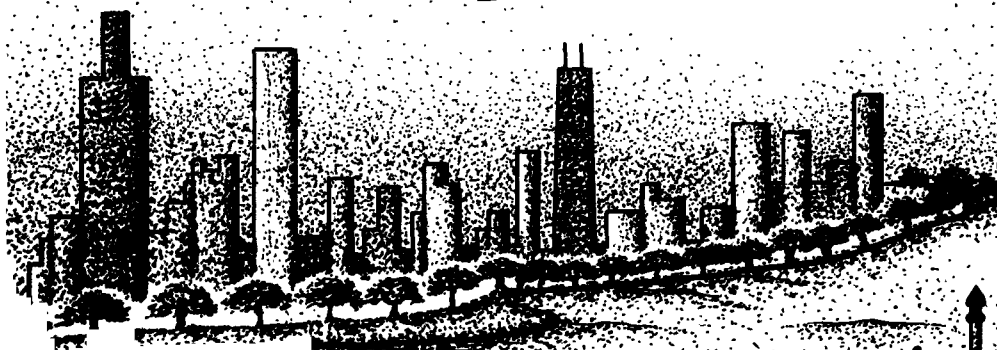
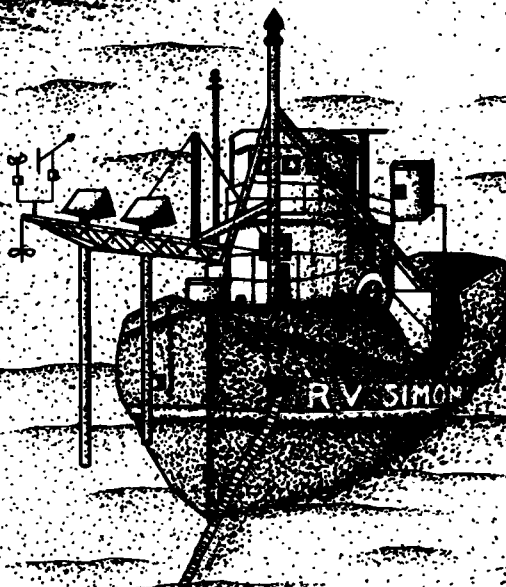


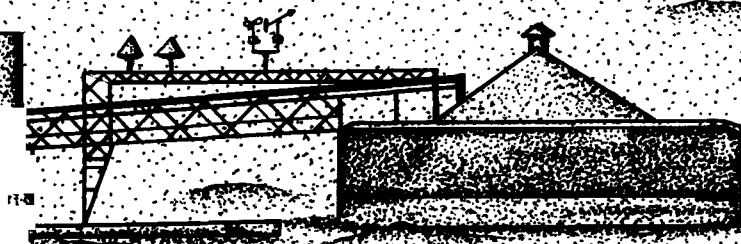
# Lake Michigan Atmospheric Loading



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SUMMARY REPORT  
FOR  
TWO YEAR PERIOD  
June 1976 - July 1978

OF

AN EXPERIMENTAL STUDY OF LAKE  
LOADING BY AEROSOL TRANSPORT  
AND DEPOSITION IN THE LAKE MICHIGAN BASIN

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## PREFACE

This summary of the first two years' data from the Lake Michigan Aerosol Loading study should be viewed as just that - a summary. We have confirmed the presented data base to be a quality one unfettered by contamination or instrument calibration errors. However, the large size of the data base has allowed us to only recently begin a detailed interpretation. It is for this reason that the present reporting is but a summary. The Interpretation section must be considered preliminary. At this writing only two of some fifteen or more scientific articles have been submitted for publication. Not only a thoroughgoing interpretation on our part but also a thorough critique by the scientific community are, thus, still wanting.

Because much of the data has not yet been analyzed only a small portion appears in this document. The oft referenced Appendix I computer printout of the complete data base is available at cost from the Principal Investigator upon approval from the U. S. EPA. The one other major data base not part of the computer printout is the NCAR air data. Because this data base is still in the raw interpretation phase it will be several months before the mesometeorological analysis is available.

We are indebted to many, many people who supported this effort. Mehul Dave' and Donald Dolske, full-time research associates, are most prominent in this regard. GSU students Mike Eason, Jil Forst, Vic Jensen, Pat McCoy, Rich Rupert, Neil Sutton and Keith Walther all contributed "flesh and bone" as well as brainpower. Grant secretaries Rebecca Borter and Elaine Sherman are especially acknowledged for their dedication in spite of the chaos presented to them. To staff of the U.S. EPA, especially Bob Bowden and Jerry Regan, we are most grateful. To Capt. McLain and his crew of the R/V Simons - thanks for bringing

us through those storms, for without you, we couldn't be writing this report. Finally, we thank the National Center for Atmospheric Research staff, especially Paul Spyers-Duran and Pete Orum for their assistance.

This work was done under U.S. EPA Grant #R00530101. I gladly accept full responsibility for this document. Any errors of omission or commission are my responsibility.

August, 1978

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## INTRODUCTION

As recognized in the original proposal for this grant project the need for meteorological and ambient air data over and on the Great Lakes is self evident upon reviewing model predictions of atmospheric loading to these lakes (Winchester, 1971, Skibin, 1973, Gatz, 1975, Sievering, 1976, and Eisenreich, 1977). Specifically, the transport processes as a function of climatology and, even more importantly, the deposition of low lying - hereafter, referred to as surface layer - ambient air constituents to Great Lakes water bodies is essential before any model calculations can be considered credible. The measurement of wet deposition as a function of over-lake rain climatology is being considered by other researchers (Bolsenga, 1974 and Murphy, 1976). The measurement of dry deposition to large lakes, especially of aerosols, has been largely neglected. A major purpose of this work is to determine the dry deposition of surface layer aerosol to Lake Michigan as a function of aerosol size and of surface layer meteorology. This surface layer meteorology or micrometeorology should be measured under sufficiently varying conditions to identify a microclimatology for aerosol dry deposition. This is so because of the much greater potential for Great Lakes loading in an unstable surface layer - i.e., when the air temperature,  $T_a$ , is less than the water surface temperature,  $T_s$ . Further, Sehmel and Hodgson (1974) found that for aerosol deposition to a water surface in a wind tunnel the rate of deposition or deposition velocity,  $V_d$ , of 2  $\mu\text{m}$  aerosols was several times that for 0.2  $\mu\text{m}$  aerosols (see Figure 1). A second purpose of this work is to determine trace metal and nutrient concentrations at representative locations on Lake Michigan to enable flux estimates. That is,

$$\text{Flux (F)} = \text{Concentration (C}_i\text{)} \times \text{Deposition Rate (V}_d\text{)}$$

where F is in  $\mu\text{g/sq. meter/second}$

$C_i$  is the concentration of constituent  $i$  in  $\mu\text{g}/\text{cubic meter}$  and

$V_d$  is the deposition velocity in  $\text{meters}/\text{second}$

Once having calculated these fluxes an overall loading in Tons/Year can be determined if a micro-and mesoclimatology for over lake waters is available. Determination of the microclimatology has been identified as a part of the first purpose of this work. An additional third purpose requires that a meso-climatology for the Lake Michigan Basin be determined. In essence this meso-climatology identifies constituent concentration as a function of location and time of year. No fully adequate way of doing this is available, primarily due to the extremely large spatial and temporal data base required. The approach used here is the intense collection of data during preselected periods of time. This data is then used to generate forward and back-trajectories at the meso-scale. With these trajectories in hand concentration variations on the lake-spatially and temporally-can be estimated and then combined with deposition velocities as a function of climatology to arrive at overall loadings.

To accomplish the three major purposes identified above a rather extensive sampling program is required. First, meteorological and aerosol sampling instruments were used aboard the R/V Simons at a midlake location-  $87^{\circ}00'$  and  $42^{\circ}00'$ - for approximately fifteen 24 hour sampling days during April to September 1977. These same instruments have been located at a City of Chicago nearshore location since May 1978. Second, aerosol samples collected on low trace metal and nutrient concentration filters have been analyzed by inductively coupled argon plasma (ICAP) emission spectroscopy

at the U.S.EPA's Central Regional Laboratory. The filters each carry only a three to six hour aerosol sample so that each filter set is obtained within a restricted micrometeorological regime. Because of this sampling requirement some trace metal filter concentrations are below ICAP detection limits.

A third major sampling developed a mesometeorological data base for trajectory analyses. In addition to obtaining National Weather Service and Coast Guard meteorological data during midlake and nearshore sampling an intense mesometeorological and aerosol concentration data base was generated through aircraft overflights in June and September of 1977 and May of 1978. This data has been supplied by the National Center for Atmospheric Research Queen Air Aircraft through an NSF supporting grant of nearly \$100,000.

The next section of this summary report reviews the data base so far collected and explains the intermediate stage of analysis which computer interpretation has afforded. To better appreciate this interpretation a brief review of the diabatic drag coefficient approach to the  $V_d$  calculation is warranted. A more complete description is found in the original proposal narrative.

Using the eddy view of atmospheric turbulence and assuming the surface layer over Lake Michigan to be a layer of constant mean aerosol flux (i.e., that the average rate at which material moves up and down is a constant with height within the surface layer) an expression for that flux is given by

$$Flux = \rho C_{DD} (\bar{a} - \bar{a}_0) (\bar{u}_a - \bar{u}_g)$$

where  $\bar{F}_A$  is the mean flux of constituent A

$\rho$  is the density of air  
 $\bar{a}$  is the mean concentration of A at some reference  
ht. within the surface layer (in this case 5 m)  
 $\bar{a}_0$  is the mean concentration of A at the air/water  
interface  
 $C_{DD}$  is the diabatic drag coefficient  
 $\bar{u}_a$  is the mean wind speed at the reference ht.  
 $\bar{u}_s$  is the flow speed of the air/water interface

The method of obtaining  $C_{DD}$  values is quite involved and is detailed in the Appendix of the original proposal. Suffice it to say that  $C_{DD}$  is determined from micrometeorological measurements of the air temperature, air/water interface temperature and of the surface layer wind speed. The mean wind speed, mean air concentration of a constituent and flow speed of the air/water interface are readily obtained. It is only regarding the air/water interface concentration of the constituent of interest that approximating assumptions need to be made. One approximation not invalid during unstable air sampling is that  $\bar{a}_0 = 0$ . This approximation is suspect for stable air sampling and clearly invalid when surface microlayers with high trace metal concentrations are present. The assumption that  $\bar{a}_0 = 0$  will first be made in the computer interpretation phase and then scrutinized in the section headed Interpretation.



## 1 DESCRIPTION OF THE DATA

The first two years of work have shown that our field study of midlake aerosol characterization and deposition, and the consequent application of the data to trace metal and nutrient loading estimations has been successful. The 1977 field program was supported by access to the R/V Simons as a midlake sampling platform, CRL's analysis of filter samples for trace metals and nutrients, and National Center for Atmospheric Research (NCAR) aircraft overflights for spatially distributed aerosol and mesometeorological data. The following section of this report is a description of the 1977 data base. Appendix A contains copies of all major computer printout components of the data.

The raw data collected on board the R/V Simons, manually calculated parameters, and results of chemical analyses from CRL have all been entered on permanent GSU computer system files. Additionally, copies of the data files are kept on magnetic tape cassettes at GSU as a safeguard against possible loss of data due to system failures. All of the computer data files have been manually edited and verified to ensure conformity to the original raw data. A series of twenty-five FORTRAN IV programs has been written to process the field data into a readable intermediate data base, presented in Appendix A and split into eight major divisions:

- A. Micrometeorology
- B. Trace Metal Concentrations in the Atmosphere
- C. Trace Metal Mass Flux
- D. Total Aerosol Mass Flux
- E. Phosphorus, Nitrate, and Sulfate Atmospheric Concentrations
- F. Phosphorus, Nitrate, and Sulfate Mass Flux
- G. Trace Metal Concentrations in Lake Water

Each of these eight divisions is described below. The description relates the raw data elements used in processing to the final printed results shown in the various tables.

#### A. Micrometeorology

The first section in this division contains micrometeorological data for each of the filter set sampling periods. The mean, standard deviation, and number of measurements in each set are shown for water surface temperature ( $T_s$ ), air temperature ( $T_a$ ), and wind speed ( $U_a$ ).  $T_s$  is measured by a downward looking infrared sensor, while  $T_a$  and  $U_a$  are measured at the five meter sampling height with standard meteorological instruments. Mean surface water current speed ( $U_s$ ) is also shown for each set.

These data enter into the calculation of the diabatic drag coefficient ( $C_{DD}$ ) which is "at the heart" of this experiment. The critical parameters for this calculation are shown (mean and standard deviation included) on the lower part of each page. They are ( $T_a - T_s$ ), the temperature difference between the air at 5 meters and the surface, and ( $U_a - U_s$ ), the difference in speed between the air at 5 meters and the surface of the lake. The stability parameter(s), a function of wind speed and ( $T_a - T_s$ ), identifies the extent to which loading to the lake is affected by micrometeorology. Results of the  $C_{DD}$  calculation were obtained manually but are now displayed in Section 1a.

The  $C_{DD}$  values are shown as a mean result with a minimum and maximum value which represents one standard deviation extremes. To additionally characterize micrometeorological conditions averaged across a filter set period, the local Richardson number ( $R_i$ ) was calculated.  $R_i$  is a measure of the tendency for turbulence initiated in the surface layer to be self-

sustaining. Lastly, the deposition velocity ( $V_d$ ) for each filter set is shown. This value is based on the mean  $C_{DD}$  for each set.

From this micrometeorological data, it is possible to exclude from further flux calculations certain filter sets. Using the criteria that  $(U_a - U_s)$  should be greater than 2.0 m/s for the  $C_{DD}$  theory to be reliable, and that  $R_i$  should be less than 0.25 (an empirical critical value, above which turbulence may be suppressed), sets 10010, 10020, 10040, 20080, 20120, 30210 must be excluded. For these sets, and during stable air summer season periods with  $(U_a - U_s) \leq 2.0$  m/s or  $R_i \geq 0.25$ , an assumption that no deposition takes place is made and is certainly conservative. Climatologically this situation occurs no more than 2.5% in March, 4% in April and May, 4.5% in June, 5.5% in July, 6.0% in August, 3.5% in September, and 3.0% in October and probably not at all in November through February (NOAA SSMO, 1975)

Section 2 of the micrometeorology printout contains the means on, and standard deviation in, wind direction data for each filter set. Also printed are barometric pressure data for the sampling periods. An assumption underlying the application of  $C_{DD}$  theory requires the wind direction to be fairly steady. No strictly quantitative definition of this steadiness is available, however. Here, a value of 30° to 40° standard deviation about the mean defines "unsteady" wind field conditions. Thus, two filter sets, 20150 and 40370, must be excluded in addition to the six above.

Although not strictly part of the microscale data base, an additional consideration for  $C_{DD}$  theory application is that relatively constant meteorology prevails for at least 5 km upwind of the sampling location during stable air conditions. (2 km or even 1 km suffices during unstable periods.) When-

ever macroscale fronts appeared on southern Lake Michigan, the related filter set was excluded. This eliminates sets 30220 and 40310. In summary, then, of the 56 total filter sets collected, ten must be excluded from flux calculations (and four were blanks), leaving 42 sets which warrant application of the  $C_{DD}$  theory and trajectory analysis.

