velocities as a function of wind direction shows that only the northwest wind had a net downward motion during the periods of this project. This coincided with the position of the ridge above the receiver. This site is something of an anomaly within the overall regional wind field.

2.4 ATMOSPHERIC NUMERICAL MODELING

2.4.1 Summary

Atmospheric numerical modeling efforts in the Atmospheric Physics Program are concentrated in two distinct but related areas. In one area focusing on cloud microphysics and chemistry, processes ranging from molecular to cloud scale and having typical time scales of less than an hour are simulated. The other area of modeling emphasizes long-range transport and deposition, with processes parameterized on scales of about 100 km in the horizontal and seasonally in time. Both areas of modeling research are currently being used for studies related to acidic deposition, although many of the techniques can be applied to other pollutants. The major effort in the detailed cloud modeling has involved preparation of a monograph on cloud physics parameterizations for the PRECP program. Recent modeling exercises in long-range transport have examined net transboundary fluxes and the effect of climatological variability on estimation of deposition and horizontal fluxes. A new effort of growing importance, climatological extension, will serve as a bridge between the two areas of modeling emphasis.

2.4.2 Long-Range Transport and Chemistry

2.4.2.1 Estimates of Long-Term Trends in Sulfur Deposition

J.D. Shannon and B.M. Lesht

[Adapted from the abstract of a paper in Proceedings, Acid Rain: Clouds over the Midwest (National Clean Air Fund) Chicago (1986).]

Knowledge of the trends in the wet and dry deposition of acidifying pollutants, principally sulfate and nitrate, over the last several decades across North America would be extremely valuable to researchers in the National Acid Precipitation Assessment Program. Unfortunately, a lengthy, unambiguous data set that would provide this record does not exist. The best long-term record is that collected at Hubbard Brook in New Hampshire, where observations have been made regularly since the middle 1960s. Unfortunately, the early Hubbard Brook data are based upon sampling with bulk collectors and thus confound wet and dry deposition input, without fully measuring total deposition. For the period of time that adequate sampling of wet deposition has occurred (roughly since the end of the last decade), the variation of emissions has been too small, about 10% overall, for emission-related changes in deposition to be easily detectable against normal climatological variations. In an attempt to quantify and separate trend contributions from emissions and climatological variations, we have applied the Advanced Statistical Trajectory Regional Air Pollution (ASTRAP) model of long-range transport and deposition to simulate the deposition of sulfur over the period 1976-1981, while allowing either or both emissions and climatology to vary. Typical results, as shown in Fig. 2.8, indicate that the variability attributable to year-to-year changes in climatology dominated the emissions changes. Over a longer period of record in which greater changes in emissions occurred, this condition might not hold, however.

FIGURE 2.8 Calculated annual wet deposition of sulfur in Columbus, Ohio, from ASTRAP simulations in which both emissions and climatology vary from year to year (solid squares), only emissions vary (open squares), and only climatology varies (circles).

2.4.2.2 Estimation of Source-Receptor Matrices for Deposition of $\text{NO}_x\text{-N}$

J.D. Shannon and B.M. Lesht

[Adapted from the abstract of a paper in *Water, Air, and Soil Pollution*, 30:815-824 (1986)]

Contributions of anthropogenic emissions of oxides of nitrogen (NO_x) from each state or province of the United States and Canada to wet and dry deposition of nitrogen within each state or province have been estimated with the ASTRAP model, previously exercised mainly in simulation of regional transport and deposition of sulfur. The model assumes linearity between emissions and deposition and applies similar parameterization methods, although with different rates, as in simulation of sulfur deposition. A deposition budget for $\text{NO}_x\text{-N}$, produced by summarizing the source-receptor matrices, is shown in Table 2.6. Sources in the United States are estimated to contribute 97% of the total $\text{NO}_x\text{-N}$ deposition in the United States, and 64% of the total deposition within Canada. Of the combined U.S. and Canadian emissions, 30% is estimated to be deposited by dry processes within their borders, 25% is estimated to be deposited by wet processes, and the remaining 45% is estimated to be exported.

TABLE 2.6 Anthropogenic $\text{NO}_x\text{-N}$ deposition budget (kT nitrogen)^a

Source	Emissions	Dry		Wet		Total	
		U.S.	Canada	U.S.	Canada	U.S.	Canada
U.S.	6147	1706	108	1335	309	3041	417
Canada	555	65	146	25	85	90	231
Total	6702	1771	254	1360	394	3131	648

^aCalculations are for 1980 emissions and 1976-1981 climatology.

2.4.2.3 Deposition of S and NO_x -N to the Great Lakes Basin

*J.D. Shannon and E.C. Voldner**

[Adapted from the abstract of a paper presented at the 5th Joint Conference on Applications of Air Pollution Meteorology (American Meteorological Society and Air Pollution Control Association), Chapel Hill, NC (1986)]

Estimating the input of both nutrient and toxic substances to the land and water of the Great Lakes Basin is a major concern of the United States and Canada under the U.S.-Canada Great Lakes Water Quality Agreement of 1978. For many substances, deposition from the atmosphere is a large or dominant source term for mass balance within the basin. While methods for routine monitoring of wet deposition are well established, it is operationally difficult or impossible to monitor continuously over the lakes themselves because of storms, ice, and the general lack of suitable platforms. Fortunately, seasonal or annual cumulative wet deposition for widely emitted atmospheric pollutants tends to be dominated by regional rather than local flow and precipitation patterns. Thus interpolation of wet-only measurements on nearby land areas is thought to provide a reasonable estimate of deposition over the lakes, although uncertainties related to lake effect precipitation systems may be significant. Input from dry deposition is much more difficult to monitor routinely; indirect methods are being applied in networks currently being established, but as yet data are insufficient for interpolation similar to that for wet deposition. The stability in the surface boundary layer can differ greatly over land and water, due to their quite different thermal inertias and resulting surface temperatures. This contrast and the different chemical reactivity of a wet surface can result in dry deposition rates over water that are quite different than over the land, and thus interpolation of terrestrial values may be quite misleading.

Alternately, a modeling approach can be used to estimate deposition input to the Great Lakes Basin. We have applied the ASTRAP model of regional atmospheric transport and deposition to calculate the deposition of sulfur and NO_x -N to each of the lakes and to its associated drainage basin. The parameterized dry deposition velocities in the ASTRAP model vary diurnally and seasonally, but not horizontally nor daily. The model cannot treat directly the differential dry deposition of land and lake, so we have taken the approach of scaling the over-water portions of the dry deposition field after initial calculation of regional fields with values typical for eastern North American land surfaces. Averaged dry deposition velocities input to the model and postcalculation scaling factors that we have chosen are shown in Table 2.7. This approach is not completely satisfactory, as it prevents the model from being mass-consistent, but the discrepancies are believed to be minor for widely distributed pollutants such as sulfur and NO_x -N.

Although wet deposition observations near the lakes are fairly sparse, particularly for the upper lakes (Superior, Michigan, and Huron), a kriging technique can be used to produce objectively analyzed wet deposition fields over the lakes and basins, which can then be integrated in a manner similar to model calculations. This allows

*Collaborator; affiliation is listed at the front of this chapter.

TABLE 2.7 Mean values of ASTRAP dry deposition velocities (cm/s) and seasonal scaling factors for the Great Lakes

Pollutant	Winter	Spring	Summer	Autumn
SO ₂	0.25	0.40	0.45	0.30
Sulfate	0.12	0.20	0.23	0.15
NO/NO ₂	0.20	0.25	0.30	0.16
NO ₃ ⁻ /HNO ₃	0.40	0.30	0.60	0.30
Scaling Factors				
Low-level mixing	1.50	0.90	0.50	1.10
Wet surface (S)	1.20	1.50	1.50	1.50
Wet surface (N)	0.83	0.67	0.67	0.67
Combined (S)	1.80	1.35	0.75	1.65
Combined (N)	1.25	0.60	0.33	0.74

comparison of modeled and "observed" wet deposition fields. Dry deposition fields are currently available only from models. A comparison of modeled and kriged deposition integrations is given in Tables 2.8 and 2.9. The differences between modeled and observed wet deposition totals tend to lie within the uncertainty of the kriged values.

2.4.2.4 Modeled Trends and Climatological Variability of the Net Transboundary Flux of Airborne Sulfur Between the U.S. and Canada

J.D. Shannon and B.M. Lesht

[Adapted from the abstract of a paper in Transactions of the Second International Specialty Conference on Meteorology of Acidic Deposition (Air Pollution Control Association) Albany, NY (1986)]

The ASTRAP model of long-range transport and deposition has been used with emission inventories and meteorological data for the period 1976 through 1981 in order to examine the trends in net transboundary fluxes associated with the moderate anthropogenic emission decrease during the period, and to estimate the seasonal and annual variability of flux calculations attributable to climatological variability. Over the six-year period, the net transboundary sulfur flux from U.S. emissions is estimated to have been about 3.2 times the corresponding net flux from Canadian emissions, with the ratio of the annual sulfur flux from the U.S. to that from Canada ranging from 2.7 to 4.4 in simulations when both climatology and emissions are allowed to vary, from 3.0 to 3.7 for simulations in which only emissions are varied, and from 2.6 to 3.9 for simulations in which only climatology is varied. Average seasonal net flux ratios ranged from 2:1 in

TABLE 2.8 Estimates of Annual Sulfur Deposition for 1980 (kT)

	Wet		Dry	
	Observed (Kriged)	Modeled	Modeled	
			Unscaled	Scaled
<u>Lake</u>				
Superior	46	21	21	30
Michigan	45	35	60	63
Huron	72	33	35	50
Erie	26	30	55	77
Ontario	23	20	34	49
Total	212	139	205	289
<u>Drainage Basin</u>				
Superior	66	27	24	-
Michigan	104	64	97	-
Huron	126	84	92	-
Erie	100	81	140	-
Ontario	73	67	89	-
Total	469	323	442	-

winter to more than 5:1 in summer. Over the period 1976 through 1981, the annual net transboundary fluxes from U.S. emissions (2210 to 2930 kT sulfur) were very close in magnitude to total sulfur emissions in Canada (2210 to 2740 kT sulfur).

The range in model estimates of the annual transboundary flux from U.S. sources, 33% of the mean, appears to have been primarily the result of climatological variability, which produced a 25% range in calculated annual fluxes, while emission changes resulted in a 13% range in transboundary fluxes. (U.S. annual emissions of sulfur also exhibited a 13% range about their mean.) On the other hand, as Canadian annual emissions of sulfur varied relatively more (21% of their mean), emission-related variability of transboundary fluxes from Canadian sources appears to have been more important than climatological variability (26% vs. 13% of their respective means).

2.4.2.5 Climatological Extension of Episodic Wet Deposition and Vertical Redistribution of Pollutants

J.D. Shannon

For modeling of acidic deposition, results from theoretical, laboratory, and field investigations have led to a consensus that highly detailed modeling capabilities are

TABLE 2.9 Estimates of Annual NO_x-N Deposition for 1980 (kT nitrogen)

Lake	Wet		Dry	
	Observed (Kriged)	Modeled	Modeled	
			Unscaled	Scaled
Superior	22	10	8	6
Michigan	24	18	22	17
Huron	33	14	14	10
Erie	11	14	18	13
Ontario	10	9	11	8
Total	100	65	73	54
Drainage Basin				
Superior	29	14	11	-
Michigan	41	34	37	-
Huron	63	28	26	-
Erie	40	37	44	-
Ontario	33	27	33	-
Total	206	140	151	-

required for at least some uses. The major modeling effort in the National Acid Precipitation Assessment Program is the Regional Acid Deposition Model (RADM), which has been developed at the National Center for Atmospheric Research with the aid of many researchers there and elsewhere. The RADM incorporates state-of-the-science treatments of key processes, but is exercised in simulations of episodes of only two or three days' duration because of the computer and input data requirements associated with the complexities. Many of the potential users of the results of atmospheric deposition modeling, however, are concerned with cumulative deposition processes over seasons or years; thus, methods are needed to relate such short-term simulations to expected long-term patterns.

The regular temporal and spatial increments of Eulerian (grid) numerical models do not neatly coincide with the temporal and spatial scales of meteorology, microphysics, and atmospheric chemistry. Because horizontal motion is normally much faster than vertical motion, grid models have a relatively coarse increment in the horizontal and a finer, sometimes variable increment in the vertical. Not all chemical species of interest are equally reactive, and it is not efficient to update calculations of concentrations of the slowly reacting species at the frequency at which the concentrations of the rapidly reacting species are updated; in effect, grid models can have different time steps for different quantities. Transport steps are a function of meteorology (wind velocity) and grid dimensions, and are normally much longer than those for chemistry. Typical grid

increments for regional models are 75-125 km in the horizontal, and 100-1000 m in the vertical. A corresponding time increment for calculating transport and diffusion might be 30 min. When averaged over a horizontal grid cell for that length of time and checked for consistency with the horizontal wind field (in order to assure conservation of mass), vertical velocities are normally small, 1 cm/s or less. However, vertical velocities of several tens of meters can occur in strong updrafts associated with thunderstorms, and the storms can reach to 15 km in some cases. The storm cells, however, are usually much smaller than the typical horizontal grid dimensions, and the updrafts are compensated for by downdrafts in surrounding air. The average vertical velocity is not a very efficient vertical transfer mechanism, but in an atmosphere with a strong vertical gradient of the species of interest, the storm scale vertical motions appear to be.

While widespread steady frontal rain through a well-mixed layer may result in relatively uniform precipitation chemistry over a wide area, many wet deposition events show large variations in both space and time. It is desirable to develop methods to extend the results of wet deposition and vertical redistribution of pollutants from the individual storm level to scales commensurate with those of RADM, and to extend the results of RADM episodic simulations to seasonal and annual climatological expectations. Our initial effort will be to conduct a thorough literature review of field and modeling studies of vertical motions and net fluxes associated with precipitating and nonprecipitating convection, and of their distributions in both space and time, in order to develop initial parameterizations appropriate for Eulerian models. We will also examine concepts on how to couple episodic simulations with long-term modeling.

2.4.3 Cloud Microphysics and Chemistry

2.4.3.1 Parameterizations of Cloud Microphysics

I.Y. Lee and M.S. Hong

We have conducted a comprehensive literature review of parameterizations of cloud microphysical processes. Our goals were (1) to understand the theoretical basis and the limitations of each parameterization in application to regional-scale modeling, (2) to examine the validity of various assumed distributions of hydrometeors, and (3) to undertake comparative studies using a detailed cloud model in order to develop new, optimized parameterizations.

Multiple regression has been used to parameterize cloud microphysical processes such as condensation, evaporation, autoconversion, and accretion as functions of mixing ratios of water vapor, cloud water, and rainwater. The bases for the regression are the solution fields from simulations of a cloud model with sophisticated microphysical processes and cloud dynamics. (The elaborate treatments make the latter model generally unfeasible for regional-scale modeling because of computation and input data requirements.) The new parameterizations are summarized in Table 2.10. The rates computed from the highly parameterized regression formulas are well correlated with the rates from the sophisticated treatments, with correlation coefficients ranging between 0.72 for the rates of condensation of rain to almost 1.0 for the rates of

TABLE 2.10 Cloud Microphysics Parameterizations^a

Rates	$e^{A_X B_Y C}$		$(s^{-1} \text{ or } cm \ s^{-1})$			Correlation Coefficient
	X	Y	A	B	C	
Condensation of Cloud Droplets	Q_c	$Q_v - Q_s$	-4.926	0.417	0.537	0.90
Evaporation of Cloud Droplets	Q_c	$Q_s - Q_v$	-6.153	0.743	0.323	0.82
Condensation of Raindrops	Q_r	$Q_v - Q_s$	-2.167	0.490	1.129	0.73
Evaporation of Raindrops	Q_r	$Q_s - Q_v$	-6.601	0.420	0.746	0.80
Autoconversion of Cloud Droplets	Q_c	$Q_v - Q_s$	0.363	2.184	0.173	0.87, $s > 0$
	Q_c	$Q_s - Q_v$	-2.824	1.878	0.076	0.97, $s < 0$
Accretion of Cloud Droplets	Q_c	Q_r	2.025	1.029	1.042	0.997
Terminal Velocity of Cloud Droplets	Q_c	$1000\rho_a$	2.562	0.236	-2.175	0.94
Terminal Velocity of Raindrops	Q_r	$1000\rho_a$	10.900	0.604	4.466	0.83

^a Q_s , Q_v , Q_c , and Q_r denote mixing ratios for saturation water vapor, actual water vapor, cloud water, and rain water, respectively. ρ_a is air density; s is supersaturation ratio.

accretion of cloud water. The very high correlations exist when the rates are determined exclusively by aerodynamic capture of drops.

2.4.3.2 Chemical and Physical Properties of Cumulus Clouds

I.Y. Lee

[Adapted from the abstract of a paper published in *Atmospheric Environment* 20:767-771 (1986).]

Numerical simulations have been carried out with a model combining aqueous chemistry with parameterizations of dynamic and microphysical processes of cumulus clouds. The model computes temporal and spatial variations in dynamic parameters, chemical species concentrations, particle spectral evolution, and pH values for drops of different sizes. A preliminary simulation produces dynamic characteristics typical of fair-weather cumulus. The largest decrease in SO_2 concentration during the 30 min of real time simulation, about 10%, occurs in the upper part of the cloud, while the corresponding SO_2 decrease in the near-cloud environment, resulting from homogeneous oxidation and detrainment, is about 2%. The dominant SO_2 oxidation pathway is kinetic oxidation by H_2O_2 . For the case simulated, the droplet pH ranges between 3.5 and 5.3 for drops larger than about 20 μm in radius, while the pH of sub- μm evaporating droplets can decrease below 2.0.

2.4.3.3 Flow-Through Chemical Reactor Model

M.S. Hong and I.Y. Lee

[Adapted from the abstract of a paper to appear in *Atmospheric Environment*]

A flow-through chemical reactor model has been used to assess the importance of various oxidation reactions and cloud processes on wet removal and redistribution of atmospheric pollutants. Investigations also have been made to examine the effect of in-cloud acidification on precipitation chemistry at the surface. For the initial and boundary conditions examined, in-cloud oxidation accounted for more than 60% of the wet-deposited acids derived from the acidification of initial SO_2 . Approximately one-half of water-soluble, non-reactive NH_3 and HNO_3 were removed by wet deposition, and the pseudo-first-order conversion rate of SO_2 to SO_4^{2-} ranged from 3 to 25% hr^{-1} . Model sensitivity studies show that the distributions of NH_3 and HNO_3 depend mainly on cloud physical parameters, while those of H_2O_2 and SO_2 depend largely on initial values of species concentrations. Various individual physical and chemical mechanisms can be the rate-limiting steps for different chemical and physical conditions at different stages of cloud evolution. For example, the mass transfer between ammonia and cloud droplets becomes negligible during the mature stages of cloud development because of fast depletion of the gas. At that point, only the accretion process between drops can change the acidity.

2.4.4 CAPTEX Simulations

I.Y. Lee

[Adapted from the abstract of a paper to appear in *Boundary-Layer Meteorology*]

Numerical studies of short-term transport and diffusion over regional distances have been made with a particle-in-cell model and compared with observations from the Cross-Appalachian Tracer Experiment. The simulated plume configurations of all seven releases show general agreement with the observed patterns. Frequency distributions of observed and predicted values are broadly similar, although correlation coefficients of points paired in space and time are poor; this results from small dislocations in predicted versus observed plume orientations. The modeled plumes generally maintain a Gaussian structure during the well-mixed-emission period, but vertical and horizontal wind shears distort the plume shapes thereafter. The simulated plume center generally lies between trajectories calculated at the 1000 and 850 mb levels; the inversion capping the planetary boundary layer constrains the simulated plume to within about 2000 m of the surface.

2.5 ATMOSPHERIC ORGANIC CHEMISTRY

2.5.1 Summary

Many forms of gaseous, vapor-phase, and nonvolatile organic substances exist in the global troposphere. They include substances associated with particular sources such as fossil fuel storage, processing, and combustion locations; natural gas and oil fields; the ocean; and vegetation. Saturated and unsaturated C_2 - C_{33} compounds, isoprene, and terpenes are examples. These substances and their reaction products play a major role in the tropospheric chemical cycles of O_3 , NO_x , H_xO_y , and CO. In order to determine the fate of organic substances in the environment, processes controlling their distribution and transformation as well as exchange rates with the biosphere, hydrosphere, and geosphere must be fully understood.

With the recent addition of a staff member expert in both organic chemistry and atmospheric processes, our efforts in this area of research are just beginning. We anticipate that elements of this new program will interact strongly with our existing expertise in environmental physics and organic geochemistry. Specific areas of interest include (1) development of sampling and analysis techniques for organic substances in air and water; (2) application of molecular marker analysis, isotopic "fingerprinting," and modeling of chemical mass balance for source identification; (3) field and laboratory investigations of vapor-particle partitioning and precipitation scavenging; (4) use of micrometeorological techniques to measure air-surface exchange rates; and (5) modeling atmospheric deposition. The following section describes an investigation that is about to be undertaken.

2.5.2 Sources of Volatile Hydrocarbons in the Urban Chicago Atmosphere

P.V. Doskey

This project is a two-year investigation funded by the Illinois Department of Energy and Natural Resources. The main objective of the study is to determine source "fingerprints" (i.e. unique chemical signatures) for C_2 - C_9 saturated and unsaturated hydrocarbon emissions from petroleum refineries, vehicles, gasoline storage and distribution facilities, and paint manufacturers. The fingerprints will be used in a chemical mass balance model to determine the contribution of each source to the hydrocarbon mixture found in the urban Chicago atmosphere. The temporal uniformity of the source fingerprints will be investigated by frequent sampling of emissions over the course of a year. Fingerprint stability will be assessed by examining the variations in hydrocarbon distributions during periods of both peak photochemical oxidation intensity and stagnant conditions. Samples of source emissions will be collected in stainless steel canisters and concentrated prior to analysis in a cryogenic trap. The individual compounds composing the mixture will be resolved and quantified by high-resolution gas chromatography with flame ionization and photoionization detection.

2.6 STUDIES OF AQUATIC SYSTEMS

2.6.1 Summary

The Atmospheric Physics Program's 1986 research on aquatic systems was divided among three major study areas: (1) analysis of Great Lakes water quality surveillance data, (2) in-situ observations of the physical and sedimentological conditions within the benthic boundary layer in Lake St. Clair, and (3) application of systems analysis to environmental problems. Although seemingly disparate, our work in each of these areas has been directed toward understanding the effects and fate of toxic and nutrient contaminants on aquatic ecosystems, in particular the Great Lakes. Support for our analysis of Great Lakes water quality surveillance data has come from the EPA's Great Lakes National Program Office. Our benthic boundary layer observations have been supported by the National Oceanic and Atmospheric Administration's Great Lakes Environmental Research Laboratory. The third project, applications of systems analysis to environmental problems, is an new outgrowth of our aquatic ecosystem modeling work, which also was supported by the Great Lakes National Program Office. In addition to our work with EPA staff members, some cooperative efforts have been made in this area with scientists from the Great Lakes Environmental Research Laboratory.

2.6.2 Analysis of Great Lakes Water Quality Surveillance Data

B.M. Lesh

The 1978 Water Quality Agreement between the U.S. and Canada calls for the parties to conduct water quality surveillance programs to collect data necessary for the ongoing assessment of the condition of the Great Lakes, as well as for improving

understanding of the Great Lakes ecosystem. Much of the data is collected by the U.S. EPA's Great Lakes National Program Office. Argonne has cooperated with EPA on analysis and interpretation of the data collected in 1983 and 1984 from Lakes Erie, Huron, and Michigan.

One of the conclusions of our analysis of the 1983 surveillance data was that the water quality in the three lakes had improved since they were last sampled in the late 1970s. This conclusion was based on decreases in the concentration of total phosphorus and chlorophyll and increases in water transparency in the open waters of the surveyed lakes. We did find, however, that the concentration of inorganic nitrogen, primarily nitrite plus nitrate, was increasing in all three lakes.

The data collected in 1984 confirmed these conclusions. Comparison of the 1984 and 1983 surveys showed considerable year-to-year variability in water temperature (Fig. 2.9). One reason for the difference between these two years was the unusually warm year of 1982-1983 associated with the occurrence of El Nino. Because many of the biological processes affecting the distribution of nutrients in the water column are related to water temperature, this may result in differences in measured concentrations that may be statistically but not environmentally significant. Thus, conclusions regarding environmental trends must be drawn carefully and with an appreciation for the natural variability in the system.

Another interesting feature of the 1983 and 1984 surveillance data is the tendency for summertime concentrations of both particulate and dissolved nutrients in the lowest ten meters of the water column to be significantly enriched relative to those in overlying waters (Fig. 2.10). Although most pronounced in Lake Michigan, this enrichment within the benthic nepheloid layer was also observed in Lake Huron and in the eastern basin of Lake Erie during both years. On the basis of vertical integration, we estimate that as much as 30% of the whole lake burden of total phosphorus and dissolved reactive silica may be suspended in this high-turbidity layer before turnover. The high concentrations of dissolved nutrient species suggest that this layer is an important site for nutrient cycling in the Great Lakes.

FIGURE 2.9 Comparison of surface water temperature in southern Lake Michigan: 1983-1984. Buoy data are from NDBO 45007. Survey data are basin averages.

FIGURE 2.10 Vertical profiles of SiO_2 , $\text{NO}_2^- + \text{NO}_3^-$, and total phosphorus in northern Lake Michigan during three cruises in 1984.

2.6.3 Benthic Boundary Layer Experiments

B.M. Lesht

The basic objective of our benthic boundary layer experiments is to make long-term in-situ observations of sedimentological and physical conditions near the sediment-water interface in order to examine the relationship between physical forcing processes and transportation of bottom sediments. Such studies are necessary to understand and, ultimately, to quantify the processes responsible for the dispersal of the fine-grained sediments that act as carriers of many classes of contaminants. Although our recent experiments have been conducted in Lake St. Clair, the shallow body of between the St. Clair and Detroit Rivers connecting Lake Huron and Lake Erie, we have also been continuing with analysis of data collected in previous years, particularly those collected within the benthic nepheloid layer in Lake Michigan.

2.6.3.1 Near-Bottom Currents and Suspended Sediment Concentration in Southeastern Lake Michigan

*B.M. Lesht and N. Hawley**

[Adapted from the abstract of a paper to appear in the *Journal of Great Lakes Research*]

In a study of sediment transport at the edge of the coastal shelf (28 m deep) in southeastern Lake Michigan, we used an instrumented tripod to make continuous observations of horizontal current velocity, temperature, and turbidity within one meter of the bottom for four weeks during October 1981. The concentration of total suspended material (TSM) 0.9 m above the bottom varied from 1 to 5 mg/L in response to coastal upwelling, surface waves, and currents that exceeded 0.28 m/s (0.7 m above the bottom) on occasion. Advection of the Grand River plume also contributed significantly to the

*Collaborator; affiliation is listed at the front of this chapter.

variations in the observed TSM concentration. Currents near the bottom were well correlated with surface winds, and, although upwelling currents transported sediments upslope, the net horizontal sediment flux during the period of observation was west-southwestward, almost directly offshore. The magnitude of the horizontal sediment flux was approximately 1000 times the magnitude of the vertical flux estimated from sediment traps deployed as part of earlier studies. We infer that local resuspension occurred roughly 20 percent of the time and that the critical mean flow speed (at 0.7 m) for resuspension of the local silty sands was about 0.18 m/s.

2.6.3.2 Sediment Resuspension and Transport in Lake St. Clair

N. Hawley and B.M. Lesht*

[Summary of a paper presented at the 1986 Annual Fall Meeting of the American Geophysical Union]

Lake St. Clair is a large (25-km-diameter), shallow (maximum depth 7 m) lake located between Lakes Huron and Erie. All of the water leaving the upper Great Lakes system (Huron, Michigan, and Superior) passes through Lake St. Clair before entering the Detroit River and the western basin of Lake Erie. We have used three instrumented tripods (one built and operated by Argonne, two built and operated by NOAA's Great Lakes Environmental Research Laboratory) designed to measure horizontal current velocity and water transparency in the lowest meter of the water column in order to study the relationship between sediment resuspension and transport and physical forcing processes active in Lake St. Clair. The tripods were deployed during three observation periods in 1986: in late spring (May-June), summer (July), and autumn (October-November).

Analysis of the results of these experiments has been concentrated on the spring deployment. We identified six episodes of sediment resuspension during the spring deployment. These are characterized by suspended sediment concentrations exceeding 6 mg/L and rapid changes in concentration with time. The ambient suspended sediment concentration in the study area during the spring deployment was about 3 mg/L. The resuspension episodes lasted between 8 hrs and 3 days and occurred either simultaneously with, or just after, episodes of increased wave action. We conclude that surface waves are an important forcing mechanism for sediment resuspension in Lake St. Clair.

2.6.3.3 Empirical Modeling of Sediment Resuspension in Lake St. Clair

*B.M. Lesht and N. Hawley**

[Summary of a paper presented at the 1986 Annual Fall Meeting of the American Geophysical Union]

We have used a simple empirical model to attempt to quantify the relationship between changes in the concentration of suspended sediment near the bottom and the

*Collaborator; affiliation is listed at the front of this chapter.

physical forcing processes in Lake St. Clair. The model, which was brought to our attention by Simons, Schertzer, and Lam of Canada's National Water Research Institute, relates the change in suspended sediment concentration in the water column to the difference between upward sediment flux due to resuspension and downward sediment flux due to settling. The model is written

$$\begin{aligned} D \, dc/dt &= R(s-s_c) - S(c-c_a) & s > s_c \\ D \, dc/dt &= -S(c-c_a) & s \leq s_c, \end{aligned} \quad (2-3)$$

where D is water depth, c is suspended sediment concentration, R is a resuspension flux parameter, s is a flow parameter assumed to force resuspension, s_c is a critical value of the flow parameter for the initiation of resuspension, S is a settling flux parameter, and c_a is an ambient suspended sediment concentration. We used data collected by the Argonne tripod to estimate the parameters of this model. During the spring deployment these data were collected in bursts at 45-min intervals. We used the standard deviation of the horizontal speed recorded during a burst as an analog of surface wave activity. The model parameters were estimated by minimizing the error between the observed suspended sediment concentration and the sediment concentration predicted by the time-integrated form of the model. Figure 2.11 shows the observed concentration time series and the predicted concentration time series. With the exception of one resuspension event that is predicted but not observed, the correspondence between the

FIGURE 2.11 Comparison of observed concentration of suspended sediment in Lake St. Clair and that predicted by equation (2-3) with the standard deviation of current speed as the flow parameter. The gaps in the observed and predicted series are due to data loss.

modeled and the observed concentration is excellent. Preliminary examination of the kinetic energy spectra of the bursts indicates that the frequency distribution of energy when the total variance is high and resuspension is inferred is qualitatively different from the distribution (with the anomalous feature) when the flow variance is high but no resuspension occurs.

2.6.4 Application of Systems Analysis to Environmental Problems

B.M. Lesht

During our work in lake ecosystem modeling and data analysis, a great potential in environmental science became apparent for application of many of the mathematical and statistical techniques commonly employed in systems analysis. These techniques include uncertainty analysis, optimization, inverse theory, nonparametric and computer-intensive statistics, and many others. Applications exist not only in modeling and data analysis, but in experimental and sampling design as well. Our work to date in this area has involved two aspects of optimization, (1) optimizing contaminant control strategies under uncertainty and (2) using formal optimization techniques to aid the design of sampling networks. The following section describes, in brief, the results of our recent efforts.

2.6.4.1 Contaminant Management Strategies for the Great Lakes: Optimal Solutions Under Uncertain Conditions

T.D. Fontaine and B.M. Lesht*

[Adapted from the abstract of a paper to appear in the Journal of Great Lakes Research]

A modeling framework combining optimization, uncertainty, and mass balance was developed to aid decision-making processes that seek to define cost-effective methods for controlling contaminant loads to the Great Lakes. The utility of the framework was demonstrated by defining an optimal phosphorus load reduction plan for the Great Lakes. An optimal plan is defined as the least-cost approach that can achieve desired phosphorus concentrations in all Great Lakes basins under realistic, stochastic phosphorus loading and removal rates. Our analysis suggests that implementation of load reduction measures recommended by the 1978 agreement, its 1983 amendments, and other plans that do not account for environmental uncertainty, may be sub-optimal. Restructuring the placement and intensity of load reduction capacities could lead to substantial annual cost savings and at the same time achieve desired phosphorus concentrations with greater probability than present strategies. Quantitatively accounting for environmental uncertainty in management models is very important.

*Collaborator; affiliation is listed at the front of this chapter.

2.6.4.2 Optimization of a Multitributary Sampling Strategy for Estimating Contaminant Loads to the Great Lakes

B.M. Lesht

Tributary loadings are a major component in the mass budget of many contaminants found in the Great Lakes. In the case of phosphorus, for example, estimates of loadings via monitored tributaries range from less than 20% to more than 90% of the total lake load, depending on lake and year. Thus, the success of efforts to determine trends in loading, or to apply a mass balance approach to pollutant evaluation and control in the Great Lakes will depend, to a great extent, on the accuracy of tributary load estimates. However, current efforts to estimate tributary loads may not be adequate for mass balance computations. Furthermore, given some criterion of performance, no adequate basis may exist for choosing the most efficient allocation of resources available for monitoring tributaries. In order to evaluate these questions, the Great Lakes National Program Office has begun a review of Great Lakes tributary sampling strategies. One major objective of this review is to provide a sound basis for recommendations for new tributary sampling programs. We have been exploring the feasibility of applying formal optimization techniques to the problem in order to provide an objective, analytical procedure for making such recommendations.

The method we have developed is a variation of linear integer programming in which a large number of alternative sampling strategies for multiple tributaries are evaluated simultaneously and an optimal subset of strategies is chosen depending on prespecified conditions, often referred to as constraints. We have considered two optimization questions: (1) What is the least expensive set of strategies for achieving a specified degree of accuracy in a load estimate? and (2) What set of strategies will produce the least amount of uncertainty in a load estimate for a fixed cost? The method produces feasible solutions for a model problem under both types of constraint (Fig. 2.12). Successful application of the method to real problems in the Great Lakes will depend on accurate estimates of the costs and uncertainties associated with each of the sampling strategies as applied to each of the tributaries of interest.

FIGURE 2.12 Results of tributary sampling optimization constrained by uncertainty and by costs.

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APPENDICES FOR CHAPTER 2**Atmospheric Physics Program**

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APPENDIX 2-A. STAFF QUALIFICATIONS

Atmospheric Physics Program

Name	Position	Highest Degree	Major	Year Received	Institution
Cook, David R.	Scientific Assistant	M.S.	Meteorology	1977	The Pennsylvania State University
Coulter, Richard L.	Meteorologist	Ph.D.	Meteorology	1976	The Pennsylvania State University
DePaul, Frank T.*	Postdoctoral Appointee	Ph.D.	Meteorology	1984	Illinois Institute of Technology
Doskey, Paul V.	Assistant Chemist	Ph.D.	Water Chemistry	1982	University of Wisconsin
Frenzen, Paul	Senior Meteorologist	Ph.D.	Meteorology	1964	The University of Chicago
Hart, Richard L.	Scientific Associate	B.S.	Mathematics	1970	Illinois Institute of Technology
Hess, Paul E.	Scientific Associate	B.S.	Physics	1958	Wheaton College
Hong, Min-Sun*	Postdoctoral Appointee	Ph.D.	Chemical Engineering	1985	University of Iowa
Lee, In-Young	Meteorologist	Ph.D.	Meteorology	1975	University of California- Los Angeles
Lesht, Barry M.	Physicist	Ph.D.	Geophysical Sciences	1977	The University of Chicago
Martin, Timothy J.	Scientific Associate	B.A.	Physics	1974	Beloit College
Policastro, Anthony J.*	Mechanical Engineer	Ph.D.	Civil Engineering	1970	Columbia University
Shannon, Jack D.	Meteorologist	Ph.D.	Meteorology	1975	University of Oklahoma
Sheih, Ching-Ming*	Meteorologist	Ph.D.	Aerospace Engineering	1969	The Pennsylvania State University
Sisterson, Douglas L.	Assistant Meteorologist	M.S.	Atmospheric Science	1975	University of Wyoming
Wesely, Marvin L.	Meteorologist	Ph.D.	Soil Science	1970	University of Wisconsin

*No longer a member of the Division.

APPENDIX 2-B. OUTSTANDING PROFESSIONAL ACTIVITIES AND AWARDS**Atmospheric Physics Program**

- R.L. COULTER--Member of American Meteorological Society's Committee on Atmospheric Measurements; session chairman (humidity measurements) at the American Meteorological Society's Sixth Symposium on Meteorological Observations and Instrumentation.
- P. FRENZEN--Professor, Department of Geophysical Sciences, The University of Chicago (Joint Appointment); member of American Meteorological Society's Committee on Boundary Layers and Turbulence.
- R.L. HART--Awarded the Argonne National Laboratory Pacesetter Award (April 1986).
- B.M. LESHT--Chairman of International Joint Commission's Lake Michigan Task Force.
- T.J. MARTIN--Awarded the Argonne National Laboratory Pacesetter Award (November 1986).
- J.D. SHANNON--Member of American Meteorological Society's Committee on Radioactivity and Atmospheric Chemistry; Argonne representative on Interagency Task Force on Acid Precipitation; member of the EPA/AMS Joint Steering Committee on Air Quality Modeling; Certified Consulting Meteorologist.
- D.L. SISTERSON--Chairman of National Atmospheric Deposition Program's Subcommittee #2 (Methods and Quality Assurance).
- M.L. WESELY--Member of EPRI Peer Review Panel on Integrated Forest Studies; member of NCAR Technical Working Group on the Regional Acid Deposition Model; session chairman (dry deposition measurements with atmospheric flux methods) at NAPAP Dry Deposition Workshop (Harper's Ferry, VA); session chairman (instrumentation) at NCAR's workshop on Facilities for Atmospheric Studies of Turbulent Exchange Processes; session chairman (physical and chemical processes for regional models) at AMS/APCA's Fifth Joint Conference on Applications of Air Pollution Meteorology; member of DOE/BES Peer Review Panel on Free-Air CO₂ Enrichment Program.
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APPENDIX 2-C. SPECIAL EVENTS ORGANIZED**Atmospheric Physics Program**

Sisterson, D.L. Chaired Environmental Research Division Workshop on Processing of Emissions by Clouds and Precipitation - PRECP-VI: Study of Convective Storms, 16 December 1986, Argonne National Laboratory, Argonne, IL.

Wesely, M.L. Cochaired and co-organized NAPAP Workshop on Dry Deposition, 25-27 March 1986, Harpers Ferry, WV.

Wesely, M.L. Organized Division seminar, held 18 June 1986, Argonne National Laboratory (Speaker: Murray Judd, Ruakura Soil and Plant Station, New Zealand; Subject: Comparative shelter strategies for Kiwifruit - A mechanistic interpretation of wind damage measurements.)

APPENDIX 2-D. EDUCATIONAL PROGRAM PARTICIPANTS**Atmospheric Physics Program**

- T. FRANK DEPAUL. Illinois Institute of Technology. Postdoctoral Appointee. Conducted field research on dry deposition of fine particles. January 1984 - February 1986.
- MIN-SUN HONG. University of Iowa. Postdoctoral Appointee. Conducted research on numerical modeling of atmospheric chemical processes. August 1985 - January 1987.
- MARY LIAW. North Central College, Illinois. Faculty Research Leave Participant. Conducted research on atmospheric lightning and in-cloud production of nitrogen oxides. June - present.
- ALAN C. BAILEY. Clemson University. Thesis Parts Program. Integrated instrumentation for making physical and chemical observations near the sediment-water interface in natural waters. July 1986 - June 1987.
- ADAM W. BURNETT. Ohio University. Thesis Parts Program. Conducted research on influence of synoptic conditions on local air chemistry. July 1985 - February 1986.
- SARA WOOD. University of Western Illinois. Thesis Parts Program. Conducted research on influence of local sources on air quality. March 1985 - present.
- JOHN R. COOLEY. University of Vermont. Undergraduate Research Program. Assisted in preparation and testing of instrumentation prior to smoke tests. June - August 1986.
- EVAN L. HELLER. State University of New York at Oswego. Undergraduate Research Program. Participated in studies of acidic wet deposition. January - April 1986.
- KATHERINE M. KANAK. University of Oklahoma, Norman. Undergraduate Research Program. Tested computer models for fog oil and HC smoke dispersion. June - August 1986.
- DAVID J. MERCER. St. John's University, Minnesota. Undergraduate Research Program. Measured air-surface exchange of pollutants and analyzed data collected. June - August 1986.
-

APPENDIX 2-E. PUBLICATIONS AND ORAL PRESENTATIONS

Atmospheric Physics Program

1. Refereed Journal Articles*

Cook, D.R. Dreaming of a white Christmas. Weatherwise 39:308-310 (1986). [DOE/OHER]**

DePaul, F.T., and C.M. Sheih. Measurements of wind velocities in a street canyon. Atmospheric Environment 20:455-459 (1986). [DOE/OHER]

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Lee, I.-Y. Numerical simulation of chemical and physical properties of cumulus clouds. Atmospheric Environment 20:767-771 (1986). [DOE/OHER]

Shannon, J.D., and B.M. Lesht. Estimation of source-receptor matrices for deposition of NO_x-N. Water, Air, and Soil Pollution 30:815-824 (1986). [EPA/ORD]

Walcek, C.J., R.A. Brost, J.S. Chang, and M.L. Wesely. SO₂, sulfate and HNO₃ deposition velocities computed using landuse and meteorological data. Atmospheric Environment 20:949-964 (1986). [EPA/ASRL]

2. Books, Book Chapters, and Collections
of Conference Proceedings

Hicks, B.B., M.L. Wesely, S.E. Lindberg, and S.M. Bromberg (eds.). Proceedings of the NAPAP Workshop on Dry Deposition, ATDL Cont. File No. 86/25, NOAA/ATDD, Oak Ridge, TN. 1986. 77 pp. [DOE/OHER]

Neff, W.D., and R.L. Coulter. Acoustic remote sounding. In: Probing the Atmospheric Boundary Layer. American Meteorological Society, Boston, MA. 1985. pp. 201-236. [DOE/OHER, EPA/ASRL]

*For all published material, names of Environmental Research Division authors are underlined. (Included are Division members who participated in a project but left the Division before the results were published.)

