

Volume Two

**ENERGY AND  
ENVIRONMENTAL  
CHEMISTRY**

Acid Rain

Edited by  
**LAWRENCE H. KEITH**

**Volume Two**

# **ENERGY AND ENVIRONMENTAL CHEMISTRY**

**Acid Rain**

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LAWRENCE H. KEITH**



**ANN ARBOR SCIENCE**  
THE BUTTERWORTH GROUP

## PREFACE

Energy and Environmental Chemistry—they are inextricably entwined. As we progress toward an increasingly industrialized and energy hungry world the demands of producing more and more energy are going to require greater care if we are to maintain a clean environment. There is no question that we will continue to produce more energy—progress demands it and people demand progress. The only question is how much we will let our continuous quest for energy affect our environment.

Learning about the effects of energy production—directly or indirectly—on the environment is one of the first steps to controlling adverse effects of that production. That's what these volumes are all about. They do not cover it all—do not even come close; the subject area is much too large and complex and we are only in the early stages of learning about the interrelations of energy and environmental chemistry. But it is hoped that the information in these books will bring us one step closer to understanding some of these relationships and hence to ultimately controlling unwanted pollution from energy production.



Lawrence H. Keith

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## ACKNOWLEDGMENTS

This is the second of a series of volumes entitled, "Energy and Environmental Chemistry." These volumes are collected papers from distinguished authors on the North American continent and abroad, and span several national and international meetings beginning with the Second Chemical Congress of the North American Continent in Las Vegas, Nevada (1980).

These symposia were jointly sponsored by the American Chemical Society's Committee on Environmental Improvement and the Division of Environmental Chemistry. However, it was only with the help of John I. Teasley and Gary E. Glass from the U.S. Environmental Protection Agency laboratory in Duluth, Minnesota, that various sessions of these symposia were organized. Without their help and commitment, the symposia, and hence this volume, could never have been accomplished.

Finally, I wish to express my appreciation to the many authors who, by their hard work, dedication and commitment, provided the main substance of this work—scientific facts and evaluations on a growing national and international problem: acid rain.



**Lawrence H. Keith's** current technical interests continue to center around analyses of organic pollutants in the environment, with emphasis on developing new methods or improving on old ones. Techniques for the safe handling of carcinogenic and/or extremely toxic materials are also an important aspect of Dr. Keith's current research efforts.

Dr. Keith was formerly involved with the selection of many of the U.S. Environmental Protection Agency's initial 129 Priority Pollutants, and he also helped to formulate some of the initial methodology for analyzing for these pollutants. He is presently involved in the selection of representative compounds and methodologies for the Appendix C Priority Pollutants and for the synfuel industry.

A member of the American Chemical Society's Division of Environmental Chemistry Executive Committee, Dr. Keith has served as secretary, alternate councilor, program chairman and chairman of the division. He is also a past chairman of the Central Texas Section of the American Chemical Society and past secretary and councilor of the Northeast Georgia Section of the American Chemical Society.

In other professional activities, Dr. Keith served as Vice-Chairman of the Gordon Research Conference on Environmental Sciences: Water, and is currently a delegate of the U.S. National Committee to the International Association of Water Pollution Research. He is also a member of the National Research Council Committee on Military Environmental Research. Dr. Keith edited the two-volume *Advances In the Identification & Analysis of Organic Pollutants In Water*, published by Ann Arbor Science.

He and his wife, Virginia, reside in Austin, Texas.

## CONTENTS VOLUME 1

### Part 1: Impact of Tar Sands and Oil Shale

1. The Alberta Oil Sands Environmental Research Program . . . . . 3  
*W. R. MacDonald, H. S. Sandhu, B. A. Munson and  
J. W. Bottenheim*
2. Management of Aquatic Environments at the Syncrude Oil  
Sands Project . . . . . 27  
*M. Aleksiuik, J. T. Retallack and K. S. Yonge*
3. Impact of Tar Sands Development on Archaeological Resources. . . 49  
*H. L. Diemer*
4. Trace Elements in Oil Shale Materials . . . . . 69  
*J. P. Fox, A. T. Hodgson and D. C. Girvin*
5. Evaluation of Mutagenicity Testing of Extracts from Processed  
Oil Shales. . . . . 103  
*J. G. Dickson and V. D. Adams*

### Part 2: Impact of Oil Spills at Sea

6. Baseline Studies for Hydrocarbons and Organic Carbon Isotope  
Ratios of Recent Sediments in the Bank of Campeche Before the  
Ixtoc-I Oil Spill. . . . . 119  
*A. V. Botello, S. A. Castro and R. Guerrero*

