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FOREWORD

A comparison of this document with previous reports of this series will reveal some substantial changes in the research performed by this Section. There have been several projects in which scientific work has evolved, creating the bases for exciting new programs. For example, the Section's work on micrometeorology was initially in support of planetary boundary layer modeling studies. In recent years, the techniques that were developed have been extended to include air pollutants, and we are now closely identified with work on the dry deposition of airborne particles and trace gases. In this area of research, three separate programs can be identified. Under EPA sponsorship, we are developing methods for parameterizing the dry deposition of acid aerosol for the MAP3S program. In a second EPA program, we are conducting field experiments to investigate the physical, chemical and biological factors that control dry deposition rates to natural surfaces. Under DOE sponsorship, we are conducting field experiments concentrating on the deposition of trace gases and particles to open water surfaces.

Similarly, our early activities in numerical modeling of transport and dispersion in the planetary boundary layer have branched into several distinct directions. The Section's Advanced Statistical Trajectory Regional Air Pollution (ASTRAP) model is an upgraded version of the STRAP model developed in the MAP3S program while MAP3S was supported by DOE. Under EPA sponsorship, ASTRAP is now being applied in regional-scale assessment studies for EPA, DOE, and the National Commission on Air Quality. While ASTRAP is being modified for investigation of regional nitrate pollution and deposition, separate modeling activities are addressing problems of pollutant behavior in clouds and in topographically complicated regions. DOE is sponsoring independent programs under its Atmospheric Studies of Complex Terrain (ASCOT) program and its multilaboratory diesel emission research program.

The breadth of current research activities is much greater than is indicated by the reports included here. As in previous years, the emphasis is on summarizing work currently in progress. For more complete accounts

of our work, the reader should refer to the open-literature publications of this Section.

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CORRECTIONS TO EDDY-CORRELATION MEASUREMENTS OF SMALL VERTICAL FLUXES IN THE ATMOSPHERIC SURFACE LAYER

M. L. Wesely

Small air-surface exchanges of trace materials can have an important effect on concentrations found in the atmosphere, especially if other removal mechanisms are severely limited. For example, concentrations of fine particles found in arid regions with very limited wet deposition might be strongly affected by dry deposition rates even if rather small. Gases such as ozone and carbon dioxide that are relatively unreactive in water have small vertical transport rates across the air-sea interface, but undoubtedly are significant in the total exchange between the atmosphere and oceans because of the vast areas considered.

In experimental field studies of air-surface exchanges, eddy-correlation techniques are often employed. The vertical flux can be calculated precisely as

$$F_c = \overline{(\rho w) 'c' } , \quad (1)$$

where ρ is air density, w is vertical wind speed, c is the mass mixing ratio, the overbar indicates a mean value, and primes indicate deviation from the mean. In practice w is usually measured rather than (ρw) , and the concentration (ρc) rather than c . Thus density variations are potentially important in evaluating the accuracy of Eq. (1). Another consideration is that mass transfer at the air-solid or air-liquid interface can cause a nonzero value of $\bar{w}$ whereas a zero value is normally assumed.

The methods of Bakan (1978), Jones and Smith (1978), and Webb et al. (1980) can be modified to evaluate the major inaccuracies found in eddy-correlation estimates. The inaccuracies are primarily caused by effects associated with the vertical fluxes of water vapor and sensible heat. These effects can be expressed in terms of a mean vertical velocity $\bar{w}$, which remains nonzero after standard eddy-correlation techniques of filtering or statistical calculations have been applied. The result is a modified equation for the

vertical flux of a trace quantity:

$$F_c = \overline{w'(\rho c)'} + \bar{w} (\bar{\rho c}) . \quad (2)$$

Expressions for $\bar{w}$ can be derived on the basis of the equation of state, Dalton's law of partial pressures and the equation of continuity for mean flow of a compressible gas over a flat surface in steady-state, homogeneous conditions. From analysis of density fluctuations due to temperature and water vapor fluctuations two terms, v_{dT} and v_{dv} , can be found to contribute to $\bar{w}$ in an additive fashion (pressure fluctuations are ignored). Another term, v_S , represents Stefan flow due to mass flow associated with evaporation or condensation of water at the surface. The expression for v_S arises from two primary assumptions, that pressure in the system is constant and that the flux of dry air at the surface is zero (although possibly nonzero aloft). Hence, $\bar{w}$ is simply

$$\bar{w} = v_{dT} + v_{dv} + v_S . \quad (3)$$

Since both the unadjusted deposition velocity, estimated as $\overline{-w'(\rho c)'}/(\bar{\rho c})$, and $\bar{w}$ are multiplied by $(\bar{\rho c})$ in order to compute components of F_c , the terms $-v_{dT}$, $-v_{dv}$, and $-v_S$ can be treated as simple additive corrections to the unadjusted deposition velocity.

Calculations show that for every 100 W m^{-2} of upward sensible heat flux, v_{dT} is increased by 0.3285 cm s^{-1} and, for every 100 W m^{-2} of upward latent heat flux, v_{dv} is increased by about 0.002 and v_S by about 0.005 cm s^{-1} . Thus, when magnitudes of deposition velocity are on the order of 0.1 cm s^{-1} or less, the effects represented by these three terms on the estimates of deposition made with the present scheme of measurement can be significant.

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TRANSPORT OF GAS AND HEAT THROUGH AIR-WATER INTERFACIAL SUBLAYERS IN THE FIELD

M. L. Wesely

At the bottom of the atmosphere, surface elements slow the wind and reduce mixing to the extent that molecular rather than turbulent diffusion tends to control vertical transport of gas and heat. The properties of the sublayers of air in this region are closely coupled to the rate of turbulent mixing aloft, but may also be changed greatly by the physical properties of the surface. Similarly, a sublayer or skin of water with limited vertical mixing exists immediately below the air-water interface. Currently, formulations intended to describe the transport of gas and heat through the sublayers are controversial. Subjects requiring further work include the interrelated effects of wind speed and surface roughness and the quantitative role of molecular diffusivity in affecting vertical transport. If these matters can be resolved, a better understanding of the air-water exchange of trace gases important in environmental studies can be achieved. Here, chemical reactions are not considered; only gases such as ozone and carbon dioxide that react very slowly with water are addressed.

If the total heat transfer through the skin of water and the corresponding temperature drop are known, the bulk transfer processes can be investigated quantitatively. Measurements of heat fluxes and temperature differences obtained experimentally in earlier studies at the Dresden cooling pond (Wesely, 1979) are analyzed here within the framework of surface renewal theory (Brutsaert, 1975; Liu et al., 1979). The values of $SPr^{-\frac{1}{2}}$ are compared with the model results and data of Liu et al. (1979) in Figure 1. The term S is an inverse transfer coefficient equal to the temperature drop across the skin divided by the temperature scaling parameter T_* , Pr is the Prandtl number and R is the surface Reynolds number. If S is not a function of R , then smooth flow can be assumed in deriving bulk parameterizations for the sublayer. This appears to be nearly the case.

FIG. 1.--Values of $SPr^{-1/2}$ measured for the aqueous sublayer at a cooling pond (dots) and compared to model results (solid line) and data (triangles) from Liu et al. (1979). The numerical value by each point is the number of contributing 10-min data-collection periods.

According to surface renewal theory, the solid line in Figure 1 should describe the transition region ($0.1 < R < 1.0$) between smooth and fully rough flow, although the discontinuity cannot be placed precisely. It is known that for data obtained in laboratory wind-water facilities, the surface renewal theory produces good results in the transition regions, except very near the discontinuity. However, the field data indicate that S is nearly constant; the appearance of smooth flow exists even though smooth flow does not apply in actuality.

The cause of the discrepancy between laboratory and field data might be related to the much greater variability in wind speeds in the atmospheric surface layer as compared to the laboratory simulations. Indeed, similar discrepancies for rougher surfaces are occasionally attributed to this effect.

Since $SPr^{-1/2}$ and R are nondimensional quantities, the relationship shown in Figure 1 can be applied to the interfacial sublayers of any two phase flows, provided that appropriate density and molecular diffusivities are selected. For application to nonreactive gases rather than heat, Pr should be replaced by the appropriate Schmidt number.

As an example, consider the case for ozone gas transfer through the water sublayer. If we assume smooth flow and apply the necessary numerical

values that can be derived from Figure 1, the resistance of the water sub-layer can be expressed as

$$r_s \approx 15 h Sc^{\frac{1}{2}} (\tau/\rho_w)^{\frac{1}{2}}, \quad (1)$$

where $Sc = \gamma/D$ is the Schmidt number with kinematic viscosity γ and diffusivity D , τ is surface stress, and ρ_w is water density. The factor $h = 4.17$ is Henry's law constant, used here in order to refer to the resistance to air concentrations and estimates of r_s found solely from atmospheric measurements. With the typical value of $u_* = (\tau/\rho_a)^{\frac{1}{2}} = 15 \text{ cm s}^{-1}$ (where ρ_a is air density) and temperatures near 20 C (which affects γ, D, ρ_w , and ρ_a), r_s is calculated to be about 3000 s cm^{-1} . This value is about 30 times larger than those found by field experiments (Wesely et al., 1980). Hence, surface chemical reactions apparently short-circuit this physical resistance and thus largely control the rate of ozone removal from the atmosphere above water.

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OZONE FLUXES MEASURED OVER SNOW, BARE WET SOIL, AND WATER

M. L. Wesely, D. R. Cook, and R. M. Williams

The dry deposition of atmospheric pollutants at the surface of the earth has a significant effect on concentrations found in the lower atmosphere. Removal of pollutants at the surface, in some cases, is the major means of cleansing the atmosphere, but then can be the major source of possibly harmful material for surface ecosystems. For both meteorological and ecological studies, it is important to understand the processes that control uptake rates, so that dry deposition rates can be computed if they cannot be measured directly. The turbulent mixing processes that transport the pollutants vertically in the atmospheric surface layer are often better understood than the relevant processes that take place at the solid or liquid side of the interfacial layers. The present effort extends work on determining the surface resistances to ozone uptake, in this case by nonvegetated surfaces.

Eddy-correlation measurements of the vertical flux of ozone, F_c , were obtained over snow, cold soil (Martinon silt loam) saturated with water, and the waters of Lake Michigan (see Table 1). Instrumentation described earlier (Wesely et al., 1978) was used with a fast-response ozone sensor employing chemiluminescent reaction with ethylene (Cook and Wesely, 1978). As described elsewhere (Wesely, 1980), adjustments to F_c were made when the flux was very small.

The deposition velocity v_d is determined as the ratio of $-F_c$ to the concentration at the height of measurement. Samples are half-hour averages, all obtained during daytime except over water where late evening data are included (see Table 1). The deposition velocities are sufficiently small that the aerodynamic resistances are apparently not very important and the deposition velocity is approximately equal to the inverse of the surface resistance r_s , which is calculated as a residual term.

The surface resistances are about 35 s cm^{-1} for snow, 11 s cm^{-1} for very wet soil, and 95 s cm^{-1} for lake water subjected to moderate winds. The value of $r_s \approx 35 \text{ s cm}^{-1}$ for snow does not appear to be dependent upon

Table 1. Summary of conditions and results. For each sample, measurements of the fluxes of momentum, heat, ozone, and, in some cases, water vapor were used to compute v_d (deposition velocity) and r_s (surface resistance). These values were then averaged to produce the values shown.

