ABSTRACTS OF REPORTS PUBLISHED IN THE ENVIRONMENTAL PROGRAMS

COVERING THE PERIOD
JANUARY - DECEMBER 1978

BROOKHAVEN NATIONAL LABORATORY
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ABSTRACTS
OF REPORTS PUBLISHED
IN THE
ENVIRONMENTAL PROGRAMS
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DEPARTMENT OF ENERGY AND ENVIRONMENT

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This 1978 Annual Abstracts represents the publishing experience over the past year of the three divisions and one group that make up the Environmental Sciences area of the Department of Energy and Environment. The abstracts are grouped according to the organization of the authors under the Atmospheric Sciences, Environmental Chemistry, and Oceanographic Sciences Division and the Land and Fresh Water Environmental Sciences Group. The range of interests and the interdisciplinary nature of the activities within Environmental Programs are demonstrated by these abstracts. Most of these activities relate in some way to the environmental effects or potential effects of energy generation. The major areas involved include:

Coastal meteorology
Physical, biological, and chemical oceanography of the coastal shelf
Analysis of marine, fresh water, and terrestrial ecosystems
Effects of acid rain and other pollutants on aquatic and terrestrial systems
Multistate Power Production Pollution Study (MAP3S), including transport and transformation experiments, data management, and modeling and analysis
Atmospheric diagnostics including the study of the chemistry of pollutants in plumes and ambient atmosphere
Basic and applied studies of atmospheric aerosol generation, composition, and behavior
Development of atmospheric tracer systems and real-time instrumentation

The objectives of the individual activities involved and the major accomplishments for 1978 are described in Annual Highlights - Environmental Programs, BNL 50977.
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INFLUENCE OF MEAN WIND DIRECTION ON SEA SURFACE WAVE DEVELOPMENT

BNL 24189

S. SETHURAMAN

Atmospheric Sciences Division

Momentum flux measurements over the Atlantic Ocean made from an air-sea interaction buoy indicate the surface drag coefficient $C_D$ to be strongly dependent on changes in mean wind direction. A change in mean wind direction is accompanied by a change in wave propagation direction in association with variations in wave steepness and stage of wave development. From simultaneous wave height spectra measurements, a critical value for the relative motion of air and sea surface is suggested beyond which the dominant waves reach fully developed stage and the drag decreases.

Program: Coastal Meteorology

Sponsor: DOE, Office of Health and Environmental Research
A knowledge of the characteristics of atmospheric turbulence in the surface layer, particularly during high wind speeds, is important in designing tall structures. This paper deals essentially with the behavior of the scales of turbulence, intensity of turbulence and wind shear within 100 m above the surface during strong winds with different meteorological conditions. The effect of surface roughness is examined by comparing the observations at an inland site with those at a coastal site and at an offshore location. Cases studied include high pressure systems, coastal storms and a hurricane.

The observations consisted of longitudinal, lateral and vertical velocity fluctuations from three stations, 1) a buoy anchored 5 km offshore near the east end of Long Island, 2) a meteorological tower at the beach, and 3) a site 18 km inland. The results indicated an increase in wind speed by a factor of about four, offshore and at the beach, as compared to inland values for onshore flows. The intensity of turbulence during the passage of a hurricane was observed to be about 35% with significant peaks in variance spectra shifted toward higher frequencies.
Structure of turbulence over water is found to change for wind speeds more than 10 to 12 m/sec. Increase in turbulence level beyond this critical wind speed is attributed to the formation of helical roll vortices. Integral scales of turbulence over water are observed to be several times larger than the corresponding overland values.
MOMENTUM FLUX AND WAVE SPECTRA MEASUREMENTS FROM AN AIR-SEA INTERACTION BUOY

BNL 24206

S. SETHURAMAN

Atmospheric Sciences Division

Momentum flux measurements by eddy correlation method and wave height measurements with a capacitance-type wave staff were carried out from a stable air-sea interaction buoy anchored 5 km off Tiana Beach, Long Island. A characteristic height of sea surface \( h_s \) was estimated from wave height spectra. A roughly linear variation of surface drag coefficient \( C_D \) with \( h_s \) was found for aerodynamically rough sea surface. Roughness length \( z_0 \) computed from the commonly adopted relationship \( z_0 = h_s / 30 \) was of the same order of magnitude as the one computed from Charnock's relationship \( \alpha u^2 \) \( / g \), where \( u^* \) is the friction velocity, \( g \) the gravitational acceleration and \( \alpha \) a constant.

Program: Coastal Meteorology

Sponsor: DOE, Office of Health and Environmental Research
Instrumentation and data acquisition system for an air-sea interaction experiment are described. The experiments were conducted with the help of a stable air-sea interaction buoy anchored five kilometers offshore in the Atlantic Ocean near Long Island. Instruments were designed to survive the hostile marine environment and maintain their calibration and relatively high frequency response. A line-of-sight RF telemetry system was used to obtain data at a fast rate. Unique power supply features, such as a wind charger and a solar panel, were used to extend the life of batteries. Future plans regarding data transmission through space satellites are presented.
CALIBRATION AND USE OF A SAIL PLANE VARIOMETER TO MEASURE VERTICAL VELOCITY FLUCTUATIONS

BNL 24299

S. SETHURAMAN, R. M. BROWN, G. S. RAYNOR and W. A. TUTHILL

Atmospheric Sciences Division

The calibrations of a sail plane variometer to measure vertical velocity fluctuations in the atmosphere boundary layer is described. Its usefulness is demonstrated with typical results from a boundary layer development study.

Program: Coastal Meteorology

Sponsor: DOE, Office of Health and Environmental Research
RESPONSE CHARACTERISTICS OF A NEW BI-DIRECTIONAL VANE

BNL 24300

S. SETHURAMAN and W. A. TUTHILL

Atmospheric Sciences Division

The design and construction of a bivane to measure horizontal and elevation angle fluctuations in the atmosphere is presented. Wind tunnel tests indicated a reasonable high frequency response. Field comparisons with a commercially available instrument gave good results. A unique feature in the design of this bivane is its ruggedness in combination with good frequency response.

Program: Coastal Meteorology

Sponsor: DOE, Office of Health and Environmental Research
Mean and fluctuating winds were measured within the atmospheric surface layer at three locations across Long Island during the landfall of Hurricane Belle on August 9, 1976. An order of magnitude increase in wind shear was observed. A friction velocity of about 133 cm/sec and an energy dissipation rate of about 130 cm²/sec³ were estimated. Mean wind speeds at the beach were found to be 3 to 5 times the corresponding wind speeds inland. A periodicity in rainfall associated with bands of thundershowers was observed. A storm surge of about 125 cm was estimated from water level records near an inlet. The records indicated the three successive stages: forerunner, hurricane surge and resurgence associated with the hurricane.
Details of instruments and data acquisition system for the 1977 air-sea experiments are described. The experiments were conducted with the help of a stable air-sea interaction buoy anchored five kilometers offshore in the Atlantic Ocean near Long Island. Instruments were designed to survive the frequency response. A line-of-sight RF telemetry system was used to obtain data at a fast rate. Unique power supply features such as a wind charger and a solar panel were used to extend the life of batteries. Future plans regarding data transmission through space satellites are presented.
Nearly all models for calculating atmospheric diffusion include parameters designed to describe the rate of diffusion in the horizontal and vertical directions. These parameters are seldom measured but are usually estimated from a known or presumed relationship to some meteorological variable which can be measured. The best estimators for short-range diffusion seem to be the horizontal and vertical fluctuations of the wind. When these are not available, diffusion parameters are most frequently estimated from temperature lapse rates, wind gustiness, or the Pasquill diffusion classes determined from synoptic observations. Several recent studies have shown poor agreement among the three methods and between measured and predicted diffusion. This study was designed to determine the amount of disagreement between the methods and to modify procedures for computing the Pasquill classes to improve agreement.

Hourly meteorological data including tower measurements and synoptic observations taken at Brookhaven National Laboratory over a two-year period were used for the study. The data included the BNL gustiness classes. Lapse rates were computed for four height intervals. The Pasquill classes were computed from the synoptic observations. Although the three measures of diffusion are not directly comparable, the percent of general agreement between each pair was calculated. The data were then analyzed to determine the conditions under which poor agreement occurred. The procedures for computing the Pasquill classes were then modified in several steps and the changes resulting from each modification examined. Complete agreement between the methods could not be obtained but the final set of modifications resulted in somewhat better agreement between the computed Pasquill classes and both measured lapse rate and gustiness classes. They also gave a more realistic distribution of stable, neutral and unstable groups. Use of the modified method is expected to give better predictions of diffusion.
The development of wind generated currents in the ocean was studied with simultaneous observations of mean wind speed, wind direction, surface wave parameters and near-surface ocean currents. The measurements were carried out during February 23-through March 14, 1976 as part of a coastal ocean boundary layer and diffusion study off Long Island, New York in the Atlantic Ocean.

The results show a high correlation between wave slope and near-surface current indicating the possibility of wave age playing a significant role in the generation of current. Wave age is known to cause variations in momentum transfer (Kraus, 1972; Sethuraman, 1978). The wind generated current was found to have a broad spectral peak as compared with tidal currents. This peak was found to occur at approximately the same frequency as wind speed spectral peak. Integral time scales associated with wind and near-surface current were about the same, indicating the dominance of wind forcing near the ocean surface for this period of observations.
FORMATION AND CHARACTERISTICS OF COASTAL INTERNAL BOUNDARY LAYERS DURING ONSHORE FLOWS

BNL 25115

GILBERT S. RAYNOR, S. SETHURAMAN, AND ROBERT M. BROWN

Atmospheric Sciences Division

The development and characteristics of coastal internal boundary layers which form as air flows from one surface to another with different roughness and temperature were investigated in 28 tests. These were made at all seasons and in both gradient and sea breeze flows but only during mid-day periods. Measurements of turbulence and temperature were taken from a light aircraft which flew traverses across Long Island at successive altitudes parallel to the wind direction. These data were used to locate the boundary between modified and unmodified air as a function of height and distance from the coast. The same measurements plus tower measurements of wind, turbulence and temperature, pilot balloon soundings and measurements of land and water surface temperatures by a remote sensing IR thermometer were used to quantify the characteristics of the modified and unmodified air.

The boundary layer slope was steep close to the land-water interface and became shallower with downwind distance. Growth of the boundary layer was initially slower with stable lapse rates upwind than with neutral or unstable conditions over the water. An equilibrium height was found in many tests except under conditions of free convection when the internal boundary layer merged into the mixed layer inland and with sea breeze conditions. The equilibrium height depended on downwind conditions and was greater with low wind speeds and strong land surface heating than with stronger winds and small land-water temperature differences. Current theoretical models are not adequate to predict the height of the boundary layer at the altitudes and distances studied but reasonably good predictions were given by an empirical model developed earlier.

Wind speed in the modified air averages about 70% of that at the coast but turbulence levels were several times higher both near the surface and aloft. These findings have important implications for diffusion from coastal sites.

Program: Coastal Meteorology

Sponsor: DOE, Office of Health and Environmental Research
EFFECTS OF CHANGES IN THE UPWIND SURFACE CHARACTERISTICS ON THE MEAN WIND SPEED AND TURBULENCE NEAR A COASTLINE

BNL 25178

S. SETHURAMAN AND G. S. RAYNOR

Atmospheric Sciences Division

Measurements of mean wind speed and longitudinal turbulence taken on a meteorological tower on the beach and on a stable air-sea interaction buoy anchored 5 km offshore in the Atlantic Ocean were compared. Observations were made simultaneously at the two sites at a height of 6 m above the surface for several days. Results indicate that the differences in mean wind speed and turbulence can be related to the development of internal boundary layers and to changes in air flow characteristics caused by variations in upwind surface features.

Boundary layer characteristics over the ocean show little diurnal change as compared with land due to lack of diurnal temperature changes of the ocean surface.