**Funding agency (abbreviations are spelled out at the end of this appendix).

Shannon, J.D., and B.M. Lesht. Modeled trends and climatological variability of the net transboundary flux of sulfur between the United States and Canada. Transactions, Second International Speciality Conference on Meteorology of Acidic Deposition, 18 March 1986, Albany, NY. 1986. pp. 28-35. [DOE/OHER]

3. Reports

Coulter, R.L., M.L. Wesely, D.L. Sisterson, T.J. Martin, R.L. Hart, D.R. Cook, P.E. Hess, E.W. Eloranta and B.B. Hicks. The DeWitt Field Study: Surface flux observations, in-situ soundings, and remote sensing of conditions affecting the behavior of the mixed layer over land. ANL/ER-85-1. Environmental Research Division, Argonne National Laboratory. 1986. [DOE/OHER, EPA/ASRL]

PolICASTRO, A.J., and W.E. Dunn. Survey and evaluation of field data suitable for smoke hazard model evaluation. ANL/ER-85-3, AD-A161 880. Prepared for U.S. Army Medical Research and Development Command. 1985 (Issued 1986). [DOD/U.S. Army]

Sheih, C.M., M.L. Wesely, and C.J. Walcek. A dry deposition module for regional acid deposition. U. S. Environmental Protection Agency Report, EPA/600/3-86/037, NTIS PB86218104. 1986. [EPA/ASRL]

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4. Published Conference Papers

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**Audience for the presentation.

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ASRL = Atmospheric Sciences Research Laboratory (in U.S. Environmental Protection Agency)
DOD = U.S. Department of Defense
DOE = U.S. Department of Energy
EH = Office of Environment and Health (in U.S. Department of Energy)
EPA = U.S. Environmental Protection Agency
FE = Office of Fossil Energy (in U.S. Department of Energy)
GLERL = Great Lakes Environmental Research Laboratory (in National Oceanic and Atmospheric Administration)
GLNPO = Great Lakes National Program Office (in U.S. Environmental Protection Agency)
NOAA = National Oceanic and Atmospheric Administration
OHER = Office of Health and Environmental Research (in U.S. Department of Energy)
ORD = Office of Research and Development (in U.S. Environmental Protection Agency)
WSMR = White Sands Missile Range

3 ENVIRONMENTAL EFFECTS RESEARCH PROGRAM

3 ENVIRONMENTAL EFFECTS RESEARCH PROGRAM

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3.1 PROGRAM OVERVIEW

T.M. Beasley

Significant changes occurred in the Environmental Effects Research Program (EERP) during 1986. Participation in the National Crop Loss Assessment Network was terminated, while a new program was initiated to identify those environmental and operational parameters that lead to the development and persistence of acidic lakes. As part of an initiative to establish an accelerator mass spectrometry facility at Argonne, initial research was begun towards building expertise in tracing and dating groundwaters by using the cosmogenically produced radionuclides ^{36}Cl and ^{14}C . While initial ^{36}Cl results have been obtained for constraining the ages of deep groundwaters underlying the Savannah River Plant in Aiken, South Carolina, the research is not yet sufficiently advanced to report here.

Work has progressed in understanding soil-plant interaction processes with added emphasis on the structural changes that occur in soils because of their association with different plant communities.

Aquatic radiochemistry research has continued to focus on understanding those processes that regulate the biogeochemical behavior of important, long-lived radionuclides in the environment.

Set out below is a brief discussion of progress in each of these programs. A more detailed account of the research can be found in the open literature publications and topical reports shown in Appendix 3-E.

3.2 BEHAVIOR OF TRANSURANIC ELEMENTS IN NATURAL WATERS

3.2.1 Summary

W.R. Penrose

The focus of this program has shifted somewhat over the past two years from environmental processes that affect the behavior of transuranic elements to the environmental processes themselves and the ways in which actinides and other environmentally distributed radionuclides can be used as tracers for these processes. The formation and fate of colloids in natural waters is particularly important, as it is a problem of considerable current interest and is easily amenable to the tracer approach. For example, experiments in Lake Trawsfynydd, U.K., and in Pond B at the Savannah River Plant have revealed a previously unobserved association of actinides with very large colloids. As before, the emphasis is on observations and experiments done primarily in the field, with laboratory experiments designed to complement or generalize the field data.

This project has been funded entirely by the U.S. Department of Energy through the Office of Health and Environmental Research.

3.2.2 Behavior of Actinides in Pond B, Savannah River Plant, SC

K.A. Orlandini, J. Bowling, John Pinder, III,* and M.W. Findlay, Jr.*

On the site of the Savannah River Plant, near Aiken, SC, are two ponds that were contaminated with radionuclides in past spills. Study of these two ponds has contributed substantially to our understanding of the behavior of transuranic nuclides, as well as that of cesium and strontium. Par Pond is the larger of the two ponds at 1040 ha; Pond B is 87 ha.

Pond B is a monomictic lake that forms an anoxic zone for several months each summer. The chemistry of this zone is dominated by iron, which is present in high concentrations in the ferrous state. The inventory of total iron (dissolved and suspended) reaches a maximum in August and September and falls to near zero from December to March. At the chemocline, upward diffusion of ferrous iron and precipitation and settling of ferric iron are presumed to form a cycle that can draw plutonium from the epilimnion downward. When the lake mixes in the fall, essentially all the iron precipitates.

Although a definite annual cycle of plutonium concentrations has been observed in Pond B, this cycle is not in phase with the iron cycle (Fig. 3.1). Plutonium concentrations in surface waters reach a maximum in early spring, and a minimum when the iron cycle is at its peak. This probably reflects the operation of the iron pump moving plutonium from the epilimnion to the hypolimnion. The total inventory, however, does not change throughout the year. In particular, the plutonium is not scavenged en masse when the lake turns over in the fall. The cesium cycle, in which cesium is displaced from sediments by ammonia, is also shown in Fig. 3.1 for comparison.

We have observed unusual behavior of curium in Pond B in the past. Occasionally dissolved curium levels were unusually high in surface waters (Fig. 3.2), and measured K_d values were unusually low (Fig. 3.3), while americium behavior was not changed. Recent observations of airborne particles by using tacky papers has demonstrated that curium often arrives by way of the atmosphere. This accounts for apparent differences in the concentrations of americium and curium in the pond. The differences in K_d can be explained if the curium requires a long time to reach equilibrium.

A similar phenomenon has since been discovered with respect to plutonium-238. Plutonium 238/239 ratios have been shown to vary with time and depth. Tacky-paper measurements have revealed airborne ^{238}Pu near the Savannah River Plant site, and so the situation seems to be analogous to that of curium and americium. The $^{238}\text{Pu}/^{239}\text{Pu}$ ratio in sediments is 0.077, and that of atmospheric input is 1.00; these ratios are sufficiently different that relative contributions of sediment and airborne sources of plutonium can be calculated. These calculations confirm that very little plutonium is mobilized from the sediments.

*Collaborator; affiliation is listed at the front of this chapter.

FIGURE 3.1 The cycle of cesium, iron, and plutonium in Pond B, Savannah River Plant site. The cycles of cesium and iron more or less coincide, but the plutonium cycle is out of phase with both. Total inventories are plotted.

3.2.3 Lake Trawsfynydd, Wales, as a Site for Experiments in Environmental Radioactivity

W.R. Penrose, K.A. Orlandini, M.B. Lovett, and B.R. Harvey**

In a collaboration with the British Ministry of Agriculture, Fisheries, and Food and the Central Electricity Generating Board, we have been studying the behavior of the actinides released from a power station located at Lake Trawsfynydd in Gwynedd, North Wales. The power station consists of twin Magnox 500-MW gas-cooled reactors with a common turbine hall. Lake water is used as the secondary coolant. Used fuel rods are cooled in a closed pond, but the ion exchange regenerates from this pond are released at a controlled rate into the cooling water and thence into the lake.

*Collaborator; affiliation is listed at the front of this chapter.

Depth Profiles of Actinides: B Pond, Aug 84

FIGURE 3.2 Concentrations of four actinides (^{239}Pu , ^{241}Am , ^{244}Cm and ^{232}Th) at different depths in Pond B, August 1984. The chemocline is at about 6 meters depth.

Although radionuclide levels are kept within British health regulations, they are sufficiently high that traces of plutonium, americium, and curium can be measured in the water. A number of common fission products are also present in some quantity (Table 3.1). The lake supports an active sports fishery on perch and trout, and the Ministry of Agriculture, Fisheries, and Food maintains continual monitoring activities on fish, water, and sediments.

Lake Trawsfynydd is a 531-ha artificial impoundment built in 1926 for a small, 26-MW hydroelectric power station. Until a recent accident, the small station was still in use. A dam about 20 meters high was built across the ravine of the Afon ("river") Prysor (Fig. 3.4).

The reactor complex began operations in 1966, making it one of the oldest continuously operating nuclear plants in Britain. Local acceptance of the plant is good, since it is the largest employer in the area and also provides the recreational fishery.

Water quality in Lake Trawsfynydd represents the extreme end of the oligotrophic spectrum. The catchment area is 92 km^2 and consists mainly of granitic rocks of approximately Upper Cambrian age. The water is very low in ions and in organic carbon (Table 3.2). Turnover time for the lake is about two months, and the reactor cycles the water every seven days while at full power.

Kd's of Actinides in Pond B: Aug 84

FIGURE 3.3 Kd values for the four actinides (²³⁹Pu, ²⁴¹Am, ²⁴⁴Cm, and ²³²Th) of Fig. 3.2. The measurements were simultaneous with those of Fig. 3.2.

TABLE 3.1 Gamma-emitting nuclides in Lake Trawsfynydd in February 1986

Cobalt-60	Ruthenium-106	Antimony-124	Antimony-125
Cesium-134	Cesium-137	Cerium-144	Europium-154
Europium-155	Lead-212	Americium-241

FIGURE 3.4 Lake Trawsfynydd, Gwynedd, North Wales. The locations A, B, and C indicate the standard sampling locations.

In spite of the increased temperature caused by the reactor, plankton blooms are limited to the summer months. This is presumably due to nutrient supply, since incoming nutrients are substantially higher in summer than winter. The surrounding landscape supports sheep grazing, which should imply a seasonal mobilization of nutrients.

Investigations on Lake Trawsfynydd have included size speciation experiments; oxidation state measurements on plutonium; and measurements of actinide concentrations in water, suspended solids, and sediments.

3.2.4 Size Speciation of Actinides in Fresh Waters

K.A. Orlandini, W.R. Penrose, and M.W. Findlay, Jr.

Earlier research, much of which has been done in this program, has demonstrated that the mobility of actinide elements in natural waters is strongly controlled by water chemistry. In the case of plutonium, oxidation state is a determinant of mobility; the

TABLE 3.2 Chemical properties of water from Lake Trawsfynydd from samples taken at Station C at the surface and just above the bottom

Parameter	Dam (Surface)	Dam (Bottom)	Units
<u>July 20-24, 1986</u>			
Oxygen	6.73	0.53	mL/L
Temperature	21.9	19.2	°C
Suspended load	7.0	61.0	mg/L
Alkalinity	7.6	11.7	mg CaCO ₃ /L
Reactive silica	1.16	1.74	mg Si/L
Phosphorus	5.0	37.5	µg P/L
Nitrate	32.4	-	µg N/L
<u>October 6, 1986</u>			
Oxygen	5.42	3.79	mL/L
Temperature	19.5	18.5	°C
Suspended load	1.4	4.0	mg/L
Reactive silica	24.9	26.1	mg Si/L
Nitrate	11.6	10.2	µg N/L
<u>March 23, 1987</u>			
Oxygen	8.4	4.6	mL/L
Temperature	11.7	9.8	°C
Phosphorus	3.0	1.0	µg P/L

Pu(V) form is soluble and weakly particle-reactive, whereas Pu(IV) is essentially insoluble and strongly particle-reactive. The proportions in the (IV) and (V) states are related to the type of water in which they are found. For all the actinides, dissolved organic carbon complexes with and enhances the apparent solubility of the (III) and (IV) oxidation states, a phenomenon that has also been observed for trace metals and hydrophobic organic compounds. Inorganic complexing agents such as carbonate are known to affect the oxidation state distribution of uranium by selective complexation.

To this picture, complex as it is, we have added yet another dimension of speciation, the selective distribution of actinides among colloids of different sizes. The availability of hollow-fiber filtration technology has allowed us to carry out rapid separations on samples of hundreds of liters, with selection of physical size down to 3000 daltons equivalent molecular weight. Hollow-fiber filtration works by forcing the water sample through a cluster of thin tubes that are lined with the porous filtration membrane. Slight back-pressure causes a fraction of the sample to be forced through the

membrane. Under normal conditions, the flow through the tube is greater than the rate of filtration, so that the movement of the sample is essentially parallel to the membrane. This prevents clogging and maintains a constant selectivity of filtration throughout the operation, while maintaining very high filtration rates.

To date, size separations have been made on water from Lake Trawsfynydd, Wales, and Pond B at the Savannah River Plant. Typically, a water sample is first filtered to $0.45\ \mu\text{m}$ with a standard micropore filter. A $0.1\text{-}\mu\text{m}$ hollow-fiber cartridge is then used to process all the water. Portions of the $<0.1\mu\text{m}$ dialysate are then passed through 100K, 30K, and 3K filters, and ferric hydroxide precipitations are made to recover the actinides in all fractions.

At Trawsfynydd, we have shown that 85-90% of the actinides that pass through the $0.45\text{-}\mu\text{m}$ filter are retained by the 30K hollow-fiber cartridge (Fig. 3.5). Although the errors are large, it appears that the remaining activity passes through the 3K filter; that is, it may be truly dissolved. (We have observed that Gd^{+3} , a large polyvalent ion similar in size and behavior to plutonium, americium, and curium, passes through a 3K filter, but is mostly retained by a 1K filter.)

FIGURE 3.5 Size speciation of $^{239,240}\text{Pu}$ in Lake Trawsfynydd. The Bailey Bridge sample was taken at site A, and the "Dam" samples at site C. The size classes are named according to the nominal molecular weight cutoffs of the hollow-fiber cartridges used.

In December of 1986, the first of a planned series of hollow-fiber separation experiments was carried out at Pond B. The fractions were analyzed for actinides as well as for iron and manganese. Americium distribution among the size fractions was correlated with that of manganese, but plutonium distribution was not correlated with that of either iron or manganese (Table 3.3).

The nature of the large actinide-binding colloids is unknown. Dissolved organic carbon is known to have a significant effect in complexing actinides and most other metals. In most waters, the bulk of the dissolved organic carbon is found in the 1K-30K molecular weight range. We do not yet, however, have a molecular size distribution of dissolved organic carbon for either Lake Trawsfynydd or Pond B.

Another possible colloid is microcrystals based on iron, manganese, or clays. When coated with a small amount of dissolved organic carbon, they would be stabilized against coagulation.

When internal standards of ^{242}Pu , ^{243}Am , and ^{230}Th are added to a sample of raw water, the standards are found to equilibrate completely with the ambient isotopes within two days. Hence, the actinides are not simply occluded in a crystal matrix, but can exchange freely.

TABLE 3.3 Size speciation of actinides in Pond B, Savannah River

	(fCi/L)			(μg/L)	
	Pu	Am	Th	Fe	Mn
<u>Dec. 86, 1.5 meters</u>					
Dissolved (<0.45μm)	0.20	0.27	0.146	22	56
0.1μ - 0.45μm	55%	20%	52%	100%	9%
100K - 0.1μm	6%	18%	11%	0%	6%
30K - 100K	2%	10%	0%	0%	2%
<30K	36%	61%	21%	0%	82%
<u>Dec. 86, 9 meters</u>					
Dissolved (<0.45μm)	0.050	0.22	0.051	173	76
0.1μ - 0.45μm	88%	27%	37%	12%	6%
100K - 0.1μm	11%	11%	63%	35%	8%
30K - 100K	0%	5%	0%	14%	2%
<30K	0%	57%	0%	39%	83%

3.2.5 A Search for Long-Lived Tin Isotopes in Areas Contaminated with Fission Products

*J.R. Penrose and T. Patton-Baker**

A recent report by the National Academy of Sciences (1983) cited tin isotopes as significant contributors of radiation dose to man from buried fission wastes in the 1000- to 100,000-yr time scale. Nuclear fission produces two isotopes of tin in significant yield: tin-121m (0.013%, beta, 0.35 MeV, 55 yr) and tin-126 (0.056%, beta, 0.25 MeV, 105 yr). Tin-126 is the isotope of concern for long-term storage, but we would expect to find the radioactivity of tin-121m to be 400 times greater.

The literature on the tin isotopes is very sparse, and that on their environmental behavior is nonexistent. In fact, the NAS report remarks that its data on tin are drawn from sparse and shaky [sic] sources. Koide and Goldberg (1985) recently reported finding tin-126 in sediment samples from several marine sources. We have attempted to develop a method for analyzing the tin isotopes.

Attempts to replicate the Koide and Goldberg method have failed. Their method depends heavily on sulfide precipitations; in our hands, many of the constituents of natural sediments interfere, and copious amounts of elemental sulfur are formed. Ferric hydroxide coprecipitation early in the procedure also seems to be somewhat less than quantitative.

We normally ash 10 g of dry sediment at 500°C and digest it with 6M hydrochloric acid. A recovery monitor of stable tin (2.0 to 5.0 mg) is added to the digest. Bromine water is also added to ensure that the tin is in the (IV) oxidation state. Iron is removed by repeated extraction with isopropyl ether until the sample is colorless. The tin is then extracted into methylisobutyl ketone and stripped into 0.1 N HCl. The extract is immediately brought to 3 M in HBr.

The tin is adsorbed from 3 M HBr onto a column of AG-1-X8 anion exchange resin. The column is washed with 3 M HBr, and the tin is eluted with 0.5 M HBr. Ferric ion (5 mg) is added, and ferric hydroxide is precipitated with sodium hydroxide and sodium bicarbonate. The ferric hydroxide precipitate, containing the tin, is centrifuged, and the ferric hydroxide is redissolved in 6 M HCl. The iron is again removed with isopropyl ether.

Cesium hexachlorostannate is precipitated by the addition of cesium chloride to the strong HCl solution. This precipitate is centrifuged and dissolved in water. Ferric iron carrier (2 mg) is added and precipitated with sodium bicarbonate. The precipitate is collected on a 2.4-cm glass fiber filter and counted in a low-background beta counter. The precipitate is redissolved and the stable tin measured by graphite furnace atomic absorption spectrometry; recovery of total tin is typically 90%. Table 3.4 shows results to date.

*Collaborator; affiliation is listed at the front of this chapter.

TABLE 3.4 ^{121m}Sn Analysis Results (pCi/g)

Sample	^{121m}Sn		$^{239,240}\text{Pu}$
Lake C, May 1986	1.34	0.05	3.52
	0.71	0.04	-
	1.32	0.05	-
	1.68	0.05	-
Lake C, Oct. 1986	0.79	0.06	4.5
	1.58	0.08	-
Irish Sea, Oct. 1977	0.40	0.04	8.8
Argonne Pond, Aug. 1983	0.17	0.03	0.003
Four Mile Creek, Dec. 1986 (Savannah River Plant)	0.17	0.04	-
	0.15	0.04	-
Pond B, Dec. 1984 (Savannah River Plant)	0.33	0.04	-
	0.28	0.03	-

More than two weeks of observation revealed neither a decrease in activity, nor any observable gamma activity. Therefore, the tin-126 was not present in detectable amounts, and there was no contamination by antimony-124 or antimony-125. Reagent blanks were found to be necessary, however, because many commercial reagent grade chemicals contained beta activity that came through the procedure.

Tin-121m is expected to occur in fission products in concentrations similar to those of plutonium. This is observed in Lake C. In Irish Sea sediment, which contains similar levels of plutonium, the tin-121m concentrations are at background levels. These differences may be due to source effects; e.g., the Sellafield effluent entering the Irish Sea may have very low tin-121m content. Alternately, the behavior of the two elements in the environment may be very different.

3.2.6 Short-term Particle Settling Rates Measured By $^{90}\text{Sr}/^{90}\text{Y}$ Disequilibrium

M.W. Findlay, Jr., K.A. Orlandini, J. Bowling, J. Pinder III,* and W.R. Penrose*

Particle settling is one of the more important mechanisms by which trace metals, radionuclides, and organic pollutants are removed from natural waters. Yet the study of particle formation and dynamics has not developed very far, mainly due to a

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dearth of effective methods. Static particle concentrations can be measured with gravimetric or optical methods, but particle settling rates can only be measured with sediment traps or inferred from radionuclide disequilibrium methods; each of these methods has its advantages and disadvantages. Disequilibrium methods, for example, are limited to time scales similar to the half-life of the daughter nuclide. In this work, we report the development of methodology to use a new radionuclide pair for the measurement of very short removal times.

Disequilibrium methods require the presence of a pair of parent-daughter nuclides. The parent must be soluble and conservative in natural waters; the daughter must be particle-reactive. The most commonly-used pairs are $^{228}\text{Ra}/^{228}\text{Th}$ and $^{238}\text{U}/^{234}\text{Th}$. The daughters have half-lives of 1.9 years and 24.1 days, respectively. If no particle removal occurs on a time scale similar to the half-life of the daughter isotope, these isotope pairs will be in secular equilibrium [the concentrations of their radioactivities (in dpm) will be identical]. If, however, the daughter nuclide is being removed from the water column at a rate similar to its own half-life, the concentration of the daughter activity will be depleted relative to that of the parent (i.e., disequilibrium will occur). Measurement of thorium daughters has been useful in determining particle removal rates in the oceans, where time scales of months and years are not uncommon. In small lakes and ponds as well as in estuaries, the time scales are much shorter, and the thorium daughter methods may not be as effective.

Atomic weapons testing has distributed the radionuclide ^{90}Sr throughout the earth at activities (in natural waters) similar to those of the actinides. This isotope decays to ^{90}Y , which is particle-reactive and has a half-life of 64 hr. We have investigated the application of this isotope pair to the measurement of rapid settling rates.

Typically, water samples of 20-100 L are filtered, and ^{90}Y is recovered separately from particles and filtrates. The water sample is saved. The strontium remains in this residue, and after several weeks the equilibrium establishes itself. A second separation and measurement of ^{90}Y yields the activity of ^{90}Sr . The rate constants of removal can be calculated from the equations:

$$r_d = D (A_p/A_d - 1) \quad (3-1)$$

$$r_s = r_d/f \quad (3-2)$$

where A_p and A_d are the activities of the parent and daughter nuclides, respectively, D is the decay constant for ^{90}Y , f is the fraction of total yttrium that is bound to suspended solids, and r_d and r_s are the removal rate constants for total yttrium and for suspended particles only.

Samples of water from Lake Trawsfynydd, Wales; Pond B, Savannah River Plant; and Saganashkee Slough, Illinois have been investigated by using this technique. Trawsfynydd and Pond B are of interest because they are already the subjects of intensive study of the dynamics of radionuclides. Saganashkee is of interest because its particle load varies from 5 mg/L to over 120 mg/L in the course of a year; its proximity to Argonne also makes it convenient for frequent sampling. Yttrium analysis is carried

out by ferric hydroxide coprecipitation, anion exchange procedures in hydrochloric and nitric acid media, and cation exchange in hydrochloric acid. The product is coprecipitated with a small amount of ferric hydroxide for beta counting. The procedure is such that thorium isotopes can be measured with very little additional effort, and so the three isotope pairs can be easily compared. Recent results are shown in Table 3.5.

The parameter r_d is the removal rate of yttrium from the water column; r_s is the removal rate of the suspended material. Both removal rates were lowest in February, when a thin sheet of ice covered the water; wind-driven particle resuspension was very slight, so suspended particle concentration was small and removal rates very low. Particle concentrations were highest in July, but removal rates were slower than in May. We suspect that this is because many of the particulates in July were living, neutrally buoyant organisms that did not passively settle through the water column.

Particle settling rates measured in Saganashkee by using thorium isotopes are instructive, although only two measurements are available. The value for ^{234}Th is much lower than that for yttrium, indicating that the settling rate measured for yttrium is

TABLE 3.5 Particle dynamics in Saganashkee Slough

	Sample Date			Units
	5/19/86	7/29/86	2/87	
Suspended solids	44	120	5.3	mg/L
^{90}Sr				
solids	28	24	5.8	fCi/L
dissolved	586	663	587	fCi/L
^{90}Y				
solids	136	280	249	fCi/L
dissolved	45	20	285	fCi/L
r_d	0.62	0.336	0.028	day ⁻¹
r_s	0.83	0.36	0.060	day ⁻¹
K_d	6.9×10^4	1.2×10^5	1.7×10^5	L/kg
By $^{238}\text{U}/^{234}\text{Th}$:				
r_d	--	0.037	--	day ⁻¹
By $^{228}\text{Ra}/^{228}\text{Th}$:				
r_d	--	-0.0005	0.007	day ⁻¹

balanced by frequent resuspensions of particles over the isotope's time scale of about a month. The value for ^{228}Th indicates the obvious: in a closed pond system, with little in the way of either sources or sinks of particles, the particle removal rate averaged over two years is zero.

Measurements at Savannah River were calculated to separate adsorption rates from particle removal rates (Table 3.6). Adsorption rates were alike between March and June; this was not surprising, since particle concentrations were similar. Particle removal rates, however, were substantially different. We assume that more of the particles in the June sample were living and actively maintained their place in the water column.

3.3 SOIL-PLANT PROCESSES PROGRAM

3.3.1 Summary

R.M. Miller

Research in this program has been directed at determining how plants adapt to the stresses imposed by their environment, and especially how these adaptations may influence community dynamics. Rather than taking an approach based upon demonstrating that change can occur, we are more interested in understanding the mechanisms behind changes in structure and function. We are addressing the following questions. How do organisms influence their environment? How do changes affect the fitness of the species initiating the change? One approach has been to use the mycorrhizal association as a means of investigating how roots influence soil aggregation and associated pore space development. Also investigated are ways these parameters influence community dynamics. The long-term goal of the program is to vertically integrate by going from the individual to community level of organization.

Beginning in the summer of 1985, effort has been directed at developing a field site at the Fermi National Accelerator Laboratory (FNAL). What attracted us to the

**TABLE 3.6 Particle removal rates at Pond B,
Savannah River Plant**

	Sampling Date		Units
	March 1986	June 1986	
Suspended solids	4.1	6.1	mg/L
Adsorption rate	0.3	0.45	day ⁻¹
Removal rate	0.055	0.006	day ⁻¹

site, in addition to its location, was the chronosequence of restored prairie that has been established there. Since 1975, portions of the area within the accelerator ring have been annually returned to prairie. A virgin tallgrass prairie also exists 6 km from FNAL. These prairies all occur on three closely related soil series. Because of these attributes, a unique opportunity for studying the mechanisms underlying community dynamics exists; time-dependent gradients have now been established in the vegetation, nutrients, mycorrhizae, and soil aggregation characteristics of both sites.

3.3.2 A Method for Measuring Externally Produced Mycorrhizal Hyphae in Soil

*R.M. Miller, J.D. Jastrow, and P.D. Olexia**

Accurate information is sparse on the amount of extramatrical mycelium produced within the soil by mycorrhizal fungi because of the difficulties involved in mycelium isolation and measurement. Many researchers (e.g., Amijee et al. 1986) have assumed that the amount of fungus produced within the root is proportional to the amount of fungus produced externally. Thus, most researchers measure only the internal portion of the association. However, a recent study in this laboratory (Miller et al. 1987) revealed no such association between internally and externally produced fungus. The number of studies measuring external mycorrhizal hyphae is exiguous. These studies, for the most part, have been limited to sandy soils (e.g., Abbott et al. 1984; Bethlenfalvay et al. 1981; Tisdall and Oades 1979). In comparison, the measurement of extramatrical hyphae in heavy soils can be tedious and time consuming. Only a few investigators have attempted such a study (Allen and MacMahon 1985). However, if mycorrhizal fungi are to be integrated into nutrient cycling and ecosystem studies, it will be necessary to quantify both the internal and external portion of the mycorrhizal fungus. Thus we initiated a study to develop a procedure to measure extramatrically produced mycorrhizal hyphae in heavy soils or in soils where colloidal materials can cause problems because of the inability to separate these small particles from the hyphae. A brief summary of this procedure, which is based on a modification of the membrane filter technique (Hanssen et al. 1974), is presented below.

A predetermined amount of soil was placed into 250 mL of water in a 600-mL beaker to which sodium hexametaphosphate was added to facilitate and maintain the dispersal of soil particles once they had been disaggregated. The soil solution was sonicated to disaggregate soil particles and to dislodge hyphae from soil and root fragments that may have remained in the sample.

Two replicate 20-mL aliquots were removed from this solution/suspension. The aliquots were centrifuged at 2700 x g for 5 min and then allowed to stop without braking. This caused larger soil particles with most of the hyphae to collect in the pellet while the clay particles remained suspended. The supernatant was decanted by pipette, and the pellet was resuspended in 50% glycerol. The resuspended material was centrifuged at approximately 75 x g for 1 min to separate hyphae from coarser soil particles; the supernatant containing the hyphae was removed by pipette as quickly as possible following centrifugation.

*Collaborator; affiliation is listed at the front of this chapter.

The supernatant was added to a filtration apparatus containing a 20- μm mesh mylar filter and subjected to mild suction. The filter collected the long hyphae and permitted the small and intermediate soil particles to pass through with the filtrate. The mylar filter was placed in a test tube with phosphate buffer containing fluorescein diacetate (FDA). The FDA-stained hyphae were dislodged from the mylar filters by placing the tube on a vortex mixer for approximately 20 s. This solution was allowed to stand for approximately 5 min, briefly mixed again to resuspend the hyphae, and decanted into the filter apparatus containing a black cellulose nitrate filter (25 mm diameter, 0.8 μm pore size). The filter was removed, air dried for approximately 30 min, mounted on a slide in low-viscosity, low-fluorescence immersion oil, and covered with a cover slip.

Hyphae were observed by using epifluorescence illumination. Lengths of hyphae were estimated made by using a gridded reticule in the ocular of the microscope as the background upon which hyphal intercepts were counted. For each filter (two filters/sample), seventy arbitrarily chosen fields of view were counted. Fields were counted at 160x with an eyepiece reticle covering an area of 0.354 mm². The 70 fields of view examined represented approximately 10% of the surface area of one filter upon which hyphae were collected. Hyphal length was calculated by using the formula of Newman (1966).

A concern in the early stages of the study was the number of fields of view required to provide an adequate measure of the hyphae on the membrane filters. The distribution of the hyphae on the filters did not appear to be random (variance:mean ratios for 70 fields of view typically ranged from 1.5-2.0 or greater). Therefore, we used a criterion of standard error as a percent of the mean to evaluate whether an adequate number of fields of view had been observed.

We found a relationship between the mean count of a field of view and the ratio of the standard error to the mean of that field (Fig. 3.6). This association indicates that the higher the average count for a field of view, the more likely that count is to be representative of the sample.

Depending upon both the soil used and the number of hyphae, the concentrations of the solutions used may be varied at a number of points throughout the procedure. Soils with many intermediate-sized particles that are not removed either by the slow centrifugation step or by passing through the mylar filter may clog the filter, making the final filtration step long and tedious or even impossible. Adjustments can be made at the initial step (in the amount of soil/volume of water), in the size of the aliquot used in the first centrifugation, at the glycerol resuspension step prior to slow centrifugation, or in the volume of buffer used for immersing the mylar filter at the FDA staining step.

3.3.3 Plant Species Associations with Changes in Soil Aggregation in Restored Tallgrass Prairie

J.D. Jastrow

The most highly aggregated soils in the United States are those that have been continually in grass for many years, because ideal conditions for both aggregate

FIGURE 3.6 The association between number of fields of view and the ratio of the standard error to the mean and its dependency on count in the field of view (---, 7.6; -.-, 4.3; ---, 3.2; ..., 1.7; —, 1.5 mean counts per field of view).

formation and stabilization exist simultaneously in the rhizosphere of grasses (Allison 1986). This is one reason why the soils that developed under prairie systems, particularly tallgrass prairie, are among the most agriculturally productive in the world. It is well known that cultivation of virgin or long-term grassland soils results in a significant loss of water-stable aggregates and often changes the distribution of aggregate size classes.

Most studies of soil aggregates have focused on preservation or improvement of soil structure and reduction of erosion in agricultural soils. Thus, most of the literature on the influence of individual plant species or species mixtures is concerned with crop or forage species. In general, these studies have shown that perennial grasses with their fine root systems, perennial legumes with their relatively rapid decomposition rates, and grass/legume mixtures are associated with greater aggregate stability than are grain and root crops.

In 1985, we initiated a study to explore the feasibility of using the dynamics of soil aggregation as a tool to assist in understanding plant-soil interactions. We hypothesized that with a restoration ecology approach, the dynamics of soil aggregation could be observed in conjunction with changes in the biological community over a

gradient in time, thereby providing insights into plant-soil interactions that might not be evident in studies conducted in mature natural systems or agricultural systems. The study was designed to determine (1) how soil aggregation changes over time when soil continuously cropped with corn (i.e., in a disturbed or degraded condition) is restored to tallgrass prairie, and (2) whether any changes in soil aggregation are associated with above- and below-ground properties, carbon and nutrient pools, and other soil physical characteristics. For comparison with the restored prairie, both an uncultivated prairie remnant and a long-term ungrazed pasture dominated by introduced Eurasian pasture grasses were also sampled.

The purpose of the initial field study was to characterize the important relationships in this system so that later studies can be designed to address specific questions concerning plant-soil interactions. The relationships between changes in aggregation and changes in the plant community, as measured by above-ground production, are presented in this section.

A prairie restoration chronosequence from continuous corn through four restored prairie plots (in the 2nd, 5th, 8th, and 11th growing seasons since planting) and a virgin prairie remnant were sampled during 17-27 June, 1985. For comparison, an ungrazed pasture (dominated by C_3 Eurasian grasses) was also sampled. All plots were located on two closely related soil series with silt loam or silty clay loam textures. Except for the prairie remnant, all plots were located within Fermi National Accelerator Laboratory (FNAL), 48 km west of Chicago. The prairie remnant was located 6 km north of FNAL.

Live above-ground plant standing crop was clipped within ten, 0.5-m² circular quadrats in each of the sampled plots. After clipping, a 10-cm-deep soil core was removed from the center of the quadrat for aggregate analysis. Phytomass samples were sorted by plant species and dried at 65°C, and dry weights were recorded by species and then pooled into six vegetation categories to facilitate comparisons across the variously aged plots. Placement of species into categories was based on the likelihood that the species would occur in an undisturbed tallgrass prairie and its ability to invade disturbed sites. The size distribution of water-stable soil aggregates was determined for entire 10-cm-deep cores by using the wet-sieving method with atmospheric-pressure wetting of the soil.

The percentage of water-stable macroaggregates (aggregates > 0.2 mm in diameter) increased with time since cultivation and was lowest in continuous corn and highest in the prairie remnant (Fig. 3.7). Above-ground live standing crop of prairie graminoids (grasses plus grasslike species such as sedges and rushes) increased with time in the restored prairie. By the eleventh growing season, aggressive prairie forbs equaled, and prairie graminoids exceeded, those found in the prairie remnant; less-aggressive prairie forbs were still present in much lower quantities than in the prairie remnant. Weedy annual/biennial forbs remained relatively constant in all prairie plots. Total live above-ground standing crop decreased between the second and fifth growing seasons as annual/biennial forbs and annual grasses declined in dominance. After the fifth growing season, total standing crop increased with time since cultivation in the restored prairie, primarily as a result of the increase in prairie graminoids.

FIGURE 3.7 Relationship between water-stable soil aggregates > 0.2 mm diameter and time since the last cultivation. For each time, $n = 10$; some values are hidden. Regression was calculated by using data for continuous corn, restored prairie, and prairie remnant (remnant age assumed to be 100 growing seasons; $n = 60$); dotted lines indicate 95% confidence intervals.

The relationship between percentage macroaggregation and vegetation composition in the restored prairie and prairie remnant was investigated by using stepwise multiple regression analysis and partial correlation analysis. Stepwise regression indicated that the prairie graminoids were the most important predictor of the percentage of macroaggregates (Table 3.7). The below-ground portion of the plant directly affects aggregation; however, it is virtually impossible to identify the species of roots extracted from soil cores. Nevertheless, changes in the relative abundances of species as measured above ground should indicate similar changes below ground. When we used partial correlation analysis to factor out the effect of time since cultivation, none of the vegetation categories was significantly correlated with the percentage of macroaggregates. This suggests that time without disturbance may be an overriding factor in macroaggregate development and that the influence of vegetation types may be far less important.

Manipulative studies will be required to determine whether the relationship between prairie graminoids and aggregation is one of cause and effect. However, we did

TABLE 3.7 Stepwise multiple regression analyses of the relationships between above-ground biomass [$\log_{10}(X+1)$ transformed] for vegetation categories and percentages of aggregates > 0.2 and > 2 mm dia. (arcsine square root transformed) in restored prairie and prairie remnant (n = 49)

Regression Model	Value ^a	F ^a	Prob > F ^a	R ²
<u>Model for aggregates > 0.2 mm dia.</u>		24.13	0.0001	0.62
Intercept	61			
Prairie graminoids	4.54	21.34	0.0001	(0.53) ^b
Aggressive prairie forbs	2.16	5.22	0.0270	(0.58)
Weedy annual/biennial forbs	-2.34	3.92	0.0540	(0.62)
<u>Model for aggregates > 2 mm dia.</u>		14.37	0.0001	0.49
Intercept	29			
Prairie graminoids	6.76	42.63	0.0001	(0.41)
Weedy perennial forbs	2.01	3.41	0.0714	(0.45)
Less-aggressive prairie forbs	-2.15	3.36	0.0733	(0.49)

^aValues are for the best three-variable model; vegetation categories are listed by order of entry into model.

^bValues in parentheses indicate R² values when each corresponding vegetation category entered the model.

investigate the relationship between macroaggregation and prairie graminoids by comparing macroaggregation in the restored prairie to that in the ungrazed pasture dominated by nonprairie graminoids. Since the ungrazed pasture was in its fourteenth growing season and multiple-aged pastures were not available for sampling, only the oldest restored prairie was compared to the pasture. On the basis of Student's t test, the percentage of macroaggregates was greater in the oldest restored prairie than in the ungrazed pasture ($P = 0.0553$), even though the restored prairie had been cultivated more recently than the pasture. This suggests that native, warm-season C_4 grasses may confer some advantage over introduced, cool-season C_3 grasses in macroaggregate development for soils in the Prairie Peninsula. Although additional studies are necessary to further investigate this hypothesis, possible mechanisms underlying the observed differences may be tied (1) to differences between C_3 and C_4 grasses in production, rooting strategies, and/or the length and timing of the active growing season, or (2) to differences in physiological properties that may affect root exudates and thus microbial populations and degradation products.

3.3.4 Influences of Plants and Associated Mycorrhizal Fungi on Soil Aggregation in Restored Tallgrass Prairie

*J.D. Jastrow, R.M. Miller, and B.D. Cook**

For most soils, the presence of physical conditions conducive to vigorous plant growth and soil biotic activity depends upon the binding of soil particles into stable aggregates of various sizes. These aggregates provide a range of pore sizes for retention of plant-available water, transmission of water and air, root growth, and soil faunal habitat. Yet it appears that plants and their associated microflora play an intimate role in the binding process and subsequent development of water-stable aggregates. Recently, Tisdall and Oades (1982) proposed a hierarchical conceptual model for aggregation in soils where organic matter is the main binding agent. In their model, microaggregates (< 0.2 mm dia.) are held together by relatively permanent inorganic means and by persistent organic binding agents. Macroaggregates (> 0.2 mm dia.), however, are bound together largely by fine plant roots and fungal hyphae, particularly the hyphae of vesicular-arbuscular mycorrhizal (VAM) fungi. To gain a better understanding of the role of plant roots and VAM fungi in the formation of water-stable soil aggregates, we used a chronosequence of restored tallgrass prairie to provide a gradient of plant and soil development on previously cultivated soils.

The prairie restoration chronosequence described in section 3.3.3 served as the study site for the present investigation. The size distribution of water-stable soil aggregates was determined for entire 10-cm-deep cores by using the wet-sieving method with atmospheric-pressure wetting of the soil. Roots were separated from 10-cm cores by flotation and sieving, and divided into coarse (> 1 mm dia.) and fibrous (<1 mm dia.) roots. For fibrous roots, root lengths and VAM-colonized root lengths were determined by the gridline intersect method. Two size classes, fine (0.2-1.0 mm dia.) and very fine (< 0.2 mm dia.), were scored. Extramatrical hyphal lengths of VAM fungi were determined by a modification of the membrane filter technique. Hyphal lengths were estimated by line intersect at 160x. Hyphae were scored as mycorrhizal if they were aseptate and branched and had the typical "knobby" appearance of hyphae that are attached to colonized roots. Calculated estimates of root surface area were determined for fibrous roots from biomass and length data.