Surface	date	No. samples	Surface conditions	Ozone conc., ppb	v_d , cm s^{-1}	r_s , s cm^{-1}
Snow	2 Feb 78	5	freezing, stable	62	0.047	20
Snow	22 Feb 78	7	freezing, neutral	64	0.027	35
Snow	24 Feb 78	12	thawing, stable	74	0.029	33
Soil	21 Mar 78	9	thawing, unstable	57	0.100	9
Soil	22 Mar 78	12	thawing, stable	50	0.084	11
Water	13 May 79	8	stable	79	0.009	112
Water	25 Jun 79	8	stable	40	0.012	80

the temperature or freshness of the surface snow (no large amounts of blowing snow were encountered during data collection). A value of $r_s^{-1} \approx 0.03 \text{ cm s}^{-1}$ for deposition velocity over snow can thus be considered representative of many snow surfaces. This is near the value of 0.02 cm s^{-1} recommended by Aldaz (1969).

The finding that $r_s \approx 11 \text{ s cm}^{-1}$ for the extremely wet soil indicates that a deposition velocity of 0.1 cm s^{-1} is a good estimate for saturated soil. This value should be considered an extreme, since the r_s for slightly moist soil is near 1 s cm^{-1} , resulting in deposition velocities slightly less than 1 cm s^{-1} in well-mixed atmospheric conditions (Turner et al., 1973). These findings indicate that the amount of ozone destroyed at the soil surface relative to the amount removed by a plant canopy above may be a function of soil moisture content.

The smallest rate of ozone removal during these experiments was recorded over Lake Michigan. Deposition velocities of about 0.01 cm s^{-1} appear to be typical. The resistance to ozone removal at the surface appears to be controlled

by chemical rather than physical processes; changing wind speeds in the range of 2 to 7 m s⁻¹ do not alter the physical properties of the surface enough to lessen seriously the very large resistance to transport of un-ionized ozone through the uppermost quasi-laminar water skin. Only with wind speeds large enough for water spray to be formed in conjunction with breaking waves might the physical resistance of the "surface" be small enough to be important.

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PRELIMINARY THEORETICAL ANALYSIS OF POLLUTANT DISPERSION IN A TWO-DIMENSIONAL STREET CANYON

C. M. Sheih

Street canyons are known to be somewhat isolated from upper air flow and to trap pollutant emissions such as automobile exhausts for extended periods. Although the problem has been studied by many investigators (e.g., Johnson et al., 1973; and Wedding et al., 1977), no analytical formulae have been developed for predicting the pollutant concentrations inside the street canyon. In the present investigation, we shall construct a set of such formulae and will outline the experiments necessary to determine the numerical constants involved.

In order to simplify the problem for a preliminary analysis, we shall consider an idealized two-dimensional street canyon as shown in Figure 1. To construct relationships that predict pollutant concentration, the turbulence velocity (q_m) and length scales (h_*) governing the pollutant transfer at the top of the street canyon must be formulated. By integration of the turbulence energy equation and various scaling arguments, one obtains

$$h_* = L(A_1 R_L - A_2)^{-\frac{1}{2}} \quad (1)$$

and

$$q_m = U_\infty (A_1 R_L - A_2)^{\frac{1}{2}} (A_3 R_L - A_4)^{-1}, \quad (2)$$

where L is the length of a city block; U_∞ is the free stream wind velocity; $R_L = U_\infty L/\nu$ is a Reynolds number; ν is the kinematic viscosity of air; and

FIG. 1.--The configuration of an idealized two-dimensional street canyon. The roof is represented by line a-b and the street by line c-d.

A_1 , A_2 , A_3 , and A_4 are constants to be determined experimentally. Assuming that the eddy diffusivity is proportional to the product of q_m and h_* , one can compute the pollutant flux across the roof level of the street canyon and obtain

$$Q = A_5 (A_1 R_L - A_2)^{\frac{1}{2}} (A_3 R_L - A_4)^{-1} U_{\infty} (C_R - C_{\infty}) \ell, \quad (3)$$

where Q is the rate of emission inside the street canyon and ℓ is the width of the street. The constant A_5 can be determined by experimental methods. Once A_5 is determined, Eq. 3 can be used to predict the pollutant concentration C_R at the upper region of the street canyon. For other locations inside the street canyon, a concentration map relating the local concentration to C_R is needed.

By physical and dimensional arguments, one can write

$$\frac{(C - C_R) U_{\infty} (\ell h)^{\frac{1}{2}}}{Q} = F_m \left(\frac{x}{\ell}, \frac{z}{h} \right), \quad (4)$$

where F_m represents a non-dimensional distribution function of the pollutant concentration. If the pollutant concentration map plotted in the format of Eq. 4 can be shown experimentally to be independent of the variation of ℓ , h , Q and ambient wind velocity, the resultant map will be universal and will provide values of F_m for other cases. Finally, since C_R can be predicted from Eq. 3, the pollutant concentration C can be computed from Eq. 4.

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A SIMPLE FORMULA FOR COMPUTING THE SEPARATION-BUBBLE LENGTH OF A TWO-DIMENSIONAL FENCE

C. M. Sheih

Introduction

Flow passing an obstacle forms a cavity region in which stream lines are separated from the surface and reattached downstream. The flow inside the separation bubble, consisting of a major vortex, is practically isolated from the main flow. If such a flow occurs in the lee of a building in an industrial complex, trapping of pollutants inside the bubble for extended periods can lead to unacceptably high concentrations (e.g., Sheih et al., 1978). Methods of describing the separation bubble in terms of flow and structural parameters are highly desirable for evaluating the environmental consequences of various building and exhaust stack alternatives. A simple formula for computing the length of the separation bubble, based upon theoretical considerations and wind tunnel studies, is described below.

If one assumes that flow conditions can be approximated by a free-jet boundary and that the growth of the mixing region is due primarily to the turbulence generated within the mixing region, then after various scaling arguments one can derive

$$(h/L)^2 = C_1 \ln(C_2 R_*) \quad , \quad (1)$$

where h is the fence height, L is the length of the separation bubble, $R_* = hu/\nu$ is a Reynolds number (where u_* is the friction velocity related to upstream flow and ν is the kinematic viscosity) and C_1 and C_2 are constants.

In order to obtain estimates of the constants C_1 and C_2 , measurements of the separation-bubble length were carried out with a series of loose strings anchored to a pair of metal strips spaced about 40 cm apart and placed behind a two-dimensional thin-plate fence. Since the wind inside and outside the separation bubble moves in opposite directions, the strings are divided at the line of reattachment into two groups, and the distance from this reattachment line to the fence is the length of the separation bubble. Choice of a proper

string size for each ambient wind velocity is very important. If the strings are too heavy, they will not move; if they are too light, they will flutter and make accurate determination of the reattachment location impossible. In the experiment discussed below, the strings ranged from very thin, light cotton thread for 5 m s^{-1} ambient wind velocity to regular shoestrings with the core thread removed for 25 m s^{-1} ambient wind velocity.

FIG. 1.--Observed ratios of fence height to separation-bubble length at various Reynolds numbers for (a) thin-plate fence and large ratio of boundary layer thickness to fence height (δ/h) by ($\bullet$) the present author with $\delta/h = 4$, ($\square$) Wilson et al. (1979) with $\delta/h = 8.6$, and ($\diamond$) Wilson et al. in water channel with $\delta/h = 4$; (b) thin-plate fence but small δ/h by ($\triangleright$) Good and Joubert (1968) with $\delta/h = 0.75$; and (c) other fence shapes by (Δ) Plate and Lin (1965) with $\delta/h = 6$; and (∇) Chang (1966) with $\delta/h = 6$. Unless stated otherwise, the experiments were conducted in wind tunnels.

Figure 1 shows the fence height normalized by the observed separation bubble length as a function of the Reynolds number. Also included are the results of other investigations with friction velocity available. The friction velocities for the data of Wilson et al. (1979) are estimated from their suggestion that the ratios of fence-height mean velocity to friction velocity are 13 and 15 for wind-tunnel and water-tunnel experiments, respectively. Plate and Lin (1965) and Chang (1966) used obstacles with wedge-shaped cross sections with various aspect ratios. If the observations shown in the figure are considered as a whole, no organized trend is evident. However, if one considers only the experiments with thin-plate fences and large ratios of boundary-layer thickness to fence height (i.e., $\delta/h > 4$ where δ is boundary layer thickness), the data points can be approximated quite well by a straight line; this suggests that the semilogarithmic formula in Eq. 1 provides an adequate description of the results within the range of Reynolds numbers investigated.

The equation developed by fitting a straight line to the data is

$$(h/L)^2 = 8.65 \times 10^{-4} \ln(534 R_*) , \quad (2)$$

which suggests a rather weak dependence of h/L on the Reynolds number. However, this might still cause some problem in physical simulations where h/L is assumed to be constant for both model and prototype. In many environmental flow investigations, the Reynolds numbers for models are about two to four orders of magnitude less than the prototype values. To justify the accuracy of the dynamic aspect of the simulation, physical modelers generally argue that the phenomenon is insensitive to Reynolds number. The validity of this assumption can be checked with our formulations. For differences of two to four orders of magnitude in Reynolds numbers between the model and the prototype (with the Reynolds number of laboratory simulations assumed to be 10^4) Eq. 2 suggests that the simulated values of h/L will be 0.82 to 0.71 times the values for the prototype. This might cause some concern if detailed flow structure is to be studied. However, if the location of the flow reattachment is the major interest, as in most applications, model results can be adjusted through the use of Eq. 2.

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A PRELIMINARY SIMULATION OF AIRFLOW MODIFICATION BY LAKE MICHIGAN

T. Yamada

The processes of transport and turbulent diffusion over Lake Michigan are particularly complex; for example, lake breezes and return flows can produce a vertical shear in the horizontal wind as large as 180 degrees, and longitudinal vortices may develop along the shoreline. During the summer the lower layers of the atmosphere over the relatively cool lake can become quite stable. This stable atmosphere and the relatively smooth water surface result in turbulence much smaller than over land; thus, a plume may travel for a long distance over the lake with little dilution. When cold air travels over the relatively warm lake during winter, the lower atmosphere becomes unstable, increasing the turbulent transfer of sensible and latent heat to the atmosphere and often producing heavy lake-effect snow.

A three-dimensional, mesoscale numerical model is being employed for better understanding of airflow modification by Lake Michigan. The model equations are almost identical to those used in Yamada (1979), except that the surface temperature is determined by solving a heat conduction equation for the soil layers, using as boundary conditions a heat energy balance at the surface and a temperature 1 m below the ground. Water temperature is kept constant and topography is assumed to be flat.

In the example to follow, integration is initiated at 0600 CST and is continued for 12 hours, with initial horizontally homogeneous fields of wind, temperature and humidity assumed. The lake temperature is 286 K. The vertical profile of the horizontal wind is logarithmic with height until it reaches the WSW geostrophic wind of 5 m s^{-1} , and above that level it remains constant. The potential temperature is assumed to be constant (288 K) in the first 250 m above the ground and then to increase above approximately 10°C km^{-1} . The vertical profile of the mixing ratio is assumed to be uniform (6 g kg^{-1}) in the surface layer and to decrease gradually with height to 2.8 g kg^{-1} at the top boundary (2320 m).