#### A'. Mesometeorology and Trajectory Analysis

Though not part of the computerized data base, National Weather Service, Coast Guard, and City of Chicago meteorological data were plotted on bi-hourly southern Lake Michigan maps along with the shipboard data at 87°00' and 42°00'. This data base, along with calculated geostrophic wind vectors at four points over the southern portion of the Lake, allowed self-consistent air parcel streamlines to be drawn on each bi-hourly map--except for the May outing, when mesometeorological conditions were too complex. Forward trajectories, initiated from Midway Airport, temporally linked the individual maps. Air parcel trend lines--both spatial (streamlines) and temporal (forward trajectories)--are thus available to relate aerosol and aerosol constituent concentrations at the midlake sampling point to source regions. An example is shown in Figure 2.

An alternative method for source identification is the use of back-trajectories. In principle a more accurate approach than forward trajectories (simply because the trajectory is initiated at the sampling point), the lack of meteorological data near to the sampling point (ship) forced the use of the ship wind vector for most of the mesoscale trajectory (i.e., to shore). An example back-trajectory is shown in Figure 3. Macroscale back-trajectories based upon the model of Heffter and Taylor (1975) were also plotted by EPA Research Triangle Park.

During the June and September 1977 and May 1978 outings, an NCAR Queen Air aircraft collected mesometeorological and vertical sounding data to enable mesometeorological analysis and improved back trajectories. These data have been received (see example midlake sounding Figure 4) and will be used over the coming months. Plans for vertical soundings to be taken on board the Simons throughout the field program failed because the Contel Corp. Metrosonde purchased for this purpose never functioned properly. Emphasis may have to be placed on the June and September 1977 and May 1978 sampling periods for which the NCAR Queen Air gave a full complement of mesometeorological data.

#### B. Trace Metal Concentration and Enrichment Factors

Trace metal concentration data is specified within each set by stage of each filter set. Figure 5 displays the collection efficiency of each stage using Misco filter media for ambient lake aerosol. It is clear that the 1  $\mu\text{m}$  and larger aerosol usually referred to as primary aerosol--is most efficiently collected by the first stage, with the remainder of the primary aerosol collected by the second stage. The third stage or backup filter most efficiently collects the 0.7  $\mu\text{m}$  and smaller aerosol--referred to as the secondary aerosol. The trace metal concentration data as a function of stage therefore carry a physical significance. That is, the first stage data identify that mass portion of the trace metal under consideration which is related to primary ( $d \geq 1.0 \mu\text{m}$ ) aerosol while the backup stage specifies the mass portion related to secondary ( $d \leq 0.7 \mu\text{m}$ ) aerosol. Note that all these trace metal concentrations have been blank corrected by subtracting the mean metal concentration of eight blank Misco

filters taken through all handling procedures except that no ambient air was drawn through them (See Table 1 for blank filter concentrations).

Section three of Appendix A, then, contains the trace metal concentration data as measured at midlake. The top portion of each page gives the "run time" for each set. This is the time in minutes over which the filters were exposed at 40 cfm to the ambient air. Also given are the results of three supportive measurements: Condensation Nuclei Counter, Integrating Nephelometer, and Total Mass Monitor data (where available from the University of Wisconsin).

A brief explanation of the filter set numbering system here will make the trace metal data in Section 3 much more readable. All samples taken during a given set have a five-digit number, which encodes the following information:

set number: A B C D E

A -- first digit corresponds to the outing number, where

1 = April 1977  
2 = May 1977  
3 = June 1977  
4 = August 1977  
5 = September 1977

BCD -- three digit sequential sampling period number,  
000 - 056 for 56 sets completed in 1977

E -- last digit corresponds to type of sample. These additional key values for the last digit will be explained when first used in each section of Appendix A.

The results of ICAP analysis were blank-corrected, Yttrium-normalized, and run time compensated, resulting in the values shown in Section 3 in units of  $\mu\text{g}$  of metal per cubic meter of air. There are four rows of data for each filter set:

ABCD1 = first stage collected aerosol  
ABCD2 = second stage collected aerosol  
ABCD3 = backup filter collected aerosol  
TOTAL = arithmetic sum of all stages

These four rows of concentration data appear in 17 columns, one for each metal analyzed for by ICAP. These concentration data form a second critical part of the data base required for performing lake loading calculations by the  $C_{DD}$  method. Too little data were obtained by ICAP analysis for Na, Cd, Co, Ni, and V to be meaningfully used in further statistical calculations. This was due to the relatively short average run time (240 minutes) for the filters which caused very low concentration elements to fall below the ICAP detection limits ( $L_d$ ). In the case of Na, a very high  $L_d$  applied from September 1977 onward effectively negated earlier reported Na results. This came about because, in an effort to be self-consistent despite changing ICAP  $L_d$  values, the highest  $L_d$  used during the April to September 1977 period was applied to the whole period. This resulted in some of the blank samples being essentially based on high  $L_d$  values. Immediately following the data for set 50560, the original data from CRL's ICAP analyses is included in the print.

From the chemical characterization viewpoint the concentration data can be looked at aggregated as an overall average for each metal. This compilation is given in Table 2.

A common term used to describe the relative contribution to trace metal mass in aerosol of a particular metal is the enrichment factor (EF). This factor is defined as a ratio of concentrations:

$$EF = \frac{\frac{\bar{c} \text{ in air of metal } x}{\bar{c} \text{ in air of standard metal}}}{\frac{\bar{c} \text{ in crustal rock of } x}{\bar{c} \text{ in crustal rock of standard metal}}}$$

Typical standard metals are Al, Fe, Na, and Ti. The most consistent and reliable results for EF were obtained by using Al as the standard. In

Table 3, overall average  $\overline{EF}$  numbers show the extent to which certain aerosol components are increased in relative concentration over that which could be expected if all of that aerosol component were crustal-derived.

It is immediately apparent from these  $\overline{EF}$  data that Pb, Zn, and Cu are extremely enriched in low lying air over the lake.

Lastly, another type of information that can be gleaned from the concentration data is the percentage of each metal's concentration associated with primary and secondary aerosol. In Table 3, note that the percentage of each metal's mass collected on the second stage filter is not identified with either primary or secondary aerosol. This is because the second stage acts to improve distinctness in primary/secondary aerosol between the first stage and backup, but does not itself represent either of these aerosol size classes clearly (see Figure 5).

### C. Trace Metal Mass Flux

The data in this section are calculated from the equation:

$$\text{Flux} = V_d \cdot C_{ij}$$

where  $C_{ij}$  is the concentration of metal  $i$  on filter state  $j$ . Note that this calculation assumes that  $V_d$  is not a function of particle size and that the concentration of aerosol metal at the air/water interface is very small compared to the air side concentration. More will be said about these two assumptions at the conclusion of the next section. The data shown in the computer printout is of value principally in comparing loading rates in one set to those in another particular set. Of more importance and impact are the values shown in Table 5. Each of the columns in Table 5 represents the results of a method of estimating a flux from the data obtained in the 1977 field program.



First, the overall average method takes the mean  $V_d$  for all non-excluded filter sets ( $0.69 \pm 0.51$  cm/s) and products this by the mean of all data on each metal. This flux is then converted to an annual loading by an overall time-area factor,  $F_{ta}$ .  $F_{ta}$  is the product of the area (of the surface to which deposition is occurring) and the time (during which deposition occurs). The area here is  $2.9 \times 10^{10}$  m<sup>2</sup> for the southern basin of Lake Michigan, and time is 0.85 year. Fifteen percent of the time on average across a year, trace or more precipitation occurs over the lake (Sievering, 1976). Thus, 0.85 year is the fraction of time when dry deposition can occur.

Second, it is possible to group filter sets together by similarities in meteorological conditions. Wind speed "bins", defined by ranges of wind speeds in meters/second as follows: 0 - 2.2, 2.3 - 3.5, 3.6 - 5.2, 5.3 - 8.5, and 8.5+, were set up. Filter sets with average wind speeds falling into these bins were grouped together, and actual  $V_d$  values for the bins were then determined. Using climatological data (NOAA SSMO, 1975),  $F_{ta}$  for each bin could be determined. The loadings for these bins were summed up to give an annual loading, which was further normalized to the 0.85 year dry deposition period. The results of this calculation are shown in the second column of Table 5.

Third, exactly as the wind speed bin calculation was done, filter sets were grouped together by temperature stability, ( $T_a - T_s$ ) or  $\Delta T$ . Bins for this parameter, in units of °C, were set up as follows:

$\Delta T \leq 0.9$ ,  $-0.9$  to  $+0.8$ ,  $1.0$  to  $2.7$ ,  $2.8$  to  $+8.1$ , and  $>8.2+$ .

This calculation results in the lowest annual loading totals of any of the three estimation methods given in Table 5.

#### D. Aerosol Mass Flux

The data in this section are sampling set totals of particle number counts, obtained from the Active Scattering Aerosol Spectrometer (ASAS). The ASAS counts aerosol particles in 15 size channels in each of four size ranges, i.e., a total of 60 size channels covering the overall range 0.09 - 3.53  $\mu\text{m}$  diameter. Table 5 is a complete listing of the geometric mean size aerosol counted in each channel. The mean flux printout in Appendix A. not only gives the total counts in each of the 60 channels for each sampling set, but also expresses a total flux in  $\text{ng} - \text{m}^{-2} \text{ sec}^{-1}$ .

The actual particle counts make up the bulk of the table. However, it is important to note that these counts must be normalized to unit time with the accumulation time shown in the upper right part of the table. This is due to the elimination of certain portions of the data when actual number counts exceeded the memory capacity of the data accumulation system of the ASAS. Thus, the total counts shown represent different total times during which the ASAS was "looking" at a given size range.

A mass flux for the total counts in each size range is given at the bottom of each page. At the left top, two non-overlap total ASAS fluxes are given. As can be seen in Table 6, there is some duplication of counts in several channels toward the ends of adjacent ASAS size ranges. These overlaps can be excluded in two ways: by excluding the higher size range overlap portion (labelled >), or by excluding the lower size range portions (labelled <). The total number counts generate mass flux results for total aerosol in the 0.09 - 3.53  $\mu\text{m}$  range by the following equation, which is an application of the  $C_{DD}$  theory:

$$\text{Flux} = \frac{\bar{\rho}_a C_{DD} \sum n 4\pi \bar{r}^3 (\bar{u}_s - u_o)}{3 V_s T_{acc}}$$

where

$\bar{\rho}_a$  = mean aerosol density,  
 assumed here =  $1.5 \text{ g/cm}^3$   
 $C_{DD}$  = diabatic drag coefficient  
 $\sum n$  = total number count  
 $u_5 - u_0$  = wind speed at 5 m, minus  
 lake surface current  
 $\frac{4}{3}\pi \bar{r}^3$  = volume of particle at  
 mean radius of size range  
 for which  $E_n$  was calculated  
 $V_s$  = sampling volume per second of  
 ASAS, a constant of  $0.28 \text{ cm}^3 \text{ s}^{-1}$   
 $T_{acc}$  = total accumulation time  
 in seconds for the size range  
 being considered

An important consideration in characterizing midlake aerosols is a description of the particle size distribution. For the  $0.09$  to  $3.53 \mu\text{m}$  diameter particles "seen" by the ASAS, this distribution is best visualized by a plot of  $\Delta n / \log \Delta r$  versus  $r$  (see Figure 6 for plots of monthly averages).

## 2. Phosphorus, Nitrate, and Sulfate Concentration Data

Concentration data for total inorganic Phosphorus, Nitrate/Nitrite, and Sulfate (hereafter P-N-S) is reported as a function of filter set and stage of each filter set. As was done with trace metal data in section B, it is possible to relate the portion of P-N-S filter concentrations to be blank corrected by subtracting the concentrations reported for filters taken through each step of the procedure except ambient air sampling.

Table 7 gives the mean concentration data of P-N-S observed during the April through September 1977 field program. It is significant that all of these potentially nutrient-available species are strongly associated with secondary aerosol ( $d \leq 0.7 \mu\text{m}$ ). The secondary aerosol, having a higher surface-to-volume ratio, may tend to make the aerosol forms of P-N-S more soluble and therefore more available to the lake biota. Also, in the form of secondary aerosol, atmospheric transformation reactions are more likely to affect the concentration and forms in which Phosphorus, Nitrogen, and

Sulfur are to be found.

Note that in Appendix A., the sample identification key for the P-N-S samples is as follows:

ABCD6	- 1st stage collected (primary aerosol)
ABCD7	- 2nd stage collected aerosol
<u>ABCD8</u>	- backup collected (secondary aerosol)
ABCDØ	- Total c of all stages

F. Phosphorus, Nitrate, and Sulfate Mass Flux

Using the same method by which trace metal fluxes and annual loadings were calculated in section C., similar results are shown for the P-N-S data. In Appendix A., the sample set derived results are shown. Table 8 is a listing of annual P-N-S loadings by overall average and micrometeorological data groupings, similar to Table 5 for trace metals. The relative importance of atmospheric route loadings of P-N-S are shown in Table 9 by comparison to water shed input and wet deposition. However, the ultimate importance for these nutrient species may be of a more subtle and insidious nature. Due to the critical roles of these nutrients in the lake ecosystem, any source of input of P-N-S will have direct effects.

G. Trace Metal Concentration in Lake Water

Two tables of trace metal concentration data are presented in Appendix A. The first table contains the results of ICAP analysis of bulk water, i.e. composite samples of water taken a 3, 5, and 7 meter depths. The second table, where the sample identification number is ABCD40, contains results for surface water samples, taken with a surface microlayer screen sampler (Elzerman, 1976). All of the water data is intended in this study to enter into the interface aerosol metal concentration term of the  $C_{DD}$  - derived flux equations. However, inadequacy of current theoretical models for transfer mechanisms of

aerosol across the air/water interface has forced this term to be assumed as small compared to the air side concentration. This assumption will be discussed in detail in the Interpretation section. Table 10 is a comparison of the mean concentrations of several metals in surface versus bulk lake water for the 5BCD<sup>4</sup> series of samples. These data clearly suggest a trend towards surface microlayer enrichment for many metals.

## II INTERPRETATION

### A. Concentrations

Since the flux is a product of specie concentration and deposition velocity, the interpretation section is divided into Concentration, Deposition Velocity, and Consequences.

The average midlake aerosol concentration was found to be  $45 \pm 10 \text{ ug/m}^3$ . About 10 to 20% of this midlake aerosol is trace metal contributed with sulfate and nitrate/nitrite each contributing another 20% or more. A comparison of aerosol mass concentration (M) with integrating nephelometer optical scattering ( $b_{\text{scat}}$ ) signals suggests that a linear regression with strong correlation exists over Lake Michigan. The equation is

$$b_{\text{scat}} = 0.298 + 0.0138M \quad (1)$$

with an  $r = 0.97$ . A strong linear correlation has been found by other researchers in urban environments (Charlson, et.al (1969), Kretzschmar (1975)), but the slope of equation (1) is much less than urban related correlations. This linear regression equation and the high correlation between  $b_{\text{scat}}$  and M suggest that fewer large aerosol may contribute to midlake mass concentration than in urban environments. If one assumes the aerosol density to be constant with aerosol size, then mass is proportional to aerosol size. One can then expect less variability in aerosol mass as measured by the integrating nephelometer for midlake aerosol. This is an important reason for the correlation coefficient of the above equation to be 0.97.

