THE UNIVERSITY OF MICHIGAN
COLLEGE OF ENGINEERING
Department of Meteorology and Oceanography

Technical Report

PARTICLE SIZE DISTRIBUTION OF CHLORINE AND BROMINE IN MID-CONTINENT AEROSOLS FROM THE GREAT LAKES BASIN

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ORA Projects 01173 and 08903

supported by:

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
U. S. PUBLIC HEALTH SERVICE
NATIONAL INSTITUTES OF HEALTH
GRANT NO. AP-00585-02
BETHESDA, MARYLAND

and

U. S. ATOMIC ENERGY COMMISSION
CHICAGO OPERATIONS OFFICE
CONTRACT NO. AT(11-1)-1705
ARGONNE, ILLINOIS

administered through:

OFFICE OF RESEARCH ADMINISTRATION ANN ARBOR

August 1969

ACKNOWLEDGMENTS

I am most grateful to Professor J. W. Winchester for suggesting the problem and for offering support and encouragement throughout. In addition, some of the chemical analyses were done with the assistance of Miss M. A. Tiffany, W. R. Matson, and K. A. Rahn; constructive criticisms were offered by R. Dams, S. J. Jacobs, D. J. Portman, K. A. Rahn, J. A. Robbins, R. G. Stevens, and W. J. Weber, Jr. Use of The University of Michigan research vessel *Inland Seas* for sampling on Lake Michigan is acknowledged. The research was supported in part by contract AT (11-1)-1705, U. S. Atomic Energy Commission and by grants AP-00585, U. S. Public Health Service, and GA-811, National Science Foundation. I am also appreciative of the educational leave and partial salary provided by the Atlantic Oceanographic Laboratory, Bedford Institute, Dartmouth, Nova Scotia, Canada.

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ABSTRACT

Bromine (Br) and chlorine (Cl) have been measured in size-fractions of atmospheric aerosols by neutron activation analysis. Previous measurements (of Br and Cl in aerosol size-fractions near the ocean and in total aerosol both near the ocean and inland) indicated that aerosol Br and Cl differ in their sources and in their roles in the atmosphere. These differences, amidst their general similarity as halogens, allow positive inferences about the sources and atmospheric processes to be made. It was anticipated that measurements of Br and Cl in size-fractions of inland atmospheric aerosols might enable one to distinguish between inland and marine sources and to elucidate the roles of Br and Cl in the atmosphere.

As background, information about sources and atmospheric processes involving aerosol Br and Cl is assembled and perspectives are established. The primary data of this study are introduced and consist of distributions of Br and Cl with particle size together with maps and records of the meteorological conditions which prevailed during sampling. For the collection of aerosols by size-fraction, cascade impactors were used. The aerosol population was thereby divided into six, seven, or eight parts by particle size. Each aerosol size-fraction was analyzed by neutron activation to determine the contained Br and Cl. (Total aerosol mass was not measured.) The present data, coupled with the findings of previous investigators, permit the formulation of a model for the roles of aerosol Br and Cl in the atmosphere. This is summarized below.

The ocean seems to generate one halogen aerosol population. This consists

of small numbers of large and giant particles rich in Cl. The characteristics of this aerosol seem consistent at different times and places. Pollution sources appear to produce several halogen aerosol populations. For example, Br-rich particles are produced in large numbers by the combustion of leaded gasoline while Cl-rich particles are copiously produced by the combustion of coal.

Inland aerosols may arise from the ocean source, the pollution sources, or both. Marine aerosols may be transported inland by fast moving weather systems however rain en route will significantly reduce their concentration because the giant sea salt particles are readily activated as cloud-droplet nuclei.

The Cl-rich particles of pollution origin are found to be active in cloud-droplet nucleation, in preference over the Br-rich particles. This is probably due to the Cl-rich particles having greater solubility.

Br, initially distributed on particles in the Aitken size range, may become distributed throughout the stable aerosol range by being first volatilized and then readsorbed on the surfaces of particles. The data imply that for this process Br is preferred over Cl. It is noted that Br is oxidized preferentially to Cl to the free halogen gas and that a common reaction which may then occur is the addition of the halogen gas at the double bond of an unsaturated hydrocarbon, expected to be present in aerosols.

The variability of the inland aerosol halogens, in contrast with the consistency of the marine aerosol, occurs because in the former case a number of distinguishable subpopulations, each affected to a different degree by the highly variable meteorological conditions, are present. In the marine environment, the same atmospheric processes are suggested to be operative but on only one halogen aerosol population and under meteorological conditions held relatively constant by the sea.

There is some evidence to suggest that the "Junge distribution" for continental aerosols arises from the mixing of many subpopulations produced by independent sources rather than from equilibrium between heterogeneous coagulation and sedimentation of particles.

CHAPTER I

INTRODUCTION

Aerosols are liquid or solid airborne particles; they are important in the atmosphere because they may influence cloud and rain formation by nucleating cloud-droplets and ice crystals (Fletcher, 1962), may affect visibility by absorbing and scattering radiation, and may present a health hazard by being deposited in the respiratory tree (Cadle, 1965). In these roles, particle concentration, composition, and size distribution are determining factors. In this study, measurements of chlorine (Cl) and bromine (Br) in size-fractions of atmospheric particles were made and used to draw inferences about the sources of these aerosols and the atmospheric processes in which they are involved. Br and Cl are rewarding of study because their sources differ in a particular way, their condensed and gaseous forms can be involved in gas-particle reactions and their compounds are not passive to cloud-physics processes. These halogen measurements are the first for size-fractions of aerosols in an inland region and it was found that, by considering these data in their environmental context, a model for the roles of aerosol Br and Cl could be constructed.

Within the limitations of time and resources available, the study was planned to document as fully as possible the range of abundance and composition of halogens in aerosols from urban and rural inland locations. In this way, the factors most directly related to variations in aerosol halogens could be identified. Controlled experimental studies of these key factors, once determined, logically follow but are beyond the scope of the present work.

A. SOURCES OF AEROSOL Cl AND Br

1. The Ocean

The ocean is the greatest natural source of aerosol Cl, although in arid areas salt crystals in the soil may also become airborne (Eriksson, 1959). Airborne sea-salt nuclei are most commonly produced as droplets from bursting bubbles; the bubbles may arise from breaking waves (Blanchard and Woodcock, 1957). The sea-salt nuclei produced fall into the large ($0.1 < r < 1\mu$) and giant ($1 < r < 10\mu$) particle size-ranges. It will emerge below that because these aerosols are relatively large, the ocean is a strong source for mass of Cl while being at the same time a weaker source for numbers of sea-salt nuclei.

From Blanchard (1963), the oceanic production rate of airborne sea-salt nuclei, for wind speed 5 m/sec, is estimated to be 10^{-11} g NaCl/(cm^2-sec) or approximately 200 g Cl/(km^2-hr). This result is shown below to be on the order of magnitude of urban pollution source strengths; therefore the ocean is a strong Cl source. Marine aerosols are found by Duce <u>et al</u>. (1967), to have mass ratio Br/Cl close to that of sea water (0.0034). The oceanic production rate of aerosol Br is therefore estimated to be ~ 1 g Br/(km^2-hr). The number of nuclei produced is given by Blanchard (1963) to be approximately 5×10^{-2}/(cm^2-sec) or 200/(cm^2-hr). If one assumes uniform mixing to an altitude of 2 km and an exposure time of 100 hr, then the resultant nuclei concentration is 0.1/cm^3. This is comparable with concentrations measured by Woodcock (1953) and Metnicks (1958) but is considerably smaller than the concentration of droplets in clouds (10 to 1000/cm^3; Twomey, 1959). Sea-salt aerosols do nucleate cloud-droplets (Woodcock and Blanchard, 1955) but they are too few in number to be the major supply of nuclei (Junge, 1963).

2. Pollution Sources—The Combustion of Leaded Gasoline

Ethyl fluid, the automobile gasoline additive containing tetraethyl lead, also contains ethylene dibromide and ethylene dichloride with the mass ratio Br/Cl = 0.39 and Cl in the amount of 0.7 g Cl/gal (cited by Winchester *et al.*, 1967). Upon combustion, the halogens form PbBrCl which is relatively volatile at combustion temperatures. This salt is dispelled in the exhaust and thus Pb, Cl, and Br are scavenged from the combustion chamber and added to the atmosphere. Stipp (1960) reports that 95% of Br produced in the United States is used in ethyl fluid. Combustion of leaded gasoline is widespread but concentrated in the cities.

As a useful example, chosen because the data are readily available, the source strength for the city of Detroit can be estimated with two assumptions: (1) Of the annual consumption of gasoline in Michigan (3.4×10^9 gal, Kirby and Moore, 1967), half is used in Detroit. This is supported by the fact that half the population of Michigan lives in Detroit. (2) Half the contained Br and Cl is emitted in aerosol particles which remain airborne (Hirschler *et al.*, 1957, and Appendix D). Thus the average rate of production of aerosol Br and Cl from the combustion of leaded gasoline in the city of Detroit is estimated to be

$$(1.7 \times 10^9 \text{ gal/yr})(0.7 \text{ g Cl/gal})(0.5 \text{ aerosol Cl/total Cl})(1.1 \times 10^{-4} \text{ yr/hr})$$

$$= 70 \text{ kg Cl/hr}$$

and, correspondingly, 80 kg Br/hr. If the city area is approximated as

1000 km^2, then the source strength can also be expressed as 70 g Cl/(km^2-hr) and 80 g Br/(km^2-hr). In comparison with unit area of ocean surface the city may be a somewhat weaker source of aerosol Cl but a much stronger source of aerosol Br.

3. Pollution Sources—The Combustion of Coal and Fuel Oil

Stenger (1964) writes

> Throughout known portions of the earth's crust, chlorine is approximately 300 times as abundant as bromine, from which it appears that the solid portion (93%) of the crust contains an average of 1.6 ppm bromine. The magnitude of this figure is substantiated by analytical data on soils, rocks and plants.

Smith and Gruber (1966) report the Cl content of several American coals to range from 0.01% to 0.5%. While Walters (1967) finds Cl to vary from 0.005 to 190 ppm in high boiling fractions of three crude oils, Smith (1962) reports about 15 ppm Cl in one analysis of fuel oil.

Again one can estimate the source-strength of the city of Detroit for the production of Cl and Br aerosols—this time due to the combustion of coal and fuel oil. The annual consumptions of coal and fuel oil in Detroit are gauged to be 15 x 10^9 kg (Young and Gallagher, 1967) and 5 x 10^9 kg (Kirby and Moore, 1967), respectively. Based on the discussion above, the Cl content of coal and oil are taken to be 0.2% and 0.002%, respectively; the Br/Cl ratio is taken to be 0.0034. Finally it is judged that 15% of the contained halogens are emitted to the atmosphere (Cuffe and Gerstle, 1967). (Precipitators and filters cause this fraction to be less than that for automobile exhaust.)

The estimated production of aerosol Cl and Br due to the combustion of coal (which can be seen to be a more important source than the combustion of fuel oil) is

$$(15 \times 10^9 \text{ kg coal/yr})(0.002 \text{ g Cl/g coal})(0.15 \text{ aerosol Cl/total Cl})(1.1 \times 10^{-4} \text{ yr/hr})$$

$$= 500 \text{ kg Cl/hr}$$

and, correspondingly, 17 kg Br/hr. Corroboration in one respect is afforded by comparison of the rate of fall-out of soluble Cl in dust in a moderately-heavily polluted area of Detroit (400 g Cl/(km^2-hr); Katz, 1952) with the above estimate for source strength taken to apply over 1000 km^2. (Consumption of coal was of the same order of magnitude in 1952 and 1968.) This comparison is corroboration if, as is not unreasonable, the airborne and dust-fall components are of approximately equal mass (Junge, 1963).

There are other sources of Cl and Br in aerosols for which the source-strengths are more difficult to estimate. Industrial processes involving the halogens may lead to some atmospheric emissions. The municipal practices of chlorinating domestic water supplies and spreading salt on roads must lead to the formation of some halogen aerosols. However one would expect that Cl would be present much more abundantly than Br and that automobile exhaust would remain the major source of the latter.

A summary of estimated source strengths is given below.

Source	g Cl/(km^2-hr)	g Br/(km^2-hr)
Leaded gasoline combustion in a city	70	80
Coal combustion in a city	500	17
Ocean surface	200	1
Pollution sources on continent-wide average (Appendix D)	0.3 to 9.5	0.3 to 1.4
Ocean contribution inland on continent-wide average (Appendix D)	10 to 100	0.04 to 0.3

The perspectives that emerge are the following: (1) The ocean is a strong and extensive source for Cl but nonetheless, industrial regions can produce Cl aerosol at comparable rates. (2) Aerosol Br is produced as rapidly over the continental United States as over the ocean and pollution contributions downwind of cities would be expected to exceed that mass of Br which is of marine origin.

B. EXISTING DATA

In an important paper, Eriksson (1959) reviewed the work on atmospheric Cl and synthesized the available data into a model for the global cycle of Cl. Atmospheric Cl from the combustion of coal and leaded gasoline was not judged to be significant on the global scale; its significance over continental United States is evaluated in Appendix D.

Junge (1963) has also reviewed the role of atmospheric Cl. The data, which included Cl concentrations in rain and in large and giant aerosol particles, suggest that giant sea-salt nuclei can penetrate far inland, that Cl particles of radius less than 1μ are generated over land and that these continental particles can penetrate marine regions.