Program: Coastal Meteorology

Sponsor: DOE, Office of Health and Environmental Research
In 1976 the Energy Research and Development Administration (ERDA) Inter-
laboratory Working Group for Data Exchange developed a standard for the
generalized exchange of data bases using magnetic tape. This subsequently
became the proposed "American National Standard Specifications for an
Information Interchange Data Descriptive File." This report describes the
development of a mechanism for conversion of SYSTEM 2000 data bases to or
from interchange files conforming to the proposed standard and vice versa.
Two phases are discussed. Phase One requires that the user supply the data-
base definition and uses loader string files for conversion. Phase Two will
be a completely automated process using the Programming Language Interface.
This phase requires no prior knowledge of the data-base structure or content
at execution time.
AN AUTOMATIC SEQUENTIAL PRECIPITATION SAMPLER

BNL 24391

GILBERT S. RAYNOR and JOHN P. MC NEIL

Atmospheric Sciences Division

An automatic sequential precipitation sampler was designed and constructed at Brookhaven National Laboratory to collect precipitation samples for chemical analysis. The sampler is designed to collect both wet and frozen precipitation and to exclude dry fallout between precipitation events. The sampler consists of a large box containing a turntable holding 30 sampling bottles. Precipitation enters through a funnel on the top of the box. Between periods of precipitation the funnel is closed by a movable cover which is actuated by a rain sensor when precipitation starts. Sample bottles are changed automatically and periodically from the time the cover opens. Times of cover opening and closing and of bottle changing are recorded on an event recorder. The sampler has operated successfully since June 1976.

Program: Effects of Acid Rain on Terrestrial Ecosystems

Sponsor: Environmental Protection Agency
An Automatic Sequential Precipitation Sampler was designed and constructed at Brookhaven National Laboratory to collect precipitation samples for chemical analysis. The sampler is designed to collect both wet and frozen precipitation and to exclude dry fallout between precipitation events. The sampler consists of a large box containing a turntable holding thirty sampling bottles. Precipitation enters through a funnel on the top of the box. Between periods of precipitation, the funnel is closed by a movable cover which is actuated by a rain sensor when precipitation starts. Sample bottles are changed automatically and periodically from the time the cover opens. Times of cover opening and closing and of bottle changing are recorded on an event recorder. The sampler has operated successfully since June 1976.
Hourly precipitation samples were collected at Brookhaven National Laboratory from June 1976 through May 1977 using an Automatic Sequential Precipitation Sampler. Conventional meteorological data were recorded for each sample period. The samples were analyzed for pH, conductivity and concentrations of sulfate, nitrate, ammonium, sodium, and chloride ions. Statistical analyses were performed of the relationships between selected chemical variables and between them and meteorological conditions. Results are presented in a series of tables.
The goal of the Multistate Atmospheric Power Production Pollution Study (MAP3S), a research program funded by the U.S. Department of Energy (DOE), is to develop and demonstrate an improved, verified capability of numerically simulating the present conditions and potential changes in pollutant concentration, atmospheric behavior and precipitation chemistry that result, or will result, from pollutants released to the atmosphere by large-scale power production processes. The program is divided into ten major tasks. Tasks 1 and 2 of the MAP3S Program Plan are concerned with the quantification of emissions of pollutants from power production and non-power production sources.

Due to the multistate nature of the MAP3S area of interest, the emissions inventory project has been based on obtaining pertinent data gathered by other agencies (EPA, FPC, state and local governments, etc.), and computerizing, correlating and updating such data. This paper describes the development of the project to date. Topics to be covered include the acquisition of both emissions and ancillary data, techniques developed for quality assurance and data updating as well as descriptions of current and future plans in both upgrading and using the inventory.
This paper presents successful experiments using finite element technique to solve the turbulent transport model proposed here for computing turbulent field and diffusion based on turbulent second-order closure scheme in the atmospheric planetary boundary layer. The model proposed here governing the mean motion, mean turbulent Reynolds stresses, mean turbulent kinetic energy, mean turbulent dissipation, mean concentration and mean concentration flux are integrated numerically. The numerical technique and the model developed have thus far only been applied to neutral lapse rate, barotropic, statistically stationary and horizontally homogeneous conditions, but extension to non-neutral and horizontally inhomogeneous conditions are obvious. The computed results are realistic and agree well with available data.
The BNL Long and Short Range Air Quality Model is described, which calculates transport, transformation and resulting pollutant concentrations for given emission inventories. Sensitivity analyses were performed on critical model parameters: chemical conversion rates, deposition velocities, release heights, mixing heights and seasons. A verification study was conducted using a complete SO\textsubscript{2} emission inventory for the East (89\% of total East SO\textsubscript{2} emissions) for 4 months (January, April, July and October). Comparison with observed SO\textsubscript{2} and SO\textsubscript{4}\textsuperscript{2-} (NASN and EPRI) for the same periods gave time averaged spatial correlations of >.7 for SO\textsubscript{2} and >.6 for SO\textsubscript{4}\textsuperscript{2-}. The model has been applied to environmental problems in energy planning, including health impact assessment, and to regional measurement program design.

Program: MAP3S Modeling and Analysis

Sponsor: Environmental Protection Agency
ATMOSPHERIC TURBULENCE AND DIFFUSION BOUNDARY LAYER TRANSPORT MODEL

BNL 25026

HSI-NAN LEE

Atmospheric Sciences Division

A finite element turbulence and diffusion transport model in the neutral atmospheric planetary boundary layer has been developed. In preliminary results the behavior of the planetary boundary layer agrees well with the available data and with the complicated existing finite difference models developed by Deardorff and Shir. The numerical technique and model developed here could be extended to a non-neutral case. Due to the advantages of accurate representation of complex geometry with the finite element method, the model could treat accurately the horizontally inhomogeneous terrain. The proposed dynamic formulation of the eddy viscosity coefficient for the momentum is particularly attractive and can provide a viable alternative approach to study the atmospheric turbulent motion and diffusion over a complicated terrain.

Program: MAP3S Modeling and Analysis

Sponsor: Environmental Protection Agency
MODELING SULFUR OXIDE CONCENTRATIONS IN THE EASTERN UNITED STATES: MODEL SENSITIVITY, VERIFICATION AND APPLICATIONS

BNL 25069

R. E. MEYERS, R. T. CEDERWALL. J. A. STORCH, AND L. I. KLEINMAN

Atmospheric Sciences Division

The BNL Long and Short Range Air Quality Model is described, which calculates transport, transformation and resulting pollutant concentrations for given emission inventories. Sensitivity analyses were performed on critical model parameters: chemical conversion rates, deposition velocities, release heights, mixing heights and season. A verification study was conducted using a complete SO₂ emission inventory for the East (89% of total East SO₂ emissions) for four months (January, April, July and October). Comparison with observed SO₂ and SO₄²⁻ (NASN and EPRI) for the same periods gave time averaged spatial correlations of > .7 for SO₂ and > .6 for SO₄²⁻. The model has been applied to environmental problems in energy planning, including health impact assessment, and to regional measurement program design.

Program: MAP3S Modeling and Analysis

Sponsor: Environmental Protection Agency
FORMATION AND TRANSPORT OF OZONE IN THE NORTHEAST QUADRANT OF THE UNITED STATES.

BNL 25292

G. D. WIGHT, G. T. WOLFF, P. J. LIOY, R. E. MEYERS and R. T. CEDERWALL

Atmospheric Sciences Division

The very high concentrations of ozone measured in Connecticut and elsewhere along the Northeast and Mid Atlantic Coast were investigated through analysis of data from the entire 1976 ozone season from nineteen northeastern and midwestern states, National Weather Service meteorological data, and air parcel trajectories. For several high ozone episodes, the relationship between the movement of and circulation within a high pressure system across the northeast quadrant of the U.S. and the buildup of ozone concentrations was clearly demonstrated. Air parcel trajectory analysis coupled with source density information was utilized for several well defined episodes in 1976 to show ozone measured at various locations throughout the study area is partially locally generated and partially transported from substantial distances.

Program: MAP3S Modeling and Analysis

Sponsor: Environmental Protection Agency
NUMERICAL METHODS IN MULTI-GRID ANALYSIS

BNL 25224

HSI-NAN LEE and RONALD E. MEYERS

Atmospheric Sciences Division

In fluid mechanics we usually deal with a system of non-linear equations (Continuity equation, momentum equation, etc.). The usual approach to such problems uses either finite-element or finite-difference equations with fixed grid size and order. In more recent years, ordinary differential equations have been solved by methods with adaptive step size and order, such as those by Gear (1971) and Byrnes and Hindmarsh (1975). The multi-level adaptive technique (Brandt, 1977) is a numerical method for solving partial differential equations. The method presented in this paper is of this kind and, since it uses a sequence of nested grids in the solution process, can be aptly described as the multi-grid method. In principle the order for this multi-grid method is that of infinite order in the sense that spatial derivatives contain information about function values on all nested grid points. Therefore, the multi-grid method has higher accuracy and efficiency than methods with the fixed grid size and order in which much computational time can be wasted. The multi-grid technique is not only applicable to finite-difference equations but also to finite-element equations. Although the advantage of the finite element method is that it represents more accurately irregular boundaries, the mechanism of implementing an efficient finite element scheme in the multi-grid method over irregular boundaries is still under investigation. For the arbitrary elements it is not clear how to construct relaxation procedures with the smoothing properties required by the multi-grid process.

An introduction to the implementation of the multi-grid method in the solution of finite difference system equations is presented and a simple time-dependent nonlinear partial differential equation is tested.

Program: MAP3S Modeling and Analysis

Sponsor: Environmental Protection Agency
The climatology of Brookhaven National Laboratory 1974-1977 is a supplement to BNL 50466, "Climatology of Brookhaven National Laboratory 1949-1973" which was prepared from data collected by the Brookhaven Meteorology Group formed in August 1948. This publication updates some meteorological summaries and includes analyses of humidity and solar radiation data not included in the original climatological report.

Results are presented in tabular form to facilitate usage. Data are given in the form of frequency distributions, percentage frequency distributions, extremes, ranges and averages as being most adaptable for further research.

Program: Meteorological Services

Sponsor: Department of Energy
Atmospheric Sciences Division

As part of a program to characterize the plant and animal life of the Laboratory site and surrounding areas, the two breeding-bird censuses taken in 1977 were repeated in 1978. Five observers made thirteen census trips to both the BNL and Westhampton plots. A decrease in rufous-sided Towhees occurred on both plots but other changes were small and not considered significant.

Program: National Environmental Research Park

Sponsor: DOE, Office of Health and Environmental Research
This paper presents successful experiments using finite element technique to solve the turbulent transport model proposed here for computing turbulent field and diffusion based on turbulent second-order closure scheme in the atmospheric planetary boundary layer. The model proposed here governing the mean motion, mean turbulent Reynolds stresses, mean turbulent kinetic energy, mean turbulent dissipation, mean concentration and mean concentration flux are integrated numerically. The numerical technique and the model developed have thus far only been applied to neutral lapse rate, barotropic, statistically stationary and horizontally homogeneous conditions, but extension to non-neutral and horizontally inhomogeneous conditions are obvious. The computed results are realistic and agree well with available data.
BROOKHAVEN NATIONAL LABORATORY LONG-TERM GAUSSIAN DISPERSION MODEL

BNL 24226

C. DOPAZO, H-N LEE and P. MICHAEL

Atmospheric Sciences Division

The Long-Term Gaussian Dispersion Model evaluated average (seasonal or annual) pollutant concentrations at ground level receptor points. The input parameters to the model are 1) the BNL joint frequency distribution of wind speed, wind direction and stability, 2) the average emission rates for both area and point sources and their geometric and physical characteristics, 3) the receptor grid configuration, 4) the assumed half-life of the particular pollutant undergoing linear chemistry, 5) deposition rate, 6) the average climatological mixing height and the average nocturnal mixing height, 7) the average air temperature, and 8) the reference height for wind speed measurements.

The main differences of this model with respect to the EPA-CDM are the following: a) BNL stability categories instead of the conventional Pasquill-Gifford stability classes are used. b) The highest and lowest central wind speeds are different from those used in the EPA-CDM. c) The area source contributions (double integrals) are analytically evaluated. EPA-CDM resorts to the numerical integration of these double integrals. d) The Briggs plume rise formulae used here are slightly different from those used by EPA-CDM. e) Pasquill's latest suggestion to obtain point source contributions as functions of the release height and the distance from the source are included here. f) Area sources far away from the receptor point are treated as point sources. g) Depositing is included as a possible mechanism for pollutant removal. h) An area source inventory with several area source dimensions can be directly treated without the need for further subdivisions of large area sources to have a unique elementary unit area.