Recovery of water-stable macroaggregates (> 0.2 mm dia.) from continuous corn through the restoration sequence occurs rapidly. These changes take place without significant change in total organic carbon from the corn field to the oldest restored prairie. Yet, within five growing seasons, the percentage of macroaggregates in restored prairie approaches that of the prairie remnant, even though organic carbon in the restored prairie is less than half of the 9.9% found in the prairie remnant. Aggregate size fractions > 1 and > 2 mm in diameter also increased with time throughout the restoration sequence. However, the percentages of these size fractions were lower in the prairie remnant than in the oldest restored prairie. The remnant also had much lower external VAM hyphal lengths than the older restored prairie plots.

*Collaborator; affiliation is listed at the front of this chapter.

All measured root and VAM parameters (from the restored prairie and prairie remnant) were positively correlated with aggregates > 2 mm in diameter, but organic carbon was not correlated at all (Table 3.8). In contrast, organic carbon was highly correlated with aggregates 1-2 mm in diameter; root parameters were weakly associated, but VAM parameters did not correlate. For aggregates 0.2-1.0 mm in diameter, both root and VAM parameters were negatively correlated, and organic carbon was marginally associated. Most relationships remained relatively unchanged when partial correlations were used to factor out the effects of parameters other than the one being considered at the time.

The data in Table 3.8 support the hierarchical conceptual model of Tisdall and Oades (1982), although they suggest that the size fractions for which fine roots and VAM hyphae temporarily physically bind macroaggregates are larger than those proposed by Tisdall and Oades for Australian soils.

Comparison of the data for external VAM hyphal lengths in the corn-through-prairie-remnant chronosequence and the ungrazed pasture with the data of Tisdall and Oades (1980) for crop rotations with periodic cultivation indicated that similar hyphal lengths are associated with greater percentages of aggregates > 2 mm in diameter (Fig. 3.8). Interestingly, data from Tisdall and Oades' 30-yr pasture and virgin soil fall within the prairie regression model. Differences between the two regression models may reflect the effects of periodic cultivation, or may be associated with differences in microaggregate (< 0.2 mm dia.) structure and/or organic matter quality between the prairie (and Tisdall and Oades' undisturbed soils) and the cultivated Australian soils.

TABLE 3.8 Correlations between aggregate size fractions and measured root and mycorrhizal parameters and soil organic carbon (n = 50)

Variable	Aggregates > 2 mm dia.		Aggregates 1-2 mm dia.		Aggregates 0.2-1 mm dia.	
	r	Prob > r	r	Prob > r	r	Prob > r
Coarse root wt (> 1 mm)	0.57	0.0001	0.44	0.0013	-0.45	0.0010
Fibrous root wt (< 1 mm)	0.71	0.0001	0.37	0.0079	-0.61	0.0001
Fibrous root length (fine; 0.2-1.0 mm)	0.71	0.0001	0.27	0.0547	-0.61	0.0001
Fibrous root length (very fine; < 0.2 mm)	0.39	0.0051	0.38	0.0059	-0.31	0.0274
Fibrous root surface area	0.60	0.0001	0.36	0.0099	-0.52	0.0001
VAM-colonized fine fibrous root length	0.57	0.0001	0.08	0.5629	-0.53	0.0001
VAM-colonized very fine fibrous root length	0.30	0.0336	0.06	0.6564	-0.31	0.0260
External VAM hyphal length	0.57	0.0001	-0.14	0.3182	-0.60	0.0001
Organic carbon	-0.06	0.6547	0.70	0.0001	0.25	0.0841

FIGURE 3.8 Relationship between external hyphal length and aggregates > 2 mm in diameter for two systems. $\circ$ and closed squares = Tisdall and Oades (1980) virgin soil and 30-year pasture, respectively.

Restabilization of macroaggregates may occur more rapidly under C_4 prairie grasses than under introduced C_3 pasture grasses, because the pasture had significantly less macroaggregates than the oldest restored prairie even though the pasture had been undisturbed for three years more. A similar response to C_4 grain sorghum and C_3 winter wheat was reported by Skidmore et al. (1986). Fibrous root weight, fine fibrous root length, external VAM hyphal length, and organic carbon did not differ between the pasture and the oldest restored prairie; however, very fine fibrous root length was significantly greater in the pasture (Table 3.9). Yet, the percentage of macroaggregates > 0.2 mm dia. was lower in the pasture than the oldest restored prairie. Examination of the aggregate size fractions indicates that the major difference occurs in the 1-2 mm fraction, which is the size fraction most strongly associated with organic carbon. This suggests that the quantity and/or quality of root exudates rather than the physical entanglement by hyphae and roots may be responsible for the observed differences in aggregation dynamics in the C_3 and C_4 grassland systems.

In conclusion, the percentage of macroaggregates measured for even the continuous corn soil was relatively high in comparison to that of soils from other regions. This phenomenon and the relatively rapid recovery of macroaggregates during prairie restoration may both be associated with a resilient microaggregate structure resulting from the conditions under which these soils formed. Although these soils have

TABLE 3.9 Comparisons of selected root and mycorrhizal parameters, soil organic carbon, and aggregate size fractions for ungrazed pasture (in its 14th growing season) and the oldest restored prairie (in its 11th growing season)

Variable	Ungrazed Pasture	Oldest Restored Prairie	t test Prob > t
Fibrous root wt ($\text{g m}^{-2} \times 10 \text{ cm}$)	669.6	601.0	0.4104
Fine fibrous root length ($\text{km m}^{-2} \times 10 \text{ cm}$)	21.9	24.9	0.4925
Very fine fibrous root length ($\text{km m}^{-2} \times 10 \text{ cm}$)	147.7	48.9	0.0001
External VAM hyphal length (m cm^{-3})	15.4	15.7	0.8528
Organic carbon (%)	4.3	4.5	0.4557
Aggregates > 2 mm dia. (%)	53.0	52.8	0.9498
Aggregates 1-2 mm dia. (%)	17.3	20.6	0.0661
Aggregates 0.2-1 mm dia. (%)	17.4	18.1	0.6674

been cultivated on and off for more than 100 years, macroaggregate structure can develop rapidly when cultivation ceases. Roots, VAM hyphae, and organic materials all appear to play a role in the development of this structure. Further, the role of native C_5 grasses in the formation and stabilization of both macro- and microaggregate structure in prairie soils needs further investigation. Such study could provide insight into how these productive soils were formed and how to better preserve and manage them.

3.3.5 Below-Ground System Development of Vesicular-Arbuscular Mycorrhiza in a Restored Tallgrass Prairie Community

B.D. Cook, J.D. Jastrow, R.M. Miller, and A.-C. McGraw*

The method typically used to quantify mycorrhizae under a field setting is measurement of the percent of roots colonized by the mycorrhizal fungus. Only within recent years have researchers begun to determine the total root length and length colonized by using the gridline intersect method (e.g., Giovannetti and Mosse 1980), though the majority of researchers do not collect samples in a manner that allows quantification of total root length on a soil volume basis. This study was conducted to determine the relationship between root and vesicular-arbuscular mycorrhizal (VAM) fungus development in a tallgrass prairie restoration chronosequence. Emphasis was placed on characterizing the relationship between root length, colonized root length, and percentage of root length occupied by the VAM fungus for differing root size classes.

*Collaborator; affiliation is listed at the front of this chapter.

Mycorrhizal fungus composition and populations along the restoration chronosequence were also determined. The study site was described in section 3.3.3.

Live, above-ground standing crop was clipped and separated by species from ten, 0.5-m^2 quadrats in each of four restored prairie plots and the virgin prairie remnant sampled from 17 to 27 June 1985. Two 20-cm-deep soil cores were removed from each quadrat, and coarse roots (roots > 1.0 mm dia.) and fibrous roots (roots < 1.0 mm dia.) were separated from the soil. Subsamples of fibrous roots were stained with Trypan blue-lactic acid and assessed for root length and length colonized by VAM fungi by using the gridline intersect method. Differentiation between fine fibrous root length (0.2-1.0 mm dia.) and very fine fibrous root length (< 0.2 mm dia.) and colonization were determined.

Spores were quantified and identified to the species level by wet-sieving and sucrose gradient procedures with a 50-g dry weight soil sample. Spore biomass values (mg m^{-2} dry weight) were calculated from mean spore diameter values.

Length of fibrous roots to a depth of 20 cm increased with time, whereas maximum fibrous root length colonized by the VAM fungus appears to have reached steady state by the fifth growing season (Fig. 3.9). This suggests that the amount of root occupied by the VAM fungus is independent of increasing root length.

The percentage of fibrous root length colonized by VAM fungi increased initially and peaked after the fifth growing season. The subsequent decline in colonization reflects an increase in fibrous root length with essentially constant colonized fibrous root length. This emphasizes the importance of presenting data for both root length and colonized root length for characterization of the below-ground system. Because the percentage of root colonized by the mycorrhizal fungus is dependent upon root length, it is essential, for field-collected samples, to determine the total length of root on a soil volume basis. Otherwise misinterpretation of the significance of colonization could easily occur. For example, one could infer from the root colonization data alone that the amount of VAM fungus within the system was decreasing with time. What appears to occur, however, is that steady-state conditions become established.

Very fine fibrous root length increased with time, whereas the fine fibrous root length remained relatively constant. Length of root colonized by the VAM fungus was greatest for very fine fibrous roots, yet percent root colonized was highest for fine fibrous roots. These trends may reflect morphological differences in the rooting systems of the individual species within the chronosequence. There appear to be positively correlated trends over time between the relative above-ground biomass of perennial *Compositae* spp. and percent root colonized, *Sorghastrum nutans* and root length colonized by the mycorrhizal fungus, and *Andropogon gerardii* and fibrous root length.

A qualitative assessment of fungal structures indicated that a greater proportion of roots obtained from plots in the second, fifth, and eighth growing seasons possessed more internal mycelia and arbuscules than did roots from the plot in its eleventh growing season or the virgin site. (The presence of arbuscules indicates the active phase of the mycorrhizal fungus.)

FIGURE 3.9 Mean fibrous root length, fibrous root length colonized by VAM fungi, and percentage of fibrous root colonized for the prairie restoration chronosequence and prairie remnant ($n = 10$; error bars represent standard errors).

Surprisingly, spore numbers and biomass levels were relatively constant across the chronosequence except for a peak at the fifth growing season and a low for the virgin prairie. No particular trend was evident for VAM fungus species composition across the gradient. *Acaulospora laevis*, *Gigaspora gigantea*, *Glomus constrictum*, *G. etunicatum*, *G. macrocarpum*, *G. microcarpum*, and several unidentified isolates were encountered across the chronosequence. *Glomus tenuis* was also encountered in roots of plants from the younger plots. *Rhizoctonia*-like microflora was characteristically encountered in roots obtained from the older plots.

3.4 HYDROLOGY AND GEOCHEMISTRY OF SURFACE COAL MINE LAKES

3.4.1 Summary

J.P. Schubert

Tens of thousands of lakes have been created in the United States on land that has been surface-mined for coal. These lakes form in surface depressions in spoil materials or in the final pits when mining operations have ceased. Most existing lakes

have water of relatively good quality and provide valuable postmining land-use benefits such as swimming, fishing, boating, and wildlife habitat. Mine lakes have even been used as water sources for irrigation, stock watering, and human consumption. However, the water in the lakes can sometimes be extremely acidic because of the oxidation and dissolution of pyritic minespoil materials. Water pH can be less than 3.0, and high concentrations of dissolved metals (particularly iron, manganese, aluminum, and zinc) and sulfate are often present.

This research program is aimed at identifying those geologic, hydrologic, geochemical, mining, or reclamation factors or processes that are primarily responsible for the existence and long-term persistence of acidic lakes. This work began in January 1986 and is funded by the U.S. Office of Surface Mining.

3.4.2 Evaluation of Existing Data

J.P. Schubert

Published and unpublished data were obtained from the U.S. Geological Survey, state agencies, coal companies, consulting companies, and university sources. On the basis of inventories of water quality data in older (pre-1975) mine lakes, over 90% of the lakes sampled in Indiana, Illinois, and Oklahoma had pH values greater than 6.0. However, 40% of the lakes previously sampled in Kansas ($n = 42$) had pH values less than 6.0 (Fig. 3.10). The higher frequency of low-pH lakes found in Kansas may be due to sampling bias (perhaps the investigators intentionally sought acidic lakes); other information and opinions indicate that a much lower percentage of acidic lakes actually exist in Kansas. Most lakes in Indiana have specific conductance values of less than 1000 $\mu\text{S}/\text{cm}$, whereas most of the lakes previously measured in Illinois had values greater than 2000 $\mu\text{S}/\text{cm}$. The pH and specific conductance data indicate that differences of water quality of mine lakes exist between states. We had hoped that poor water quality could be generally associated with specific regions (e.g., counties) or coal seams that were mined. Presumably, geochemical factors such as high pyrite content in the overburden would be limited to specific regions or stratigraphic units. However, when the data for each state were plotted and contoured by using the SURFACE II program (Sampson 1975), no clear spatial trends of water quality were apparent within each state.

Correlation analyses between water quality variables (pH, specific conductance) and lake morphometric variables (length, width, maximum depth) showed that specific conductance is positively correlated ($P < 0.05$) with length ($r = 0.27$) and depth ($r = 0.42$) of mine lakes in Illinois. However, no significant correlations exist for the Indiana lakes. Therefore, it is unclear whether lake morphometric variables have any influence on water quality.

FIGURE 3.10 Histograms of lake pH values determined during past lake surveys. Sources of data: Bobo, 1979; Voelker, 1985; Pope and Diaz, 1982.

3.4.3 Investigation of Twenty-One Lake Sites in the Eastern U.S.

J.P. Schubert

The qualitative information and data from previous coal mine studies indicated that a wide range of factors significantly affect water chemistry in mine lakes. Examples include (1) the geochemistry of spoil materials (e.g., pyrite content, carbonate mineral content, base saturation of clay minerals), (2) the physical characteristics of spoil materials (e.g., texture, spatial distribution, compaction, thickness, and areal extent of each spoil type), (3) the hydraulic characteristics of spoil materials and soil cover (e.g., hydraulic conductivity, porosity, infiltration rates), and (4) the watershed characteristics (e.g., large vs. small watersheds, topography, lake in high or low topographic position).

The second phase of this research includes a study, in moderate detail, of 21 lakes in the eastern U.S.; the pH values of these lakes range from very acidic (pH = 2.55) to alkaline (pH = 8.10). Each lake was visited once between February and May 1987. Activities at each site included (1) collection of soil and spoil samples from auger holes, (2) collection of water and bed sediments from the lake, (3) single-ring infiltration tests

on the soils and pumping tests of the auger holes, (4) measurement of surface slopes and shape characteristics of the watershed, and (5) determination of the morphometric characteristics of the lake. The water, soil, spoil, and lakebed sediment samples are currently being analyzed for a large number of physical and chemical parameters. When all laboratory analyses are completed, multivariate statistical analyses of the data will be conducted to identify which of the physical, geochemical, hydrologic, or reclamation factors have the greatest influence on lake water chemistry. These statistical relationships will be used to construct predictive models that can be used to estimate water quality of a lake prior to construction.

3.4.4 Detailed Studies at Goose Lake Mine Site, Illinois

J.P. Schubert

An intensive investigation is currently being conducted at a reclaimed surface coal mine in Grundy County, Illinois. The mined area was graded and successfully revegetated in the 1970s. However, five small, very acidic lakes still persist despite past attempts to neutralize two of the lakes. Water infiltrating into the spoils and flowing into the lakes via shallow groundwater pathways is the principal mechanism of continued acidity production and transport. Over 50 piezometers have been installed at the site over the past ten years in an effort to determine hydraulic properties, hydraulic gradients (Fig. 3.11), and geochemical properties of the spoil materials.

Recently, our efforts have focused on rainstorm events, infiltration, and short-term fluctuations in the water table as contributing factors to persistent acidity. Infiltrating water reaches a low pH as it passes through the upper 50 cm of spoil materials, but the high concentrations of acidity and dissolved metals are not attained until the water has passed further down into the spoil profile. Rapid fluctuations of water levels in the lakes and the piezometers indicate a good hydraulic connection between the lakes and the spoil materials and rapid transfer of water between the two during storm events. Efforts are now being made to calculate the rapid fluxes of water and solutes occurring during storm events and to simulate the groundwater-lake hydrologic system by using finite-difference numerical modeling.

3.5 NATIONAL CROP LOSS ASSESSMENT NETWORK

3.5.1 Summary

P.M. Irving

The National Crop Loss Assessment Network (NCLAN) was established by the U.S. Environmental Protection Agency in 1980 to investigate the impacts of ozone (O_3), sulfur dioxide (SO_2), and nitrogen dioxide (NO_2) on the yield of important agricultural crops. Most research has been limited to effects of O_3 , although some work on interactions of $O_3 + SO_2$ and $SO_2 + NO_2$ has been accomplished with additional assistance from the Electric Power Research Institute. Argonne National Laboratory has

FIGURE 3.11 Potentiometric surface of shallow ground-water at Goose Lake mine site, Grundy County, IL. (Contour lines are in meters above an arbitrary local datum.)

been responsible for the research in the Central States Region of the United States and has investigated the impacts of O_3 , SO_2 , NO_2 , or their combinations on field corn, soybeans, winter wheat, grain sorghum, and alfalfa.

1986 marked the final year of field studies within the NCLAN program; work performed at Argonne is summarized below. Data from the research accomplished at Argonne and the other NCLAN sites will be used in national assessment activities to advise policymakers on issues such as air quality standards.

3.5.2 Studies on the Interaction of Ozone with Drought Stress or with Sulfur Dioxide on Soybeans and Corn

P.M. Irving, L.W. Kress, W. Prepejchal, and H.J. Smith

Crop plants growing in a typical field situation are exposed to multiple stresses during the growing season. Ozone is one of those stresses in many areas of the United

States. To evaluate potential interactions of O_3 with other stresses, we conducted dose-response field investigations of corn exposed to O_3 and drought stress, and of soybeans exposed to O_3 and SO_2 . Responses measured included physiological and biochemical parameters as well as harvested yield.

The results from our research on two important crop plants indicate that measures of physiological and biochemical parameters can be essential aids in furthering understanding of the impacts of air pollutants and other stresses. These measurements can be used to explain the influence of exposure dynamics (e.g., sequence and magnitude of stress in relation to growth stage), because they may reflect a more immediate response to stress as opposed to the integrated response apparent in growth and yield measurements. These measurements may also point to possible mechanisms that explain growth and yield response to stress.

Our measurements of certain physiological and biochemical responses support the yield responses of field corn exposed to O_3 and SO_2 . We observed an early stimulation and later reduction of chlorophyll by O_3 , which indicates a more rapid senescence (or aging) of leaves as a result of O_3 exposure -- a response frequently noted. Our results indicate that the highest SO_2 dose used in our study predisposed corn plants to chlorophyll degradation from O_3 exposure. The SO_2 effect on chlorophyll did not appear to result in effects on photosynthetic rates. In contrast, the effects of O_3 on chlorophyll in late August were highly correlated with effects on photosynthesis and yield. The measurements made in late August suggest that field corn yield is reduced by O_3 through an effect on photosynthetic processes during the reproductive stage, resulting in decreased amounts of carbohydrates available for translocation to the developing kernel. This observation is in agreement with results for winter wheat and for soybeans reported by other NCLAN investigators. Any stress to the corn plants from the SO_2 exposure appeared to be minor and was not reflected in significant yield impacts (Fig. 3.12). In contrast, the O_3 exposures significantly reduced the grain yield of corn, although the difference in yield between plants in charcoal-filtered air (0.016 ppm O_3 , 12-hr mean) and ambient O_3 (0.042 ppm, 12-hr mean) was small (1.5%, Fig. 3.12). These results for field corn exposed to O_3 were similar to those reported previously by our group.

Our studies with soybeans indicate that the damaging effects of O_3 on crop yield may be reduced or negated when the plants are subjected to a severe drought stress during the late reproductive stage (pod-fill). In fact, at 12-hr average O_3 levels > 0.073 ppm, there were no differences in seed yield between drought-stressed and well-watered soybean plants, even though yield in charcoal-filtered air (0.014 ppm O_3) in the dry plots was 32 percent lower than in the wet plots (Fig. 3.13). Soybean root biomass in the dry plots, however, was affected to a greater degree by the O_3 exposure than in the wet plots (Fig. 3.14).

Damage to the leaf from O_3 results in a greater demand, and greater sink, for carbohydrates for repair functions. The occasional stimulation of photosynthetic rates by O_3 exposure observed in this study early in the growing season supports this concept. The greater demand for carbon compounds in the leaf reduces allocation to the root; thus the O_3 impact on root biomass is large. Furthermore, the photosynthesis data from both the corn and soybean experiments indicate that O_3 damage to the C-fixing process in

FIGURE 3.12 Grain yield of field corn as a function of daily O_3 and intermittent SO_2 exposure. Two standard errors are indicated for the mean response of the three SO_2 levels.

leaves is cumulative, with negative impacts observed later in the growing season when total O_3 dose is higher than at earlier growth stages. The O_3 -caused reduction in photosynthetic rates during grain and pod production undoubtedly contributed to the observed reductions in yield.

Soybean yield loss from O_3 in the well-watered plots in this study is similar to that observed in previous experiments. The results from these two studies indicate that when soil moisture is adequate, soybean yields are affected by ambient levels of O_3 to a much greater degree than are field corn yields (15.6% vs. 1.5%). Our data suggest that O_3 response functions may be improved by incorporating a factor that describes plant moisture status.

We conclude that at ambient exposure levels, SO_2 has little or no influence on the yield response of corn to O_3 , but that drought plays a major role in reducing the damaging effects of O_3 on soybean yield.

FIGURE 3.13 Seed mass of soybeans in irrigated (wet) and non-irrigated (dry) plots as a function of O_3 concentration. Two standard errors of the mean are indicated.

3.6 ACCELERATOR MASS SPECTROMETRY PROGRAM

3.6.1 Summary

D. Elmore

In early 1986, the Environmental Research Division began an initiative to establish a National Accelerator Mass Spectrometry (AMS) Facility at Argonne. The installation would use the FN tandem accelerator that presently serves as the injector for the Argonne Tandem Linear Accelerator System (ATLAS). The principal applications of the facility would be for research in the geosciences in which the long-lived radioisotopes ^{10}Be , ^{14}C , ^{26}Al , ^{36}Cl , and ^{129}I would be measured in small, natural samples provided by university, government, and industry-based scientists. Emphasis would be placed on the heavier isotopes such as ^{36}Cl and ^{129}I , which cannot presently be measured at cosmogenic levels by Tandetrans. However, the time ultimately allocated to the measurement of each isotope would depend on the needs of the research community. The latest instruments and techniques developed over the past ten years at several laboratories around the world would be incorporated in order to achieve the best possible precision, sensitivity, and sample measurement capacity. Sample preparation

FIGURE 3.14 Root mass to a depth of 20 cm for soybeans in irrigated (wet) and non-irrigated (dry) plots as a function of O₃ concentration. Two standard errors of the mean are indicated.

capability would be available for each of the radioisotopes. The schedule for Phase I of the project calls for the first measurements in 1989 and the completion of the computer automation system in 1990. In Phase II of the project, starting in 1991, the tandem will be upgraded with new acceleration tubes and a gas stripper; this will allow improved transmission for ¹⁰Be and ¹²⁹I, lower interference, and increased reliability. The project is envisioned as a cooperative effort between the U.S. Department of Energy and the National Science Foundation (NSF).

3.6.2 The Need for a National Accelerator Mass Spectrometry Facility

D. Elmore

It is now ten years since the first AMS measurements were reported, and we are beginning to see the magnitude of the impact on earth sciences. The number of samples requiring analysis is increasing at a rapid pace, and it is clear that the capacity in the United States is not adequate. There are four active facilities in the United States that are shared with basic nuclear physics (University of Pennsylvania, University of Rochester, University of Washington, and Argonne National Laboratory), and one dedicated radiocarbon facility (University of Arizona). The capacity of the shared

facilities is not high because beam time is limited and much of the available time and effort is used for development of new analytical methods.

In spite of the facts that almost all accelerators used by AMS worldwide were built in the United States and that most of the early development of the method was carried out here, we are falling behind the other countries in application of the method. Only one AMS facility exists in the United States while there are accelerators dedicated to AMS in Canada, England, France, Japan, New Zealand, and Switzerland. In addition, another 12 shared facilities are outside the United States.

Participants at a workshop held in March 1985 (AMS, 1985) concluded that to regain the leadership role, the Arizona Tandetron facility should be upgraded to obtain greater capacity, and support should be increased for the shared facilities. Furthermore, a dedicated national facility is needed. This facility should be based on a larger accelerator capable of the full range of technique development as well as dedicated analysis time. Since that workshop, the NSF Division of Ocean Sciences has shown interest in funding an additional AMS facility dedicated to oceanographic measurements, principally for radiocarbon.

The proposed Argonne facility is shown in Fig. 3.15. Buildup of the AMS facility has been split into Phase I (three years) and Phase II (two years). The first year of Phase I will be devoted primarily to hiring, design, and procurement. Capability for measuring AMS samples starts in mid-1989, and the AMS facility reaches full capacity in 1991. The primary objective for Phase II is to upgrade the tandem to include the installation of a Pelletron charging system, new accelerator tubes, and terminal pumping.

Because the proposed facility will be a national facility dedicated to AMS, new components will be designed and built, without compromise, so as to meet the requirements for high precision, sensitivity, and capacity. Consultants will be retained from the top AMS laboratories around the world to help incorporate the latest designs developed over the past decade.

A detailed discussion of the applications of AMS measurements in environmental, biological, and material sciences research has recently been published (Elmore 1987). There is little doubt that the technique holds great promise for advancing understanding of processes where rare elements and long-lived radionuclides (at extremely low concentrations) can serve as tracers of those processes. Exploitation of this potential will depend upon the availability of facilities such as the one proposed for Argonne.

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FIGURE 3.15 Layout of proposed AMS facility. The negative ion injector is shown as located in 1991. The gas stripper will not be available until the upgrade in 1991.

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APPENDICES FOR CHAPTER 3
Environmental Effects Research Program

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APPENDIX 3-A. STAFF QUALIFICATIONS

Environmental Effects Research Program

Name	Position	Highest Degree	Major	Year Received	Institution
Beasley, Thomas M.	Acting Program Manager	Ph.D.	Oceanography	1968	Oregon State University
Findlay, Melvin W.*	Assistant Soil Scientist	M.S.	Soil Science	1985	Northwestern University
Irving, Patricia M.	Ecologist	Ph.D.	Botany	1979	University of Wisconsin
Jastrow, Julie D.	Environmental Scientist	M.S.	Agronomy	1979	University of Illinois
Kress, Lance W.*	Ecologist	Ph.D.	Plant Pathology	1978	Virginia Polytechnic Institute and State University
Miller, R. Michael	Ecologist	Ph.D.	Botany and Microbiology	1975	Illinois State University
Orlandini, Kenneth A.	Scientific Associate	B.S.	Chemistry	1957	University of Illinois
Penrose, William R.	Biochemist	Ph.D.	Biological Chemistry	1969	University of Michigan
Prepejchal, William*	Scientific Assistant	B.S.	Electrical Engineering	1972	Illinois Institute of Technology
Schubert, Jeffrey P.	Hydrogeologist	M.S.	Geology	1978	The Pennsylvania State University
Smith, Harry J.*	Scientific Assistant	M.S.	Plant Pathology	1976	The Pennsylvania State University

*No longer a member of the Division.

APPENDIX 3-B. OUTSTANDING PROFESSIONAL ACTIVITIES AND AWARDS**Environmental Effects Research Program**

- T.M. BEASLEY--Member, Editorial Board, Journal of Environmental Radioactivity, 1986-present.
- T.M. BEASLEY--Member, Executive Committee, Global Environmental Research Council, U.S. Department of Energy, 1987.
- M.W. FINDLAY, JR.--Co-recipient of the Federal Laboratory Consortium 1987 Special Award for Excellence in Technology Transfer, May 1987.
- R.M. MILLER--Co-recipient of an Argonne National Laboratory Pace Setter Award, November 1986.
- R.M. MILLER--Member, Editorial Board, Restoration and Management, 1985-1989.
- R.M. MILLER--Public Awareness Representative to the American Institute of Biological Sciences for the Mycological Society of America, 1986-1990.
- W.R. PENROSE--Co-recipient of the Federal Laboratory Consortium 1987 Special Award for Excellence in Technology Transfer, May 1987.
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APPENDIX 3-C. SPECIAL EVENTS ORGANIZED

Environmental Effects Research Program

Beasley, T.M. Organized a workshop to develop a plan for a Department of Energy global environmental research program, 8-12 June 1987, Argonne National Laboratory, Argonne, IL.

Elmore, D. Co-organized the Fourth International Symposium on Accelerator Mass Spectrometry, 27-30 April 1987, Niagara-on-the-Lake, Ontario, Canada.

Miller, R.M. Co-organized the workshop Using Mycorrhizae in Plant Research, 9 June 1986, University of Rhode Island, Kingston, RI.

APPENDIX 3-D. EDUCATIONAL PROGRAM PARTICIPANTS**Environmental Effects Research Program**

- C.J. ALDERINK. Henderson State University. Undergraduate Research Program. Conducted research on the hydrology and geochemistry of surface coal mine lakes. June - August 1987.
- C. ANTHONY. North Central College. Undergraduate Research Program. Conducted research on nutrient distribution in prairie soils. January - April 1986.
- J.R. BERNHARDT. Illinois Institute of Technology. Undergraduate Research Program. Conducted research on the hydrology and geochemistry of surface coal mine lakes. June - August 1987.
- T. CHOI. York High School. Post-High School Research Program. Conducted research on soil respiration in tallgrass prairie. June - August 1987.
- B.D. COOK. Huntington College. Undergraduate Research Program. Conducted research on roots and mycorrhizal fungi in a prairie chronosequence. January - September 1986.
- V. COVAS. North Central College. Undergraduate Research Program. Conducted research on nutrient allocation in stressed plants. January - April 1986.
- E. DRINGMAN. Carroll College. Undergraduate Research Program. Conducted research on tin levels in the aquatic environment. September - December 1986.
- G. DUHL. Highland Park High School. Post-High School Research Program. Conducted research on development of a soil moisture model. June - August 1987.
- D.L. DUNN. Clemson University. Thesis Parts Participation Program. Tested a technique for isolating cadmium from large samples of natural water by using Cd-109 tracer. August 1986.
- L.A. DURHAM. Purdue University. Graduate Research Program. Conducted research on hydrology and geochemistry of surface coal mine lakes. January - August 1987.
- D. EATON. The Fort Valley State College. Summer Faculty Research Program. Evaluated the physiological effects of ozone and drought stress on soybeans. June - September 1986.
- S.L. EGGERT. University of Wisconsin. Undergraduate Research Program. Conducted research in aquatic radiochemistry. August 1987 - present.
- R. FRANSON. University of Chicago. Dissertation Research. Conducted research on below-ground interactions in plants. Finalized December 1986.
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- D. FRISON. Mississippi Valley State University. Undergraduate Research Program. Studied the effects of ozone and drought stress on chlorophyll concentration in field-grown soybean plants. June - August, 1986.
- E.L. FUGE. University of Minnesota. Thesis Parts Program. Studied the role of mycorrhizae in toxic soil. March 1986.
- G.S. GHUMAN. Savannah State College. Faculty Research Program. Conducted studies involving mycorrhizae and trace metal acquisition. July - September 1986.
- D.M. GLOVER. Wartburg College. Undergraduate Research Program. Conducted research in aquatic radiochemistry. June - August 1987.
- T. HABEGGER. University of Illinois. Undergraduate Research Program. Conducted research on the effects of mycorrhizae on phosphorus uptake. June - August 1986.
- L.G. HANSHAW. Alcorn State University. Faculty Research Program. Conducted research on the evaluation of the physiological effects of ozone and drought stress on soybeans. July - September 1986.
- T.A. HARRIS. Lindenwood College. Undergraduate Research Program. Conducted research on the hydrology and geochemistry of surface coal mine lakes. June - August 1987.
- D.W. HOLT. University of Kentucky. Graduate Research Program. Conducted research on the hydrology and geochemistry of surface coal mine lakes. January - November 1987.
- F.J. JANZEN. Colorado State University. Thesis Parts Program. Conducted research on the influence of water and temperature on carbohydrates, proteins, and fatty acids in embryonic and hatching snapping turtles. January 1986.
- R. KLAPER. Wheaton North High School. ARCO High School Teachers' Program. Conducted research on below-ground interactions in a prairie chronosequence. June - August 1987.
- R. MEIER. University of Minnesota. Thesis Parts Program. Conducted research on mycorrhizal analysis such as the determination of percent infection in a root, isolation and identification of fungal spores, and methods of staining fungal structures. March 1986.
- S. NELSON. Mississippi Valley State University. Undergraduate Research Program. Conducted research on the effects of mycorrhizal fungi on root anatomy. June - September 1987.
- J. PILLAI. Hirsch High School. ARCO High School Teachers' Program. Conducted research on the determination of mycorrhizal fungus hyphae in desert soils. June - September 1986.
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- D. RAMITO. University of Illinois. Undergraduate Research Program. Conducted research on root hair distribution in a prairie grass. June - August 1986.
- M. RATHOUZ. Boston University. Undergraduate Research Program. Conducted research on mycorrhizal fungus hyphae extraction from soils. June - August 1986.
- C.B. RENZULLI. University of Chicago. Graduate Research Program. Conducted research on USE leaf-area analyzer. December 1985 - May 1986.
- C.R. REYNOLDS. Northern Arizona University. Graduate Research Program. Conducted research on the hydrology and geochemistry of surface coal mine lakes. January - August 1987.
- R.L. RYBKA. University of Akron. Undergraduate Research Program. Conducted research to identify the factors and processes that control water quality in lakes on strip-mined lands. January - April 1986.
- K. SKUBAL. Lockport High School. Post-High School Research Program. Conducted research on aggregation in prairie soils. June - August 1987.
- T.P. SRIHARAN. Selma University. Faculty Research Program. Conducted research to evaluate the physiological effects of ozone and drought stress on soybeans. July - August 1986.
- K.D. STRONG. Andrews University. Undergraduate Research Program. Conducted research on trace metal acquisition by mycorrhizal fungi. September - December 1986.
- G.A. SZUMLAS. Iowa State University. Undergraduate Research Program. Conducted research in aquatic radiochemistry. May - August 1986.
- G.T. TISUE. Clemson University. Faculty Research Program. Conducted research in aquatic trace metal chemistry. June - August, 1986; June - August, 1987.
- K. VON DER HEIDE. Northern Illinois University. Undergraduate Research Program. Conducted research on mycorrhizal fungus hyphae extraction from heavy soils. January - June 1987.
- D.B. WALTON. University of Chicago. Thesis Parts Program. Conducted field research on the ecology of a small butterfly species, the Pearl Crescent (*Phyciodes tharos*). September 1985 - September 1986.
- C.M. WICKS. University of Virginia. Graduate Research Program. Conducted research on the hydrology and geochemistry of surface coal mine lakes. January - May 1987.
- S.A. WILLIS. Bridgewater State College. Undergraduate Research Program. Conducted research on the engineering feasibility and the geological, hydrological, and ecological considerations of placing low-level radioactive wastes in underground mined cavities. January - April 1986.

E.P. ZOVINKA. Roanoke College. Undergraduate Research Program. Conducted research on the effect of ozone and drought stress on physiological processes in field-grown soybean plants. June - August, 1986.

T. WU. Institute for Radiation Protection, People's Republic of China. IAEA Fellow. Conducted research in aquatic radiochemistry. December 1986 - July 1987.

APPENDIX 3-E. PUBLICATIONS AND ORAL PRESENTATIONS

Environmental Effects Research Program

1. Refereed Journal Articles*

Carpenter, R., T.M. Beasley, D. Zahnle, and B.L.K. Somayajulu. Cycling of fallout (Pu, ^{241}Am , ^{137}Cs) and natural (U, Th, ^{210}Pb) radionuclides in Washington continental slope sediments. *Geochimica et Cosmochimica Acta* 51:1897-1921 (1987). [DOE/OHER]**

Elmore, D., and F.M. Phillips. Accelerator mass spectrometry for measurement of long-lived radioisotopes. *Science* 236:543-550 (1987). [DOE/NSF]

Elmore, D., N.J. Conard, P.W. Kubik, H.E. Gove, M. Wahlen, J. Beer, and M. Suter. ^{36}Cl and ^{10}Be profiles in Greenland ice: Dating and production rate variations. *Nuclear Instruments and Methods B29*:207-210 (1987). [DOE/NSF]

Fabryka-Martin, J., S.N. Davis, and D. Elmore. Applications of ^{129}I and ^{36}Cl in hydrology. *Nuclear Instruments and Methods B29*:361-371 (1987). [NSF/DOE]

Fehn, U., S. Tullai, R.T.D. Teng, D. Elmore, and P.W. Kubik. Determination of ^{129}I in heavy residues of two crude oils. *Nuclear Instruments and Methods B29*:380-382 (1987). [Texaco Corp./NSF/DOE]

Huh, C.A., and T.M. Beasley. Profiles of dissolved and particulate thorium isotopes in the water column of coastal southern California. *Earth and Planetary Science Letters* 85:1-10 (1987). [NSF/DOE]

Irving, P.M. Gaseous pollutant and acidic rain impacts on crops in the United States: A comparison. *Environmental Technology Letters* 8:451-458 (1987). [DOE/ER]

Kress, L.W., J.E. Miller, and H.J. Smith. Impacts of ozone and sulphur dioxide on soybean yield. *Environmental Pollution (Series A)* 41:105-123 (1986). [EPA]

Kubik, P.W., D. Elmore, U. Fehn, and F.M. Phillips. Accelerator mass spectrometry of ^{36}Cl , ^{129}I , and ^{187}Os . *Nuclear Instruments and Methods B24*:676-681 (1987). [NSF/DOE]

*For published material, the names of all Environmental Research Division authors are underlined. (Included are Division members who participated in a project but left the Division before the results were published.)

