Conference on
Health Effects of Atmospheric Salts and Gases of Sulfur and Nitrogen in Association with Photochemical Oxidant

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Edited by
T. Timothy Crocker, M.D.
Community and Environmental Medicine
College of Medicine
University of California, Irvine

Health Effects of Atmospheric Salts and Gases of
Sulfur and Nitrogen in Association with Photochemical Oxidant

SPEAKERS

Yves Alarie, Ph.D.
Department of Occupational Health
Graduate School of Public Health
University of Pittsburgh

Robert Charlson, Ph.D.
Department of Atmospheric Chemistry
University of Washington

Jack Hackney, M.D.
Medical Sciences Service
Rancho Los Amigos Hospital
Downey, California

George Hidy, Ph.D.
Program Manager, Air Quality Research
Rockwell International Corporation
Thousand Oaks, California

James D. MacEwen, Ph.D.
Toxic Hazards Research Unit
University of California, Irvine
Dayton, Ohio

Jack Calvert, Ph.D.
Department of Chemistry
Ohio State University

Robert Frank, M.D.
Department of Environmental Health
School of Public Health and Community Medicine
University of Washington

Thomas Hauser, Ph.D.
National Environmental Research Center
United States Environmental Protection Agency

Carl Shy, M.D.
Director, Institute of Environmental Studies
University of North Carolina

T. Timothy Crocker, M.D.
Department of Community and Environmental Medicine
College of Medicine
University of California, Irvine

PARTICIPANTS

Stanley Rokaw, M.D.
California Thoracic Society
Los Angeles

Edward Lee, Ph.D.
Department of Chemistry
University of California, Irvine

G. Scott Samuelsen, Ph.D.
Environmental and Resources Engineering
School of Engineering
University of California, Irvine

Archie Wilson, M.D.
Department of Medicine, College of Medicine
University of California, Irvine

Stanley Galant, M.D.
Department of Pediatrics
College of Medicine
University of California, Irvine

James N. Pitts,
Statewide Air Pollution Research Center
University of California, Riverside

Edmond Vernot
Toxic-Hazards Research Unit
University of California, Irvine
Dayton, Ohio

William Clark, Ph.D.
Air Quality Research, Rockwell International Corporation
Los Angeles, California

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FOREWARD

The motivation for this report was the desire of the members of the Air Resources Board and of Dale Hutchison, then Director of Research, State of California Air Resources Board, to combine information on aerosol composition in the South Coast Air Basin of California with available information on the health effects of the aerosols combined with gaseous photochemical pollutants. Acting for the Air Resources Board, Dale Hutchison had guided the development of a research program to characterize aerosols by the most comprehensive methods possible. The findings of this program strengthened previous demonstrations of significant quantities of particulate sulfates and nitrates, especially in downwind parts of the Air Basin. Reports from the CHESS study of the Environmental Protection Agency had begun to appear on the possible health impact of particulate sulfates. Hutchison reasoned that the presence of sulfates and nitrates in California air might potentiate adverse effects of oxidant and oxides of nitrogen. He foresaw that the California South Coast Air Basin could become a meeting place for two previously separate species of air pollution: the photochemical oxidative variety well-known in Southern California and the reducing variety dominated by sulfur oxides, historically identified with London and the north-central and northeastern United States.

Dale Hutchison's death on August 29, 1973, prevented him from participating in the development of his ideas, but his foresight was acute as demonstrated by the fact that he and the scientific directors in federal agencies began at about the same time to bring the perceptions of people in the technologies relevant to air pollution together to examine new findings in that field.

The purpose of the present report was to assemble existing data related to health effects of particulate sulfates (and nitrates where available) and to

review epidemiologic and experimental studies of effects of combined air pollutants. Relevant information on atmospheric chemistry was also sought. As of the time the Conference was held to generate the report, the data available were not as advanced, either in actual data gathering or in presentation, as they became during the six months following the Conference. The report, therefore, contains the conferees' submissions plus an attempt by the convenor to incorporate abstracts from EPA documents and to develop a chapter reviewing data pertinent to experimental studies of particulate sulfates. A summary of conclusions and recommendations for future research was compiled and represents Volume I of the Report. This volume is submitted for circulation. The manuscripts presented by individual conferees are assembled in Volume II, entitled Reference Documents.

Research findings from epidemiologic studies of sulfates and nitrates were presented at the Conference by a representative of EPA, but future plans were not. These plans are emerging within an existing network of community-based programs set up directly by EPA. New sources of information regarding research plans of federal and private research agencies are also emerging, as well as new assessments by the National Academy of Sciences. As research policy is developed by the Air Resources Board of the State of California, these sources will be scanned to assure that policy decisions take account of national trends.

As for any report seeking to review an active area of research and public concern, the data and interpretations in the present report may not be a comprehensive source of new information (since newer reports are appearing) but may serve as a compilation of information adequate to show what data do not need to be gathered again or to point out areas in which there is need for further study.