The log-log plot of ASAS aerosol counts (see Figure 6) confirms the IN data in suggesting that midlake aerosol concentration may be dominated by secondary aerosol. A best fit straight line to such log-log plots results in a slope of -2 to -3 for urban polluted and rural continental air. Marine air and upper

level air often exhibit slopes of -3 to -4. The fact that the average slope for the 1977 field program is -3.25 is strong confirmation that the midlake aerosol is depleted of primary aerosol. Further resolution of the data base gives slopes of -2.3, -3.4, -3.3 and -3.8 for May, June, August and September data respectively. The stable air of the May Outing forces many of the secondary aerosol to remain above the thermal internal boundary layer (described later) while increasing the number of primary aerosol by suppressing dispersion within the surface layer. Except in this strongly stable air the slope of the log-log plots support the conclusion that secondary aerosol predominate the midlake aerosol.

This conclusion explains the predominance of trace metal on the backup filter even for metals such as Fe and Zn (see Table 4). If the concentration of metals is dominated by that portion associated with the secondary aerosol one might conjecture that much of these metal concentrations in the atmospheric surface layer at midlake is man derived. Lake derived contributions would tend to be associated with large aerosols (Duce, 1976 and MacIntyre, 1974). By using average crustal rock trace metal concentrations for rock most prevalent in the Great Lakes basin (Wedepohl, 1971) and the average bulk water trace metal concentrations measured during the 1977 field program the percent of each trace metal that is derived can be estimated. Using Al again as the reference metal in air and Mg as the reference metal in Lake Michigan waters, the resulting estimates are shown in Table 11. That 90% and more (99.9% of Pb) of several metal midlake concentrations are neither crustal nor lake derived is quite dramatic. One is tempted to relabel "unexplained" as "anthropogenic". However, one should not rule out the possibility that large lake-derived aerosols may fractionate in air to create small aerosol with metal concentrations no longer representative of their relative concentrations in lake water (Duce, 1976).

Correlation coefficients using filter set average concentrations of metals, P,  $\text{NO}_3^-$  and micrometeorological data are shown in Table 12. Any correlation coefficient 0.7 or greater is circled. Almost no correlation of micromet data with metal P or  $\text{NO}_3^-$  data is found, whereas inter metal and  $\text{NO}_3^-$  correlation is quite prevalent. The correlation of P with other data is present but usually not with high correlation. The generally negative correlation between wind speed and other variables indicates lower midlake concentrations with higher wind speeds. However, the small magnitude suggests very little dependence on this factor. The high correlation of  $\text{NO}_3^-$  with  $\Delta T$  supports the notion that in situ chemical generation of  $\text{NO}_3^-$  is significant.

The correlation coefficient matrix of Table 12 does not well identify groups of factors that may be co-related. Factor analysis is a statistical technique which can give additional information by using linear combinations of the factors in the correlation coefficient matrix. A preliminary use of factor analysis has identified the following elemental groups:

- Group 1 - Cu, Fe, Mn, Mo, Pb, Zn and Mass
- Group 2 - Ca, Mg, Al, Ba, Fe, Mn and Ti
- Group 3 - Ti, P and  $\text{SO}_4^{--}$
- Group 4 -  $\text{NO}_3^-$ ,  $\text{SO}_4^{--}$  and  $\Delta T$

The first group is clearly the secondary aerosol metals. Note that mass is correlated with these metals. The second group is the primary "soil derived" aerosol. Pollutant and lake-derived source contributions may, however, contribute to this group. Group 3 may be a lake-derived source and group 4 is clearly the chemically (in air) generated aerosol. Of the 90% or more "unexplained" elements in Table 11 only Ti is not part of Group 1. This grouping by factor analysis is strong evidence that, except for Ti, the lake-derived large aerosol fractionation is not a contributor to the otherwise anthropogenic source of the metals Cu, Pb, Zn, Mn, Mo and Fe.



Another fruitful way to view the metal concentrations is through the use of scatter-diagrams (Rahn, 1976). Quite characteristic patterns appear when the enrichment factor for a metal of interest is plotted versus the concentration of the reference metal - in this case Al. An example is shown in Figure 7, the scatter-diagram of Pb versus Al. Note that data collected in April 1977 is also plotted here even though it was not used in loading calculations. This scatter-diagram is not significantly different from that found in other literature. The area within the dashed line is where the bulk of other reported Pb enrichment factor data resides. Data points below the dashed line are not uncommon and indicate cases in which the Pb concentration is about equally contributed to by primary and secondary aerosols. Data points to the upper left of the dashed line are rare. A goodly number of June, August and September data points appear in this area. This is strong evidence that the primary aerosol containing 40% or more of the atmospheric Al concentration is depleted before the midlake sampling point. In addition, relatively little Pb has been depleted. Thus, a very large Pb enrichment factor with a low Al concentration results.

A second scatter-diagram is presented in Figure 8 - that for Ti. Most researchers have reported a trend toward constant enrichment factor. The data of Figure 8 suggests instead a trend toward constant concentration. This would indicate that a relatively constant source of Ti is present at midlake. Either the lake is indeed a source for Ti or despite all precautions the Simons effluent may have been a contaminant source. That the lake is a source for Ti is also supported by the factor analysis results and the data of Table 4. Fully 40% of the Ti concentration at midlake is associated with the primary aerosol. This portion of the Ti concentration is

likely to be lake-derived as against contaminant derived. Other scatterdiagrams not shown give additionally useful interpretation. One particular example is the scatterdiagram for Mg which substantiates the very strong source the lake is for mid-Lake Michigan Mg concentrations. The use of Mg as our lake source reference metal is, therefore, substantiated.

The preceding discussion of trace metal and P, N, S specie as well as mass and number concentration is incomplete without an understanding of the mesometeorology surrounding the concentration data base. As pointed out in the Introduction the concentration data must be viewed as a function of location and time of year. Though some of this mesoclimatological view can be obtained from the previous discussion it is the trajectory analyses at the mesoscale that can best generate mesoclimatology data needed for a good understanding of spatial and temporal variability in concentration. Some preliminary analysis will be reviewed here.

A first useful parameter for mesoclimatology is the so called dispersion factor, the product of the mixing height and mean wind speed. Edwards and Wheat (1978) have shown this dispersion factor to be well correlated with atmospheric lead concentrations in Denver. A correlation between monthly mean dispersion factors across a 42-month period concludes that variability in the dispersion factor alone accounts for 69% of the variability in the lead concentrations. Monthly mean mixed layer wind speeds would have given a better correlation. Still better would be to use emission factors producted by the inverse of the dispersion factor.

Data for the southern basin of Lake Michigan may not suffice to determine emission factors (although this will be scrutinized). However a four year record of low level soundings at Midway Airport does allow the determination

of mean mixed layer winds and of the mean mixed layer height. Use of the mean mixed layer winds makes their extrapolation to the southern basin much more acceptable. By the two major periods over Lake Michigan (i.e., warm season - May through October and cold season - November through April) the mixed layer heights are 1400 m in the warm season and 850 m in the cold season. The mean mixed layer winds are 6.8 m/s in the warm season and 7.8 m/s in the cold season. Thus, the dispersion factor is 9520 in the warm season and 6630 in the cold season. Concentrations of metals such as Pb are then proportional to the inverse of the dispersion factor. This level of disaggregation is, of course, not sufficient to specify a concentration mesoclimatology for the southern basin of Lake Michigan. One could disaggregate by month although the concentration climatology is more likely to be dependent upon air mass type. An analysis of the Midway soundings by air mass type tentatively has concluded:

Warm Season - 30% continental polar, 1500 m MLH  
35% maritime tropical, 1275 m MLH  
25% uncertain, 1150 m MLH

Cold Season - 15% continental arctic, 1000 m MLH  
25% maritime polar, 900 m MLH  
10% maritime tropical, 875 m MLH  
25% uncertain, 775 m MLH

10% of the warm season and 25% of the cold season air masses can be designated washout air masses due to precipitation of 0.01" or more.

Clearly, further consideration will have to be made of the meteorological data base in the southern basin of Lake Michigan. In particular, soundings at Midway must be compared to those taken over Lake Michigan by the NCAR aircraft to obtain a mesoclimatology of the dispersion factor. Analysis such as the foregoing should eventually lead to a statement on the concentration climatology over Lake Michigan.

## B. Deposition Velocity

Use of the diabatic drag coefficient theory has given a grand average  $V_d$  encountered during the 1977 field program of  $0.8 \pm 0.5$  cm/sec. Extreme values were 0.09 and 1.66 cm/sec. Means for the May, June, August and September Outings were  $0.22 \pm 0.14$ ,  $0.28 \pm 0.17$ ,  $0.89 \pm 0.31$  and  $1.12 \pm 0.40$  respectively. This  $V_d$  is obtained by first determining a neutral drag coefficient for the wind speed regime in which one sampled (See Figure 9). Then a ratio of diabatic to neutral drag coefficient is obtained for the temperature stability regime present during sampling (See Figure 10). As already pointed out, the diabatic drag coefficient approach should give good results except when  $(\bar{u}_a - \bar{u}_s) \leq 2$  m/s or the local Richardson number,  $R_1$ , is greater than 0.25. At these values surface drag and surface layer turbulence have been suppressed to the point that a laminar sublayer may develop at the air/water interface. Once this phenomenon occurs there is likely to be little or no deposition occurring. Only a few such cases appear in the 1977 data base.

The mean  $V_d$  by Outing (0.22, 0.28, 0.89 and 1.12) compare favorably with other data found. Sehmel and Sutter (1974) found values of 0.01 cm/s and larger for deposition of particles of density  $1.5 \text{ gm/cm}^3$  depositing on a water surface in a wind tunnel. However, a strong dependence on surface roughness was found. Cawse (1974) found  $V_d$  of 0.1 cm/s and larger for a filter surface exposed to ambient air. The real environment surface of Lake Michigan not only affords substantial roughness compared to a wind tunnel having a water surface but also may afford other and more efficient mechanisms for deposition than a filter surface exposed to ambient air. In particular, a recent study by Stulov, et. al. (1978) considers the efficiency of collision of aerosols with water surfaces. It was shown that at a clean water surface all collisions are effective

and lead to aerosol transfer into the water medium. However, when aerosols collide with other aerosols previously deposited on the water surface they usually rebound. Thus a  $V_d$  of 0.2 up to 1.0 cm/s and larger is certainly feasible.

The work by Stulov also addresses the assumption that  $\bar{a}_0 = 0$ . It was noted in the Introduction that this assumption was made for all calculations in the Description of Data section. Mass flux calculations using the ASAS number concentration data can safely assume  $\bar{a}_0 = 0$  for the surface of Lake Michigan rarely affords a significant probability for aerosol-aerosol collisions. Possibly when the laminar sublayer is present aerosol may collide with aerosol instead of the water surface itself. However, in these instances  $V_d$  has already been assumed to be zero. Further support for the appropriateness of  $\bar{a}_0 = 0$  is given by the work of Meszaros (1977). She has found that 90% of summer continental aerosol not unlike that seen over Lake Michigan and in the size range  $0.02 \leq r \leq 100 \mu\text{m}$  is water-soluble and 50% or more is water-soluble in winter months.

Regarding specie specific fluxes the  $\bar{a}_0 = 0$  assumption is more difficult to accept. However, the combination of arguments applied to metal concentrations earlier also applies here. The Table 11 result suggesting 1.0% or less of Pb, Zn, Cu, Mn, Fe and Ti and only 2% of Mo midlake concentrations are lake-derived is a strong indicator that the air/water interface concentrations of these metals are generally far less than that measured at the 5m height. The tentative grouping of metals by factor analysis supports the notion that these metals, except for the anomalous case of Ti, are not lake-derived despite the possible fractionation of large lake-derived aerosol into less than  $1 \mu\text{m}$  diameter aerosol. More importantly, the work of Stulov (1978) and of

Meszaros (1977) suggest a near 100% efficiency of collision and better than 50% water solubility of aerosols throughout the year. Thus, the number concentration of aerosol and mass concentration of non-volatile, non-reactive elemental species should change across the air/water interface. Of course, the exception to this rule is when the laminar sublayer prevails and greatly reduces the probability of collision between aerosol and the lake surface.

Under the assumption of a smooth continuum of concentration the profile method of measuring  $V_{dp}$  (call it  $V_{dp}$ ) may be applied. The principle behind this method requires that measurements of the concentration of interest be made at two heights. If the instrumentation used does, in fact, discriminate between the concentrations at the two heights, call them H for high position and L for low, then a mean profile method deposition velocity,  $V_{dp}$  is determined by:

$$\bar{V}_{dp} = \bar{u}_5 C_{DD} \frac{\bar{c}_H - \bar{c}_L}{\sqrt{\frac{H}{5}} - \sqrt{\frac{L}{5}}}$$

where  $\bar{u}_5$  is the wind speed at the standard 5 m height.

During the 1977 field program measurement of  $V_{dp}$  was attempted for aerosols, and effectively for at least the metals Pb, Zn, Cu, Mn, Fe and Mo, by use of ASAS number concentration data at  $H = 6.5$  m and  $L = 3.7$  m. Preliminary analysis of the profile data showed over half of the data had to be discarded because the ship was not sufficiently close to being a fixed platform. This, despite the fact that  $\bar{V}_{dp}$  means for 30 minutes and more were sought after. The ship's rise and fall with wave action caused the  $\bar{c}_H$  and  $\bar{c}_L$  values to fall within one standard deviation of each other. Only nine profile measurements gave statistically significant  $\bar{c}_H - \bar{c}_L$ . However, the nine remaining cases do give substantial insight into the question of  $a_o \approx 0$ .

One case had  $\bar{u}_5 = 4.7$  m/s and  $(\bar{T}_a - \bar{T}_s) = 2.0^\circ$  C. Using Figures 9 and 10,  $C_{DD} = 1.16 \times 10^{-3}$ . This then gives a  $\bar{V}_d = 0.58$  cm/s. By using the number concentration data of the ASAS in the above equation the following  $\bar{V}_{dp}$  were calculated:

$$\begin{aligned}\bar{V}_{dp} &= 1.09 \text{ cm/s} & 0.75 \text{ } \mu\text{m} < D < 3.5 \text{ } \mu\text{m} \\ \bar{V}_{dp} &= 0.36 \text{ cm/s} & 0.25 < D < 0.75 \text{ } \mu\text{m} \\ \bar{V}_{dp} &= 0.62 \text{ cm/s} & 0.10 \text{ } \mu\text{m} < D < 0.25 \text{ } \mu\text{m}\end{aligned}$$

Consideration of the nine profile case studies suggest:

$$\begin{aligned}\frac{9}{10} \bar{V}_d & \quad \bar{V}_{dp} (0.75 < D < 3.5 \text{ } \mu\text{m}) < \bar{V}_d \\ \frac{7}{10} \bar{V}_d & \quad \bar{V}_{dp} (0.25 < D < 0.75 \text{ } \mu\text{m}) < \bar{V}_d \\ \frac{8}{10} \bar{V}_d & \quad \bar{V}_{dp} (0.10 < D < 0.25 \text{ } \mu\text{m}) < \bar{V}_d\end{aligned}$$

The deposition velocity seems, indeed, to vary with aerosol size but not as strongly as Sehmel and Hodgson (1974) suggest. However, the conclusions from these profile measurements must be considered quite tentative.