**Funding agency (abbreviations are spelled out at the end of this appendix).

Kubik, P.W., D. Elmore, T.K. Hemmick, H.E. Gove, U. Fehn, R.T.D. Teng, S. Jiang, and S. Tullai. Accelerator mass spectrometry at the University of Rochester. Nuclear Instruments and Methods B29:138-142 (1987). [NSF/DOE]

Leavy, B.D., F.M. Phillips, D. Elmore, P.W. Kubik, and E. Gladney. Measurement of cosmogenic $^{36}\text{Cl}/\text{Cl}$ in young volcanic rocks: An application of accelerator mass spectrometry in geochronology. Nuclear Instruments and Methods B29:246-250 (1987). [NSF/DOE]

McGraw, A.-C., and J.W. Hendrix. The influence of soil fumigation and source of strawberry plants in population densities of spores and viable propagules of endogonaceous mycorrhizal fungi. Plant and Soil 94:425-434 (1986). [DOE/OHER]

Miller, R.M., A.G. Jarstfer, and J.K. Pillai. Biomass allocation in an *Agropyron smithii* *glomus* symbiosis. American Journal of Botany 74:114-122 (1987). [DOE/OHER]

Norris, A.E., K. Wolfsberg, S.K. Gifford, H.W. Bentley, and D. Elmore. Infiltration at Yucca Mountain, Nevada traced by ^{36}Cl . Nuclear Instruments and Methods B29:376-379 (1987). [DOE/NSF]

Orlandini, K.A., W.R. Penrose, and D.M. Nelson. Pu(V) as the stable form of oxidized plutonium in natural waters. Marine Chemistry 18:49-57 (1986). [DOE/OHER]

Penrose, W.R., D.N. Metta, J.M. Hylko, and L.A. Rinckel. The reduction of of plutonium (V) by aquatic sediments. Journal of Environmental Radioactivity 5:169-184 (1987). [DOE/OHER]

Purdy, C.B., A.C. Mignerey, G.R. Helz, D.D. Drummond, P.W. Kubik, D. Elmore, and T.K. Hemmick. ^{36}Cl : A tracer in groundwater in the Aquia formation of southern Maryland. Nuclear Instruments and Methods B29:372-375 (1987) [Camille and Henry Dreyfus Foundation/NSF/DOE]

Teng R.T.D., U. Fehn, D. Elmore, T.K. Hemmick, P.W. Kubik, and H.E. Gove. Determination of Os isotope and Re/Os ratios using AMS. Nuclear Instruments and Methods B29:281-285 (1987). [NSF/DOE]

2. Books, Book Chapters, and Collections of Conference Proceedings

Alberts, J.J., J.W. Bowling, and K.A. Orlandini. The effect of seasonal anoxia on the distribution of ^{238}Pu , $^{239,240}\text{Pu}$, ^{241}Am , ^{244}Cm , and ^{137}Cs in pond systems of the southeastern United States. In: Environmental Research on Actinide Elements. J.E. Pinder, III, J.J. Alberts, K.W. McLeod, and R.G. Schreckhise (eds.). CONF-841142 (DE86008713). National Technical Information Service, Springfield, VA. 1987. pp. 371-390. [DOE/OHER]

Beasley, T.M. Transuranic radionuclides in the Columbia River: Sources, inventories, and geochemical behavior. In: Environmental Research on Actinide Elements. J.E. Pinder, III, J.J. Alberts, K.W. McLeod, and R.G. Schreckhise (eds.). CONF-841142 (DE86008713). National Technical Information Service, Springfield, VA. 1987. pp. 255-271. [DOE/OHER]

Irving, P.M. Comparison of the effects of wet and dry deposition on crops in the United States. In: Aerosols. S.D. Lee, T. Schneider, L.D. Grant, and P.J. Verkerk (eds.). Lewis Publishers, Chelsea, MI. 1987. pp. 1378-1389. [EPRI]

Irving, P.M. Effects on agricultural crops. Chapter 6. In: The Causes and Effects of Acidic Deposition. National Acid Precipitation Assessment Program Interim Assessment. Volume IV. NAPAP - 87/04, National Technical Information Service, Springfield, VA. 1987. pp. 1-50. [ER]

Irving, P.M. Effects of acidic deposition and associated gaseous pollutants on human health and visibility. Chapter 10. In: The Causes and Effects of Acidic Deposition. National Acid Precipitation Assessment Program Interim Assessment. Volume IV. NAPAP - 87/04, National Technical Information Service, Springfield, VA. 1987. pp. 1-83. [ER]

Miller, R.M. The ecology of vesicular-arbuscular mycorrhizae in grassland and shrublands. In: Ecophysiology of VA Mycorrhizal Plants. G.R. Safir (ed.). CRC Press, Boca Raton, FL. 1987. pp. 136-170. [DOE/OHER]

Nelson, D.M., R.P. Larsen, and W.R. Penrose. Chemical speciation of plutonium in natural waters. In: Environmental Research on Actinide Elements. J.E. Pinder, III, J.J. Alberts, K.W. McLeod, and R.G. Schreckhise (eds.). CONF-841142 (DE86008713). National Technical Information Service, Springfield, VA. 1987. pp. 27-48. [DOE/OHER]

3. Reports

Gilbert, T.L., N.K. Meshkov, J.P. Schubert, L.E. Trevorrow, and C. Yu. Planning for greater-confinement disposal. Volume 1: Alternatives and methods. Low-Level Radioactive Waste Management Handbook Series. DOE/LLW-53T. U.S. Department of Energy. August 1986. [DOE]

Gilbert, T.L., N.K. Meshkov, J.P. Schubert, and L.E. Trevorrow. Planning for greater-confinement disposal. Volume II: Appendices. Low-Level Radioactive Waste Management Handbook Series. DOE/LLW-58T. U.S. Department of Energy. September 1986. [DOE]

Hossain, T.Z., D. Elmore, H.E. Gove, T.K. Hemmick, P.W. Kubik and S. Jiang. Neutron activation/accelerator mass spectrometry: A new technique for measuring light elements in ultrapure materials. Report URNSRL-326. University of Rochester. 1987. [Kodak/DOE]

Irving, P.M. Report on the Crop Response Workshop of the National Acid Precipitation Assessment Program. 17-18 April 1986, Chicago, IL. Sponsored by the Interagency Task Force on Acid Precipitation. 1986. [EPA,EPRI]

Phillips, F.M., and D. Elmore. Chlorine-36 in hydrogeology: New applications through accelerator mass spectrometry. Report URNSRL-315. University of Rochester. 1987. [NSF/DOE]

Rogers, R.D., J.W. McConnell, Jr., M.W. Findlay, and E.C. Davis. Lysimeter data from EPICOR-II waste forms - Fiscal Year 1986. EGG-TMI-7417; INEL Informal Report to U.S. Nuclear Regulatory Commission. 1987. [NRC]

Schubert, J.P., W.S. Vinikour, and D.K. Gartman. Effects of gas-pipeline construction on the Little Miami River aquatic ecosystem. Final Report (September 1983 - April 1985). GRI-86/0024, Gas Research Institute, 1985. [GRI]

Vinikour, W.S., and J.P. Schubert. Effects of gas-pipeline construction on the aquatic ecosystem of Canada Creek, Presque Isle County, Michigan. Final Report (September 1984-July 1986). GRI-87-0027, Gas Research Institute, January 1987. [GRI]

4. Published Conference Papers

Irving, P.M. The influence of moisture stress on the response of soybeans to ozone and of sulfur dioxide on the response of corn to ozone. In: Peer Review of the Air Ecology Research Program. Volume 1: Background and Summary Material. 1-3 April 1987, Corvallis Environmental Research Laboratory, Corvallis, OR. 1987. (in press). [EPA]

5. Published Abstracts, Notes, Reviews, Comments, Letters

Franson, R. Model of belowground interactions between two oldfield herbs. American Journal of Botany 75(5):680 (1986). [DOE/OHER]

Franson, R., and R.M. Miller. The effect of mycorrhizal fungi on competition between plants: Testing the appropriate hypothesis. American Journal of Botany 73(5):667 (1986). [DOE/OHER]

Miller, R.M., and J.D. Jastrow. Influence on soil structure supports agricultural role for prairies, prairie restoration. Restoration and Management Notes 4:62-63 (1987). [DOE/OHER]

Miller, R.M. Book Review "Invertebrate-Microbial Interactions." J.M. Anderson et al., (eds.). American Scientist 74:86 (1986). [DOE/OHER]

Penrose, W.R., and K.A. Orlandini. Factors governing the association of radionuclides with organic colloids and particles. Extended abstract of presentation delivered to ISIS Seminar, Transport of Contaminants in the Subsurface: The Role of Organic and Inorganic Colloidal Particles. 5-8 October 1986, Manteo, NC. 1987. pp. 30-33. [DOE/OHER]

Oral Presentations*

Beasley, T.M. The biokinetic behavior of ^{95m}Tc in juvenile coho salmon, *Onchorhynchus kisutch* (Walbaum). Presented at Behavior of Technetium in Terrestrial and Aquatic Environs: Workshop on Research Status and Needs. U.S. Department of Energy, 5-10 May 1986, Seattle, WA. [Scientists] [DOE/OHER]

Beasley, T.M. The use of ^{36}Cl in dating and tracing old groundwaters. Presented at Workshop on Subsurface Microbiology, U.S. Department of Energy, 15 July 1986, Gaithersburg, MD. [Scientists, program managers] [DOE/OHER]

Beasley, T.M. New directions for measuring long-lived radionuclides in environmental and biological materials. Presented at 32nd Annual Conference on Bioassay, Analytical, and Environmental Radiochemistry. National Bureau of Standards, 21-23 October 1986, Gaithersburg, MD. [Scientists] [DOE]

Beasley, T.M. Initial results of age dating waters of the Tuscaloosa aquifer using ^{36}Cl . Presented at Workshop on Subsurface Microbiology, U.S. Department of Energy, 15 July 1987, Gaithersburg, MD. [Scientists, program managers] [DOE]

Cook, B.D., J.D. Jastrow, R.M. Miller, and A.-C. McGraw. Belowground-system development of VA mycorrhiza in a restored tallgrass prairie community. Poster presentation at the Seventh North American Conference on Mycorrhizae, 3-8 May 1987, Gainesville, FL. [Conference attendees] [DOE/OHER]

Elmore, D. A search for supermassive isotopes and measurement of cosmogenic radioisotopes on the Rochester tandem. Presented at the Nuclear Science Seminar, Institut für Mittelenergiephysik, ETH-Honggerberg, 17 June 1986, Zurich, Switzerland. [Scientists, students] [DOE]

Elmore, D. A tandem accelerator as a detector for anomalously heavy isotopes and fractionally charged particles. Nuclear Physics Seminar presented at the University of Rochester, 18 September 1986. [Faculty, students] [DOE]

*For oral presentations, the person making the presentation is underlined.

**Audience for the presentation.

Elmore, D. A tandem Van de Graaff accelerator as a detector for supermassive isotopes and fractionally charged particles. Presented at the International Center for Theoretical Physics, 23 June 1986, Trieste, Italy. [Scientists, students] [DOE]

Elmore, D. Cosmogenic radioisotopes measured with a tandem accelerator. Presented at the Department of Experimental Physics, Universita Degli Studi, 23 June 1986, Trieste, Italy. [Faculty, students] [DOE]

Elmore, D. Plans for a dedicated AMS facility centered around the Argonne FN tandem. Presented at the Workshop on Techniques in Accelerator Mass Spectrometry, 30 June-1 July 1986, Oxford, England. [Conference attendees] [DOE]

Elmore, D. $^{186}\text{Os}/^{187}\text{Os}$ isotope ratios. Presented at the Workshop on Techniques in Accelerator Mass Spectrometry, 30 June-1 July 1986, Oxford, England. [Conference attendees] [DOE]

Elmore, D. Experience with all-electrostatic TAMS. Presented at the Workshop on Techniques in Accelerator Mass Spectrometry, 30 June-1 July 1986, Oxford, England. [Conference attendees] [DOE]

Elmore, D. ^{36}Cl and ^{129}I geochemistry. Presented at the Sixth International Conference on Geochronology, Cosmochronology, and Isotope Geology, 30 June-4 July 1986, Cambridge, England. [Conference attendees] [DOE]

Elmore, D. A tandem accelerator as a detector for anomalously heavy isotopes and fractionally charged particles. Nuclear Physics Seminar presented at the University of Rochester, 18 September 1986, Rochester, N.Y. [Faculty, students] [DOE]

Elmore, D. Accelerator mass spectrometry of ^{36}Cl , ^{129}I , and ^{187}Os . Presented at the Ninth Conference on the Application of Accelerators in Research and Industry, 10-12 November 1986, Denton, TX. [Conference attendees] [DOE]

Elmore, D. Accelerator mass spectrometry. Presented to the Geoscience Directorate, National Science Foundation, 3 February 1987, Washington, DC. [Program managers, administrators] [DOE]

Elmore, D. Plans for an AMS facility based on the FN tandem. Presented to The Heavy Ion Discussion Group, Argonne National Laboratory, 13 February 1987, Argonne, IL. [Scientists] [DOE]

Elmore, D. Accelerator mass spectrometry applications using long-lived radionuclides. Presented at the Conference on Innovation in Ecology: Technology and Theory, U.S. Department of Energy, 21-22 April 1987, Gaithersburg, MD. [Conference attendees] [DOE]

- Elmore, D. Measurements of ^{36}Cl in Greenland ice. Presented at the Fourth International Symposium on Accelerator Mass Spectrometry, 27-30 April 1987, Niagara-on-the-Lake, Ontario, Canada. [Conference attendees] [DOE]
- Elmore, D. Neutron activation/accelerator mass spectrometry for measuring light elements in semiconductor materials. Presented at Eastman Kodak Company, 24 August 1987, Rochester, NY. [Scientists, managers] [DOE]
- Franson, R., F. Janzen, and R.M. Miller. The effect of mycorrhizal fungi on competition between plants: Testing the appropriate hypothesis. Presented at Annual Meeting of the Botanical Society of America, 10-14 August 1986, Amherst, MA. [Conference attendees] [DOE/OHER]
- Irving, P.M. Preview of assessment report for crops. Presented at the National Acid Precipitation Assessment Program Annual Meeting, 9-13 June 1986, Greenbelt, MD. [Government agency managers, scientists] [DOE/OAP]
- Irving, P.M. Summary of crop response to acidic deposition. Presented at the National Acid Precipitation Assessment Program Annual Meeting, 9-13 June 1986, Greenbelt, MD. [Government agency managers, scientists] [DOE/OAP]
- Irving, P.M. Response of crop plants to air pollutants. Presented to the U.S. Department of Agriculture Environmental Effects Technical Committee, 19 June 1986, Washington, DC. [Scientists] [DOE/OAP]
- Irving, P.M. Crop effects research. Presented at the U.S. - Federal Republic of Germany Research Coordination Meeting, 14 October 1986, Washington, DC. [Scientists, program managers, government] [DOE/OHER]
- Irving, P.M. Acidic deposition effects on crops. Presented at the National Atmospheric Deposition Program Annual Meeting, 28-30 October 1986, Atlanta, GA. [Scientists] [DOE/OHER]
- Irving, P.M. NAPAP state-of-the-science report. Presented at the National Atmospheric Deposition Program Annual Meeting, 28-30 October 1986, Atlanta, GA. [Scientists] [DOE/OHER]
- Irving, P.M. Status of the National Acid Precipitation Assessment Program. Presented at the Tenth Symposium on Flue Gas Desulfurization, 18-21 November 1986, Atlanta, GA. [Scientists, program managers] [DOE/OHER]
- Irving, P.M. The physiological effects of ozone and water stress on soybeans and of ozone and sulfur dioxide on corn. Presented at a Peer Review of the Air Ecology Research Program, Corvallis Environmental Research Laboratory, 1-3 April 1987, Corvallis, OR. [Scientists, administrators] [DOE/OHER]
- Irving, P.M. Biotic stress interactions with air pollutants. Presented at the Ninth Annual Air Pollution Workshop, 27 April-1 May 1987, Helena, MT. [Scientists] [DOE/ER]

Irving, P.M. Overview of the U.S. National Acid Precipitation Assessment Program. Presented at the Symposium on the Effects of Air Pollution on Terrestrial and Aquatic Ecosystems, 18-22 May 1987, Grenoble, France. [Scientists] [DOE/ER]

Irving, P.M. Gaseous pollutants and acidic rain impacts on crops in the United States: A comparison. Presented at the International Acid Rain Conference, 1-4 September 1987, Lisbon, Portugal. [Scientists] [DOE/ER]

Irving, P.M., L.W. Kress, W. Prepejchal, and H.J. Smith. The influence of moisture stress or sulfur dioxide exposure on physiological processes in soybeans and corn exposed to ozone. Presented at the International Conference: Assessment of Crop Loss from Air Pollutants, 25-29 October 1987, Raleigh, NC. [Scientists] [DOE/ER]

Jastrow, J.D., R.M. Miller, and B.D. Cook. Influence of roots and VA mycorrhizal fungi on soil aggregation in restored tallgrass prairie. Poster presentation at the Seventh North American Conference on Mycorrhizae, 3-8 May 1986, Gainesville, FL. [Conference attendees] [DOE/OHER]

Kress, L.W. Selection and care of rooting media and trees for controlled exposure experiments. Presented at the Workshop on Controlled Exposure Techniques and the Evaluation of Tree Responses to Airborne Chemicals, U.S. Environmental Protection Agency, 4-5 February 1986, Atlanta, GA. [Scientists] [EPA]

Kress, L.W. Air pollution stress to ecosystems. Presented at the Division of Educational Programs, Student Research Participation Program, 12 February 1986, Argonne National Laboratory. [College students] [EPA]

Kress, L.W. Pollutant interactions. Presented at Eighteenth Air Pollution Workshop, 15-17 April 1986, Chicago, IL. [Scientists] [EPA, EPRI]

Kress, L.W. Relevance of controlled exposure data. Presented at Eighteenth Air Pollution Workshop, 15-17 April 1986, Chicago, IL. [Scientists] [EPA, EPRI]

Kress, L.W. Acid rain and ozone effects to vegetation. Presented to Associated Colleges of the Chicago Area (ACCA) Program on Global Climate, 7 October 1986, Argonne IL. [Chicago area adult education students] [EPA, EPRI]

McGraw, A.-C. The balance of mutualism in mycorrhizal symbiosis: Consequences of living in the real world. Presented at seminar jointly sponsored by Phi Sigma Society and Biology Department, Illinois State University, 30 January 1986, Normal, IL. [Faculty, graduate students] [DOE/OHER]

McGraw, A.-C. Variability in morphology of spore progeny from single spore isolates of the *Glomus monosporum/mosseae* complex. Presented at Annual Meeting of the Mycological Society of America, 10-14 August 1986, Amherst, MA. [Conference attendees] [DOE/OHER]

McGraw, A.-C., and R.M. Miller. Interactive effects of mycorrhiza, plant nutrient-limiting growth conditions, drought, and plant genotype. Presented at Joint Session of the Botanical Society of American and Mycological Society of America, 8-14 August 1986, Amherst, MA. [Conference attendees] [DOE/OHER]

Miller, R.M. The survival dynamics of beneficial microbes. Presented at Joint Session of the Botanical Society of American and Mycological Society of America, 8-14 August 1986, Amherst, MA. [Conference attendees] [DOE/OHER]

Miller, R.M. A mycorrhizal fungus-influenced, host biomass allocation response in *Agropyron smithii*. Presented to Horticulture Department, Purdue University, 9 October 1986, West Lafayette, IN. [Faculty, students] [DOE/OHER]

Miller, R.M. Microbiology and surface mining. Presented to Plainfield School District Accelerated Science Program, 8 November 1986, Plainfield, IL. [High school teachers, students] [DOE/OHER]

Miller, R.M. Mycorrhizal fungus-mediated biomass allocation in *Agropyron smithii*. Presented to Department of Plant Pathology, Kansas State University, 13 November 1986, Manhattan, KA. [Faculty, students] [DOE/OHER]

Miller, R.M. Mycorrhizae influence fitness in the grass *Agropyron smithii*. Presented at the Department of Botany and Plant Pathology, Michigan State University, 13 April 1987, East Lansing, MI. [University faculty, students] [DOE/OHER]

Miller, R.M. Management of mycorrhizae in semi-arid environments. Presented at the Seventh North American Conference on Mycorrhizae, 3-8 May 1987, Gainesville, FL. [Conference attendees] [DOE/OHER]

CODES FOR FUNDING AGENCIES

DOE = U.S. Department of Energy
 EPA = U.S. Environmental Protection Agency
 EPRI = Electric Power Research Institute
 ER = Energy Research (in U.S. Department of Energy)
 GRI = Gas Research Institute
 NRC = U.S. Nuclear Regulatory Commission
 NSF = National Science Foundation
 OPA = Office of Program Analysis (in U.S. Department of Energy)
 OHER = Office of Health and Environmental Research (in U.S. Department of Energy)

4-1 / 4-2

**4 ORGANIC GEOCHEMISTRY AND ENVIRONMENTAL
INSTRUMENTATION PROGRAMS**

4 ORGANIC GEOCHEMISTRY AND ENVIRONMENTAL INSTRUMENTATION PROGRAMS

<u>Program Staff</u>	<u>Title</u>
V.C. STAMOUDIS	Program Manager/Chemist
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W.J. BUTTNER	Assistant Electrochemist
P. HESS*	Scientific Associate
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W.R. PENROSE*	Biochemist
K.C. PICEL	Assistant Environmental Scientist
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Collaborators

R. BATTIN, North Central College, Naperville, IL
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4.1 PROGRAM OVERVIEW

V.C. Stamoudis (Program Manager)

The Organic Geochemistry group is doing research in the area of analytical organic chemistry as it applies to health, the environment, geoscience, and control technology for energy-related hazardous waste materials. During calendar year 1986 and the first half of 1987, the group operated with program cutbacks. However, it continued operating through partial research development funds and temporary personnel support through the Division of Educational Programs (DEP).

The areas of research covered during this period include (1) computer-assisted gas chromatographic, qualitative, and quantitative analyses of coal-derived complex mixtures; (2) chemodynamic measurements in complex organic mixtures to study the transport and transformation processes that determine the movement and fate of chemicals in the environment; (3) bioassay-directed characterization of mutagenic polycyclic aromatic hydrocarbons in coal-derived materials; (4) chemical and toxicological evaluation of condensates from mild coal gasification processes; (5) development of rapid (high-pressure liquid chromatography) characterization techniques for primary aromatic amines in coal-derived liquids by using specific electrochemical detectors; (6) study of flame ionization detector response factors and chemical structure in gas chromatography; (7) development of a simple, portable device for preconcentrating airborne aromatic amines to be analyzed by portable liquid chromatography; (8) initial uptake and release studies of perchloroethylene and trichloroethylene in pine needles; (9) application of stable carbon isotope techniques in tracing environmental pollutants; (10) development of control technology for hydrazine fuels by neutralization with hypochlorite II.

The Environmental Instrumentation group is engaged in research to develop and build prototype field-portable devices and instruments for the detection, identification, and quantification of volatile hazardous gases in a variety of environmental and workplace settings.

Work during this period focused on (1) building five prototype field-portable, rugged instruments with updated hardware and software of the chemical parameter spectrometer (CPS-100);* (2) improvements of the CPS-100 instrument through advanced branching algorithms for single chemical identification and mixture-resolving algorithms for identifying binary or tertiary mixtures; (3) feasibility study towards interfacing gas chromatography (mixture resolving power) to the CPS-100 instrument (characterization power) for application in analyzing fire-generated hazardous vapors and other toxic vapor mixtures; (4) development of amperometric gas microsensors with exceptionally high repeatability, sensitivity, and selectivity for a variety of applications; (5) feasibility of using simple permeation-absorption devices for sampling and preconcentrating hazardous air contaminants.

**The CPS-100 instrument is based on measuring 16 characteristic signals (the chemical parameter spectrum) generated by an array of four electrochemical sensors after the sample is pretreated by passing through two hot/cold wire filaments operated in four different modes.*

4.2 COMPUTER-ASSISTED GAS CHROMATOGRAPHIC ANALYSIS OF COAL-DERIVED COMPLEX MIXTURES

*V.C. Stamoudis, K.C. Picel, and V.J. Vlastnik**

Coal-derived liquids are very complex organic mixtures containing mostly one- to five-ring polynuclear aromatic hydrocarbons (PAH): O-, S-, and N-PAH, both endocyclic (heterocyclic) and exocyclic (e.g., hydroxy-, amino-, keto-, and cyano-); and straight- and branched-chain aliphatic and alicyclic hydrocarbons, both saturated and unsaturated. Complete analysis of these mixtures requires elaborate fractionation procedures and state-of-the-art instrumental techniques.

Recent advances in the efficiency of gas chromatography (GC) columns and improvements in related hardware, and especially software, have facilitated rapid and accurate analysis of complex organic mixtures. By applying manufacturer-supplied software (calibrated-peak methods) and custom software based on retention indices (RI), most of the classes of chemicals in these mixtures (Stamoudis and Demirgian 1985) can be analyzed both qualitatively and quantitatively. Sample prefractionation is essential because it accomplishes two things: it produces simpler mixtures for GC analysis, and it separates constituents by chemical class, which aids automated identification. In the analysis of any new material, existing sample preparation procedures are validated for the material or modified to produce well-resolved chemical class fractions. Representative samples and their subfractions are characterized by GC/mass spectrometry (GC/MS) before analysis by computer-assisted GC.

The GC analysis method developed combines the features of conventional calibrated-peak methods, which require a standard calibration mixture of analytes, and a method based on RI values. The combined method consists of four steps. In the first step, targeted peaks in the sample are identified by their expected retention times, and their concentrations are calculated on the basis of the response factor of the respective standard chemical. A Hewlett-Packard Model 5880A GC equipped with Level 4 BASIC, a Grob-type split/splitless injector, and a flame ionization detector was used for this study. However, any computer-controlled GC could be adapted to this method.

In the second step, peaks not identified in the calibrated-peak report are processed and documented by the RI method. A data communication interface is used to transmit this calibrated report to a Perkin-Elmer 3600 data station (Demirgian 1984). A BASIC program then calculates an RI value and concentration for each peak on the basis of its relative position between bracketing standards.

In the third step, the analysis report containing the names of the calibrated peaks, RI values, and concentrations of all peaks is transferred via modem to a mainframe computer (IBM 3033). By using Statistical Analysis Systems (SAS) programming, the analysis report is matched against a data base containing RI values for about 1000 coal-related compounds. The data base is divided into ten chemical classes, any number of which can be included in the matching process. Appropriate selection of

**Collaborator; affiliation is listed at the front of this chapter.*

chemical classes in relation to the subfraction type being analyzed is important for making accurate identifications and for eliminating superfluous matches. Data base entries within a specified RI window are reported for corresponding GC peaks. The appropriate match is selected for each peak after consulting GC/MS data and other pertinent information.

Data management, the final step of the method, takes advantage of the information in the computerized RI data base. Entries in the data base contain, in addition to chemical name and RI value, a class code (0 through 9), an alkyl substitution code (CO, C1, C2, ... Cn), and a three-digit ring code indicating the total number of rings, number of aromatic rings, and number of alicyclic rings, respectively. Through the use of these codes, sample composition data for related components are graphically displayed in the form of bar or pie graphs. This way, various coal-related materials can be readily but comprehensively compared.

Computer-assisted GC analysis has been applied in the analysis of a coal-liquefaction standard material from the SRC-II process (CMR-1) as well as coal-gasification condensates from the Morgantown Energy Technology Center (METC) fixed-bed gasifier and from the Grand Forks Energy Technology Center (GFETC) slagging, fixed-bed gasifier. These materials are qualitatively similar in composition and were prefractionated by using the same procedure. Samples of the material (2 g) were initially fractionated by liquid/liquid extraction at extreme pH into acid, base, and neutral fractions. The neutral fraction was further fractionated into chemical class subfractions by silica gel column chromatography.

For each material, the subfractions were analyzed by computer-assisted GC as described above. Figure 4.1A is an SAS-generated bar graph comparing the three above-mentioned materials by abundances of PAH (class 2), O-PAH (class 6), and S-PAH (class 7) in the aromatic subfractions (F2). In Fig. 4.1B, the three materials are compared by abundances of compounds of various ring number, by using the ring codes in the data base. The numbers in the bars show the chemical class codes of the components represented. The high levels of two-ring aromatics in CRM-1 are notable, whereas the two gasifier condensates have higher levels of three- and four-ring compounds. Lastly, Fig. 4.1C, also produced from the codes in the data base, compares the materials by alkyl substitution levels.

The ability to display compositional data graphically, made possible by the data base coding of each substance analyzed in the materials, is particularly useful for comparing various coal-derived materials. The method can also be used to analyze a series of samples of similar composition for a large number of components. By using RI values in conjunction with spectrometric data, peaks can be identified with increased confidence. Further, by assigning each GC peak an RI number, the peaks are documented chromatographically for future reference.

This methodology will be extremely useful in studies of new mild gasification technologies where large numbers of samples will likely be generated. Applications may include studies of product stability and upgrading, as well as the effects of various process conditions on product composition.

FIGURE 4.1 Comparison of three coal-conversion materials by aromatic subclass composition (A), ring number distribution (B), and alkyl substitution (C).

4.3 CHEMODYNAMIC MEASUREMENTS IN COMPLEX ORGANIC MIXTURES

K.C. Picel and V.C. Stamoudis

Chemodynamics is the study of the transport and transformation processes that determine the movement and fate of chemicals in the environment. To model the behavior of complex organic mixtures in the environment, measurements are needed of chemodynamic parameters such as distribution coefficients and Henry's constants, as well as volatilization, biodegradation, and photolysis rates. The application of computers to capillary column GC makes it possible to measure the chemodynamic parameters of the numerous components of complex organic mixtures. We have developed a methodology for making such measurements and discuss herein its application to the measurement of coal oil/water distribution coefficients and to the identification of photosensitive components in aqueous solutions of a coal oil reference material (CRM-1).

Experimental studies of complex organic mixtures are best conducted by using whole crude mixtures. The conditions of an actual discharge are simulated, and the behavior of individual constituents is more realistic than it would be in experiments using single compounds or simple mixtures. In addition, solute interactions and the bulk properties of the mixture (e.g., light attenuation and toxicity) are taken into account.

In the approach we developed, a crude coal oil was used in conventional experiments for measuring chemodynamic constants. The crude oil acts as a standard against which changes in composition are measured. In most chemodynamic experiments, relative concentrations (equilibrium constant measurements) or relative changes in concentration (rate constant measurements) are measured, eliminating the need for making highly accurate measurements of absolute concentrations. Studies can therefore be conducted by using a GC with a flame ionization detector and a few representative standards in conjunction with GC/MS identifications of mixture constituents. Once documented by its RI value or relative retention time and its mass spectrum, a substance can be tracked throughout an experiment.

Samples from chemodynamic experiments were fractionated by applying the minimum number of steps necessary to produce well-resolved fractions by capillary GC. In sample fraction analysis, GC/MS identifications were used to create multiple-reference-peak, retention time calibration tables in the data system of the GC (Hewlett Packard 5880A). The sample fractions generated in the experiments were analyzed to produce a suite of GC reports containing compound names and concentrations. To facilitate data processing and interpretation, the GC reports were transferred electronically via a laboratory microcomputer (Perkin Elmer 3600) to a mainframe computer (IBM 3033). On the mainframe, data were processed by using SAS software. The SAS output was readily screened to identify photosensitive constituents. For photosensitive compounds, time-dependent concentration data were used to compute photolysis rate constants.

Chemodynamics was used to measure coal oil/water distribution coefficients (K_D) of CRM-1 components and to identify photosensitive components. For both studies, CRM-1 was equilibrated with distilled water (2 g/L) for several days. K_D values were measured for about 200 bulk components by analyzing several replicates of the

equilibrated aqueous layer and the original oil. The range of $\log K_D$ values measured by this technique was from 2 to 6. Acidic and basic components had the lowest values, with $\log K_D$ values in the range of <2 to 3.5, while aromatic hydrocarbons of one to five rings had values ranging from 4.2 to 6.2.

In the photolytic study, oil-equilibrated water was exposed in 1-L flasks (Pyrex) to sunlight (in triplicate) for up to three hours. Data for concentration versus exposure time were obtained for about 200 bulk components, including four targeted PAH. Table 4.1 is a sample of the tabulated data generated by SAS. Results of the study show that (C_0 - C_3)-phenols, (C_0 - C_4)-anilines, (C_0 - C_5)-pyridines, (C_0 - C_2)-quinolines, and one- to three-ring aromatic hydrocarbons (except anthracene) were not degraded measurably in the three-hour exposure. In contrast, (C_0 - C_3)-indoles, (C_0 - C_1)-carbazoles, and the four- and five-ring targeted PAH degraded significantly in the same period. For all these components, initial first-order rate constants and projected half-lives were calculated. Comparing these rates with those obtained in distilled water for individual compounds revealed inhibition of photolysis rates for PAH and carbazole, and sensitization for indoles, in the aqueous coal-oil matrix (Picel 1985).

The benefits of this methodology are readily apparent. With high-resolution chromatography and computer data transfer and processing, it was possible to analyze many replicates of samples containing large numbers of components. In addition, data editing was greatly facilitated by having all the raw data in a computer data base. As a result, the behavior of many compounds was studied rapidly under realistic conditions in a limited number of experiments. This methodology will be applied in future studies of the chemodynamic behavior of organic mixtures of environmental interest.

TABLE 4.1 SAS-generated table of aqueous concentration versus exposure time for isomers of carbazole and methyl carbazole^a

Isomer	MCO	SCO	MC30	SC30	MC90	SC90	MC180	SC180
CARBAZOLE1	416.74	18.382	391.50	30.649	322.22	28.114	285.39	20.559
CARBAZOLE2	28.08	0.811	24.43	1.644	17.89	1.832	13.66	1.486
CARBAZOLE3	38.86	5.259	31.06	1.044	22.73	3.138	14.46	2.468
Cl-CARBZL1	32.57	0.909	29.99	2.940	24.35	2.198	19.79	2.164
Cl-CARBZL2	34.80	1.972	28.67	2.384	19.26	1.790	13.98	1.278
Cl-CARBZL3	30.12	1.830	26.08	2.300	19.97	1.724	16.72	1.612
Cl-CARBZL4	16.15	0.734	14.12	0.801	10.81	1.521	8.96	1.158

^aMCO, MC30, MC90, and MC180; and SCO, SC30, SC90, and SC180 are the mean concentrations ($\mu\text{g/L}$, three observations) and standard deviations, respectively, for increasing exposure times (min).

4.4 BIOASSAY-DIRECTED CHARACTERIZATION OF MUTAGENIC POLYCYCLIC AROMATIC HYDROCARBONS IN A COAL-DERIVED MATERIAL

V.C. Stamoudis and D.A. Haugen*

Conversion of coal to liquid or gaseous fuels results in the formation of complex mixtures of carcinogenic and noncarcinogenic chemicals. Among these are numerous PAH and their alkyl homologs. To identify the carcinogenic PAH in complex organic by-products of coal gasification, we measured the mutagenic activities of fractions obtained by preparative and semi-preparative high-performance liquid chromatography (HPLC). Mutagenic activity was measured in the Ames assay with *Salmonella typhimurium* strain TA98 and Aroclor-induced rat liver S-9 for metabolic activation. The composition of mutagenic fractions was determined by GC, GC/MS, HPLC, and UV-visible spectrophotometry.

Before chromatographic analysis, the coal gasification tar was dissolved in methylene chloride and extracted successively with aqueous HCl and NaOH to remove basic and acidic components, respectively (Fig. 4.2). The remaining neutral components were fractionated by preparative silica HPLC to yield three major fractions of mutagenic PAH. These fractions were each subjected to semi-preparative reversed-phase HPLC (RP-HPLC). Chemicals were eluted with an acetonitrile-water gradient. For each separation, duplicate portions of each of approximately 100 fractions were assayed for mutagenic activity. Approximately 20 major mutagenic fractions were obtained. Analysis of these fractions by GC and GC/MS indicated that some mutagenic fractions contained primarily single components such as cyclopenta[cd]pyrene and benzo[a]pyrene.

As was predicted from the chromatographic behavior of reference chemicals, the more complex mutagenic fractions were composed of PAH and alkyl-PAH, all having approximately the same total carbon number (aromatic plus aliphatic), but a range of aromatic carbon numbers. The results of RP-HPLC analysis of silica fraction 7 (S7) are shown in Fig. 4.3. The composition of one of the mutagenic fractions, S7-R55, is shown in Table 4.2.

The mutagenic mixtures of PAH and alkyl PAH obtained by RP-HPLC were resolved further by either (1) RP-HPLC (elution with acetonitrile-water) with an alternate packing having different selectivity or (2) normal-phase HPLC (NP-HPLC) with a bonded amino column eluted with 2% methylene chloride in hexane. Elution from the amino column was largely independent of the degree of alkylation, allowing further resolution of the PAH and alkyl PAH that coeluted in the RP-HPLC system.

Resolution of fraction S7-R55 (see Fig. 4.3 and Table 4.2) in the NP-HPLC system is shown in Fig. 4.4. GC analysis of the three mutagenic fractions (S7-R-55-N23, -N24, and -N25) is shown in Fig. 4.5, along with analysis of the fractions from which they were derived (S7 and S7-R55). The identities of the mutagenic PAH as methylenechrysene and methylenebenz[a]anthracene (Figs. 4.4 and 4.5) were determined on the basis of their mass and UV-absorbance spectra.

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FIGURE 4.2 Extraction scheme for coal gasification tar.

FIGURE 4.3 HPLC analysis of fraction S7. A_{313} , at 313 nm; bars, mutagenic activity; inset, analytical load of fraction S7.

Similar series of complementary chromatographic separations (Fig. 4.2) were applied to the isolation of other mutagenic PAH. These included chrysene, benz[a]anthracene, and dibenzanthracenes, as well as their respective methyl and methylene homologs; cyclopenta[cd]pyrene and methyl homologs; benzo[a]pyrene, benzo[fluoranthene], and their isomeric methyl homologs; indeno[1,2,3-cd]pyrene; benzo[ghi]perylene; anthanthrene; and dibenzpyrene isomers. Of these compounds, most of the specifically identified unsubstituted PAH, as well as isomers of the generically identified alkyl PAH, have been previously shown to be carcinogenic.

This stepwise series of bioassay-directed chromatographic procedures that enabled the isolation and identification of mutagenic and carcinogenic PAH present in a complex mixture would be applicable to analysis of other PAH-containing mixtures. Success in using bioassay-directed characterization requires iterative fractionation and bioassay testing to direct the selection of the most favorable set of complementary chromatographic systems.

TABLE 4.2 Composition of mutagenic RP-HPLC fraction S7-R55

Component	Carbon Number	
	Total	Aromatic
C ₆ - and C ₇ -naphthalenes	16,17	10
C ₅ - and C ₆ -biphenyls	17,18	12
C ₄ - and C ₅ -fluorenes	17	12
C ₃ -phenanthrenes/anthracenes	17	14
C ₂ -pyrenes/fluoranthene	18	16
C ₂ -dihydropyrenes	18	16
Methylbenzofluorenes	17	16
Methyl(chrysenes/benzanthracenes)	17	18
Methylcyclopenta[cd]pyrenes	17	18
Methylene(chrysenes/benzanthracenes)	19	18

FIGURE 4.4 NP-HPLC resolution of fraction S7-R55.

FIGURE 4.5 GC analysis of fractions S7 and S7-R55 and three mutagenic fractions derived from them. C_n , number of alkyl carbons; numbers in parentheses, molecular weight of parent PAH.

4.5 CHEMICAL AND TOXICOLOGICAL CHARACTERIZATION OF MILD GASIFICATION CONDENSIBLES

K.C. Picel, and V.C. Stamoudis

The Department of Energy through its Morgantown Energy Technology Center (METC) is in the process of developing an advanced, continuous "mild coal gasification" process, a concept that is envisioned to open new markets for coal in transportation, light industrial, and commercial sectors. The process is so named because the operating conditions applied during the coal conversion are mild compared to those used in conventional gasification processes. Mild gasification is done in a sealed reactor at atmospheric pressure and relatively low temperatures. Mild gasification produces three products: a fuel gas that could be a substitute for natural gas, a liquid fuel with several properties similar to No. 2 diesel fuel, and a coke-like material called char that could be used as a solid fuel.

We are examining the chemical composition, toxicological properties, and upgrading possibilities of the liquid product. Chemical and toxicological characterization was performed on a liquid sample that was obtained from the United Coal Company (UCC; Reston, VA) mild gasification pilot plant. By using well-documented rapid chemical and toxicological characterization techniques specifically developed at Argonne for process stream characterization and coal-derived liquids, we have analyzed over 200 major constituents of the material and have measured the mutagenic potential of acidic, basic, and neutral chemical fractions.

In the chemical analysis of the UCC liquid, a sample of the condensible product was first dried (water was 54% by weight) and then fractionated into acidic, basic, and neutral fractions by successive extractions with strong base and strong acid. Chemical analysis was then performed on each fraction by capillary GC. Constituents were identified by using a retention index and by GC/MS.

The mutagenic activities of the three pH-separated fractions were determined by the Ames plate-incorporation method with *Salmonella typhimurium* strain TA98. Aroclor 1254-induced rat liver S-9 was used for metabolic activation. The mutagenicity (revertents/ μ g) of benz[a]pyrene was also measured in each assay as a positive control.

The recoveries of mass and mutagenicity in the three pH-separated fractions are given in Table 4.3. The total recoveries were 86.6% of original mass and 59% of original mutagenicity. In this sample, the level (1.8%) of acids (phenols) is quite low, a property necessary for good fuel quality. The bases (mainly nitrogen heterocyclics) accounted for 4.6%, and the neutrals made up 80.2% of the condensibles.

The neutral fraction, which made up the bulk of the material, was composed principally of two- to six-ring PAH. There was little alkylation or heterocyclic content. About 15% by weight of the sample was made up of four- to six-ring PAH, which is undesirable from a toxicity standpoint, because this fraction contains many well-established carcinogens and mutagens. Distillation and hydrogenation are two processes that can reduce levels of mutagenic PAH. The former is much cheaper than the latter.

The basic fraction contains the bulk of the recovered mutagenicity of the sample, although it represents only a minor fraction of the mass. This high specific mutagenicity is due primarily to the presence of low levels of highly mutagenic primary aromatic amines (PAA). Mutagenic PAA (which represent only a few percent of the basic fraction, the bulk of which is composed of endocyclic nitrogen compounds) can also be removed by distillation or hydrogenation.

TABLE 4.3 Mass and mutagenicity balance of pH fractionation of United Coal Company mild gasification liquid

Fraction	% Mass	Mutagenicity	
		rev/ μ g	%
Original oil	(100)	35.1	(100)
Acids	1.8	0.6	< 0.1
Bases	4.6	313	41
Neutrals	80.2	8.0	18
	<u>86.6</u>		<u>59</u>

The acid fraction in this particular liquid represents a minor fraction of the mass and has insignificant mutagenicity. The fraction is of concern mainly from the standpoint of fuel quality and stability. Acidic constituents, which are principally phenols, are effectively removed by hydrogenation, as are many of the other heterocyclic species that degrade fuel quality.

The initial chemical and toxicological characterization of the UCC mild gasification condensable product reveals a material that has several qualities of a useful fuel such as high energy content and fairly low heteroatom content, but also is significantly mutagenic in its crude state. With the appropriate upgrading steps, an environmentally acceptable product could probably be produced. We expect that upgrading will also improve product stability and fuel quality. Efforts now should be focused on testing those upgrading processes with the greatest potential for commercialization such as distillation and hydrogenation.

4.6 DEVELOPMENT OF A RAPID CHARACTERIZATION TECHNIQUE FOR PRIMARY AROMATIC AMINES IN GASIFIER CONDENSATES

V.C. Stamoudis, K.C. Picel, R.F. Lee, and S. Zaromb*

The objective of this study was to apply short-column (3-cm) liquid chromatography with electrochemical detection (LC-EC) to the analysis of a variety of gasifier condensates and base fractions thereof in a search for correlations between various chromatographic peaks and sample mutagenicity values (Ames *Salmonella* assay).

In the analysis of tars by LC-EC, chromatograms were produced containing four to five distinct peaks, which correlated in retention time to PAA standards of one to three rings. The LC-EC peaks from base fractions of representative tar samples were collected, extracted, and analyzed by GC/MS. The identifications and approximate concentrations of PAA and alkylated PAA present in each LC-EC peak were determined. Each LC-EC peak typically contained isomeric unsubstituted PAA and a suite of alkyl substituted (up to three carbons) derivatives. Peak #1 contained (C₀-C₃)-anilines; peak #2, (C₀-C₃)-aminonaphthalenes; peak #3, (C₀-C₁)-aminobiphenyls; peak #4, (C₀-C₁)-aminofluorenes; and peak #5, aminophenanthrenes and aminoanthracenes. The concentrations of total PAA in each peak as determined by GC/MS corresponded fairly well to the concentrations represented by the peak areas from the LC-EC, indicating that the EC detector response was due only to PAA in the base fraction.