Measurements of atmospheric Br and I are less plentiful and are reviewed by Duce et al. (1965). They have measured Cl, Br, and I in rains and large and giant aerosols at various altitudes in Hawaii. Duce et al. (1967) provide a suite of more detailed size-spectra for Cl, Br, and I in large and giant marine aerosols near sea-level in Hawaii. As mentioned previously these aerosols show the average mass ratio, Br/Cl, to be on the order of the value in sea-water, 0.0034, but real variations between 0.001 and 0.01 are observed. Keane and Fisher (1968) have measured Cl and Br in filter aerosols from three locations in Britain. Their filters probably retained some of the Aitken particles as well as large and giant particles. The values for Br/Cl range from 0.005 in a relatively unpolluted coastal region to 0.035 in polluted areas. The time-series variations of Cl and Br in the polluted areas correspond only on occasion.

Lininger et al. (1966) collected aerosol particles by cascade impactor in the coastal city of Cambridge, Massachusetts. Br/Cl ranged from 0.01 to 0.3, and high values are attributed to particulate lead halide from automobile exhaust. However since Br/Pb was usually less than the value in leaded gasoline, the data suggest that Br is lost from the aerosol in the atmosphere. Winchester et al. (1967) measured Cl, Br, and I in snow and filter aerosols from Fairbanks, Alaska. Their samples were collected under conditions of strong temperature inversion which restricted the dilution volume for pollutants. Their data provide a reference for the relative concentrations and evolution of Cl, Br, and I in aerosols from automobile exhaust and the combustion of coal.

Lee and Patterson (1969) have presented a one-week average of cumulative size distributions for aerosol Cl from each of three locations, both coastal and inland.

With respect both to their sources and to the atmospheric processes which modify Cl and Br in aerosols, particle size distribution is a key parameter, Junge (1963) has shown that size distributions of marine and continental aerosols are fundamentally different. He chooses to express the distributions as the number or volume of aerosol particles per unit logarithmic size-range. Moreover he has recognized a "universal" mean distribution for atmospheric aerosols in populated continental areas. The "Junge distribution," n(r), can be approximated by

$$n(r) = \frac{dN}{d(\log r)} = C\cdot r^{-\beta} \qquad 0.1\mu < r$$

where N is the number of particles of radius less than r, C is a scaling factor and the empirical constant $\beta \approx 3$.

Following Junge (1963), aerosol surface area and volume distributions are expressed as

$$s(r) = 4\pi r^2 n(r)$$

and

$$v(r) = \frac{4}{3}\pi r^3 n(r)$$

respectively. Then the "Junge surface area distribution" is

$$s(r) = 4\pi r^2\cdot C\cdot r^{-3} = B\cdot r^{-1}$$

and the "Junge volume distribution" is

$$v(r) = \frac{4}{3}\pi r^3 \cdot C \cdot r^{-3} = B'$$

where B and B' are scaling factors. Thus, on the average in populated continental areas, the size distribution of aerosol surface area is observed to vary inversely with particle size while the size distribution of aerosol volume is observed to be constant with particle size.

Friedlander (1960) has offered a dimensional analysis similarity theory in explanation of the occurrence of the "Junge distribution." This theory involves dynamic equilibrium between coagulation and sedimentation of aerosol particles. Junge (1969) suggests that such a dynamic equilibrium cannot generally be approached over the requisite size range, 0.1 to 100μ, at a rate faster than the rate of change of meteorological conditions. His explanation is that the observed distribution arises not by heterogeneous coagulation so much as by the mixing (without coagulation) of aerosols from many independent sources both natural and anthropogenic. The situation envisaged is that the aerosol populations from each source may be distributed approximately log-normally in volume (as dispersion aerosols tend to be (Fletcher, 1962)) and that the resultant mixture might display a broad log-normal distribution, nearly constant over the stable aerosol range.

For continental aerosols there is approximately equal volume (or mass if density be assumed constant) in the large ($0.1 < r < 1\mu$) and giant ($1 < r < 10\mu$) particle size-ranges. The data for marine aerosols on the other hand show the mass to be greatest for giant particles, falling off sharply in the large particle size-range (Junge, 1963). Consequently, one may be able to distinguish between aerosols of marine and continental origin from size-distributions of Cl and Br. For instance, if Cl and Br in continental aerosols are distributed in some correspondence with the total mass, then continental Cl will be found in the large as well as the giant size-range whereas marine Cl will be concentrated on the giant particles. This can be tested with the present data.

C. ATMOSPHERIC PROCESSES

1. Preferential Loss of Br

Evidence is accumulating which suggests that as an aerosol ages Br may be lost from the particles preferentially to Cl. Duce et al. (1965) find Br/Cl values significantly less than the sea-water ratio in samples collected by aircraft over the sea. They discuss the possibility that photochemical oxidation of Br^- in preference to Cl^- might occur in the aerosol particle and afford a mechanism by which Br could escape as Br_2.

Lininger et al. (1966), who sampled aerosols in Cambridge, Massachusetts, find that their results suggest the escape of Br from the particles by reactions in the atmosphere. Winchester et al (1967) find preferential loss of Br in pollution aerosols from Fairbanks, Alaska. Pierrard (1969) studied the photochemical decomposition of PbClBr, a component of automobile exhaust, and found gaseous Br to be produced at twice the rate for gaseous Cl. The data of this study will be examined for evidence of preferential Br loss.

2. Cloud-Droplet Nucleation

Aerosol particles are eventually removed from the atmosphere by either dry or wet fallout. Wet fallout may occur by washout below the cloud (giant particles), by attachment to droplets within the cloud (through Brownian motion or Facy (1958) effect (Aitken particles)) or by cloud-droplet nucleation and subsequent rainout. The latter process is likely most important (Junge, 1963) and is of special interest in this study.

Cloud-droplet concentrations range from 10 to 1000/cm^3 (Twomey, 1959). The concentration of aerosol particles which are potential cloud-droplet nuclei must almost always exceed 10/cm^3 (Jiusto, 1967). The presence of cloud depends primarily on the availability of liquid water or ice. If liquid water is available, then aerosol particles may be activated as cloud-droplet nuclei. Rain may be formed after droplets or ice crystals have achieved sufficient size by condensation to grow rapidly by coagulation. The giant soluble particles will be activated first and followed by smaller or less soluble particles if the amount of available liquid water is maintained at a sufficient level. Giant soluble particles may, by their own efficient growth, deplete the supply of liquid water available and thus prevent the activation and growth of smaller particles. In any case, if the supply of available liquid water is exhausted, droplet growth by condensation is arrested.

The growth of a soluble aerosol particle by cloud-droplet nucleation (hereafter abbreviated CDN) and condensation of water vapor is described by Köhler curves (Figure 1). These show the existence of a critical supersaturation above which the particle grows markedly. The critical supersaturation increases for

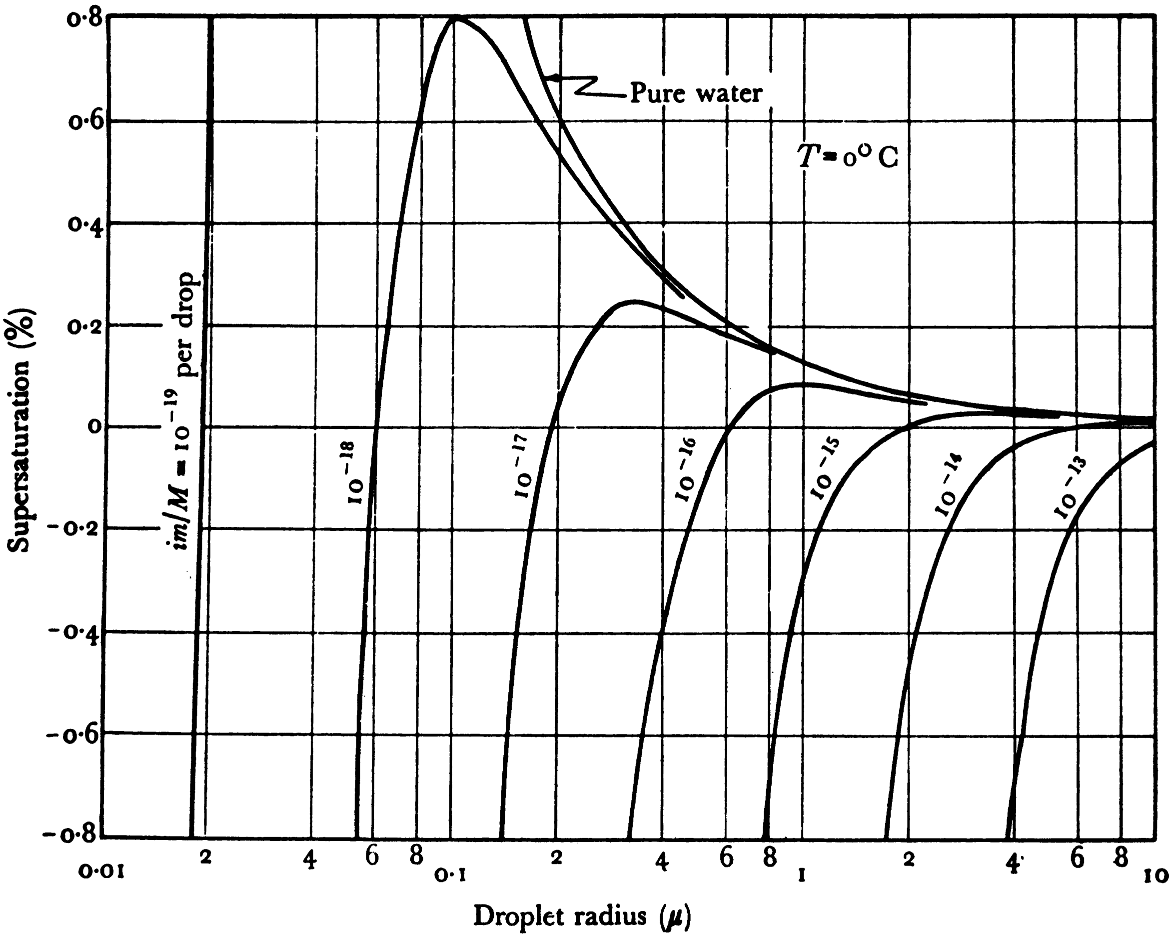

Figure 1. Equilibrium supersaturation as a function of droplet radius for water droplets, each containing mass m of solute of molecular weight M and van't Hoff factor i (after Fletcher, 1962).

decreasing particle size. Mordy (1959) explains that the rapid growth of the large and giant particles is due to their hygroscopicity (i.e., to their solubility which reduces the vapor pressure over the droplet) while the smaller particles depend for their modest growth on the supersaturation. Mordy then points out that a gap will appear in the aerosol number- or mass-spectrum as the hygroscopic particles grow by condensation away from the smaller particles. He calculates the dividing line between the activated and the nonactivated nuclei to be in the range, 0.05 to 0.5μ radius. A similar development is envisaged by Neiburger and Chien (1960). Junge (1963) has given a schematic diagram of the effect on the continental aerosol distribution of CDN; this diagram is reproduced in Figure 2.

In Figure 2 the "Junge distribution" is included. Let us consider simultaneously the distribution of marine aerosols which is shown in Figure 3 (curve 3). Starting at small radii, the marine distribution rises sharply to a peak in the large particle range, at a size fully tenfold larger than that of the continental distribution. In the giant range, both distributions fall off together. Now let us examine the process of CDN. Variations of critical supersaturation with particle size and solubility are summarized in Figure 2 and show the soluble giant particles to be most readily activated. Therefore one would expect the majority of the marine aerosols, because of their size and solubility, to be readily activated. As this occurred, these particles would grow larger. In the case of the continental aerosols, a gap would develop between the activated and unactivated particles. If the supersaturation were to be further increased, another wave of continental nuclei would be activated;