CONCLUSIONS WITH RECOMMENDATIONS FOR RESEARCH

General Statement

The conference participants prepared brief summaries of their own data after the individual presentations and ensuing discussion had singled out specific elements for emphasis. These summaries are presented below in a section entitled Summaries of Individual Reports. A more specific set of conclusions and recommendations were prepared from these summaries, from the complete reports presented in Volume II: Reference Documents, and from discussion during the conference. In addition, pre-publication copies of in-house EPA documents submitted by several conferees were used as sources of information and as input in recommending research policy. Volume I entitled Conclusions with Recommendations for Research represents the portion of the report of interest to most readers and the chapters constituting the submissions of conferees are bound separately as Volume II.

Conclusions and Recommendations

A. Experimental Systems for Evaluation of Biologic Effects of Aerosols and Gases

1. Acute studies of effects of particulates and gases

Measurements of airflow resistance in guinea pigs appears to evaluate reliably the action of airborne chemicals, particularly on the larger conducting airways. Some reservations are in order when considering the contribution of each portion of the respiratory tract (upper and lower) to the total increase in resistance and to the various mechanisms involved in this reaction to inhaled chemicals. Acute responses to particles and gases have been found for SO_2 at about 1 ppm (with variation among investigators), for H_2SO_4 at 1 mg/m^3, for soluble salts of catalytic metals plus SO_2 and for NaCl plus SO_2 at a relative humidity above 72%.

Some findings by this system have not been confirmed in other animals or normal humans, indicating the need to test particulates in additional species and in human subjects. The latter type of work would aid in confirming epidemiologic findings. Most animal studies have used concentrations far above ambient.

Recommendation: Acute effects of particulates and gases need to be evaluated in additional animal systems by measurement of responses characteristic of site of deposition of aerosols. Based on the chemical composition of aerosols (see below), the studies should include sulfuric acid, sulfurous acid, sulfates, bisulfates, sulfites and bisulfites of weak bases (ammonia, others), nitrates and metals (Zn, Fe, Cu, Pb, Mn, others).

2. Experimental exposure conditions

Many experimental exposure trials with particulates have failed to measure some of the following elements: physical state and shape of aerosol particles, water solubility, hygroscopicity, deliquescent behavior, relative humidity of the exposure air and pH of the aerosol. Similar omissions exist for epidemiologic studies with the added problem that molecular species of aerosol components have not been defined in enough detail. Some reactions among or between gases, aerosols and chamber walls may also occur in experimental exposures, hence the molecular state of aerosols must be defined as precisely as possible at the moment of inhalation.

Recommendation: Aerosols used in experimental studies require accurate and comprehensive characterization. Atmospheric conditions during

exposure (as relative humidity, contaminating gases) should be identified and controlled. Molecular states of aerosols should be identified, especially in mixed-gas aerosol studies, to account for reactions occurring during residence in atmospheric exposure systems.

3. Factors influencing synergism among particles and gases

Synergism arising from mixtures of SO_2 and a submicronic, physiologically inert aerosol of NaCl has been demonstrated in guinea pigs, but not in man or the cat. The physiological parameter relied upon in virtually all of these studies was respiratory mechanics in the guinea pig, i.e., pulmonary flow resistance and compliance. In recent experiments, several factors were noted that might contribute to synergism. These include relative humidity, pH and bisulfite ion in the absence of sulfate ion or sulfuric acid. Other factors to be considered are the influence of ambient temperature on the change in flow resistance, the role that heavy metal catalysts may play in converting SO_2 to higher oxidative states, the effect of metals as such, and the relative importance of SO_2 and the aerosol concentrations in producing the synergistic response. Finally, it is suggested that these experiments be extended to human subjects.

Recommendation: Studies of synergism among particles and air pollutant gases should be extended with control of exposure conditions as described in 2, above. Human studies should be undertaken when preliminary animal studies have been done.

4. Relevance of long-term exposure to chronic disease

Long-term exposures of animals have demonstrated that the air pollutant gases ozone, SO_2 and NO_2 and aerosols of sulfuric acid with or without particles induce stable anatomic and functional abnormalities of the lung. All studies have used concentrations well above ambient but the expectation is warranted that pollutants effective as single components will produce greater effects in combination and that synergistic effects, if present, will be relevant to chronic progressive lung disease.

Recommendation: Synergism among pollutant aerosols and gases should be sought not only in acute exposures, simulating adverse effects in diseased or sensitive persons, but also in exposures of long enough duration to identify anatomic abnormalities consistent with development of chronic lung disease.

5. Human studies relevant to air quality criteria

Ten of 14 normal human subjects varied in their reactions to 0.5ppm ozone for 2 to 4 hours. Five showed no response while 5 experienced discomfort and some abnormality of pulmonary function. This effect was more marked upon a second successive day of exposure.

Four "reactive" subjects developed discomfort and abnormalities of pulmonary function at 0.37 ppm and 0.5 ppm but not at 0.22 ppm ozone. Cumulative effects were noted over 2 weeks of successive exposure.

Recommendation: Additional studies of confirmed asthmatics or of persons with known sensitivity to inhalant irritants are desirable as a means to establish the level of ozone which adversely affects such persons. Mixed pollutants, including aerosols and gases, should be studied in normal and sensitive subjects when preliminary studies in animals indicate probable effective levels.