Until further profile measurements are made a tentative conclusion regarding  $\bar{a}_o$  is that it is likely to be less than one-quarter of  $\bar{a}$  and may, in fact, often be so much smaller than  $\bar{a}$  that one can assume  $\bar{a}_o \approx 0$ . This conclusion applied to the results presented in Table 5 would cause a reduction in these estimated annual dry deposition loadings of no more than 25% to as little as no reduction at all.

If the deposition velocities calculated by the diabatic drag coefficient method assuming  $\bar{a}_o \approx 0$  can now be considered sufficiently accurate for loading estimates, one can proceed to the final interpretative step regarding  $\bar{V}_d$ . A review is necessary to determine the "goodness of fit" between the 1977 field program micrometeorology and the microclimatology that prevails over the southern basin of Lake Michigan.

Filter sets were grouped together according to averaged micrometeorological conditions for the time the sets were taken. Two parameters were used, each in a separate aggregation scheme: temperature stability ( $T_a - T_s$ ), and mean wind speed ( $\bar{u}$ ). An at least ten-year-long record of synoptic conditions over the lake (NOAA SSMO, 1975) was used to determine the April to September frequency of occurrence ( $F_o$ ) for given values of each parameter. "Bins" were set up to correspond with reported ranges of values for ( $T_a - T_s$ ) and  $\bar{u}$ , and the filter sets were then sorted into these "bins".

The ( $T_a - T_s$ ) bins are based directly on values and ranges for air/sea temperature difference reported in the climatological history. Thus, calculating an annual  $F_o$  was a matter of arithmetically summing the monthly-mean values. It should be noted here that the historical data reports air/water temperature difference whereas the micrometeorological data of this work is for air/surface temperature difference.  $T_s$ , in this work, was measured by a downward looking infrared sensor and represents a true surface temperature. During periods of intense insolation, and particularly in the presence of organic surface films,  $T_s$  may be somewhat higher than the water temperature. The result is a possible bias in the  $F_o$  for the ( $T_a - T_s$ ) bins towards more stable conditions. This bias would lead to lower estimates for total annual loadings, because  $F_o$  will be larger for the stable bins, which have lower average deposition velocities. Table 13A shows the data for the ( $T_a - T_s$ ) bins. Each bin is identified by a range of values for ( $T_a - T_s$ ),  $^{\circ}\text{C}$ . The next row is the  $F_o$  values corresponding to climatological data (NOAA SSMO, 1975). The number of actual sets in each bin is given, and an average  $V_d$ , cm/s for those sets is shown in the last row. For each metal, mean concentrations,  $\bar{c}$ , for each bin were found, and



annual loadings were calculated from this equation:

$$\text{Bin Loading} = \bar{V}_d \cdot F_o \cdot c \cdot A \cdot k$$

$$\begin{aligned} \text{where: } A &= \text{area of southern basin} = 2.9 \times 10^6 \text{ m}^2 \\ k &= \text{constant to correct units} \end{aligned}$$

Finally, the five bin loadings in metric tons/yr. were summed to give an annual loading for the 0.81 year the  $F_o$  values for April to September represent. The result was normalized to 0.85 year loadings to compare with other dry deposition calculations of this work. The normalization of the  $(T_a - T_s)$  bin loadings tends to further bias the results toward a least-likely total annual loading; as can be seen from Table 13A, our data is unstable-case deficient. There is a six-fold increase in  $\bar{V}_d$  from the most to least stable bin, and more unstable ( $T_a - T_s < 0$ ) data would likely result in a bin with a still higher  $\bar{V}_d$ . Bin loading from that unstable data would substantially increase the annual loading total.

Table 13B shows the  $\bar{u}$  bins, similar to the  $(T_a - T_s)$  bins discussed above. Bin loadings and annual lake loadings were calculated in the same manner as for the temperature stability result. In the case of climatological data for  $\bar{u}$ , the historical record was not reported in units or ranges conveniently compatible with our own data. By calculating annual  $F_o$  values for the reported ranges, and plotting cumulative  $F_o$  versus  $\bar{u}$ , it was possible to interpolate  $F_o$  values for the "bins" used in this work. The  $\bar{u}$  bins are based very closely on the Beaufort wind scale increments. Note that again, as for the  $(T_a - T_s)$  result, our data is severe (high  $\bar{u}$ ) condition deficient, and leads to a least-likely total annual loading. If more high wind data were available, a higher  $\bar{V}_d$  bin would result and increase the final sum loading substantially.

### C. Consequences

Given the data generated and interpretation to date some discussion of the consequences of the present results is certainly warranted. Though no person on the grant project team is in a position to assess these impacts we hope others may do so. There are a few literature sources which may help the reader in this assessment.

At first thought a diffuse area source of toxic metals depositing on the lake's surface might be thought of less damaging to the lake ecosystem. However, several Great Lakes biological researchers have suggested (in private communiques) that lower organisms in the near surface waters or in the sediment may ingest significant amounts of trace metals such as Pb due to the atmospheric source. Bioaccumulation may then result in toxic levels of these metals in edible fish.

Pb is a most important candidate for investigation regarding atmospheric inputs. The enrichment factor of over 3300 and essentially zero concentration contribution from other than anthropogenic sources make it the most lethal - potentially - of the elements analyzed in this data base. Patterson, et. al. (1976) find a small Pb flux to the oceans. Yet ecosystem impacts are noted. They also point out the selective food chain transport of Pb between albacore and marten. MacIntyre (1974) identifies a major ecosystem impact when the laminar sublayer is present. Under this condition of greatly reduced transport, airborne metals may collect in a surface microlayer with enrichment factors greater than 10000.

Pb accumulation in freshwater fishes is a strong function of lake chemistry (Torrey, 1976). For example, Merlini and Pozzi (1977) studied the accumulation

of Pb by an edible freshwater fish at pH 7.5 and pH 6.0. Although the sites of lead concentration were not altered, the fish concentrated almost three times more Pb at the lower pH than at the higher pH. Whether the Pb remains in particulate form or dissolves is certainly another significant factor. Each of the metals have unique pathways into edible freshwater fish. With the sharp increase in coal utilization for energy production the next decades, the impact of atmospheric trace metals on Great Lakes waters will surely increase.

The impact of nutrients input to the lake via the atmospheric route may be more direct than the impact of metals. In a phosphorus-limited ecosystem, an addition of that nutrient in small particle or soluble form will cause an immediate response by the primary producers. Moreover, in areas of the lake far removed from nutrient sources other than the atmosphere, the availability and relative concentrations of nutrient materials may differ from that of near shore regions. The implications for the diversity in and abundance of aquatic biota are not well known. It is hoped that atmospheric loading impacts will be increasingly addressed in the literature.

### III FUTURE WORK

Review of the present data base suggests at least three areas for improvement:

1. more unstable surface layer data and nearshore concentration measurements
2. more and better measurements of  $V_d$
3. the development of trajectory analysis programs and a meso-climatology for aerosol transport

The comparison of the 1977 field program micrometeorology with Lake Michigan's southern basin climatology has shown the need to obtain data in high wind speeds ( $\bar{u} > 10$  m/s) and late fall or winter months ( $T_a - T_s < -2^\circ\text{C}$ ). Such data will be very difficult to obtain at midlake but may be reasonable at a nearshore fixed platform. For this reason and to characterize the near-shore aerosol concentrations the 1978 field program is taking place at a City of Chicago water intake crib 2 miles offshore. This sampling should create a data base to address the first area for improvement.

The second area may be more difficult to address. However, the profile method has already given better data at the crib's permanent platform sampling site. Several studies of the mass transfer coefficient from liquid to air (Cohen, et. al., 1978, Duce, et. al., 1977, Brtko and Kabel, 1976) may result in an accurate statement of the  $\bar{a}_o$  correction to earlier flux calculations.

Lastly and most difficult will be the determination of concentration variability both spatially and temporally. Some consideration was given to this question at the conclusion of section II A. Section I A' described the forward and back trajectory analyses being plotted on southern Lake Michigan maps. The manual plotting of back trajectories (example, Figure 3) will allow the designation of 95% confidence, three-dimensional source regions from which the

aerosol sampled at midlake originated. If emissions data is available for the designated source region one can then calculate the product of emission factor and the inverse of the dispersion factor for each filter set. A determination can then be made as to whether the variability in midlake concentration is highly correlated with this product. If so, computerized back trajectories using the NCAR aircraft and NOAA SSMO data bases will be used to attempt developing a mesoclimatology for the southern basin of Lake Michigan. This mesoclimatology will be relatively easier to define for cold season conditions. During the warm season the development of thermal internal boundary layers and lake breezes makes the situation much more complicated. However, with the goal being a mesoclimatology for concentration variability on a temporal and spatial basis the task may be feasible if not reasonable.

## REFERENCES

- Bolsenga, S. N.: 1974, private communication, Great Lakes Environmental Research Laboratory, Ann Arbor, Michigan.
- Brtko, W. J. and Kabel, R. L.: 1976, Water, Air and Soil Pollution, 6, 71.
- Cawse, P. A., 1974: A Survey of Trace Elements in the U.K., 1972-73. U. K. At. Energy Auth. Rep. AERE-R7669. Harwell, 95 pp.
- Charlson, R. J., Ahlquist, N. C. and Selvidge, H.: 1969, Jour. of Air Pollut. Control Assoc., 10, 937.
- Cohen, Y., Cocchio, W. and MacKay, D.: 1978, Environ. Sci. and Tech., 12, 553.
- Duce, R. A.: Sea-Air Exchange Study, SEAREX, Univ. of Rhode Island, Kingston, R. I.
- Duce, R. A., et. al.: 1976, Trace Metals in the Marine Atmosphere, in Marine Pollutant Transfer, Toronto; Heath, 77.
- Edwards, H. W. and Wheat, H. G.: 1978, Environ. Sci. and Tech., 12, 687.
- Eisenreich, S. J., Emmling, P. J. and Beeton, A. M.: 1977, J. Great Lakes Res., 3, 291.
- Gatz, D. F.: 1975, 'Estimates of Wet and Dry Deposition of Chicago and Northwest Indiana Aerosols into Southern Lake Michigan', ICMSE Conf. on the Great Lakes, Argonne, Ill., March, 1975.
- Heffter, J. L. and A. D. Taylor, 1975: "A Regional-Continental Scale Transport Diffusion and Deposition Model," NOAA Tech. Memo. ERL-ARL-50.
- Kretschmar, J. G.: 1975, Atmos. Environ., 9, 931.
- MacIntyre, F.: 1974, Chemical Fractionation and Sea-Surface Microlayer Processes in The Sea, 5, Marine Chemistry, New York: Wiley, 245.
- Merlini, M. and Pozzi, G.: 1977, Environ. Pollut., 12, 167.
- Meszaros, A.: 1977, Atmos. Environ., 11, 1075
- Murphy, T. J. and Doskey, P. V.: 1976, J. Great Lakes Res., 2, 60.

- NOAA: 1975, Summary of Synoptic Meteorological Observations for Great Lakes Areas, Vol. 3, Lake Michigan. National Oceanic and Atmospheric Administration, National Climatic Center, Asheville, N. C.
- Patterson, C., et. al.: 1976, Transport of Pollutant Lead to the Oceans and Within Ocean Ecosystems, in Marine Pollutant Transfer, Toronto; Heath, 23.
- Rahn, K.: 1976, The Chemical Composition of the Atmospheric Aerosol, Grad. School of Oceanography, Univ. of Rhode Island, Kingston, R. I., 265 pp.
- Sehmel, G. A. and W. H. Hodgson: 1974, "Predicted Dry Deposition Velocities," in Atmosphere-Surface Exchange of Particulate and Gaseous Pollutants - 1974 Symposium. Battelle Pacific Northwest Laboratory, Richland, Wash., pp. 399-422.
- Sehmel, G. A. and Sutter, S. L.: 1974, J. Rech. Atmos., III, 911.
- Shepherd, J. G.: 1974, Atmospheric Environment, 8, 69.
- Sievering, H.: 1976, Water, Air and Soil Pollution, 5, 309.
- Skibin, D.: 1973, Water, Air and Soil Pollution, 2, 405.
- Steen, B.: 1977, Atmospheric Environment, 11, 623.
- Stulov, L. D., Murashkevich, F. I. and Fuchs, N.: 1978, J. Aerosol Sci., 9, 1.
- Torrey, M.: 1976, Chemistry of Lake Michigan, Vol. 3 of Environmental Status of the Lake Michigan Region, ANL/ES-40, Argonne Natl. Labs., Argonne, Ill.
- Wedepohl: 1971, Geochem. Acta, 10, 999.
- Winchester, J. W. and Nifong, G. D.: 1971, Water, Air and Soil Pollution, 1, 50.

Metal	Blank		Typical Sample	
	Backup	Cascade	Backup	Cascade
Ca	6150	1970	6875	11250
Mg	565	220	1315	1320
Al	285	125	1110	875
B	5605	1725	6990	3070
Ba	12	5	25	35
Cu	25	10	100	70
Fe	850	370	2810	1820
Mn	30	10	160	80
Mo	28	10	55	10
Pb	130	55	1605	200
Ti	45	20	75	45
Zn	190	100	725	245

Table 1. Trace Metal Concentrations for Typical Sample Filter and Blank Misco Cellulose Filters,  $\mu\text{g/l}$  in 25 ml ICAP Sample



Number of Sets C > L <sub>d</sub>	Metal	1st Stage $\bar{c}$ (Primary Aerosol)	Backup $\bar{c}$ (Secondary Aerosol)	Total $\bar{c}$ (1st, 2nd and Backup stages)
30	Ca	.67	.06	1.03
47	Mg	.125	.065	.253
51	Al	.07	.072	.201
38	B	.124	.120	.352
33	Ba	.003	.002	.007
43	Cu	.001	.006	.016
45	Fe	.130	.170	.406
46	Mn	.007	.011	.022
20	Mo	.000	.002	.003
49	Pb	.006	.127	.153
46	Ti	.004	.003	.009
50	Zn	.008	.046	.072

Table 2. 1977 Overall Average Trace Metal Concentrations,  
μg/cu. m

Trace Metal	$\overline{\text{EF}}$ (Al = 1.0)	"Background" Marine Aerosol EF (Duce, 1976)
Pb	3380	180
Zn	520	22
Cu	145	11
Mn	9	-
Mg	11	2
Ca	8	-
Fe	4.5	1
Ba	2.5	-
B	7	-
Ti	1.5	-
Mo	1.3	-

Table 3. Overall Average Enrichment Factors for 1977 Aerosol Metal Samples

Element	Percent Primary ( $d > 1.0 \mu\text{m}$ )	Percent Second Stage	Percent Secondary ( $d \leq 0.7 \mu\text{m}$ )
Ca	65	29	6
Mg	50	24	26
Al	35	29	36
B	35	31	34
Ba	43	28	29
Cu	8	56	36
Fe	32	26	42
Mn	29	22	49
Mo	7	13	80
Pb	4	13	83
Ti	40	31	29
Zn	11	26	63

Table 1. Elemental Association with Primary/Secondary Aerosol at Midlake.