7. Investigation of the Transport and Fate of Petroleum Hydrocarbons from the Ixtoc-I Blowout in the Bay of Campeche—Sampling and Analytical Approaches. . . . . 129  
*P. D. Boehm, D. L. Fiest, K. Hausknecht, J. Barbash and G. Perry*
8. Distribution of Hydrocarbons in Water and Marine Sediments after the Amoco Cadiz and Ixtoc-I Oil Spills. . . . . 161  
*M. Marchand, J.-P. Monfort and A. Cortes-Rubio*
9. Biodegradation of Crude Oil in a Marine Environment—General Methodology . . . . . 185  
*D. Ballerini and J. P. Vandecasteele*
10. Biodegradation of Hydrocarbons in Mousse from the Ixtoc-I Well Blowout . . . . . 199  
*R. M. Atlas, G. E. Roubal, A. Bronner and J. R. Haines*
11. Chemical Characterization of Ixtoc-I Petroleum in Texas Coastal Waters . . . . . 219  
*R. S. Scanlan, J. K. Winters and P. L. Parker*
12. Characterization of Azaarenes in Ixtoc-I Oil by Gas Chromatography and Gas Chromatography/Mass Spectrometry . . . 233  
*I. R. DeLeon, E. B. Overton, G. C. Umeonyiagu and J. L. Laseter*
13. Comparative Embryotoxicity and Teratogenicity of Petroleum and Petroleum Substitutes to Insects Developing in Contaminated Substrates . . . . . 249  
*B. T. Walton, M. V. Buchanan and C.-H. Ho*

### Part 3: Impact of Fugitive Hydrocarbon Emissions

14. Fugitive Hydrocarbon Emissions from Petroleum Production Operations. . . . . 261  
*W. S. Eaton, F. G. Bush III, J. Coster and J. C. Delwiche*
15. Reduction of Fugitive Volatile Organic Compound Emissions by On-Line Maintenance . . . . . 275  
*R. C. Weber, G. J. Langley and R. G. Wetherold*

16. Response Factors for VOC Analyzers Used in Fugitive Emission Monitoring. . . . . 293  
*G. E. Harris and B. A. Tichenor*
17. Airborne Hydrocarbon Emissions from Landfarming of Refinery Wastes—A Laboratory Study . . . . . 321  
*J. L. Randall, B. F. Jones, D. D. Rosebrook, R. G. Wetherold, R. A. Minear, L. P. Provost and E. W. Cunningham*

#### Part 4: Impact of Lurgi Coal Gasification

18. Characterization of Emissions from a Lurgi Coal Gasification System at Kosovo, Yugoslavia . . . . . 343  
*K. J. Bombaugh, K. W. Lee and T. K. Janes*
19. A Comparison of Organics Collected from the Ambient Air with the By-products of a Lurgi Coal Gasification Plant. . . . . 363  
*K. W. Lee, K. J. Bombaugh, C. H. Williams, Jr., D. S. Lewis and L. D. Ogle*
20. GC/MS Characterization of Trace Organic Compounds in the Ambient Aerosol Associated with a Coal Gasification Plant at Kosovo, Yugoslavia . . . . . 377  
*C. H. Williams, Jr., K. J. Bombaugh, P. H. Lin, K. W. Lee and C. L. Prescott*
21. Characterization of Vapor- and Particulate-Phase Organics from Ambient Air Sampling at the Kosovo Gasifier. . . . . 395  
*W. H. Griest, C. E. Higgins, R. W. Holmberg, J. H. Moneyhun, J. E. Caton, J. S. Wike and R. R. Reagen*
22. Carbonaceous Aerosol in the Vicinity of a Lurgi Gasifier. . . . . 411  
*J. J. Huntzicker, R. L. Johnson, J. J. Shah and E. Heyerdahl*
23. Particle Size Distributions of Trace Element Emissions Near a Coal Gasification Plant in Kosovo, Yugoslavia. . . . . 425  
*L. C. S. Bouéres, J. W. Winchester and J. W. Nelson*
24. Collection and Characterization of Ambient Aerosols Downwind from a Commercial Lurgi Coal Gasification Facility. . . . . 433  
*W. D. Balfour, K. J. Bombaugh, L. O. Edwards and R. K. Patterson*