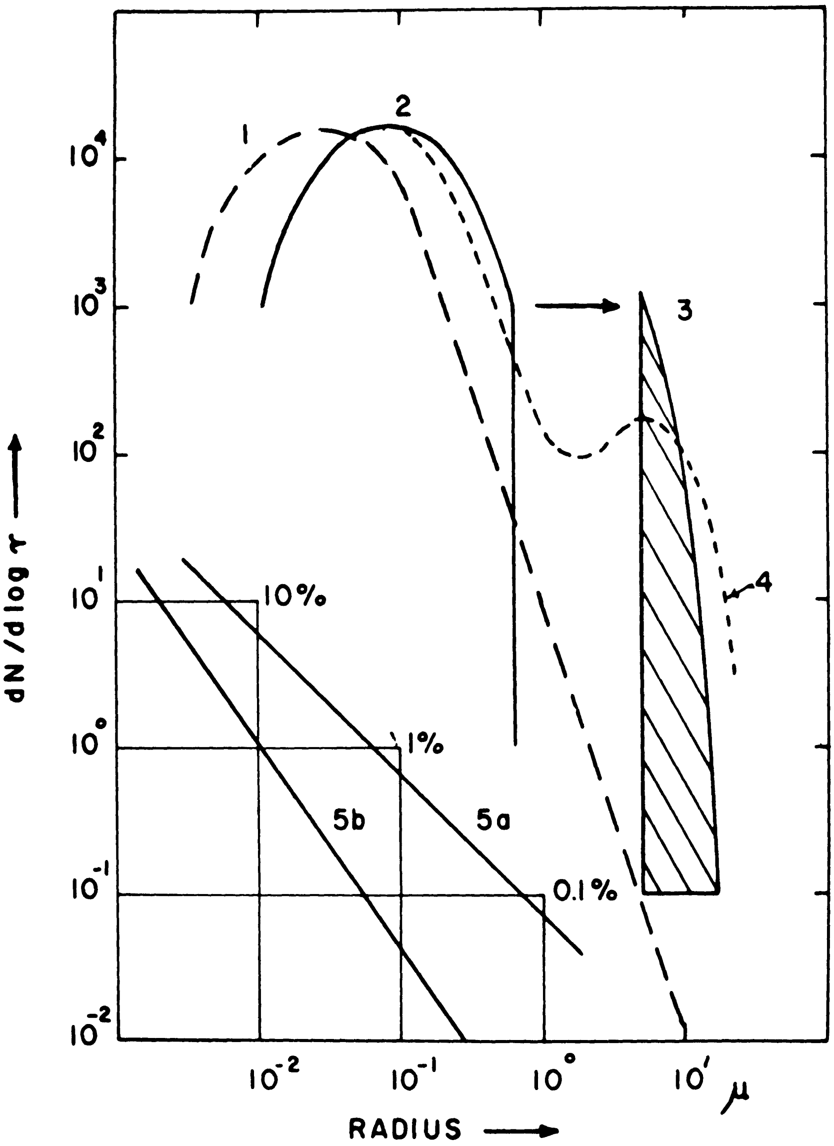

Figure 2. Schematic diagram of activated and unactivated condensation nuclei for continental aerosols: Curve 1, continental aerosol distribution at 70% relative humidity. Curve 2, unactivated condensation nuclei at 100% relative humidity. Curve 3, cloud droplets formed around activated condensation nuclei, according to Mordy (1959). Curve 4, expected combined distribution of unactivated nuclei and cloud droplets for clouds with an inhomogeneous temperature field, coagulation, and mixed nuclei. Curve 5, critical supersaturation as a function of radius at 100% relative humidity; curve 5a, insoluble but wettable particle (Thomson formula); curve 5b, NaCl particle. The difference between curves 5a and 5b is enhanced due to particle growth below 100% relative humidity (after Junge, 1963).

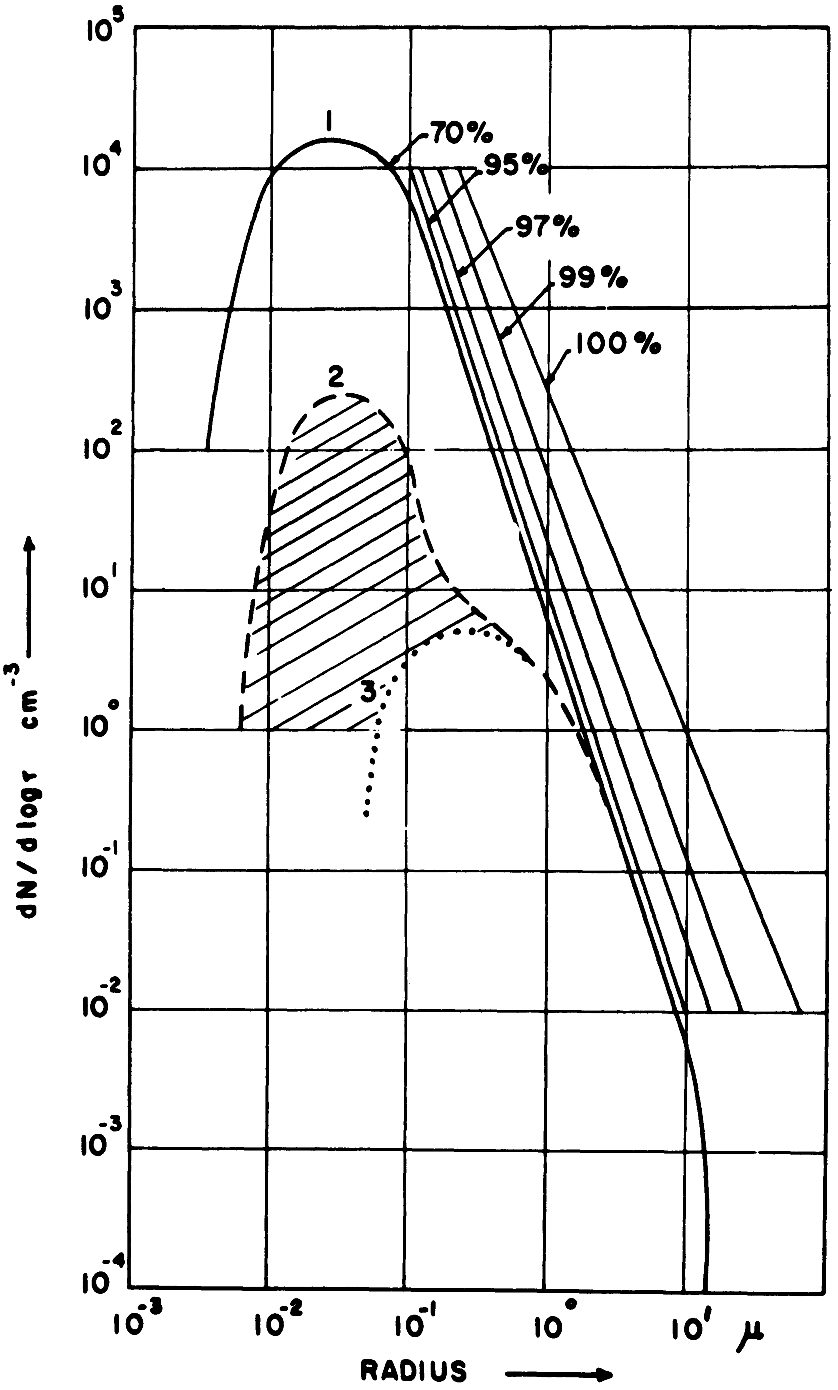

Figure 3. Model size distributions for atmospheric aerosols. Curve 1, continent. Curve 2, ocean. The part of the curve below 1μ is estimated. Curve 3, sea-spray component of the maritime aerosol. The hatched area between curves 2 and 3 represents the non-sea-spray component over the ocean.

The straight lines indicate the shift of the continental log radius-number distributions curve due to particle growth by humidity for mixed particles of about 20% soluble material (after Junge, 1963).

however, the nucleating ability of the marine aerosol would not be likewise sustained.

Source-strength and size-distribution can now be related with respect to CDN. The ocean, a source of large and giant particles in limited numbers, may be of reduced importance as a source of CD nuclei compared to pollution sources which produce large particles in prolific numbers.

Twomey (1959) distinguishes between cloud-droplet nuclei and condensation nuclei. The former act to nucleate cloud-droplets at the supersaturations of 1% or less encountered in nature; the latter are activated in expansion chambers where supersaturations are on the order of 100% (Fletcher, 1962). Therefore it is not certain that condensation nuclei from pollution sources (e.g., from automobile exhaust (Neuberger, 1952)) are CD nuclei and few measurements of cloud-droplet nuclei exist. In fact Twomey's (1959) observation at Sydney, Australia, was that pollution particles did not contribute significantly to CDN. He suggested that crystals of soluble material from drying soils were the most important component of the nuclei population in Australian continental air masses.

On the other hand, Jiusto (1967) has compared CD nuclei concentrations at Hilo, Hawaii, and Buffalo, New York, and finds the former premise to be verified; that is, the pollution particles, because of their strength in numbers, and despite their distribution mainly in the large and Aitken range, provide CDN nuclei in concentrations more than ten times those in the marine atmosphere.

While continuing to discuss CDN, let us shift attention from the total aerosol to the Cl component of the aerosol. Woodcock and Blanchard (1955) find sea-salt Cl to be involved in nucleation of rain drops. Junge (1963) concludes that the sea-salt particles are activated in company with Aitken and large particles not composed of sea-salt so that not more than 10% of the cloud-droplets will have grown around sea-salt particles. The present data afford an indication of whether or not Cl and Br in pollution aerosols are important for CDN.

In summary, this survey of the evidence for the sources and atmospheric processes involving Cl and Br in aerosols has provided the following background information:

(1) The ocean as a source for aerosol Cl is strong mass-wise but weak with respect to the numbers of particles produced.

(2) The continental United States is on the average a weak source for Cl mass but in industrialized areas the source-strength can surpass that of the ocean. Moreover, even on continent-wide average the number of particles produced per unit area over land exceeds the number produced over the ocean.

(3) The continental United States has an average source-strength for Br mass comparable to that of the ocean and in excess of the latter in pollution-generating areas.

(4) Marine Cl aerosols are large and readily activated as CD nuclei. Therefore rain-out and wash-out processes must act efficiently to remove them from the atmosphere. Nonetheless sea-salt particles could conceivably dominate the inland Cl aerosol if the flow of air from the ocean inland were swift, with little precipitation en route, and along a trajectory which avoided large cities. A swift flow would transport

particles with minimal loss by sedimentation although giving rise to dilution by mixing. However the marine aerosols arise from such an extensive source that dilution due to horizontal mixing, at least, would be much less effective than in the case of a plume from a city. Precipitation en route would substantially reduce the concentration of sea-salt aerosols; pollutants injected by large cities would mask marine Cl and Br aerosol.

(5) There is evidence for the loss of Br preferentially to Cl from marine and pollution aerosols.

(6) There is a need for study of the possible CDN role of Cl and Br in pollution aerosols.

CHAPTER II

THE EXPERIMENTAL TECHNIQUES

A. DATA COLLECTION AND PRESENTATION

The aerosol data are listed in Tables B-3 and B-4 of Appendix B. The basic data consist of the concentrations and standard deviations of Cl, Br, I and, in a few cases, Pb, in nanograms per cubic meter of air. Tables B-1 and B-2 list operating details with the filter data and meteorological conditions for the periods of sampling. In Table B-3 the data for each stage in the run, from Stage A at the top of the impactor to Stage Z, the filter are listed in series. In Table B-4 the impactor data are totalled and presented together with the filter data.

The impactor run numbers (e.g., Run 2:GR:II) have three parts. The first is the number of the run in chronological order of collection. The second part gives initials which identify the sampling site. The third part identifies the month in 1968 during which the run was made.

The sampling sites for these inland aerosols are labelled on the map of Figure 4. The initials GR stand for George Reserve, a parcel of land, partly wooded and located in a rural part of southeastern Michigan near the village of Pinckney and managed by The University of Michigan as a preserve. The site was used to obtain aerosols free from recent exposure to urban pollution.

The code, EE, indicates a run made at the East Engineering Building of The University of Michigan. The building is located in Ann Arbor which is a city of about 100,000 people. The sampling site is on the building's roof, about 30 m above street level.

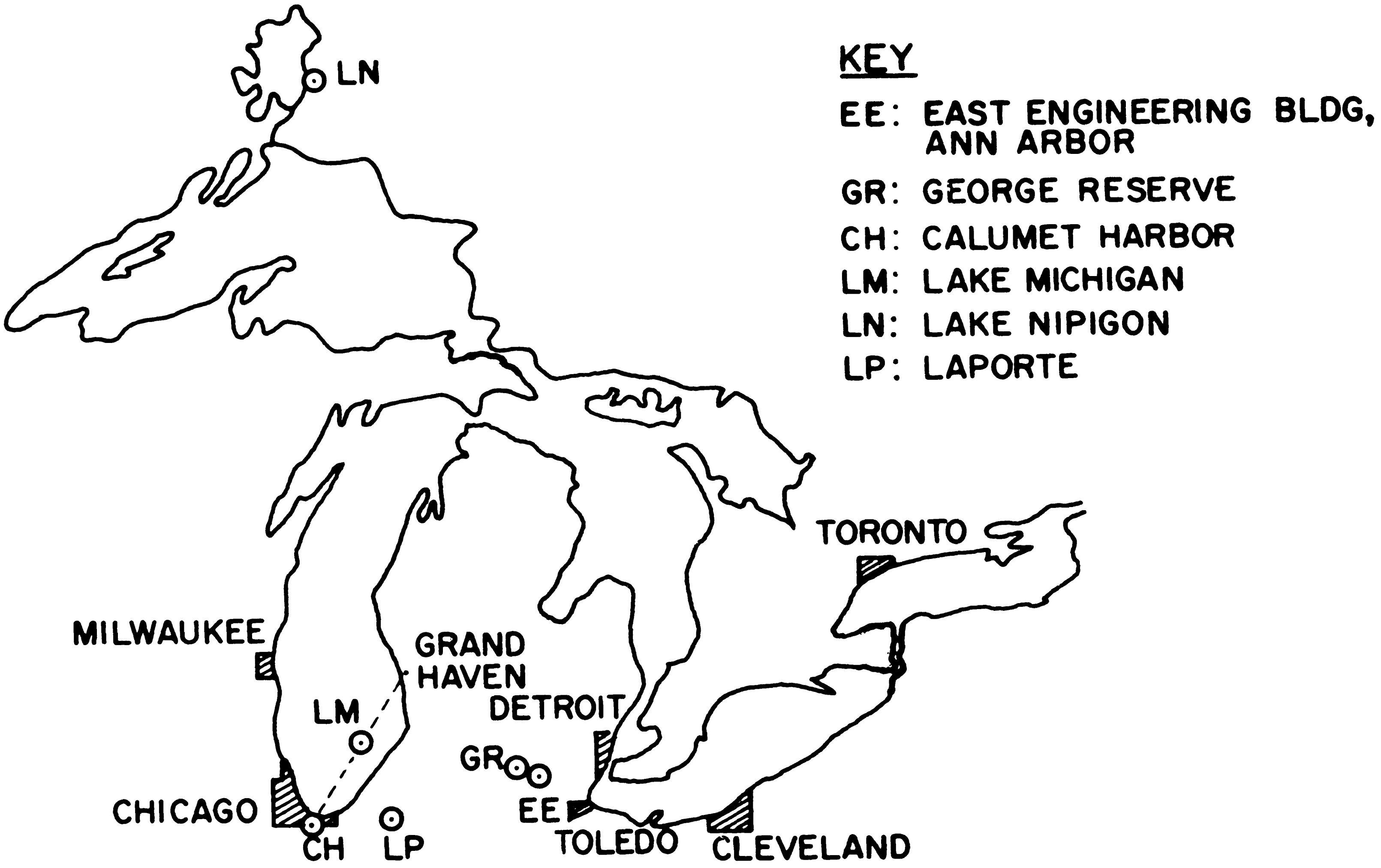

Figure 4. The locations of the sampling sites and neighboring large cities.