Element	Overall Average Loading, T/yr.	Wind Speed Loading, T/yr.	$\Delta T$ Bin Loading, T/yr.
Pb	825	710	465
Zn	390	340	230
Cu	86	39	35
Mn	120	89	59
Mg	1365	1030	815
Ca	5550	3340	2050
Fe	2190	1650	1090
Ba	38	27	16
B	1895	1955	1386
Ti	49	57	45
Mo	16	12	8

Table 5. Estimated Annual Dry Deposition Loadings of Southern Lake Michigan Basin

Size Channel	Size Range Number			
	0	1	2	3
1	.763	.335	.182	.098
2	.960	.365	.198	.113
3	1.157	.395	.214	.124
4	1.353	.425	.230	.134
5	1.550	.455	.246	.142
6	1.746	.485	.262	.149
7	1.943	.515	.278	.156
8	2.139	.545	.294	.163
9	2.335	.575	.310	.170
10	2.531	.605	.326	.176
11	2.727	.635	.342	.183
12	2.923	.663	.358	.190
13	3.112	.692	.374	.198
14	3.286	.721	.390	.206
15	3.450	.750	.406	.216

Table 6. Geometric Mean Aerosol Diameter ( $\mu\text{m}$ ) of ASAS Counting Channels

<u>Specie</u>	Primary Aerosol		2nd Stage		Secondary Aerosol		Total c
	<u>c</u>	<u>(%)</u>	<u>c</u>	<u>(%)</u>	<u>c</u>	<u>(%)</u>	
total P	5	(16)	8	(24)	20	(60)	32.4
NO <sub>3</sub> <sup>-</sup>	726	(12)	1064	(18)	4158	(70)	5948
SO <sub>4</sub> <sup>-2</sup>	208	( 4)	336	( 6)	4872	(90)	5416

Table 7. 1977 Data Averages for P-N-S Concentration, ng-m<sup>-3</sup>, and Aerosol Size Association, per cent.

<u>Specie</u>	<u>Overall Average Dry Loading</u>	<u>Wind Speed Bin Calculation</u>	<u>ΔT Bin Calculation</u>
total P	170	160	100
$\text{NO}_3^-$	32000	22500	20500
$\text{SO}_4^{2-}$	29000	20500	18500

Table 8. P-N-S Annual Loadings by Atmospheric Dry Deposition.

Specie	Loadings, $10^6$ kg/yr		
	Dry Deposition <sub>(1)</sub>	Precipitation <sub>(2)</sub>	Run-Off <sub>(3)</sub>
Ca	2050		490000
Mg	815		134000
Al	575	560	13000
Cu	35	20	140 <sup>(5)</sup>
Fe	1090	950	1450
Mn	59	53	250
Pb	465	88	100
Ti	45	59	100
Zn	230	52	180 <sup>(5)</sup>
total P	100	1000 <sup>(4)</sup>	4500 <sup>(4)</sup>
NO <sub>3</sub> <sup>-</sup>	20500		
SO <sub>4</sub> <sup>-2</sup>	18500		

Table 9. Annual Loading of Lake Michigan Comparison of Several Loading Routes.

1. This Work - Southern Basin only, 1977.
2. Gatz, 2nd ICMSE Conf. on G.L., 1975.
3. Winchester & Nifong, W,A,SP, 1, 50+, 1975.
4. Murphy & Doskey, EPA - 600/3-75-005, 1975.
5. Robbins, 2nd ICMSE Conf. on G. L., 1975.



Metal	Surface Sample Concentration, $\mu\text{g/l}$	Bulk Sample Concentration, $\mu\text{g/l}$	Ratio Surface/Bulk
Ca	30928	29806	1.04
Mg	8872	8589	1.04
B	55	68	.81
Ba	10	10	1.0
Co	1	-	
Cu	4	3	1.33
Fe	37	24	1.54
Mn	1	-	
Mo	3	3	1.0
Pb	8	6	1.33
Ti	3	3	1.0
Zn	20	16	1.25

Table 10. Comparison of Trace Metal Mean Concentrations in Surface and Bulk Water Samples (September, 1977 samples).

<u>Element</u>	<u>Average Crustal Conc(ppm)*</u>	<u>Average Bulk Water Conc(ppb)**</u>	<u>Percent Crustal (%)</u>	<u>Percent Lake Derived (%)</u>	<u>Percent "Unexplained" (%)</u>
Al	78300	37.5	100	0	0
Mg	13900	8728	14	86	0
Ca	28700	29900	7	73	20
Fe	35000	46.3	24	0.4	75.6
Mn	690	2.6	8.1	0.3	91.6
Mo	1.0	3.3	0.1	2.0	97.9
Ti	1.3	2.4	<0.1	0.7	99.3
Cu	30	4.8	0.3	0.4	99.7
Zn	60	17.7	0.2	0.7	99.1
Pb	15	7.5	<0.1	0.1	99.9

\* Wedepohl (1971)

\*\* 1977 grand average of more than 40 bulk water samples

Table 11. Percentage of Trace Metals Identified as Crustal, Lake Derived and "Unexplained"

# CORRELATION COEFFICIENTS MATRIX

Mg	(.75)	(.83)	.67	(.83)	(.95)	(.84)	.45	.54	(.70)	.59	-.21	-.38
Al	(.80)	.68	(.87)	(.88)	(.80)	.60	(.92)	.57	(.70)	.04	(.70)	
Cu	(.74)	(.77)	(.87)	(.88)	(.80)	.60	.48	.57	(.72)	.13		
Fe	(.83)	(.73)	(.77)	(.88)	(.95)	(.81)	.69	.34				
Mn	(.82)	(.73)	(.77)	(.88)	(.76)	(.81)	.46	.07				
Pb	(.70)	.67	.67	(.94)	(.80)	.45						
Ti	.57	.50	.55	.50	.67	.45						
Zn	(.74)	.63	.66	(.93)	(.88)	(.92)						
P	.40	.40	.45	.51	.69	.48						
$\text{NO}_3^-$	.69	.69	(.70)	(.71)	(.76)	(.81)						
WS	-.21	-.18	-.23	-.20	-.14	-.13						
$\Delta T$	.45	.58	.66	.42	.46	.39						
Ca												

Table 12. Correlation Coefficients among metal, P,  $\text{NO}_3^-$ , WS and Temp using 42 Filter Sets' Data.

Range of $(T_a - T_s)$ , °C	< -0.9	-0.8 to +0.9	1.0 to 2.7	2.8 to 8.1	> 8.2
$F_o$ , fraction of year*	0.26	0.09	0.05	0.22	0.19
Number of sets, this bin	8	17	9	3	5
$\bar{V}_d$ cm/s	1.04	.95	.48	.21	.15

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Table 13A. Temperature Stability Bins of Filter Set Data

Range of $\bar{u}$ , m/s	< 2.2	2.3 to 3.5	3.6 to 5.2	5.3 to 8.5	> 8.6
$F_o$ , fraction of year*	0.04	0.16	0.15	0.29	0.24
Number of sets, this bin	4	7	9	19	4
$\bar{V}_d$ , cm/s	.03	.20	.44	.98	1.54

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Table 13B. Wind Speed Bins of Filter Set Data

\* NOAA SSMO, 1975.

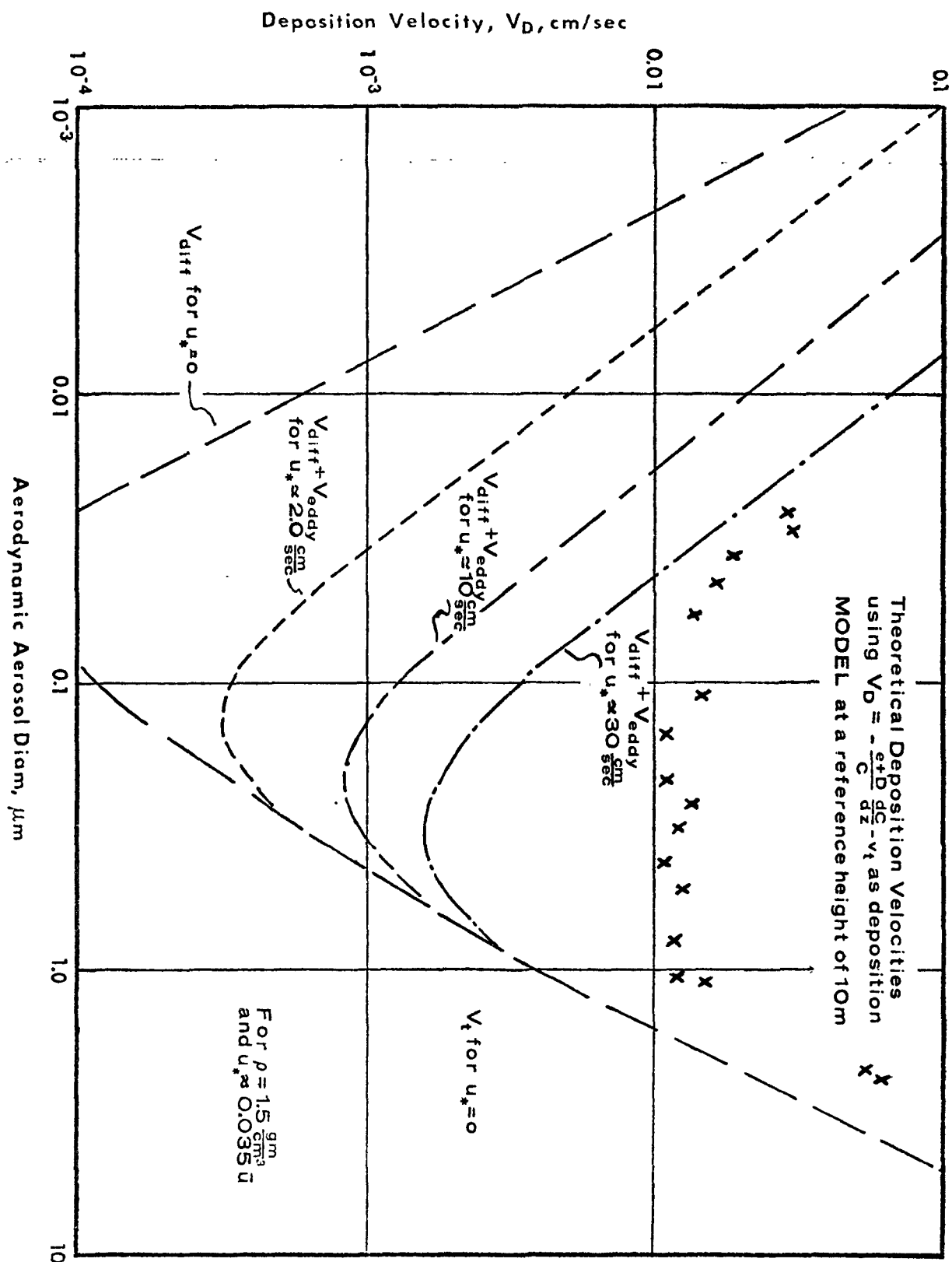


Figure 1. Theoretical Aerosol Deposition to a Water Surface as a Function of Aerosol Size. Note the experimental data points (x) measured by Sehmel and Sutter (1974) for particles of density  $1.5 \text{ gm cm}^{-3}$  depositing on a water surface in a wind tunnel.