B. Epidemiologic data for sulfates and nitrates

Epidemiologic data collected within the Community Health and Environmental Surveillance System (CHESS) afforded the opportunity to compare the effects of atmospheric SO_2, total suspended particulates (TSP) and suspended sulfates on daily symptom status of groups of asthmatics and subjects with cardiopulmonary disease. During the first year of CHESS studies, asthma panels were followed for a period of four to eight months in the Salt Lake and New York CHESS areas. A cardiopulmonary panel was similarly studied for eight months in New York. In the best judgement of the investigators involved in the first year of CHESS studies, significant worsening of symptom status in these diseased panels could be attributed to 24-hour suspended sulfate exposures as low as 8 to 10 $\mu g/m^3$.

Additional analyses have correlated aggravation of asthma with nitrates and temperatures above or below 40^oF. Thresholds of 2.16, 7.63 and 20.4 $\mu g/m^3$ were reported at temperatures above 40^oF in 4 New Jersey communities, Queens and the Bronx, respectively. The observed health effects may be attributable to one of the following:

1. The atmospheric precursors of sulfate. These include, among others, bisulfite, sulfite, acid sulfate, sulfurous and sulfuric acid aerosols.

2. Atmospheric precursors of nitrates. These include PAN, nitrites, possibly nitric acid.

3. The acidity of the aerosol in which aerosols are found.

4. Specific molecular sulfate or nitrate compounds such as ammonium nitrate or sulfate, zinc ammonium sulfate, ferric sulfate and nitrate and others. One, rather than another, of these chemical compounds may be responsible for the biologic reactivity attributed to sulfate and nitrate measured merely as anions.

5. The small physical size of salt aerosols, reported to be less than one micrometer in diameter.

6. Relative humidity and temperature.

Recommendation: Well-controlled laboratory exposures of animals first and of humans subsequently are required to establish causal relationships of the several sulfate and nitrate precursors, various end products, and acid aerosols with the kinds of adverse responses observed in epidemiologic studies. Animal models of asthma and human cardiopulmonary disease would make toxicologic studies more relevant to the epidemiologist.

Epidemiologic observations should continue to test whether the sulfate and nitrate health effect relationship is consistent at different times and in a variety of environmental and geographic conditions.

The air monitoring laboratory must provide the level of analysis needed to identify various sulfate and nitrate precursors, acid aerosols and the various sulfate and nitrate end products occurring in the atmosphere.

C. Formation and analysis of atmospheric controls

1. Atmospheric analyses of sulfates

Samples collected on glass fiber paper and analyzed by controlled vaporization of the sample into a computer-controlled, high resolution

mass spectrometer have been shown to contain compounds such as H_2SO_4, NH_4HSO_4, $(NH_4)_2$ and $NaHSO_4$. Because of the temperatures involved in the vaporization, the integrity of the glass fiber filter sample is a very major problem. Analytic values may be obtained, but their accuracy is in doubt for these reasons:

Sulfates

a. Collection of sulfate from all types of polluted air is not reliable because of formation of factitious sulfate during collection.

b. Water-insoluble sulfates are not extracted in the analytical procedure.

c. Not only is the integrity of the sample in doubt but the sample may not have a reasonable shelf life, i.e., it may be susceptible to further reactions, as with NH_3.

d. Current and new types of field monitors are expensive to buy and maintain, undergo rapid obsolescence and require competent field calibration. This problem is considerably enhanced with monopollutant analyzers.

H_2SO_4

In collection on glass fiber filters, the fibers may catalyze the oxidation of SO_2 to SO_3 and can also neutralize the H_2SO_4 at the surface of the glass fiber sheet.

In collection of particulate H_2SO_4 in aqueous solutions and in extraction of particulate H_2SO_4 with water, it is possible that dissolving basic particles will neutralize some of the H_2SO_4. This problem in collection would be even more serious in monitoring methods consisting of short-time collection and elution, where the precision would vary over a wide range dependent on the amount of soluble basic material caught with each batch of H_2SO_4.

In any methods involving heat, artifact formation could ensue. Thus, ammonium sulfate would be measured as H_2SO_4. Other compounds, such as organic sulfates, sulfonates, sulfites and sulfones could also interfere.

Recommendation: The following research and development tasks are recommended.

a. Develop an in-situ H_2SO_4 measurement method.

b. Verify existing manual compliance test methods for SO_3 and H_2SO_4.

c. Develop Raman scattering and/or fluorescence technique for analysis of particulate sulfate in-situ.

d. Conduct a study of particulate/filter/H_2SO_4/sulfate interactions, temperature dependence of sulfate, conversion on probes and filters, verifications of true particulate sulfate (as distinct from condensible H_2SO_4).

e. Develop a reliable method for total sulfate, and evaluate collection techniques for atmospheric sulfates in the presence of SO_2 and other critical pollutants.

2. Atmospheric analysis of nitrates

The majority of the nitrate concentration data available in the U.S. has been acquired by analysis of particulate matter samples obtained using the Hi Vol sampler with glass fiber filters. Such a technique provides only a limited indication of the nature of the air sample. Fully satisfactory methods for routine use in measuring particulate nitrate, PAN, nitric acid, nitrous acid, nitrogen dioxide, and nitrogen pentoxide are not yet available.