LM stands for Lake Michigan. Several runs were made on board The University of Michigan research ship, Inland Seas, on Lake Michigan between Grand Haven and Calumet Harbor. The samplers were isolated from fresh pollution sources by the expanse of water. Thus processes operating on aged aerosols could be studied.

CH identifies runs made in Calumet Harbor, Chicago, a harbor which extends inland from Lake Michigan to docks surrounded by heavy industry and overpassed by expressways. The aerosols collected there do reflect these conditions.

LN refers to Lake Nipigon. Runs were made on the lakeshore at the provincial park in order to establish the background aerosol concentrations in inland air not yet exposed to pollution sources. However, continuous southerly winds during our visit, rather than the northwesterlies we had hoped for, may have brought some aged pollution aerosols from the south.

LP signifies La Porte, Indiana. The sampling site here was in the middle of the municipal airfield. It was hoped that westerly winds would prevail so that our samples might bear on the La Porte weather anomaly (Changnon, 1968). Actually southerly winds were encountered.

AG, or automobile garage, identifies runs made at my home garage, 30 m from the street in a residential part of Ann Arbor. These runs were made for the purpose of sampling automobile exhaust, both in the ambient aerosol from the street traffic and fresh from the exhaust pipe of a car.

In order to estimate the sources of the aerosol sampled, and the path, speed and meteorological conditions of its journey from source to sampler, a kind of trajectory analysis was undertaken. For example, Figure 21 consists basically of the North American surface weather map (National Weather Records

Center, Asheville, N. C.) upon which have been sketched dots joined by straight lines accompanied by an arrow and a number. The lines indicate the estimated path of the air which was sampled at the time indicated by the number e.g., 0700 hr. The prime on the number signifies that the arrival time is a day later than map date or a day later than the arrival time on another, unprimed, trajectory number. The arrows show the directions of travel; the dots show the position of the air at 3- or 12-hr intervals. Winds at the 850-millibar level (12-hr) were used in those cases where, by the high surface winds and alignment of surface and upper air flows, rapid transport over great distances was likely. In cases where air masses were moving slowly or where weather features were of local extent, geostrophic winds at surface level (3-hr) were used.

To supplement the description of meteorological conditions obtainable from the trajectory maps, Table B-2, Appendix B, lists ranges of meteorological data at a nearby station during the period of sampling. These data were abstracted from the records of Local Climatological Data, National Weather Records Center, Asheville, N. C. The station referred to for collections made at the East Engineering Building was Willow Run Airport (15 km east of Ann Arbor).

B. AEROSOL SAMPLING INSTRUMENTS

Cascade impactors were used to collect aerosols by size fractions. These instruments (Figures 5 and 6) consist of a series of jets—each of which is followed by a plate for collecting the particles. The principle of operation is this: as the air is accelerated through the jet, the more dense aerosol particle is also accelerated and, being relatively massive, acquires high axial momentum; upon reaching the neighborhood of the collector plate the air flow curves around; however, the aerosol particle only curves to the extent that its radial momentum—developed by the drag of the curved flow—can overcome its existing axial momentum. If the axial momentum remains a significant component of the resultant momentum, the particle will impact upon the impactor plate. If the particle is liquid or tarry or the plate wet or sticky, the particle will stick. If the particle does not stick or if the radial momentum comes to dominate the axial momentum, the particle will travel around the plate and into the next stage. Here the jet is reduced in area; consequently the axial velocity and particle momentum become higher than in the previous stage. Again the air flow curves around the plate. By construction the jet-to-plate distance is large enough so that any increase in particle radial momentum is less than the increase in its axial momentum. Thus a particle which is not sufficiently massive, either because of low density or small size, to impact on the first stage will, in the second stage, have axial momentum more likely to dominate radial momentum and result in impaction. The fractionation continues through six or seven stages—the jet decreasing in area at each stage. Finally the air passes through an in-line filter (Gelman, Type A).* In this work the cascade impactors used were the Scientific Advances, Inc., Model CI-S-6** (Figure 5) and the Andersen Air Sampler,*** Model 0203—modified to seven stages (Figure 6).

Mercer (1963) has considered methods of calibrating cascade impactors.

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*Gelman Instrument Co., P.O. Box 1448, Ann Arbor, Mich. 48106.

**Scientific Advances, Inc., 1400 Holly Ave., Columbus, Ohio.

***Andersen Air Samplers, 1423 S. 2nd. West, Salt Lake City, Utah.

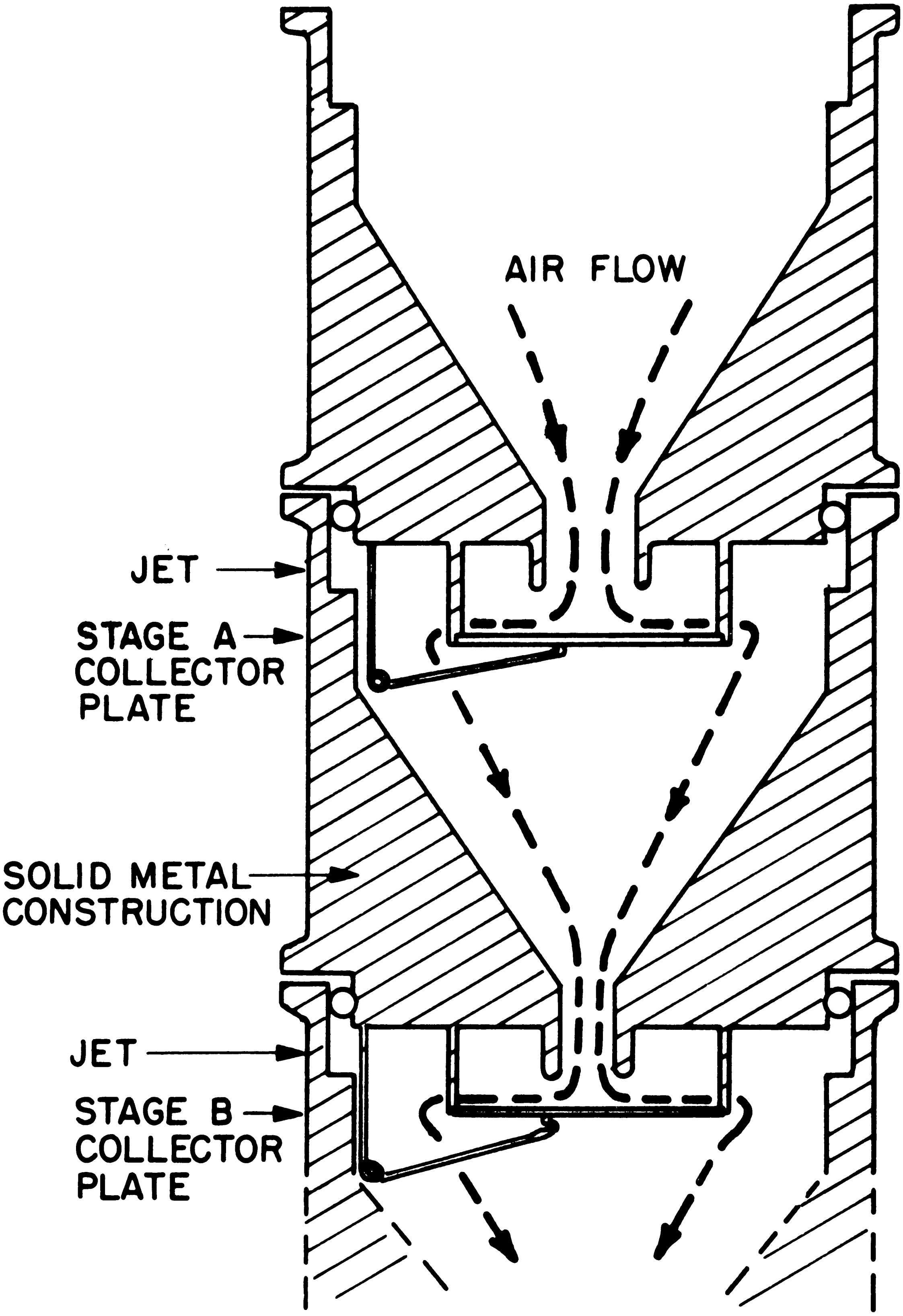

Figure 5. Schematic view of two of the six stages of the Scientific Advances Inc. cascade impactor, Model CI-S-6.

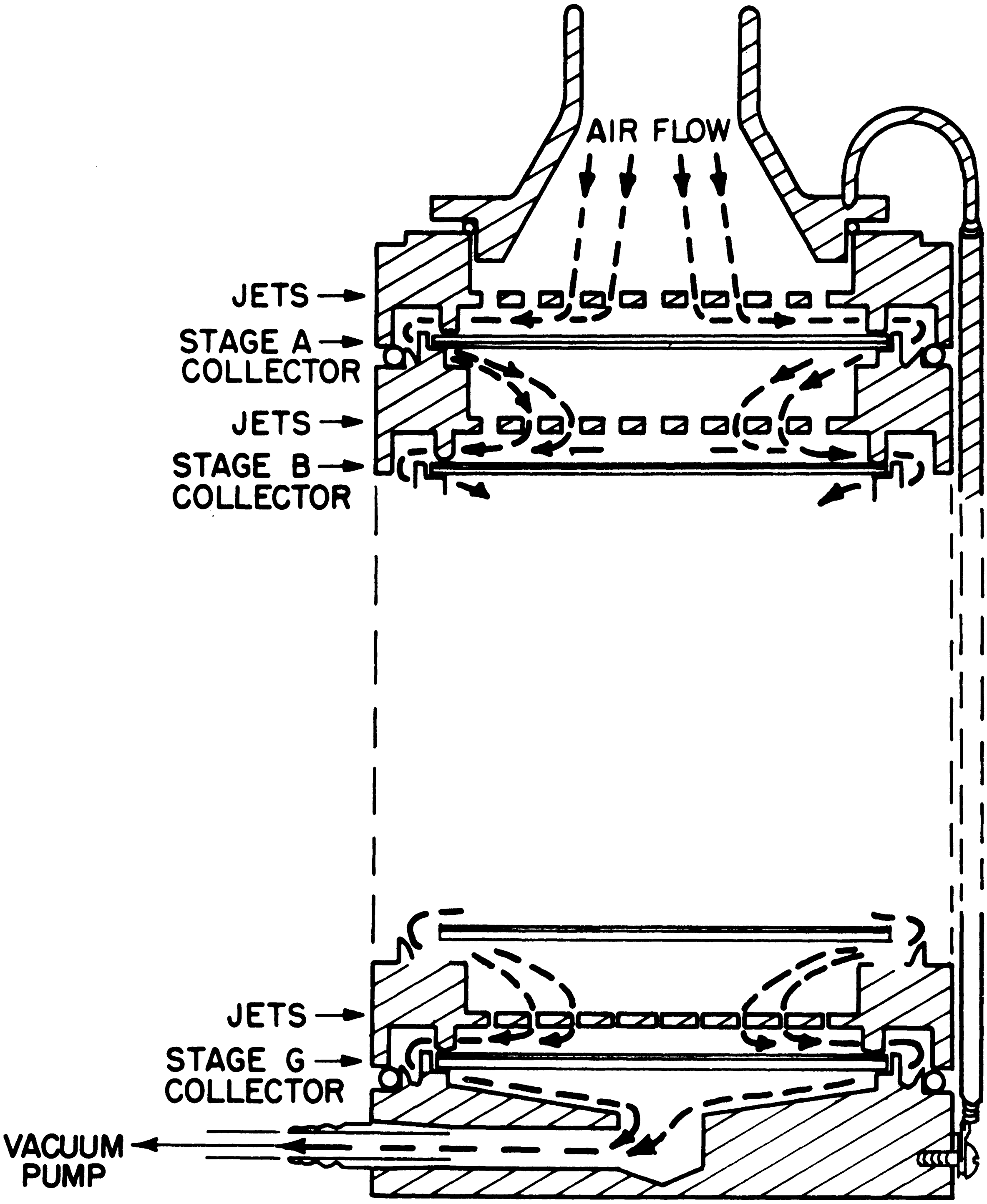

Figure 6. Schematic view of the Andersen Sampler, Model 0203 cascade impactor.