Figure 28.  
Forward Traj.  
Analysis

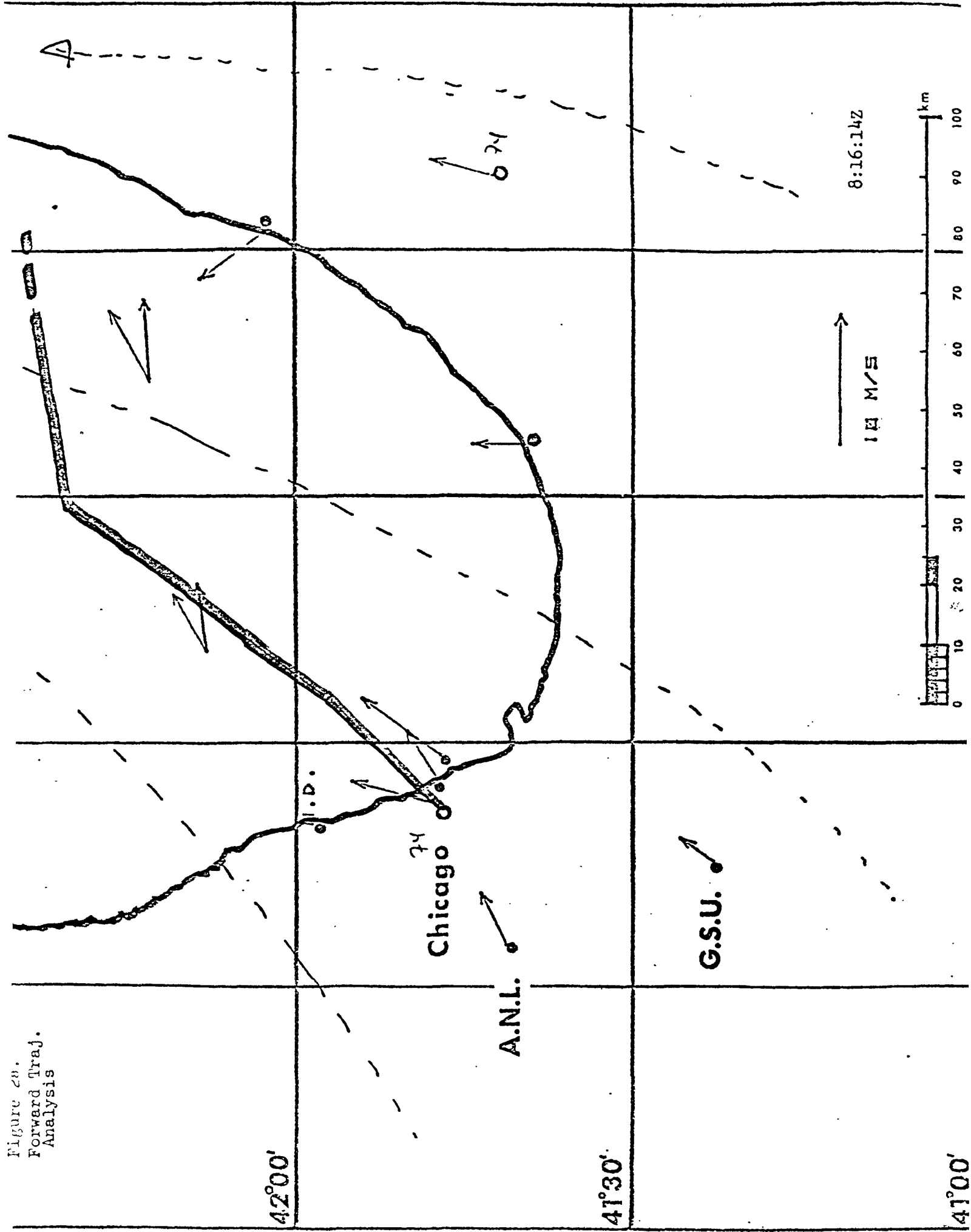


Figure 2b.  
Forward Traj.  
Analysis

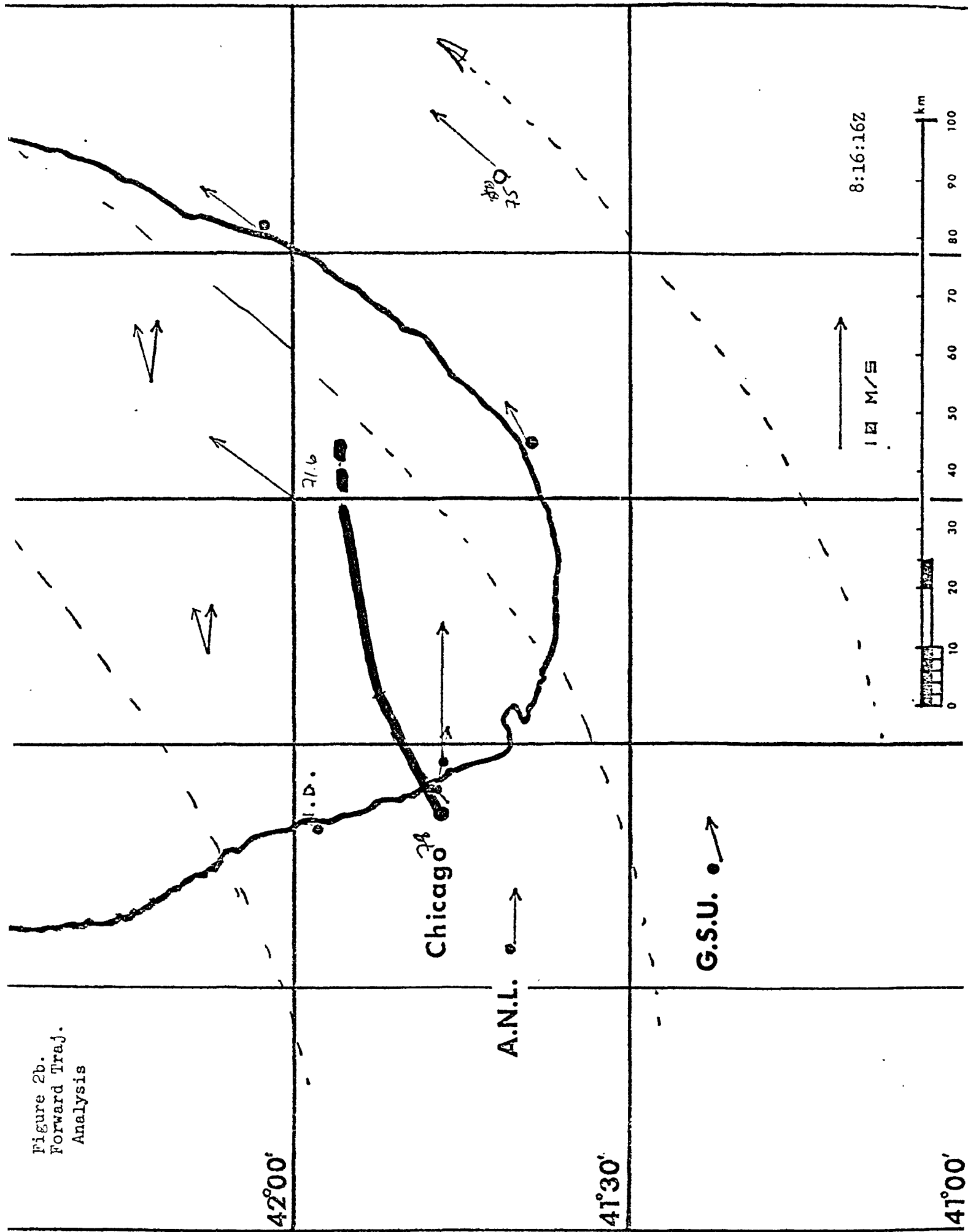


Figure 3.  
Example Back  
Trajectory

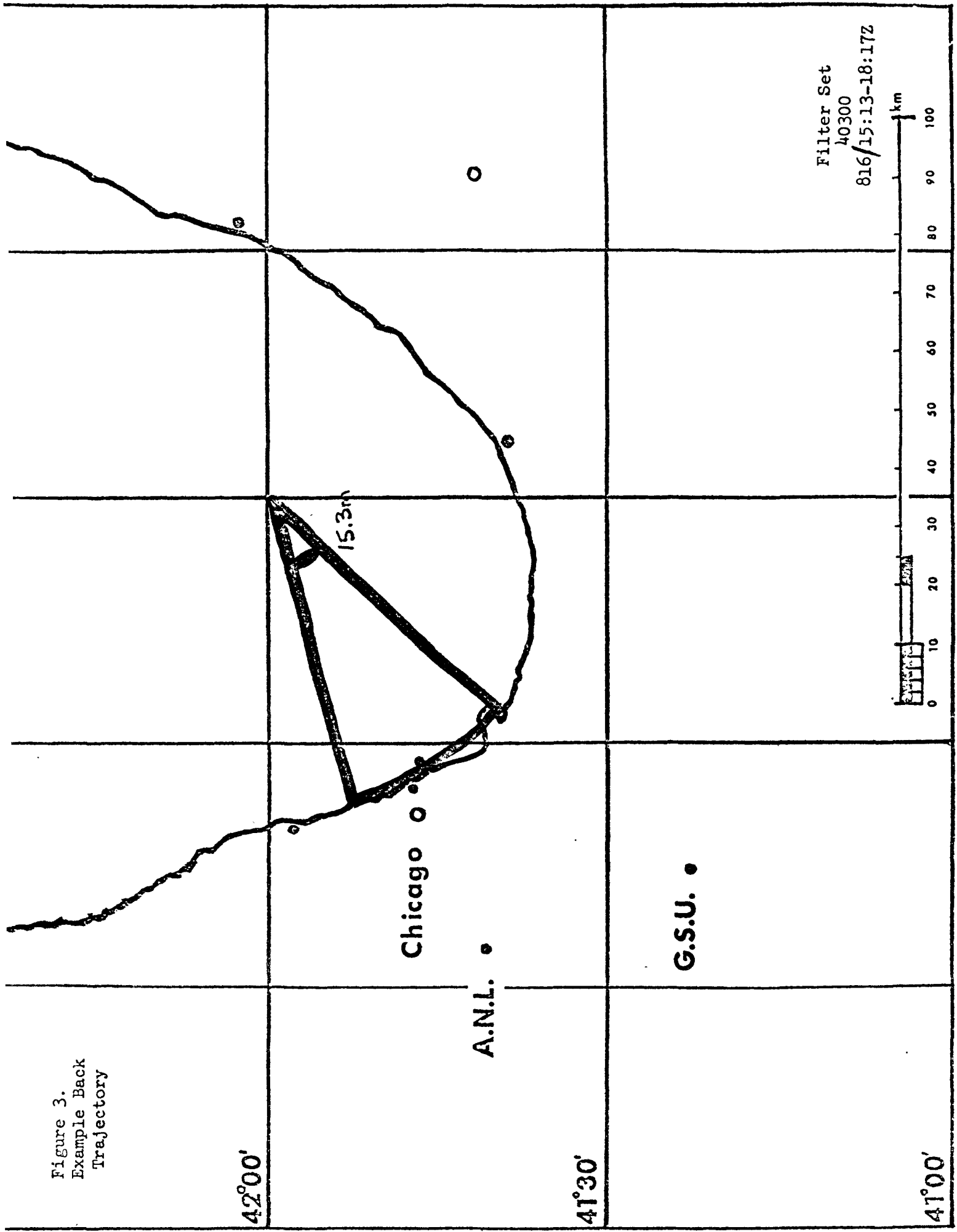
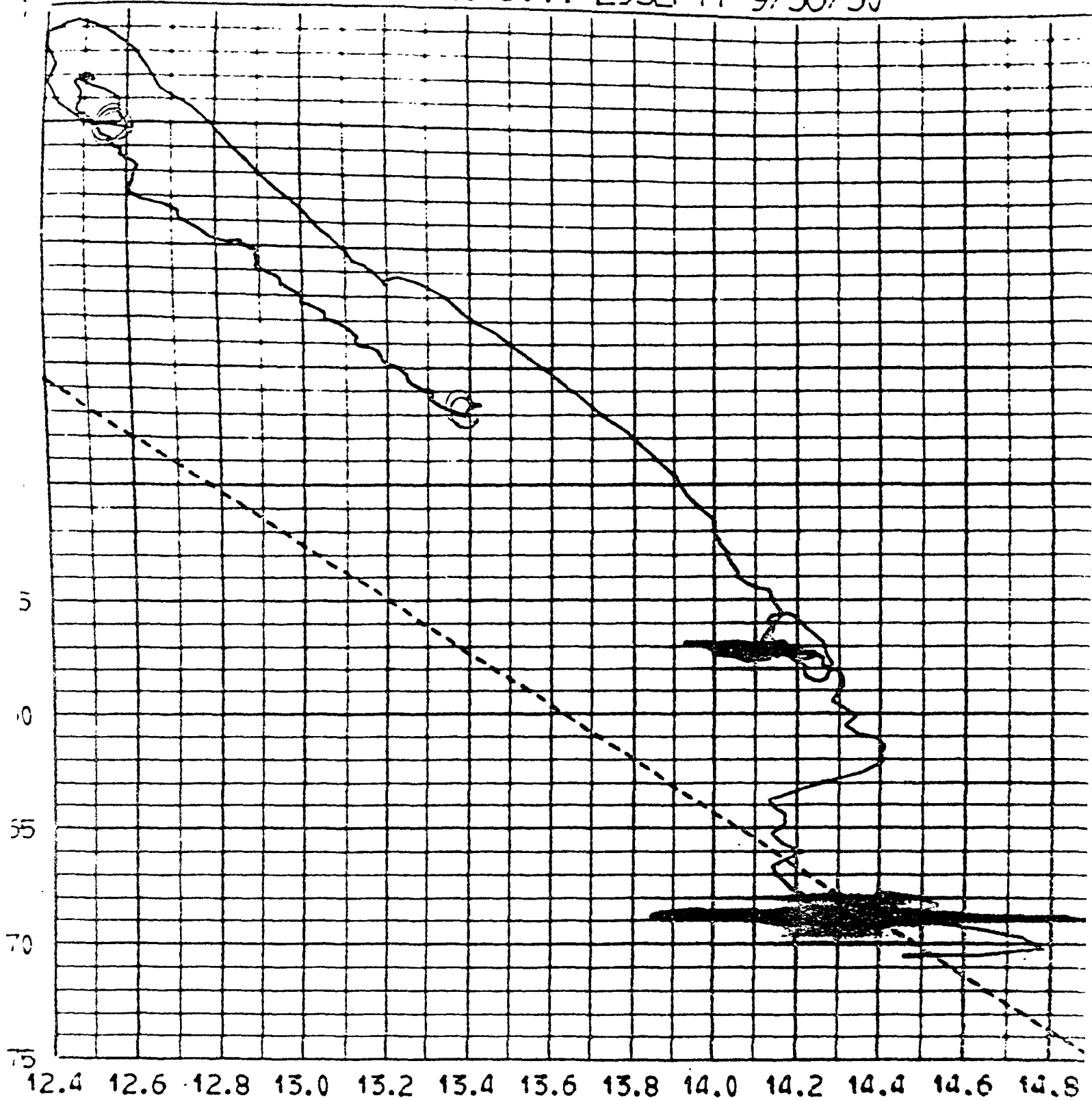




Figure 4. Example Midlake Sounding

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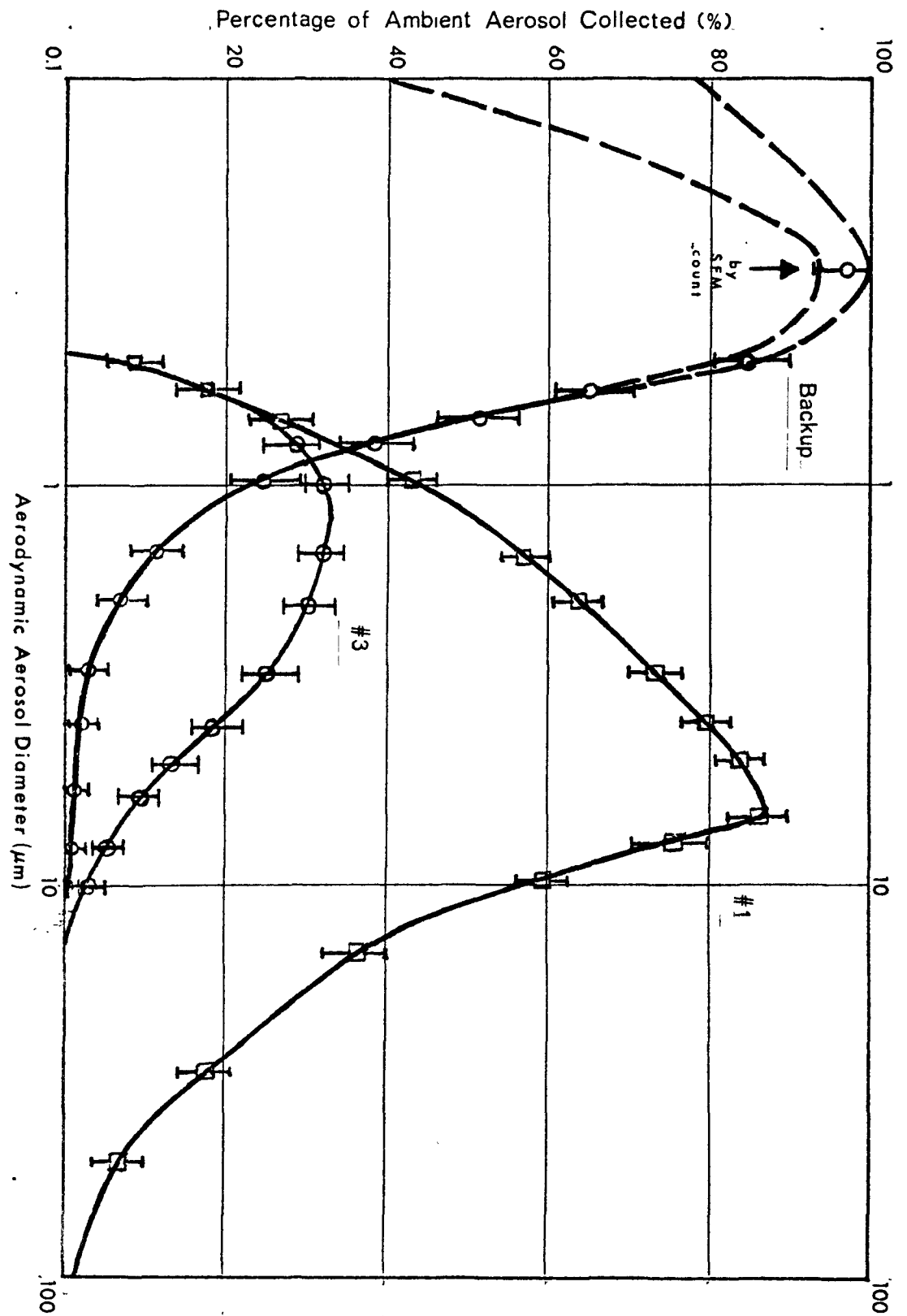


Figure 5. Aerosol Collection Efficiency of Misco Filter Sierra #1, #3 and Backup Cascade Combination.