- Index . . . . . 445



## CONTENTS VOLUME 2

### Part 1: Point Source Effects

1. The Effects on the Environment of Fossil Fuel Use  
by Electric Utilities . . . . . 3  
*E. Kleber, A. Dasti and A. Gakner*
2. Plume Washout Around a Major Coal-Fired Power Plant:  
Results of a Single Storm Event . . . . . 11  
*N. C. J. Chen, R. E. Saylor and S. E. Lindberg*
3. Some Evidence for Acid Rain Resulting from HCl Formation  
During an Expendable Vehicle Launch from Kennedy Space  
Center . . . . . 23  
*B. C. Madsen*

### Part 2: Regional Effects

4. Deposition and Transport of Heavy Metals in  
Three Lake Basins Affected by Acid Precipitation in  
the Adirondack Mountains, New York . . . . . 33  
*D. E. Troutman and N. E. Peters*
5. Distribution of Mercury and Fourteen Other Elements  
in Remote Watersheds in the Adirondack Mountains . . . . . 63  
*G. W. Fuhs, M. M. Reddy and P. P. Parekh*
6. Precipitation Analysis in Central New Mexico . . . . . 89  
*C. J. Popp, C. M. Jensen, D. K. Brandvold and L. A. Brandvold*
7. Chemical Source, Equilibrium and Kinetic Models of Acid  
Precipitation in Southern California . . . . . 103  
*H. M. Liljestrand and J. J. Morgan*

8.	Atmospheric Deposition of Nitrogen and Sulfur in Northern California . . . . .	123
	<i>J. G. McColl</i>	
9.	Acid Precipitation Impact Assessment in Minnesota Derived from Current and Historical Data . . . . .	147
	<i>S. A. Heiskary, M. E. Hora and J. D. Thornton</i>	
10.	Chronology of Atmospheric Deposition of Acids and Metals in New England, Based on the Record in Lake Sediments . . . . .	177
	<i>S. E. Johnston, S. A. Norton, C. T. Hess, R. B. Davis and R. S. Anderson</i>	
11.	Relationships of Chemical Wet Deposition to Precipitation Amount and Meteorological Conditions . . . . .	189
	<i>G. S. Raynor and J. V. Hayes</i>	

### Part 3: Theoretical Considerations

12.	Critique of Methods to Measure Dry Deposition . . . . .	205
	<i>B. B. Hicks, M. L. Wesely and J. L. Durham</i>	
13.	An Integrated Approach to Acid Rainfall Assessments . . . . .	225
	<i>J. L. Schnoor, G. R. Carmichael and F. A. Van Schepen</i>	
14.	Acidification of Rain in the Presence of $\text{SO}_2$ , $\text{H}_2\text{O}_2$ , $\text{O}_3$ and $\text{HNO}_3$ . . . . .	245
	<i>J. H. Overton, Jr., and J. L. Durham</i>	
15.	The Influence of Gas Scavenging of Trace Gases on Precipitation Acidity . . . . .	263
	<i>M. Reda, Y. Adewuyi and G. R. Carmichael</i>	
16.	Preliminary Results of an Eight-Layer Regional Assessment Model Applied to the Problem of Acid Rain . . . . .	287
	<i>W. E. Davis</i>	
	Index . . . . .	301

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## **PART 1**

### **POINT SOURCE EFFECTS**

#### **CHAPTER 1**

### **THE EFFECTS ON THE ENVIRONMENT OF FOSSIL FUEL USE BY ELECTRIC UTILITIES**

**E. Kleber, A. Dasti and A. Gakner**

Federal Energy Regulatory Commission  
Washington, DC 20426

Recent technical reports have highlighted growing concern about the "acid-rain" problem. Brezonik et al. [1] made pH determinations on rain-water in Florida during a recent year, where isolated measurements ranged to a low of 3.76, and volume-weighted measurements ranged from an average of 4.60 to a high of 5.80. Lewis and Grant [2] made measurements in Boulder County, Colorado, over a recent three-year period which indicated a drop in pH from 5.4 to 4.6 over that time span.

The causes and implications of these measurements have been argued vigorously, and much attention has been directed to the electric utility industry, especially because of its combustion of coal with a high sulfur content for power generation. However, the inadequacy of data sufficient for reaching scientific conclusions has become apparent, and led to the recent enactment of federal legislation directed toward more thorough evaluation of cause and effect. This legislation is contained in the Energy Security Act [3], signed June 30, 1980. Title VII of the act is the Acid Precipitation Program and Carbon Dioxide Study.\*

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\*The act established a ten-year program to carry out the provisions of Title VIIA, with the formation of a Task Force, having as joint chairmen the Secretary of Agriculture, the Administrator of the Environmental Protection Agency, and the Administrator of the National Oceanic and Atmospheric Administration. The latter is also named as the director of the research program established by this act.