For our purposes he recommends the determination of collection efficiency as a function of particle size for each stage. He also suggests criteria for satisfactory resolution and collection of particles by size. These criteria are expressed nondimensionally in terms of the calibration data. The calibration of the Scientific Advances impactor (hereafter abbreviated SA) was carried out by Mitchell and Pilcher (1959) (Figure 7). The performance of the Andersen Sampler (hereafter abbreviated AS) was measured by Flesch _et_ _al_. (1967) (Figure 8) and Lundgren (1967). From these calibration data our calculations show that both impactors surpass the minimum requirements suggested by Mercer (1963).

Air was drawn through the impactors by an electric vacuum pump (Gelman, Catalog no. 25002)* at rates of 12.5 and 28 liters/min for the SA and AS impactors, respectively.

In time of rain a shield was fitted or, alternatively, the impactor was operated in a standard U.S. Weather Bureau meteorological shelter. The conclusion was reached, after the sampling was begun, that the collecting plates should be made sticky to assure retention of particles after impaction. The evidence is presented in Appendix A.

In Appendix B, Table B-1 shows, for each run, the sampling period (usually tens of hours), the air volume sampled, the impactor used, and information as to whether a filter was used and whether the collecting plates were made sticky. In the first two runs the particles were collected on the surfaces of glass plates. Subsequently the technique was found to be improved by using thin

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*Gelman Instrument Co., P.O. Box 1448, Ann Arbor, Mich. 48106.

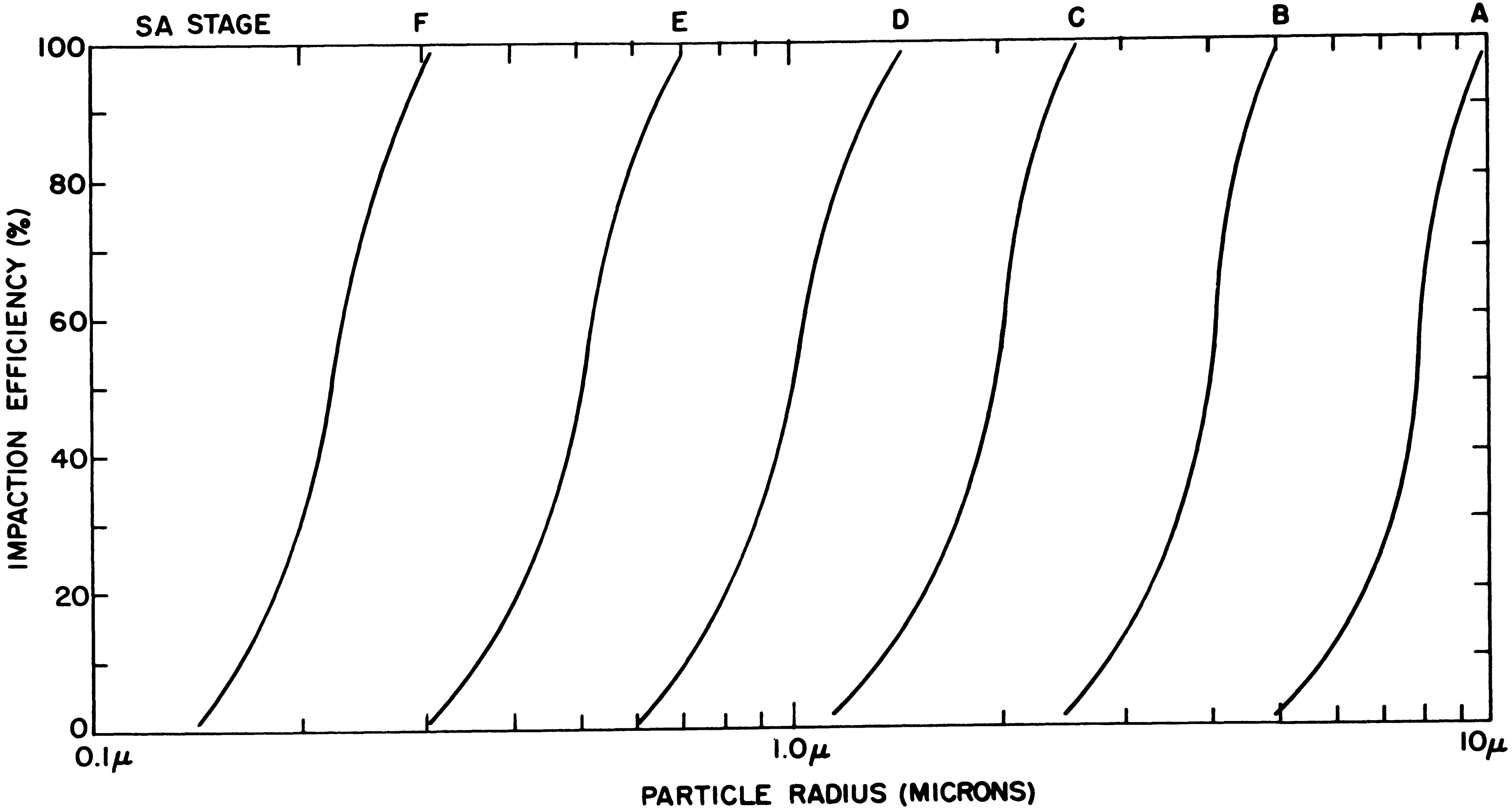

Figure 7. Efficiency curves for the SA impactor (after Mitchell and Pilcher, 1959).

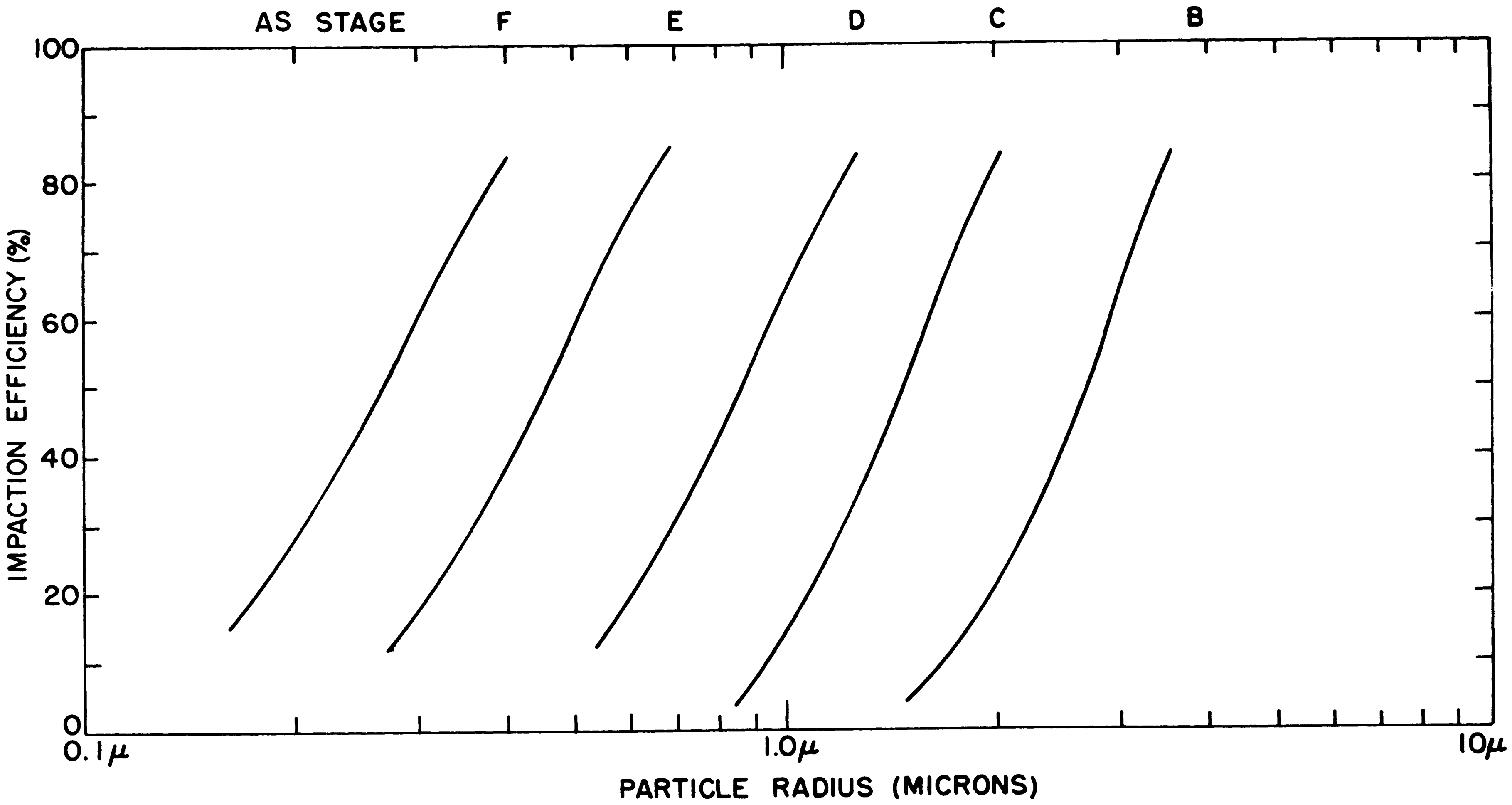

Figure 8. Efficiency curves for the AS impactor (after Flesch et al., 1967).

polyethylene discs over the plates. The collecting surfaces were first washed with warm concentrated nitric acid and rinsed in distilled water. Then if they were to be made sticky they were thinly coated with glycerol and installed in the impactor. At the conclusion of a run the polyethylene discs were transferred to disposable plastic Petri dishes for storage until the time of analysis. For those collections made on glass, the aerosol sample was washed with distilled water into a clean polyethylene vial for storage.

C. CHEMICAL ANALYSIS

Cl, Br, and I were determined using neutron activation analysis and two radiochemical and radioactivity measurement procedures. The first technique involved chemical separations and β-detection; the second, γ-detection with some preparatory chemistry.

A portion of the polyethylene disc with its aerosol sample was irradiated in a flux of approximately 2×10^{12} neutrons/cm^2/sec in a pneumatic tube of the Ford Reactor, Phoenix Memorial Laboratory, The University of Michigan. After irradiation (usually for 30 min), the two techniques diverged. For β-detection the sample was dissolved off the disc in water. Aliquots of this solution were taken for Cl and Br+I according to the procedure of Duce and Winchester (1965). Cl, Br, and I were each separated as silver halide precipitates and were counted individually using an end-window proportional counter. The mass of a halogen in the sample was determined from the count-rate by comparison with standards taken through the same procedure.

For γ-detection the irradiated sample on polyethylene, was rinsed with scraping into a KCl-KBr carrier solution. The solution was made reducing by adding a few drops of 0.5M sodium meta-bisulphite solution. After addition of silver nitrate the composite silver halide precipitate from this solution was placed on either a NaI or a Ge(Li) scintillation crystal for γ-counting using a multichannel analyzer and comparison with standards.

The inland aerosols were, for two reasons, somewhat difficult to treat via the β-method: (1) The aerosols often contained a manganese component which appeared as a contaminant in the Cl aliquot. (2) The high value of Br/Cl led to some Br interference, also in the Cl aliquot, because of incomplete evaporation of Br. In addition, unless one is experienced in wet chemistry there is a risk of over-oxidizing at one point in the Br separation. Later, when it became feasible, γ-ray spectrometry was used, both for new samples and for deriving corrections to the β-results, around 30% in the Cl and Br samples. These alteration were systematic and usually small (e.g. 30%) compared to the range of variation in the Cl and Br size-spectra (e.g. 1000%) (Appendix A). Also the results are reproducible to with ±2 standard deviations with sticky slides (Runs 13 and 14) or high humidity (Runs 35 and 36) and to within ±3 standard deviations with dry slides and low humidity (Runs 9 and 10).

For a few impactor runs a portion of the sample was measured for its lead content using anodic stripping voltammetry with a composite mercury-graphite cathode (Matson _et_ _al_., 1965). Lead ions, as well as several other cations, are electroplated into a thin Hg film on the surface of the graphite cathode from a solution of the sample in which the electrodes are immersed. Then the negative voltage across the cell is swept in the positive direction toward zero, and the cations are stripped off the cathode, one element at a time. Each element leaves the cathode in a surge of Faradaic current. The surges are separate and occur at particular cell voltages which are related to the electrode potential for the cell reaction through the Nernst equation (Daniels and Alberty, 1966). The charge measured by a strip-chart recorder for each element is directly related to the amount of the element in the sample.

CHAPTER III

RESULTS

In this chapter, both previously existing and present measurements of aerosol halogen size-spectra are introduced. The Br and Cl data from Duce et al. (1967), collected from a tower on the windward beach in Hawaii, are reproduced in Figures 9 and 10. These spectra of halogens in size-fractions of fresh marine aerosols are compared with the present results for inland aerosols.