Program: Transport and Transformation Experiments (MAP3S)

Sponsor: Environmental Protection Agency
A radio-controlled air sampling system was developed for sampling tracer gases at an array or remote, portable sampling stations. Each sampling station contains a receiver-decoder, a battery pack and three evacuated metal cylinders fitted with hand-operated toggle valves, radio-controlled latching solenoid valves and critical orifices. The transmitting station includes an encoder and a FM base station radio. It may be operated from a fixed based with a tower-mounted antenna or from an aircraft for greater distances. Distance is limited only by line of sight transmission. Three sets of samples may be taken at any selected time and for any selected duration within the volume limitations of the sampling cylinders and the flow limitations of the critical orifices. Each set is simultaneous at all sampling stations. Samples may be either continuous or intermittent. The system has been tested in the field and operated as designed.
A COMPARATIVE STUDY OF DIFFUSION CLASSIFICATION BY LAPSE RATE, GUSTINESS AND A MODIFIED PASQUILL METHOD

BNL 24844

GILBERT S. RAYNOR and JANET V. HAYES

Atmospheric Sciences Division

Nearly all models for calculating atmospheric diffusion include parameters designed to describe the rate of diffusion in the horizontal and vertical directions. These parameters are seldom measured but are usually estimated from a known or presumed relationship to some meteorological variable which can be measured. The best estimators for short-range diffusion seem to be the horizontal and vertical fluctuations of the wind. When these are not available, diffusion parameters are most frequently estimated from temperature lapse rates, wind gustiness, or the Pasquill diffusion classes determined from synoptic observations. Several recent studies have shown poor agreement among the three methods and between measured and predicted diffusion. This study was designed to determine the amount of disagreement between the methods and to modify procedures for computing the Pasquill classes to improve agreement.

Hourly meteorological data including tower measurements and synoptic observations taken at Brookhaven National Laboratory over a two-year period were used for the study. The data included the BNL gustiness classes. Lapse rates were computed for four height intervals. The Pasquill classes were computed from the synoptic observations. Although the three measures of diffusion are not directly comparable, the percent of general agreement between each pair was calculated. The data were then analyzed to determine the conditions under which poor agreement occurred. The procedures for computing the Pasquill classes were then modified in several steps and the changes resulting from each modification examined. Complete agreement between the methods could not be obtained but the final set of modifications resulted in somewhat better agreement between the computed Pasquill classes and both measured lapse rate and gustiness classes. They also gave a more realistic distribution of stable, neutral and unstable groups. Use of the modified method is expected to give better predictions of diffusion.

Program: Transport and Transformation Experiments (MAP3S)

Sponsor: Environmental Protection Agency

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Results of recent soundings made with an instrumented aircraft in the Multistate Power Production Pollution Study (MAP3S) show the extent of variability in concentration and distribution measurements within, at the interface, and above the mixed layer. Correlation of the measurements to meteorological parameters provide some understanding of the variability found in the data. The results include time integrated values of sulfate concentrations at selected altitudes above ground level at several locations in the northeastern United States. The data provide additional measurements of the ratios of $\text{SO}_4 / \text{SO}_2$ in the area of investigation.

Program: Transport and Transformation Experiments (MAP3S)

Sponsor: Environmental Protection Agency
Submicron particles in the atmosphere consist almost entirely of various combinations of sulfate and ammonia. Depending upon the composition and relative humidity, these aerosols may exist in the form of solution droplets or as dry crystals composed of either pure \((\text{NH}_4)_3\text{H(SO}_4)_2\) or mixed salts such as \((\text{NH}_4)_3\text{H(SO}_4)_2\) and \(\text{HN}_4\text{H}_2\text{SO}_4\). Previous work has shown that the equilibrium size of mixed-salt aerosols can readily be calculated as a function of relative humidity, provided that the pertinent thermodynamic properties of the bulk system under consideration are available. This paper presents the measured optical and thermodynamic properties essential for making growth calculations for \((\text{NH}_4)_3\text{H(SO}_4)_2\) aerosols. For experimental purposes, letovicite was prepared in solution by dissolving reagent grade \((\text{NH}_4)_2\text{SO}_4\) in triple distilled water and adding \(\text{H}_2\text{SO}_4\) in stoichiometric proportions. The purity of the crystallized salt was verified by x-ray diffraction. Aliquots of this stock solution were diluted to various concentrations and the refractive index, density and water vapor pressure measured as a function of temperature for each dilution. A least-squares computer program was used to best fit the water vapor pressure data in the usual form of \(\ln p\) vs. \(1/T\). From the water vapor pressure at \(25^\circ\text{C}\), the deliquescence point of letovicite was determined to be 69.3% R.H. in good agreement with the value of 68.5 ± 1% obtained from aerosol growth experiments.
The phase transformation and subsequent droplet growth of the mixed-aerosols NaCl-KCl and (NH₄)₂SO₄-H₂SO₄ were investigated in a continuous flow apparatus at 25°C and 30°C as a function of relative humidity. Monodisperse salt aerosols (d = ~ 0.5 μm, σg = 1.07-1.13) were prepared and mixed with N₂ carrier gas at controlled humidities. The particle-size distribution of the aerosol before and after growth by water vapor condensation was continuously monitored with an optical particle counter. It was found that mixed-salt aerosols were characterized by stage-wise growth when the relative humidity in the atmosphere was increased. The onset of growth took place at a specific deliquescence humidity determined by the water activity at the eutonic composition. Thus, mixed NaCl-KCl aerosols deliquesce at 73.8 ± 0.5% r.h. regardless of initial compositions. For sulfate aerosols containing 0.75 to 0.95 mole fraction (NH₄)₂SO₄ (the balance being H₂SO₄), the onset of growth occurs at 89.0 ± 0.5% r.h. In the composition range of 0.5 to 0.75, a deliquescence humidity of 39.0 ± 0.5% is noted. Below 0.5 mole fraction, however, the mixed-sulfate aerosols are expected to exhibit hygroscopic properties on the basis of thermodynamic considerations.

Program: Aerosol Chemistry and Dynamics

Sponsor: DOE, Office of Health and Environmental Research
DELIQUESCENCE PROPERTIES OF MIXED SULFATE AND NITRATE AEROSOLS IN A MOIST ATMOSPHERE

BNL 24846

I. N. TANG and H. R. MUNKELWITZ

Environmental Chemistry Division

The paper describes the work in progress at Brookhaven National Laboratory to study the growth of aerosols composed of mixed inorganic salts. Sub-micron monodisperse salt aerosols having a log-normal size distribution with \( \sigma_g \) ranging from 1.07 to 1.13 are prepared by mobility separation. The deliquescence properties and particle size change as a function of relative humidity are investigated in a specially designed continuous flow apparatus. Data on the phase transformation and subsequent droplet growth have been obtained for aerosols of various internal mixtures of sulfates and nitrates which are of environmental interest. The results are discussed in terms of the thermodynamic properties of the aerosol systems.

Program: Aerosol Chemistry and Dynamics

Sponsor: DOE, Office of Health and Environmental Research
DELIQUESCENCE PROPERTIES AND PARTICLE SIZE CHANGE OF HYGROSCOPIC AEROSOLS

BNL 25028

I. N. TANG

Environmental Chemistry Division

Ambient aerosols frequently contain large proportions of hygroscopic inorganic salts such as sulfates and nitrates, which may induce adverse health effects upon inhalation. The inhaled salt particles are invariably exposed to a humid environment; their deposition along the respiratory tract will necessarily depend upon the size change resulting from water vapor condensation. This paper discusses the deliquescence properties of pure and mixed salt aerosols and the particle size change as a function of relative humidity. Experimental results are presented for the growth of mixed chlorides (NaCl-KCl), mixed sulfates (H₂SO₄-(NH₄)₂SO₄), and mixed (NH₄)₂SO₄-NH₄NO₃ aerosol systems. It is shown that the behavior of the mixed salt aerosols in a moist atmosphere can be predicted from phase diagrams and pertinent thermodynamic properties of the bulk solutions. The evaporation of a saline droplet in an atmosphere of decreasing humidities is also investigated experimentally. The onset of recrystallization of the salt from a supersaturated aerosol takes place at a reproducible relative humidity for chlorides, but not for sulfates and nitrates. The significance of the results in terms of nucleation theory is discussed.

Program: Aerosol Chemistry and Dynamics

Sponsor: DOE, Office of Health and Environmental Research
A NEW AIRBORNE AEROSOL SAMPLING SYSTEM

BNL 24192

WILLIAM H. MARLOW and ROBERT W. GARBER

Environmental Chemistry Division

The aerosol instrumentation and measurement methodology presented in this paper will be of interest both to those concerned with transport and transformation of particulate air pollution and to workers in the field of aerosol instrumentation. An airborne size-discriminatory sampling system with size distribution measurement for use aboard an aircraft is described. The filter sampling system operates at a total volumetric flow of approximately 200 lpm and consists of a sequential train of a virtual impactor, a slit-to-cylinder impactor, and a diffusion processor. Size distributions are determined in as little as 10 seconds by a modified GE CNC with a diffusion battery consisting of parallel packs of fine mesh wire screen. By careful calibration for particle removal, the "diffusion" battery method has been extended beyond its customary 0.1 µm limit.

Program: Aerosol Measurements and Microphysics

Sponsor: DOE, Office of Health and Environmental Research
Sampling and characterization needs for HTP aerosols are defined and discussed according to sample representativeness, sample integrity, artifacts of measurement and validity of the signal. It is argued that for a measurement method to be adequately defined and therefore have meaning, each of these questions must be addressed. Consequently, a rigorous calibration procedure is an integral part of the design. A candidate HTP probe system for mass determination and how it addresses these questions is described.
We develop a formalism for treating chemical reactions in stack plumes whose constituents are being diluted as the reaction proceeds, in order to examine the dependence of the ultimate extent of reaction upon the interplay between dilution and chemical reaction. This treatment is developed first for plumes of uniform cross section and is then extended to plumes of arbitrary cross section. It is shown that the rate of plume expansion exerts a controlling influence upon reactions that are higher than first-order in plume constituents, and that chemical reactions are quenched at high expansion rates. The conditions that lead to quenching depend only upon the order of reaction and the rate of expansion and are independent of the details of the reaction mechanism. For the concentration of a conservative tracer diminishing with time proportionately to $t^{-n}$, a $p$-th order reaction is quenched for $n(p-1)>1$ and unquenched for $n(p-1)\leq1$. The meteorological stability classes that would lead to quenching of second- and third-order reactions are considered.

The formalism that is developed is applied to a reexamination of SO$_2$ oxidation data obtained in studies of the Northport, N.Y. oil-fired and Sudbury, Ontario nickel-smelter plumes to ascertain the extent to which observed decreases in reaction rates may be ascribed either to dilution or to depletion of a catalyst or other reactive species that is co-emitted and co-diluted with SO$_2$. This reexamination confirms that the mechanism of oxidation was higher than first-order in plume constituents and strongly suggests second-order. The data are consistent with the second-order mechanism for a wide range of assumed catalyst/SO$_2$ ratio. It is thus established that no inference may be drawn from such data concerning catalyst depletion as a mechanism for limiting the in-plume reaction.
Aerosol samples collected in New York during August 1976 and February 1977 with high volume and diffusion samplers were analyzed for strong acid, ammonium, sulfate and nitrate.

Ammonium-sulfate correlation was exceptionally high in all respirable size fractions with average \( \frac{NH_4^+}{SO_4^{2-}} \) molar ratio about 1.5 in summer and about 2 in winter. Diurnal and seasonal variations in sulfate composition were investigated.