FIG. 1.--The horizontal wind field at a height of 4 m at 1800 CST. The length of an arrow is proportional to the wind speed; one grid length indicates 2 m s^{-1} .

FIG. 2.--The same as in Figure 1 except at a height of 250 m.

FIG. 3.--Wind vector hodograph at the midpoint between Milwaukee and Muskegon.

The horizontal wind fields at 1800 CST at 4 and 250 m are shown in Figures 1 and 2. The initial WSW winds have been modified considerably by the variation in temperature and roughness from the land to the water. A wind vector hodograph for the midpoint between Milwaukee (MIL) and Muskegon (MUS), shown in Figure 3, is consistent with observations taken over the lake with a tethered balloon (Wylie and Young, 1979). Measurements were taken under conditions similar to the simulation here, i.e., the geostrophic wind was approximately 5 m s^{-1} and the maximum temperature difference between water and land was approximately 11°C .

Lake effects become considerably greater if the geostrophic wind is weaker. For simulations (not shown) with a geostrophic wind of 2 m s^{-1} , the surface wind direction offshore of Gary (GAR) is directly opposite that of the imposed geostrophic wind. Other interesting simulation features, which are consistent with observations by Wylie and Young (1979), are that the surface air temperatures downwind of the lake are approximately 2°C cooler than the upwind temperatures, owing to the advection of air cooled by the lake and reduction of incoming solar radiation from the east. The lower surface temperatures result in smaller buoyancy fluxes, and hence atmospheric turbulence downwind. The much smaller turbulence over water due to atmospheric stability and small surface roughness is also confirmed.

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MODELING OF NOCTURNAL DRAINAGE FLOW

T. Yamada

An improved capability of modeling transport and diffusion of energy-related pollutants over complex terrain is a prime objective of the Atmospheric Study in Complex Terrain (ASCOT) program of the U. S. Department of Energy. An initial ASCOT field experiment to investigate nocturnal drainage flow was conducted during the summer of 1979 over the California Geysers geothermal area. The complex topography results in highly variable wind and turbulence fields. Vertical motion, shear-generated turbulence, and meandering of horizontal winds all become important for realistic simulations of dispersion of hydrogen sulfide released in the atmosphere during the conversion of geothermal energy into electric power.

In this study, a three-dimensional, simplified second-moment turbulence-closure model previously used to simulate air flow over Gaussian-shaped mountains (Yamada, 1978) and a large cooling pond (Yamada, 1979), has been modified to simulate nocturnal drainage flow over the Geysers area. The simulation example is for the case of a westerly geostrophic wind. A comparison of the wind fields at 500 and 850 m elevation (Figures 1 and 2), clearly shows convergence of downslope flow into a valley and veering of wind with height. Wind directions near the ground appear to be controlled by the local slope, while winds aloft approach geostrophic flow. Drainage winds simulated along the slopes in the northwest are much greater than those in the southwest, primarily because of the difference in the inclination. Calculated winds within 100 m of the surface in the northwest and south depart as much as 45 degrees from the generally westerly winds aloft. The simulated surface winds qualitatively agree with observations (not shown); however, the observed wind speeds are in general much smaller. The primary cause for the overprediction of surface wind speeds is attributed to the irregular ground coverage of trees typically 20 m in height. Thus, drainage flow may have been decreased considerably by drag. Although the immediate vicinities of observation towers are relatively clear, most observation sites are surrounded by trees.

FIG. 1.--Computed horizontal winds at 500 m MSL.
An arrow of one grid length indicates 10 m s^{-1} .
Terrain contours are at 100 m intervals, with the
lowest contour at 400 m.

FIG. 2.--Same as in Figure 1 except at 850 m MSL.

FIG. 3.--Computed winds in the vertical cross section through A-A in Figure 1.

FIG. 4.--Computed winds in the vertical cross section through B-B in Figure 1.

Speed and directional convergence results in vertical motions, which can be computed from the mass conservation equation. Maximum downward motion ($\sim 4 \text{ m s}^{-1}$) occurs over the downslope, while maximum upward motion ($\sim 1 \text{ m s}^{-1}$) occurs at the convergence zone over the valley. The winds in the vertical cross section through line A-A in Figure 1 are plotted in Figure 3 with an exaggerated vertical scale. The complex nature of the flow is revealed, with wind maxima evident in the surface layer along the downslopes. A north-south cross section (Figure 4) clearly shows flows draining down both slopes and then converging and rising in the valley. In general, airflow follows surface contours but with considerable deviation due to vertical motion caused by horizontal convergency and divergence.

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NUMERICAL SIMULATION OF MESOSCALE MOTIONS OVER THE EASTERN UNITED STATES WITH A PLANETARY BOUNDARY LAYER MODEL

I. Y. Lee

A planetary boundary layer (PBL) model in which cloud formation and air chemistry are simulated (Lee and Swan, 1977; Swan and Lee, 1979) has been modified to balance the competing aims of computational economy and realistic treatment of significant macro- and micro-physical processes. Basic equations in a σ -coordinate system are integrated vertically through the boundary layer to produce a set of equations representing the mean values in the PBL. Equations for the surface pressure tendency and the w -velocity at the top of the PBL are derived by applying the equation of continuity and the principle of conservation of mass across the interface between the PBL and the free atmosphere. A prognostic equation for the PBL depth, which corresponds to the surface inversion layer plus the remnants of the previous day's mixing layer during nighttime and to the mixing layer during daytime, reveals dynamic processes such as convergence in the boundary layer as well as the entrainment through the interface. The turbulent fluxes through the interface are parameterized by integrating the PBL equations through the infinitesimally thin layer at the top of the boundary layer. The formation or dissipation of clouds is parameterized according to the moisture budget in the PBL. The surface temperature simulates a diurnal cycle.

A test run was carried out for the eastern United States, with a topographic resolution of $1/3$ degree. The initial σ value of about 0.9 indicated a PBL thickness of 700 m. The specified initial winds were northwesterly at 7 m s^{-1} in the PBL, with a vertical gradient in the free atmosphere of $50 \text{ m s}^{-1} \sigma^{-1}$. The potential temperature was initially 292° K in the PBL with a vertical gradient in the free atmosphere of $30^\circ \text{ K } \sigma^{-1}$. The mixing ratio of water vapor was 5 g kg^{-1} in the PBL and decreased rapidly in the free atmosphere. The initial state of the PBL represented July fair-weather conditions, and thus PBL variations were created mainly by the forcing of radiative heating and topography.

FIG. 1.--Simulated PBL depth in meters over the eastern United States.

FIG. 2.--Simulated mean winds in the PBL over the eastern United States.

The fields of simulated PBL depth and mean wind for predawn conditions (Figures 1 and 2) indicate an overall behavior of the PBL clearly interpretable in terms of generally understood phenomena. As expected, the horizontal variation of the PBL depth is very small over the ocean and is large over land, in particular over the Appalachians where the PBL depth becomes as shallow as a few tens of meters. The PBL winds can be seen to be blocked by the Appalachians, to drain downslope and to be channelled through the valleys.

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EFFECTS OF AEROSOL CHARACTERISTICS ON CLOUD DROPLET EVOLUTION

I. Y. Lee

The growth of aerosol particles by condensation has been studied numerically with an air parcel model that allows entrainment of drier air and aerosol particles. Two types of aerosols, collected at Mainz, Germany in 1966 (M66) and (M70) are used as initial conditions in numerical simulations (Fig. 1). This procedure circumvents some unrealistic features that often entered previous computations due to unrealistic assumptions about size distribution or chemical composition of the aerosol particles.

The major difference between the present model and earlier models lies in the treatment of the equation describing the activity of water. Here, following Hanel (1976), the activity may be written as

$$a_w = \exp[-\beta_n m_n / m_w] \quad (1)$$

where m_n denotes the total mass of aerosol, m_w the mass of water associated with the aerosol and β_n the associated hygroscopicity. The value of β_n is determined from an empirical relationship

$$\beta_n = B_0 + B_1 \left[\frac{m_n}{m_w} \right]^{\frac{1}{2}} + B_2 \left[\frac{m_n}{m_w} \right] + B_3 \left[\frac{m_n}{m_w} \right]^{3/2} \quad (2)$$

where B_0 , B_1 , B_2 , and B_3 are constants.

The total number of particles in M70 is five time greater than in M66, and the water soluble mass fraction (m_s/m_n) and the concentrations of larger particles are also greater for M70. In both cases, clouds develop to about 3000 m vertical extent with maximum updraft velocity, supersaturation ratio and liquid water mixing ratio of about 4 m s^{-1} , 0.1% and 3 g kg^{-1} , respectively. The drop size distributions near the cloud top (Fig. 2) show that the drop size mode for drops $> 2 \text{ } \mu\text{m}$ is greater for M66, due mainly to the smaller concentration of M66 aerosol available for activation, but that M70 aerosol can produce large drops ($r > 20 \text{ } \mu\text{m}$) with concentrations greater than 1000 m^{-3} . Therefore, we may conclude that the initiation of rain by

collision and coalescence is more likely when the aerosols are of the M70 type.

FIG. 1.--Initial aerosol size distribution.

FIG. 2.--Drop size distributions near cloud top.

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A COMPARISON OF SODAR AND KYTOON DERIVED WIND SPEEDS

R. L. Coulter

In July, 1979 during the Central Illinois Rainfall Chemistry Experiment (CIRCE), the Atmospheric Physics Section utilized two methods of measuring wind profiles in the planetary boundary layer (PBL) to heights in excess of 500 m: a kytoon-borne instrument package which measures pressure, temperature, dew point, wind speed, and wind direction; and the ANL Doppler sodar, which evaluates wind speed from the frequency shifts of a back-scattered acoustic signal.

The wind sensor on the kytoon instrument package is a three-cup anemometer with a start speed of less than 1 m s^{-1} . A dc tachometer provides a signal proportional to the cup rotation rate and thus the wind speed. This output is integrated for a short time with a capacitor to reduce brush noise. Therefore, the values transmitted and stored are short-term (less than 5 s). During convective conditions the kytoon may oscillate; the anemometer may be affected by the motions, and the pressure and associated height for a particular wind measurement may be in error, for the two are not sampled simultaneously.

The sodar used in this experiment consisted of a single separated transmitter and receiver and thus was sensitive to only a single component of the horizontal wind. The position of the transmitter was varied to orient the sodar system along the wind direction (observed from kytoon and pibals) as much as possible. It was not possible to orient the transmitter and receiver along all possible wind directions, nor, of course, to change the relative angle with height. Thus, the wind direction sensed by the kytoon has been used to correct for the difference between the direction of the sodar baseline (between the transmitter and receiver) and the direction of the wind vector at each height. The sodar is sensitive to wind speeds averaged over layers 10 to 20 m thick because of the finite duration of the acoustic energy transmitted. For comparison purposes, the data have been averaged over 25 m height intervals for 5 to 15 min. This implies approximately 30 to 90 instantaneous samples

FIG. 1.--A comparison of winds derived from the sodar and the kytoon. Horizontal lines indicate the variation in kytoon results when several successive values were taken. The numbers indicate the day the data were taken: 1) July 12, 2) July 13, 3) July 15, 4) July 16, 5) July 17, 6) July 18.

at each height, since the system transmitted once every 5 s, alternating between vertical and horizontal directions.