The arithmetic mean for nitrates as measured at the NASN stations with the Hi Vol sampler for a 5-year period (1966-1970) for those urban sites where all data were available ranged from 0.57 to 7.57 $\mu g/m^3$ -- the highest being in Los Angeles and the lowest in Concord, New Hampshire.

Available data are not sufficient to describe diurnal variations; however, limited data and theoretical considerations suggest that significant diurnal cycles may occur, similar to that of ozone, particularly in the Los Angeles area. If this were the case, the daily maximum concentration should be significantly higher than the annual average -- possibly orders of magnitude higher.

Data on the size distribution of nitrates in the atmosphere are limited. Available data indicate that the nitrate aerosol particles are normally 2 μm or less in diameter.

Recommendation: a) An adequate routine monitoring system for nitrates should be developed and implemented. Based on possible health effects, specific emphasis should be given to those geographical areas which currently experience annual average nitrate concentrations on the order of 3 to 5 $\mu g/m^3$ or greater. This will require the development and evaluation of suitable nitrate measurement techniques. Information concerning size distribution and chemical characterization should be either implicit in the concentration measurement or these parameters should be studied directly. Standard siting, sampling, preparation and analysis procedures should be established for the monitoring network.

b) An extensive research effort is recommended to obtain an understanding of the nitrate aerosol formation, transport and removal processes in urban atmospheres. Particular emphasis should be given to determining the controlling rates of reaction as a function of precursor concentrations, and the transfer mechanisms (atmospheric removal) between the atmosphere, water and soil. An integral part of this effort should be the chemical and physical characterization of nitrate aerosols in the different urban areas.

3. Atmospheric aerosol measurements in Southern California

Preliminary results of the Atmospheric Characterization Experiment (ACHEX) indicate that the transformation of sulfur in the gas to sulfur in the aerosol particles is not exclusively a photochemical process. A possible conversion mechanism might invoke the absorption of SO_2 on soot or other carbon material and subsequent oxidation by adsorbed oxygen or other oxidizing agents. No experimental evidence was found for the homogeneous nucleation of new particles in the L.A. basin. It is thought that the dominant mechanism is the heterogeneous growth of existing particles. Most of this growth appears to occur in the particle size range from 0.1 to 1.0 μm. The results of sampling near the Harbor Freeway in downtown L.A. indicated that the primary particle size range associated with automobile exhaust was from 0.01 to 0.1 μm in diameter. It is thought that these primary particles contributed by the automobile can grow into the light scattering size range between 0.1 and 1.0 μm by the transformation of material from the gas phase to the particulate state and by coagulation of smaller particles to form particles in the larger size range. No specific chemical data are available for the large number concentration of particles between 0.01 and 0.1 μm which can serve as nuclei for aerosol growth. Chemical composition of particles 0.6 μm-MMD and above indicate the presence of water-soluble sulfate, bisulfate, sulfuric acid and nitrates in association with metals (Zn, Fe, Cl, Pb, Ca, Na, K) and carbon as well as with organic acids and aldehydes.

Recommendation: Chemical evaluation of primary particles from mobile and stationary sources is needed as well as analysis of chemical reactions producing light scattering particles. Data support heterogeneous reactions leading to particles containing sulfate and nitrate as well as carbon, metals and hydrocarbons.

4. Theoretical factors in aerosol formation

An evaluation has been made of the theoretically possible rates of homogeneous reactions which convert SO_2 to sulfate and NO_x to nitrate in a simulated sunlight-irradiated, NO_x-hydrocarbon-SO_2-polluted atmosphere. The present kinetic interpretations suggest that photochemical aerosol formation can be initiated by homogeneous reactions at rates which are in line with the observed rates of sulfate and nitrate salt formation in the urban atmosphere.

Either SO_3 or sulfuric acid formation in the urban atmosphere should initiate the growth of an aerosol droplet. This growth will be controlled by many factors including the humidity, the rate of condensation of the supersaturated vapor, the rate of capture of gaseous organic pollutant molecules (olefins, aldehydes, epoxides, etc.) and their conversion to polymeric or low vapor pressure products within the acid droplet, the rate of capture of ammonia and other basic molecules or particles (ZnO, Fe_2O_3, PbO, EdO, $CaCO_3$, etc.) or the halides of the metals as well as the rate of capture of nitric acid, etc.

There are several possible heterogeneous paths of conversion of SO_2 and NO_2 to the sulfate and nitrate salts which are often invoked by atmospheric scientists and which may occur at a significant rate in the atmosphere. Present kinetic data do not allow a realistic evaluation of their relative significance in the smoggy urban atmosphere at this time.

Recommendation: Homogeneous as well as heterogeneous reactions leading to formation of sulfates and nitrates involve many active intermediate products as well as metals and hydrocarbons as potential primary reactants. Experimental confirmation of key molecular events with and without particles is needed using natural atmospheres, atmospheric reaction chambers and simulation models.