Program: Atmospheric Diagnostics

Sponsor: DOE, Office of Health and Environmental Research
Simultaneous measurements of atmospheric particulate sulfate and SO$_2$ were made by tandem filter sampling during manned balloon flights. The balloon permitted measurement of chemical species evolution while following a given air mass. On the June 8, 1976 flight, the balloon encountered a relatively stagnant air mass, remaining above St. Louis County for most of the day before being carried off by nocturnal winds. Concentrations of sulfate and SO$_2$ remained relatively constant during an eight-hour period. Processes responsible for concentration changes were examined to set bounds upon the oxidation rate of SO$_2$. The data are consistent with an oxidation rate as low as zero and no greater than 4% hr$^{-1}$.
Sodium chloride-impregnated cellulose filters collected nitric acid vapor from ambient atmospheres at efficiencies of ca 90% per filter when placed downstream from pretreated quartz particulate filters in a high-volume sampler. Efficiencies increased with decreasing linear flow velocity and appeared not to be a function of HNO₃ concentration. No adsorption of NO₂ on the NaCl-impregnated filters with retention as nitrate was observed. Conversion of NO₂ to nitrate on quartz (either retained as nitrate or released as artifact nitric acid) was negligibly low—less than 1% of incident NO₂ was removed. At high humidities adsorption of HNO₃ on the quartz pre-filter can become significant; for example, about 18% of 2 ppb HNO₃ was removed at 85% RH. However, adsorption losses can be minimized by desorption in a post-collection sampling period using drier air. Quartz filters which were pre-loaded with ambient particulates by 16 hour hi-vol sampling lost nitrate when exposed to aerosol H₂SO₄. Losses ranged from ~3-22 µg NO₃⁻/mg H₂SO₄ or ~1-40% of total particulate nitrate. Potassium carbonate-impregnated cellulose filters may be placed in series downstream from quartz and NaCl papers without loss of sulfur dioxide on preceding filters. 
GENERAL CONSIDERATIONS ON HOW RAINWATER MUST OBTAIN SULFATE, NITRATE AND ACID

BNL 25114

LEONARD NEWMAN

Environmental Chemistry Division

Some general statements and observations are made concerning $SO_x$ and $NO_x$ emissions in connection with the ratio that appears in aerosols, and the concentrations found in ambient air and rainwater. Based on these considerations and the acidity of aerosols and rainwater it can be concluded that it does not appear possible for rainwater to obtain its sulfur and nitrogen from aerosol sulfate and nitrate both because the ambient concentrations of the aerosols are too low and the acidity is insufficient to account for that found in rainwater. In contrast it can be shown that rainwater must obtain an appreciable fraction of its sulfur and acidity by incorporation of sulfur dioxide and that the nitrogen and its acidity could come from either nitrogen dioxide or nitric acid. Inferences can be made that in-cloud processes must be important for this incorporation of the sulfur or nitrogen dioxides. Finally it was shown that the average oxidation rate of sulfur dioxide in the atmosphere must be of the order of 0.5% per hour. The importance of making nitric acid and ammonia concentration measurements in the atmosphere are clearly indicated along with in-cloud measurements of the species in question.

Program: Atmospheric Diagnostics

Sponsor: DOE, Office of Health and Environmental Research
A detailed chemical and meteorological data base has been accumulated for the New York City subregion using improved analytical methodologies for sulfur- and nitrogen-containing aerosol constituents, as well as conventional gaseous chemical, meteorological, and aerosol size-classifying instrumentation. Seasonal and temporal variations in measured parameters within the subregion have been statistically evaluated. Data confirming the disparate nature of coarse particles (>2 μm), fine particles (0.08–2 μm), and Aitken nuclei (<0.08 μm) is remarkably consistent. Associations of sulfate levels with fine particulate parameters are uniformly strong, but seasonal, temporal and spatial variations are observed in correlations between sulfate and strong acid, gaseous precursors and air mass backward trajectories. The potential impact of recently developed techniques for continuous aerosol sulfur, sulfuric acid, nitric acid and ammonia on the characterization of aerosols may be substantial.
EVALUATION OF DETECTION OF TAGGED BLASTING CAPS UTILIZING THE U.S. CUSTOMS SERVICE AUTOMATED BAGGAGE EXAMINER AND THE BROOKHAVEN CONTINUOUS ELECTRON CAPTURE MONITORS

BNL 24959

RUSSELL N. DIETZ, GUNNAR I. SENUM and ROBERT W. GOODRICH

Environmental Chemistry Division

Utilizing the Brookhaven electron capture continuous monitors and the U.S. Customs Service Automated Baggage Examiner, these tests conclusively demonstrated that a tagged blasting cap of the design emission rate (1 nCi/min) can be adequately and reliably detected in 15 minutes or less after being placed within a typical suitcase.

Program: Explosives Tagging

Sponsor: Bureau of Alcohol, Tobacco and Firearms / Aerospace Corporation
Three types of monitors or detecting instruments for determining the presence of perfluorinated taggants have been developed and validated in field studies. Each of the three versions—a portable continuous real-time monitor, a portable concentrating chromatograph, and a fixed station high sensitivity chromatograph—have been utilized for detecting these types of compounds in atmospheric tracer studies.

The portable continuous monitor, which has a detection capability of two parts of taggant in one trillion parts of air (2 pp 10^12), has been used in three field tracer studies in the past 18 months, operating on-board aircraft. In a scenario such as continuous on-line screening of checked and hand-carried luggage at airport environments, the sensitivity and response time are more than adequate. Confirmation of the method applied to conveyor belt suitcase screening has been demonstrated.

A small concentrating field instrument was developed and field tested more than a year ago. Five minute repetitive sampling rates are estimated to ultimately provide limits of detection for the taggant compounds at about 5 pp 10^16 and could be extended as much as another 50-fold lower. Applications potentially include detecting vapor tagged explosives in meeting rooms, corridors and passageways, and on-board aircraft.
VAPOR TAGGING OF ELECTRIC BLASTING CAPS WITH PERFLUORINATED COMPOUNDS

BNL 25051

G. I. SENUM, R. P. GERGLEY, M. GREENE AND R. N. DIETZ

Environmental Chemistry Division

Vapor tagging of electric blasting caps (EBC) is accomplished with the use of perfluorocarbon taggants. These taggants are absorbed in either the present EBC end closures or in substitute fluoroelastomeric end closures in approximately 5-10% of the total weight of end closure. The specific taggants have been chosen to allow a 0.5 to 5 nanoliter per minute vapor taggant emission rate from the tagged EBC over a 5 year lifetime.

The taggant emission rates from tagged EBC have been experimentally observed to be well described by a taggant emission rate model. This model provides for experimental selection of the proper taggant for projected lifetimes of ten years based on just several months of observed emission measurements.

Another model has been derived which can predict the taggant concentrations in various realistic scenarios such as room, building, lockers, etc. The model takes into consideration the effect of barriers such as boxes, suitcases, etc., in impeding the release of the taggant vapors from the tagged EBC into the scenario and the dilution effect of the scenarios air circulation system. Taggant concentrations have been experimentally determined using a 425 liter sampling chamber with various barriers and the results are used with the model to predict various scenario taggant concentrations.

Program: Explosives Tagging

Sponsor: Bureau of Alcohol, Tobacco and Firearms/Aerospace Corporation
CONTINUOUS DETERMINATION OF AMMONIA AT AMBIENT ATMOSPHERIC CONCENTRATIONS USING FLUORESCENT DERIVATIZATION

BNL 25027

ROGER L. TANNER and JOSEPH LEPORE

Environmental Chemistry Division

Ambient atmospheric concentrations of ammonia, although critical in studies of formation and transport of aerosol sulfur and nitrogen compounds, are difficult to measure by existing techniques. A new method is reported for ammonia based on its derivatization by o-phthalaldehyde at pH 10 in the presence of the reducing agent, mercaptoethanol. The resulting, strongly fluorescent derivative may then be determined quantitatively using a conventional fluorimeter with a limit of detection for ammonia in aqueous solution of <1 ng/ml. The system may be adapted for continuous analysis by incorporation of a delay flow-through midget impinger and a particulate filter upstream from a reagent addition permits the determination of as little as 1 ppb of gaseous ammonia with 10-min time resolution.

Preliminary measurements of ambient ammonia levels on Long Island, New York were made and, combined with aerosol sulfate composition measurements made simultaneously, illustrate the value of real-time ammonia data in evaluating the chemical homogeneity of secondary sulfate-containing aerosols.

Program: Fragile Molecules

Sponsor: DOE, Division of Basic Sciences
DETERMINATION OF PARTS PER BILLION CONCENTRATIONS OF AQUEOUS NITRATE BY DERIVATIZATION GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTION

BNL 25116

ROGER L. TANNER, RUBY FAJER and JEFFREY CAFNEY

Environmental Chemistry Division

An analytical method is described for determining nanogram quantities of nitrate in microliter aqueous extracts of a variety of environmental samples. The method is based on the reaction of nitrate with an electron capture sensitive benzene analog to form a substituted nitrobenzene derivative which may be separated and analyzed by gas chromatography with electron capture detection (GC-ECD). Its application to aqueous nitrate determination in the $2 \times 10^{-7}$ to $2 \times 10^{-4}$ M range (10 ppb – 10 ppm) is demonstrated.

Use of 2,3,5,6-tetrafluoroanisole as the ECD-sensitive derivatizing agent and substitution of trifluoromethanesulfonic acid for 83% H$_2$SO$_4$ as the acid catalyst are shown to improve both nitration reaction efficiency and the overall precision of the method. Attention to experimental detail allows determination of $2 \times 10^{-7}$ M nitrate with ±10% precision and accuracy.

In the analysis of aqueous extracts of airborne particulate samples, low results were frequently obtained. A more detailed study revealed serious negative halide interferences, and the mechanism of bromide interference was elucidated through GC/MS/computer analysis. Addition of silver ion to remove halide interference was evaluated.

Program: Fragile Molecules

Sponsor: DOE, Division of Basic Sciences
GEOLOGY OF OIL AND GAS IN WESTERN SIBERIA
(TRANSLATION OF SELECTED SECTIONS)

BNL 50908

E. T. PREMUZIC

Environmental Chemistry Division

An extensive report of the studies carried out in the Western-Siberian Plateau is presented. Paleogeographic, hydrogeological and geochemical data are reviewed from a mechanistic point of view directed at distribution, magnitude and time of petroleum and gas formation and accumulation. Particular attention is given to the current Soviet methodology in search and prospecting for gas and oil deposits.

Program: Geosciences

Sponsor: DOE, Division of Basic Energy Sciences
The characteristics of a photoacoustic detection system for measurement of ambient trace atmospheric pollutants at CO$_2$ laser frequencies are analyzed and described. Several photoacoustic variables are optimized in this study. An alternate-traverse acoustic cell to eliminate cell window signals is described. An ac biased 16 cm$^2$ microphone is used. The modulation frequency dependence of the acoustic signal and a theoretical analysis is also presented. Trace gas interferents limit the practical sensitivity of the system, however, even with interferents present, a minimum measurable pressure change of 8.09 x 10$^{-10}$ atmospheres and absorptivity of 2.8 x 10$^{-9}$/cm was obtained. Techniques to minimize effects of interferents are reported along with the methodology of the photoacoustic technique in trace gas measurements.
AN EVALUATION OF THE MODIFIED EPA METHOD 6 FLUE GAS SAMPLING PROCEDURE

BNL 24367

RUSSELL N. DIETZ, ROBERT F. WIESER and LEONARD NEWMAN

Environmental Chemistry Division

The character of primary sulfate emissions (i.e., $\mathrm{H}_2\mathrm{SO}_4$ and water soluble sulfate salts) must be determined with flue gas sampling methods that differentiate between the acid form and the less noxious sulfates, both for consideration of potential health effects and for determination of the mechanisms and parameters which affect the magnitude and distribution of such emissions.

As presently recommended, the Modified EPA Method 6 does not provide for specific determination of sulfate particulates and $\mathrm{H}_2\mathrm{SO}_4$. A Brookhaven modification, based on an islinetically-sized nozzle and quartz fiber filter assembly, has been shown to quantitatively collect, in situ, all the particulate sulfate. Sulfuric acid was quantitatively passed through the filter for subsequent collection. There was no spurious formation of acid by oxidation of $\mathrm{SO}_2$ on the filter. Problems associated with sub-isokinetic particulate sampling, leading to significant positive sulfate measurement errors, will be discussed.