To test the capability of the instrument to detect amines directly in crude tar samples, such a sample was run along with its base fraction. The chromatograms from both runs were quite similar, and both analyses gave similar concentrations of PAA, indicating that the technique may be directly applicable to crude samples. When crude tars are analyzed, however, the LC column requires back-flushing to remove uneluted sample before another run can be made.

*Collaborator; affiliation is listed at the front of this chapter.

Base fraction mutagenicities (revertants/ μg , Ames *Salmonella* assay) for a variety of gasifier tar base fractions as well as a base fraction from shale oil were compared to the intensities (PAA concentrations) of LC-EC peaks 2 through 5 produced from the base fractions. In general, samples with high mutagenicity had relatively high intensities for all LC-EC peaks. The correlation, however, was best between mutagenicity and the intensity of peak #5, which contained aminophenanthracenes and aminoanthracenes. This result both supports the hypothesis that three-ring PAA are the most important mutagens in gasifier tar base fractions, and indicates that the LC-EC technique may be a means of quickly characterizing the types and levels of PAA in gasification condensates, thus giving an indication of their expected mutagenicities.

The LC-EC technique should be useful in future studies of coal liquid detoxification and upgrading where the principal mutagens targeted for removal are PAA. The technique will supplement and perform a screening function for more costly and time-consuming detailed chemical and toxicological assays.

4.7 FLAME IONIZATION DETECTOR RESPONSE FACTORS AND CHEMICAL STRUCTURE IN GAS CHROMATOGRAPHY

K.C. Picel, A.D. Jorgensen, V.J. Vlastnik,* and V.C. Stamoudis*

The flame ionization detector (FID) is the detector of choice for the gas chromatographic analysis of hydrocarbons and other species with oxidizable carbons. We studied FID response to a wide variety of organics found in coal liquids and containing heteroatoms (N, S, O), relative to that obtained for a pure hydrocarbon, naphthalene. The purpose of the study is to determine whether the measured relative response factors (area response per ng of compound:area response per ng naphthalene) are in agreement with those expected from a simple approximation and, if not, to what degree they differ and whether the difference is systematic. This study will significantly improve our ability to perform automated quantitative analysis of coal liquids.

Measurements of relative response factors were made by preparing a stock standard solution of the chemical of interest from neat (> 98% pure) material. Aliquots of stock solutions of about ten compounds of interest and naphthalene were combined in a mixture at the 50 ng/ μL level. This mixture was then analyzed in triplicate by using a new fused-silica capillary column (30 m x 0.32 mm DB-5) and an FID. The relative response factors were computed from the integrated areas and injected amounts. For each set of compounds, this process was repeated two or more times, starting with neat materials and with preparation of fresh stock solutions and mixtures.

We have thus far measured relative response factors for 72 components making a more or less complete data set for characterizing coal liquid heterocyclics. The data set includes 28 N-heterocyclics (five containing two nitrogens), 35 O-heterocyclics (seven containing two oxygens), one compound containing both N and O, three S-heterocyclics, four alkanes, and an alkyl aromatic (trimethylbenzene).

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The basis for response of an FID, in theory, is that the detector responds only to oxidizable carbons in a compound. For our initial approximation, we assumed no response for carbons bonded to O, N, or S in heterocyclic compounds. Using only the molecular formula for a compound, this approximation will predict the relative FID response of a heterocyclic compound to a pure hydrocarbon, in our case, naphthalene.

The results of our study on 72 compounds show that the initial approximation predicts relative response factors to a fair degree of accuracy, typically within 10% of the experimental value. We have observed, however, systematic differences between the predicted and experimental values. In the majority of cases, the experimental values were slightly higher than predicted, indicating a partial response from the heteroatom-bonded carbon. This partial response, which contributes to the effective carbon number, was quite consistent among members of the same chemical family, e.g., pyridines and quinolines.

Briefly, our results for N-heterocyclics show a partial response of about 30% for the N-bonded carbon, although there were small differences between 1°, 2°, 3°, and nitrile N. Compounds with oxygen-bonded carbons had partial carbon responses ranging from near zero for ketones and alcohols, up to about 40% for ethers and esters (for each of two carbons). The data for sulfur-containing compounds, although limited, show a partial carbon response approaching unity, indicating little hindrance of oxidation of the sulfur-bonded carbon.

These relative-response-factor values constitute a data base for coal liquids that will allow accurate prediction of relative response factors for almost any heterocyclic of interest for use in future automated GC analysis of coal liquids. We are currently testing the stability of the relative response factors to changes in the flow rates of the air and hydrogen flame gases. Preliminary data show an insensitivity to air flow rates at a given hydrogen flow rate.

4.8 PRECONCENTRATION OF AIRBORNE PRIMARY AROMATIC AMINES FOR ANALYSIS BY A PORTABLE LIQUID CHROMATOGRAPH

S. Zaromb, T. Otagawa, J.R. Stetter, and K. Quandt**

4.8.1 Introduction

In order to detect very low airborne concentrations of the highly mutagenic and carcinogenic PAA by using a recently reported (Otagawa et al. 1986) LC-EC method, a high degree of preconcentration of the hazardous constituent(s) must be achieved. The use of sorbents like charcoal, Tenax, or polymer resins has several objectionable features, such as the necessity for sample desorption and sorbent-reconditioning steps, possible introduction of interfering contaminants, or the requirement of sorbent cleanup and solvent extraction steps that are unsuitable for a portable monitor. Collecting

*Collaborator; affiliation is listed at the front of this chapter.

amines on acidified silica gel has been successful (Wood and Anderson 1975), but requires two solutions with different pH values -- one of low pH to protonate and trap amines on a chemically reactive surface and one of high pH to elute them into the LC-EC. Such complexity is inappropriate for a field instrument.

Three alternative preconcentration techniques were evaluated: injecting air directly into an absorbing solution; cryogenic or cold-trap sampling; and circulating the air sample past a permeation-type absorber. The efficiency with which airborne aniline vapor was collected into a small volume of liquid suitable for LC-EC analysis was determined for different sampling conditions. Aniline was chosen because it is the most difficult PAA to condense, having the lowest melting point and the highest vapor pressure.

4.8.2 Experimental Design

The LC-EC system and preparation of the mobile phase and liquid standard samples were described elsewhere (Otagawa et al. 1986). The mobile phase was a solution of 35% (vol) tetrahydrofuran in a aqueous (pH 2.2) phosphate buffer. A sample of 10 ppm aniline in air, prepared by injecting liquid aniline with a motor-driven syringe pump into a stream of hot air and collecting the air in aluminum-foil-covered Teflon gas-sampling bags, was used in most experiments.

The bubbler-type sampler consisted of a porous Teflon tube (Gore-Tex TB001, 1 mm i.d., 0.4 mm wall thickness, 3.5 μ m maximum pore size, 70% porosity, W. L. Gore & Associates, Inc., Elkton, MD) immersed in 1 mL of the mobile phase solution. Pyrex glass wool was packed at the tip of the tube to increase the surface area of the gas-solution interface. In a modified bubbler, a 24-cm-long Gore-Tex TB001 tube immersed in 2-3 mL of the mobile phase solution was substituted for the glass wool. The air sample was introduced by using a portable air pump located upstream from the sampler. After passing the air sample through the solution for a specified time, 200 μ L of the solution was collected with a syringe and directly injected into the LC-EC.

The cryogenic sampler comprised a thermoelectric device (3 cm x 1.5 cm, Model CP1.0-63-06L, Melcor Materials Electronic Products Corp., Trenton, NJ) attached to a 20-cm-long by 1-mm-i.d. stainless steel tube, which constituted the sample collector as well as the injection sample loop for the LC-EC. The cold surface of the thermoelectric device was attached to the sample loop and the hot surface to a Model 641 heat sink with a thermally conductive, electrically nonconductive zinc oxide paste, Thermal Compound, Part No. 120-2 (both made by Wakefield Engineering, Inc., Wakefield, MA). The heat sink was immersed in a 1-L water reservoir to maintain the hot surface at room temperature, while the sample loop was covered by an asbestos insulator at the cold surface. One end of the sample loop was cemented to the LC-EC sample injector (Model 7125, Rheodyne, Inc., Cotati, CA).

The permeation apparatus consisted of an aluminum-covered 1-L or 5-L Teflon sampling bag having an inlet valve connected to a permeation absorber and an outlet valve connected to a circulating pump. The outlet of the pump was connected to the inlet of the absorber, thereby forming a closed flow circuit. The absorber consisted of an

outer polyethylene tube, about 1 cm i.d., and an inner 15-cm length of Gore-Tex tubing (TB001) terminating at solid (nonporous) inlet and outlet nipples. The inner tubing was filled with the aqueous mobile phase, which could not pass through the hydrophobic pores and which absorbed the aniline from the circulating air sample. The volume of liquid required to fill this tubing was 0.12 mL, a good size for direct LC analysis.

4.8.3 Results and Discussion

With both bubbler-type samplers, aniline collection efficiency was always less than 1%. The efficiency decreased as the flow rate was increased from 10 mL/min to 25 mL/min. Slower flow rates were not tested because sampling times in excess of 10 min would not be practical for quick field analyses.

With the cryogenic sampler to achieve a collection efficiency of $\geq 80\%$, the sampling loop temperature should be $\leq -10^\circ\text{C}$, and the air sample volume should not be much greater than 10 mL. With larger volumes, achieving satisfactory collection efficiencies would require a sampling loop with a larger effective wall area.

For the permeation absorber to work satisfactorily, air leaks must be prevented, and all the components in contact with the air sample must be of inert and nonabsorbent materials. When these conditions were met or approached, we obtained collection efficiencies of 60-100% for 1-L and 5-L samples containing 1 ppm or 5 ppm of aniline.

4.8.4 Conclusions

The effectiveness of either cryogenic or permeation-absorption sampling for analyzing aniline vapor in dry air by LC-EC has been demonstrated. The collection method is simple and relatively fast and can be easily automated and adapted to a portable monitor. The 10-mL upper limit for the volume of air that can be satisfactorily sampled with the present cryogenic sample loop translates into a detection limit of 4 ppb aniline in air. The larger air sample volume possible with the permeation absorber translates into a detection limit of 0.01 ppb aniline, if the extrapolation of our preliminary results is valid.

4.9 ACCUMULATION OF PERCHLOROETHYLENE AND TRICHLOROETHYLENE IN PINE NEEDLES

J.V. Bonilla, M. Williams, G. Flanagan,* D. Frison,* and V.C. Stamoudis*

Perchloroethylene (PCE), trichloroethylene (TCE), and related compounds are suspect cancer agents, and their presence in the environment poses a potential hazard to people and other living organisms. PCE and TCE are used as solvents in a variety of

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applications, mainly in metal degreasing, textile cleaning, and solvent extraction processes, and as carrier solvents for pesticides and insecticides.

The major part (~85%) of the produced PCE and TCE is released into the environment. For example, in 1975, the emission of PCE alone into the air was estimated to be 450 kilotons/year. Therefore, atmospheric and groundwater contamination are a major problem with these compounds, especially because they are rather persistent in the environment (not easily metabolized or biodegraded).

The presence of PCE and TCE in the environment is especially severe at the Department of Energy's Savannah River Laboratory (SRL) area, Aiken, SC, where a system that strips these compounds by aeration of groundwater is in operation to produce emissions in conformance with environmental regulations.

It might be possible to assess the extent of the deposition and spreading of TCE, PCE, and related compounds by measuring their concentrations in pine needles located near their sources. That is, pine needles might monitor these compounds in the environment. Interestingly, little work has been done on the behavior of PCE and TCE in soils, groundwater, or plants.

The basic purpose of this study was to evaluate the uptake of PCE and TCE by pine needles and their subsequent release back to the environment. To do this, we created in the laboratory a microcosm in which we exposed small live pine trees to different concentrations of PCE and TCE for 24-hr periods and then exposed them to a clean environment and periodically sampled branches over several days to monitor the chemicals. TCE and PCE analysis was performed by capillary GC.

Preliminary results indicate that pine needles absorb PCE and TCE very efficiently (~200 $\mu\text{g/g}$ and 150 $\mu\text{g/g}$ respectively) in an initially saturated environment. The concentration decreases rapidly during the first few hours of exposure to a clean atmosphere, but after about 6 hr it levels off. In fact, foliar accumulation of PCE persisted in pine trees over several weeks to a steady level of about 10 $\mu\text{g/g}$. This was also the case when the trees were exposed to lower concentrations. However, TCE decreased to levels below detection limits over a period of two weeks. The fact that PCE is more efficiently absorbed and retained in the pine needles may explain why the extracts from field samples (SRL) show only PCE and no detectable quantities of TCE.

Because of the large octanol-water partition coefficient of TCE ($K_{ow} = 339$) and PCE ($K_{ow} = 398$), these chemicals are expected to be soluble in lipids and other nonpolar organic substances like plant waxes. Indeed, bioaccumulation of TCE and PCE has been reported to occur in the lipid-rich tissues of both man and animals. Yet, a significant concentration remains after 3-4 weeks of exposure to a clean environment.

By using the octanol-water partition coefficient (K_{ow}) and the Henry's law constants (air-water partition coefficient, H), we estimated a partition coefficient for PCE and TCE between octanol and air. We used the assumption that octanol is a good organic surrogate for plant wax to predict the relative concentrations of PCE and TCE in pine branches. Literature values for K_{ow} and Henry's law constants are listed in Table 4.4. The octanol-air partitioning coefficient (K_{oa}) for TCE and PCE was

TABLE 4.4 Data for TCE and PCE (at 25°C unless otherwise stated)

Compound	MW	b.p. (°C)	Vapor Pressure ^a P _a	Henry's Law Constant		K _{oa}		
				Calc.	Exp. ^b (20°C)	K _{ow}	Calc.	Exp. ^c
TCE	131.4	87	9.87	1.3 1.169	9.04	339 287.5	260	273
PCE	165.8	121	2.48	2.94 1.03	2.0	398 386	135	260

^aVapor pressure correlations for low-volatility environmental chemicals (MacKay et al. 1982).

^bExperimental values from MacKay et al. (1982).

^cCalculated from experimental values of MacKay et al. (1982).

calculated on the basis of the ratio K_{ow}/H , by using the two lowest and highest values listed in the literature for H . Caution must be exercised with the above approach because octanol may not be an appropriate surrogate for plant wax, and also because reliable data for the value of H are not available (Table 4.4).

Theoretical considerations of vapor pressure and the highest values of H listed in Table 4.4 would suggest that TCE would be present in the pine needles at a much higher concentration than would PCE. When the lowest values of H are used, however, the opposite would be expected. These results suggest that the mechanisms of deposition of TCE and PCE in pine needles may be fairly complex and may be a function not only of air-organic phase partitioning but also of other factors including irreversible absorption in the plant wax.

The preliminary results of this study indicate that pine trees could potentially be used to monitor the persistence of PCE and TCE in the environment and to predict the accumulation of these and related compounds.

A study in more depth should be undertaken to further determine the factors that affect PCE and TCE absorption in pine needles and the stability and/or transformation mechanisms of these chemicals once they are absorbed in the pine needles. It is also necessary to determine the rate at which these pollutants are absorbed by the plant, and how the plant responses influence the pollutant concentration in the environment.

4.10 APPLICATION OF STABLE CARBON ISOTOPE ANALYSIS IN ENVIRONMENTAL RESEARCH

J.V. Bonilla and V.C. Stamoudis

The use of stable isotopic fractionation as a means of studying environmental processes is well known. During the past year, we employed stable carbon isotopy in two pilot projects. The first was to evaluate the relationship between $\delta^{13}\text{C}$ and the chemical structure or degree of alkylation (number of aliphatic carbons) of aromatic hydrocarbons produced in synthetic oils. The second was to determine the degree to which starting materials and/or processing techniques uniquely label environmentally important chemicals with characteristic $\delta^{13}\text{C}$ values. If such labeling occurs, sourcing of these chemicals might be possible.

4.10.1 Correlation Between Chemical Structure and $\delta^{13}\text{C}$ Values of Aromatic Hydrocarbons

Three samples were obtained from a coal gasification plant for these studies. They represented material from a lignite coal gasified at the Mellon Institute Reactor at temperatures of 600°C, 800°C, and 1000°C. Other reactor conditions were as follows: carrier gas, He; pressure, 3 atm; and residence time, 1.3 min. Extensive chemical analysis on these samples was reported by Fillo et al. (1983). The general features observed after analysis of the aromatics are shown in Figs. 4.6 and 4.7. The bar graph in Fig. 4.6 shows the relative amounts of aromatic hydrocarbons for each ring structure in each of the three samples, which differed only in the reactor temperature. The ratios of 440 compounds (chrysenes) to 220 compounds (naphthalenes and biphenyls) or 110 compounds (benzenes) in the samples are markedly higher at 1000°C than at 800°C or 600°C. The concentration of the compounds containing alicyclic rings (i.e., the sum of 211, 321, and 431 compounds) reaches a maximum at 800°C.

Another trend seen is the degree of alkylation of the sample material at various temperatures. In Fig. 4.7, the subscript indicates the number of aliphatic carbons in the structure. The content of monoalkylated and dialkylated compounds (i.e., the sum of chromatographable C_1 and C_2 compounds) in the sample is the largest for runs 71 and 72. In other words, the degree of alkylation decreases with increasing gasification temperature of the sample.

The above trends in chemical composition of the aromatics could be related to specific process conditions. Furthermore, the chemical differences resulting from differences in processes seem to be reflected in $\delta^{13}\text{C}$ values (Table 4.5), which may be related to the aromatic compound's degree of alkylation, to the ring structure, or to both. The relative enrichment of the aromatic fraction with increasing gasification temperature is probably due mostly to dealkylation, as the low $\delta^{13}\text{C}$ value for the saturated fraction suggests. This is a good explanation assuming that the saturated fraction results from dealkylation of the coal structure moieties.

FIGURE 4.6 Analysis of total organics in combined oils versus ring structure for Mellon Institute (MI) reactor runs 1, 22, 3. (In the three-digits ring index, first digit = total rings, second digit = aromatic rings, third digit = alicyclic rings.) From Fillo et al. 1983.

FIGURE 4.7 Analysis of total organics of combined oils versus alkyl substitution for Mellon Institute (MI) reactor runs 1 (600°C), 2 (800°C), and 3 (1000°C). From Pillo et al. 1983.

Figures 4.6 and 4.7 show that with increasing reactor temperature, the degree of aromatization and ring number increase, while the degree of alkylation decreases. Examination of the $\delta^{13}\text{C}$ values for the aromatic fractions (Table 4.5) suggests a relationship between the aromatic structure (aromaticity and number of rings) and the degree of alkylation. The lower-ring-number (highly alkylated) compounds are depleted in ^{13}C relative to the higher-ring-number (less alkylated) components. This point deserves further study.

4.10.2 Sourcing

The fact that the isotopic signature of a product may reflect the isotopic properties of the starting material and/or the process it has undergone can potentially allow environmental pollutants to be traced to their source(s). To empirically examine this hypothesis, PCE and TCE samples from several suppliers were analyzed for their stable carbon isotope composition. The results are shown in Table 4.6. Only the $\delta^{13}\text{C}$ values for PCE from Ultrascientific and Fluka are similar. A reasonable hypothesis is that PCE and TCE obtained from Kodak were manufactured from natural gas, the PCE from Ultrascientific from marine oil sources, and the Fisher samples from terrestrial oil sources. Unfortunately, suppliers do not reveal the sources of their products, so we cannot, at this time, confirm this hypothesis.

From our initial measurements, stable carbon isotopes appear to be a potentially powerful tool for chemical sourcing when the same chemicals are produced by different companies.

4.11 NEUTRALIZATION OF HYDRAZINE FUELS WITH HYPOCHLORITE II

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The U.S. Air Force uses large quantities of hydrazine (N_2H_4), monomethyl hydrazine (MMH), 1,1-dimethylhydrazine or unsymmetrical dimethylhydrazine (UDMH), and Aerozine-50 (AE-50, a 50:50 mixture of hydrazine and UDMH) in a number of applications, including auxiliary power units, small thrusters, and space launch vehicles. The toxic nature of these fuels dictates that they must be treated and then disposed of carefully in the event of accidental spills or contamination.

TABLE 4.5 Stable carbon isotope values for the aromatic fractions from a coal gasification plant

Run	Gasifier Temperature ($^{\circ}\text{C}$)	$\delta^{13}\text{C}^a$
1	600	-24.90
2	800	-24.73
3	1000	-23.75

$\delta^{13}\text{C}$ values are relative to the Pee Dee Belemnite (PDB) standard.

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TABLE 4.6 Stable carbon isotope values for PCE^a and TCE^b from different suppliers

PCE Supplier	$\delta^{13}\text{C}^c$	TCE Supplier	$\delta^{13}\text{C}^c$
Ultrascientific	-25.9	-----	-----
Kodak	-35.2	Kodak	-35.28
Fluka	-24.4	Fluka	-25.35
Fisher	-28.4	Fisher	-33.23

^aGas analysis of the combustion products of PCE shows pure CO₂ as the only gaseous product (>99.6%). CO₂ from PCE was analyzed at Argonne, where the uncertainty (1 standard deviation) was ± 0.1 . CO₂ from TCE was analyzed at Indiana University. One instrument standard deviation was ± 0.05 .

^bGas analysis of the combustion products of TCE shows CO₂ and water as the only gaseous products.

^cThe $\delta^{13}\text{C}$ values are reported relative to PDB standard and are corrected for ¹⁷O contribution.

One approach to treatment and disposal is to allow the hydrazine fuel to react with a suitable oxidizing agent prior to disposal. The oxidation of hydrazine itself has been studied for over 80 years, and the Air Force has also performed extensive research on the environmental effects of hydrazine fuels in both aqueous and gaseous phases. Using hypochlorite solution to neutralize fuel spills after dilution with water and prior to disposal has been previously recommended. This technique provides a relatively simple way to deal with small spills. Previous work at Argonne (Brubaker et al. 1985) has shown that the neutralization reaction of methyl-substituted hydrazine fuels with hypochlorite does not proceed to completion with the formation of nitrogen, gas, water, and innocuous organic products, as does reaction of hydrazine, but rather results in a complex mixture that contains mutagenic substances. There is, therefore, concern regarding the toxicity and environmental significance of the products of the hypochlorite neutralization procedure.

Analytical results in Tables 4.7-4.9 indicate that nitrosamines [nitrosodimethylamine (NDMA), nitrosoethyl-methylamine (NEMA), and nitrosodiethylamine (NDEA)] can be produced by the neutralization of methylated hydrazine fuels with

TABLE 4.7 Nitrosoamine levels from the MMH-hypochlorite reaction^a

Run	Condition	Sample	Moles ClO^- per Mole Fuel	Nitrosoamine Concentrations (ppm)		
				NDMA	NEMA	NDEA
1	12% Methanol	1	8.1	-	-	-
2	Normal	1	1.9	-	4.9	2.1
		2	4.5	-	2.1	1.5
		3 ^b	4.5	-	2.1	0.8
3	pH = 1.8	1	3.3	-	-	-
4	T = 44°C	1	3.3	-	6.0	2.7
5	T = -10°C	1	2.7	-	-	-
6	12% Methanol	1	2.1	-	6.1	1.7
7	Blank	1	0.0	-	-	-

^aUnless otherwise noted, all samples were extracted from the reaction mixture within one hour of the completion of the reaction.

^bExtraction after aging for seven days.

hypochlorite. The main goals of this work were to quantify the nitrosamines produced under a variety of experimental conditions and to identify other products of environmental significance resulting from hydrazine neutralization.

In almost all of our experiments, detectable amounts of NDMA, NEMA, or NDEA were found. The addition of excess bleach and the aging of the final reaction mixtures in general reduced levels of, but did not completely eliminate nitrosamines. Temperature variations did not have large effects on the levels of the nitrosamines produced, although their low temperatures tended to suppress nitrosamine formation. On the other hand, nitrosamine formation tended to be enhanced by the presence of methanol. Nitrosamine formation seemed to be completely suppressed by the addition of mineral acid to a pH of approximately 2.0 prior to neutralization with hypochlorite. Under all conditions examined, the neutralization of all methylated hydrazine fuels considered yielded a rather complex final mixture, and a large fraction of these constituents were not identified. A more detailed description of the results from this project appears elsewhere (Brubaker et al. 1987).

TABLE 4.8 Nitrosoamine levels from the UDMH-hypochlorite reaction^a

Run	Condition	Sample	Moles ClO ⁻ per Mole Fuel	Nitrosoamine Concentrations (ppm)		
				NDMA	NEMA	NDEA
1	Normal	1	5.1	5.3	d	-
		2	9.9	6.5	d	-
		3 ^b	5.1	3.2	d	-
		4 ^b	9.9	0.8	-	-
2	Normal	1	1.2	49.2	-	-
		2	4.6	8.1	-	-
		3 ^b	4.6	2.6	-	-
		4 ^c	4.6	3.0	-	-
3	pH = 2.1	1	5.0	-	-	-
4	T = 44°C	1	5.7	7.3	d	-
5	T = -10°C	1	4.0	7.0	-	-
6	12% Methanol	1	8.5	11.0	-	-
7	Reverse Add.	1	5.7	6.9	3.6	-
8	Oxygen Free	1	7.1	3.8	-	-
9	Blank	1	0.0	-	-	-

^aUnless otherwise noted, all samples were extracted from the reaction mixture within one hour of the completion of the reaction.

^bExtracted after aging the reaction mixture for seven days.

^cExtracted after aging the reaction mixture for fourteen days.

^dPossible small amount coeluting with another compound.

4.12 A PORTABLE INSTRUMENT FOR MULTIPLE COMPOUND DETECTION AND ANALYSIS

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In response to a need by the U.S. Coast Guard and other agencies to monitor levels of toxic chemical vapors frequently encountered in chemical spills, we have been

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TABLE 4.9 Nitrosoamine levels from the AE-50-hypochlorite reaction^a

Run	Condition	Sample	Moles ClO ⁻ per Mole Fuel	Nitrosoamine Concentrations (ppm)		
				NDMA	NEMA	NDEA
1	Normal	1	5.1	1.7	12.2	-
		2	10.0	1.0	1.6	-
		3 ^b	5.1	1.3	0.5	-
		4 ^b	10.0	0.3	0.3	-
2	pH = 2.0	1	3.5	-	-	-
3	T = 45°C	1	4.9	1.9	2.0	-
4	T = -9°C	1	5.2	2.9	c	-
5	12% Methanol	1	5.0	2.4	c	-
6	Blank	1	0.0	-	-	-

^aUnless otherwise noted, all samples were extracted from the reaction mixture within one hour of the completion of the reaction.

^bExtracted after aging the reaction mixture for seven days.

^cPossible small amount coeluting with another compound.

developing a portable toxic vapor analyzer. Details of an earlier prototype instrument have been previously described (Stetter et al. 1984a, 1984b, 1984c; 1985b; Stull et al. 1986). This instrument (a "chemical parameter spectrometer") measures 16 independent signals (chemical parameters) and quantifies a sample by comparing its response to a predetermined library. The present instrument model, which weighs about 9.0 kg (including battery pack and heavy-duty case) and has dimensions of 31.5 cm x 32.1 cm x 23.5 cm, is truly portable. It has been designed to be used with only a few operator-initiated commands and has microprocessor-controlled data acquisition, analysis, and identification. Moreover, emphasis was placed upon designing a rugged instrument able to easily withstand the levels of abuse likely to be encountered in the field. Prototypes have been delivered to the U.S. Coast Guard and other agencies for evaluation.

4.12.1 Instrumentation and Methods

4.12.1.1 Instrument Design and Construction

The instrument has been extensively improved since the first prototype was introduced. During the early stages of development, we tested various electronic circuit

designs and instrument configurations and finally used circuitry that had been constructed in-house. While the use of homemade electronics was essential in order to evaluate performance and demonstrate the viability of the instrument, such circuitry is neither as rugged as is necessary for use in the field nor conducive to large-scale production. Moreover, the construction of the instrument as a single unit rendered it difficult to service. Indeed, most problems associated with the instrument's performance were directly related to the actual physical construction.

In the past two years, the problems associated with the initial portable units have been addressed. The connectors were chosen for ruggedness. All electronics were mounted on computer-designed, printed circuit boards and equipped with test points to facilitate servicing by qualified technicians. All of the electronic subsystems of the unit were laid out on individual circuit boards. This modular design allows rapid replacement of boards in the event of a failure of one of the subsystems and renders the instrument easy to service. The sensor housings were physically redesigned, as were the pneumatics of the instrument. The entire unit was packaged inside a sturdy steel carrying case (31.5 cm x 32.1 cm x 23.5 cm). A removable and rechargeable battery pack was fitted into the bottom panel of the carrying case. The total unit now weighs 9 kg.

4.12.1.2 Microprocessor Control of the Portable Unit

In the original prototype unit, built in 1984, microprocessor control was achieved by using technology that had been available since 1976. Data acquisition and analysis are now controlled by a high-speed, low-power, state-of-the-art microprocessor (CMOS 8088) with 64 kbytes of memory. This microprocessor is essentially identical to that used in the IBM PC. The unit may be programmed in high-level languages; it is now programmed in the computer code "C." The library searches are now performed at a rate of about 150 comparisons per minute, about ten times that in the original unit. The operating software is directly accessible to an IBM PC via an RS232 port. The unit is not currently programmed to run via external computer control, but it can be. At present, 32 kbytes of memory are used for the 25-compound library and algorithms. The unit is designed so that the memory can be expanded to 512 kbytes without any modification of the hardware, thus allowing implementation of more sophisticated software.

Data analysis is performed via comparison of the normalized response patterns of test runs with those stored in the library. The microprocessor computes the Euclidean distance between the 16-element vectors of the sample and library files. Identification and reliability are based upon closeness of fit; quantification is performed from a comparison of the net (not normalized) signals in the strongest channel of the identified compound. The analysis algorithm is essentially identical to that described by Stetter et al. (1985a).

4.12.1.3 Probe Design and Features

Stored inside the top panel of the case is a hand-held sampler probe. The probe, which is a new feature in the instrument, allows for direct sampling of vapors on site. The probe is easily connected to the pneumatics and electronics of the instruments.

Mounted directly inside the probe are an oxygen detector and a combustible gas detector. In the event that low levels of oxygen or high concentrations of combustible gases are encountered, both audible and visual alarms are set off. A red and green light indicates unsafe levels of combustible gas and oxygen, respectively. The alarm thresholds may be adjusted to appropriate levels by trained personnel.

4.12.1.4 Sensors and Sensor Arrays

As with the earlier prototype instrument, the detection technology employs three-electrode amperometric sensors. The sample gas is monitored simultaneously by an array of four sensors, each biased to a different operating potential. The array comprises two sensors with gold working electrodes biased to -200 mV and +300 mV (vs. a Pt-air reference), one sensor with a platinized platinum working sensor biased to +200 mV, and a commercial electrode (National Draeger, model 45950k) with a platinum black working electrode biased to 0 mV. The modular design also encompasses the sensor array, which is replaced as a unit. The array housing is 12.7 cm x 10.6 cm x 7.6 cm and includes the filament chamber as well as the potentiostat and current amplifier circuit board.

The array monitors the currents induced by untreated samples and also measures the responses of the four sensors to the sample (pyrolyzed by heated noble metal filaments). Operationally, sequential sensor responses are determined with the sample gas passing over a rhodium filament heated to 750°C and to 1000°C and over a platinum filament heated to 900°C. Such treatment converts electrochemically inactive compounds like benzene into electrochemically active products. The observed sensor response to the pyrolyzed sample is highly reproducible and dependent only upon the composition of the sample gas. Thus, by measuring the response of the four sensors in each of the four modes of operation, 16 signals (chemical parameters) are obtained. The typical concentration range for gas detection is about 10 to 200 ppm, although lower detection limits are attainable for certain chemicals. Normalization of the net current yields response patterns as histograms. Such histograms are graphic representations of the data stored in the instrument's library to which test runs are compared.

4.12.2 Operating Modes and Performance Evaluation

As a self-contained unit, the instrument's operation is simple and does not require extensive training. Operator commands, which are displayed on a liquid crystal display (with a backlight to facilitate use in the dark), are initiated by four push-button switches located on the front panel. The commands are simple and self-explanatory. The instrument can perform in three operator-controlled modes: (1) IDENT (identify), (2) UNIV (universal), and (3) SELECT. In the IDENT mode, the sample gas is qualitatively analyzed to identify the toxic vapor present and to determine its concentration. SELECT mode is designed to verify the presence or absence of a specific (operator-selected) chemical in the environment. UNIV mode monitors the sample for the presence of any undetermined compounds. For libraries of up to 25 compounds, the instrument correctly identifies test samples 90% of the time (Stetter et al. 1985a, 1985b). By using an

advanced algorithm, an identification success of 80% was obtained for 65-compound libraries and a 90% success for a library of 40 compounds (Zaromb et al. 1986a).

4.12.3 Conclusion

An accurate, lightweight, truly portable toxic-vapor analyzer has been designed and constructed for industrial applications. This is a rugged instrument capable of performing an analysis within five minutes. Customized libraries can be readily installed in the instrument to fulfill the specific needs of a client. While this particular unit was designed to monitor levels of toxic chemicals commonly encountered at spill sites or near storage vessels, the technology that was developed can be applied to other applications, including monitoring the environment around chemical plant sites or detecting solvents associated with clandestine drug laboratories.

4.13 IMPROVEMENTS IN FIELD-USABLE CHEMICAL PARAMETER SPECTROMETER (CPS-100) INSTRUMENTS

S. Zaromb, R. Battin, D. Domin,* and J. Privette**

4.13.1 Advanced Identification Algorithms

In order to extend the capabilities of the CPS instrument and to improve its reliability, two advanced identification algorithms were developed in 1986, a branching algorithm that extends the applicability of the present CPS sensor array to the identification of > 50 compounds and a mixture-resolving algorithm for resolving mixtures of up to three detectable compounds.

4.13.2 Branching Algorithm

The present CPS instruments use the relative strengths of 16 sensor responses or "parameters" obtained by operating four different electrochemical sensors in four different modes to generate response patterns or "parameter spectra" characteristic of each compound. Sensor responses to electrochemically inactive compounds are obtained in three of the four operating modes in which such compounds are partly preoxidized or pyrolyzed by passage over a noble metal filament heated to an elevated temperature (Stetter et al. 1985b). The resulting parameter spectrum is presently processed by a pattern-matching algorithm (PA) that computes the 16-dimensional Euclidean distance between the measured spectrum and a library of pattern vectors previously determined for up to 30 different compounds.

An alternative computational approach may extend the capability of the CPS to mixtures of detectable compounds (Zaromb and Stetter 1986). A third approach, presented here, combines the present 16-dimensional PA with a preliminary branching algorithm (BA) in order to extend the capability of the CPS to the identification of any one of up to about 100 different compounds. In the BA, a given set of compounds is

divided into smaller subsets according to initial sensor responses, generation of negative (electroreducing) signals in any of the four different sensing modes, and the rates of decay of sensor signals after discontinuance of exposure to a tested compound. These spectral features are used first to assign an unknown compound to an appropriate subset and thereafter to identify it by PA. The branching greatly reduces the computation time and assures that, as the number of candidate compounds increases, parts of the 16-dimensional space do not get so crowded that a high probability of misidentifications results.

The BA improved the percentage of correct identifications for a library of 40 compounds (Zaromb et al. 1986a) and subsequently for other libraries of up to 65 compounds. In all cases, the percentage of correct identification improved significantly.

A total of 65 compounds in 208 test runs yielded a ratio of 135:30 correct:incorrect identifications with branching, as compared to a ratio of 107:58 without branching (i.e., 82% versus 65% correct identifications). The data for 43 runs have not been included in these totals because the test compounds appeared in the branching only once, which would *ipso facto* yield a perfect identification. If these runs are included in the totals, the yield of correct identifications is 86%. Of the 30 misidentifications with the branching algorithm, at least 40% involved chemically related compounds (*o*-xylene or toluene in lieu of *p*-xylene; CHCl_3 in lieu of $\text{Cl}_2\text{C}=\text{CCl}_2$ or vice versa; acetone for isopropanol; ethyl acetate for acetone; ethylene oxide or ethyl acrylate for butyraldehyde; tetrahydrofuran for ethylene oxide; ammonia or *sec*-butyl amine for ethyl amine).

The 82% yield of correct identifications with the BA (as compared with a 65% yield without branching) was achieved by excluding the data from one of the four sensors. Further improvements in the percentage of correct identifications may result from replacement of the defective sensor and also from refinements in the algorithm.

4.13.3 Mixture-Resolving Algorithm

A mixture-resolving algorithm (MRA) was written, debugged, and applied to a data set for mixtures of up to three detectable compounds. Defective data sets (exhibiting excessive variability or nonlinearity) for some of the runs were eliminated from the evaluation. These included all acrylonitrile-containing mixtures. For the remaining runs, the mixture-resolving algorithm computed not only the concentrations but also their probable errors, by using the approach outlined by Zaromb and Stetter (1985). In ten runs, the computed results included compounds not present in the prepared mixture; nevertheless, agreement within error limits is good, as the error bars for the absent compounds are comparable to or greater than the computed concentrations. In eight of the 66 runs, some or all of the listed compounds (as computed) differed from those in the prepared mixture, and the computed concentrations of the compounds actually present differed from the prepared concentrations by at least a factor of two. The results of these eight runs are regarded as poor. Four runs showed good qualitative but poor quantitative agreement, in that the compounds listed by the algorithm were correct, but the concentration computed for at least one differed from the prepared concentration by at least a factor of two. Finally, in three runs, substantially correct

concentrations were listed for one or two compounds, but the results were incomplete in that at least one compound was erroneously eliminated by the algorithm.

All in all, qualitative agreement was good (no poor or incomplete results) in 55 of the 66 runs (83.3%), and quantitative agreement was good in 51 of the 66 runs (77.3%). These somewhat encouraging results were obtained with a limited data set comprising various combinations of up to three out of five possible compounds.

4.13.4 Future Prospects

The BA could be retrofitted into the already-delivered CPS-100 prototypes, which would improve the reliability of the identifications obtained with these instruments. The MRA will require further work before it can be usefully applied to the resolution of unknown mixtures under field conditions. However, a simplified version of the MRA could be used to resolve overlapping peaks from a gas chromatograph (GC) in a GC/CPS system.

4.14 APPLICATION OF GC/CPS TO FIRE-GENERATED HAZARDOUS VAPORS AND OTHER TOXIC VAPOR MIXTURES

W.J. Buttner, D. Domin, V.C. Stamoudis, and S. Zaromb*

4.14.1 Introduction

A major emphasis of the Instrument Group of the Environmental Research Division has been the development of a portable toxic vapor analyzer (CPS-100). The CPS-100 can identify and monitor trace levels (1 to 500 ppm) of a wide variety of hazardous chemicals. Although identification efficiencies of 90% are achieved for libraries of up to 26 compounds, the portable CPS-100 instrument is presently unable to easily analyze mixtures. A more detailed description of the present CPS-100 prototype was presented in Section 4.12.

In many hazardous situations, however, a variety of toxic vapors would probably be present. For example, the combustion products of many common materials expose fire fighters to a wide range of toxic vapors. An instrument that could perform quick and accurate analyses of mixtures would be a powerful tool. The Center for Fire Research at the National Bureau of Standards has funded a program to expand CPS-100 capabilities to include mixture analysis.

Two approaches are being developed simultaneously. Algorithms are being developed to analyze CPS data for multiple components; these algorithms assume that the resulting CPS signals are formed from linear contributions of each component in a mixture. A generalized algorithm for up to five components has been developed with

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favorable results. This algorithm, however, requires significantly more computing power and memory space than is available in a portable unit. Regardless of sophistication, these algorithms will become increasingly unreliable as the number of components in the mixture increases.

In a parallel effort, a prototype interfaced gas chromatograph/CPS (GC/CPS) instrument has been constructed. Instrumentation of this nature, coupled with the chemically selective detection technology afforded by CPS, will allow for separation of complex mixtures into single components or simple mixtures. Major advantages of the use of GC/CPS for mixture analysis are (1) identification of each chromatographic peak (including overlapping peaks due to two or three closely spaced compounds) on the basis of the multiple responses of the CPS detection in addition to the GC retention time (RT); (2) quantification of partially resolved components by use of the multiple response generated by CPS; and (3) detection, but not identification, of unexpected spurious components with RT values identical to chemical species stored in the library of the CPS detector.