In each diagram, the impactor stage designations are displayed along the abscissa with particle size increasing to the right. Since the 50%-effective-cut-off radii increase approximately twofold for each impactor stage from F to A (Figures 7 and 8), the abscissa is, in effect, logarithmic in radius. The ordinate on the left (e.g., Figure 11) is the scale of concentration of Cl and Br mass, i.e., nanograms of the elements on the aerosol particles of one size fraction in 1 m^3 of air. The ordinate on the right is the scale for the mass ratio of Br/Cl in grams per gram. The dotted sloped line (with r^{-1} dependence) in the lower portion of each graph is used in Chapter IV as an aid to interpretation. If Cl(r) is the Cl concentration in all particles of radius less than r, then this line has the equation

$$\log_{10}\left(\frac{d\ Cl(r)}{d\ \log_2 r}\right) = -(\log_{10} 2)\cdot\log_2 r + K$$

where K is a scaling factor; the left-hand side is equivalent to the ordinate and $\log_2 r$, to the abscissa variable in our diagrams.

A. RUNS 4 to 11:HAWAII

The data of Figures 9 and 10 show the Hawaiian marine aerosols to have mass ratio Br/Cl equal approximately to the value for sea-water and character consistent from run to run—in fact the uniformity is remarkable. The spectra of Run 8:HAWAII are representative and are included in Figure 11 for ready comparison with inland aerosols. When the Cl spectrum of Run 8:HAWAII is converted from Cl mass on particles of known radius range to the equivalent number of NaCl particles in those ranges of radii, the data correlate well with those of Woodcock (1953) and Metnieks (1958) for sea-salt particles from Hawaii and Ireland, respectively. Therefore Run 8:HAWAII may be quite representative of Cl in marine aerosols and the uniformity of spectral shape is suggested to be general.

In Figure 11, by way of contrast, two inland runs, 2:GR:II and 35:EE:IX can be seen to differ from Run 8:HAWAII and from each other.

B. RUN 2:GR:II (FIGURE 11)

This run was collected at George Reserve, a rural site in southeastern Michigan. Trajectory analyses (Figures 21 and 22) from the flow pattern at 850 mb for the period of this run indicate the air to have travelled from the Arctic—at times from the region of the Labrador Sea—in a period of one to three days. The total Cl concentration in the impactor size-range for Run 2: GR:II is 10% of that for Run 8:HAWAII. Also the Cl spectral shapes differ; compared to Run 8:HAWAII, the Cl spectrum of Run 2:GR:II is shifted to the larger particle sizes. The total Br concentrations in the impactor size-range are nearly the same in the two cases and the Br spectral shapes are similar. The ratio Br/Cl is, on the smaller inland particles, much greater than on the fresh marine aerosol but decreases as particle size increases so that the values are comparable on Stages A and B.

C. RUN 35:EE:IX (FIGURE 11)

This run was collected at the East Engineering Building during a period of thunder showers. Trajectory analysis (Figure 23) shows the air flow to have been slowly northward from Ohio, ahead of a cold front. The total Cl concentration, in the impactor size-range, is greater than in Run 2:GR:II. Moreover the distribution of Cl shows concentrations greatest on the smaller-sized particles in direct contrast to the results of Run 2:GR:II. The total Br concentration, in the impactor size-range, is more than thirtyfold greater in Run 35:EE:IX than in Run 2:GR:II. Further, the Br distribution mirrors the Cl distribution even to its gaps and peaks. The mass ratio Br/Cl for Run 35:EE:IX is relatively invariant with particle size and from four to thirty times larger than corresponding values for Run 2:GR:II. Compared to Run 8:HAWAII, Run 35:EE:IX has somewhat less Cl mass but much greater Br concentration, both distributed on smaller sized particles, and much higher Br/Cl values.

D. RUNS 3, 4, 5, and 6:EE:III (FIGURE 12)

These runs were collected in sequence (with interruptions) from March 7 to 14, 1968. For Runs 3 and 4:EE:III, the air trajectories (Figure 24) were, for at least part of the time, swiftly northward from the Gulf of Mexico; the air sampled had not yet spawned precipitation. Dry-bulb temperatures and dew-point temperatures at Willow Run Airport increased with the arrival of the southern air.

For Run 5:EE:III, the trajectories (Figure 25) of air sampled (wind direction) varied rapidly although wind speeds were not extremely high. Under these conditions it was judged preferable to estimate trajectories using the surface-level pressure patterns for geostrophic winds at 3-hr intervals. The Willow Run temperatures indicate that air of long-distance continental trajectory was sampled for approximately 85% of the period and air with both ocean and continental trajectory, for 15% of the time. The latter may have spawned some precipitation.

For Run 6:EE:III, the air trajectory (Figure 26) was once again from the Gulf of Mexico to Michigan in about 24 hr. Dry-bulb temperatures and dew-point temperatures again rose at Willow Run Airport.

Runs 3, 4, 5, and 6:EE:III show characteristics more akin to those of Run 2:GR:II than to Run 35:EE:IX although some similarities with the latter are noticeable. The Cl concentrations, on particles of radius greater than 0.2μ, are relatively high and comparable with those of Run 8:HAWAII. The Cl is distributed, as in Run 2:GR:II, mainly on the giant particles. This pattern is distinct and reproduced throughout the sequence. The Br concentrations exceed those of Run 2:GR:II. For Runs 3 and 4:EE:III, the Br concentration is greatest on the smaller particles; for Runs 5 and 6:EE:III, more resemblance to the peaked distribution of Runs 2:GR:II and 8:HAWAII is shown. With respect to the ratio Br/Cl, the values for Stage A in these four runs are quite low (0.004) and approach those of Runs 2:GR:II and 8:HAWAII. On subsequent impactor stages, however, the ratios rise: for Runs 3, 4, and 5:EE:III, as high (Br/Cl = 0.1) as in Run 35:EE:IX; for Run 6:EE:III, to intermediate values (Br/Cl = 0.06).

E. RUNS 15, 16, and 19:LM:V (FIGURE 13)

These runs were collected on two consecutive days from shipboard in the southern basin of Lake Michigan. The synoptic trajectories (Figure 27) show the air to have moved southward at moderate speed over some inhabited regions. The sampling sites on Lake Michigan may have afforded considerable isolation from pollution sources. The characteristics of the data are intermediate between those of Runs 2:GR:II and 35:EE:IX. Total concentrations of Cl and Br, in particles of radius greater than 0.2μ, are comparable with those of Run 2:GR:II. However the spectral shapes, with the small particles being Br-rich and the giant Cl-rich particles being masked or absent, resemble Run 35:EE:IX more than 2:GR:II.

F. RUNS 37 TO 41:AG:IX (FIGURE 14)

This sequence of runs represents a preliminary step toward the set of controlled experiments which will be required to answer the questions opened by the present data. These runs sampled automobile exhaust during aging as a test for preferential Br loss.

For Run 37:AG:IX, the garage was empty and its doors were open; thus what was sampled was the background aerosol 30 m from a city street. The relative humidity exceeded 80% and rainshowers occurred. Afterward, exhaust from an automobile engine burning a premium gasoline was injected into the garage for a period of 10 min. During this time Run 38:AG:IX was made. The automobile was removed and the garage doors were closed, although a little daylight was admitted through the windows. The exhaust aged for two and one-half hours and was sampled intermittently in Runs 39, 40, and 41:AG:IX.

In Run 37:AG:IX the Cl and Br spectra are similarly shaped, having concentrations highest on the small particles and showing a gap at about 0.2μ. The Br/Cl ratios are somewhat lower than for Run 35:EE:IX. The filter fractions of Runs 38 to 41:AG:IX show striking variation in Br/Cl. This is illustrated in Figure 15. The ratio is high (Br/Cl = 0.3) in particles freshly produced by combustion of leaded gasoline and, over a time interval of about 40 min, decreases by more than tenfold.

G. RUNS 17 and 18:CH:V (FIGURE 16)

The aerosol data show very high concentrations for both Br and Cl in Calumet Harbor which is an industrial section of south Chicago. The Br/Cl values are comparable with those of Run 35:EE:IX and vary similarly for each run although the ratio of total Br to total Cl is significantly higher for Run 17:CH:V than for Run 18:CH:V.

The size-distributions show Br-rich and Cl-rich small particles with the masses of Br and Cl decreasing in the larger particle size-ranges. It is noteworthy that the Br and Cl distributions are all similarly shaped.

The collection of Run 17:CH:V extended over late afternoon and evening. Run 18:CH:V was collected subsequently, from 0300 to 0600 hr EST. The synoptic meteorological conditions were little changed from those of Figure 27. The relative humidity did rise above 90% during Run 18:CH:V but skies were clear and winds, light.

H. RUNS 9, 12, and 13:EE:V (FIGURE 17)

During the period of Run 9:EE:V, the air from a high pressure cell was moving slowly southward in Michigan (Figure 28); haze was observed from the East Engineering Building. This air had not spawned rain within at least 24 hr. Relative humidity was less than 50% during daylight. However the next day, during Run 12:EE:V, the wind direction changed and trajectories approached Ann Arbor from the southwest (Figure 29); atmospheric stability, as gauged from the variance of wind direction (Baulch, 1962), decreased; and traces of rain were associated with the air mass sampled. Run 13:EE:V was collected two days after Run 12:EE:V during the passage of a low (Figure 30). Rainshowers and thunderstorms were experienced.

The Cl and Br distributions for these three runs all show concentrations highest on the small particles. In fine structure, Run 13:EE:V shows more gap and peak, sawtooth character than do Runs 9 and 12:EE:V. The variations of Cl concentration and Br/Cl mass ratio are intriguing. From Run 9 to Run 12:EE:V, Cl is significantly reduced although the Br concentrations are comparable. From Run 12 to Run 13:EE:V, Cl and Br are reduced by about 60% although the values of Br/Cl are preserved.

I. RUNS 31 and 32:LN:VIII, 33:LP:IX, 35 and 36:EE:IX (FIGURES 13 and 18)

During both Lake Nipigon runs the synoptic-scale flow (Figure 31) was northward from the midwestern United States without rain. Haze was observed at the site but skies were mostly clear.

For Run 33:LP:IX, La Porte, the air sampled had likely spawned rain within the previous two days while moving slowly northward up the Mississippi Valley (Figure 32).

Runs 35 and 36:EE:IX were simultaneous; the former with sticky slides, the latter with dry slides. Run 35:EE:IX has been presented in Figure 11 but can also be usefully included in this group. The air mass sampled (Figure 23) had moved slowly northward from Ohio and Indiana preceding a cold front with which were associated thundershowers. The wind records from the meteorological tower on the East Engineering Building showed winds variable from southerly to easterly. Relative humidity exceeded 80% for half, and 70% throughout, the sampling period.

Again all the spectra have the same general shape with the Cl- and Br-rich particles being concentrated in the smaller size-fractions. The La Porte aerosol has Cl and Br/Cl higher than in the Lake Nipigon aerosols. Compared with Run 33:LP:IX, Runs 35 and 36:EE:IX have similar Cl and Br/Cl values. The gap and peak structure in the last two runs, Cl and Br together, is striking. Moreover, the correspondence between them indicates a satisfactory degree of reproducibility.

J. RUNS 21 TO 24:LM:V (FIGURE 19)

These runs were sampled in sequence from shipboard in the southern basin of Lake Michigan. From Figure 33 it can be seen that, on the synoptic scale, air was moving slowly over southern Lake Michigan from the east and southeast. Run 21:LM:V was collected under conditions of smudge-colored haze, then overcast and light fog. During Run 22:LM:V, the fog thickened. Fog and rain were experienced during Run 23:LM:V. The fog was dissipating and there was no rain during Run 24:LM:V.

The Br distributions show, in general, a fall-off of concentration with increased particle size although a marked gap and peak appear superimposed on the Br distribution of Run 23:LM:V. The Br concentrations, totaled over the impactor range (the impactor being shielded against the entry of rain drops), show relatively little change from run to run. The Cl concentration, similarly totaled, is significantly less for Run 23:LM:V (during rain) than for the other runs. The Cl distributions all have peaks and gaps.

K. RUNS 43:EE:V AND 44:EE:V (FIGURE 20)

During both these runs, strong low pressure systems were controlling Michigan weather (Figures 34 and 35). For about half the hours in each sampling period, precipitation was recorded at Willow Run Airport.

These Cl and Br spectra are similarly shaped; their most striking feature is a wide gap from approximately 0.3μ to 3μ particle radius in Run 43:EE:XI and 0.3μ to 1μ radius in Run 44:EE:XII. Moreover Br/Cl ratios are extremely high (> 1), especially in the small particle sizes. In the A- and B-stage fractions, the Br/Cl values decrease and tend toward the values for the precipitation. (Rain was collected concurrently with the aerosol sampling of Run 43:EE:XI; snow was collected just before the period of Run 44:EE:XII.) The precipitation in each case had Br/Cl lower than that of any aerosol fraction.