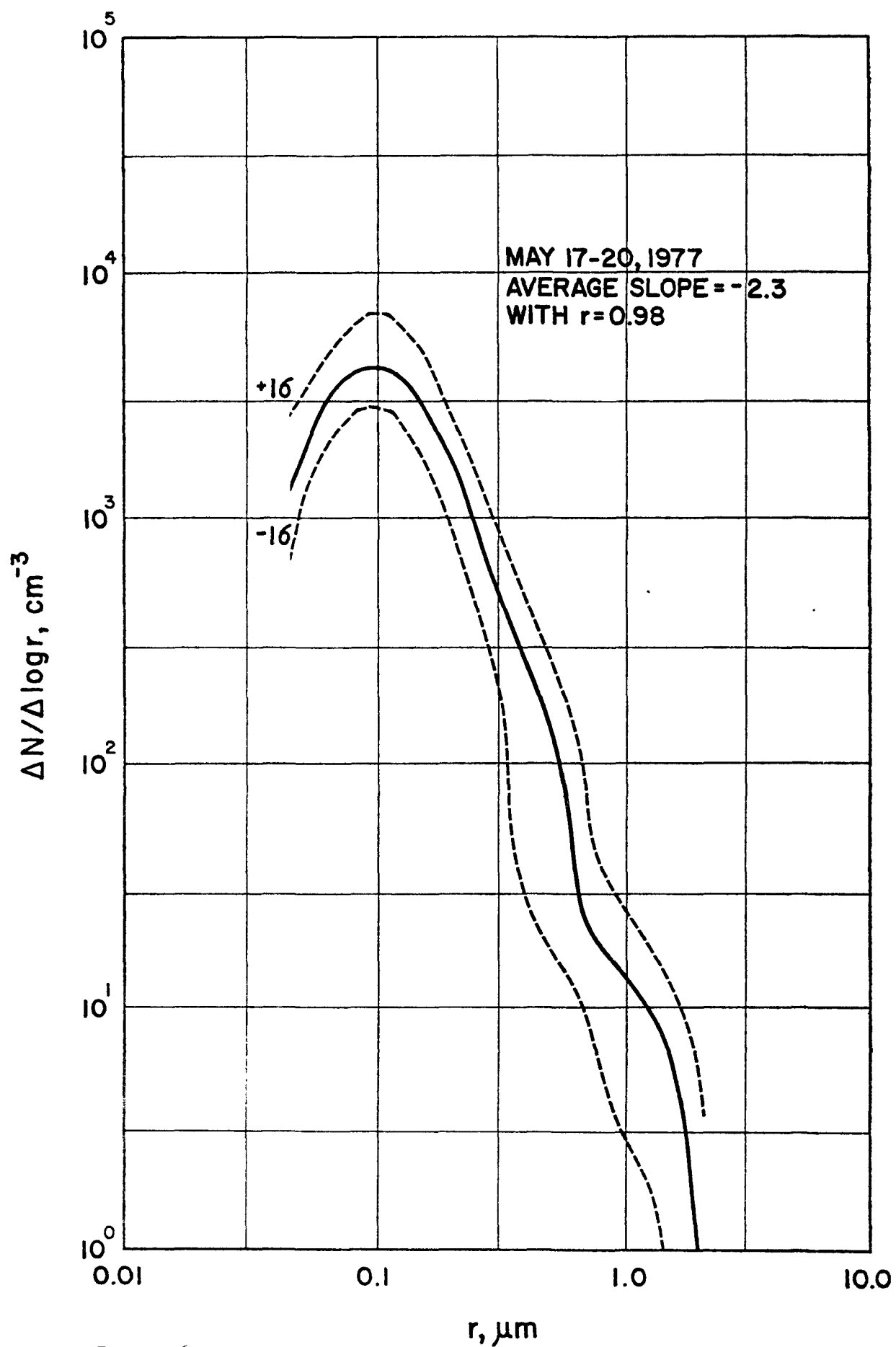


Figure 6a. Plot of ASAS counts for May Outing.

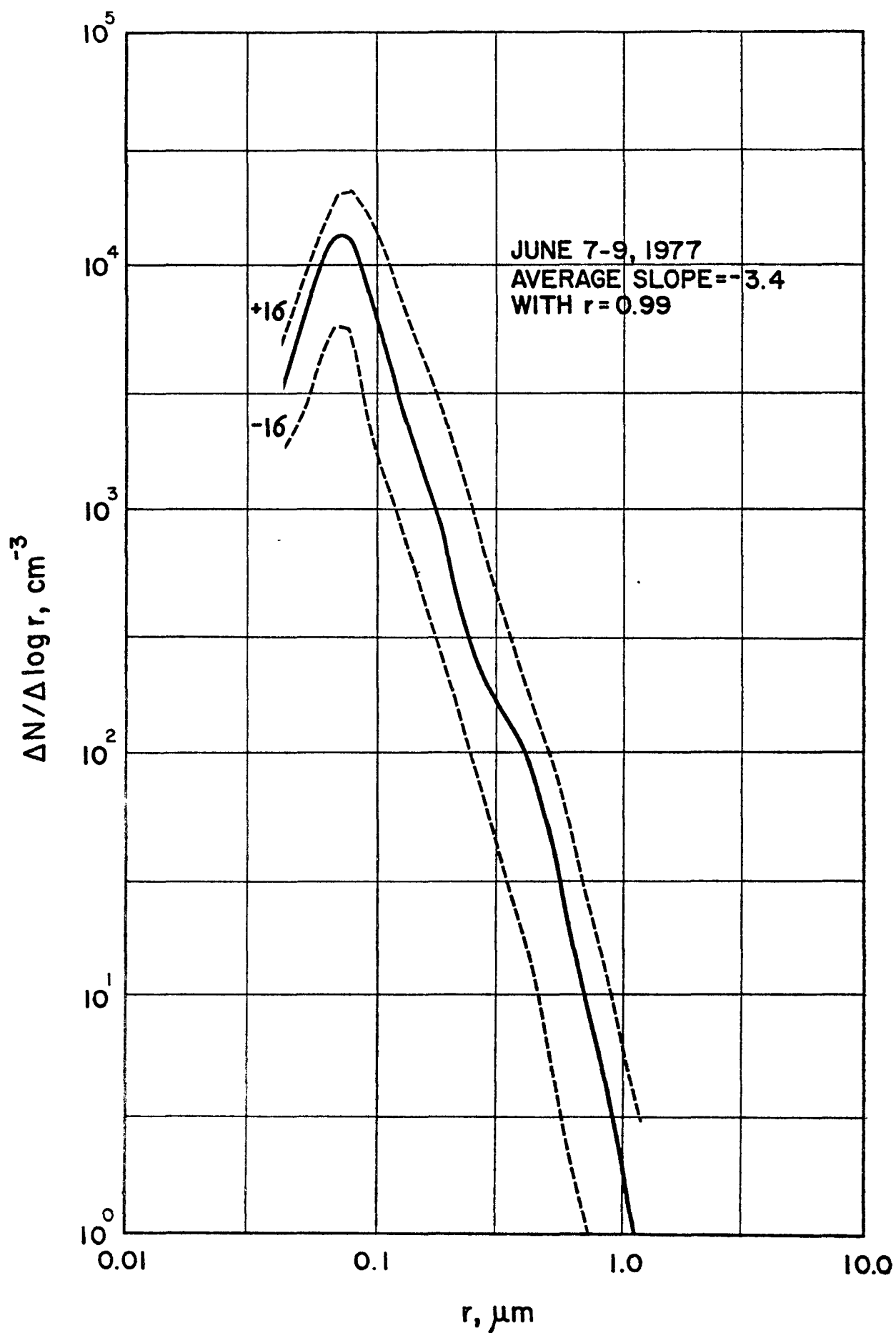


Figure 6b. Plot of ASAS counts for June Outing.

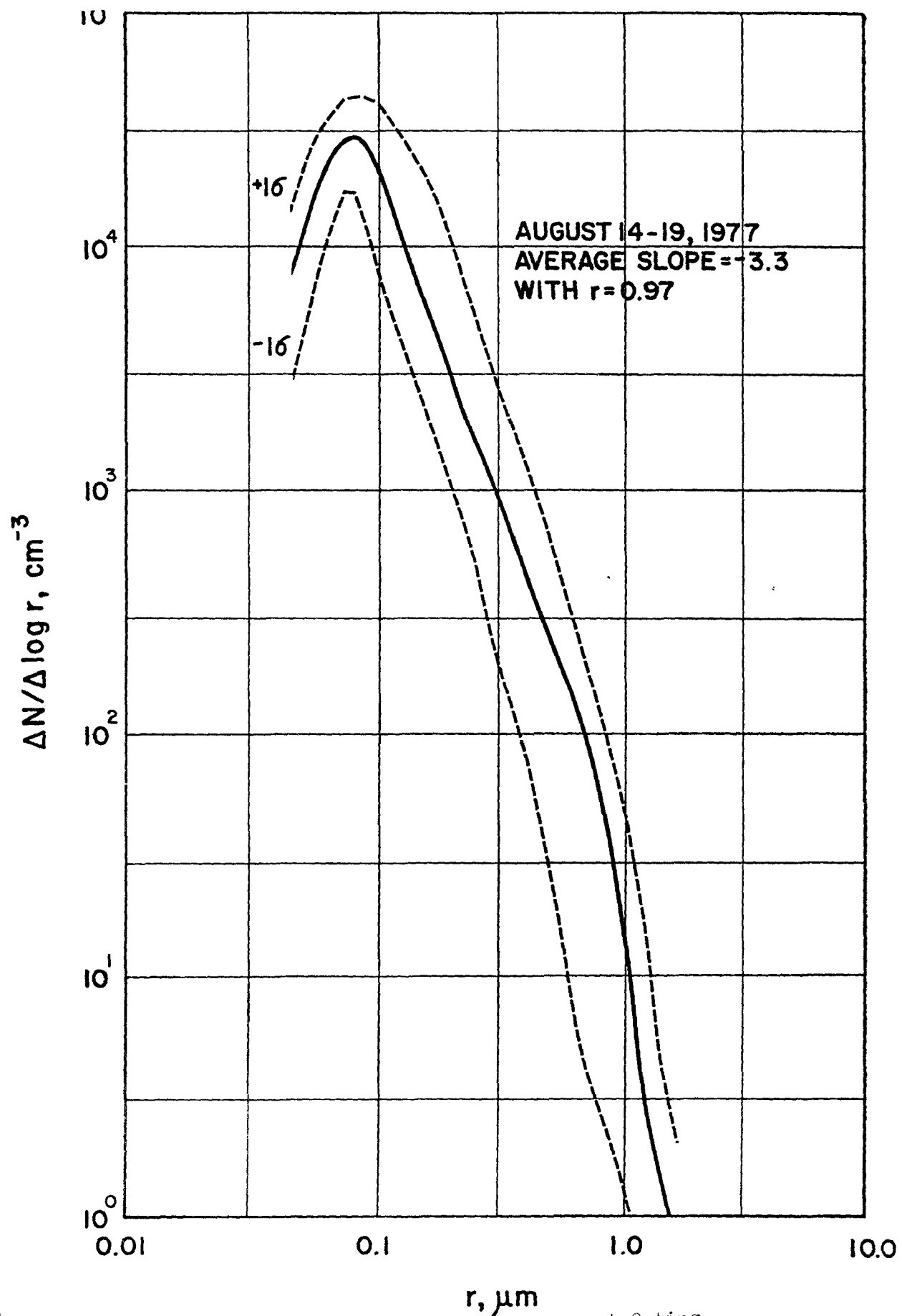


Figure 6c. Plot of ASAS counts for August Outing.

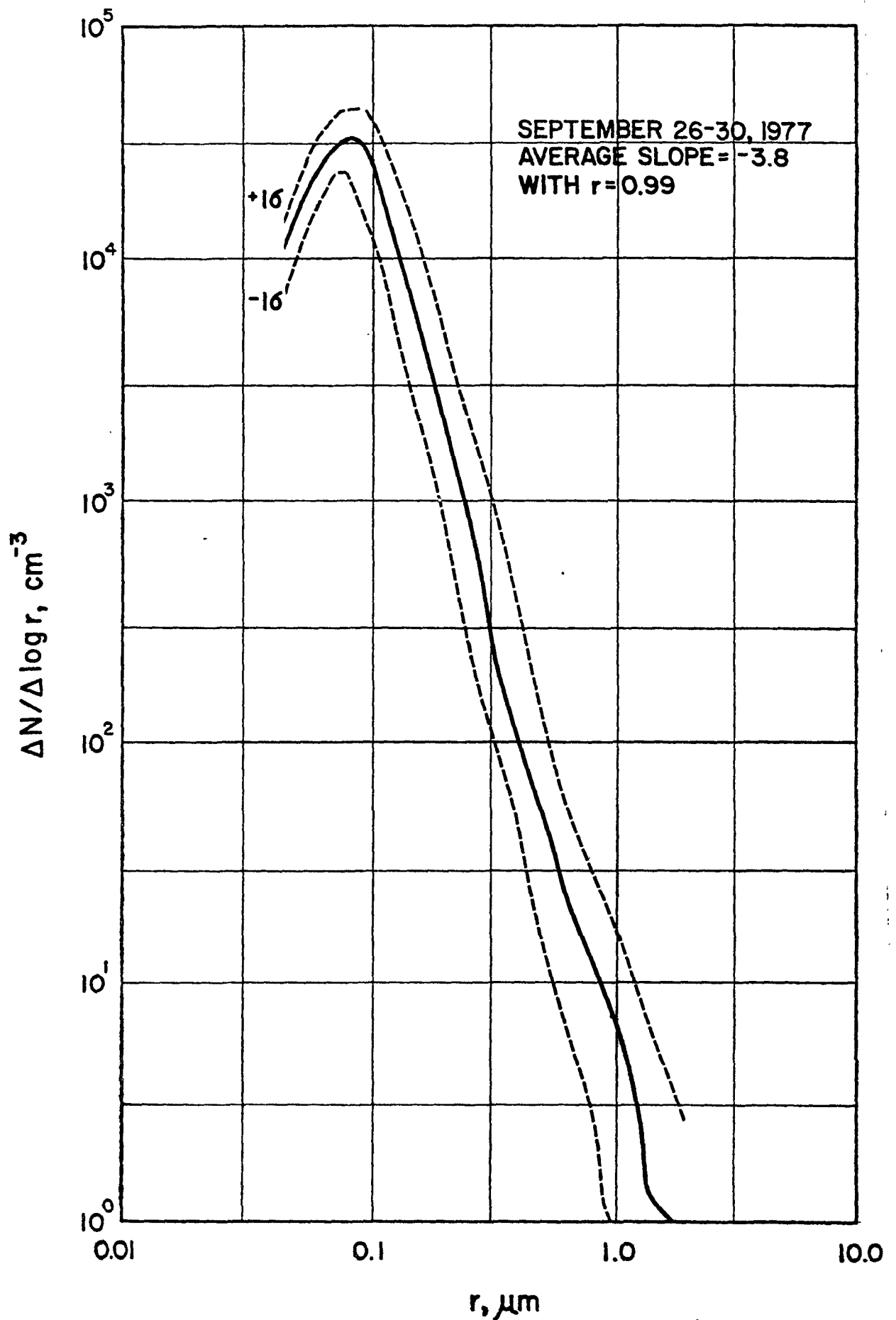


Figure 6d. Plot of ASAS counts for September Outing.