#### 4 POINT SOURCE EFFECTS

Subtitle A of Title VII of the act is known as the Acid Precipitation Act of 1980. One objective is the development of a comprehensive research plan to identify causes and effects, and to identify actions to limit or ameliorate the harmful effects of acid precipitation.\*

Acid precipitation may be significantly affected by the electric utilities' use of sulfur-bearing fossil fuels. The data that follow are based on information available in Department of Energy (DOE) records.

In 1972 the Federal Power Commission (now the Federal Energy Regulatory Commission) initiated a new data-collection system, which required filing of monthly reports (form 423) to the DOE of cost and quality of fuels for electricity-generating plants. In its present form, this report requires the filing of information on fossil-fuel shipments received by each electric-power producer (both private and public) for each of its electric-generating plants with a total combined (steam-electric, combustion turbine and internal combustion engine) generating capacity of 25 MW or more. The information provided by the utility for each delivery of fuel during the reporting month includes the following:

- Type of plant: steam turbine, combustion turbine, internal combustion engine
- Purchase type: (coal and oil) spot purchase, new contract, contract under which price is changed because of automatic price adjustment, all other contracts
- Contract expiration: within the next 24 months
- Fuel type: coal, oil, gas
- Coal mines: type (underground or surface);  
                  origin (state and Bureau of Mines coal-producing district)
- Fuel source: coal—name of mine and county of origin;  
                  oil—supplier and refinery or port of entry  
                  gas—pipeline or distributor, producing area or port of entry
- Quantity received: tons, barrels, MCF
- Quality received: Btu content, sulfur content, ash content
- Delivered price: cents per million Btu.

The data as received are entered on a computer which makes possible retrieval in diverse ways. Reports summarizing some of the data are issued monthly (e.g., [4]). Annual reports, which include a variety of special studies, also are published. The first annual report was published in 1975 [5] covering the years 1973 and 1974. Subsequent reports have been expanded to include

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\*Section 704 provides for the development of the plan and its submission in draft form to the Congress and for public review by December 30, 1980, and in final form by April 15, 1981. The plan is to include programs in 14 subareas of research, development and assessment.

additional, most frequently, requested analyses, and have been published annually since then [6].

With this wealth of data available, attention has been focused on the sulfur content of the fuels, and some of the possible implications of combustion of these fuels with the corresponding introduction of sulfur-containing species into the atmosphere. These data are shown here in a series of tables which represent the maximum potential for sulfur dioxide emissions into the atmosphere by fuel combustion. These are based on the assumption that the entire sulfur content of the fuel is converted into sulfur dioxide, all of which finds its way into the atmosphere. Ignored for the purposes of this calculation are estimations of any quantities that do not enter the atmosphere by virtue of either retention of any portion of the sulfur in the ash, or the removal of sulfur oxides by stack gas scrubbing.

The data in Table 1 put into perspective the reliance of the electric utility industry on coal as a source of fossil fuel for the generation of electricity. The data cover the period since 1962 in five-year increments. Generation from fossil fuel sources was based on the Btu content of the fuels; nuclear and hydro generation were calculated from kWh statistics, using a conversion factor of 10,000 Btu/kWh. The major portion of the increase in electricity generation in the decade of the 1960s was from the increased use of fossil fuel; in the 1970s, following the oil embargo, increases in total electricity generation and in fossil-fuel demand have been very small.

Detailed data for the period 1975-1979 are also shown in Table 1. Whereas total generation increased at a 3.9% annual rate, coal-fired generation increased at a 6.2% annual rate. (The data included for 1980 are based on extrapolations from five months of statistics.) The decrease in 1978 in coal-fired generation does not represent a real trend—it was caused by an unusually long (four-month) strike by coal miners in the East. The drop in oil-fired electricity generation is real, caused by the deliberate push for economic and political reasons to switch away from oil as a fuel source. The dip in hydro-generation in 1977 was caused by a severe water shortage in the western United States that year.

Total national emissions of sulfur dioxide, using the aforementioned assumptions, are shown in Table 2. In general, one can observe that the increasing tendency to use coals of lower sulfur content has resulted in relatively constant levels of total sulfur dioxide emissions, despite significant increases in coal quantities delivered. Contributions to total sulfur dioxide emissions by oil utilization have been much smaller, and on a national basis, do not alter the totals markedly.