5. Dissemination of acid sulfates

Based on an optical, in situ method, it has been shown possible to identify and to semi-quantify H_2SO_4 and/or NH_4HSO_4 as the major submicrometer aerosol constituent in St. Louis in summer. The South Coast (CA) aerosol clearly is not currently dominated by H_2SO_4, but if high sulfur fuel were used it might be. Instead of the few percent sulfate presently found, the St. Louis constitution of about 50% submicrometer particles as various acid sulfates could emerge. The role of NH_3 in this system is currently unknown but presumably important. Methods are needed for NH_3 analysis.

Unlike SO_2, the SO_4-aerosol is distributed over wide geographic areas. The removal distance (1/e) for SO_2 and its oxidation products appears to be of the order of 1000 Km. Sulfuric acid and acid sulfates may be imposed on cities by rural sources (power generation) as well as from urban stationary and mobile sources.

Recommendation: Distribution patterns of aerosols must be recorded over areas as great as 1000 Km from sources of sulfur emissions. This requirement presumably applies also to oxides of nitrogen and nitrates.

Experimental Systems for Evaluation of Biologic Effects of Aerosols and Gases. Acid Mists, Salts of S and N, Synergism Between Salts and NO_2 and Other Gases.

Yves Alarie, Ph.D.

Nerve endings lining the respiratory tract are easily accessible to inhaled airborne chemicals. Stimulation of these nerve endings results in reflex reactions which can be evaluated in unanesthetized laboratory animals with adequate methodology and used to predict, at least qualitatively, the type of reaction to be expected in humans.

Measurement of decrease in respiratory rate in mice appears to evaluate reliably. The action of airborne chemicals can be of use in predicting at what concentration sensory irritation will occur in humans as well as predicting the time-response pattern of the reaction during continuous or repeated exposures.

Measurements of airflow resistance in guinea pigs appears to evaluate reliably the action of airborne chemicals, particularly on the larger conducting airways. Some reservations are in order when considering the contribution of each portion of the respiratory tract (upper and lower) to the total increase in resistance and to the various mechanisms involved in this reaction to inhaled chemicals.

Measurements of increase in respiratory rate in laboratory animals appears to be reliable to evaluate the action of airborne chemicals on the deeper pulmonary structures.

It is interesting to note that NO_2 and sulfuric acid mist, which are considered deep lung irritants (as opposed to sulfur dioxide which is primarily an upper respiratory tract irritant) induced similar types of effects. The distribution of pulmonary ventilation was impaired, the respiratory rate was increased and decreases in arterial blood oxygen were observed. Modifications of the distribution of ventilation indicates an effect primarily on the peripheral conducting

airways. The increase in respiratory rate may be attributed to stimulation of pulmonary receptors although other factors may have contributed.

Sulfur Oxides and Particles: Effects on Pulmonary Physiology in Man and Animals

Robert Frank, M.D.

Synergism arising from mixtures of SO_2 and a submicronic, physiologically inert aerosol of NaCl has been demonstrated in guinea pigs, but not in man or the cat. The physiological parameter relied upon in virtually all of these studies was respiratory mechanics, i.e., pulmonary flow resistance and compliance. Recently, we undertook a series of experiments designed to examine factors that might contribute to synergism. The first of these factors was relative humidity (RH). NaCl aerosol is deliquescent. Below RH of 68%, the aerosol is dry; above RH of 72%, the aerosol is a droplet. Lightly anesthetized guinea pigs were exposed to one of six modes: SO_2 (1 ppm) at low (<40%) and high (>90%) RH, NaCl aerosol (1 $\mu g/m^3$) at low and high RH, and the mixture at low and high RH. The only mode associated with a significant increase in flow resistance (R_L) was the mixture at high RH. The pH of the droplet in the latter mode was about 3.5. Evidence was adduced that the droplet contained bisulfite ion, but no sulfate ion or sulfuric acid. Other factors to be studied are the influence of ambient temperature on the change in R_L, the role that heavy metal catalysts may play in converting SO_2 to higher oxidative states, and the relative importance of SO_2 and aerosol concentrations in producing the synergistic response. Finally, it is suggested that these experiments be extended to human subjects.

Effects of Sulfur Oxides in Animals and Man

T. Timothy Crocker, M.D.

The limited toxicity of SO_2 is based on extraction by moist mucosal surfaces where the gas is presumably dissolved to form sulfurous acid. Surfaces nearest the nose and mouth are affected directly and sensory reflexes produce bronchoconstriction. The local effect is suppression of mucociliary transport and mucosal swelling with possible impairment of defense against infection. Remote bronchoconstriction does not apparently require that SO_2 reach beyond the larynx. Bronchoconstriction may not be relevant to progressive chronic lung disease if it is initiated only by SO_2 or by aerosol particles too large to reach deeper airways. Bronchoconstriction could be highly incapacitating in persons with high reflex reactivity of bronchi, as asthmatics, or in persons with limited lung reserve due to prior cardiopulmonary disease.