The isopropyl alcohol (IPA) used to collect the $\mathrm{H}_2\mathrm{SO}_4$ vapor in many cases contained sufficient oxidant to produce 10-fold positive errors or more when actual flue gas acid levels were less than 1 ppm. In addition, stripping experiments demonstrated the presence of dissolved $\mathrm{SO}_2$ equivalent to 1 to 3 ppm of flue gas acid even after 16 to 32 minute purging periods. The significance of these errors and attempted corrective procedures will be presented. It was concluded that for flue gas $\mathrm{H}_2\mathrm{SO}_4$ less than 5 ppm, the controlled condensation procedure was preferred to that of the IPA methodology.

Program: Stack Emissions from Fossil Fueled Combustion Sources

Sponsor: Environmental Protection Agency
Any voluntary or legislated action taken to control sulfates should be based at least in part on a thorough knowledge of the character of primary sulfates (i.e., H₂SO₄ and water soluble sulfate salts) and an understanding of the principal variables which govern the magnitude of those emissions.

A system comprising isokinetic flue gas sampling for particulate sulfate on an in situ quartz fiber filter assembly followed by controlled condensation for H₂SO₄ collection was used primarily at a high (2.5%) sulfur-content oil-fired power unit. Speciation during collection demonstrated that the ESP, depending on efficiency, reduced particulate sulfate generally by 50 to 90%.

Particulate sulfates at a low (0.3%) sulfur-content oil-fired unit decreased almost in proportion to the decrease in sulfur-content of the oil. Sulfuric acid concentrations were found to correlate well with excess furnace O₂ over the range investigated (0 to ~ 2% O₂). A good correlation was also found for particulate sulfate and H₂SO₄ at the ESP inlet, with an indication of sulfate formation controlled both in the flame region and the high temperature heat transfer region. Elemental and carbon analyses indicated the principal metals in the soluble fraction (Mg and V) nearly accounted for the total measured soluble sulfates. The insoluble fraction was composed primarily of MgO, V₂O₅ and carbon.

Program: Sulfate Formation in Oil-fired Power Plant Plumes

Sponsor: Electric Power Research Institute, Empire State Electric Energy Research Company and Long Island Lighting Company
Continuous and discrete sources of buoyancy are studied. Previous approaches are mentioned and the main ingredients of the problem are introduced. The motion of buoyant fluid bodies in isolation from their surroundings can be described using an intermittency function; this methodology parallels the conditional sampling techniques commonly utilized in experimental shear flow turbulence; the interaction between the isolated region and the surroundings explicitly enters the equations as mass, momentum and energy exchange due to both entrainment and molecular effects. The average conditioned partial differential equations for buoyant jets are then obtained; integration of these equations over a cross section of the jet yields the integrated ordinary differential equations of motion. A clear distinction between average local and global entrainment rates is established. Convergence problems in previous formulations are absent in the present one. A simple derivation of a generalized Rayleigh transport theorem or Leibnitz rule for nonmaterial volumes is presented, and specialized to the study of discrete instantaneous releases of buoyant fluids. The instantaneous dump of discrete masses of sulfuric acid into water is then investigated; the thermal field generated by the heat of dilution induces an upward buoyancy opposing the downward force due to concentration contrasts (double-diffusive turbulent convection). Taylor's simple entrainment assumption is utilized to study the blob evolution and predictions are compared with some preliminary available experiments.
A large spill of sulfuric acid in water is a likely possibility in marine accidents involving cargo vessels carrying large quantities of concentrated sulfuric acid and oleum. Although the consequences of such a spill accident could be detrimental to man and the environment, it is not possible at present to make a realistic assessment of the extent of damage because of the sparsity of data in existence. Moreover, the physical and chemical processes associated with a large spill appear to be very complicated, and no predictive method is presently available for use as guidance in setting up emergency response procedures in case of an accident.

As a prelude to a study of sulfuric acid release in maritime spill accidents under the sponsorship of the United States Coast Guard, the present report is prepared which contains mainly an extensive literature survey in the pertinent areas of fluid mechanics and aerosol dynamics. In addition, several spill scenarios are described to indicate the scope of the investigation. Two types of acid spills are considered: I, accidents in which no appreciable amount of acid aerosols is produced, and II, accidents in which the major safety hazards are associated with acid aerosol generation. Important parameters controlling the spill phenomena are delineated for subsequent laboratory measurements. A compilation of the sources of the physical and chemical properties of concentrated $\text{H}_2\text{SO}_4$ and oleums is also included.
MODELING HOMOGENEOUS OXIDATION OF ATMOSPHERIC SO\textsubscript{2} BY A SUROGATE CHEMICAL MECHANISM (SCHEME)

BNL 24383

S. Z. LEVINE and S. E. SCHWARTZ

Environmental Chemistry Division

The formulation of effective control strategies for atmospheric sulfur pollutants, in large part, upon the use of regional transport models to understand the complex processes of chemical transformation and transport of these pollutants. Such models will in turn require the incorporation of a kinetic mechanism describing the homogeneous gas-phase oxidation of SO\textsubscript{2}; however, the practical usefulness of the mechanism is limited to a minimum number of modeled species because of the computational burden involved in solving a large set of differential equations for a coupled diffusion-advection-reaction problem. To meet these computational constraints, we have developed a Surrogate CHEmical MEChanism (SCHEME) incorporating only 12 chemical species. This model has been developed using a more detailed ATMospheric MOdel for Sulfur (ATMOS) which incorporates 30 species and generalized hydrocarbon chemistry. SCHEME accurately reproduces the simulation results of ATMOS, but with a savings of \( \geq 80\% \) in execution time.

For a simulated six-hour irradiation \( (z = 40^\circ) \) these mechanisms predict an SO\textsubscript{2} oxidation rate of \( \sim 3\% \text{ hr}^{-1} \) which occurs principally by reaction with HO, HO\textsubscript{2} and RO\textsubscript{2} free-radicals. The relative contributions of these reactions to the total oxidation rate change markedly with time.

Program: Transport and Transformation Experiments (MAP3S)

Sponsor: Environmental Protection Agency
Homogeneous gas-phase reactions of pollutants in the troposphere, i.e., the formation of photochemical smog and the oxidation of \( \text{SO}_2 \), occur to a great extent by elementary reactions involving chain carrying free-radicals (HO, \( \text{HO}_2 \), RO, RO\(_2\), RCOO\(_2\) whose concentrations are governed by the concentrations of trace molecular constituents including \( \text{NO} \), \( \text{NO}_2 \), \( \text{CO} \), \( \text{O}_3 \) and organics, as well as sunlight. The reaction kinetics of such a multi-species, multi-reaction system is commonly modeled by a set of coupled ordinary nonlinear differential equations in the concentrations of the species, and such treatment has been rather successful in modeling these concentrations as measured in "smog chamber" experiments. However, for the purpose of modeling chemical transformations in the ambient atmosphere, which requires incorporating a reaction mechanism within an atmospheric transport model, it is necessary to develop a mechanism that includes a minimum number of chemical species, since the computational time and cost involved in solving the set of partial differential equations describing the diffusion-advection-reaction problem increases dramatically with the number of species modeled. In order to meet the time and cost constraints of an atmospheric transport model, we have constructed a 12-species Surrogate CHEmical MEchanism (SCHEME) incorporating reactions for the homogeneous gas-phase oxidation of \( \text{SO}_2 \). A preliminary but much more detailed and comprehensive ATmospheric Model for Sulfur (ATMOS) has been used to generate SCHEME and test its applicability to a broad range of chemical conditions. SCHEME accurately reproduces the results of ATMOS and does so with a 5-fold decrease in execution time. For all 12 species modeled by SCHEME, there is close agreement with the concentration profiles predicted by ATMOS, even when the initial concentrations of \( \text{NO}_x \), \( \text{SO}_2 \), or olefin are changed by an order of magnitude. Additionally, the kinetic relationships used in the construction of SCHEME may be used at little additional computational cost to algebraically determine concentration profiles for many of the deleted species.

Program: Transport and Transformation Experiments (MAP3S)

Sponsor: Environmental Protection Agency
The definitions of the residence times describing the removal of materials from natural reservoirs, i.e., the mean age, the mean transit time, and the turnover time, have been extended to encompass time-dependent rates of introduction and removal. This treatment leads to two sets of such residence times, the first based upon the time at which the material enters the reservoir, and the second based upon the material present in the reservoir at any given observation time. The former quantities are properties only of the rates of removal processes, whereas the latter reflect also the time dependence of the introduction of the material into the reservoir. Relationships are examined among the several residence times, as well as to the burden of material in the reservoir attributable to a given rate of introduction. Additionally, the several definitions are extended to encompass secondary materials, i.e., materials formed in situ as a consequence of reactions of materials directly introduced.

The above framework is applied to a consideration of the residence times and burdens of atmospheric SO$_2$ and sulfate aerosol, for assumed time-dependent rates of SO$_2$-to-sulfate conversion and dry deposition. It is found that even for such rates exhibiting strong diurnal modulation, as expected from considerations of photochemical reaction rates and atmospheric stability, the turnover times and atmospheric burdens of SO$_2$ and sulfate exhibit relatively little diurnal modulation, unless the fraction of SO$_2$ removed per day substantially exceeds 50%. These considerations suggest that it may be adequate for many purposes to model such processes according to their diurnal average rate coefficients.

Regarding secondary materials, one further useful quantity is the relative burden, or the ratio of the amounts of secondary to primary materials present in the reservoir. This quantity is directly comparable to ratio of the observed concentrations of these materials and thus serves as an additional condition that must be satisfied by models describing their transformation and removal.
THE USE OF WETLANDS FOR TREATING WASTES—WISDOM IN DIVERSITY?

BNL 24519

KAREN BLUMER

Land and Freshwater Environmental Sciences Group

Two artificial wetland systems consisting of linear configurations of a marsh-pond and a meadow-marsh-pond have been treating sewage in continuous operation for four years. Data from the past two and one-half years suggest that the trapping of nutrients may be increased by increasing the number of biotopes in the flow sequence.

For the entire system, the retention of phosphorus and nitrogen per unit area of wetland appears greater when a variety of eco-components are used in sequence than if only one type of system is used. By increasing the physical and biological barriers to nutrient movement, an increase in the number of habitats (and ecological niches) is achieved. This seems to be especially important when hydrologic flow alternates between drought and flood, and in a temperate climate with dramatic seasonal temperature differences.

The implication for the Kissimmee watershed, beset with the problems of high seasonal nutrient flushes, is that a management strategy which includes the intermittent use of diverse wetland ecosystems can be expected to achieve a greater degree of nutrient retention than a strategy which attempts to optimize a single type of ecosystem, for example, a marsh alone. Practical applications may include such simple measures as providing ponds to alternate with marsh wetlands, or designing wetlands with island meadows in appropriate sequences.

Program: Ecosystems Engineering

Sponsor: Rockefeller Foundation
The guarding of natural community diversity, more than being of deep concern to an ardent few, may provide a vital contribution in attempting to reduce pollution of natural systems through the use of wetlands. Preliminary data analysis from two Brookhaven wetland models operating continuously over the past four years suggest that increased diversity may be one of the major factors in the startling ability of certain wetland systems to retain high amounts of nutrients.

According to preliminary analysis of total phosphorus, increasing the number of biotopes, or ecocomponents, in a flow sequence will increase the ability of systems to take up and retain a greater amount of nutrients than would a continuous, single ecosystem of the same size. Although the reasons for increased efficiency by compartmentalization may be many—such as order, size of the component, tempering effect by the initial components, etc.—there is the suggestion based on Brookhaven models that biotope—and consequently biotic—diversity plays a great if not critical part. Practical applications to wetland management are offered.
AN AUTOMATIC SEQUENTIAL PRECIPITATION SAMPLER

BNL 24391

GILBERT S. RAYNOR and JOHN P. MC NEIL

Atmospheric Sciences Division

An automatic sequential precipitation sampler was designed and constructed at Brookhaven National Laboratory to collect precipitation samples for chemical analysis. The sampler is designed to collect both wet and frozen precipitation and to exclude dry fallout between precipitation events. The sampler consists of a large box containing a turntable holding 30 sampling bottles. Precipitation enters through a funnel on the top of the box. Between periods of precipitation the funnel is closed by a movable cover which is actuated by a rain sensor when precipitation starts. Sample bottles are changed automatically and periodically from the time the cover opens. Times of cover opening and closing and of bottle changing are recorded on an event recorder. The sampler has operated successfully since June 1976.