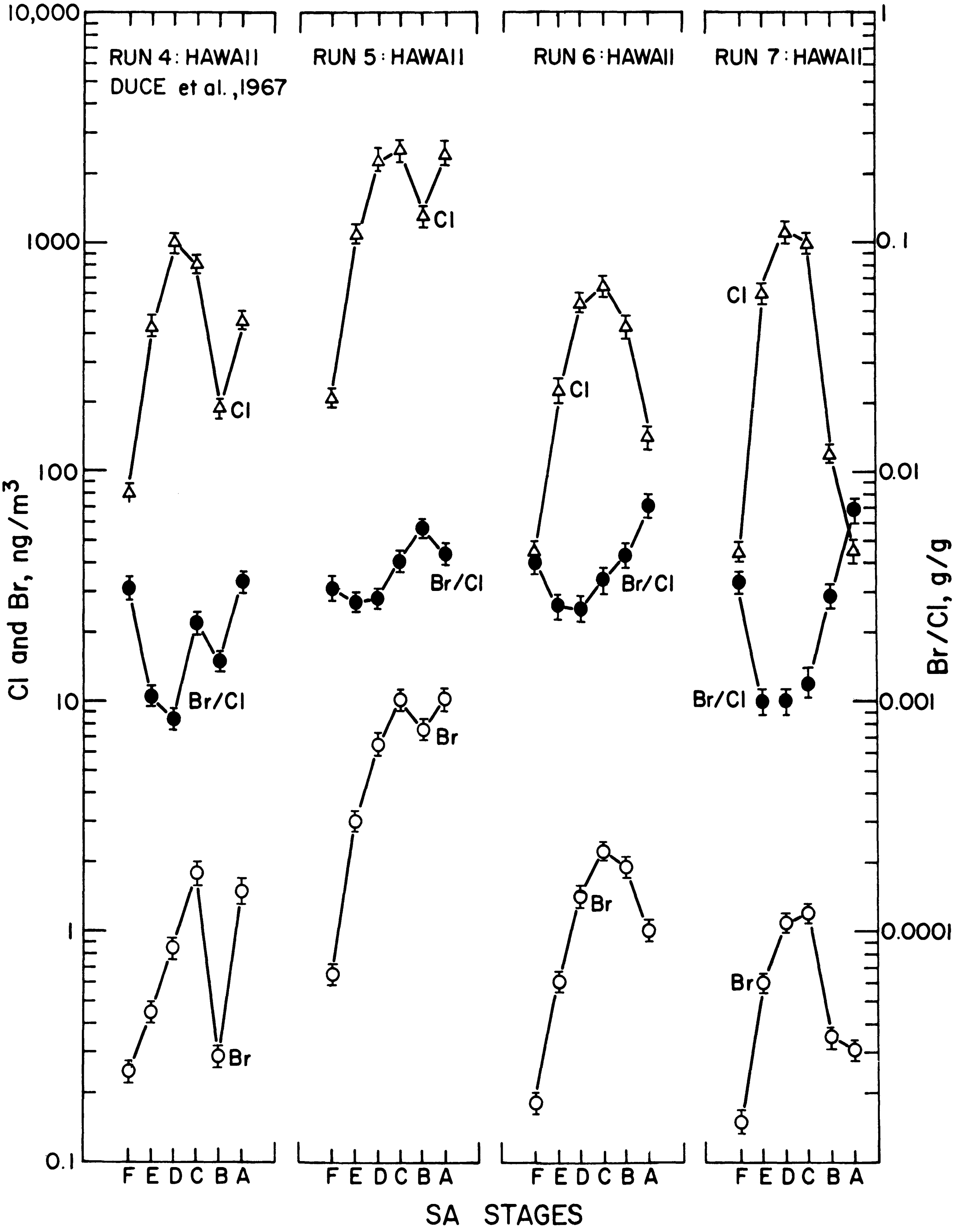

Figure 9. Cl and Br size-spectra: Runs 4, 5, 6, and 7:HAWAII.

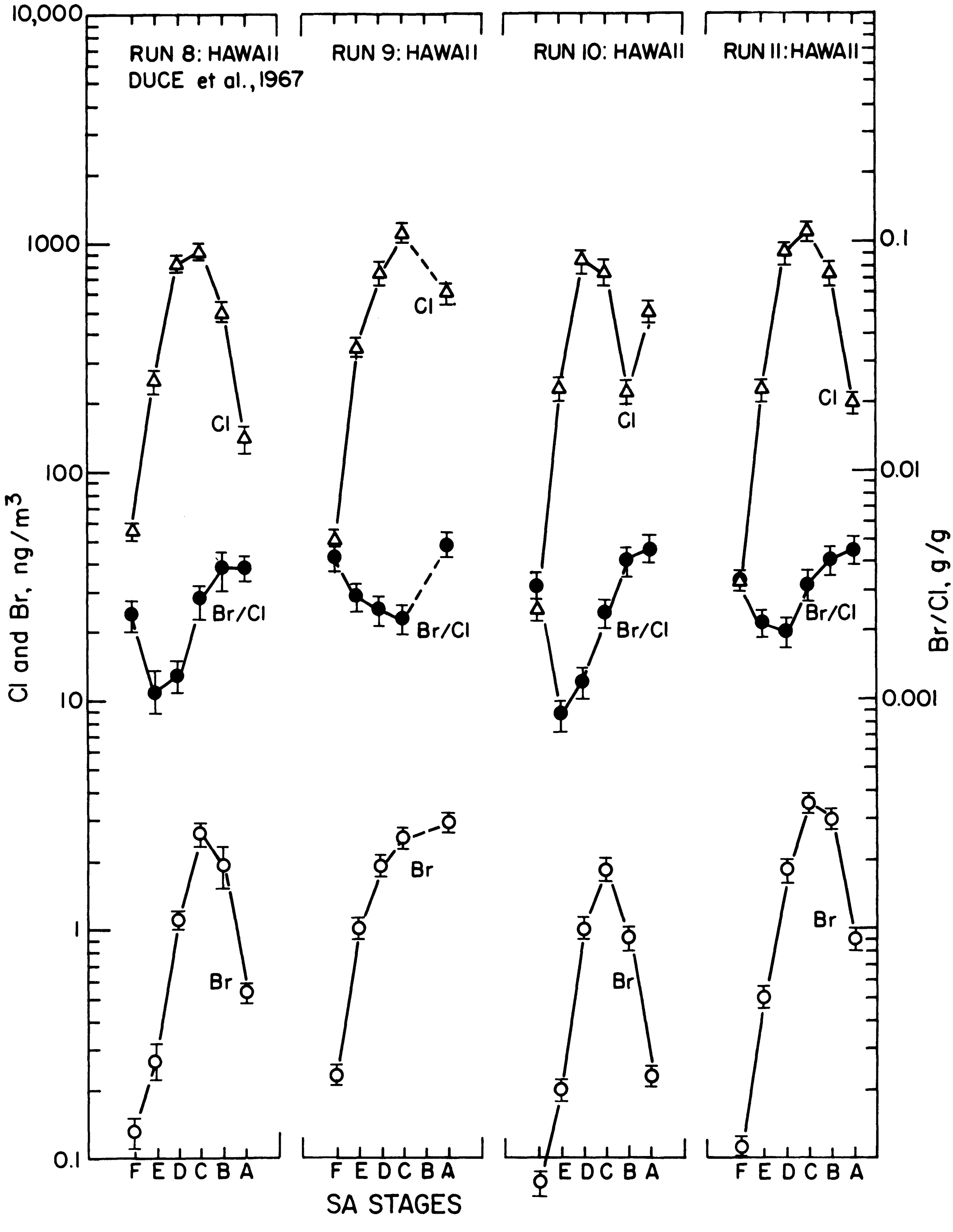

Figure 10. Cl and Br size-spectra: Runs 8, 9, 10, and 11:HAWAII.

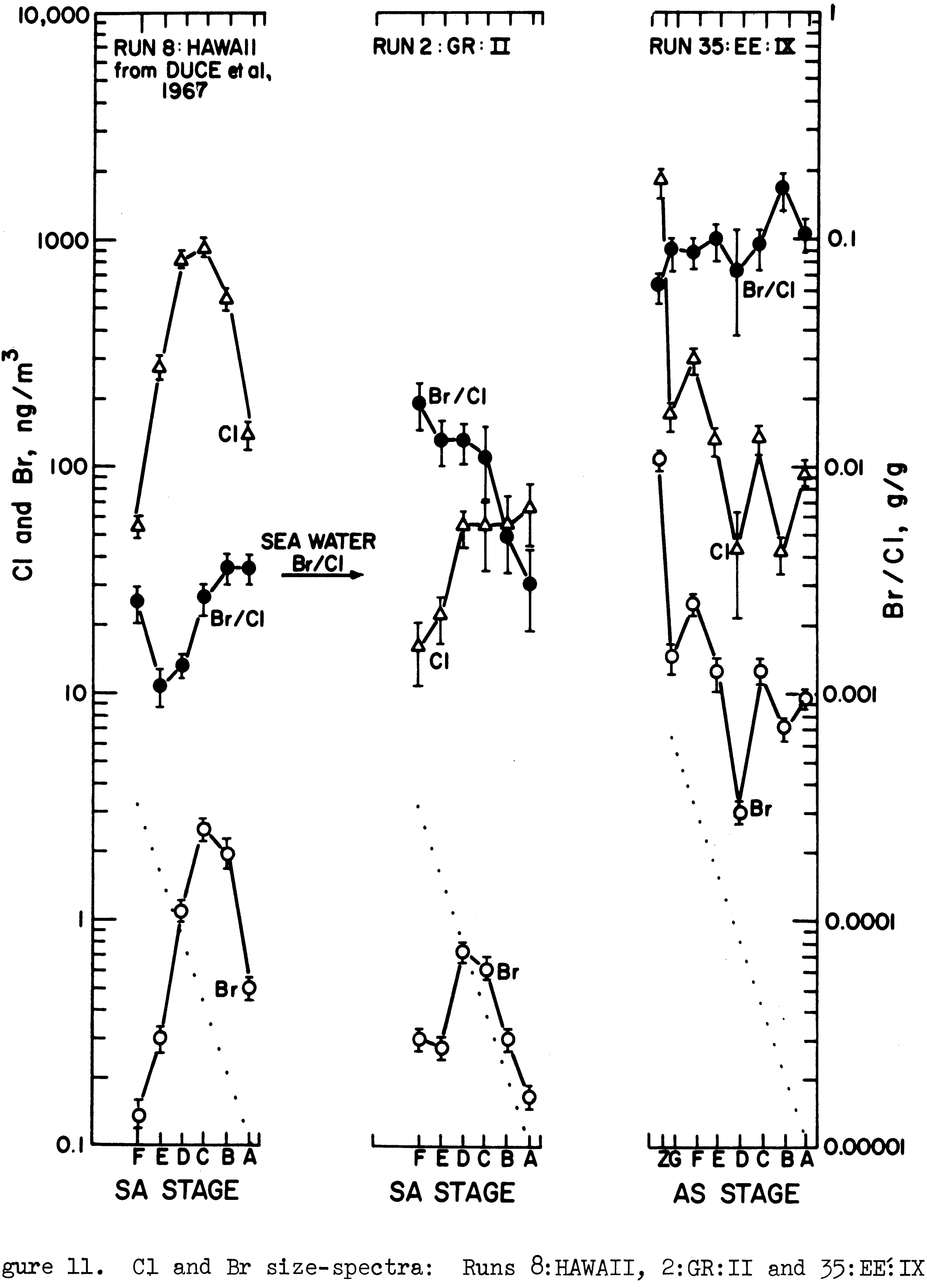

Figure 11. Cl and Br size-spectra: Runs 8:HAWAII, 2:GR:II and 35:EE:IX.

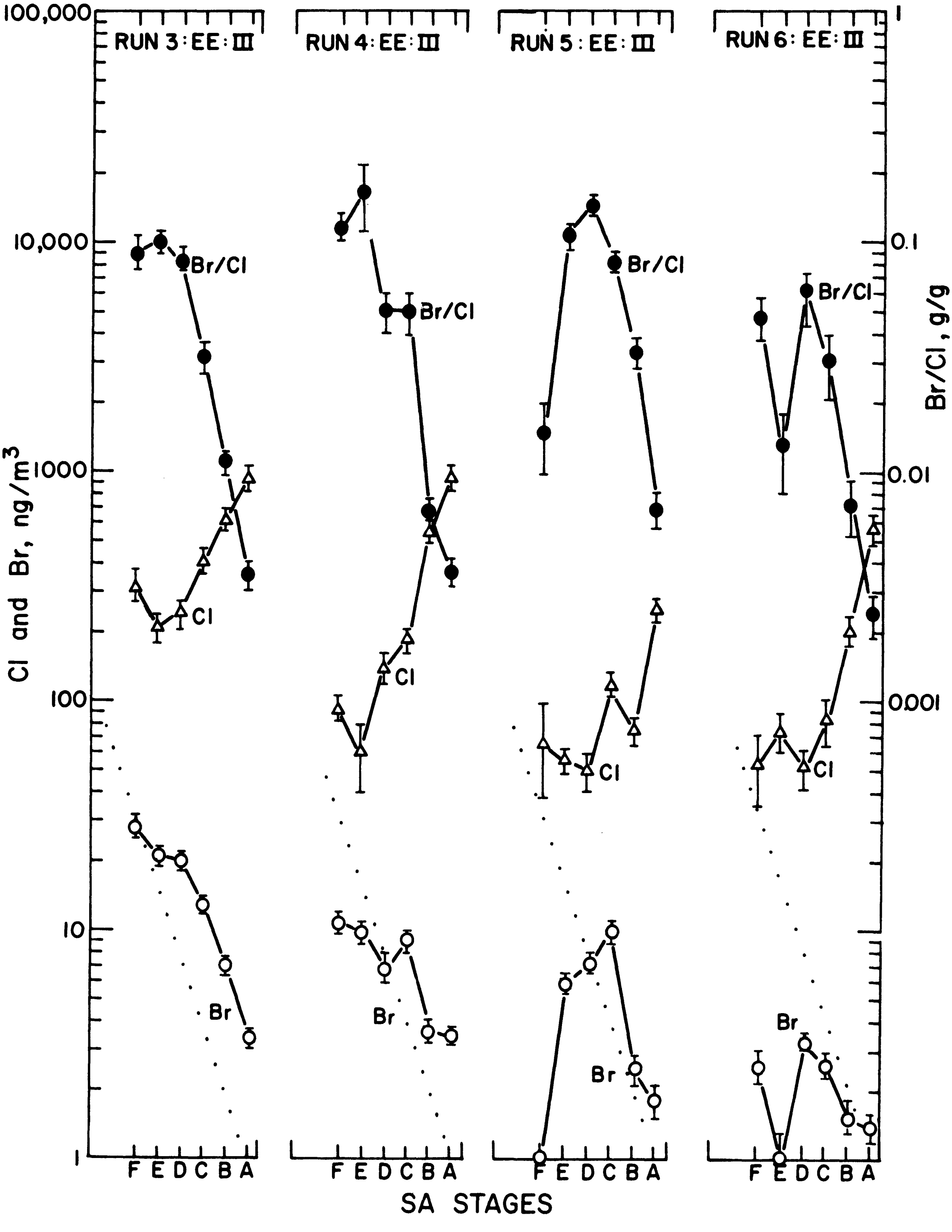

Figure 12. Cl and Br size-spectra: Runs 3, 4, 5, and 6:EE:III.