Sulfur dioxide absorbs on particles and dissolves in watery aerosols. Sulfurous acid so formed is more irritant than SO_2. Oxidation of SO_2 to SO_3 (hence to H_2SO_4) occurs in the atmosphere. Acidic aerosols so formed are a toxic hazard during whatever time H_2SO_4 or HSO_4 can be inhaled. At such times, the irritant potency of sulfur oxides rises by about 3 to 9-fold (or possibly by 400-fold) above the potency of SO_2. The potential for damage to small airways is increased as particle size of acid aerosols is reduced from 3 to about 0.5 um and may be still greater near 0.1 um.

Chronic lung disease associated with long-term exposure to SO_2 or H_2SO_4 can be produced in experimental animals but requires 10 to 400-fold higher than ambient quantities. The pathogenetic effect of oxides of sulfur alone is probably not sufficient to produce chronic human airway disease but oxides of sulfur in the form of sulfate particles may be candidates as pathogens if associated with metallic cations some of which have direct irritant potency. An example is ferric but not ferrous ion. Chronic effects of aerosols of such metals have not been reported. The irritant potency of metallic sulfates and H_2SO_4 together may be great enough to warrant study as pathogens in chronic lung disease.

Ozone, NO_2 and CO in Healthy Adults and Ozone Dose Response in Reactive Adults

Jack Hackney, M.D.

Human volunteers were exposed to realistic levels of individual and mixed pollutants at elevated temperatures ($88^{o}F$), at 35% relative humidity and with intermittent moderate exercise. The pollution levels and meteorological conditions were chosen to approximate a smoggy summer in the Los Angeles South Coast Air Basin. Because of the response to O_3 alone, studies on mixtures were performed.

Fourteen subjects were exposed to 0.5 ppm O_3 in this study. Ten of these were classified as 'normal'. Of these ten, four showed few or no ill effects after 4 hours exposure. A fifth showed no apparent decrement in pulmonary function after two hours exposure. The degree of change varied with the individual; and in three of the five, the change did not become apparent until the second successive day of exposure. Thus, effects of two successive days' exposure were cumulative to a significant degree.

The four additional subjects, classified as 'reactive' on subjective grounds, had increased symptoms and function decrement after 4 hours exposure to 0.5 ppm O_3. All four 'reactive' subjects also showed changes with 0.37 ppm O_3. All four 'reactive' subjects also showed changes with 0.37 ppm O_3, but not with 0.22 ppm. A cumulative effect of successive exposure over 2 weeks was also suggested by the results.

We conclude that there is wide variation in sensitivity to short term O_3 exposure in 'normal' and subjectively reactive subjects. In addition, we found evidence of cumulative effects on repeated exposure.

Health Consequences of Sulfur Oxides

Carl M. Shy, M.D.

Epidemiologic data collected within the Community Health and Environmental Surveillance System (CHESS) afforded the opportunity to compare the effects of

atmospheric SO_2 total suspended particulates (TSP) and suspended sulfates on daily symptom status of groups of asthmatics and subjects with cardiopulmonary disease. During the first year of the CHESS studies, asthma panels were followed for a period of four to eight months in the Salt Lake and New York CHESS areas. A cardiopulmonary panel was similarly studied for eight months in New York. Our combined results indicate that variations in daily suspended sulfate levels were more consistently associated with aggravation of disease status in asthmatics and cardiopulmonary subjects than was true for SO_2 or TSP. These data are reported in detail in Health Consequences of Sulfur Oxides: A Report from CHESS 1970-1971. The important point about these CHESS data is the emergence of a pattern of aggravation of daily symptom status, under varying conditions of temperature and geographic location, in relation to daily suspended sulfate levels. Daily SO_2 and TSP levels simply did not provide as consistent a relationship with symptom status. In the Salt Lake Basin, where the effects of TSP and suspended sulfate on asthma were partitioned, and where the TSP concentrations were equal, a higher asthma attack rate was observed on those days when sulfate concentrations were higher (above 8 to 10 $\mu g/m^3$). Thus, it appeared that atmospheric sulfate levels were a stronger determinant than TSP of symptom status in asthmatics and cardiopulmonary subjects. In the best judgement of the investigators involved in the first year of CHESS studies, significant worsening of symptom status in these diseased panels could be attributed to 24-hour suspended sulfate exposures as low as 8 to 10 $\mu g/m^3$. Since these sulfate-symptom relationships were manifested even in low exposure communities in which concentrations of SO_2 and TSP were below the national primary standard, there was evidence that suspended sulfates emanating from point or urban sources penetrated well beyond the suburban fringes and adversely affected individuals living in more distant communities.

At this point in time, several alternative explanations should be mentioned to account for the observed sulfate-health effect relationships. Recall that suspended sulfates represent an anion, not a specific chemical compound, and that

the anion is itself the end product of a series of atmospheric reactions. Thus, the observed health effects may be attributable to one of the following:

1. The atmospheric precursors of sulfate. These include, among others, bisulfite, sulfite, acid sulfate, sulfurous and sulfuric acid aerosols.

2. The acidity of the aerosol in which sulfates are found.

3. Specific molecular sulfate compounds such as ammonium sulfate, zinc ammonium sulfate, ferric sulfate and others. One, rather than another, of these chemical compounds may be responsible for the biologic reactivity attributed to sulfate concentrations.