For comparative purposes, it may be noted that the U.S. Environmental Protection Agency (EPA) has estimated [7] that the total emissions of  $\text{SO}_x$  (x not specified) including those from nonelectric sources have ranged from  $24,500 \times 10^3$  tons in 1950 to  $29,900 \times 10^3$  tons in 1976, with a high of

# 6 POINT SOURCE EFFECTS

Table 1. Generation ( $10^{15}$  Btu) by the Electric Utility Industry: By Primary Sources of Energy

	Coal	Oil	Gas	Total Fossil	Nuclear	Hydro	Grand Total <sup>a</sup>
1962	4.66	0.58	2.03	7.27	0.02	1.75	9.04
1967	6.90	1.01	2.83	10.75	0.08	2.30	13.13
1972	8.39	3.14	4.11	15.63	0.58	2.81	19.04
1977	10.55	3.83	3.19	17.57	2.51	2.20	22.28
1975	9.33	3.07	3.11	15.51	1.73	3.00	20.24
1976	9.86	3.31	3.03	16.20	1.91	2.84	20.95
1977	10.55	3.83	3.19	17.57	2.51	2.20	22.28
1978	10.13	3.72	3.23	17.08	2.76	2.81	22.65
1979	11.89	3.02	3.35	18.27	2.55	2.80	23.63

<sup>a</sup>Includes all other sources.

Table 2. Sulfur Dioxide Emissions

	Coal		Oil		Total SO <sub>2</sub> (10 <sup>3</sup> ton)
	10 <sup>6</sup> ton	% S	10 <sup>6</sup> bbl	% S	
1975	431.1	2.2	468.9	1.0	1,600
1976	454.9	2.07	508.3	1.0	1,800
1977	490.4	1.95	584.4	0.9	1,800
1978	476.2	1.79	568.6	1.0	2,000
1979	556.6	1.73	489.0	1.0	1,700
1980 <sup>a</sup>	630	1.58	385	1.0	1,300
					20,600
					20,600
					20,900
					19,000
					20,900
					21,200

<sup>a</sup>Extrapolated from data for the first five months of the year.



$32,700 \times 10^3$  tons in 1973. The EPA attributes the principal source of the  $\text{SO}_x$  to fuel combustion from stationary sources.

National data can be disaggregated to provide regional information. Summaries of total sulfur dioxide emissions (again with assumptions utilized) as compiled by geographic regions are shown in Table 3. Total contributions for each region in 1979, as a percentage of the national totals are shown in Table 4. Aggregations of the data may be made in many ways: one such would show that power plants east of the Mississippi were responsible for 83% of total sulfur dioxide emissions nationally while providing only 62% of electricity generation.

One feature of the regional data is the indication of the relative constancy of total sulfur dioxide emissions from electric utility power plants over the past five years. The only exceptions are in three geographic regions with less than 10% of total emissions—New England, West South Central, Mountain—where there has been some increase in recent years. Further detailed data analyses may be made using any mode of aggregation to provide an input into specific studies such as those cited [1, 2].

It is interesting to combine sulfur dioxide emission data with rainfall data. If one assumes that: (1) all the sulfur dioxide emitted to the atmosphere is quantitatively converted to sulfur trioxide; (2) the latter is quantitatively converted to sulfuric acid by contact with rainwater; and (3) all the sulfuric acid reaches the earth as acid rain with no precipitation in dry form as neutral sulfate dusts; then the maximum acidity of the corresponding rain due to sulfuric acid can be calculated. Table 5 shows the results of these calculations using 1977 data for rainfall. West of the Mississippi, the calculations of sulfuric acid content in rainfall yield concentrations of  $0.5$  to  $2.5 \times 10^{-6}$  molal; east of the Mississippi, the concentrations are calculated to range from  $2$  to  $17 \times 10^{-5}$  molal. Calculations may be made for any geographic area: for example, data for the state of Florida, using all of the assumptions above, show a sulfuric acid concentration of  $5 \times 10^{-5}$  molal.

Future trends may also be forecast with the aid of these data.

1. Coal usage will accelerate significantly. A recent analysis prepared in this office [9] indicates that demand due to new plants will be for an additional 170,000 tons of coal in 1983 (a 25% increase) and 395,000 tons by 1988 (>50% increase). (These do not take into account any reduction in demand due to retirement of old plants.)
2. There will be an increasing trend toward use of low-sulfur coal, to the extent that much more low-sulfur Western coal can be made available. The net effect of these two factors will be a relative constancy in total emissions of sulfur dioxide to the atmosphere, paralleling the trends of recent years.
3. The effects of the installation of flue gas desulfurization systems may be ignored for the near-term future. Data summarized by the EPA [10] indicate that, as of March 1980, 10% of the capacity of all coal-fired units have the capability to scrub sulfur dioxide. Operationally, however, the percentage of coal-fired scrubbed electric generation is much less.