4.14.2 Results

Table 4.10 lists several of the compounds that have been analyzed in the prototype GC/CPS. Figure 4.8 depicts representative CPS response patterns. The response patterns of the sensors were initially obtained in three modes of operation: (1) electrochemical analysis of the GC eluent subsequent to passage through the flame ionization detector (FID; corresponding to channels 1-4 in Fig. 4.8), (2) electrochemical analysis of the GC eluent without exposure to a heated filament or the FID (corresponding to channels 5-8 in Fig. 4.8), and (3) electrochemical analysis of the eluent as it passed through the column and over a heated platinum coil but bypassed the FID (corresponding to channels 9-12 in Fig. 4.8). Subsequently, to optimize selectivity, a fourth mode of operation was added in which the eluent was exposed to a heated rhodium filament prior to electrochemical analysis (corresponding to channels 13-16). The electrochemical sensors consisted of two gold electrodes, biased to -200 mV and +300 mV (vs. a Pt-air reference); a Pt electrode biased to +200 mV, and a commercial Pt electrode (National Draeger model ES 45950K) biased to 0.00 mV. As with the CPS monitoring of the steady-state response of single compounds, the transient response patterns generated are highly selective. For most of the compounds tested to date, sufficient resolution is obtained with the GC column to minimize the need for the mixture-resolving algorithms. However, two sets of binary mixtures that were

TABLE 4.10 Compounds analyzed by prototype GC/CPS

Compound	RT (min)
Acetone	0.91
Acetonitrile	2.12
Acrolein	0.89
Acrylonitrile	2.14
Benzene	1.67
Ethyl Acetate	1.33
Isobutyraldehyde	1.02
Toluene	3.39

FIGURE 4.8 CPS patterns obtained for the indicated compounds. RT is the GC retention time as measured by the FID. Channels 1 to 4 are the electrochemical response of the FID eluent, 5 to 8 are the electrochemical response to the eluent by-passing the Pt filament and FID, and 9 to 12 are the electrochemical response to eluent partially pyrolyzed at a heated platinum filament.

tested did not yield baseline resolution from the GC column, but had CPS responses that allowed identification.

The trace in Fig. 4.9 demonstrates the improved selectivity of the CPS detector. Figure 4.9B shows the nonselective response of the FID detector to a liquid acetonitrile:benzene (1:1 by volume) mixture. Although two distinct peak maxima were obtained, baseline resolution was not. Figure 4.9A depicts a sensor response (the commercial sensor monitoring the eluent passing over the heated platinum filament, corresponding to channel 12 in Fig. 4.8) arising primarily from benzene with negligible interference from acetonitrile. Similarly, Fig. 4.9C depicts a sensor response (the high-potential gold sensor monitoring the eluent passing through the FID, corresponding to channel 2 in Fig. 4.8) to acetonitrile. This demonstrates the ability of the CPS to simultaneously and selectively detect multiple components.

The nearly overlapping peaks shown in Fig. 4.9 for an acetonitrile-benzene mixture would have probably been fully resolved with lower concentrations of the two components. The high concentrations arose from the use of liquid samples pending acquisition of a gas injector port; such levels are not likely to be encountered in the

FIGURE 4.9 (A,B,C) Illustrative CPS responses to a benzene-acetonitrile mixture. (A) Current-time response of a commercial CO detector when the GC eluent was passed over a heated platinum filament. (B) FID response. (C) Current-time response of a gold sensor (biased to +300 mV vs. an air reference electrode) to the eluent from the FID.

vapor phase. With the lower vapor concentrations achievable with the gas injector port, overlapping peaks should be relatively rare. However, acetone-acrolein had nearly identical retention times, and a 1:1 mixture by volume eluted through the column was observed as a single peak by the FID. These two compounds have distinct CPS histograms (Fig. 4.8). The response of channel 7 (the platinum sensor monitoring the untreated eluent) was due solely to acrolein; this response would serve as a highly selective marker for acrolein. The presence of acetone (or other chemical species) could then be determined from the CPS response corrected for the contribution of acrolein. In the case of acetone and acrolein, complete resolution of the GC peaks would probably not be obtained even at significantly lower concentrations; the use of the CPS detector system eliminates the need for complete (or partial) separation.

4.14.3 Conclusions

An interfaced GC/CPS instrument would be a powerful and inexpensive tool for the analysis of mixtures. The feasibility of such an instrument has been demonstrated only for a bench top GC instrument, but the technology should be readily applied to existing portable GC units. An interfaced GC/CPS unit would have several additional advantages. Libraries for the conventional (steady-state) CPS instrument are presently built by running each gas separately, a time-consuming (expensive) process. In a natural extension, the GC/CPS would build CPS libraries by using standard mixtures rather than single compounds, as is presently done. The 26-compound library of response patterns in the present CPS units might be not only expanded but also generated in a fraction of the time now needed.

Standard mixtures would allow for complete and facile calibration of the sensor array in the GC/CPS, and would correct for long-term drift in the sensor response. A more subtle application of GC/CPS technology would be the rapid assessment of a sensor's sensitivity and relative selectivity for various compounds of interest. This would allow grouping of similar sensors, which then might be potentially used interchangeably in existing arrays.

4.15 AMPEROMETRIC MICROSENSORS FOR CHEMICAL DETECTION

*W.J. Buttner and J.R. Stetter**

4.15.1 Introduction

The first modern amperometric gas sensor was the Clark electrode (Clark et al. 1953). In successive decades, many improvements were made in this device, and by the 1970s a wide range of amperometric gas sensors had been developed for many toxic compounds (Bay et al. 1972a, 1972b; La Conti et al. 1981). As the understanding of these sensing systems continues to improve, better stability, smaller (microsensor) size,

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greater sensitivity, and superior selectivity will result. Already, amperometric detection has achieved ppb-level sensitivity for certain analytes (e.g., SO_2 and NO_2 ; Stetter et al. 1977).

The decided advantages of microelectronic electrochemical sensors include reduced cost, reduced size, and faster response time. In addition, much greater control of the device is possible. In view of these advantages, we have been developing microsensor technology for use in personal and collective air purification systems (e.g., gas masks) through a contract from the U.S. Army Chemical Research and Development Center.

4.15.2 Microfabricated Sensors

Nafion (DuPont trademark) was chosen as the substrate for the electrode structures described above. The microsensor system is suitable for a H_2S , NO_2 , NO , or SO_2 detector (La Conti et al. 1981), and it has been used for many years in practical sensors for such gases (Buttner et al. 1987). This sensor system uses a Nafion solid polymer electrolyte that is more likely to be compatible with integrated microsensor fabrication processes than would liquid electrolytes such as sulfuric acid and propylene carbonate.

Three configurations of test sensors were fabricated: (1) "standard" sensors in which an existing amperometric gas sensor design was used; (2) several different sensors with standard counter and reference electrode designs but with microfabricated working electrodes deposited on Nafion sheets; and (3) structures consisting entirely of microfabricated electrodes and spin-coated Nafion electrolyte film. The microfabricated working electrodes used in this study were square grids (6 mm on a side); the grid density varied according to the parameters outlined in Table 4.11. This allowed the relative reactivity of each sensor design to be measured and each step to be monitored in the conversion of the "standard" amperometric sensor to the integrated microfabricated sensor geometries. This set of experiments led to (1) identification of the important sensor/process design parameters and test protocols, (2) development of

TABLE 4.11 Microfabricated working electrode configurations

Metal Grid Width	Grid Spacing	Number of Holes	Total Inner Perimeter	Ratio (P_i/P_o)
125 μm	200 μm	289	231 mm	9.6
0.55 mm	0.55 mm	25	55 mm	2.3
2.0 mm	2.0 mm	1	8 mm	0.3

the required process technology for microfabrication, and (3) understanding of the chemical sensor's analytical performance in the process of miniaturizing both its chemistry and the geometry.

4.15.3 Standard Design vs. Sensors with Microfabricated Working Electrodes

The current densities of the three working electrode geometries (Table 4.11) and the standard sensor differed by more than an order of magnitude upon first testing. The initial results are summarized in Table 4.12. The sensitivity of the sensor is very dependent upon the structure of the sensing electrode. Each of these four sensors was fabricated with a platinized platinum mesh counter and reference electrode pressed into the Nafion before deposition of the gold working electrodes.

The fine-grid electrode sensor produced an initial signal approximately 11 times that of medium-grid sensors for H_2S and NO . The initial background signals for the two sensing microelectrodes were approximately the same. Signal intensities for these sensors changed substantially with time. While the signal intensity for the medium-grid sensor increased slightly after three weeks, the signal for the fine-grid design decreased significantly. More importantly, however, the signal-to-background (S/B) ratio improved for both sensors. No significant signal was observed for the coarse-grid design. The relative signal obtained for three sensors (the standard sensor and the microfabricated sensors with the fine and medium grids), normalized to the strongest signal, indicates that the electrochemistry is essentially the same for all of the gold electrodes. All experimental parameters (e.g., gas concentration, flow rate, cell bias) were constant during this experiment.

4.15.4 Response of Microfabricated Electrodes

The net current response induced by the sample gas, which in this case was 200 ppm of H_2S , was significantly smaller for a fully microfabricated sensor than that of the "standard" design sensor. The S/B ratio, however, was excellent, and more importantly, the response time of the minaturized system was much faster. The rise and recovery times (from 10 to 90% change) for the microsensor were 1 and 2.5 seconds, respectively; those for the standard sensor were 3.7 and 3 seconds, respectively. This difference can be easily explained by the volume of sensor and electrolyte that must be equilibrated to reach steady state.

4.15.5 Conclusions

In summary, we have fabricated several new amperometric electrochemical sensor structures and compared the analytical characteristics of the resultant sensors. The results have several important implications:

- (1) Methodology can be developed to fabricate amperometric electrochemical sensors by using electronic device technology. Physical structures of the entire sensor were fabricated by using

TABLE 4.12 Sensor signal for various gas mixtures^a (μA)

Gas Mixture	Medium Grid			Fine Grid			Standard Sensor		
	S	B	S/B	S	B	S/B	S	B	S/B
Day 1									
92 ppm NO/N ₂	0.22	0.30	0.73	2.38	0.28	8.5	---	---	---
83 ppm H ₂ S/N ₂	2.5	0.30	8.3	27.1	0.28	96.8	---	---	---
Day 2									
92 ppm NO/N ₂	0.879	0.10	8.5	0.24	0.01	12.0	3.2	0.1	32
83 ppm H ₂ S/N ₂	2.98	0.10	28.9	2.7	0.02	136	14.7	0.1	147
49 ppm NO ₂ /air	0.17	0.10	1.65	0.02	0.02	1.0	0.63	0.1	6.3
8.2 ppm SO ₂ /air	0.02	0.10	0.19	0.036	0.02	1.8	0.1	0.1	1.0
200 ppm CO/air	0.00	0.10	0.00	0.00	0.02	0.0	0.0	0.1	0.00
100 ppm HCN/air	spike	0.10	---	spike	0.02	---	spike	0.1	---

^aThe sensor was operated at a constant potential of +300 mV versus the Pt/air reference electrode; the "standard" porous gold electrode sensor was tested for comparison with the microelectrodes. S = signal; B = background.

microfabrication technology, with the resulting amperometric sensor, including the electrolyte, being only a few millimeters square and a few micrometers thick.

- (2) Electrochemical responses were obtained for model micro-fabricated working (sensing) electrodes. This means that the structures fabricated have significant electrocatalytic activity; the qualitative nature of the activity is independent of geometry, while the quantitative catalytic activity is extremely dependent upon the geometry.
- (3) The response time and S/B ratio can be substantially improved over existing amperometric sensors.
- (4) Sensor characteristics may be "engineered" by development of the fabrication technology by precise control of the sensor geometry and materials of construction.

We should be able to build precise structures with exceptionally high repeatability and also to engineer sensitivity and selectivity for a given application.

4.16 A SIMPLE PERMEATION ABSORBER FOR SAMPLING AND PRECONCENTRATING HAZARDOUS AIR CONTAMINANTS

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4.16.1 Background and Scope

We have developed a portable liquid chromatograph (LC) for the detection, identification, and quantification of low concentrations of highly mutagenic and carcinogenic PAA that may be encountered in synthetic fuel processes, dyestuff and pesticide manufacture, and other industries and commerce (Otagawa et al. 1986, 1987). In conjunction with that work, we evaluated alternative sampling means that preconcentrate PAA vapors in air and provide a suitable interface between air samples and the portable LC (Zaromb et al. 1986b).

This led to the invention and evaluation of an alternative method of preconcentrating vapors of PAA and possibly also of other hazardous compounds, on the basis of the unidirectional permeation of such vapors through a selectively permeable membrane into a small volume of absorbing solution that is suitable for direct injection into a liquid or gas chromatograph or other analytical instrument (e.g., a mass spectrometer). Besides the advantages of relative simplicity and rapidity, the use of a properly chosen liquid extractant should have the further benefits of selectivity and

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irreversibly trapping and stabilizing those absorbed vapors that would remain highly volatile or reactive in an adsorbed state.

Although our experiments were performed mainly with aniline, for comparison with the cryogenic sampling approach (Zaromb et al. 1986b), we expect that the preconcentration technique should be applicable to other PAA vapors and to many other hazardous compounds (e.g., the hydrazines).

4.16.2 Progress in 1986

The permeation apparatus consisted of an aluminum-covered, 1-L or 5-L polytetrafluoroethylene sampling bag having an outlet valve connected to a permeation absorber and an inlet valve connected to a circulation pump. The outlet of the pump was connected to the outlet of the absorber, forming a closed flow circuit. The absorber consisted of an outer polyethylene tube, about 1 cm i.d., and an inner 15-cm length of 1-mm-i.d. microporous polytetrafluoroethylene tubing terminating at solid (nonporous) inlet and outlet nipples. The portion of each nipple extending outside the outer polyethylene tube was closed off with a polyethylene stopper or a rubber septum through which a syringe needle could be inserted to inject or withdraw an extractant liquid. The inner tubing was filled with an aqueous solution that could not pass through the hydrophobic pores but absorbed the aniline permeating from the circulating air sample. The volume of liquid required to fill this tubing was 0.12 mL, a size appropriate for direct LC analysis.

The critical parameter used in evaluating the performance of a preconcentrator sampler is the collection efficiency, ϵ , which is the ratio of the amount of an analyte that is actually collected to the total amount of the analyte contained in the volume of air that was passed through the sampler. We measured ϵ by using our LC system (Otagawa et al. 1986). Chromatographed aniline peaks of standard and of collected liquid samples were measured, and the theoretical peak height and area corresponding to 100% collection efficiency were calculated for each experiment. For each test sample, the ratio of measured to calculated theoretical peak heights or areas gave the approximate collection efficiency.

The permeation absorber can be used in two alternative modes -- a recirculating, multiple-pass mode and a single-pass mode, without recirculation. A theoretical model of the permeation absorption sampler yields the following relation between the collection efficiencies ϵ_r and ϵ_{nr} of a single permeation absorber in a loss-free recirculating mode and in a non-recirculating mode, respectively:

$$\epsilon_r = 1 - e^{-N\epsilon_{nr}}, \quad (4-1)$$

where N , the number of passes, is given by the relation

$$N = vt/V, \quad (4-2)$$

v is the flow rate (in L/min) of the analyte-containing air sample of volume V (in L) past the permeation absorber, and t is circulation time (in minutes). If analyte losses occur in the recirculating system (as a result of leaks or chemical reactions), equation 4-1 assumes the form:

$$\epsilon_r = \frac{\epsilon_{nr}}{\epsilon_{nr} + K_L} (1 - e)^{-(\epsilon_{nr} + K_L)}, \quad (4-3)$$

where K_L is a loss rate factor.

Figure 4.10 shows the variation of ϵ_r with N for a flow rate of 2.3 L/min. The scatter of the experimental points is attributable primarily to the method of sample preparation and secondarily to variability of the loss rate factor K_L and to other errors. At the flow rate of 2.3 L/min and 5.6 passes (Fig. 4.10) the measured collection efficiency was $84 \pm 20\%$. The value of ϵ_{nr} deduced from Fig. 4.10 and equation 4-3 is in the range of 0.4-0.5 (40-50%).

4.16.3 Conclusions

In view of its fairly high estimated collection efficiency, the non-recirculating mode offers several important advantages over the recirculating mode. These include

- (1) A much shorter sampling time;
- (2) A far simpler sampling procedure;
- (3) A much simpler system; and hence
- (4) Fewer sources of error (elimination of most potentially reacting or adsorbing contacting surfaces, which is especially important at low analyte concentrations).

FIGURE 4.10 Dependence of ϵ on n for $v = 2.3$ L/min

The permeation-type absorber offers significant advantages over the other samplers studied. It can be used with an arbitrarily high volume of air sample, which translates into a high preconcentration ratio (about 200 for a 5-L volume). The high preconcentration ratio translates in turn into high sensitivity (< 1 ppb [by volume] in air with our portable LC system). Moreover, its collection efficiency is not affected by humidity. The permeation absorption procedure for sampling and monitoring PAA in dry or humidified air with a portable LC instrument is simple, relatively fast (5-10 minutes), and adaptable to automation.

The permeation absorption sampler has been tested in practice only with aniline samples in recirculating modes and with a mixture of PAA in a non-recirculating mode. However, according to our theoretical model, this sampler should also be applicable to other types of compounds. Basic analytes, such as the highly carcinogenic hydrazines [N_2H_4 , $N_2H_3CH_3$, $N_2H_2(CH_3)_2$] should be readily absorbed in the acidic extractant. Other extractants may be developed to absorb other vapors (e.g., a basic extractant for acidic vapors).

An extractant liquid may be selected to react rapidly with the analyte to effect a change that can be measured photometrically (e.g., colorimetrically, with a dye, or by chemiluminescence). This could yield a very small and lightweight, yet highly sensitive, near-real-time, self-contained analytical instrument.

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APPENDICES FOR CHAPTER 4

**Organic Geochemistry and Environmental
Instrumentation Program**

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APPENDIX 4-A. STAFF QUALIFICATIONS

Organic Geochemistry and Environmental Instrumentation Programs

Name	Position	Highest Degree	Major	Year Received	Institution
Bonilla, Jose	Postdoctoral Appointee	Ph.D.	Analytical Chemistry	1986	The University of Oklahoma
Buttner, William J.	Assistant Electro- chemical Engineer	Ph.D.	Chemistry	1982	Michigan State University
Otagawa, Takaaki*	Postdoctoral Appointee	Ph.D.	Physical Electro- Chemistry	1982	Texas A&M University
Picel, K.C.	Assistant Scientist	Ph.D.	Environmental Health Sciences	1985	The University of Michigan
Stamoudis, Vassilis C.	Environmental Chemist	Ph.D.	Organic Chemistry	1973	Michigan State University
Zaromb, Solomon	Electrochemical Engineer	Ph.D.	Physical Chemistry	1954	Polytechnic Institute of Brooklyn

*No longer a member of the Division.

APPENDIX 4-B. OUTSTANDING PROFESSIONAL ACTIVITIES AND AWARDS

**Organic Geochemistry and Environmental
Instrumentation Programs**

- S. ZAROMB--Invited lecture on "Alkaline Aluminum-Air Batteries," Alcoa Laboratories Centennial Electrochemistry Seminar, 1-15 June 1986, Farmington, PA.
- V.C. STAMOUDIS--Invited lecture on "Bioassay-Directed Characterization of Energy-Related Complex Mixtures," University of Michigan, 12 June 1986, Ann Arbor, MI.

APPENDIX 4-C. SPECIAL EVENTS ORGANIZED**Organic Geochemistry and Environmental
Instrumentation Programs**

STAMOUDIS, V.C. Organized and conducted a symposium on "Health and Environmental Effects of Complex Organic Mixtures," 192nd National Meeting, American Chemical Society, Division of Environmental Chemistry, 7-12 September 1986, Anaheim CA.

APPENDIX 4-D. EDUCATIONAL PROGRAM PARTICIPANTS**Organic Geochemistry and Environmental
Instrumentation Programs**

- R. BATTIN. North Central College. Undergraduate Research Program. Assisted in the development and testing of algorithms and sensor arrays for the analysis of mixtures of hazardous compounds in air. January 1986 - July 1987.
- S. BECKER. Murray State University. Undergraduate Research Program. Assisted in the assembly of a portable toxic vapor analyzer developed for the U.S. Coast Guard. January 1986 - January 1987.
- W. BELISLE. Alabama State University. Undergraduate Research Program. Assisted in the development and fabrication of electrochemical microsensors for the detection of hazardous gases. June 1986 - August 1986.
- B. BRUNSMAN. University of Nebraska. Undergraduate Research Program. Assisted in adapting liquid chromatography to electrochemical detectors for the analysis of mutagenic components in coal-derived materials. June 1986 - August 1986.
- J. CARILLO. Plainfield High School. Pre-College Summer Student. Assisted in fabricating and evaluating sensory devices for the detection of volatile pollutants. June - August 1987.
- D. DOMIN. Illinois Benedictine College. Undergraduate Research Program. Performed various tests of the responses of sensor arrays to up to 100 different hazardous compounds and to mixtures of such compounds in air. June 1986 - July 1987.
- A. FERMAINT. University Interamericana. Undergraduate Research Program. Assisted with the development of a preconcentrator device for analyzing low-level hazardous vapors in air. June 1986 - August 1986.
- G.M. FLANAGAN. Elmhurst College. Undergraduate Research Program. Assisted in sample preparation and analysis of energy-related materials by computer-assisted gas chromatography. September 1986 - present.
- M. FIESMAN. College of St. Francis. Undergraduate Research Program. Assisted in liquid chromatography measurements and in mutagenicity testing of coal-conversion materials. January 1986 - May 1986.
- D. FRISON. Mississippi Valley State University. Undergraduate Research Program. Assisted in chemical analysis and toxicological characterization of coal liquids and environmental samples. January - April 1987.
- C. GENTRY. Murray State University. Undergraduate Research Program. Assisted in the construction, testing, and evaluation of electrochemical sensors and sensor arrays. May 1986 - July 1987.

- N. IMBROCK. College of St. Francis. Undergraduate Research Program. Assisted in fabricating electrochemical methane sensors and in mutagenicity testing of coal conversion material. January 1986 - September 1986.
- L. MITNAUL. Benedict College. Undergraduate Research Program. Assisted in the development and testing of improved sensors for the detection of hazardous gases. June 1986 - August 1986.
- M. PORTELLOS. Allegheny College. Undergraduate Research Program. Studied the effects of flow rates on relative response factors in the analysis of energy-related complex mixtures by gas chromatography. June - August 1987.
- J. PRIVETTE. College of Wooster. Undergraduate Research Program. Assisted in writing computer algorithms to process data gathered by the CPS-100. June 1986 - August 1986.
- T. REEME. University of Illinois. Undergraduate Research Program. Assisted in documenting the protocols used in characterizing complex, coal-derived material by computer-assisted gas chromatography. June 1986 - September 1986.
- L. RICE. South Carolina State College. Undergraduate Research Program. Assisted in the development of a preconcentrator device for analyzing low-level hazardous gases. June 1986 - August 1986.
- C. SNYDER. Elmhurst College. Undergraduate Research Program. Assisted in the analysis of coal-conversion materials by gas and liquid chromatography. June 1986 - October 1986.
- V. VLASTNIK. Illinois Benedictine College. Undergraduate Research Program. Assisted in the analysis of coal-conversion materials by computer-assisted gas chromatography and gas chromatography/mass spectrometry. January 1986 - September 1986.
- M. WILLIAMS. University of Pittsburgh. Undergraduate Research Program. Assisted in chemical and biological/toxicological characterization of energy-related complex mixtures. June - August 1987.
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APPENDIX 4-E. PUBLICATIONS AND ORAL PRESENTATIONS

Organic Geochemistry and Environmental Instrumentation Programs

1. Refereed Journal Articles*

- Haugen, D.A., and V.C. Stamoudis. Isolation and identification of mutagenic polycyclic aromatic hydrocarbons from a coal gasifier condensate. *Environmental Research* 41(2):400-419 (1986). [DOE/METC/FE]
- Haugen, D.A., V.C. Stamoudis, M.J. Peak, and A.S. Boparai. Isolation of aminophenanthrene from a mutagenic coal gasification condensate. *Environmental Research* 39:60-73 (1986). [DOE/OHER/FE]
- Otagawa, T., J.R. Stetter, and S. Zaromb. Portable liquid chromatograph for analysis of primary aromatic amines in coal-derived materials, *J. Chromatography* 360(1):252-259 (1986). [DOE/OHER/FE]
- Swanson, M.S., D.A. Haugen, C.A. Reilly, Jr., and V.C. Stamoudis. Protection of uridine diphosphoglucuronic acid and DT-diaphorase against the cytotoxicity of aromatic hydrocarbons isolated from a complex coal-conversion material. *Toxicology and Applied Pharmacology* 84:336-345 (1986). [DOE/OHER]

2. Books, Book Chapters, and Collections of Conference Proceedings

- Picel, K.C., M.S. Simmons, and V.C. Stamoudis. Sunlight photolysis of selected indoles and carbazole in aqueous coal-oil systems. In: *Photochemistry of Aquatic Environmental Systems*, R.J. Zika and W.J. Cooper (eds.). Symposium Series 327, American Chem. Society, Washington, DC. 1987. pp. 44-60. [DOE/METC/FE]

*For published material, the names of all Environmental Research Division authors are underlined. (Included are Division members who participated in a project but left the Division before the results were published.)

**Funding agency (abbreviations are spelled out at the end of this appendix).

3. Reports

Reilly, C.A., Jr., K.E. Wilzbach, J.R. Stetter, D.A. Haugen, F.R. Kirchner, V.C. Stamoudis, M.J. Peak, T. Matsushita, A.S. Boparai, and R.E. Jones. Synfuels environmental research program for high-Btu coal gasification: Health effects summary report. ANL/SER-7. Argonne National Laboratory. October 1986. [DOE/OHER/FE]

Stamoudis, V.C. Chemical and toxicological characterization of Morgantown Energy Technology Center fixed-bed gasifier materials. DOE/MC/49533-1809 (ANL/SER-6). U.S. Dept. of Energy. June 1986. [DOE/METC/FE]

4. Published Conference Proceedings

Brubaker, K.L., J. Bonilla, V.C. Stamoudis, A.S. Boparai, and C.T. Snyder. Products of the neutralization of hydrazine fuels with hypochlorite, II, In: Proceedings of the 1987 JANNAF Safety and Environmental Protection Subcommittee Meeting, 5-7 May 1987, NASA/Lewis Research Center, Cleveland, OH. 1987. (in press). [U.S. Air Force]

Buttner, W.J., R.D. Battin, S.E. Becker, D.S. Domin, C.R. Gentry, W.P. McDowell, W.R. Penrose, S. O'Malley, V.C. Stamoudis, J.R. Stetter, J.O. Stull, R.J. Voogd, and S. Zaromb. A portable instrument for multiple compound detection and analysis. In: Proceedings of the 4th Technical Seminar on Oil Spills, 10-12 February 1987, Environment Canada, Toronto, Canada. 1987. pp. 295-301. [U.S. Coast Guard]

Demirgian, J.C., V.C. Stamoudis, J.R. Stetter, K. Brubaker, and R. Cole. Application of GC/FTIR to environmental degradation study. 1986 Pittsburgh Conference of Analytical Chemistry and Applied Spectroscopy, March 1986, Atlantic City, NJ. Paper No. 472. 1986. [U.S. Air Force]

Haugen, D.A. and V.C. Stamoudis. Characterization of mutagenic polycyclic aromatic hydrocarbons in a coal-derived material. 192nd Meeting of the American Chemical Society, Division of Environmental Chemistry, 7-12 September 1986, Anaheim, CA. ACS Series, Vol. 26, No. 2, 1986. pp. 74-77. [DOE/OHER/FE]

Picel, K.C., and V.C. Stamoudis. Chemodynamic measurements in complex organic mixtures using computer-assisted capillary gas chromatography. 192nd Meeting of the American Chemical Society, Division of Environmental Chemistry, 7-12 September 1986, Anaheim, CA. ACS Series, Vol. 26, No. 2. 1986. pp. 26-29. [DOE/METC/FE]

Stamoudis, V.C., K.C. Picel, and V.J. Vlastnik. Computer-assisted gas chromatography and data management system for analysis of coal-derived complex mixtures. 192nd Meeting of the American Chemical Society, Division of Environmental Chemistry, 7-12 September 1986, Anaheim, CA. ACS Series, Vol. 26, No. 2. 1986. pp. 22-25. [DOE/METC/FE]

Zaromb, S., R. Battin, W.R. Penrose, J.R. Stetter, and V.C. Stamoudis. Extending the capabilities of the portable chemical parameter spectrometer to identification of up to 100 compounds. In: Proceedings of the Second International Meeting on Chemical Sensors, J.L. Ancouturier et al. (eds.). 7-10 July 1986, University of Bordeaux, Bordeaux, France. 1986. pp. 739-742. [U.S. Coast Guard]

Zaromb, S., W.J. Buttner, V.C. Stamoudis, D. Domin, and J. Privette. Feasibility study of field detection and analysis of the toxic products of combustion. In: Proceedings of the Annual Conference on Fire Research, 3-6 November 1986, National Bureau of Standards, Gaithersburg, MD. 1986. pp. 40-43. [CFR/NBS]

Zaromb, S., T. Otagawa, J.R. Stetter, and K. Quandt. Preconcentration of airborne primary aromatic amines for analysis by a portable liquid chromatograph. 192nd Meeting of the American Chemical Society, Division of Environmental Chemistry, 7-12 September 1986, Anaheim, CA. ACS Series, Vol. 26, No. 2. 1986. pp. 14-17. [DOE/OHER/FE]

5. Published Abstracts, Notes, Reviews, Comments, and Letters

Stamoudis, V.C.. Analysis of energy-related complex mixtures: Computer-assisted gas chromatography and data management systems (Abstract). EPA Symposium on the Application of Short-Term Bioassays in the Analysis of Complex Environmental Mixtures, October 1986, Durham, NC. Abstract Booklet, Paper No. 2. 1986. p. 7. [DOE/METC/FE]

6. Patents

U.S.P. 4,670,405, June 2, 1987, Sensor Array for Toxic Gas Detection, J.R. Stetter, S. Zaromb, and W.R. Penrose.

U.S.P. 4,591,414, May 27, 1986, Method of Determining Methane and Electrochemical Sensor Therefor, S. Zaromb, T. Otagawa, and J.R. Stetter.

CODES FOR FUNDING AGENCIES

CFR = Center for Fire Research (in National Bureau of Standards)
DOE = U.S. Department of Energy
FE = Fossil Energy (in U.S. Department of Energy)
METC = Morgantown Energy Technology Center
NBS = National Bureau of Standards
OHER = Office of Health and Environmental Research (in U.S. Department of Energy)

5-1/5-2

5 FUNDAMENTAL MOLECULAR PHYSICS AND CHEMISTRY

5 FUNDAMENTAL MOLECULAR PHYSICS AND CHEMISTRY

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5.1 PROGRAM OVERVIEW

Mitio Inokuti, Program Manager

The research of the Fundamental Molecular Physics and Chemistry Program deals with the properties of molecules that are related to their interactions with photons, electrons, and other charged particles. Specifically, we deal with photons ranging from the visible region to the far-vacuum-violet region, and with electrons of energies ranging from several electron volts to hundreds of electron volts. From this broad area of research we choose topics of study that meet the needs of the agencies that support our work--primarily the Office of Health and Environmental Research (U.S. Department of Energy) and secondarily the Office of Naval Research (U.S. Department of Defense) and National Bureau of Standards (U.S. Department of Commerce).

A major thrust of our research is to provide fundamental data needed in radiation research. For example, we attempt to determine cross sections for the interactions of electrons and photons with molecules. Such data are indispensable for microscopic analysis of the physical action of radiation on any matter, including the biological cell and its constituents. The same data are also required in theoretical dosimetry. Another major thrust of the Fundamental Molecular Physics and Chemistry Program is to develop methods for detecting and characterizing molecular species, including excited states, radicals, and other unstable species. To this end, resonance-enhanced multiphoton ionization spectroscopy is being developed to elucidate dynamics of electronic excited states. This technique is important in advanced measurement science because of its high sensitivity and selectivity.

The following reports on our research work are classified into four general areas: theoretical studies in radiation physics and chemistry (section 5.2), electron collision studies (section 5.3), photophysics studies with multiphoton resonant absorption (section 5.4), and photophysics studies in the vacuum ultraviolet (section 5.5).

5.2 THEORETICAL STUDIES IN RADIATION PHYSICS AND CHEMISTRY

5.2.1 Summary

We conduct theoretical studies on elementary processes that occur in molecules subjected to ionizing radiations. These studies concern two general areas: (1) the cross-section data for collision processes, and (2) application of these data to the analysis of the initial stage of radiation actions.

The first area may deal with a large variety of collision processes involving a variety of incident particles. However, electrons are the most important because they appear abundantly as secondary particles in matter upon the incidence of any ionizing radiation. Photons in the far ultraviolet and soft x-ray regions are also important because they interact most strongly with any matter and because of the close relation between the photoabsorption and inelastic collisions of fast charged particles. Thus, our work on the cross-section data concerns electrons, other fast charged particles, and far-ultraviolet photons.

In the second area, we concentrate on the theory of the yields under ionizing radiation of initial molecular species such as ions and excited states. The work in this area starts with the knowledge of relevant cross-section data and involves analysis of the consequences of many collision processes both for matter itself and for the electrons and other charged particles generated in matter.

In both of the areas, we have made considerable progress. In particular, we have made a breakthrough in the second area, in a generalization of the Spencer-Fano theory of electron degradation to time-dependent cases, which are exemplified by some recent pulse radiolysis experiments. Section 5.2.8 represents the initial report on this topic; fuller accounts of the work will soon appear in the form of journal publications. In the first area, we made notable progress in renewed work on the theory of electron-molecule collisions and molecular photoionization (section 5.2.5).

5.2.2 Analytic Representation of Secondary-Electron Spectra

M. Inokuti, M.A. Dillon, J.H. Miller, and K. Omidvar**

[Summary of a paper published in *Journal of Chemical Physics* 87:6967-6972 (1987)]

The secondary-electron spectrum, or the energy distribution of the ejected electrons produced by charged-particle impact, is crucial information for the microscopic modeling of radiation actions. We show here a general method for systematizing a bulk of data on secondary-electron spectra into a small number of indices. Our method is based on the firm theoretical grounds of full examination of the mathematical physics involved.

The Bethe theory (Inokuti 1971) leads to an expression of the form

$$d\sigma/d\epsilon = 4\pi a_0^2 z^2 (R/T) [A(\epsilon) \ln T + B(\epsilon)] \quad (5-1)$$

for the secondary-electron spectrum $d\sigma/d\epsilon$ resulting from the collision of a particle with charge ze at speed v . Here $T = mv^2/2$, $R = me^4/2\hbar^2$ is the Rydberg energy, $a_0 = \hbar^2/me^2$ is the Bohr radius, and ϵ is the kinetic energy of the secondary electron. The coefficient $A(\epsilon)$ is closely related to the spectrum of dipole oscillator strength. An analytic form suitable for fitting $A(\epsilon)$ is known from the earlier work by Dillon and Inokuti (1981, 1985); briefly, $A(\epsilon)$ can be expressed in terms of a polynomial in variable $g = \epsilon/(\epsilon + I)$, where I is the relevant ionization energy. Following up an earlier analysis (Dillon et al. 1985), we have now shown that $B(\epsilon)$ can be expressed in the same way. For both $A(\epsilon)$ and $B(\epsilon)$, it is advisable to multiply the polynomial with a suitable simple function of ϵ so that the behavior at $\epsilon \rightarrow 0$ is explicitly fixed. Illustrative treatments of recent experimental data demonstrate the success of our approach.

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5.2.3 Absence of Resonances in the Elastic Scattering of Electrons in Molecular Solids

U. Fano, J.A. Stephens,* and M. Inokuti*

[Summary of a paper published in *Journal of Chemical Physics* 85:6239-6240 (1986)]

Sanche and Michaud (1983, 1984) reported on experiments that probed interactions of slow electrons with molecules in thin films. They found that effects of resonance, or the temporary attachment of an electron to a molecule, are almost as conspicuous in solid thin films as they are in the gas phase. For instance, electron transmission spectra in solid molecular nitrogen show a peak at about 1.2 eV that is due to a resonance; in gaseous nitrogen, the same resonance occurs at about 2 eV. More specifically, the resonance shows up clearly in the vibrational-excitation channel in both gas and solid. However, in the elastic-scattering channel, the resonance is undetectable in solid, while it is conspicuous in gas.

Our interpretation of the above finding relates to resonance in a gas. An incident electron of specific kinetic energy (e.g., 2 eV in nitrogen) has a high probability of being captured into a vacant orbital of the target molecule (π_g in nitrogen), then making many revolutions and eventually escaping. The temporary presence of this additional electron causes a significant change in the adiabatic potential that governs nuclear motion. Thus, the resonance leads to a high probability of change in nuclear motion, e.g., of vibrational excitation, especially with more than one quantum. Nevertheless, the electron may also leave the molecule in the initial state of nuclear motion, thus escaping with the same kinetic energy as it had before the collision.

In a solid or in any condensed matter, the resonance occurs in roughly the same way as in the gas, because it is chiefly governed by short-range interactions of the electron with the molecule and is little influenced by neighboring molecules. In contrast, the decay of the resonance depends on the neighboring molecules. The resonance, once formed, is a localized negative-ion state that distorts the position, the orientation, and the internal structure of neighboring molecules, through the process of electric polarization. The polarization causes some nuclear motion and therefore some inelasticity of the electron scattering. (An elastic scattering via resonance would involve polarization upon electron escape, which is extremely unlikely because of the many degrees of freedom involved.)

We propose to call this phenomenon "electric-polarization hysteresis" and will discuss its implications for electron behavior in condensed matter. The phenomenon represents a general condensed-phase effect hitherto unnoticed.

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5.2.4 Generalized Oscillator Strength of the Hydrogen Molecular Ion

*M. Kimura**

[Adapted from the abstract of a paper published in *Physical Review A* 35:4101-4107 (1987)]

The generalized oscillator strength (GOS) of H_2^+ was calculated comprehensively for both discrete-discrete and discrete-continuum transitions by using exact Born-Oppenheimer wavefunctions. The calculation presumed the Born-Oppenheimer separation, giving the GOS dependence upon the internuclear distance and the angle between the molecular axis and the momentum transfer, in addition to dependence upon the energy and the magnitude of momentum transfer. The theoretical study of the molecular GOS is extremely rare even for discrete excitation and is virtually nonexistent for continuum transitions. Our study served as a guideline for full understanding of the molecular GOS in general, although no experimental results on the key aspect (the dependence of the GOS upon the momentum transfer) are available for comparison with theory.

5.2.5 Theoretical Study of Electron-Molecule Collisions and Molecular Photoionization by the Continuum Multiple Scattering Method

H. Sato, K. Fujima,* and M. Kimura**

Applications of the continuum multiple scattering method (CMSM) (Dill and Dehmer 1974; Davenport 1976; Bloor and Sherrod 1986) have proved to be successful in fully elucidating various experimental observations in electron-molecule collisions and molecular photoionization. In particular, the method is useful for studying larger molecules that are not readily amenable to other theoretical approaches such as the R-matrix method and the coupled-channel method (Rescigno et al. 1979). Both an advantage and disadvantage of CMSM is the partitioning of the molecular field into three regions: each atomic sphere (region I), the spherical region surrounding the whole molecule (region III), and the interstitial region (region II). For regions I and III, the spherically symmetric part of the potential is used. For region II, the potential is approximated by a constant known as the muffin tin potential.

Generally, the potential in each region of space comprises direct and exchange electrostatic potentials plus a polarization potential. The direct term is determined from a self-consistent field (SCF) ground state charge distribution of the molecule, and the exchange term is determined by using various local exchange approximations including the Slater- X_α form. Wave functions are numerically determined by matching across these boundaries. Unlike the commonly used version, we have adopted the discrete-variable (DV) X_α method (Averill and Ellis 1973) to describe discrete electronic states for larger systems. The DV X_α method is better than its predecessor in that (1) the DV X_α method uses a more realistic SCF potential in region II than the simpler

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muffin tin potential used in the predecessor; and (2) numerical basis functions as well as functional basis functions can be used in implementing the DV X α method. We have developed a new CMSM code and have conducted systematic studies of electron-molecule collisions and molecular photoionization for a larger class of molecules, e.g., ethylene, ethane, propane, benzene, and pentane. In particular, our study of the cross section of momentum transfer for electron collisions with three isomers of pentane revealed interesting characteristics that interpret recent experimental findings (Freeman et al. 1979).

5.2.6 Survey and Compilation of Data on Stopping Power Conducted by the International Commission on Radiation Units and Measurements

*M. Inokuti and M. J. Berger**

[Adapted from the abstract of a paper published in Nuclear Instruments and Methods in Physics Research B 27:249-255 (1987)]

One of the principal objectives of the International Commission on Radiation Units and Measurements (ICRU) is to recommend internationally acceptable values of physical quantities relevant to radiation measurements and radiological dosimetry. Among a large variety of the physical quantities treated by the ICRU, the stopping power is one of the most fundamental. In 1984, the ICRU issued Report No. 37 concerning stopping power for electrons and positrons. Currently the ICRU is preparing a report on data for protons and alpha particles. Work planned for the future concerns heavier charged particles, which include most importantly carbon, oxygen, and nitrogen ions resulting from neutron irradiation of human tissues. The task requires, in addition to mere collection of published data, critical evaluation of those data for their reliability, precision, and accuracy. The critical evaluation in turn requires full knowledge of experimental and theoretical methods for the determination of stopping power. Our work pointed out key issues and major unsolved problems involved in the determination.

5.2.7 Electron Degradation and Yields of Initial Products

M. Kimura, M. Inokuti, and M.A. Dillon*

When charged particles pass through matter, they interact with atoms and molecules in matter to generate ions, excited states of atoms and molecules, as well as electrons. These products subsequently react with atoms and molecules in matter, leading to chemical and biological effects in general. Electrons are most abundantly produced in the degradation of charged particles in matter. Hence, understanding the action of an energetic electron on matter is of fundamental importance in radiation physics. Electron degradation spectra and ion yields for pure substances have been studied frequently in the past by means of the Fowler equation, the Spencer-Fano equation, and the Monte Carlo method. These three treatments, which belong to two quite different theoretical categories, are considered to be compensatory rather than

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competitive. However, the Spencer-Fano method, which gives degradation spectra $y(T_0, T)$, provides the most information about degradation mechanisms of electrons in matter.