Program: Effects of Acid Rain on Terrestrial Ecosystems

Sponsor: Environmental Protection Agency
The acidification of freshwaters as a consequence of acid precipitation is a major environmental problem in several areas of North America and Scandinavia. Damages to aquatic flora and fauna are extensive, but our quantitative knowledge of the severity is not great. Perhaps of greatest interest is effects of acidification on aquatic processes such as primary production and decomposition. Data obtained from experimental operations in both natural and artificial stream channels indicate that algal productivity and removal are simultaneously inhibited by low pH.

Program:  Effects of Acid Rain on Terrestrial Ecosystems

Sponsor: Environmental Protection Agency
Experimental data demonstrate that foliar applied simulated acid rain of pH levels of 3.1 and below produced 1) leaf lesions, 2) decreased leaf expansion, 3) premature defoliation, 4) a decreased number and mass of pods per plant, a decreased number and mass of pods per plant in pinto bean. These production parameters are correlated with pH levels that produce 1) decreased rates of leaf expansion, 2) an increased percentage of leaf lesions, and 3) altered nutrient leaching rates of first trifoliate leaflets.
Relative rates of nutrient penetration, nutrient leaching and cell permeability of acid-rain-sensitive, first trifoliate leaves of Phaseolus vulgaris were examined. In buffer solutions, $^{35}\text{SO}_4^{2-}$ penetrated leaves faster at pH 2.7 than at 5.7. In contrast, $^{86}\text{Rb}^+$ pervaded faster at the higher pH, and $^3\text{H}_2\text{O}$ entered foliage at similar rates at all pH levels tested. When plants were exposed to simulated rains of various pH levels, calcium, nitrate and sulfate were preferentially leached from whole leaves by low pH, whereas potassium, ammonium and zinc were leached preferentially at pH 5.7 and 3.4 compared with 2.7 and 2.9. Isotope tests indicated that leaf cells were more permeable to $^{35}\text{SO}_4^{2-}$ and $^3\text{H}_2\text{O}$ at pH 2.7 than at higher pH levels, but were more permeable to $^{86}\text{Rb}^+$ at higher pH levels. These results suggest a wide diversity of leaf and cell permeability responses to various ions after exposure to acid rain. In general, an overall increased rate of nutrient leaching at more acidic levels was correlated with a lower adaxial leaf resistance during leaf development. This decrease in adaxial leaf resistance may allow gaseous pollutants to enter leaves more rapidly.
Microbial denitrification in acid and acidified soils was studied by measuring the rate of N$_2$O production. At neutral pH, the rate of denitrification was very rapid and N$_2$O was not detected after a few days, indicating further reduction to N$_2$. The rate of denitrification was rather slow in acid soils and, at greater acitudes, N$_2$O accumulated in the incubation vessel. The results suggest that N$_2$O can be generated from natural acid soils, such as forest soils, and from the acidified soils that result from acid rain.
IMPACTS OF ACID PRECIPITATION ON DECOMPOSITION AND PLANT COMMUNITIES IN LAKES

BNL 25066

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The production of fish or other animal life in a lake is ultimately dependent upon the availability of both allochthonous and autochthonous organic materials. Bacterial biomass derived from the decomposition of organic detritus is a major pathway by which these organic materials are transferred to higher trophic levels. Numerous studies indicate that microbial decomposition is severely reduced at pH levels encountered in lakes affected by acid precipitation. This results in an abnormal accumulation of coarse organic detritus on lake bottoms and an accelerated rate of sediment accumulation. An inhibition of the microbiota or a reduction in the formation of microbial biomass can have a direct impact on the animal communities of lakes and may effect the supply of food organisms for fish. In waters affected by acid precipitation, major changes occur within plant communities. In some acidified lakes macrophyte communities dominated by Lobelia and Isoetes have regressed, while Sphagnum has expanded as dense mats. Heavy growths of filamentous algae occur in many acidified lakes and streams. Experimental stream work indicates that such accumulations may be due to an inhibition of grazing invertebrates and reduced microbial decomposition, processes which contribute to the rate at which benthic algae may be removed. These problems are being addressed by the Adirondack Lakes Project (ALP), a cooperative research effort by several private, state and Federal research agencies. One goal of the ALP study is to provide a quantitative assessment of the effects of acidification on biotic processes.

Program: Effects of Acid Rain on Terrestrial Ecosystems

Sponsor: Environmental Protection Agency
Experiments were performed to measure the pH-sensitive steps in nodulation and symbiotic nitrogen fixation by *Pisum sativum* and isolate RP-212-1 of *Rhizobium leguminosarum*. An aeroponic system with rigorous pH control was used to obtain numerous effective nodules. After exposure to various pH levels, the following responses were measured: (1) legume root growth and development, (2) survival and growth rate of a single effective bacterial isolate, (3) degree of nodulation, (4) rate of nitrogen fixation, (5) plant biomass, and (6) nitrogen content of plants. Both bacterial growth and root development were adequate at all pH levels from 4.8 to 6.6, but efficient nodulation and nitrogen fixation did not occur at pH 4.8 and below. The processes required for symbiosis were about 80 times as sensitive to acidity as either bacterial growth or root growth alone. Nodulation was the most acid-sensitive step.
An Automatic Sequential Precipitation Sampler was designed and constructed at Brookhaven National Laboratory to collect precipitation samples for chemical analysis. The sampler is designed to collect both wet and frozen precipitation and to exclude dry fallout between precipitation events. The sampler consists of a large box containing a turntable holding thirty sampling bottles. Precipitation enters through a funnel on the top of the box. Between periods of precipitation, the funnel is closed by a movable cover which is actuated by a rain sensor when precipitation starts. Sample bottles are changed automatically and periodically from the time the cover opens. Times of cover opening and closing and of bottle changing are recorded on an event recorder. The sampler has operated successfully since June 1976.
Atmospheric Sciences Division

Hourly precipitation samples were collected at Brookhaven National Laboratory from June 1976 through May 1977 using an Automatic Sequential Precipitation Sampler. Conventional meteorological data were recorded for each sample period. The samples were analyzed for pH, conductivity and concentrations of sulfate, nitrate, ammonium, sodium, and chloride ions. Statistical analyses were performed of the relationships between selected chemical variables and between them and meteorological conditions. Results are presented in a series of tables.

Program: Effects of Acid Rain on Terrestrial Ecosystems

Sponsor: Environmental Protection Agency
SOME POTENTIAL EFFECTS OF ACID RAIN ON FOREST ECOSYSTEMS:
IMPLICATIONS OF A COMPUTER SIMULATION

BNL 50889

D. B. BOTKIN AND J. D. ABER

Land and Freshwater Environmental Sciences Group

Potential effects of acid precipitation on forest productivity and species composition were considered through the use of the JABOWA forest growth simulator. Physiological studies suggest that current levels of acid rain would result in a mortality of 5.5% or less of tree leaf tissue, depending on the species. Such reductions produce non-significant changes in the total productivity of the simulated forest. Significant changes in total productivity and relative species composition do occur at much higher levels of effects and are discussed. The simulations reported here consider only effects due to species interactions and direct impact on leaves; no changes and soil chemistry are assumed.

Program: Effects of Acid Rain on Terrestrial Ecosystems

Sponsor: Environmental Protection Agency
The EPA and the State Department sponsored a workshop (University of Minnesota, April 1978) on possible impacts of an 800-MW coal-fired power plant to be built near Atikokan, Ontario. It is feared that the emissions of SO₂ will lead to the deposition of sulfuric acid and result in the acidification of freshwaters in nearby parks and wilderness areas.

It appears that all trophic levels are affected by acidification. Reduced decomposition is evidenced by an unusual accumulation of coarse organic debris and plant remains in acidified waters. Field and laboratory experiments indicate that microbial activity is reduced and that the recycling of materials is greatly impeded at low pH. This may interfere with nutrient supplies to plants, and decrease the microbial biomass available to higher trophic levels.

Phytoplankton densities appear to decrease in acidified lakes and there is a reduction in some species of macrophytes. On the other hand, Sphagnum and benthic filamentous algae have been observed to greatly increase in some cases. Total primary productivity of lakes and streams may actually increase because of such dense growths on the bottom.

Zooplankton and benthic invertebrate communities become less complex as acidity increases. This may in part be due to reduced food supplies (bacteria, phytoplankton), but direct inhibition by H₂SO₄ has also been demonstrated. This removal of fish food organisms may exacerbate damage to fisheries, especially in the pH range of 5 to 6. When a lake loses all fish because of low pH, a few species of invertebrates may become very abundant.

Salamanders sensitive to acidity are being eliminated from small ponds or temporary pools in the region around Ithaca, N.Y. Species of frogs in some lakes are also being eliminated. These are important predators on invertebrate pests and are themselves prey for higher trophic levels. A listing of step functions for damages caused by decreasing pH is provided.

Program: Effects of Acid Rain on Terrestrial Ecosystems

Sponsor: Environmental Protection Agency
ELUTION EFFICIENCY OF BEEF EXTRACT FOR THE RECOVERY OF POLIOVIRUS FROM WASTEWATER EFFLUENTS

BNL 24355

EDWARD F. LANDRY, JAMES M. VAUGHN, MC HARRELL Z. THOMAS and THOMAS I. VICALE

Land and Freshwater Environmental Sciences Group

The efficiency of poliovirus elution from fiberglass cartridge (K27), epoxy-fiber glass-asbestos filters (M780), and pleated cartridge filters was assessed using 3% beef extract (pH 9.0) or 0.1 M glycine (pH 11.5). Poliovirus type I, strain LSc, was seeded into 20-25 gallon samples of treated sewage effluent and concentrated using a filter adsorption-elution technique. Virus elution was accomplished by using either two 660-ml aliquots of 3% beef extract (pH 9.0), or two-1 l aliquots of 0.1 M glycine (pH 11.5). In all experiments, beef extract was found to be the superior eluant, yielding a mean recovery efficiency of 85%, with recoveries ranging from 68 to 100%. Elution with 0.1 M glycine (pH 11.5) resulted in a mean recovery efficiency of 36%. The variable range of recoveries with beef extract could not be significantly improved by varying the type of beef extract or by extending the elution time to 30 minutes.

Second-step reconcentration of 1 liter seeded sewage effluent and renovated wastewater samples indicated that organic flocculation was a more efficient method for virus recovery than inorganic flocculation. Beef extract concentrations of less than 3% were found to be efficient in the recovery of poliovirus from renovated wastewater.

Program: Fate of Human Viruses in Groundwater Recharge Systems

Sponsor: Environmental Protection Agency
THE 1978 BREEDING BIRD CENSUSES

BNL 50933

GILBERT S. RAYNOR

Atmospheric Sciences Division

As part of a program to characterize the plant and animal life of the Laboratory site and surrounding areas, the two breeding-bird censuses taken in 1977 were repeated in 1978. Five observers made thirteen census trips to both the BNL and Westhampton plots. A decrease in rufous-sided Towhees occurred on both plots but other changes were small and not considered significant.

Program: National Environmental Research Park

Sponsor: DOE, Office of Health and Environmental Research
A SURVEY OF HUMAN VIRUS OCCURRENCE IN WASTEWATER RECHARGED GROUNDWATER
ON LONG ISLAND

BNL 23874

J. M. VAUGHN, E. F. LANDRY, L. J. BARANOSKY, C. A. BECKWITH, M. C. DAHL
and N. C. DELIHAS

Land and Freshwater Environmental Sciences Group

Treated wastewater effluents and groundwater observation wells from three
sewage recharge installations located on Long Island were assayed on a
monthly basis for indigenous human enteroviruses and coliform bacteria for
a period of one year. Viruses were detected in groundwater at sites where
recharge basins were located less than thirty-five feet above the aquifer.
Results from one of the sites indicated the horizontal transfer of viable
viruses through the groundwater aquifer.