The wind speeds derived from the two sensors for 6 of the 14 days of CIRCE are compared in Figure 1. Data have been omitted when the wind direction was different from the transmitter receiver baseline by more than 45° or when wind direction changed rapidly with height. The horizontal lines indicate the variation in kytoon wind speeds when several successive measurements were taken at one position. Over all, the sodar wind speeds agree well with the kytoon values. However, positive sodar values (defined as wind moving from the transmitter toward the receiver) are low in comparison to the kytoon values, although the number of samples for this case is small. Because of the temporal and spatial averaging differences between the sodar and kytoon systems, some variability is to be expected. Since there was only a single axis for sodar derived wind speeds, the agreement must be considered very encouraging.

The expansion of the sodar to include an additional transmitter at an angle to the present baseline eliminates the need for separate wind direction information to derive sodar winds. A second comparison will be carried out in the spring between the full three-dimensional system and the kytoon. During the experiment the kytoon will be maintained at a single height long enough to evaluate both sets of wind speeds accurately. In addition several different techniques for Doppler wind estimates of PBL winds will be explored.

SODAR SYSTEM FUNCTION AND ERROR ANALYSIS

R. L. Coulter and E. Roth

The determination of turbulence variables (e.g., C_T^2 and C_V^2 , the temperature and velocity structure parameters) from sodar amplitude measurements is critically dependent upon knowledge of the bistatic system function, which relates the power received to the power transmitted and to system geometric variables (see Coulter, 1978). The strength of the scattered return is dependent upon the transmitter and receiver beam patterns (described by directivity functions $F_T(\Theta, \phi)$ and $F_R(\Theta, \phi')$, where Θ is the angle between the vertical plane containing the baseline and a point in space and ϕ and ϕ' are the angles between the baseline and a point in space as seen from the receiver and transmitter, respectively (see Figure 1).

The beam patterns are frequency dependent, becoming sharper around the elevation angles ϕ_0 and ϕ'_0 as the frequency increases. The total amount of scatter contributing to the returned signal at a given instant is determined by integrating over an ellipsoid of revolution with foci at the transmitter and

FIG. 1.--Bistatic sodar geometry for transmitter T and receiver R. The angles defined in the text are indicated.

FIG. 2.--System functions S_T and S_V for the Argonne sodar at two different frequencies. Note the sharper character at higher frequencies due to the more peaked character of the antennae directivities at higher frequencies.

receiver and the semimajor axis ($2A$) equal to the total travel distance of the acoustic energy received at any instant. This ellipsoid is the locus of points having equal travel time from transmitter to receiver.

In order to evaluate C_T^2 and C_V^2 , the dimensionless system functions S_T and S_V , which combine features of the transmitting and receiving antennae with the scattering cross section (Kristenson, 1978), must be integrated over the pulse length in space (Figure 2 is an example of this result). The peak values of the system functions occur near the value of A corresponding to the intersection of the centers of the beam patterns of the two antennae, where $F_T(0, \phi) = F_R(0, \phi') = 1$. The system functions decrease as A becomes larger or smaller than this intersection value as the product of E_T and F_R decreases rapidly toward zero. Thus, there is a limited range over which values for C_V^2 can be obtained. This range is determined by the height range over which the gain from S_T and S_V maintains a signal larger than the background noise level. This in turn is a function primarily of ϕ_0 and F_R if $\phi_0' = \pi/2$, which is usually the case. As ϕ_0 increases, the maximum height and the minimum height increase. On the other hand, as the transmitter beam pattern

FIG. 3.--Error estimates due to assumed azimuthal pointing angle errors for the transmitter. The horizontal axis is the ratio of the ellipse semimajor axis to the baseline. Error increases with frequency (dashed line) because of the narrower beam patterns. When the transmitter and receiver directivity functions are assumed identical to the receiver directivity (dotted lines), the error increases dramatically.

becomes broader, the maximum height increases and the minimum decreases. This can be seen from a comparison of system function curves for different acoustic frequencies (Figure 2). Higher frequencies result in narrower beam patterns and thus a smaller height range from which measurable signals are received. Once S_T and S_V have been evaluated, C_T^2 and C_V^2 can be calculated.

In reality, errors in the positioning of the transmitting antenna can lead to the use of incorrect values for the system functions. In order to evaluate the sensitivity to these errors, various errors in the azimuth pointing angle have been assumed. One must take care in transferring the azimuth error (δ) into errors in θ , as an azimuthal pointing error manifests itself in two ways; the amount of the shift is dependent upon ϕ , i.e., $\delta = \delta \cos(\phi)$, and the amount of the shift perpendicular to the vertical plane containing ϕ_0 is given by $\theta \cos(\delta)$. Thus, there is no error for points directly over the

transmitter ($\phi = \pi/2$); similarly, if the transmitter is pointed 90° from the correct direction (an unlikely occurrence), the shift perpendicular to the plane containing ϕ_0 is zero. The necessity for including variations in directions perpendicular to the plane containing ϕ_0 is due to the generalization of F_T to allow for an asymmetric beam pattern in the transmitter. Figure 3 illustrates the error in θ that occurs for various errors in azimuth pointing angle. For broad F_t functions the error is not excessively large until shifts of 10° occur. However, as F_t becomes narrower, or as the breadth of F_t approaches that of F_r , the errors become significant at smaller azimuth errors. It is also apparent that the maximum error occurs in the region of the intersection of the antenna boresights. This is usually the region of most interest but also the region where two sharply peaked functions must coincide in order to obtain the most reliable data.

It is clear that the accurate determination of turbulence variables from sodar amplitude information is dependent both upon accurate determination of directivity functions F_t and F_r and upon the accuracy with which the two antennae are pointed. The required directional accuracy is in turn a function of the directivity functions involved. Since these functions are themselves a function of frequency, care must be taken in the selection of the proper frequency as well. Doppler shift information, on the other hand, is not directly affected by errors in pointing angle except through the necessity of having a large signal-to-noise ratio. It is not necessary to know the absolute magnitude of the signal return in order to derive wind information.

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ROTATING PHASOR DOPPLER ESTIMATES

R. L. Coulter and T. J. Martin

The use of the Doppler frequency shift of electromagnetic or acoustic radiation for the measurement of atmospheric wind speeds is well known. Many methods for making the initial frequency shift estimate are available, ranging from tracking filters to complex covariance techniques, but each method has problems. A promising method for obtaining an instantaneous frequency estimate, a necessity for measurement of vertical velocity profiles using sodar, is described below.

The Argonne sodar receiver derives in-phase (I) and quadrature-phase (Q) signals from the return signal; the first of these components is in phase with the transmitted signal, the second is 90° out of phase. These two signals can be combined into a single phasor (R), described by

$$R(t) = (I(t)^2 + Q(t)^2)^{\frac{1}{2}} \exp(i\phi(t)), \quad (1)$$

where

$$\phi(t) = \tan^{-1} (Q(t)/I(t)). \quad (2)$$

The time derivative of Eq. 2 is the Doppler frequency. Here ϕ is calculated from samples of Q and I at a 200 Hz rate by using a function available from a table for the arctangent and multiplying it by the sample rate. This method, an order of magnitude faster than using the arctangent function provided in the FORTRAN library for our microcomputer, is a necessity for on-line calculation of wind speeds. Since an estimate of ϕ is available for each sampling interval, the values can be averaged over any desired length of time (or, equivalently, height interval) and averaged with samples from later acoustic pulses. However, the high frequency noise created in such operations presents a problem.

Another possible problem with this method is the effect of noise on the probability distribution or spectrum calculated from Eq. 2. In order to investigate this problem, a model was constructed to simulate any desired

signal phasor and then combine it vectorially with other signal phasors as well as a noise signal. The noise signal is a randomly generated phasor of normally distributed phase (with selectable mean and standard deviation) and uniformly distributed amplitude (between selectable limits). Thus, probability distributions and spectra of Doppler frequency for any given signal-to-noise ratio (SNR) can be calculated and compared to that which one might expect from a known signal alone. The advantages of this model are that existing routines and programs for real-time data collection in the sodar system are used, and that the random noise signal can be tailored to replicate the ambient noise characteristic of any location.

Figure 1 illustrates the probability distribution and spectrum one might expect to see with a mixture of seven signals of differing frequencies (modeling the signal return) and random noise, with a SNR of 1.2. Note that the frequencies of the mean and the peak of both curves are shifted toward zero from what one might expect with the seven signals alone. For simple cases such as a constant amplitude, constant phase noise vector combined with a fixed frequency signal vector, the shift as a function of SNR can be predicted analytically.

The model was run for various values of SNR, and the mean frequency was determined, as shown in Figure 2, as well as the analytical result (used to verify the model) for the case mentioned above. We see that while the mean frequency is indeed shifted toward zero, the shift is not so large as that for the constant phase and amplitude case. More importantly, the shift is well defined and easily calculated as a function of SNR.

Therefore, it appears that for cases where $\text{SNR} > 3$, the Doppler frequency derived from the rotating phasor method of calculation is quite reliable, and when $0.5 < \text{SNR} < 3$, the anticipated shift can be estimated and corrections made to wind speeds derived under low signal amplitude situations.

FIG. 1.--Probability distribution and spectrum of frequency shift for a mixed signal plus random noise. Vertical axis is linear in amplitude.

FIG. 2.--Mean frequency shift calculated from the model under various SNR. Curve A is the predicted shift for a single signal plus a noise vector of constant phase and amplitude; curve B results from a single signal and a noise vector of random phase and amplitude; curve C represents the case of Figure 1 and various values of SNR, with predictions for mean frequency shift calculated from the probability distribution. Curve D ($\bullet$) represents the same case as curve C, except with predictions for mean frequency shift calculated from the spectrum.

AUTOCORRELATION AND SPECTRA OF REGIONAL-SCALE TURBIDITY

J. D. Shannon and M. L. Wesely

A regional network of ten silicon-cell pyranometers, which detect total and diffuse radiation and thus measure turbidity indirectly, was designed in part through objective sensor-placement techniques (Shannon et al., 1978) and was established as part of MAP3S during the fall and winter of 1976-1977. The sensor-placement optimization method used a correlation structure function (CSF) derived from a previous turbidity network of Volz synphotometers. The pyranometer network operated during 1977 and 1978, although at rather low efficiency in data recovery. A network re-evaluation, which considered both data recovery rates and a CSF derived from pyranometer network data, was made with data from 1977 (Shannon and Wesely, 1979).

Further insight into the temporal structure of daily average turbidity may be gained through analysis of the autocorrelation function (ACF) and variance spectrum. Data from April through October of 1977 and 1978 are examined, as regional haze episodes are more common during warmer weather.

The approach used here is to compute an ACF for ANL observations over the two seven-month periods, and an ACF for all observations combined. The latter method assumes that the ACF of daily turbidity is not a function of location. The reason that other sampling sites are not treated separately can be seen in the limited number of observations obtainable during the total sampling period of 428 days (Table 1).

The lack of data continuity, due to instrument problems or cloud conditions, has several significant effects on the ACF. Auto correlation estimates for consecutive lags are more independent, but the sample ACF has a greater variation about the true ACF. In addition, the total exclusion of data for the months November through March causes calculations for lags around 180 days to be solely from spring-fall data pairs. Although meteorological considerations lead us to expect an annual variation in regional turbidity, which should result in negative values of the true ACF around lags of 180 days, the sample ACF cannot reflect this.