4. The small physical size of sulfate aerosols, reported to be less than one micrometer in diameter.

Intelligent and economical selection of appropriate control strategies may crucially depend on identifying the exact chemical substance responsible for the observed sulfate-health effect relationship. This identification requires a systematic and coordinated application of toxicologic, clinical and epidemiologic research to the sulfate issue. Epidimiologic studies alone cannot sort out the many variables involved in a natural community exposure setting. Well-controlled laboratory exposures of animals, first, and humans are required to establish causal relationships of the several sulfate precursors, various sulfate end products, and acid aerosols with the kinds of adverse responses observed in epidemiologic studies. Animal models of asthma and human cardiopulmonary disease would make toxicologic studies more relevant to the epidemiologist. At best, the epidemiologist can continue observations to demonstrate that the sulfate-health effect relationship is consistent at different times and in a variety of environmental and geographic conditions. The laboratory must provide the level of control needed to separate out the effects of various sulfate precursors and of acid aerosols from the various sulfate end products occuring in the atmosphere. At the present time, a second year of CHESS results are being analyzed in the same communities as well as in new CHESS areas, to determine whether the sulfate findings will be consistent from year to year.

Data relating nitrate concentrations in several CHESS study sites to increased

incidence of asthma and bronchitis have been recently developed. Brief references to these findings is made in an addendum (abstract from "Summary Report on Atmospheric Nitrates", EPA) to the report of Dr. Hauser.

Monitoring for Oxides of Sulfur and Nitrogen and Related Salts

Thomas R. Hauser, M.D.

Any decision based on ambient air monitoring data, whether it be in the field of air quality management, standard setting, compliance, enforcement or criteria development is only as good as the validity of the data used to make that decision. Without the assurance that measurements obtained truly describe the existing conditions under observation the validity of any conclusion must remain doubtful.

There are many analytical methods available to monitor for oxides of sulfur and nitrogen and related salts. EPA has initiated an "equivalence program" to assist in determining the interrelatibility of air monitoring data for sulfur dioxide, carbon monoxide, oxidants, hydrocarbons, and nitrogen dioxide. Thus far, regulatory proposals have been written for SO_2, CO and O_x while interim equivalency guidelines have been written for HC and NO_2. The proposed operations of the equivalency program is discussed in the report accompanying this presentation.

The problem of interrelatibility of data can be exemplified by SO_2 monitoring activities. At present, there are over 60 SO_2 monitors available from 30 instrument manufacturers involving 13 distinctly different principles of analysis.

Sampling location and intake lines are just as important as the analytical method. For example, measurement of NO_2, NO_x and O_3 may very well be in error if residence time in the sampling line is greater than about 1-2 seconds, and the errors may be large. Proper designs have been formulated and should be standardized.

The current status of air monitoring technology is described with references and the analytical techniques used by the NASN for monitoring SO_2, particulate sulfate, nitrogen dioxide, and particulate nitrate are presented in the addendum

to the document submitted for this conference.

Data was presented indicating that the sulfate, nitrate, chloride and ammonium ions present in air particulate matter were predominantly associated with sub-micron particles. In addition, most of the sulfate, nitrate, chloride and lead found in auto exhaust particulates were found in particles predominantly sub-micron in diameter.

The annual report of air quality and emission trends obtained from the national air monitoring program was reviewed. Abstracted data from that report were presented in an EPA "Summary Report on Suspended Sulfates and Sulfuric Acid Aerosols." The relevant section of that summary is included as an addendum to the document submitted for this report.

In addition, the summary, conclusions, recommendations for research and plans for work to be done in evaluating the environmental impact of nitrates, nitrites, PAN and other nitrogenous pollutants were abstracted from the "Summary Report on Atmospheric Nitrates", an EPA document. These data are included as an addendum to the report presented for the conference.

Theory of Formation and Properties of Photochemical Aerosols

G. M. Hidy, M.D.

Preliminary results of the Atmospheric Characterization Experiment (ACHEX) project indicate that the transformation of sulfur in the gas to sulfur in the aerosol particles is not exclusively a photochemical process. Little difference in the ratio of sulfur in the gas phase to the total sulfur in the particles was found between night and daytime sampling periods or for high and low ozone concentrations. A possible conversion mechanism might invoke the absorption of SO_2 on soot or other carbon material and subsequent oxidation by absorbed oxygen or other oxidizing agents.

In general, the aerosol to gas phase sulfur concentration ratio ranged between

0.3 and 0.6 during the day in locations away from strong local sources. Near local sulfur sources the ratio was measured to be as low as .05 and at night during stagnant conditions the ratio exceeded 1.0.

No experimental evidence was found for the homogeneous nucleation of new particles in the L.A. basin. It is thought that the dominant mechanism is the heterogeneous growth of existing particles. Most of this growth appears to occur in the particle size range from 0.1 to 1.0 μm.

The results of sampling near the Harbor Freeway in downtown L.A. indicated that the primary particle size range associated with automobile exhaust was from 0.01 to 0.1 μm in diameter. It is thought that these primary particles contributed by the automobile can grow into the light scattering size range between 0.1 and 1.0 μm by the transformation of material from the gas phase to the particluate state by coagulation of smaller particles to form particles in the larger size range.