Program: Section 208, Federal Water Pollution Control Act

Sponsor: Nassau-Suffolk Regional Planning Board
A SURVEY OF HUMAN ENTEROVIRUS OCCURRENCE IN FRESH AND MARINE SURFACE WATERS ON LONG ISLAND

BNL 24088

J. M. VAUGHN, E. F. LANDRY, M. Z. THOMAS, T. J. VICALE and W. F. PENELLO

Land and Freshwater Environmental Sciences Group

A variety of surface water systems including a lake, a creek and two marine embayments, were analyzed on a monthly basis for indigenous human enteroviruses and coliform bacteria. Findings are discussed in terms of the probable pollution sources to each system and their relationship to data from previous studies.

Program: Section 205, Federal Water Pollution Control Act

Sponsor: Nassau-Suffolk Regional Planning Board
THE OCCURRENCE OF HUMAN ENTEROVIRUSES IN A GROUNDWATER AQUIFER RECHARGED WITH TERTIARY WASTEWATER EFLLUENTS

BNL 24431

J. M. VAUGHN and E. F. LANDRY

Land and Freshwater Environmental Sciences

A two-year study of the impact of human viruses on a tertiary treatment-groundwater recharged system located on Long Island is currently nearing completion. Raw influents, chlorinated tertiary effluents and groundwater from beneath a uniquely designed recharge basin were assayed on a weekly basis for the presence of indigenous human enteroviruses and coliform bacteria. While high concentrations of viruses were routinely isolated from sewage influents, the chlorinated tertiary effluents were positive for virus in only 3 of 20 samples. In spite of the high quality effluent being recharged, viruses were detected in the groundwater aquifer on several occasions indicating their ability to percolate through the recharge basin. This finding was confirmed by the results of two poliovirus seeding experiments carried out at the field installation. At both high (75-100 cm/hr) and low (6 cm/hr) infiltration rates seeded polioviruses were detected at all sampling levels as well as in the groundwater aquifer, 7.62 m below the recharge basin. It would appear that lower infiltration rates promote better virus removal in the specific type of soil used in this study.

Program: Section 208, Federal Water Pollution Control Act

Sponsor: Nassau-Suffolk Regional Planning Board
Land and Freshwater Environmental Sciences Group

A limited virus survey was conducted in Arthur Kill at the request of the New York State Power Authority. The purpose of the study was to provide background information on ambient human enteric virus occurrence in the waters of the Kill. The survey was part of a larger program designed to determine the likely public health and environmental hazards which would result from the use of Kill water for power plant coolant.

Human viruses were routinely isolated from the two sampling stations under study. Virus concentrations did not exceed 6.7 virus pfu/gal in any of the samples. Among isolates identified from sample material were various poliovirus, coxsackievirus and ECHOvirus serotypes.

PROGRAM: Viral Analysis in Arthur Kill

SPONSOR: Equitable Environmental Health, Inc.
SOME PHYSICAL PROCESSES AFFECTING THE DISTRIBUTION OF PRIMARY PRODUCTION IN THE NEW YORK BIGHT

BNL 24176

T. S. HOPKINS and J. J. WALSH

Oceanographic Sciences Division

The spatial distribution of chlorophyll in the waters of the New York Bight changes its characteristic length scale conformation from late winter to early fall. Accompanying these changes are successions in the dominant phytoplankton type and in the characteristic physical processes. The phytoplankton are represented by fast growing diatoms in March that are distributed in an along-shore chlorophyll maximum located inshore of the shelf-slope front or approximately over the 80 m isobath. In May, dinoflagellates dominate the phytoplankton composition and are distributed in shelf-wide patches of 10-50 km length scale. Normally during summer, the phytoplankton biomass consists of nanoplankton located in a nearshore band. However, under certain summer conditions, as for example in 1966, 1968, 1974 and 1976, the phytoplankton biomass is in a shallow band of ceratium located in the thermocline at about the 1-5% light level.

The causal physical processes accompanying these phytoplankton distributions are summarized. The relative importance of advection is discussed specifically and for the case of the May distribution it is shown that the field patchiness is sustained by significant interaction between the characteristic growth rate and the characteristic velocity field.

Program: Coastal Transport and Diffusion

Sponsor: DOE, Office of Health and Environmental Research
The thermohaline dynamics of the Gulf of Maine are analyzed from the two year, eight cruise, data set of Colton, Marak, Nickerson and Stoddard, 1968. Six water masses are described: the Maine Surface Water, Maine Intermediate Water, and the Maine Bottom Water as interior water masses; and the Scotian Shelf Water, the Slope Water, and the Georges Bank Water as exterior water masses. Particular attention is given to the formation and disposition of the Maine Intermediate Water. Salt balance, T-S volume, and T-S drift analyses are used to provide transport and mixing estimates for the year 1966. The Slope Water entered at depth through the Northeast Channel at a rate of 2600 km$^3$/yr; while the Scotian Shelf Water entered the surface and intermediate layers, mostly during winter intrusions, at a rate of 5200 km$^3$/yr in a 3:7 ratio, respectively. The Maine Intermediate Water tends to collect over the Wilkinson Basin during the stratified season to exit via the Great South Channel during early spring and summer. Comparisons are made between the estimated winter heat loss of 280 Ly/d and the observed heat losses of 230 Ly/d (surface layer) and 260 Ly/d (surface and intermediate layers). An upper bound for the Scotian Shelf Water contribution is 70 Ly/d. It is concluded that the Maine Intermediate Water is produced locally and that it is exported in significant quantities.
An instrumented, semi-rigid, spar buoy was moored in the nearshore region off Shinnecock, Long Island, in October 1976. The mooring had four sensor packages at distributed depths recording velocity, conductivity, and temperature over hourly intervals. The averaged data was radioed to the Brookhaven National Laboratory. The operating period extended for 41 days.

The results of the velocity and temperature sensors are presented in this report as: 1) time series, 2) daily mean velocity vectors, 3) progressive vector diagrams, and 4) histograms of speed and direction. The instrumentation is described and a discussion of error is presented.
The biomass and ammonium and urea release rates of zooplankton and fish were measured in the coastal upwelling ecosystem off northwest Africa. Zooplankton of 102 to 505 μm in size dominated the biomass nearshore, while zooplankton larger than 1000 μm were the major component offshore. Fish populations were estimated to have a biomass of about 40–60 g wet weight m⁻² over the shelf and sometimes slightly larger at the shelf break. The zooplankton and fish supplied at an average of 44 and 27% of the ammonium demand of the phytoplankton and an average of 25 and 14% of the total nitrogen required by the phytoplankton. This upwelling area is unusual among eutrophic systems that have been studied as having such a large percentage of the nitrogen necessary for primary production supplied as ammonium by zooplankton and fish.
A SIMULATION STUDY OF BIOLOGICAL RESPONSES TO ENVIRONMENTAL CHANGES
ASSOCIATED WITH COASTAL UPWELLING OFF NORTHWEST AFRICA

BNL 24204

STEVEN O. HOWE

Oceanographic Sciences Division

A time dependent, two-dimensional model of upwelling and its effects on
nutrient and phytoplankton fields off northwest Africa is described. Changes
in phytoplankton cell numbers, particulate carbon, nitrogen, chlorophyll and
silica are simulated as a function of concentrations of nitrate, ammonium
and silicate, and intensity of photosynthetically active radiation. Grazing
losses occur to one species of herbivorous fish and two size classes of zoo-
 plankton. Results from simulation experiments show a flux of nutrient-rich
water into the euphotic zone supporting high rates of primary production
seaward of a turbid nearshore region. High ammonium concentrations, occurring
in the nearshore region, are shown to be sensitive to physical circula-
tion processes and phytoplankton uptake rates. Simulated rates of primary
production may exceed the observed rates and the losses attributed to physio-
logical mortality and ingestion by herbivores. An underestimate of the sig-
nificance of grazing related to the vertical distribution and feeding behavior
of the zooplankton is tentatively identified as the factor responsible for
the discrepancy between observed and simulated results.

Program: Coastal Upwelling Ecosystem Analysis (CUEA)

Sponsor: International Decade of Ocean Exploration/National Science Foundation
Larval survival of individual anchovy is better off the northern coast of Peru during the austral winter season when a motile algal food supply is available. Concentrations of the dinoflagellate food of the first feeding anchovy larvae appear to be reduced less often by wind events in the north than in the south. Under \textit{El Niño} conditions, more of the adult anchovy are found south within a less favorable spawning habitat, in terms of dilution and food quality, where there is evidently less larval survival and subsequent recruitment to adult stocks. Latitudinal excursions of larval clupeid distribution off California have also been associated with warm water anomalies. Moreover, the change in organic loading off Peru in response to such phenomena can be detected with chemical tracers such as nitrite. Monthly transients of oxygen demand appear to be related to removal of grazing stress at \textit{El Niño} scale of variability. A longer interannual trend of increased oxygen demand also appears to be associated with an increase in \textit{zooplankton} biomass and a decline of the Peru anchovy fishery. The sardine species of the clupeid pair off Peru may be increasing in number, with the implication that natural oscillations of clupeid populations may be accelerated by overfishing.
VERTICAL DISTRIBUTION OF ZOOPLANKTON IN RELATION TO AN OXYGEN MINIMUM OFF PERU

BNL 24549

DAVID C. JUDKINS

Oceanographic Sciences Division

In March 1977 a high yield pump was used to collect zooplankton at discrete depths to 85 m at three stations located 10, 25 and 110 km off the Peruvian coast (~15°S). Vertical profiles of dissolved O₂ obtained by bottle casts revealed a minimum layer (O₂ concentrations ≤ 0.1 ml/liter) which approached within 25-35 m of the surface at 10 km and within 50-65 m at 25 km. At 110 km, O₂ values exceeded 1.0 ml/liter throughout the upper 85 m. Vertical abundance patterns in zooplankton corresponded closely to the O₂ profiles. Most zooplankters (including the dominant copepods Oithona plumifera, Oncaea sp. Paracalanus parvus, Centropages brachiatus, Calanus chilensis, and Acartia tonsa) were restricted to the oxygenated waters above the minimum at the 10 and 25 km sites, as opposed to the situation at the 110 km location where they tended to be more broadly distributed throughout the upper 85 m. Although most species were virtually absent from waters with O₂ values ≤ 0.1 ml/liter, the vertical ranges of a few forms (e.g., polychaete larvae and Eucalanus attenuatus) extended well into the minimum.

Program: Coastal Upwelling Ecosystems Analysis (CUEA)

Sponsor: International Decade of Ocean Exploration/National Science Foundation
An in situ fluorometer was moored at 10 meters for two time periods in August and September 1977 in the New York Bight for a total of 21 days. The mooring consisted of a battery pack which acted as an anchor, PVC spars, in situ data processor, FM radio telemetry system and fluorometer. A second mooring containing current meters, salinographs and thermistors was moored in close proximity. The data were telemetered at 20 minute intervals to a shore-based computer for real time display and storage. The fluorometer data records show good correspondence with shipboard measurements of fluorescence determined with an in situ profiling fluorometer and chlorophyll pumping system. The range of fluorescent variation observed over the two sampling periods of 10 and 11 days was equivalent to about 3 μg chlorophyll a liter⁻¹. Increases in the fluorescence observed over a period of 3 or 4 days were probably related to increases in chlorophyll a concentration, while the high frequency changes were probably caused by tides. Spectra of the data show dominant peaks at the semidiurnal tidal frequency. Differences between the fluorescence and the temperature-salinity spectra are probably related to biological activity rather than advection.