Table 1. Number of observations of daily average turbidity from April through October of 1977 and 1978.

<u>Station</u>	<u>Total Observations</u>
Argonne, Illinois	224
Brookhaven, New York	176
Burlington, Vermont	65
Miami, Ohio	100
Oak Ridge, Tennessee	193
St. Louis, Missouri	106
Guelph, Ontario	122
Pellston, Michigan	77
State College, Pennsylvania	174
Lynchburg, Virginia	63

Since the ACF is symmetric about zero, only half the ACF need be plotted. The ACF for ANL observations and for combined observations (Figures 1 and 2) clearly display the effects of mixing the synoptic scale (3 to 7 days) and the biased sample of the annual scale, with the additional complication of intermediate scales associated with shifts of upper-air steering patterns; correlations show a sharp drop in the first few days, but do not drop to zero or negative values until a lag of about 90 days.

An advantage of transforming the ACF to the spectrum is that adjacent values of the spectrum are essentially independent. One problem that often arises with finite realizations of the spectrum, however, is the wide variation of sample values about the true spectrum. This can be reduced with a filtering function or lag window, but the bias becomes greater. The spectra (Figure 3) produced by applying a Bartlett lag window of half-width 10 days (Jenkins and Watts, 1968) to the ACF for ANL and for the combined observations show the effects of turbidity scales > 2 days directly (shorter scales cannot be resolved from daily averages). The peaks in the spectra are due to the synoptic variations (peak frequency 0.2 d^{-1}) and possibly to shifts in steering patterns (peak frequency $\approx 0.06 \text{ d}^{-1}$).

FIG. 1.--Autocorrelation function for daily turbidity average for ANL observations during the warmer months of 1977 and 1978.

FIG. 2.--Autocorrelation function of daily turbidity average for the entire MAP3S network during the warmer months of 1977 and 1978.

FIG. 3.--Spectral density, plotted in energy-conserving form, for daily turbidity averages of entire MAP3S network (solid line) and ANL (dashed line).

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ESTIMATING WET AND DRY DEPOSITION OF TOTAL SULFUR ON THE REGIONAL SCALE

J. D. Shannon

Air pollution modeling has emphasized the distribution of atmospheric concentrations of pollutants, with wet and dry removal considered only as depletion factors, if at all. However, increasing emphasis is now being given to the ecological effects of the chemistry of deposited pollutants, and thus wet and dry deposition are being examined as source terms for ecosystem modeling. One of the capabilities of the Advance Statistical Trajectory Regional Air Pollution (ASTRAP) model (Shannon, 1979a) is the simulation of the regional-scale patterns of long-term cumulative wet and dry deposition of pollutant sulfur.

One of the three subprograms of ASTRAP is a numerical integration of the diffusion equation to produce normalized one-dimensional vertical profiles of pollutants. In the integration, which is performed separately for different effective emission heights, diurnal patterns of dry deposition velocity are specified for SO_2 and SO_4^- (Figure 1). The subprogram cycles through these diurnal patterns five times during the integration for various starting times, and then averages the resulting vertical profiles and dry deposition increments as functions of plume age. The dry deposition of SO_2 and SO_4^- can be maintained in separate budgets, or combined into dry deposition of total sulfur. It should be noted here that, while ASTRAP varies dry deposition velocities diurnally, the identical cycle is repeated each day (i.e., the pattern represents a typical day and not a particular day) and there is no horizontal variation of the pattern.

Another subprogram of ASTRAP calculates horizontal dispersion statistics from the distribution of a series of simulated tracers released from each source. While the tracers are undergoing transport, they may encounter precipitation. If so, total sulfur is removed from the hypothetical normalized tracer mass according to the half power of the precipitation amount (Hicks and Shannon, 1979). Part of the sulfur removed can be transported into the free

FIG. 1.--Dry deposition velocities for SO_2 (o) and sulfate (x) used in ASTRAP simulations during summer.

FIG. 2.--Rate of wet deposition (solid line) and transport to the free troposphere (dashed line).

FIG. 3.--Example of ASTRAP simulation of long-term wet and dry deposition of total sulfur, in which the parameterizations of Figures 1 and 2 are used.

troposphere by the convective activity instead of being deposited at the surface (Figure 2). Statistics of the mean position and spread of deposited tracers as function of source and plume age are maintained.

When the concentration and deposition subprogram of ASTRAP combines the results of the above two subprograms with an emission inventory, cumulative dry deposition and cumulative wet deposition are expressed as a grid of point values of total sulfur deposited. The point values are scaled by the areas represented by the grid cells to produce the mass of sulfur deposited by wet or dry processes. Since the grid cells can be identified as within or outside an area of interest in a manner similar to that used in computing net horizontal mass flux (Shannon, 1979b), the relative importance of wet and dry deposition within a region can be compared (Figure 3).

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COMPUTING THE LONG-TERM, REGIONAL-SCALE NET HORIZONTAL MASS FLUX OF POLLUTANT SULFUR

J. D. Shannon

Transport of air pollutants across political boundaries is the subject of increased interest in both North America and Europe, primarily due to the questions associated with acid rain or chemical deposition. One important step in evaluating the problem is to investigate large-scale relationships between source and receptor regions. Such relationships can include relative or absolute contributions to atmospheric concentrations and wet and dry deposition of pollutants, and the net mass flux of pollutants from one region into the other. The Advance Statistical Trajectory Regional Air Pollution (ASTRAP) model (Shannon, 1979) has been modified and improved in order to calculate such budget items for sulfur pollutants.

The initial step necessary in calculation of regional budget terms is definition of the receptor region of interest by a description of its borders. Since ASTRAP calculates pollutant concentration and deposition fields for an externally defined rectangular grid, the boundary of the region is expressed mathematically as maximum and minimum values of X along each Y row and maximum and minimum values of Y along each X column. The boundary thus is a series of connected line segments parallel to the X or Y axes. If the grid is dense relative to the major features of the border, the approximation of the border is quite accurate. An example of the technique, considering the eastern half of the United States as the area of interest, is shown in Figure 1.

The ASTRAP model consists of three basic components: a one-dimensional (vertical) numerical integration that calculates normalized surface concentrations, airborne sulfur, and accumulation of dry deposition as a function of time since release (plume age); a two-dimensional (horizontal) dispersion subprogram that calculates the normalized long-term horizontal plume and wet removal from the statistics of a series of simulated tracer particles released from each source; and a concentration and deposition subprogram

FIG. 1.--The solid boundary indicates the ASTRAP area of interest, the eastern United States.

Table 1: Horizontal flux calculations

Source location	Effective height, m	Relative net mass flux into Canada
Southern Ohio	0-50	14.9
Southern Ohio	400-500	21.2
Central Tennessee	0-50	8.5
Central Tennessee	400-500	12.3

that combines an emission inventory with the normalized horizontal and vertical dispersion statistics to produce concentration and deposition fields. In the horizontal dispersion calculations, each tracer particle is identified by its current X value and the value corresponding to its previous position. The Y value for the current and previous positions are then compared with the corresponding border Y values along the identified X columns. If the tracer goes from without to within the region of interest during the time step, the

contribution to the net mass flux is positive; if the tracer exists the region during the step, the contribution is negative. If the tracer remains inside or outside the region during the time step, there is no flux contribution. Similar comparisons are made with the border X values along each Y row.

The border crossings are totaled by border, source, and plume age. The results are then scaled by the source emission rate and the airborne budget in order to estimate a net mass flux. The net flux resulting from a different source inventory or vertical mix of sources can be examined by simply changing the source inventory in the simulation.

Some examples of the statistics estimated with this techniques are shown in Table 1. Net horizontal mass flux is decreased if removal by wet and dry processes is increased before reaching the boundary of interest; thus, the net horizontal mass flux is less for low level sources and for sources further from the border.

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SOME OBSERVATIONS ON SULFUR SCAVENGING RATIOS

B. B. Hicks

Scavenging ratios are frequently used to relate concentrations of chemical constituents in precipitation to concentrations of the same quantity in air. Although these ratios depend on many other factors, they provide an attractively simple method for including wet removal processes in numerical simulations of regional air pollution. However, scavenging ratios also can be used to study the basic processes by which air pollutants are scavenged by and concentrated in precipitation.

Scavenging of small particles is especially efficient in convective storm systems, such as those which typify summer rainfall in the midwestern USA. Many studies have shown that scavenging ratios of about 400 should be expected in the case of pollutants that originate near the surface, and values of about 800 are characteristic of material derived from the free troposphere aloft (such as fallout radionuclides). The case of NaCl is particularly interesting, since this wettable and hygroscopic compound is usually present as particles that are substantially larger than the so-called accumulation size range normally associated with sulfate aerosol. Scavenging of sodium chloride particles is therefore quite efficient; scavenging ratios of about 600 seem typical. If studies of some other quantity indicate greater values, then it would be necessary to postulate some mechanism more effective than that which scavenges large, hygroscopic sea-salt particles.

The highly scattered results on particle scavenging in the United Kingdom reported by Cawse (1974) yield geometric means that are not greatly dissimilar from observations in the Midwest, ranging from about 240 ($\pm 38\%$) for lead to 400 ($\pm 44\%$) for selenium. However, the data of Cawse indicate ratios of 1460 ($\pm 68\%$) for sulfate and 1630 ($\pm 41\%$) for nitrate. The suggestion that both quantities are scavenged about five times more efficiently than other particles is hard to rationalize unless some kind of in-cloud SO_2 conversion is postulated. The following points are especially relevant.

1. The finding of a seemingly enhanced sulfate scavenging efficiency is not unique to the Cawse data set.
2. Scavenging of sea salt is not usually found to be enhanced, thus indicating that the mechanism involved in sulfate scavenging enhancement is additional to all those chemical and physical processes that contribute to the removal of the larger and hence more active NaCl particles.
3. Selenium is not removed with the high scavenging ratio of sulfate, but rather as one of the particulate trace metals. It should be noted that selenium and sulfur compounds are chemically similar although the former are more active. SeO_2 is not a common atmospheric constituent.

The alternative hypothesis that precipitation contains a large sulfur contribution from scavenged SO_2 which is transformed by in-cloud mechanisms to $\text{SO}_4^{=}$ remains to be tested. In order to demonstrate the likelihood of this mechanism, Figure 1 presents annual cycles of total sulfur scavenging ratios, derived from atmospheric and precipitation chemistry data reported for Poland by Hryniewicz (1979) and for the Canadian midwest by Nriagu and Coker (1978). The data show excellent agreement and indicate summer scavenging ratios in the range 400 - 500, precisely as expected. Thus, summer rainfall appears to remove total sulfur from the atmosphere as if all the sulfur were associated with those accumulation size particles that carry trace metals, and almost as rapidly and efficiently as large sea-salt particles. (Note that the values graphed are evaluated as total sulfur based on SO_2 concentrations only, neglecting airborne particulate sulfur which in this case appears to have been small.)