We have examined electron degradation spectra and initial yields of various species in binary mixtures including Ar - H₂, CO₂ - H₂, and Ar - H₂O by using numerical solutions of the Fowler equation and the Spencer-Fano equation. The yield of any species resulting from complete degradation of electrons in a binary mixture is given by

$$N_i^X(T) = n^X \int_0^T dT' y(T_0, T') \sigma_i^X(T'), \quad (5-2)$$

where $N_i^X(T)$ represents the yield of i species of X substance in the mixture, n^X is the number density of X substance, and $\sigma_i^X(T')$ is the cross section of changing state to i of an X substance at energy T . The solution of the Fowler equation directly provides $N_i^X(T)$, while the Spencer-Fano equation gives degradation spectra $y(T_0, T)$. Obviously, degradation spectra $y(T_0, T)$ contain far more information of dynamics than does the yield itself. Hence, a detailed study of electron degradation spectra in binary mixtures is a primary object in the present work. Our calculated results for $y(T_0, T)$ as well as $N_i^X(T)$ help to elucidate the mechanism of electron degradation in binary mixtures.

5.2.8 Analytical Time-Dependent Treatment of Electron Degradation: Electronic Excitation of N₂ Molecules by Subexcitation Electrons in He or Ne Gases

M.A. Dillon, M. Kimura, and M. Inokuti*

[Summary of a paper presented at the 39th Annual Gaseous Electronics Conference, Madison, Wisconsin, 7-10 October 1986. A full paper will appear in Radiation Physics and Chemistry.]

The electron degradation spectrum (EDS) is the key element in the description of the elementary processes induced by ionizing radiation. The original study by Spencer and Fano (1954) gave a time-independent representation, applicable to stationary irradiation. However, recent experiments follow the kinetics of formation and decay of excited states in pulse-irradiated gases (Cooper et al. 1982). In response to this work, we developed a time-dependent version of the Spencer-Fano equation. The new equation has been used to model the moderation of subexcitation electrons in He or Ne and the competing formation of the C ³π_u state of N₂ solute. We have tested the sensitivity of the EDS to cross-section data used to derive the EDS.

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5.2.9 Radiation-Energy Partition Among Mixture Components: Current Ideas on an Old Question

A.J. Swallow and M. Inokuti*

[Adapted from the abstract of a paper to appear in *Radiation Physics and Chemistry*]

We have reviewed the basis of the familiar idea that the energy partition among mixture components in the initial stage is governed by the total electron fraction. For many problems in radiation chemistry, use of the valence electron fraction is better. More detailed treatments of recent developments indicate that the concept of energy partition has limitations for determining the yields of initial molecular species that appear under irradiation.

5.2.10 Electron Capture in Ion-Molecule Collisions at Intermediate Energy

*M. Kimura**

[Summary of a paper published in *Nuclear Instrumentation and Methods in Physics Research B24/25:101-105 (1987)*]

In contrast to the flourishing experimental and theoretical studies of ion-atom collisions, comprehensive theoretical studies of ion-molecule collisions are extremely rare. Undoubtedly, difficulties in obtaining accurate electronic wavefunctions and the complexity of practical computations are responsible. With knowledge of collision dynamics obtained from ion-atom collisions (Kimura 1986a), however, the distinct mechanisms of close and distant collisions can also be applied to the study of ion-molecule collisions. For a close collision where the molecular complex of a colliding system may play an important role in a collision event, explicit representation of the whole ion-molecule system is indispensable to the correct determination of the collision dynamics.

Technology commonly used by the quantum chemistry community can be adapted to obtain reasonably accurate ion-molecular system wavefunctions and adiabatic potentials. For a distant collision where the molecular nature of a target does not greatly influence the collision dynamics, a simple model analogous to an ion-atom system describes the collision dynamics reasonably well. Practically, the charged ion-molecule collision system for ions of lower charge ($Z = 1, 2$) belongs to the former category, while the system for ions of higher charge ($Z \geq 3$) is in the latter. We have applied the diatoms-in-molecules method as well as the more sophisticated multi-configuration SCF method to obtain accurate molecular wavefunctions and potential surfaces as functions of internuclear distances and molecular orientations in order to study a close collision (Kimura 1985; Kimura et al. 1986). (See Fig. 5.1.) We used a pseudopotential method to represent the molecule-ion core, which allowed us to treat a molecule as an "atom" having an ionization potential of a target molecule. This treatment is quite adequate to

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describe an ion-molecule collision system for a distant collision (Kimura 1986b; Kimura and Lane 1987). (See Fig. 5.2.) We used these two models to simulate electron capture in ion-molecule collisions in the energy range from 0.1 to 25 keV/amu.

5.2.11 Quantum Defect Values for Positive Atomic Ions

C.E. Theodosiou, M. Inokuti, and S.T. Manson**

[Summary of a paper published in Atomic Data and Nuclear Data Tables
35:473-486 (1986)]

The asymptotic quantum defects, at the ionization limit, of s, p, d, and f atomic orbitals have been calculated in the Hartree-Slater approximation for all ionization stages of all ions with atomic number $Z \leq 50$. The quantum defect value is a key index for short-range interactions of an electron with an ion core; it summarizes various spectral and collisional data. In particular, the term values of a Rydberg series are compactly characterized by the quantum defect. The significance of the results has been fully discussed in a separate paper by Theodosiou et al. (1986). Our theoretical results show good agreement with available spectral data. Thus, our results should provide a good estimate for many applications, especially where experimental results are absent.

5.3 ELECTRON COLLISION STUDIES

5.3.1 Summary

The interaction of ionizing radiation with matter first generates secondary electrons. These secondary electrons degrade in energy through elastic and inelastic collisions and act as carriers of energy, subsequently producing a large variety of reactive species (often called initial products) that start the chain of chemical reactions eventually leading to the net radiation effects, including biological changes. Thus, the measurement of the specific energy transferred per collision between electrons and molecules (or atoms), together with the probability of such energy transfer per collision, is of prime importance for studies of the effects of energy deposition in matter by ionizing radiation.

The purpose of our research is to measure cross sections for inelastic scattering of electrons in order to characterize those mechanisms important in energy-degradation processes. The resulting data can be used to estimate yields of irradiation products, to identify spectroscopically the energy levels of states initially excited in the target, and to test predictions or further develop electron scattering theory. The generalized oscillator strength derivable from the measured cross sections describes the response of the target to fast-charged-particle impact and, in the limit of small momentum transfer, yields the optical oscillator strength. Moreover, measured generalized oscillator

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A close collision: $\text{H}^+ + \text{H}_2(X^1\Sigma_g^-) \rightarrow \text{H}(1s) + \text{H}_2^+(2s\sigma_g)$

FIGURE 5.1a Probability times impact parameter versus impact parameters for $\text{H}^+ + \text{H}_2$ collision as a function of θ at $E = 1$ keV.

FIGURE 5.1b Electron capture cross sections in $\text{H}^+ + \text{H}_2 \rightarrow \text{H} + \text{H}_2^+$ collisions. Theory: solid line. Experiment: o, x.

A distant collision: $N^{7+} + H_2(X^1\Sigma_g) \rightarrow N^{6+}_{(n\ell)} + H_2^+(1s\sigma_g)$

FIGURE 5.2a Electron capture probability vs. impact parameter for $N^{7+} + H_2$ collisions at $E = 5$ keV.

FIGURE 5.2b Electron capture cross sections in $N^{7+} + H_2$ collisions. Theory: solid line. Experiment: $\circ$.

strengths can be used to calculate intermolecular energy transfer cross sections as well as singlet-triplet energy differences. Both topics are of fundamental importance in radiation chemistry and biology.

One of the techniques we use to study such electron collision processes is called electron energy loss spectroscopy. Specifically, we shoot an electron beam of known energy at a target molecule and measure the intensity differential of the scattered electrons in terms of both energy transfer and scattering angle. This technique, a form of spectroscopy, gives the energy levels of the atom or molecule. By measuring how many electrons lose specific amounts of energy, we are able to determine the probability of each excitation event.

Electron collision studies are truly multidisciplinary. The data we obtain are often of immediate relevance to programs other than basic radiation research. For example, analogous processes occur in gas discharge lasers, plasma etching of microchips in the electronics industry, terrestrial and planetary atmospheres, and stellar atmospheres. Our electron collision studies in the past year have been directed toward all of these fields.

In 1986 we converted some previously reported electron energy loss spectra that we had obtained in the forward scattering direction into photoabsorption cross sections. Normalization of our data to optical spectra has allowed us to obtain absolute photoabsorption cross sections in energy regions well outside those easily obtained by conventional photoabsorption experiments. In addition, we report here several measurements of progressively larger molecules, a systematic study that has facilitated spectral interpretation and revealed many new optically allowed and optically forbidden transitions. Finally, we present our first data on energy deposition in the DNA base adenine. These measurements demonstrate the viability of our technique of measuring energy deposition in single molecules in the gas phase and reveal connections with measurements made in the condensed phase. A complete, detailed understanding of the electronic structure of the heterocyclic DNA bases will, however, require a systematic study of the electronic structure of the other four bases, guanine, cytosine, thymine, and uracil. This program of systematic measurements continues.

5.3.2 Direct Observation of 157-nm "Laser" Photons from the $f^3\Pi_g$ State of F_2 by High-Resolution Electron Impact

D. Spence, H. Tanaka, M.A. Dillon, and K. Lanik**

[Summary of a paper published in Journal of Physics B 19:L569 (1986)]

By using variable-energy, high-resolution electron impact techniques, we have directly observed for the first time the emission of 157.5-nm "laser" photons from the $f^3\Pi_g$ state of F_2 , which has long been conjectured to be (Woodworth and Rice 1978), though only recently was energetically located in (Hoshiba et al. 1985), the upper laser level in molecular fluorine. The results of our experiments are shown in Fig. 5.3, which

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FIGURE 5.3 Excitation function for production of 157.5-nm fluorescence radiation in F_2 as a function of incident electron energy between 8.5-14.5 eV.

is a plot of 157.5-nm photon yield from F_2 as a function of the energy of a high-resolution exciting electron beam.

Figure 5.3 clearly shows four upward breaks in the yield of 157.5-nm photons, each of which corresponds energetically with the known location of one of four electronic states of F_2 . These states are the $f^3\Pi_g$ state located by Hoshiba et al. (1985) at 11.62 eV, the $CDE^1\Sigma_u^+$ states at 12.85 eV (Colbourne et al. 1976), an unidentified transition observed at 14.0 eV by Hoshiba et al. (1985), and the $I^1\Sigma_u^+$ state at 14.127 eV (Colbourne et al. 1976). The background level corresponds on an average to about 8 photons per channel, which translates to about 1 dark photon per 10 seconds.

The 17.5-nm fluorescence observed between 11.6 and 12.89 eV can only come from the $f^3\Pi_g$ state, because electron energy loss spectra show that this is the only state excited in this energy regime under the present experimental conditions (Hoshiba et al. 1985).

5.3.3 Momentum Transfer Dependence of the $(6\sigma)^2 \rightarrow (6\sigma, n\pi)$ Window Resonance in N_2O

M.A. Dillon, D. DeMille, and D. Spence*

[Summary of a paper published in Journal of Electron Spectroscopy and Related Phenomena 42:67 (1987)]

Scattered electron spectra of N_2O with 200-eV electrons have been recorded in an energy loss regime of 17 eV to 21 eV, corresponding to excitation from the 6σ orbital. In this region, the shape of the $(6\sigma, n\pi)$ window resonance series shown in Fig. 5.4 exhibits a strong variation over a scattering angle range of 3° to 9° . For the $n = 3$ member, this variation is attributed to a change in the resonance profile index from about -0.2 to +0.9 (Fig. 5.5). Although profile index sign reversals have been measured in ejected electron spectra, their interpretation is difficult. The scattered electron aspect of our measurement lends itself to a more straightforward interpretation as a sign reversal in the transition amplitude for excitation to the modified discrete state, and our measurements provide one of the first clear-cut examples of this effect.

5.3.4 Observation of Rydberg Transitions from the Inner Valence Shell of Ethane

M.A. Dillon, H. Tanaka, and D. Spence*

[Summary of a paper published in Journal of Chemical Physics 87:1499 (1987)]

The electronic spectrum of ethane is the most important of those for the saturated hydrocarbons because (1) it contains much discrete structure by which theory may be tested, and (2) orbital assignments in ethane can be used as a starting point for the analysis of higher alkanes (Robin 1974a; Robin 1985; Sandorfy 1976; Lombos 1974). Transitions from the valence shell of ethane have been investigated by a variety of techniques including photoabsorption (Raymonda and Simpson 1967; Koch and Skibowski 1971) and electron impact (Lassettre et al. 1969; Johnson et al. 1979) methods, both of which reveal much vibronic structure in electronic bands converging to the first ionization potential (IP).

In a study using electron energy loss spectroscopy, we reported for the first time the existence of similar vibrational progressions preceding the fourth IP and resulting from excitation from the inner valence shell. Our results, shown in Figs. 5.6 and 5.7, reveal one diffuse structure and a progression of ten vibrational bands in a range of 4 eV below, and to some degree overlapping, the $^2A_{2u}$ ion threshold. Evidence indicates that the observed transitions belong to the symmetry-forbidden Rydberg series $(2a_{2u})^2 \rightarrow (2a_{2u}, n\sigma \text{ or } n\pi)$.

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FIGURE 5.4 Electron impact spectrum of N_2O for incident electrons of 200 eV recorded at indicated scattering angles. Arrows point to the emergence of new features in the larger-angle spectrum.

5.3.5 Photoabsorption Cross Section of XeF_2 from 150 to 275 nm by Forward-Scattering Electron Energy Loss Spectroscopy

D. Spence, H. Tanaka, and M.A. Dillon*

[Summary of a paper to appear in *Journal of Applied Physics*]

Despite the importance of the photoabsorption cross section of XeF_2 for some excimer lasers, only one set of data in the energy range 180 to 210 nm seems to have been published (Black et al. 1981). Moreover, the general trend of the measured cross section at wavelengths greater than 175 nm in two published conventional photoabsorption experiments is somewhat discordant (Black et al. 1981; Jortner et al. 1963). In an attempt to clarify these differences, we have reexamined the photoabsorption cross section between 150 and 275 nm by using a different technique, high-incident-energy, forward-scattering, electron energy loss spectroscopy. Such a forward-scattering

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FIGURE 5.5 Variation of shape parameters q_1 ($3p\sigma$) and q_2 ($3p\pi$) of the data shown in Fig. 5.4 as a function of momentum transfer K .

FIGURE 5.6 Electron energy loss spectrum of ethane recorded with electrons of 200 eV kinetic energy at scattering angles of 3° and 9° , giving a global view of structures between 6 and 26 eV. Vertical bars indicate the excitation region converging to the fourth ionization threshold.

spectrum is, when modified by a well-defined scaling factor, equal to the photoabsorption cross section (Inokuti 1971; Inokuti et al. 1978; Johnson et al. 1979). A unique aspect of our technique is that the transmission function of the apparatus is independent of the electron energy loss over very wide energy ranges, so that instrumental transmission corrections similar to those required by optical measurements are unnecessary.

A typical energy loss spectrum obtained in XeF_2 for an incident electron energy of 200 eV and energy losses between 4 and 23.5 eV is shown in Fig. 5.8. From this spectrum we derived a relative photoabsorption cross section, normalized to two previous measurements that used conventional photoabsorption techniques (Fig. 5.9). Our data show good agreement with an early measurement (Jortner et al. 1963) over the entire spectral range, but significant disagreement with more recent data (Black et al. 1981) for wavelengths greater than 175 nm. The cause of this discrepancy is uncertain. However, in photoabsorption measurements, the instrumental transmission efficiency is generally a strong function of wavelength, and a precise knowledge of the absolute value of the efficiency is essential and difficult to obtain. In contrast, in our experimental technique, the transmission is constant and no correction other than a minor, well-defined aperture correction is needed.

FIGURE 5.7 Expanded spectrum in the region between the vertical bars in the 9° spectrum of Fig. 5.6, recorded independently, showing the diffuse structure and progression of vibrational bands discussed in the text.

FIGURE 5.8 Electron energy loss spectrum of XeF_2 free of Xe impurities obtained for electrons with 200 eV incident energy scattered in the forward direction (± 0.034 radians) and for energy losses between 4 and 23 eV.

FIGURE 5.9 Comparison of the photoabsorption cross section of XeF_2 obtained in the present experiment (solid curve) with those obtained previously by Black et al. (solid triangles) and by Jortner et al. (solid circles). All data have been arbitrarily normalized at 158 nm to the value $4.2 \times 10^{-16} \text{ cm}^2$ obtained by Jortner et al. and reanalyzed by Black et al.

5.3.6 Electron Energy Loss Spectroscopy of Disilane

M.A. Dillon, D. Spence, L. Boesten, and H. Tanaka**

[Summary of a paper submitted to Journal of Chemical Physics]

In recent years, the electronic structure of disilane has come under increased scrutiny because of its convenience as a starting point in the analysis of the higher saturated silanes (Robin 1974b; Robin 1985; Bock et al. 1976) as well as its importance in chemical plasma deposition mechanisms (Perrin et al. 1982, 1984). Information about the electronic structure of disilane has been obtained from photoelectron spectroscopy (Xu et al. 1983; Price 1968) and photoabsorption spectroscopy (Itoh et al. 1986) by using synchrotron radiation. In supplementary studies, appearance potentials of excited fragments (Perrin and Aarts 1980) and fragment ions (Potzinger and Lampe 1969; Chatham et al. 1984) have been measured for a substantial range of incident electron energies.

The present investigation, which uses electron energy loss spectroscopy as a probe of the electronic spectrum of disilane, generally supports the results of previous

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reports. In addition, the use of low- and medium-energy electrons facilitates the search for spin- and symmetry-forbidden transitions and extends the optically allowed regime beyond the LiF cutoff.

Electron energy loss spectra of disilane have been recorded over an excitation energy range of 20 eV with incident electrons of 20 and 200 eV energy for scattering angles of 0° - 90° . Every transition detected except one appears at an energy consistent with the first observed members of the Rydberg series, converging to one of four possible ion states. The first two observed transitions belong to $(2a_{1g})^2 \rightarrow 1,3(2a_{1g}, 4s)$ dipole forbidden channels appearing at excitation energies of about 6.3 eV and 7.05 eV for the triplet and singlet, respectively. Our results support the identification of additional forbidden transitions as well as a possible low-lying valence transition. Typical energy loss spectra obtained in disilane at three different scattering angles for incident electrons at 200 eV are shown in Fig. 5.10. A synopsis of our analysis of these spectra is given in Table 5.1.

5.3.7 Energy Deposition in Nucleic Acid Bases: Adenine

M.A. Dillon, H. Tanaka, and D. Spence*

The electronic properties of nucleic acid bases have been investigated by a variety of means including ultraviolet spectroscopy (Clark et al. 1965) and electron scattering by thin films (Isaacson 1972). The same methods were also used to estimate high-energy electron collision cross sections and optical oscillator strength distributions. In spite of this progress, the response of the bases to interaction with slow electrons remains one of the challenging problems of radiation biology. In order to investigate the scattering of low- and intermediate-energy electrons by biologically important compounds including nucleic acids, we have modified an electron spectrometer to facilitate the spectral analysis of vaporizable solids. An example of results obtained so far (Fig. 5.11) shows energy loss spectra of adenine recorded at scattering angles of 3° and 6° with incident electrons of 200 eV kinetic energy. The spectra were produced by interaction of the incident electrons with a beam of gaseous adenine generated by an effusive jet and oven maintained at 250°C .

Although all of the peaks in Fig. 5.11 may be attributed to $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ transitions, confirmation of such specific assignments awaits the acquisition and analysis of spectra correlating the electronic properties of a series of nucleic acids, including thymine and uracil.

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FIGURE 5.10 Electron energy loss spectra of disilane recorded with incident electrons of 200 eV at three scattering angles. The variation of momentum transfer K over each spectrum is given under the angle designation. The inset in the zero-angle spectrum is the photoelectron spectrum in the neighborhood of the peak intensity, shifted in energy to coincide with the $1E_u$, $1A_{2u}$ peak at 9.46 eV. The vertical lines mark the locations of forbidden transitions. Connected lines near the top of each spectrum indicate John-Teller splitting of possible molecular states designated in the zero-angle spectrum, and the energy regions of the four lowest ionization potentials are indicated at the bottom of the figure.

TABLE 5.1 Assignment of features in Fig. 5.10. W is the energy location, T is the term value, and n^* is the effective quantum number.

Configuration	$W(\text{eV})$	$T(\text{eV})$	n^*
$[2a_{1g}, 4s] \ ^3A_{1g}$	6.3	4.43	----
$[2a_{1g}, 4s] \ ^1A_{1g}$	7.05	3.53	1.96
$[2a_{1g}, e_u \text{ or } a_{2u}] \ ^1E_u, \ ^1A_{2u}$	7.6	2.93	2.15
$[2a_{1g}, 4p] \ ^1E_u, \ ^1A_{2u}$	8.36	2.17	2.50
$[1e_g, 4p] \ ^1E_u, \ ^1A_{2u}$	9.46	2.33 9.86	2.42
$[1a_g, 5p] \ ^1E_u, \ ^1A_{2u}$	10.65	1.15	3.44
$[1e_u, 4p] \ ^1A_{1g}, \ ^1E_g$	10.9	2.0	2.6
$[1e_u, 5p] \ ^1A_{1g}, \ ^1E_g$	11.73	1.17	3.41
$[1a_{2u}, 4s] \ ^1A_{2u}$	13.2 (onset) 14.17 (peak)	3.25	2.05
$[1a_{2u}, 5s] \ ^1A_{2u}$	15.0 (onset) 15.2 (peak)	1.45	3.06

FIGURE 5.11 Electron energy loss spectra in adenine obtained with an incident electron energy of 200 eV for energy losses between 2.5 and 27.5 eV at two different scattering angles.

5.3.8 Electronic Properties of Homologous Freons of Atmospheric Interest

M.A. Dillon, H. Tanaka, and D. Spence*

We have used electron beams to probe the electronic structure of both major and minor atmospheric constituents with special emphasis on contaminants related to stratospheric ozone reduction. An application of the energy loss technique is illustrated in Figs. 5.12 and 5.13, which compare energy loss spectra of CF_4 and CF_3H obtained with incident electrons of 200 eV and recorded at scattering angles of 3° and 9° . The pairs of spectra demonstrate how the angular behavior of bands in a highly symmetric molecule can aid in the spectral interpretation of homologous molecules. The 9° spectrum in Fig. 5.12 reveals a band, indicated by the arrow, that must correspond to a symmetry-forbidden transition. The term value (~ 3.6 eV) and excitation energy (~ 14.8 eV) indicate a Rydberg orbital transition of the type $(1e)^4 + (1e)^3 3s$. This enables us to identify the corresponding optically allowed transition in the spectrum of CF_3H (arrows, Fig. 5.13). Indeed, the band in CF_3H is a superposition of two broad peaks; we have chosen the one with an angular trend similar to the band found in the CF_4 spectrum.

FIGURE 5.12 Electronic spectrum of CF_4 from 10 to 29 eV obtained by electron energy loss spectroscopy at two scattering angles. The arrow indicates the emergence of a symmetry-forbidden transition in the 9° spectrum, whose location indicates it to be a Rydberg orbital transition of the type $(1e)^4 + (qe)^3 3s$.

*Collaborator; affiliation is listed at the front of this chapter.

FIGURE 5.13 Electron energy loss spectra of CF_3H from 9 eV to 28 eV obtained at two scattering angles. The arrows indicate an allowed transition of CF_3H , which corresponds to the forbidden transition of Fig. 5.12.

5.4 PHOTOPHYSICS STUDIES WITH MULTIPHOTON RESONANT ABSORPTION

5.4.1 Summary

The purpose of this program is to develop and use resonantly enhanced multiphoton ionization (REMPI) with mass spectrometry (MS), photoelectron spectrometry (PES), and fluorescence spectrometry to study molecular photophysics and photochemistry at the quantum-state-specific level. The combination of the highly selective excitation technique and the variety of detection methods results in a powerful approach to the study of basic atomic and molecular physics and chemistry. In general, a tunable "pump" laser is used to excite a target molecule to a resonant intermediate level, and a second (or perhaps a second and a third) independently tunable "probe" laser is used to study the various physical and chemical transformations of the excited state. As an example, the probe laser may lead to ionization of the resonant intermediate state, and the products of the ionization event may be monitored by ion mass analysis or by electron kinetic energy analysis as a function of all pertinent parameters. Alternatively, a delayed probe laser can be used to examine the decay of a selected excited state at variable time intervals after the initial excitation, thus following the internal transformations or decay mechanisms as a function of time. It is also possible to use the probe laser to study the spectra and chemical reactions of fragments (such as free radicals) formed by the action of the pump laser on a radical precursor. Often, this is one of the most efficient ways of producing and studying the properties of free radicals.

During the past year, we have performed a variety of types of experiments. Such work includes (1) REMPI-MS studies of the spectroscopy of atomic and molecular excited states and quasibound states that cannot be accessed from the ground electronic state by using single-photon excitation techniques; (2) REMPI-PES studies of the photoionization dynamics of excited states; (3) REMPI-MS and REMPI-PES studies of the decay mechanisms of excited states; and (4) the production and study of photofragments (particularly fragments such as atomic carbon, nitrogen, sulfur, or iodine that are difficult to produce by using conventional techniques) with both REMPI-MS and REMPI-PES.

5.4.2 Wavelength-Dependent Photoelectron Spectra of Rotationally Resolved Autoionizing Levels of Nitric Oxide

S.T. Pratt, P.M. Dehmer, and J.L. Dehmer

[Summary of a paper published in *Journal of Chemical Physics* 85:5535 (1986)]

As is discussed in section 5.4.7, we have used direct two-photon excitation to probe previously unobserved Rydberg states in nitric oxide (NO). In the present study, we focus on the NO $9d\sigma\pi$, $v'=2$ band, which is shown in Fig. 5.14. The figure displays sharp rotational structure, and the observed levels can autoionize into both the $\text{NO}^+ X^1\Sigma^+$, $v^+=0$ and $v^+=1$ continua. We have determined the wavelength dependence of the photoelectron spectrum and the photoelectron angular distribution for several rotational lines within the band. These data can be used to determine the photoelectron branching ratio for the autoionizing peaks as well as for the direct ionization continuum, allowing a

FIGURE 5.14 The two-photon ionization spectrum of supersonically cooled NO between 2655 and 2665 Å.

detailed examination of the photoionization dynamics. In particular, several workers have shown (Berry 1966; Bardsley 1967; Nielsen and Berry 1968; Berry and Nielsen 1970) that if the autoionizing Rydberg state has a potential curve similar to that of the corresponding ionic state, the autoionization probability will be largest for the process with the smallest allowable change in the vibrational quantum number of the ion core. This gives rise to the $\Delta v = -1$ propensity rule when such a process is allowed. However, an important breakdown of the vibrational propensity rule occurs when the autoionizing level interacts with a third channel, which could be a Rydberg series converging to a different ionization limit, a predissociative valence state, or any number of other possibilities. In such a case the nominally isolated, vibrationally autoionizing level can no longer be treated as a simple resonance, and should be treated in a multichannel framework. Perhaps the best example is multichannel quantum defect theory (Giusti-Suzor and Jungen 1984). Further, in this case the conditions for the vibrational propensity rule are no longer valid, and strong violations of propensity rule behavior may be observed. Thus, the present measurements allow us to assess the extent of this type of perturbation in the $9d\sigma^+ \pi$, $v'=2$ levels.

Figure 5.15 shows the photoelectron angular distributions for the $v^+=1$ peak at four different wavelengths. Here the 78048.4 cm^{-1} distribution corresponds to the peak of an autoionizing resonance, while the other distributions correspond to increasing distances off resonance. On resonance the $v^+=1$ angular distribution is far more isotropic than any of the off-resonance distributions. The photoelectron branching ratios show a similar sharp resonant behavior over the autoionizing feature, with a strong increase in the $\text{NO}^+ \text{ } ^1\Sigma^+$, $v^+=1$ branching ratio on resonance, in accord with the $\Delta v = -1$ propensity rule. An analysis of the data indicates that the autoionization mechanism leads to approximately 96% $\text{NO}^+ \text{ } ^1\Sigma^+$, $v^+=1$, in contrast with approximately 71% $v^+=1$ in the direct ionization continuum. Future studies on a more extensive number of rotational lines and for different values of principal quantum number n should contribute to the understanding of autoionization processes in NO.

5.4.3 Three-Photon Excitation of Autoionizing States of Atomic Krypton and Xenon Between the $^2P_{3/2}^0$ and $^2P_{1/2}^0$ Fine-Structure Thresholds

S.T. Pratt, J.L. Dehmer, and P.M. Dehmer

Recently, Gangopadhyay et al. (1986) reported calculations of the three-photon ionization spectra of Xe in the energy region between the $\text{Xe}^+ \text{ } ^2P_{3/2}$ and $^2P_{1/2}^0$ fine-structure thresholds. These calculations show distinct resonant structures corresponding to $J=1$ and $J=3$ autoionizing Rydberg series of xenon converging to the $\text{Xe}^+ \text{ } ^2P_{1/2}^0$ threshold. For this reason, we have recorded the experimental three-photon ionization spectrum of Xe in the same spectral region. For linearly polarized light, four different Rydberg series are allowed by the selection rules for three-photon transitions, and all four of these series are observed. These correspond to the $ns'[1/2]_1^0$, $nd'[3/2]_1^0$, $nd'[5/2]_3^0$, and $ng'[7/2]_3^0$ Rydberg series. All four series have $\text{Xe}^+ \text{ } ^2P_{1/2}^0$ ion cores. The notation $n\ell'[K]_J^0$ corresponds to $j_c\ell$ coupling, in which the angular momentum of the ion core, j_c , is coupled to the orbital angular momentum of the Rydberg electron, ℓ , to give K , which is then coupled to the Rydberg electron's spin to give J .

FIGURE 5.15 The photoelectron angular distributions following two-photon ionization of NO for the $\text{NO}^+ \text{X } 1\Sigma^+, v^+=1$ peak at four different energies. The experimental data are given as solid circles ($\bullet$). The solid line (—) represents a best fit to the functional form $1 + \beta P_2(\cos\theta) + \gamma P_4(\cos\theta)$, and the dotted line ($\cdot \cdot \cdot$) represents a best fit to the functional form $1 + \beta P_2(\cos\theta)$.

Figure 5.16 shows the three-photon ionization spectrum of Xe obtained by using linearly polarized light between 2791.00 Å and 2800.75 Å. Two members of three different Rydberg series are clearly discernible; these correspond to the sharp $ns'[1/2]_1^0$ and $nd'[5/2]_3^0$ series, and the broad $nd'[3/2]_1^0$ series. In this spectral range, the intense $ns'[1/2]_1^0$ peaks obscure the members of the $ng'[7/2]_3^0$ series. At lower n , these two series are resolved, as is shown in Fig. 5.17. Figure 5.17 also shows that with circularly polarized light the $J=1$ series becomes forbidden, and only the $J=3$ series is observed. With circularly polarized light, the higher $ng'[7/2]_3^0$ series members are also observed.

The three-photon ionization spectrum of atomic Kr has also been recorded in the region just above the $\text{Kr}^+ 2P_{3/2}^0$ threshold, and it displays structure analogous to that observed in Xe. However, the low-lying members of only three series are present in the spectrum, and the members of the $nd'[5/2]_3^0$ series are not observed.

Photoelectron spectra and photoelectron angular distributions have been determined for a number of resonances in the xenon and krypton spectra. The photoelectron spectra all show a single peak corresponding to the production of Xe^+ or

FIGURE 5.16 Three-photon ionization spectrum of atomic Xe between 2800.75 Å and 2791.00 Å obtained by using linearly polarized light

$\text{Kr}^+ 2\text{P}_{3/2}^{\circ}$. No evidence of above-threshold ionization is observed in any of these spectra. In the future, we will compare the photoelectron angular distributions with the theoretical results (Gangopadhyay et al. 1986).

5.4.4 Photoionization Dynamics of Excited Molecular States: Photoelectron Angular Distributions and Rotational and Vibrational Branching Ratios for $\text{H}_2 \text{C } ^1\Pi_u, v = 0 - 4$

S.T. Pratt, P.M. Dehmer, and J.L. Dehmer

[Summary of a paper published in Journal of Chemical Physics 85:3379 (1986)]

We previously presented photoelectron spectra following three-photon-resonant, four-photon (3+1) ionization of H_2 via the $\text{C } ^1\Pi_u, v'=0-4, J'=1$ levels, in which the spectra were recorded along the polarization axis of the laser ($\theta=0^\circ$) (Pratt et al. 1984). The $\text{C } ^1\Pi_u$ state of H_2 is the lowest-lying singlet Rydberg state converging to the $\text{H}_2^+ \text{X } ^2\Sigma_g^+$ ground electronic state. As is expected on the basis of Franck-Condon factors, photoionization via a particular vibrational level v' of the $\text{C } ^1\Pi_u$ state leads to a photoelectron spectrum that is strongly peaked at the ionic vibrational level $v^+=v'$. Calculations performed by Dixit et al. (1984a) were in good agreement with the

FIGURE 5.17 The three-photon ionization spectra of atomic Xe near the $9s'[1/2]_1^0$ autoionizing resonance obtained by using linearly and circularly polarized light. The spectra are plotted so that the relative peak heights reflect the approximate relative intensities of the peaks in the two spectra.

experimental results for the lower vibrational levels, although significant differences were observed for the higher vibrational levels. In an effort to clarify these discrepancies and to provide more detailed dynamical information, we have now presented the photoelectron angular distributions for (3+1) ionization via the same $C^1\Pi_u$, $v'=0-4$, $J'=1$ levels as before. In addition, the present measurements allow the determination of the angle-integrated branching ratios, which could not be evaluated from the $\theta=0^\circ$ measurements alone.

The photoelectron angular distributions for the $v^+=v'$ photoelectron peaks following (3+1) ionization via the $C^1\Pi_u$, v' , $Q(1)$ transitions are shown in Fig. 5.18. The distributions for different vibrational levels are quite similar, although the lower- v' distributions are somewhat narrower than the higher- v' distributions. The angular distributions have also been determined for all of the off-diagonal photoelectron peaks with sufficient intensity to achieve reasonable statistics.

FIGURE 5.18 Photoelectron angular distributions for the $v^+=v'$ photoelectron bands following (3+1) ionization of H_2 via the $C^1\Pi_u, v'=0-4 + X^1\Sigma_g^+, v''=0, Q(1)$ transitions. Data points are shown as diamonds (◆).

Recently, Dixit (1986) and Dixit et al. (1984b) have calculated photoelectron branching ratios and angular distributions for (3+1) ionization of H_2 via the $C^1\Pi_u, v'=0-4, Q(1)$ transitions. The agreement with experimental results for the $v^+=v'$ distributions is remarkably good. Unfortunately, the agreement is not as good for the off-diagonal photoelectron angular distributions. In particular, for a given value of v' , the theory (Dixit et al. 1987) predicts an increase in anisotropy with increasing v^+ . Thus, relative to the $v^+=v'$ peak, the theory predicts more isotropic distributions for $v^+<v'$ and more anisotropic distributions for $v^+>v'$. In general, for a given value of v' , the theoretical values of γ show little variation, and the increase in anisotropy with increasing v^+ is due to an increase in the β values. The increase in anisotropy with increasing v^+ in the theoretical angular distributions is in contrast to the decrease in anisotropy for $v^+>v'$ in the experimental angular distributions. Thus, while the agreement of the theoretical calculations with the experimental observations for the diagonal angular distributions is encouraging, some improvements in the theoretical model of the process are clearly necessary in order to obtain better agreement for the off-diagonal angular distributions.

The photoelectron spectra obtained following (3+1) ionization of H_2 via the $C^1\Pi_u$, $v'=4R(0)$ and $R(1)$ transitions at $\theta=0^\circ$ are shown in Fig. 5.19. The $\theta=0^\circ$ vibrational branching ratios are quite similar to those of the $v'=4 Q(1)$ spectrum reported previously (Pratt et al. 1984), although the $v^+=v'$ peak appears somewhat stronger in the R-branch spectra.

Of particular interest in the photoelectron spectra of Fig. 5.19 is the ratio of the relative intensity of the $N^+=4$ to the $N^+=0,2$ photoelectron peaks in the $R(0)$ spectra for the different vibrational bands [as well as the ratios of the relative intensities of the $N^+=5$ to the $N^+=1,3$ photoelectron peaks in the $R(1)$ spectra]. For example, in the $v^+=v'$ photoelectron band in the $R(0)$ spectrum, the $N^+=4$ peak is quite small, while in the $v^+\neq v'$ bands the $N^+=4$ peaks are much more intense relative to the corresponding $N^+=0,2$ peaks. In addition, the $v^+=3, N^+=4$ photoelectron peak is nearly the same intensity as the $v^+=4, N^+=4$ photoelectron peak, in dramatic contrast to the dominant behavior of the $v^+=4, N^+=0,2$ rotational peaks over the $v^+=3, N^+=0,2$ peaks. Similar behavior is observed for the $N^+=5$ photoelectron peaks in the $R(1)$ spectrum. If we consider only parity-favored processes in the angular momentum transfer formulation of the photoionization dynamics (Dill 1976; Fano and Dill 1972; Dill 1972), the $N^+=4$ and 5 peaks in the $R(0)$ and $R(1)$ spectra, respectively, require the value of the angular momentum transfer to be $j_t=3$, while, with one exception, the lower N^+ peaks may arise from $j_t=1$ and 3. [The $N^+=0$ peak in the $R(0)$ spectrum can only arise from $j_t=1$.] The increase in the relative intensity of the high N^+ values in the off-diagonal bands seems to indicate a different mechanism for ionization to the $v^+\neq v'$ continua than to the $v^+=v'$ continua.

In order to provide some physical interpretation to the angular momentum transfer formulation, it is useful to divide the photoionization process into two steps, (1) the photoabsorption step, and (2) the subsequent escape of the photoelectron from the ion core. In step (1), the angular momentum transfer for photoionization of the $C^1\Pi_u$ state of H_2 is limited to $j_t=1$. Only in step (2) can angular momentum transfer between the escaping photoelectron and the residual ion core produce $j_t=3$ processes as well as $j_t=1$ processes. Thus, it appears that such angular momentum transfers in step (2) become relatively more important for $v^+\neq v'$ than for $v^+=v'$, indicating some difference in the dominant mechanism for ionization into alternative vibrational final states.

The $H_2 C^1\Pi_u$, $v'=0-4$, $Q(1)$ photoelectron angular distributions that we presented provide a detailed basis for comparison with theoretical calculations aimed at producing an understanding of the excited-state photoionization dynamics of molecular hydrogen. Although the only currently available calculations are in excellent agreement with the $v^+=v'$ photoelectron angular distributions, the agreement with the off-diagonal angular distributions is relatively poor. In particular, the decrease in anisotropy in the experimental angular distributions on either side of the $v^+=v'$ photoelectron peak is not reproduced in the calculations. Thus, although significant progress in describing excited-state photoionization dynamics has been made, improvements in the theoretical model are needed to achieve the desired level of understanding. The $H_2 C^1\Pi_u$, $v'=4$, $R(0)$ and $R(1)$ photoelectron spectra introduce a number of new questions about the $C^1\Pi_u$ photoionization dynamics. In particular, the strongly v^+ -dependent rotational branching ratios at $\theta=0^\circ$ seem to reflect different mechanisms for the ionization processes in the $v^+=v'$ and the $v^+\neq v'$ spectra. Thus, both the photoelectron angular distributions and the

FIGURE 5.19 Photoelectron spectra of H_2 determined along the laser polarization axis ($\theta=0^\circ$) and at the wavelengths of the resonant three-photon $C^1\Pi_u, v'=4 \leftarrow X^1\Sigma_g^+, v''=0, R(0)$ and $R(1)$ transitions.

v^+ -dependent rotational branching ratios presented here indicate that the photoionization dynamics of the $C^1\Pi_u$ state of H_2 are more complicated than was originally expected. We hope that these experimental data will provide the stimulus for future theoretical developments.

5.4.5 Photoelectron Studies of Resonantly Enhanced Multiphoton Ionization of H_2 Via the $B'^1\Sigma_u^+$ and $D^1\Pi_u$ States

S.T. Pratt, P.M. Dehmer, and J.L. Dehmer

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We previously reported resonant multiphoton ionization photoelectron spectra (REMPI-PES) of molecular hydrogen via the $B^1\Sigma_u^+$ (Pratt et al. 1983) and $C^1\Pi_u$ (Pratt et al. 1984) electronic states. The $B^1\Sigma_u^+$ and $C^1\Pi_u$ represent the lowest-lying states of these symmetries and correspond to the electron configurations $1s\sigma_g 2p\sigma_u$ and $1s\sigma_g 2p\Pi_u$, respectively. With the aim of providing experimental results on the photoionization of additional excited states of H_2 , we have now determined the three-photon-resonant, four-photon (3+1) ionization REMPI-PES spectra via the $B'^1\Sigma_u^+$, $v'=0-2$ and $D^1\Pi_u$, $v'=0,1$ levels. The $B'^1\Sigma_u^+$ and $D^1\Pi_u$ electronic states correspond to the configurations $1s\sigma_g 3p\sigma_u$ and $1s\sigma_g 3p\Pi_u$, respectively; i.e., they are the next members of the Rydberg series whose lowest levels are the $B^1\Sigma_u^+$ and $C^1\Pi_u$ states.