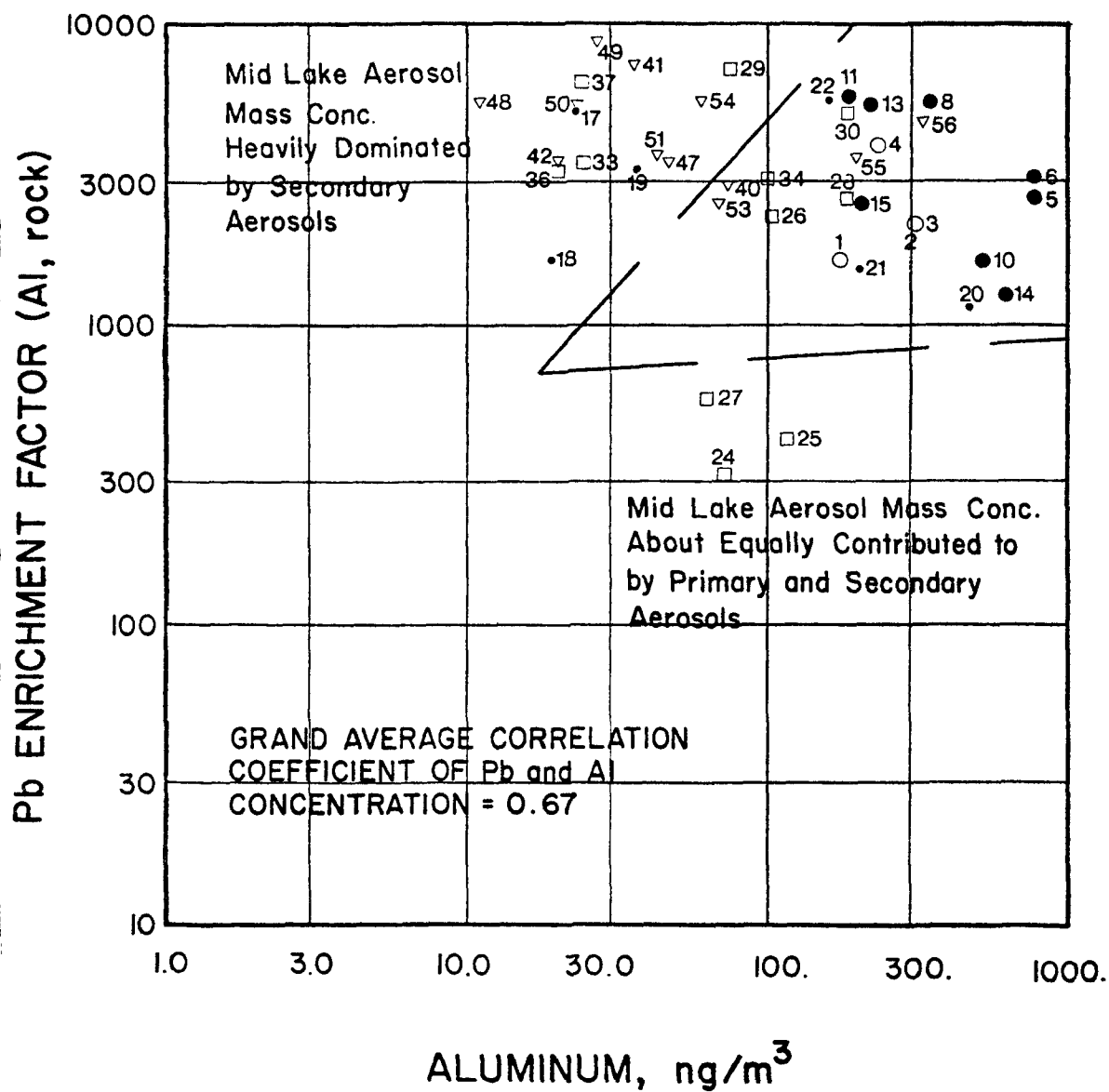


Figure 7. Scatter-diagram for Pb.

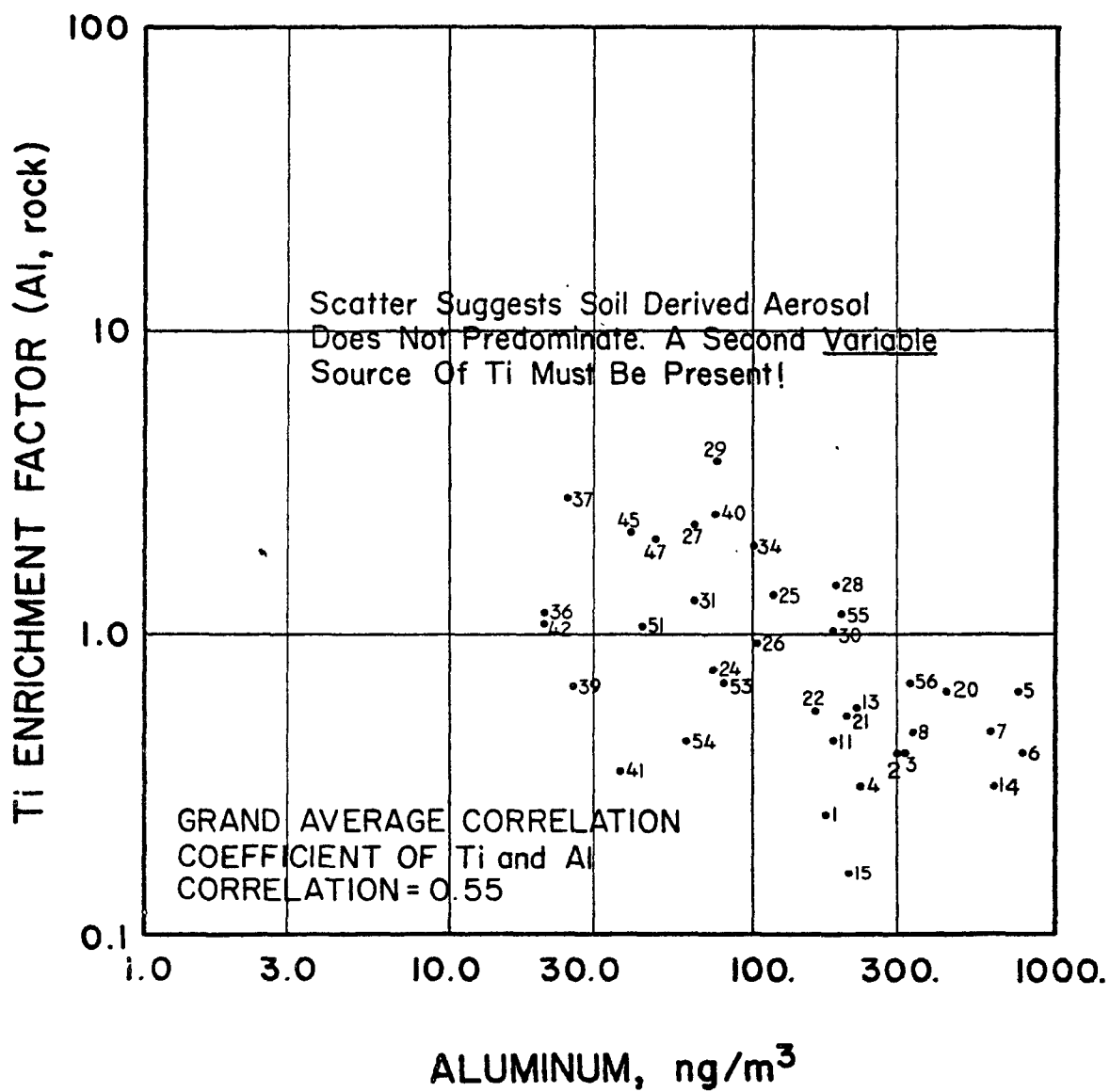


Figure 8. Scatter-diagram for Ti.



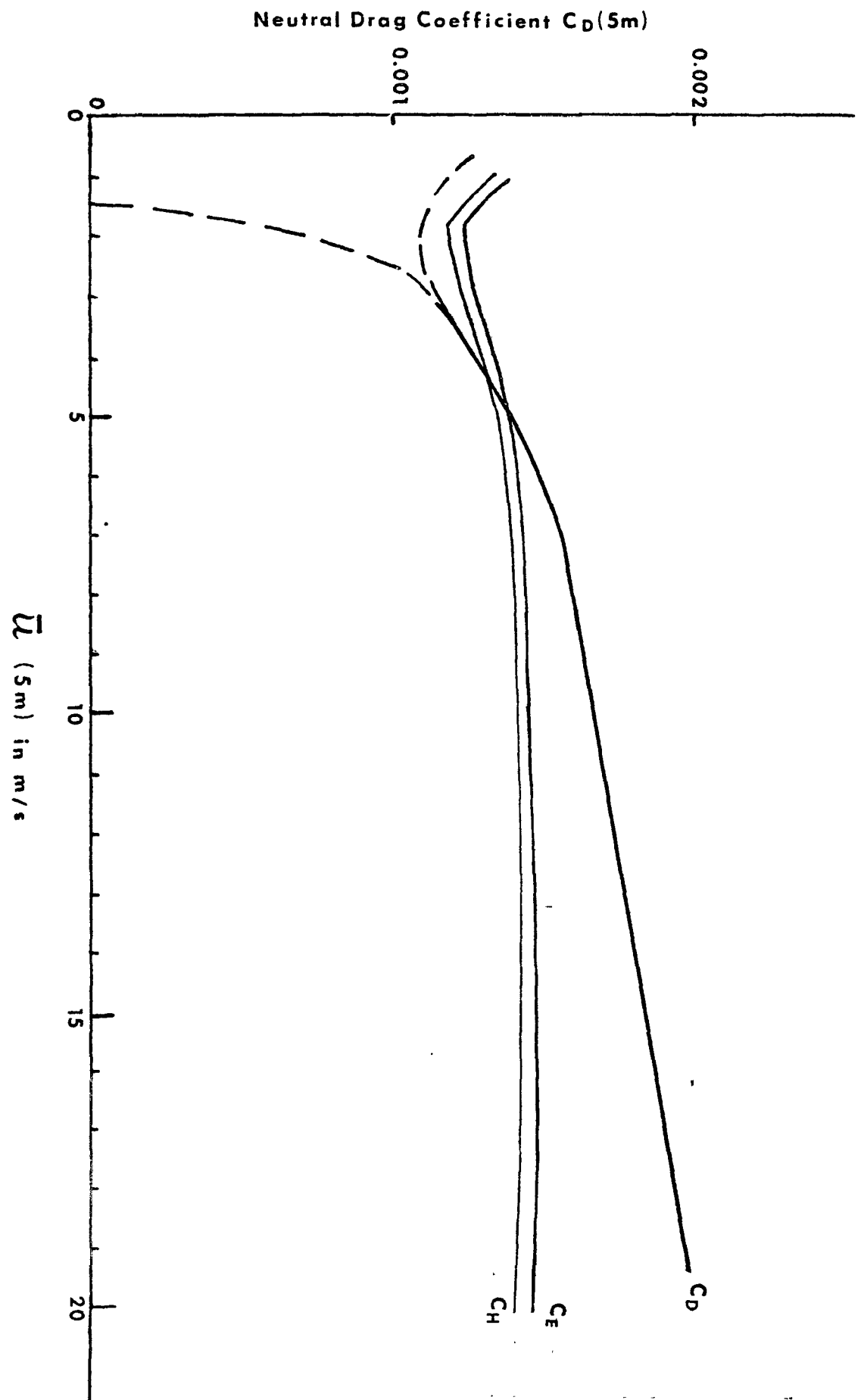


Figure 9. Neutral Drag Coefficient at 5 m Height

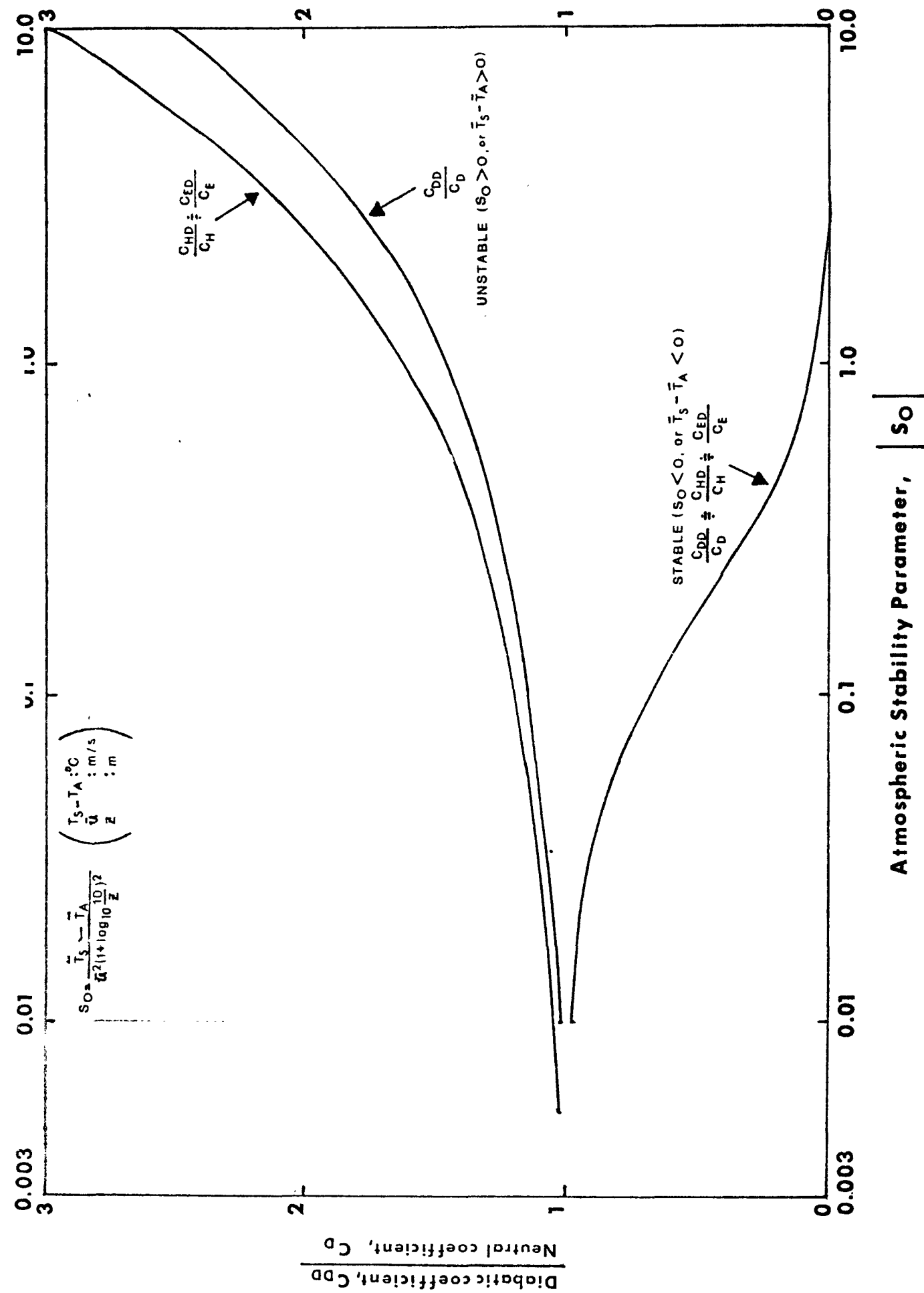


Figure 10. Diabatic Drag Coefficient Ratio to Neutral Drag Coefficient versus the Stability Parameter.