Program: Food Chain Dynamics

Sponsor: DOE, Office of Health and Environmental Research
The ingestion of a calanoid copepod, Centropages typicus, feeding in natural seawater has been measured with a Coulter Counter and compared with laboratory derived rates using monospecific algal cultures as food. The laboratory- and field-derived relationships between particle concentrations and ingestion rate are similar, but only on rare occasions were natural particle concentrations sufficiently high to allow attainment of a maximum daily ration. On two occasions ingestion rates were also estimated from measurements of gut fluorescence in freshly captured C. typicus. This method suggested higher intake rates of phytoplankton than were found with the Coulter Counter method but rates were still lower than the maximum possible rates. Some technical difficulties probably reside in each method, but both approaches appear to illustrate that C. typicus does not usually obtain a maximum daily ration from the phytoplankton. However, estimates of food requirements from egg production rates of C. typicus show that the measured ingestion rates account for only 1/3 to 2/3 of the food required, suggesting that a major portion of the daily diet comes from carnivory and that obtaining a maximum daily ration may not be a rare event.
Centropages typicus and Pseudocalanus sp. are the two predominant copepods in the continental shelf waters immediately south of Long Island, New York. The estimated in situ rate of egg production for C. typicus ranged from 5 to 230 eggs female$^{-1}$ day$^{-1}$ during this study. Variability was partly attributed to seasonality in water temperature and partly to seasonality in the physiological condition of individual females. It could not be shown that the egg production capability varied seasonally due to food related factors. Egg production by Pseudocalanus sp. probably is from 1 to 10 eggs female$^{-1}$ day$^{-1}$. The two reproductive strategies result in average abundances of adults that are approximately the same, although peaks occur at different times of the year, indicating that C. typicus has a higher mortality between the egg and adult stages than Pseudocalanus sp.
Zooplankton taxa were counted in 8 to 19 samples from each of 11 cruises in the New York Bight between September 1974 and September 1975. Major seasonal events were an influx into the region of tropical-subtropical copepod species during autumn 1974 and summer 1975, an offshore (> 50 m water depth) zooplankton abundance maximum dominated by the pteropod Limacina retroversa, a second offshore maximum in May dominated by the copepods Pseudocalanus sp., Calanus finmarchicus, and Oithona similis, and an onshore (< 50 m water depth) maximum in July dominated by the copepods Centropages typicus and Temora longicornis. The offshore maxima occurred during or shortly after the local spring phytoplankton bloom (March-April). Advection of pteropod and copepod stocks into the region from the northeast probably contributed to these peaks. The July C. typicus-T. longicornis peak was associated with summer warming of the water column within the highly productive waters in the Bight apex and off the New Jersey coast. Comparison of our results with a study conducted in 1959-1960 shows that the copepod fauna was dominated by essentially the same species during the two periods.
The utilization of NH$_4$ and NO$_3$ by natural phytoplankton communities were determined in the New York Bight during a spring bloom dominated by Ceratium tripos. Higher percent dark uptake rates of NH$_4$ and less light-dependent uptake rates of NH$_4$ and NO$_3$ characterized the inshore C. tripos communities. The ambient NH$_4$ concentration was higher at the shelf break and this was reflected in a greater percent dependence on NH$_4$ for primary production there (70%) than that observed inshore (59%). The higher ambient NH$_4$ concentration at the shelf break corresponded to a greater zooplankton biomass (~8 times) than that found inshore. Ammonium regeneration from zooplankton at the shelf break accounted for ~62% of the regenerated production (i.e., based on NH$_4$) while inshore, regenerated NH$_4$ from zooplankton, benthos and bacterioplankton accounted for 38 to 53% of the phytoplankton requirements.
The size and number of photosynthetic units were determined as a function of light intensity in two marine phytoplankton: Skeletonema costatum, a diatom, and Dunaliella tertiolecta, a chlorophyte. In the diatom, light-shade adaptation is characterized by changes in the size, but not the number of photosynthetic units, while in D. tertiolecta, primarily the number, but not the photosynthetic unit size is altered. Both strategies appear to be effective in harvesting and transferring light energy to photosynthetic reaction centers; however, the Dunaliella strategy appears to be more effective at high light intensities. Apparently these strategies represent an evolutionary divergence in photosynthetic adaptation.
CHLOROPHYLL TURNOVER IN *SKELETONEMA COSTATUM*, A MARINE PLANKTON DIATOM

BNL 25376

PAUL G. FALKOWSKI

Oceanographic Sciences Division

$^3$H- and $^{14}$C-5-aminolevulinic acid were incorporated into the chlorophylls of *Skeletonema costatum*, a marine plankton diatom. In the stationary phase of growth, the tetrapyrrole-based pigments reached steady-state labeling after 10 hours. Under conditions of exponential cell division and chlorophyll accumulation, $^3$H was rapidly lost from the labeled chlorophylls and was replaced with $^{14}$C derived from 4-$^{14}$C-5 aminolevulinic acid. The kinetics of isotope dilution suggest recycling of tetrapyrrole precursors and/or two pigment pools, containing both chlorophyll $a$ and chlorophyllide $c$, one which turns over rapidly (10 hours) and another which turns over more slowly (100 hours). Turnover times varied from 3 to 10 hours for chlorophyll $a$ and from 8 to 26 hours for chlorophyllide $c$. The data suggest the dynamics of chlorophyll metabolism in *S. costatum* and explain the diatom's ability to undergo light-shade adaptation within a generation time.
The Middle Atlantic Continental Shelf (MACS), surrounded by a region of high population density and energy use, may potentially be affected by the development of natural energy resources on the shelf itself or within the region and the location of energy facilities upon or adjacent to the shelf. A goal of the ERDA research program in this region is to optimize energy development while minimizing deleterious environmental effects.

The aim of this meeting was to bring the ERDA-MACS region contractors together for mutual enlightenment on the ongoing research programs and to plan future actions in light of ERDA's interests. This report grew out of the deliberations within the three workshop groups set up to accomplish this latter goal. We first deal with the assessment of the principal stresses and how they may be transferred in the ecosystem or to man. Next, contractor capabilities and research facilities are summarized. This is followed by a statement on the potential for multi-group or multi-agency research coordination. The Appendix contains research summaries from the present contractors.
The second annual meeting of DOE, Oceanographic Contractors in the Mid-Atlantic Coastal Region was held at the Brookhaven National Laboratory on 7-8 March 1978. The purposes of this meeting were to provide a forum for information exchange among contractors and agency representatives and to plan for effective coordination of the various programs. The meeting included a series of statements of individual contractors' recent accomplishments and future plans plus statements by representatives of DOE and several other agencies as to agency goals, priorities and research interests. This report consists of research summaries submitted by the individual contractors.

Program: Northeast Oceanography Coordination

Sponsor: DOE, Office of Health and Environmental Research
Fractionation of the stable carbon isotopes, $^{13}$C and $^{12}$C, was measured in thirteen species of marine phytoplankton representing major phylogenetic divisions. $\delta^{13}$C values range from -5.5 to -29.7 $\%\text{o}$ and unlike in terrestrial plants do not cluster into two major groups. The variations in $\delta^{13}$C values do not appear to be primarily related to variations in temperature, pH, carbon availability, or chemical composition. It is suggested that the wide range is most readily explained by multiple paths of carbon fixation in marine unicellular algae. The path of carbon in photosynthesis appears to depend, to some extent, upon environmental conditions.
Several lobster pounds and adjacent areas in Southern Nova Scotia were examined for the occurrence and distribution of chitinoclastic bacteria from June 1973 to May 1974.

During the year, the chitin digesting population ranged $10^0 - 10^3$ bacteria/ml in the water samples, while in the bottom mud, the counts varied from $10^0 - 10^7$ bacteria/g. The incidence of chitinoclastic bacteria followed the seasonal temperature curve with maximum values being recorded during the summer and fall at all stations. Chitinoclastic bacteria constituted 0-10% of the total heterotrophic population, but increased occasionally to 50-100% in the summer. The low densities of chitinoclasts encountered in the pounds during the fishery season suggest that the microbial contribution from lobsters to the pounds is negligible.

Program: Primary Production and Utilization

Sponsor: DOE, Office of Health and Environmental Research
The hydrographic, particle size, and microbiological data from the Atlantic Coastal Experiment I R/V Knorr Cruise held 24-30 January 1975 are given in this report. The observations, methods of collection, and methods of measurement are described. This cruise was designed to provide biological and physical measurements to help define continental shelf process in the New York Bight area.
This report contains the tabulated hydrographic, productivity and zooplankton data from the Atlantic Coastal Experiment I R/V Atlantis II cruise of 26 March - 9 April 1975. This cruise was designed to compile a nitrogen budget for the spring bloom in the New York Bight with preliminary identification of the importance of different nitrogen sources in relation to the event and diel time scales of variability on the continental shelf. The various observations made, method of collection and analyses are described.
STUDIES OF δ-AMINOLEVULINIC ACID DEHYDRASE FROM SKELETONEMA COSTATUM, A MARINE PLANKTON DIATOM

BNL 24490

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Oceanographic Sciences Division

The accumulation of δ-aminolevulinic acid and activities of δ-aminolevulinic acid dehydrase were examined in the marine diatom, Skeletonema costatum, grown in the presence of levulinic acid. Levulinic acid concentrations greater than 10 mM affect growth, morphology, and inhibit chlorophyll synthesis. The algae recover from the effects of levulinic acid after 48 h of exposure. The recovery is characterized by increased cellular chlorophyll content, decreased δ-aminolevulinic acid accumulation, decreased 3-(3,4-dichlorophenyl)-1,1-dimethyl urea-enhanced in vivo fluorescence, and the induction of a levulinic acid-activated δ-aminolevulinic acid dehydrase which does not follow Michaelis-Menten kinetics. The data indicate that levulinic acid blocks may be ineffective in vivo, and that δ-aminolevulinic acid is metabolized to amino and dicarboxylic acids. δ-aminolevulinic acid dehydrase activities are used to estimate the capacity for chlorophyll synthesis. Results suggest this diatom may be capable of rapid chlorophyll turnover, allowing the plant to light-shade adapt on the time scales appropriate to vertical mixing rates in the sea.

Program: Primary Production and Utilization

Sponsor: DOE, Office of Health and Environmental Research
Using two indices of chlorophyll synthesis (δ-aminolevulinic acid dehydrase activity and the incorporation of 4-14C aminolevulinic acid into chlorophyll a), turnover times for the photosynthetic pigment are estimated at 5-20 h in a marine diatom. Further, our analysis of chlorophyll a:P700 ratios suggest that the size, but not the number, of the photosynthetic units is changing as a function of light intensity. The chlorophyll turnover time is comparable to the excursion time of phytoplankton from the base of the euphotic zone to the surface in winter months. In conjunction with these laboratory data, field data indicate that in the winter, vertical mixing processes strongly dampen the effects of light adaptation and production is statistically equivalent throughout the euphotic zone. In the summer, however, primary production is markedly influenced by water structure, and light-shade adaptation is a means by which this can be investigated. These data are discussed in relation to general models of primary production.
The uptake and mineralization of dissolved free amino acids by the microbial communities in waters south of Long Island during September 1976 were investigated using a $^{14}$C-labeled algal protein hydrolysate. Concentrations of dissolved primary amines ranged from <100 to 700 n mol liter$^{-1}$. The overall mean rate of amino acid total uptake (net uptake plus carbon mineralization) was 4.8 n mol liter$^{-1}$ h$^{-1}$ were observed in surface waters in the apex of the New York Bight and associated with chlorophyll maxima in waters near the Long Island South Shore. The amino acid total uptake rate in the top 30 m was approximately equal to the estimated sum of phytoplankton and zooplankton amino acid release rates. Positive correlations were observed between several parameters, including amino acid uptake rate, chlorophyll $a$, direct counts of bacteria and concentrations of dissolved primary amines. A mean of 14.4% of the substrate taken up by the plankton was mineralized to CO$_2$. Size fractionation experiments indicated that organisms of bacterial size were responsible for most of the amino acid uptake. Amino acid carbon mineralization and estimated bacterial secondary production in surface waters averaged about 1.6% and 16%, respectively, of particulate primary production. It was estimated that approximately 2.5% of phytoplankton nitrogen demand might be satisfied by heterotrophic mineralization of dissolved free amino acids under these conditions.