The photoelectron spectra obtained following (3+1) ionization of H_2 via the $Q(1) D^1\Pi_u$, $v'=0 + X^1\Sigma_g^+$, $v''=0$; $Q(1) D^1\Pi_u$, $v'=1 + X^1\Sigma_g^+$, $v''=0$; and $R(1) D^1\Pi_u$, $v'=1 + X^1\Sigma_g^+$, $v''=0$ transitions are shown in Fig. 5.20. The $Q(1) D^1\Pi_u$, $v'=0$ spectrum shows an intense $v^+=0$ photoelectron peak, a weak $v^+=1$ peak, and vanishing intensity for the remaining v^+ peaks. The $Q(1) D^1\Pi_u$, $v'=1$ spectrum displays a strong $v^+=1$ photoelectron peak with weak $v^+=0, 2$, and 3 sidebands. The intensities of all other v^+ peaks are negligible, with the exception of the $v^+=9$ photoelectron peak. The $Q(1)$ line of the $D^1\Pi_u$, $v'=1 + X^1\Sigma_g^+$, $v''=0$ transition is blended with the $Q(1)$ line of the $C^1\Pi_u$, $v'=9 + X^1\Sigma_g^+$, $v''=0$ transition; the ionization of the $C^1\Pi_u$, $v'=9$ level gives rise to the relatively intense $v^+=9$ photoelectron peak.

Qualitatively, the photoelectron spectra of Fig. 5.20 conform to expectations based on the Franck-Condon factors for the photoionization of a Rydberg state with a potential curve similar to that of the corresponding ionic state. In such a case, the Franck-Condon factors for the $v^+=v'$ transitions are nearly unity, and the dominant ionization pathway then leads to the production of ions with vibrational quantum numbers $v^+=v'$. The spectra of Fig. 5.20 also show strong resemblances to the photoelectron spectra obtained following (3+1) ionization of H_2 via the $C^1\Pi_u$, $v'=0, 1$ levels (Pratt et al. 1984). This is expected because the $D^1\Pi_u$ is the next number in the $n p \pi$ Rydberg series. However, although the qualitative agreement between the experimental results and the Franck-Condon factors is good, as in the case of the $C^1\Pi_u$ spectra (Pratt et al. 1984), the quantitative agreement is poor.

FIGURE 5.20 REMPI-PES spectra of H_2 determined at the wavelengths of the resonant three-photon $D^1\Pi_u, v'=0 \leftarrow X^1\Sigma_g^+, v''=0, Q(1)$; $D^1\Pi_u, v'=1 \leftarrow X^1\Sigma_g^+, v''=0, Q(1)$; and $D^1\Pi_u, v'=1 \leftarrow X^1\Sigma_g^+, v''=0, R(1)$ transitions.

The potential curve of the $B' \ ^1\Sigma_u^+$ Rydberg state differs significantly from that of the $H_2^+ X \ ^2\Sigma_g^+$ state, with the value of ω_e significantly lower for the former state [$\omega_e(B' \ ^1\Sigma_u^+) = 2039.52 \text{ cm}^{-1}$ and $\omega_e(X \ ^2\Sigma_g^+) = 2321.70 \text{ cm}^{-1}$] (Huber and Herzberg 1979). Consequently, the $B' \ ^1\Sigma_u^+$ photoelectron spectra are not expected to be as strongly peaked at $v^+ = v'$ as the $D \ ^1\Pi_u$ spectra. The photoelectron spectra obtained following (3+1) ionization via the $R(1) \ B' \ ^1\Sigma_u^+, v'=0-2 \leftarrow X \ ^1\Sigma_g^+, v''=0$ transitions are shown in Fig. 5.21. As in the $D \ ^1\Pi_u$ photoelectron spectra, the qualitative agreement between the Franck-Condon factors and the experimental intensities is good. However, the quantitative agreement is again poor, and in each of the spectra of Fig. 5.21, the intensity of what is theoretically predicted to be the most intense peak is redistributed into the other channels in the experimental spectra.

The discrepancies between the simple Franck-Condon predictions and the observed photoelectron spectra for the $D \ ^1\Pi_u$ and $B' \ ^1\Sigma_u^+$ electronic states can be caused by a number of dynamical effects that have been enumerated in detail earlier (Pratt et al. 1984). More detailed theoretical calculations, such as those made for the REMPI-PES spectra via the $C \ ^1\Pi_u$ electronic state (Dixit et al. 1984a), are clearly needed to assess the relative importance of the different effects. Such calculations will improve our understanding of excited-state photoionization dynamics in molecular hydrogen.

5.4.6 Molecular Photoionization and Photodissociation Dynamics with Multiphoton Ionization - Photoelectron Spectroscopy

P.M. Dehmer, J.L. Dehmer, and S.T. Pratt

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Resonantly enhanced multiphoton ionization (REMPI) of molecules has been used for over a decade to obtain detailed spectroscopic information on excited neutral states. With the addition of photoelectron spectrometry (PES) to analyze the kinetic energy of the ejected electrons, it is possible to determine the branching ratios into different electronic, vibrational, and rotational levels of the product ion and to focus directly on the dynamics of both the multiphoton ionization process and the photoionization of excited-state species.

As does single-photon PES, REMPI-PES relies on the determination of the kinetic energy and angular distributions of the ejected photoelectrons to provide information on ionic energy levels and the dynamics of the photoionization process. However, significant differences exist between the single-photon process and the corresponding REMPI process. In a typical single-photon process, one photon is used to ionize a thermal distribution of vibrational and rotational levels of the ground electronic state of a target molecule. In contrast, in a typical (m+n) REMPI-PES study, a single vibrational and rotational level of an excited resonant intermediate state is prepared by m-photon (usually m=1 to 3) excitation with radiation from a pump laser, and this excited state is subsequently ionized by an n-photon (usually n=1) process with radiation either from the pump laser or from a second, independently tunable probe laser.

FIGURE 5.21 REMPI-PES spectra of H_2 determined at the wavelengths of the resonant three-photon $B'^1\Sigma_u^+, v'=0-2 \leftarrow X'^1\Sigma_g^+, v''=0$ R(1) transitions.

The most significant advantages of REMPI-PES over single-photon PES arise from the characteristics of pulsed laser excitation and ionization sources, i.e., high peak power, short pulse duration, high wavelength resolution, and significant wavelength tunability. Use of the appropriate combination of tunable pulsed lasers should allow preparation and subsequent ionization of virtually any resonant intermediate state. In addition, photoelectron spectroscopy can probe the products of the decay of the resonant intermediate state.

Single-photon PES experiments have been used to provide information on ionic energy levels, the dynamics of photoionization from the ground state, and (when a variable-frequency light source is used) the photoionization branching ratios and angular distributions as a function of ionizing wavelength, including branching ratios across resonances in the ionization continuum. REMPI-PES offers several important advantages over single-photon PES for these types of studies. In particular, REMPI-PES provides higher wavelength resolution, which improves photoelectron kinetic energy resolution, enables the preparation of a resonant intermediate state in a single rotational and vibrational level, and enables the detailed study of branching ratios as a function of wavelength across individual rotational autoionizing resonances in the ionization continuum. In addition, REMPI-PES permits the study of the dynamics of photoionization from excited states, the determination of the photoelectron spectra of transient species or minor species that occur in the presence of a large concentration of a species with an interfering photoelectron spectrum, the study of the photoelectron spectra of the products of photodissociation or predissociation, the study of time-resolved intramolecular energy transfer processes, and the observation of both resonant intermediate states and final ionic states that might be symmetry-forbidden in single-photon excitation.

5.4.7 Two-Photon Spectroscopy of the nd Complexes of Nitric Oxide

S.T. Pratt

The analysis of the two-photon ionization spectrum of rotationally cooled nitric oxide (NO) determined at high resolution in the region between the $\text{NO}^+ X^1\Sigma^+, v^+=0$ and 2 thresholds (2500-2680 Å) has progressed from our preliminary results of last year. The present two-photon ionization spectrum is completely different from the corresponding single-photon ionization spectrum owing to the differences in selection rules for one- and two-photon absorption. The spectrum is also significantly different from the optical-optical double resonance spectrum. Although the $n=7-11$ members of the nd Rydberg series converging to the $\text{NO}^+ X^1\Sigma^+, v^+=1$ and 2 thresholds have been identified, the detailed analyses of these bands are difficult owing to the highly perturbed nature of the nd Rydberg complexes in NO. However, recent calculations by Ch. Jungen (1986) on the rotational energy levels of the nd complexes strongly suggest that these bands correspond to the previously unobserved $nd\pi^-$ components. We are currently attempting to calculate two-photon rotational line intensities in order to confirm these assignments.

5.4.8 Rotational and Vibrational Branching Ratios from Resonantly Enhanced Multiphoton Ionization-Photoelectron Spectroscopy of H_2 via the $C^1\Pi_u$ State

M.A. O'Halloran, S.T. Pratt, P.M. Dehmer, and J.L. Dehmer

Photoelectron spectra have been obtained following three-photon-resonant, four-photon (3+1) ionization of H_2 via the $C^1\Pi_u$, $v'=0-4$ states. These spectra were determined by using a magnetic bottle electron spectrometer (Kruit and Read 1983), which measures angle-integrated photoelectron intensities with 50% collection efficiency for electrons with kinetic energies up to 10 eV. The present experiment confirms and extends our previously reported results (Pratt et al. 1984; Pratt et al. 1986), which were obtained with a hemispherical electron energy analyzer.

The $C^1\Pi_u$ state is the lowest Rydberg state converging to $H_2^+ X^2\Sigma_g^+$. In the (3+1) multiphoton ionization process discussed here, the production of the ionic vibrational state with $v^+=v'$ is the dominant channel, but a significantly greater population is observed in the off-diagonal channels ($v^+\neq v'$) than is predicted either by Franck-Condon overlap or by *ab initio*, Hartree-Fock level calculations. This is illustrated in Fig. 5.22, which compares the vibrational branching ratios obtained in the present experiment for (3+1) excitation via $C^1\Pi_u$ [Q(1) transition], with those calculated by Dixit et al. (1984a). The vibrational branching ratios obtained for excitation of all observed intermediate levels were qualitatively the same as those shown for excitation via Q(1) transitions, indicating that neither perturbations of the intermediate state by the $B^1\Sigma_u^+$ state, nor accidental resonances at the four-photon energy with sharp autoionizing structure in the continuum, can explain the significant disagreement between experiment and calculation.

As the vibrational quantum number of the resonant intermediate state increases, a pattern of increasing change of both the vibrational and rotational states of the ion relative to those of the resonant intermediate state is observed (Figs. 5.23 and 5.24). If the ion and photoelectron are considered in Hund's case (d) coupling, and only s- and d-partial waves are considered, then parity selection rules determine that the allowed values of change of rotational quantum number, $\Delta N = [N^+(H_2^+) - J'(C^1\Pi_u)]$, are $\Delta N = 0, \pm 2$ for Q-branch excitation and $\Delta N = \pm 1, \pm 3$ for R-branch excitation. For (3+1) ionization via $C^1\Pi_u$, $v'=0$, no evidence is observed of photoelectron peaks corresponding to larger changes in rotational quantum number (Fig. 5.23). As the vibrational quantum number of the intermediate level increases, the intensity of the photoelectron peaks corresponding to larger changes of rotational angular momentum increases (Fig. 5.24). These peaks tend to be significantly larger for the off-diagonal vibrational bands ($v^+\neq v'$), indicating that the photoionization dynamics that produce changes of vibrational energy in the ion relative to the intermediate state also involve larger exchanges of angular momentum between the ion and the departing photoelectron.

FIGURE 5.22 Vibrational branching ratios determined for three-photon-resonant, four-photon ionization of H_2 via $\text{C } ^1\Pi_u, v'$ [Q(1) transitions]. Calculation is that of Dixit et. al. (1984a).

5.4.9 Resonantly Enhanced Multiphoton Ionization of Atomic Nitrogen via the $3p \ ^2S_{1/2}^o$ Level

S.T. Pratt, P.M. Dehmer, and J.L. Dehmer

[Adapted from the abstract of a paper published in Physical Review A 36:1702 (1987)]

The two-photon-resonant, three-photon (2+1) ionization spectrum of atomic nitrogen was determined in the region of the $2s^2 2p^2 ({}^3P) 3p \ ^2S_{1/2}^o$ state. A single laser was used to produce nitrogen atoms in the excited $2s^2 2p^3 \ ^2D_{3/2,5/2}^o$ levels by multiphoton dissociation of nitrous oxide (N_2O) and also to probe the two-photon ${}^2S_{1/2}^o + {}^2D_{3/2,5/2}^o$ transitions. In addition, the photoelectron spectrum and the photoelectron angular distribution were obtained for excitation via the ${}^2S_{1/2}^o + {}^2D_{5/2}^o$ transition. The photoelectron spectrum shows a single peak corresponding to the production of the $\text{N}^+ \ ^3P$ ground state. The ${}^2S_{1/2}^o$ intermediate state cannot be aligned, and it should be possible

FIGURE 5.23 Photoelectron spectra determined at the wavelengths of three-photon-resonant $\text{H}_2 \text{C } ^1\Pi_u, v'=0 + \text{X } ^1\Sigma_g^+, v''=0$, Q(2) and R(3) transitions. Spectra of individual vibrational bands were recorded separately. Relative areas of vibrational bands are set equal to the vibrational branching ratios.

to obtain a theoretical photoelectron angular distribution by using a simple one-electron model. The validity of this approximation for this important first-row atom could then be tested by using higher-level calculations.

5.4.10 Photoionization Dynamics of Excited Molecular States. $\text{D}_2 \text{C } ^1\Pi_u$

S.T. Pratt, P.M. Dehmer, and J.L. Dehmer

[Adapted from the abstract of a paper published in *Journal of Chemical Physics* 87:4423 (1987)]

We have determined the three-photon-resonant, four-photon (3+1) ionization spectra of D_2 via the $\text{C } ^1\Pi_u, v'=0-4$ levels. In addition, we have determined the photoelectron spectra and photoelectron angular distributions for the Q(3) lines in the $\text{C } ^1\Pi_u, v'=0-3$ bands, and the photoelectron spectra for the Q(1) lines in the $\text{C } ^1\Pi_u, v'=0-4$ bands. These studies were performed in an effort to understand the discrepancies between the theoretical and experimental results for the analogous processes in H_2 . In particular, the isotopic studies allow an assessment of the validity of the Born-Oppenheimer approximation (i.e., the separation of nuclear and electronic motion) in the H_2 spectra. The Born-Oppenheimer approximation has been made in all previous calculations of molecular multiphoton ionization, and the present study is an important test of this assumption.

FIGURE 5.24 Photoelectron spectra determined at the wavelengths of three-photon-resonant $H_2\ C\ 1\Pi_u, v'=4 + X\ 1\Sigma_g^+, v''=0$, Q(1) and R(1) transitions.

5.5 PHOTOPHYSICS STUDIES IN THE VACUUM ULTRAVIOLET

5.5.1 Summary

Photophysics studies in the vacuum ultraviolet generally have two broad objectives. The first is to determine the spectroscopy of excited neutral states and ionic states. The second is to explore the dynamics of the photoionization processes. The work summarized below emphasizes basic studies of small molecules, including weakly bound van der Waals complexes. Various techniques are employed, including photoionization mass spectrometry using a Hopfield continuum light source, triply differential electron spectrometry using synchrotron radiation, and fluorescence polarization studies.

5.5.2 Electrostatic and Spin Orbit Autoionization in HCl

H. Lefebvre-Brion, P.M. Dehmer, and W.A. Chupka**

We used for HCl the theory of spin orbit autoionization, including vibrational effects (recently applied to the interpretation of the photoionization spectrum of HBr between the $X\ 2\Pi_{3/2}$ and $X\ 2\Pi_{1/2}$ ionization thresholds). Preliminary calculations reproduce well the energy positions of the first peaks observed in the photoionization cross sections, but cannot explain the anomalies in the intensities. These anomalies are assumed to be due to the highest vibrational levels of the $V\ 1\Sigma^+$ ionic state.

The Rydberg states of the series converging to the $A^2\Sigma^+$ state are autoionized by electrostatic interaction with the continuum of the $X^2\Pi$ state. We used a multichannel quantum defect theory with ab initio calculations of the electronic quantities to study the autoionized peaks in the wavelength region of 770-900 Å. We showed that progression II is due to the $d\sigma^1\Sigma^+$ states and progression I to the $d\pi^1\Pi$ states. This is in disagreement with previous assignments.

5.5.3 Photoionization of Rotationally Cooled H_2O and D_2O

*P.M. Dehmer and D.M.P. Holland**

Despite considerable effort, the vacuum UV absorption spectra of H_2O and D_2O in the region of the ionization continuum still are not well understood. In particular, the discrete structure in the absorption and ionization spectra have not yet been quantitatively assigned to specific Rydberg states. The ground state configuration of H_2O is $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2^1A_1$, and the He I 584 Å photoelectron spectrum consists of the states produced by ionization of the outermost three orbitals. The ionization potentials of these orbitals are 12.6223 eV (982.27 Å) for the X^2B_1 state, 13.8417 eV (895.74 Å) for the A^2A_1 state, and 17.178 eV (721.77 Å) for the B^2B_2 state. The ionization processes consist of the corresponding three direct ionization processes as well as autoionization of Rydberg series converging to these limits. In the current study, we have added to the large body of work already existing for H_2O and D_2O by determining the first photoionization spectra of the rotationally cooled molecules; we found that rotational cooling significantly enhances the Rydberg structure with respect to the direct ionization background. In addition, our spectra are the highest-resolution (0.065 - 0.11 Å) photoionization spectra reported to date for these species.

While the major part of the photoionization occurs by the direct process, significant structure due to autoionization is also present. These Rydberg states undergo simultaneous competitive decay to neutral products. Predissociation is the most likely competing process for this state, although fluorescence can be dominant in certain cases.

Steplike structure is observed in the region of the X^2B_1 ionization threshold corresponding to the formation of the ion in the (0,0,0), (0,1,0), and (1,0,0) vibrational levels of the X^2B_1 state. The fact that these steps are clearly displayed at the vibrational limits is evidence that the major fraction of the Rydberg states converging to these thresholds decays by processes other than autoionization, because the principle of continuity of oscillator strength through a convergence limit requires that no steps appear in the ionization efficiency curve if these Rydberg states are totally autoionized.

Considerable structure exists in the region from the ionization threshold to 700 Å. Identification of the structure is suggested on the basis of quantum defects and on the similarity to the band shapes in the photoelectron spectrum. The structure in the region near the threshold (900-990 Å) consists of two Rydberg states converging to the 2A_1 state of the ion. A sharp Rydberg state is observed in the region from 920-980 Å, which is

*Collaborator; affiliation is listed at the front of this chapter.

assigned as the 5s state. The bands of this Rydberg state show a clear alternation in appearance, characteristic of a bent-to-linear transition. This trend is similar to that observed in other bent-to-linear transitions, most notably the $A^2A_1 - X^2B_1$ emission spectrum of H_2O^+ . In this same region, another stronger and broader state is observed at slightly shorter wavelength; this may be the 3d or the 4p state.

In addition, a vibrational progression is observed in the region from 800-860 Å, which is probably the 3s Rydberg state converging to the 2B_2 state of the ion. Vibrational progressions also are observed in the region from 700-800 Å with $n^* = 2.66$; these also converge to the 2B_2 state of the ion.

5.5.4 Vibrationally Resolved Photoelectron Angular Distributions for H_2 in the Range $17 \text{ eV} \leq h\nu \leq 39 \text{ eV}$

A.C. Parr, J.E. Hardis,* S.H. Southworth,* C.S. Feigerle,* T.A. Ferrett,*
D.M.P. Holland,* F.M. Quinn,* B.R. Dobson,* J.B. West,* G.V. Marr,* and
J.L. Dehmer*

[Summary of an article to appear in Physical Review A.]

Vibrationally resolved photoelectron angular distributions have been measured for photoionization of H_2 over the range $17 \text{ eV} \leq h\nu \leq 38 \text{ eV}$ by using independent instrumentation at two synchrotron radiation facilities. The present data greatly extend and add vibrational resolution to earlier variable wavelength measurements. The average magnitudes of the asymmetry parameters continue to lie significantly lower than those for independent-electron calculations. Incipient, broad structure is observed for the first time, possibly indicating the effects of channel interaction with dissociative, doubly excited states of H_2 . Neither the average magnitude nor the wavelength-dependent structure appears to vary strongly with final vibrational channel.

5.5.5 Fluorescence Polarization Studies of Autoionization in CS_2

E.D. Poliakoff, J.L. Dehmer, A.C. Parr,* and G.E. Leroi**

[Adapted from an article published in Journal of Chemical Physics 86:2557 (1987).]

We measured the polarization of the CS_2^+ ($A^2\Pi \rightarrow X^2\Pi$) transition following photoionization of CS_2 with synchrotron radiation in the range $875 \text{ Å} < \lambda_{\text{exc}} < 967 \text{ Å}$. Autoionization features prominent in the fluorescence polarization spectrum were investigated in detail. The spectral assignments of the absorption spectrum by Ogawa and Chang (1970) are supported by the current measurements. Although fluorescence excitation and fluorescence polarization profiles normally align precisely, exceptions have been found for many resonances ($\sigma_u \rightarrow nd\pi$, $n > 3$), and comparisons between the lineshapes are given for several features.

*Collaborator; affiliation is listed at the front of this chapter.

5.5.6 Resonance Structure in the Vibrationally Resolved Photoelectron Branching Ratios and Angular Distributions of the $2\pi^{-1}$ Channel of NO

S.H. Southworth, A.C. Parr,* J.E. Hardis,* and J.L. Dehmer*
[Abstract of an article submitted to Journal of Chemical Physics]

We determined vibrationally resolved photoelectron angular distributions and branching ratios for $\text{NO}^+ (2\pi^{-1}) X^1\Sigma^+$ by using synchrotron radiation in the range $h\nu = 11.5\text{--}26$ eV. Normally weak vibrational levels were strongly enhanced below 18 eV, and the photoelectron asymmetry parameters and branching ratios displayed a vibrationally dependent, broad spectral structure over $h\nu \approx 11\text{--}18$ eV. These observations may reflect the presence of the expected σ shape resonance. However, various interchannel coupling mechanisms may also be involved. Resonance structure in the photoelectron asymmetry parameters is also observed in the $h\nu \approx 19\text{--}22$ eV region. This structure is probably associated with Rydberg excitations of the 4σ orbital.

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APPENDICES FOR CHAPTER 5**Fundamental Molecular Physics and Chemistry**

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APPENDIX 5-A. STAFF QUALIFICATIONS

Fundamental Molecular Physics and Chemistry Program

Name	Position	Highest Degree	Major	Year Received	Institution
Dehmer, Joseph L.	Senior Physicist	Ph.D.	Chemical Physics	1971	University of Chicago
Dehmer, Patricia M.	Senior Chemist	Ph.D.	Chemical Physics	1972	University of Chicago
Dillon, Michael A.	Physicist	Ph.D.	Physical Chemistry	1965	University of Notre Dame
Inokuti, Mitio	Senior Physicist	Ph.D.	Applied Physics	1962	University of Tokyo
Kimura, Mineo	Visiting Scientist	Ph.D.	Chemical Physics	1981	University of Alberta
O'Halloran, Maureen A.	Postdoctoral Appointee	Ph.D.	Physics	1986	Stanford University
Pratt, Stephen T.	Chemist	Ph.D.	Chemistry	1982	Yale University
Spence, David	Physicist	Ph.D.	Physics	1967	University of Newcastle-Upon-Tyne
Tomkins, Frank S.	Consultant	Ph.D.	Physical Chemistry	1942	Michigan State University

APPENDIX 5-B. OUTSTANDING PROFESSIONAL ACTIVITIES AND AWARDS

- J.L. DEHMER--Member, Editorial Board, Journal of Electron Spectroscopy, 1986-; Advisory Committee, "New Opportunities in Chemistry: An International Symposium on the Uses of Synchrotron Radiation in Chemistry," 1986-1987; Member, National Research Council Committee on Atomic and Molecular Sciences, 1983-86; Chairman (1985-1986) Gordon Research Conference on Electron Spectroscopy.
- P.M. DEHMER--Member, Executive Committee, American Physical Society Division of Electron and Atomic Physics, 1979, 1981-84, 1986-89; Member, American Physical Society Committee on Opportunities in Physics, 1984-1986; Member, American Physical Society Committee on Constitution and Bylaws, 1986-1988; Member, Editorial Board, Review of Scientific Instruments, 1985-1987; Chairperson, Selection Committee for the Presidential Young Investigator Award, Physics Division, National Science Foundation, 1986; Chairperson, Gordon Research Conference on Multiphoton Processes, 1986; elected to terms on the Council of the Gordon Research Conferences (1987-1989) and the Council of the American Physical Society (1987-1990).
- M. INOKUTI--Member of the International Commission of Radiation Units and Measurements (ICRU), 1985-1989; Member of the Science and Technical Talent Pool, Committee on Interagency Radiation Research and Policy Coordination (CIRRPC), 1985; Associate Member, Local Organizing Committee for the Tenth International Conference on Atomic Physics, August 1986, Tokyo, Japan.
- S.T. PRATT--awarded the Argonne National Laboratory Pacesetter Award in July 1985.

APPENDIX 5-C. SPECIAL EVENTS ORGANIZED

- J.L. DEHMER, Chaired Gordon Research Conference on Electron Spectroscopy, 18-21 July 1986, Brewster Academy, Wolfeboro, New Hampshire.
- P.M. DEHMER, Chaired Gordon Research Conference on Multiphoton Processes, 9-13 June 1986, Colby Sawyer College, New London, New Hampshire.
- M. INOKUTI, Hosted meeting of the Report Committee on Stopping Power and Ranges for the International Commission on Radiation Units and Measurements (ICRU), 22-24 October 1986, Argonne National Laboratory.
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APPENDIX 5-D. EDUCATIONAL PROGRAM PARTICIPANTS

HIROSHI TANAKA. Visiting Foreign Scholar. Department of General Science, Faculty of Science and Technology, Sophia University, Tokyo, Japan. July 1986 - August 1986.

APPENDIX 5-E. PUBLICATIONS AND ORAL PRESENTATIONS

Fundamental Molecular Physics and Chemistry Program

1. Refereed Journal Articles*

Bichsel, H., M. Inokuti, and D.Y. Smith. Mean excitation energy for stopping power of metallic aluminum: Comments on McGuire's article. *Physical Review A* 33:3567-3571 (1986). [DOE/OHER]**

Dehmer, P.M., S.T. Pratt, and J.L. Dehmer. Gerade electronic states of Xe_2 observed using resonantly enhanced multiphoton ionization. *Journal of Chemical Physics* 85:13-24 (1986). [DOE/OHER, DOD/ONR]

Eggarter, E.. Theory of initial yields of ions generated by electrons in binary mixtures. *Journal of Chemical Physics* 84:6123-6128 (1986). [DOE/OHER]

Fano, U., J.A. Stephens, and M. Inokuti. Absence of resonances in the elastic scattering of electrons in molecular solids. *Journal of Chemical Physics* 85:6239-6240 (1986). [DOE/OHER]

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Lefebvre-Brion, H., P.M. Dehmer, and W.A. Chupka. Vibrational effects in the spin-orbit autoionization of HBr. *Journal of Chemical Physics* 85:45-50 (1986). [DOE/OHER, DOD/ONR]

Naleway, C., M. Inokuti, M.C. Sauer, Jr., and R. Cooper. Theoretical study of the time dependence of the production of excited N_2 by subexcitation electrons in rare-gas mixtures. *Journal of Physical Chemistry* 90:6154-6158 (1986). [DOE/OHER]

Pratt, S.T. Photoelectron spectroscopy of Rydberg states of atomic iodine. *Physical Review A* 33:1718-1724 (1986). [DOE/OHER, DOD/ONR]

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*For published material, the names of all Environmental Research Division authors are underlined. [Included are Division members who participated in a project but left the Division before the results were published.]

**Funding agency (abbreviations are spelled out at the end of this appendix).

- Pratt, S.T., P.M. Dehmer, and J.L. Dehmer. Photoionization dynamics of excited molecular states: Photoelectron angular distributions and rotational and vibrational branching ratios for $\text{H}_2\text{C}^1\Pi_u$, $v=0-4$. *Journal of Chemical Physics* 85:3379-3385 (1986). [DOE/OHER, DOD/ONR]
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- Southworth, S.H., A.C. Parr, J.E. Hardis, and J.L. Dehmer. Channel coupling and shape resonance effects in the photoelectron angular distributions of the $3\sigma_g^{-1}$ and $2\sigma_u^{-1}$ channels of N_2 . *Physical Review A* 33:1020-1023 (1986). [DOE/OHER, DOD/ONR]
- Southworth, S.H., A.C. Parr, J.E. Hardis, J.L. Dehmer, and D.M.P. Holland. Calibration of a monochromator/spectrometer system for the measurement of photoelectron angular distributions and branching ratios. *Nuclear Instrumentation Methods A* 246:782-786 (1986). [DOE/OHER, DOD/ONR]
- Spence, D., H. Tanaka, M.A. Dillon, and K. Lanik. Direct observation of 157 nm laser photons from the $f^3\Pi_g$ state of F_2 by high resolution electron impact. *Journal of Physics B* 19:L569-L573 (1986). [DOE/OHER]
- Stephens, J.A., D. Dill, and J.L. Dehmer. Shape resonances in the photoionization of CF_4 . *Journal of Chemical Physics* 84:3638-3646 (1986). [DOE/OHER]
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2. Books, Book Chapters, and Collections of Conference Proceedings

- Inokuti, M., and M.A. Dillon. What formulas are good for representing dipole and generalized oscillator-strength spectra? In: *Physics of Ionized Gases*. M.M. Popović and P. Krstić (eds.). World Scientific, Singapore. 1986. pp. 3-22. [DOE/OHER]

3. Reports

Environmental Research Division Annual Report. Fundamental Molecular Physics and Chemistry. January 1984 - December 1985. ANL-86-15, Chapter 5. Argonne National Laboratory. 1986. [DOE, DOD]

4. Published Conference Papers

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Lin, C.D., W. Fritsch, and M. Kimura. An overview of low-energy ion-atom collisions. In: Proceedings of International Seminar on Dynamic Processes of Highly Charged Ions, 21-24 August 1986, Wako, Saitama, Japan. 1986. pp. 3-13. [DOE/OHER, OBES]

Pratt, S.T., P.M. Dehmer, and J.L. Dehmer. Photoionization and predissociation of excited states of NeXe, ArXe, KrXe, and Xe₂. In: Advances in Laser Science. I. American Institute of Physics Conference Proceedings No. 146. W.C. Stwalley and M. Lapp (eds.). American Institute of Physics, New York. 1986. pp. 493-494. [DOE/OHER, DOD/ONR]

5. Published Abstracts, Notes, Reviews, Comments, and Letters

Dehmer, J.L., P.M. Dehmer, S.T. Pratt, M.A. O'Halloran, and F.S. Tomkins. Experimental REMPI studies of small molecules (Abstract). In: Proceedings of NASA Workshop on Atomic Oxygen Effects, Jet Propulsion Laboratory, 10-11 November 1986, Pasadena, CA, Book of Abstracts, p. 12 (1986). [DOE/OHER, DOD/ONR]

Dillon, M.A., and M. Inokuti. Time-dependent treatment of the yields of initial products and electron slowing down (Abstract). 34th Annual Scientific Meeting, 13-17 April 1986, Las Vegas, NV, Book of Abstracts. p. 51 (1986). [DOE/OHER]

Dillon, M.A., M. Inokuti, J.H. Miller, and K. Omidvar. Analytic representation of secondary-electron spectra resulting from electron and proton impact (Abstract). 34th Annual Scientific Meeting, 13-17 April 1986, Las Vegas, NV, Book of Abstracts. p. 54 (1986). [DOE/OHER]

- Dillon, M.A., M. Kimura, and M. Inokuti. Analytical time-dependent treatment of electron degradation: Electronic excitation of N_2 molecule by subexcitation electron in He or Ne gases (Abstract). 39th Annual Gaseous Electronics Conference, 7-10 October 1986, Madison, WI, Book of Abstracts. p. 158 (1986). [DOE/OHER, OBES]
- Dillon, M.A., H. Tanaka, and D. Spence. Electron energy loss spectra of disilane from 5-25 eV (Abstract). 39th Annual Gaseous Electronics Conference, 7-10 October 1986, Madison, WI, Book of Abstracts. p. 93 (1986). [DOE/OHER]
- Inokuti, M. The 1986 Annual Meeting of the International Commission on Radiation Units and Measurements (ICRU) (Note), Isotope News (in Japanese), No. 390. 1986. p. 9 (1986). [DOE/OHER]
- Inokuti, M. Book Review of: Bird of Passage. Recollections of a Physicist, by R. Peierls. In: Parity (in Japanese) 1(7):91 (1986). [DOE/OHER]
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- Kimura, M. The generalized oscillator strength for one-electron diatomic molecules (Abstract). 39th Annual Gaseous Electronics Conference, 7-10 October 1986, Madison, WI, Book of Abstracts. p. 156 (1986). [DOE/OHER, OBES]
- Kimura, M., and M. Inokuti. Yields of initial products and electron degradation spectra in binary mixtures under electron irradiation (Abstract). 34th Annual Scientific Meeting, 13-17 April 1986, Las Vegas, NV, Book of Abstracts. p. 54 (1986). [DOE/OHER, OBES]
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- Shirai, T. Ionization of Rydberg atoms in thermal collisions with polar molecules (Abstract). 39th Annual Gaseous Electronics Conference, 7-10 October 1986, Madison, WI, Book of Abstracts. p. 148. [DOE/OHER]
- Southworth, S.H., J.E. Hardis, A.C. Parr, C.S. Feigerle, B.R. Dobson, F.M. Quinn, J.B. West, and J.L. Dehmer. Photoionization of H_2 : Vibrationally resolved photoelectron angular distribution. Bulletin of the American Physical Society 31:937 (1986). (Program of the Seventeenth Meeting of the Division of Atomic, Molecular, and Optical Physics, 18-20 June 1986, Eugene, OR.) [DOE/OHER]

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6. Oral Presentations*

Dehmer, J.L. Probing excited states of atoms and molecules using resonant multiphoton ionization. Presented at Chemistry Department Seminar, University of Tennessee, 6 May 1986, Knoxville, TN. [Faculty and students]** [DOE/OHER]

Dehmer, J.L. Resonantly enhanced multiphoton ionization of molecules. Presented at Chemistry Division Seminar, Oak Ridge National Laboratory, 7 May 1986, Oak Ridge, TN. [Scientists] [DOE/OHER]

Dehmer, J.L., P.M. Dehmer, and S.T. Pratt. Resonantly enhanced multiphoton ionization of molecules. Presented at the DOE (OHER and OBES) Workshop on Advanced Laser Technology for Chemical Measurements Workshop, 29 April - 1 May 1986, Seattle, WA. [DOE program managers and contractors] [DOE/OHER]

Dehmer, J.L., P.M. Dehmer, S.T. Pratt, M.A. O'Halloran, and F.S. Tomkins. Experimental REMPI studies of small molecules. Presented at the NASA Workshop on Atomic Oxygen Effects, Jet Propulsion Laboratory, 10-11 November 1986, Pasadena, CA. [Scientists] [DOE/OHER]

Dehmer, P.M. Spectroscopy and dynamics of rare gas dimers using VUV and multiphoton ionization techniques. Presented at 191st National American Chemical Society Meeting, 13-18 April 1986, New York, NY. [Scientists] [DOE/OHER, DOD/ONR]

*For oral presentations, the person who made the presentation is underlined.

**Audience for the presentation.

Dillon, M.A. Fundamental mechanisms in electron energy deposition processes as the basis for radiation chemistry and biology. Presented at the 19th Radiological and Chemical Physics Contractor's Meeting, 23-24 April 1986, Oak Ridge, TN. [Contractors and scientists] [DOE/OHER]

Dillon, M.A. Series of lectures on the topics of electron impact processes and radiation physics. Presented at Chengdu University of Science and Technology, 21 October - 2 November 1986, Chengdu, China. [Faculty, students] [DOE/OHER]

Dillon, M.A., M. Inokuti, and D. Spence. Presentations to the Functional Review of the Biomedical and Environmental Programs, 15 January 1986, Argonne National Laboratory. [Laboratory Director and others from the Office of the Director, ANL] [DOE/OHER]

Dillon, M.A., and M. Inokuti. Time-dependent treatment of the yields of initial products and electron slowing down. Presented at the 34th Annual Scientific Meeting, 13-17 April 1986, Las Vegas, NV. [Scientists] [DOE/OHER]

Dillon, M.A., and M. Inokuti. Analytic time-dependent treatment of electron degradation: Excitation of solute nitrogen molecules by subexcitation electrons in helium or neon. Presented at the Gordon Research Conference on Radiation Chemistry, 23-27 June 1986, Wolfeboro, NH. [Scientists, faculty, and students] [DOE/OHER]

Dillon, M.A., M. Kimura, and M. Inokuti. Analytical time-dependent treatment of electron degradation: Electronic excitation of N_2 molecule by subexcitation electron in He or Ne gases. Presented at the 39th Annual Gaseous Electronics Conference, 7-10 October 1986, Madison, WI. [Faculty, students, scientists] [DOE/OHER]

Dillon, M.A., H. Tanaka, and D. Spence. Electron energy loss spectra of disilane from 5-25 eV. Presented at the 39th Annual Gaseous Electronics Conference, 7-10 October 1986, Madison, WI. [Faculty, students, scientists] [DOE/OHER]

Inokuti, M. Theory of the ionization yield by radiation. Presented at Ruder Boskovic Institute, 15 September 1986, Zagreb, Yugoslavia. [Faculty, students, scientists] [DOE/OHER]

Inokuti, M. Survey and compilation of stopping-power data conducted by the International Commission on Radiation Units and Measurements. Presented at the Second Workshop on Stopping Power on Low-Energy Ions, 18-19 September 1986, Linz, Austria. [Scientists] [DOE/OHER]

Inokuti, M., M.A. Dillon, J.H. Miller, and K. Omidvar. Analytic representation of secondary-electron spectra resulting from electron and proton impact. Presented at the 34th Annual Scientific Meeting, Radiation Research Society, 13-17 April 1986, Las Vegas, NV. [Scientists] [DOE/OHER]

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Inokuti, M., C.E. Theodosiou, and S.T. Manson. Systematics of threshold phase shifts, or quantum defects, for atomic ions. Presented at the Tenth International Conference on Atomic Physics, 25-29 August 1986, Tokyo, Japan. [Scientists, faculty, students] [DOE/OHER]

Kimura, M. Rydberg atom-molecule collisions. Presented to the Physics Department of Rice University, 9 September 1986, Houston, TX. [Faculty, students] [DOE/OHER, OBES]

Kimura, M. Small angle differential cross sections in ion-atom, molecule collisions. Presented to the Physics Department and Joint Institute for Laboratory Astrophysics, University of Colorado, 11 September 1986, Boulder, CO. [Faculty, students, scientists] [DOE/OHER, OBES]

Kimura, M. The generalized oscillator strength for one-electron diatomic molecules. Presented at the 39th Annual Gaseous Electronics Conference, 7-10 October 1986, Madison, WI. [Faculty, students, scientists] [DOE/OHER, OBES]

Manson, S.T., M. Inokuti, and C.E. Theodosiou. Systematics of energy levels and other properties of highly charged ions. Presented at the International Seminar on Dynamic Processes of Highly Charged Ions, 21-24 August 1986, Susono, Shizuoka-ken, Japan. [Scientists] [DOE/OHER]

O'Halloran, M.A. Comments on Papers No. 4 and 10. Royal Society of Chemistry Faraday Discussion No. 82, "Dynamics of Molecular Photofragmentation," 15-17 September 1986, Bristol, England. [Faculty, students, scientists] [DOE/OHER]

O'Halloran, M.A., S.T. Pratt, J.L. Dehmer, and P.M. Dehmer. Photoelectron energy analysis following resonantly enhanced multiphoton ionization of H_2 via the $C\ ^1\Pi_u$ state. Presented at the Gordon Research Conference on Multiphoton Processes, 9-13 June 1986, New London, NH. [Scientists, faculty, and students] [DOE/OHER]

Pratt, S.T. Multiphoton ionization of diatomic molecules. Presented at the Gordon Research Conference on Multiphoton Processes, 9-13 June 1986, New London, NH. [Scientists, faculty, and students] [DOE/OHER]

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Shirai, T. Ionization of Rydberg atoms in thermal collisions with polar molecules. Presented at the 39th Annual Gaseous Electronics Conference, 7-10 October 1986, Madison, WI. [Faculty, students, scientists] [DOE/OHER]

Spence, D., D. DeMille, and M.A. Dillon. Profile index reversal in the $6\sigma \rightarrow n\rho\pi$ window resonances of N_2O . Presented at the Tenth International Conference on Atomic Physics, 25-29 August 1986, Tokyo, Japan. [Scientists, faculty, students] [DOE/OHER]

Spence, D., H. Tanaka, M.A. Dillon, and K. Lanik. Direct observation of 157.5 nm "laser" photons from the $f\ ^3\Pi_g$ state of F_2 . Presented at the 39th Annual Gaseous Electronics Conference, 7-10 October 1986, Madison, WI. [Faculty, students, scientists] [DOE/OHER]

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