In the colder months, scavenging ratios referred to SO_2 drop to about 100 - 200, probably as a direct consequence of a diminished efficiency of in-cloud capture and/or conversion of SO_2 . Hales and Dana (1979) report maximum concentrations of unoxidized SO_2 dissolved in rain in the winter months, in support of the contention that reduced conversion causes the lower winter scavenging ratios of Figure 1. It does not appear that the winter sulfur scavenging ratio is overwhelmingly weighted towards particulate scavenging, however, since the Polish data do not differ greatly from the

FIG. 1.--Solid circles and error bars: geometric mean scavenging ratios derived directly from data on sulfur concentrations in rain and sulfur dioxide concentrations in air at Canadian stations in the vicinity of the Great Lakes (Nriagu and Coker, 1978). Open circles: scavenging ratios derived from average concentrations of total sulfur in precipitation and in air, as reported for Poland by Hryniewicz (1979) for the year 1976. Shaded bands: long-term average sulfur scavenging ratios evaluated for Poland, over warm and cold six-month periods (see Hryniewicz, 1979).

Canadian even though the former are derived from atmospheric sulfur concentrations that include particles whereas the latter are not.

The nitrate data reported by Cawse are not significantly different from his high sulfate values. It is tempting to attribute this to in-cloud processes similar to those that appear to dominate in the case of sulfur, as has been postulated by Marsh (1978), but until nitrate information similar to the sulfate data of Figure 1 becomes available the possibility of a fortuitous result cannot be rejected.

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AN OVERVIEW OF ARGONNE'S PARTICIPATION IN CIRCE

B. B. Hicks

The evolution of the planetary boundary layer (PBL) was studied in some detail in the 1975/6 Sangamon and 1977 AMBIENS (see previous Annual Reports) experiments. During 1979, these field investigations of fundamental features of the PBL were continued in another of the sequence of coordinated, multi-laboratory experiments conducted under the auspices of the Multistate Atmospheric Power Production Pollution Study (MAP3S). In July 1979, the Central Illinois Rainfall Chemistry Experiment (CIRCE) was conducted in the Bloomington area by workers from Argonne National Laboratory, Brookhaven National Laboratory, Pacific Northwest Laboratory, and the University of Wisconsin. CIRCE was designed to take advantage of several other large experiments; these concurrent studies were known as VIN (denoting the main participants, from the University of Virginia, the Illinois State Water Survey, and the National Hurricane and Experimental Meteorology Laboratory) and SCORE-79 (the Summer Chemistry of Rain Experiment). Figure 1 shows the areas of major interest of these experiments.

Although CIRCE was intended as a study of convective rainfall and in-cloud scavenging processes, supporting investigations evaluated the use of ground-based remote probing methods to measure vertical velocities in the PBL. Such data is required in order to document pollutant fluxes into convective clouds. During CIRCE, both optical LIDAR and acoustic SODAR methods were tested.

As in the previous PBL experiments conducted by this laboratory, emphasis was also placed on the need to test recently-developed models of the growth of the morning mixed layer. Investigations were also conducted of the nocturnal low-level wind maximum (or jet) which is characteristic of pre-dawn flow in the Midwest during summer. This jet may well provide a mechanism for rapid horizontal transport that is not indicated by and cannot yet be predicted from routine surface meteorological observations. Also in common with previous practice, a large body of supporting micrometeorological data was

FIG. 1.--The area of the VIN/SCORE-79 study, showing the internal area of intensive precipitation monitoring (cross-hatched) and the region of major interest to participants in CIRCE (circled).

FIG. 2.--Details of PBL sounding schedule for the CIRCE experiment. Ascending and descending soundings by kytoon are shown schematically, as are ascent-only soundings by WHAT-system radiosondes. Heights are in meters. Solid bars at the bottom of each profile set indicate periods during which acoustic sounding data are available; bars at the top of each set show periods of LIDAR operation.

obtained. In particular, eddy fluxes of heat, moisture, momentum and ozone were measured routinely.

Figure 2 shows the extent of the observations made during CIRCE. The intense PBL observations extended over a ten-day period, during which significant rainfall was recorded on only one day. Thus the scavenging aims

of CIRCE were largely foiled. However, conditions were excellent for the PBL studies of interest to the ANL research team.

Thanks are due to the residents of Weldon, Illinois, for their friendly assistance during the course of the experiment, and especially to Messrs. Lester Riddle and Howard Poff who agreed to the use of their property as observation sites. Without their help, this experiment would not have been possible.

THE INTERPRETATION OF PRECIPITATION STATISTICS

B. B. Hicks

Recent attempts to relate the chemical composition of precipitation to concentrations of contaminants in air have generated some intriguing statistical questions. Many of these questions arise from uncertainty about how best to combine results obtained from studies of the highly irregular precipitation process. To a considerable extent, the purpose of the study imposes the solution to many of these questions. For example, if the intent is to investigate the washout of atmospheric sulfur dioxide by falling raindrops, a process that is known to be pH dependent, then rainfall-weighted averages of pH values are likely to be appropriate for statistical analysis. On the other hand, in ecological studies the intent is often to evaluate the total flux of some selected chemical component to the surface, in which case rainfall-weighted average concentrations are more appropriate. Thus some studies make use of averaged pH data, while others employ averages derived from hydrogen ion concentrations.

A further complication arises when the spatial variability of rainfall events is considered. Hales and Dana (1979) provide an extensive table of rainfall chemistry data obtained during the 1972 and 1973 METROMEX experiments in the vicinity of St. Louis, Missouri. Ranges in concentration are reported as a factor of about 30 for sulfate, nearly 100 for nitrate, and 700 for hydrogen ion concentration. In such circumstances, it is difficult to see how the results obtained at any single sampling station can be interpreted in terms of spatial averages by any averaging procedure.

Spatial variability within events has a large effect on the apparent correlation coefficient r between concentrations of some quantity in rainfall, C_r , and corresponding values in air, C_a . It is convenient to introduce new variables $x = \ln(C_a)$ and $y = \ln(C_r)$; in practice, air quality variables usually have a log-normal distribution. Then the correlation coefficient is calculated from n values as

$$r = \frac{\sum x'y'}{n s_x s_y}, \quad (1)$$

where primes denote deviations from sample means and s_x and s_y are standard deviations. There is little loss of generality in considering the logarithmic quantities in this context. In the limit in which variations are small the value of r derived by manipulating x and y will be the same as that obtained by the usual linear procedure.

It is informative to consider the total variance in rainfall concentration to be made up of several independent contributions: (i) that due to variations in air concentration, s_{y1}^2 , (ii) that due to uncertainties in sampling the precipitation, s_{y2}^2 , and (iii) a residual contribution due to other factors such as changes in rainfall rate and cloud properties. Then the total variance can be expressed as

$$s_y^2 = s_{y1}^2 + s_{y2}^2 + s_{y3}^2. \quad (2)$$

Consider an experiment in which all of the rain from individual events is sampled (i.e. $s_{y2} = 0$), yielding a correlation coefficient r_a between concentrations in total precipitation and concentrations in air. The covariance $\frac{1}{n} \sum x'y'$ can then be written as

$$\frac{1}{n} \sum x'y' \approx r_a s_{y1} s_{y1}, \quad (3)$$

provided there is insignificant contamination introduced by variables falling into the residual category (iii), i.e. $s_{y3} \ll s_{y1}$. If other factors are taken to be independent of air concentrations, then the expected covariance will be unaffected by "noise" imposed on the rainfall concentration data by sampling inadequacies or any other cause. Then the apparent correlation coefficient will be as defined in (1) with $s_y^2 = s_{y1}^2 + s_{y2}^2 + s_{y3}^2$. Then, it follows that

$$r = r_a / (1 + s_{y2}^2/s_{y1}^2 + s_{y3}^2/s_{y1}^2)^{1/2}. \quad (4)$$

The precipitation chemistry network data presented by Hales and Dana (1979) provide sufficient detail to test the inferences of Eq. 4. Nine events were studied by a network that provided up to 81 samples across an area of about 4500 km², near St. Louis, Missouri. Data were obtained during the METROMEX experiments of 1972 and 1973. The reported sulfate concentrations

vary widely with both time and space; the overall geometric mean concentration is $50.1 \mu\text{m/L}$, with a logarithmic standard deviation of 0.616 (corresponding to a factor of about 3.4 between plus and minus one standard deviation limits). Their Table 9 (of rainfall-weighted average concentrations) yields a geometric mean of $61.3 \mu\text{m/L}$, with a logarithmic standard deviation of 0.395 (a factor of about 2.2 for ± 1 s.d.). However, the mean standard deviation within events was 0.507 — a factor of 2.8 for ± 1 s.d. It should be noted that the variances are not precisely additive, since $(0.395)^2 + (0.507)^2 = (0.643)^2$, rather than $(0.616)^2$. Several factors contribute to this discrepancy; none is sufficiently important to worry about here.

Let us suppose that half of the observed variance between events was due to changes in air chemistry and half to some combination of meteorological factors. Then it appears that we can approximate s_{y1} , s_{y2} , and s_{y3} by 0.28, 0.51, and 0.28 respectively. Substitution into Eq. 4 indicates that $r \approx 0.43 r_a$. Thus, even if we assume that concentrations in rain are linearly dependent on concentrations in air and experimental error is negligible, sampling location effects and meteorological influences combine to reduce the apparent correlation coefficient to a maximum value of about 0.43. It should be emphasized that the same mathematics will apply to the relationship between concentrations in rain and meteorological factors, since we have assumed here that variations in air quality and in meteorology cause effects of similar magnitude on concentrations in precipitation. While this assumption might be appropriate for the convective situations that are typical of the North American Midwest, it might well be inappropriate in other circumstances.

The correlation coefficients tabulated by Sisterson (1980) for the Argonne site tend to lie in the range 0.3 to 0.5, much as predicted above. In this case, the relevance of standard tests of statistical significance become rather questionable, since it is clear that explaining a relatively small proportion of the total variance might indeed represent an excellent result. The usual methods of accounting for the effects of other sources of variance (e.g. partial correlation) cannot be applied, since sufficient spatial data are almost always lacking.

The case of widespread rainfall is of some interest, even though less frequent in the Midwest. In this case, we might suspect that the spatial variability of concentrations in rainfall will be greatly reduced, so that the variance observed between events will be dominated by the effects of changes in air chemistry and meteorology. If we assume that there is no spatial variability within events and that the observed variance is equally attributable to chemical and meteorological factors, then Eq. 4 indicates that correlation coefficients between concentrations in air and in rain might be as great as 0.7. Garland (1978) reports values obtained at two sites in England between January and June 1973. Correlation coefficients of 0.68 and 0.62 were found, considerably higher than values reported in the American Midwest but substantially as predicted for the steady, synoptic rainfall that is characteristic of the English environment.

In conclusion, it should be stressed that studies of the relationship between rainfall quality and air chemistry cannot be expected to yield high correlation coefficients. Moreover, results obtained in England point to substantial differences between the nature of precipitation scavenging in western Europe and in the American midwest. These differences are, as must be expected, based on the prevailing meteorology, especially the precipitation regimes of the two areas.

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STATISTICAL INVESTIGATION OF ACID RAIN AT ARGONNE NATIONAL LABORATORY

D. L. Sisterson

In recent years, this Laboratory's continuing study of scavenging of atmospheric pollutants by rainfall has focused on the case of environmentally active pollutants, such as trace metals and sulfate. During 1977, studies of rainfall acidity were initiated by the Ecological Sciences Section (ESS) as part of their terrestrial ecology program. The data from these studies have been used in a study of rainfall acidity by this section, (a) to determine whether rainout or washout is the primary process for the removal of pollutants contributing to the acidity of rain, and (b) to investigate the relationship between the chemical properties of the rain samples and the air quality and meteorological conditions prior to storm development.