We do not know what the pre-existing nuclei for aerosol growth are. Although we have chemical composition data for particles less than 0.6 μg, we have no specific chemical data for the large number concentration of particles between 0.01 and 0.1 μm which can serve as nuclei for aerosol growth.

Modes of Formation of the Salts of Sulfur and Nitrogen in an NO_x-SO_2Hydrocarbon Polluted Atmosphere

Jack G. Calvert, Ph.D.

An evaluation has been made of the theoretically possible rates of homogeneous reactions which convert SO_2 to sulfate and NO_x to nitrate in a simulated sunlight-irradiated, NO_x-hydrocarbon-SO_2-polluted atmosphere. These studies suggest that the following elementary homogeneous reactions probably occur at significant rates in the urban atmosphere:

$$HO + SO_2 \text{ ---------} HOSO_2 \qquad (60)$$

$$HO_2 + SO_2 \text{ --------} HO + SO_3 \qquad (53a)$$

$$HO + NO_2(+M) \text{ ----------} HONO_2(+M) \qquad (14)$$

$$N_2O_5 + H_2O \text{ ----------} 2HONO_2 \qquad (3)^*$$

In theory the occurrence of reaction 60 would be followed by subsequent rapid reactions which will form sulfuric acid, peroxysulfuric acid, and other potentially interesting and chemically reactive compounds such as $HOSO_2O_2NO_2$, a mixed anhydride of sulfuric and nitric acids. The latter species, predicted in theory but not yet observed experimentally, is an inorganic analogue to the peroxyacetylnitrate formed on irradiation of NO_x-hydrocarbon mixtures in the atmosphere.

The present kinetic study suggests that photochemical aerosol formation can be initiated by homogenous reactions at rates which are in line with the observed rates of sulfate and nitrate salt formation in the urban atmosphere.

Either SO_3 or sulfuric acid formation in the urban atmosphere should initiate the growth of an aerosol droplet. This growth will be controlled by many factors including the humidity, the rate of condensation of the supersaturated vapor, the rate of capture of gaseous organic pollutant molecules (olefins, aldehydes, epoxides, etc.) and their conversion to polymeric or low vapor pressure products within the acid droplet, the rate of capture of ammonia and other basic molecules or particles (ZnO, Fe_2O_3, PbO, CdO, $CaCO_3$, etc.), or the halides of the metals as well as the rate of capture of nitric acid, etc.

There are several possible heterogeneous paths of conversion of SO_2 and NO_2 to the sulfate and nitrate salts which are often invoked by atmospheric scientists and which may occur at a significant rate in the atmosphere. Present kinetic data do not allow a realistic evaluation of their relative significance in the smoggy urban atmosphere at this time.

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* Reaction may occur at a significant rate only in an aerosol droplet.

$H_2SO_4/(NH_4)\ SO_4$ Background Aerosol: Optical Detection in the St. Louis Region

R. J. Charlson, Ph.D.

In order to understand how to control secondary pollutants in air such as H_2SO_4 aerosol, it is necessary to develop an understanding of the relationship between source and the effect. The connection between these requires a knowledge of the molecular structure and size distribution of submicrometer material.

Ordinary chemical analyses do not provide adequate molecular information, and methods that do are still limited to research applications. Nonetheless, the molecular composition controls the following:

a. toxicity
b. water solubility
c. hygroscopicity
d. deliquescent behavior
e. refractive index
f. physical state and shape of particles

Toxicity is of obvious importance to living organisms, as is water solubility, while hygroscopicity and deliquescent behavior govern the growth of particles within the airways of animals due to high humidity there. Hygroscopicity, deliquescent behavior and refractive index are important to the problem of visibility while physical state and shape of particles is probably important for gas-particle interaction.

Based on an optical, in situ method, it has been shown possible to identify and to semi-quantify H_2SO_4 and/or NH_4HSO_4 as the major submicrometric aerosol constituent in St. Louis in summer.

This discovery heightened the need for understanding its source, which is probably oxidation of SO_2, and it also heightened the need for a better understanding of its health effects. Also, to what extent are St. Louis and the South Coast (CA) of Bay Area regions comparable with respect to acid sulfate? Today the South Coast (CA) aerosol clearly is not dominated by H_2SO_4, but if high sulfur fuel

were used it might be. Instead of the few percent sulfate presently found (with low-sulfur fuels) we could find the St. Louis constitution of $\geq$ 50% submicrometer particles as various acid sulfates.

There is thus a clear need to understand tha atmospheric molecular chemistry of sulfate and its health effects. Both acute and chronic exposures should be studied.

The role of NH_3 in this system is currently unknown but presumably important. Methods are needed for NH_3 analysis.

The spatial dependence of SO_4=aerosols by traditional chemical analysis and the new optical measurements both show that, unlike SO_2, the SO_4=aerosol is distributed over wide geographic areas. The removal distance (1/e) for SO_2 and its oxidation products appears to be of the order of 1000 Km while the spacing of sources is much smaller. As a result, the SO_4= is found well outside of cities. Indeed, it may be imposed on cities by rural sources (power generation) and it may not be primarily an urban entity.