During the non-winter months of 1977 and 1978, ESS collected 85 precipitation samples at ANL. Each rain sample was measured for pH and titrated with NaOH to determine the strong, weak, and total acid concentration from Gran's plots (Irving, 1978). Concentrations of sulfate were evaluated for some rain samples by wet-chemical methods (Tissue and Kacoyannakis, 1975). During the collection period, no concurrent air-quality measurements at ANL were available. Instead, air-quality data (coefficient of haze or elemental carbon, reactive hydrocarbons, CO, SO₂, NO_x, and O₃) were obtained from an Environmental Protection Agency air monitoring station in Joliet, 22 km south-southwest of ANL. Since sulfate was not monitored, visibility measurements at Midway airport, 22 km northeast of ANL, were used as a surrogate; sulfate is a primary constituent of the aerosol that reduces urban visibility. Meteorological data from ANL (wind direction, wind speed, relative humidity, rain rate, rain amount, rain duration, and time of rain) and the Total Totals Index (derived as explained by Sisterson, 1979) were chosen to characterize storm intensity and to test alternate rainout and washout hypotheses. Six-hour averages of air-quality and meteorological variables were considered representative of ambient conditions prior to storm development. Of the 85

rain samples collected, only 29 were clearly single event samples. A correlation analysis between rainfall chemical properties and meteorological and air quality information was performed on the subset of single event samples.

Table 1. Statistically significant correlations between rain chemistry and air quality and meteorological data.

Dependent variable	Independent variable	Correlation Coefficient	Number of points	Significance level, %
Hydrogen ion Concentration	CO	+0.484	28	1
	COH	+0.439	21	5
	(Visibility) ⁻¹	-0.438	28	5
	O ₃	-0.406	22	5
Strong acid Concentration	COH	+0.790	16	1
	O ₃	-0.361	22	5
	CO	+0.356	20	5
Sulfate concentration (in rain)	Storm type	-0.660	12	1

The only statistically significant correlation (Table 1) detected between rainfall chemistry and meteorological parameters indicates the expected dependence of sulfate concentration in the rain on the storm type; 44% of the variance is attributable to differences in storm type. As indicated by simple dilution models, the more intense the storm the lower the sulfate concentration in the rain. While correlation coefficients are quite small in this study,

Hicks (1979) shows that such correlations cannot be ignored. Visibility is significantly correlated with the hydrogen ion activity determined from measured pH and accounts for 19% of the variance; but visibility is not correlated with the strong, weak, or total acid concentrations. The lack of significant correlation between visibility and strong acid concentration may be due to the fact that Midwestern urban aerosols are dominated by neutral ammonium sulfate, which does not contribute to the acidity of the rain. The

correlation between visibility and hydrogen ion concentration, however, is surprising, and no simple explanation can be offered.

The correlation between hydrogen ion and strong acid concentrations is lower than would be expected. Although it is assumed that only strong acids determine the pH of a sample in Gran's procedure, weak acids (both organic and inorganic) are known to affect the dissociated hydrogen ion concentration. Acid titration performed on some of the rain samples indicates the presence of weak acids with dissociation constants similar to the pH of rain samples (pH 3.8 to 4.1).

The rainfall chemistry data yield statistically significant correlations with some unexpected air quality variables. As carbon monoxide and the coefficient of haze (a measurement of elemental carbon) increased and as ozone decreases, the strong acid concentration and hydrogen ion concentration both increase. The correlation of atmospheric carbon concentration with strong acid and hydrogen ion concentration in rainfall might support the hypothesis of the presence of weak organic acids in the rain samples, since these acids have dissociation constants similar to the pH of the rain and are interpreted as strong acids in the titration procedure.

Precipitation samples were also collected during 1979. It is hoped that added air quality instrumentation at the ANL site will minimize any effects of spatial separation in the comparison of rain chemistry to air quality data.

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pH MEASUREMENTS OF RAIN

D. L. Sisterson and P. M. Irving

Improper measurements of pH can result in errors as large as 50% in calculation of the concentration of dissociated hydrogen ions in solutions (Galloway, et al., 1979). While the acidity of a solution is typically expressed as pH, defined as $-\log [H^+]$ where $[H^+]$ is the hydrogen ion concentration, pH electrodes respond to the hydrogen ion activity $[H_a^+]$. In the discussion below, pH will be redefined as $-\log [H_a^+]$ both in text and equations (as discussed in Feldman, 1956).

FIG. 1.--Combination pH electrode.

The combination electrode (Figure 1), the type most commonly used for pH measurements of rain, combines the indicating and reference electrodes in one unit. The indicating glass electrode consists of an internal sealed tube containing a standard solution and a silver-silver chloride half-cell. The

immersion tip of this tube is a special glass bulb across which an electrical potential proportional to the $[H_a^+]$ of the sample is developed. The silver-silver chloride reference electrode, which provides a stable reference potential and completes the circuit, is enveloped in a 4 molar potassium chloride (KCl) solution, saturated with silver chloride. A ceramic junction allows flow of the KCl electrolyte from the reference electrode to establish a salt "bridge" or electrical contact with the sample.

To convert $[H_a^+]$ to $[H^+]$ the hydrogen ion activity coefficient A of the sample and of the buffer solutions in which the electrode is calibrated must be known. This coefficient is a function of the strength I of the sample and buffer solutions. For solutions where 10^{-5} molar $< I < 10^{-3}$ molar (typical of most precipitation samples), the Debye-Huckel expression for water at 25°C can be used to estimate $[H^+]$

$$[H^+] = \frac{[H_a^+]}{A} = (10^{-pH})(10^{\frac{1}{2}I}) \quad (1)$$

Within the above range of ionic strength Debye-Huckel approximation is accurate within 0.002 to 0.020 pH units. The ionic strength of standard buffer solutions used for calibration of the pH electrode fall into the upper range (10^{-3} molarity). Precipitation samples typically fall into the lower end of this range; however, some samples collected in relatively clean environments are as low as 10^{-6} molar, and others collected near the ocean and containing appreciable amounts of sea spray are well above 10^{-3} molar. In these cases, different expressions relating $[H_a^+]$ to $[H^+]$ should be used.

Operationally, pH electrodes approximate $[H_a^+]$ of a solution by the Nernst equation, which relates the potential measured by the pH electrode in a standard buffer solution to the rain sample by

$$pH_{rs} = pH_{bs} + \frac{(E_{rs} - E_{bs})F}{2.3 RT} \quad (2)$$

where pH_{rs} is the hydrogen ion activity of the rain sample, pH_{bs} is the hydrogen ion activity of the buffer solution, E_{rs} is the potential measured in the rain sample, E_{bs} is the potential measured in the buffer solution, F is Faraday's constant, R is the gas constant and T is absolute temperature.

In practice, the flow of KCl ions through the ceramic junction also creates a liquid-junction potential, E_{lj} , which represents the difference between junction potentials generated by the large differences in ionic strength of the rain samples and buffer solutions. This additional potential difference can cause errors larger than 0.04 pH units (Galloway et al., 1979), particularly in the case of rain samples collected near the ocean or in relatively clean areas. This error can be reduced by calibrating the pH electrodes in dilute solutions of strong acids or by increasing the ionic strength of the test solution by adding an inert salt such as KCl. However, the acid standards have no buffering capacity and must be routinely calibrated by titration, while trace contaminants in the KCl can greatly affect the pH of the rain sample.

Stirring a sample during pH measurement produces a "streaming" potential that can result in an error as large as 0.50 pH units. This error can be eliminated by thoroughly agitating the rain sample and allowing the solution to come to rest immediately before the pH measurement is made. Only after the meter reading is stable should the pH value be recorded.

The preferred way to determine the acidity of rain samples is by titration and construction of titration curves in the manner developed by Gran (1952). The principle behind Gran's plot is that when the hydroxyl ion forms, the titrant will act preferentially with the hydrogen ions in solution rather than with the hydrogen ions still undissociated with the weak acid anion. This procedure is accurate for determination of the strong, weak, and total acid concentrations of a rain sample unless weak acids are present. The latter may have dissociated constant at pH values of the rain. Therefore, acid titrations are necessary to determine the presence of the weak acids (Tissue, 1975). Because acid and base titrations involve stirring of the solution, the streaming potential will be large. Gran's procedure does not rely on the accuracy of values indicated by the pH electrode, but only on the differences in pH indications with successive additions of the titrant. Thus, streaming and liquid-junction potentials (as long as the stirring rate is constant) do not affect the measurement of the strong, weak, and total acid concentrations of

the rain sample.

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COMPARISON OF THE ACIDITY OF RAIN SAMPLES FROM ACM AND PNL PRECIPITATION COLLECTORS

D. L. Sisterson and G. T. Tissue

During the summer of 1979, a Battelle Pacific Northwest Laboratory (PNL) precipitation collector of the kind used in the MAP3S precipitation chemistry network and a commercially produced Aerochem Metrics (ACM) precipitation collector were operated at Argonne prior to commencement of sampling for the National Atmospheric Deposition Program and as part of an ongoing scavenging study under MAP3S. A study was made to determine the difference in acid concentration between rain samples collected by these two devices. Titrations were performed on 9 of the 12 rain events sampled by both collectors, with the procedure developed by Gran (1952) which allows comparison of the strong acid (A_s), weak acid (A_w), and total acid (A_t) concentrations. Two samples contained insufficient amounts of rain to titrate, and one sample became contaminated after collection.

The PNL collector features a polyethylene funnel and bottle assembly designed to minimize desorption and absorption of volatile species after collection. The funnel tapers from a diameter of 24 cm to an opening of 2.5 cm to which a 1 L polyethylene bottle is attached. The ACM collector resembles the more familiar Health and Safety Laboratory (HASL) design and uses a 13 L polyethylene collection bucket 28.6 cm in diameter.

The rain sensor for each collector consists of a 34 cm² stainless steel grid positioned above, but insulated from, a stainless steel plate. Water droplets bridging the gap between grid and plate complete a circuit to open the collector to rain. A heater warms the sensor plate during the wet cycle to increase the rate of evaporation and reduce open time of the collector after the cessation of rain.

Because the grid spacing on the PNL collector is smaller than that on the ACM apparatus, less rainfall is necessary to activate the PNL collector, which therefore opens sooner. The PNL collector has been observed to close sooner after a precipitation event, but it also cycles frequently in fog or dew. A

collector open during non-raining periods exposes the sample to contamination by dry deposition.

The PNL and ACM collectors were placed approximately 5 m apart in an open, grassy field. Rain samples were removed from the collectors after each rain event during the day. When rain occurred during the night, the samples were removed the following morning. Rain samples collected during the weekend were not removed from the collectors until morning. Each sample was then titrated as outlined elsewhere (Irving et al., 1979).

Rainfall sample acidity is summarized in Table 1. Six of 9 PNL rain samples had lower concentrations of strong acids, A_s , than ACM samples, but the average of the normalized differences [(PNL-ACM)/PNL] between the two collectors was not significantly different from zero. Each PNL sample had more weak acid, A_w , and total acid, A_t , than ACM samples, with an overall average of 15.0% higher A_w and 11.8% higher A_t per event after normalization.

Table 1. Comparison of titrated rain samples collected by PNL by ACM precipitation collectors. Sample 36 was collected during a weekend and not analyzed until Monday morning; evaporation may have been significant.

Sample No.	Amount of rain, mm	Calculated pH		Strong acid, 10^{-4} eq L^{-1}		Weak acid, 10^{-4} eq L^{-1}		Total acid, 10^{-4} eq L^{-1}	
		PNL	ACM	PNL	ACM	PNL	ACM	PNL	ACM
30	27.94	4.07	4.05	0.848	0.892	3.358	3.250	4.206	4.142
31	5.59	4.11	4.23	0.777	0.589	3.472	2.755	4.249	3.344
32	12.45	4.68	4.44	0.211	0.367	11.618	10.251	11.829	10.618
34	7.11	3.96	3.89	1.104	1.282	1.909	1.706	3.013	2.988
35	17.02	4.02	4.29	0.950	0.513	3.420	2.654	4.379	3.167
36	45.21	4.57	4.50	0.272	0.317	2.103	1.982	2.375	2.299
37	7.37	4.01	4.00	0.968	1.006	2.353	1.556	3.321	2.562
38	4.57	3.87	3.81	1.359	1.536	4.782	3.648	6.141	5.184
39	14.73	3.98	4.00	1.040	0.996	2.319	2.243	3.359	3.239

The acid concentration in rainfall is usually greatest at the beginning of a storm; thus PNL samples should contain a higher A_s because the PNL collector tends to open before the ACM collector during a precipitation event. Volatile (weak) acids should be retained more completely in the PNL samples because the funnel-bottle system inhibits gas exchange. As a result, the PNL collector should yield a higher A_t . In fact, the PNL samples did have higher A_w and A_t , but A_s was not significantly different. Differences in A_s between PNL and ACM samples for the same rain event were occasionally large.

No single explanation accounts for these differences. On the one hand the frequent cycling of the PNL collector, particularly during fog or dew, may expose the rain sample to species such as ammonia, ammonium bisulfate, or ammonium sulfate, which neutralize strong acids and/or increase the total acid concentration of the rain sample. On the other hand, the ACM samples collect rain in large buckets; even after the heaviest of rains, only a very small percentage of the bucket is filled, exposing a large surface area of the sample to the air. Enhanced exchange of volatile species between the sample and the head space might have many consequences, such as the loss of sulfurous acid or its conversion to sulfuric acid. Evaporation losses may be expected to be more serious with the ACM collector. In this study, however, 8 of 9 rain samples were collected within 6 hours after the rain stopped. Therefore, evaporation should not have contributed significantly to the observed results. Finally, the funnel of the PNL collector system may be a source of contamination, for it cannot be changed with the collection bottle, but must be rinsed regularly with deionized water. Otherwise, the frequent cycling of the collector leads to an accumulation of contaminants.

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CONTINUED EVALUATION OF THE TOTAL TOTALS INDEX AS AN AID TO FORECASTING THUNDERSTORM ACTIVITY IN NORTHERN ILLINOIS

D. L. Sisterson

Tests of the operational value of the Total Totals Index (TTI) as a predictor of thunderstorms within a 100 km radius of Argonne (see Sisterson, 1977; 1978) were continued during the 1979 thunderstorm season. These data have been used to quantify storm intensity as well as to prepare for rainfall collection for ongoing studies of wet deposition at ANL (Sisterson, 1979). As in previous years, the upper-air data used to compute TTI values, the 0600 CST sounding at Peoria, Illinois, were supplied by the National Weather Service office in Chicago.

The TTI is defined as (850 mb temperature - 500 mb temperature) + (850 mb dew point temperature - 500 mb temperature). Generally TTI values of < 40 indicate a relatively stable atmosphere; values > 50 indicate a highly unstable atmosphere. These critical values of the TTI are both geographically and seasonally dependent. In the 1979 study the critical TTI value for thunderstorm development was empirically determined to be 40 (43 in 1977, 42 in 1978). Severe weather occurrences were included as thunderstorms in this study. Since the TTI at Peoria is valid as a predictor for ANL only for southwesterly winds, only days with southwesterly flow were considered in the present analyses. During the 102-day study period, southwesterly winds (180 to 270° at the Peoria 850 mb level) occurred on 44 days.

A comparison of the TTI forecasts with observations is shown in Table 1. A chi-square test indicates significance at the 1% level. The skill score S, defined by $S = [(R-E)/(T-E)]$, where R is the number of correct forecasts, T is the total number of forecasts, and E is the corresponding number of correct forecasts that could have occurred by chance, is 0.38. Table 2 shows the frequency of events observed for all other wind directions. The flow was southwesterly on 43% of the study days, but 81% of all thunderstorms occurred when winds were from this direction. Thunderstorms occurred on 41% of the days with southwesterly winds, but only 10% of all other days.

Table 1. A comparison of 1979 TTI forecasts with
in conditions of southwesterly flow

Forecasts	Observations	
	No thunderstorms	Thunderstorms
TTI value		
< 40	11	0
≥ 40	15	18

Table 2. The distribution of 1979 thunderstorm days
by wind direction.

Wind direction	No thunderstorms	Thunderstorms	Total days
Southwesterly	26	18	44
All other	52	6	58
Total	78	24	102

Figure 1 contains a plot of the components of the TTI, convective instability versus static stability. The 45° line through the origin represents saturation at 850 mb, with the short lines parallel to it representing 850 mb dew-point depression lines. Lines of constant TTI are orthogonal to the dew-point depression lines. Fifty-five percent of the cases contained in the boundaries formed by the saturation and TTI - 40 lines represent occurrences of days with thunderstorm activity. In almost half of the cases, no thunderstorms occurred for values of TTI within these boundaries. These occasions are mostly explained by fronts having passed through Peoria but not reaching the Chicago area and these situations could not be determined a priori.

FIG. 1.--Plot of convective instability ($T_{d850} - T_{500}$) versus static stability ($T_{850} - T_{500}$), where T_{d850} is the 850 mb dewpoint temperature and T_{850} and T_{500} are the 850 and 500 mb temperatures at Peoria. Four no-thunderstorm points with abscissa values less than 5 are not plotted. Open circles represent no thunderstorms; solid circles represent thunderstorms.

In three years of testing, the Peoria TTI has provided an early means for assessing potential thunderstorm activity within a 100 km radius of ANL under conditions of southwesterly flow. Although thunderstorm activity

only occurred 55% of the time it was forecast in the 1979 study (77% in 1977, 63% in 1978), a forecast of no thunderstorms was correct 100% of the time. For winds from the other three quadrants, no thunderstorm activity occurred on 90% of the days regardless of the TTI values. Thus, the TTI provides a simple, objective assessment of the conditions to be expected later in the day.

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VARIATIONS IN THE AMBIENT OZONE CONCENTRATION DURING SOLAR ECLIPSE

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On 26 February 1979, a partial solar eclipse (approximately 80% of totality) provided an opportunity to observe the strikingly dynamic nature of ozone photochemistry. Ozone concentrations were monitored by a McMillian Model 1100 chemiluminescent ozone sensor, which is used routinely at ANL to monitor the ambient ozone concentration at a height of 3.7 m. The sensor lag time plus the time required for a 90% response to an imposed change in the ozone concentration is less than 10 s. Total solar radiation is measured nearby with an Eppley pyranometer.

During the daylight hours of 26 February, the wind direction was north to north-northeast at speeds between 4 and 8 m s⁻¹. Nephelometer data indicate that b_{scat} values were less than $1 \times 10^{-5} \text{ m}^{-1}$ until the late afternoon. Thus, no significant sources of pollution lay immediately upwind and pollution levels were low. About one hour after sunrise, the sun passed behind clouds, as can be seen in Fig. 1, and remained partially obscured for almost 2 hr. By 0915 CST the sky was practically clear and remained so throughout the remainder of the day. The eclipse began, reached a maximum, and ended at about 0936, 1052, and 1210 CST, respectively.

Figure 1 shows changes in total (direct plus diffuse) insolation and ozone concentration measured during the eclipse. The decrease in radiation follows the anticipated form. The changes in ozone concentration can be explained by examining the 3 fastest reactions involving nitric oxide (NO), ozone (O₃), and nitrogen dioxide (NO₂) (Leighton, 1961).

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Since these three reactions are faster than other reactions involving the oxides of nitrogen (NO_x), a steady state exists where the formation and destruction rates for NO_2 are equal; thus, $k_3[\text{O}_3][\text{NO}] = j(\text{NO}_2)[\text{NO}_2]$. Brackets denote concentration, k_3 ($= 0.00024 \text{ ppb}^{-1} \text{ s}^{-1}$; Hampson and Garvin, 1978) is the rate constant for reaction (3), and $j(\text{NO}_2)$ is the photolysis rate of NO_2 , which is directly related to the intensity of solar radiation. The steady state equation can be rearranged to give

$$[\text{O}_3] = j(\text{NO}_2)[\text{NO}_2]/k_3[\text{NO}]. \quad (4)$$

Thus, a reduction in $j(\text{NO}_2)$ should be accompanied by a reduction in both $[\text{NO}]$ and $[\text{O}_3]$ as they react with each other. Air quality data indicates that $[\text{NO}_2]$ was probably about 51 ppb^* . If $j(\text{NO}_2)$ is estimated to have been

FIG. 1.--Ozone concentration in ppb and total solar radiation in W m^{-2} on 26 February 1979.

* Concentrations of NO and NO_2 were determined from air quality data from Chicago, IL and Joliet, IL, 22 km south-southwest of Argonne. These data were modified to allow for local sources of NO in these urban areas, i.e. $[\text{NO}_2]$ was slightly increased and $[\text{NO}]$ was substantially decreased.

0.013 s^{-1} (Harvey et al., 1977), then at 1052 CST, in the presence of the eclipse, Eq. 4 yields an NO concentration of 19 ppb. If, in the absence of the eclipse, $j(\text{NO}_2)$ is estimated to have been 0.0065 s^{-1} (Harvey et al., 1977) and if the sum of [NO] and $[\text{NO}_2]$ remained constant, then Eq. 4 indicates NO_2 and NO concentrations of 37 and 33 ppb, respectively. Thus, the decrease in $[\text{O}_3]$ of 15 ppb is approximately matched by the conversion of NO to NO_2 ($33 - 19 = 14$ ppb).

With an approximate value for [NO], the expected lag time L between changes in the solar intensity and changes in $[\text{O}_3]$ can be calculated from (Hampson and Garvin, 1978)

$$L = (j(\text{NO}_2) + k_3[\text{NO}] + k_3[\text{O}_3])^{-1}. \quad (5)$$

The resulting lag time is about 100 s at the rapidly changing peak of the eclipse; this is consistent with the observed minima in Fig. 1, which are estimated to be less than two minutes apart. Time lags at the more gradual onset and end of the eclipse are thought to be the result of natural variations in the ambient $[\text{O}_3]$.

The data collected during the eclipse show the labile behavior of ozone in the boundary layer; researchers who use ozone as an atmospheric tracer or who measure the ozone concentration downwind of pollution sources should be aware of the related implications regarding the effects of variable cloudiness on the concentration of ozone over the regional areas commonly used in these types of studies. The effect of cloudiness on photochemical reactions in surface air has been noted previously (Harvey et al. 1977) but this might be the first observation of large changes in the ozone concentration resulting from a solar eclipse.

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