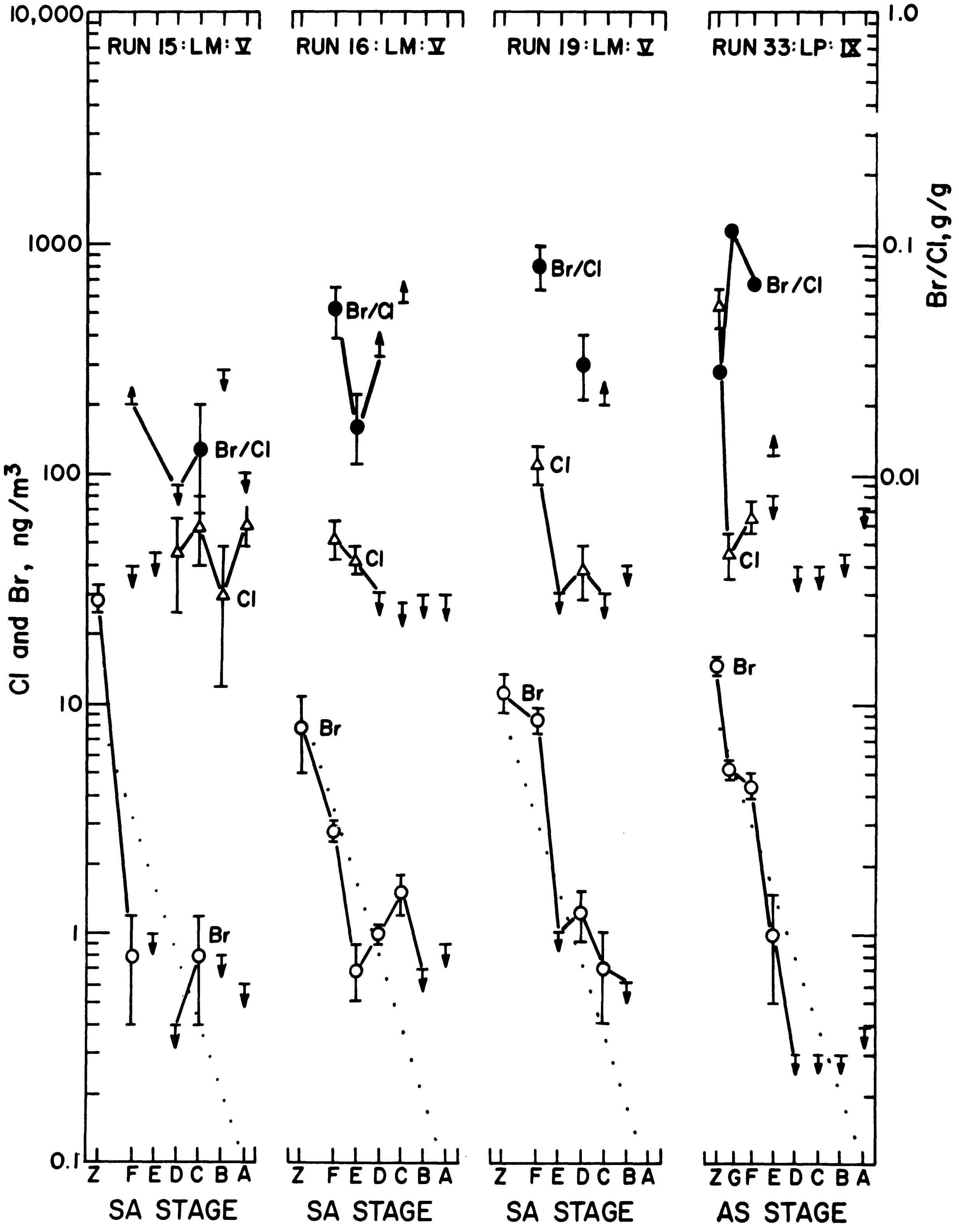

Figure 13. Cl and Br size-spectra: Runs 15, 16, and 19:LM:V and 33:LP:IX.

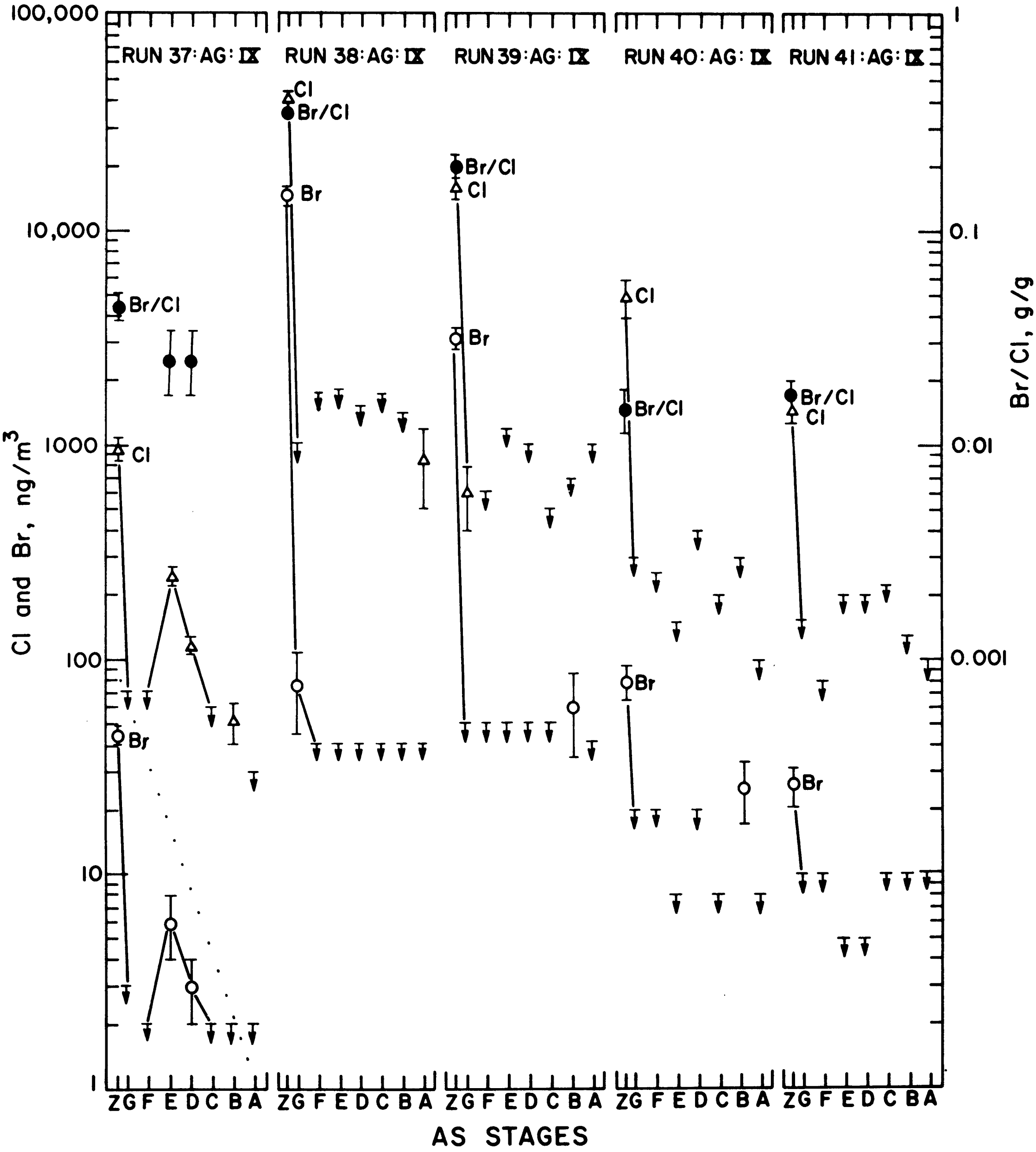

Figure 14. Cl and Br size-spectra: Runs 37, 38, 39, 40, and 41:AG:IX.

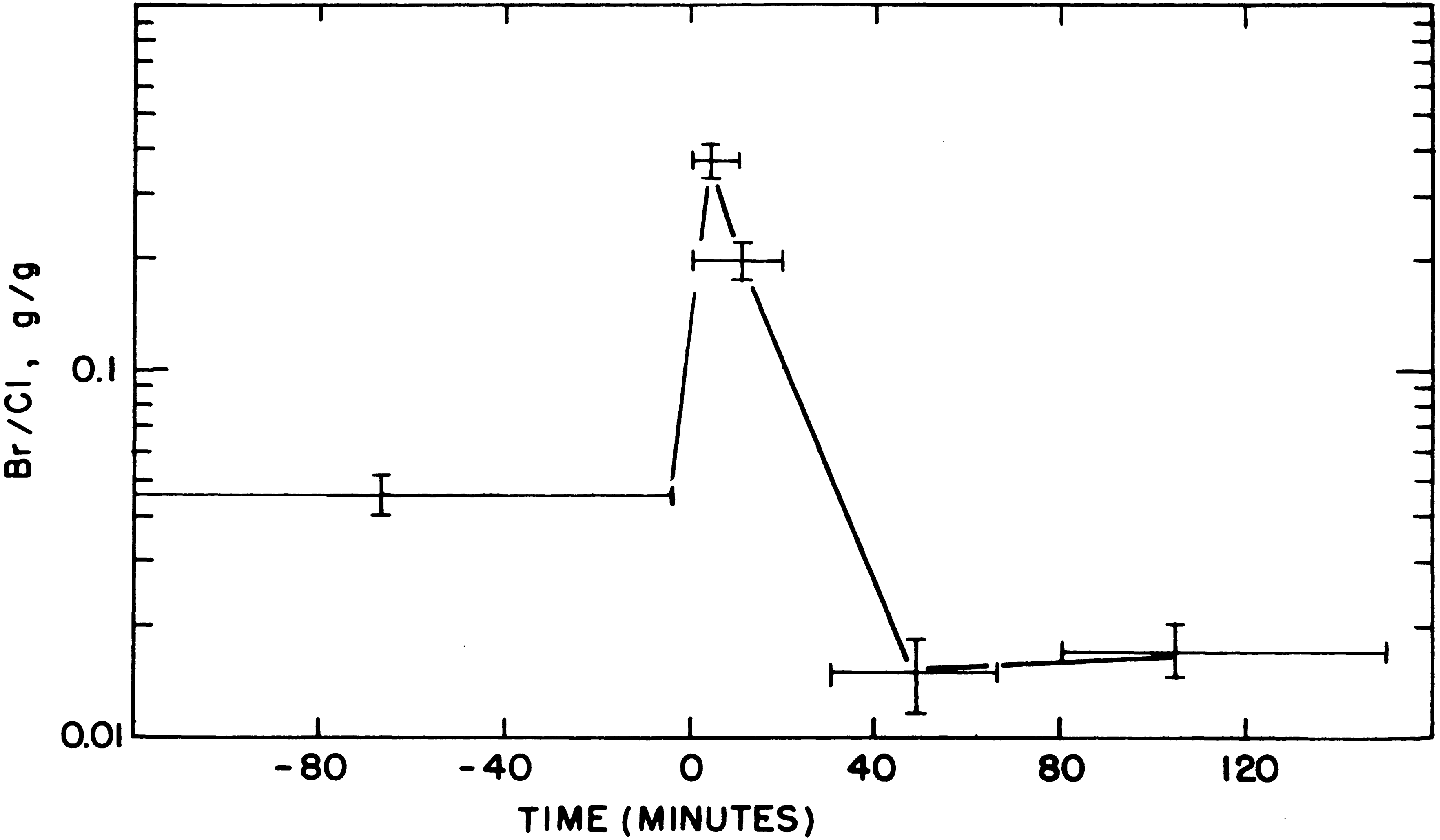

Figure 15. The time variation of the Br/Cl ratio in very small automobile exhaust particles introduced fresh at time zero.

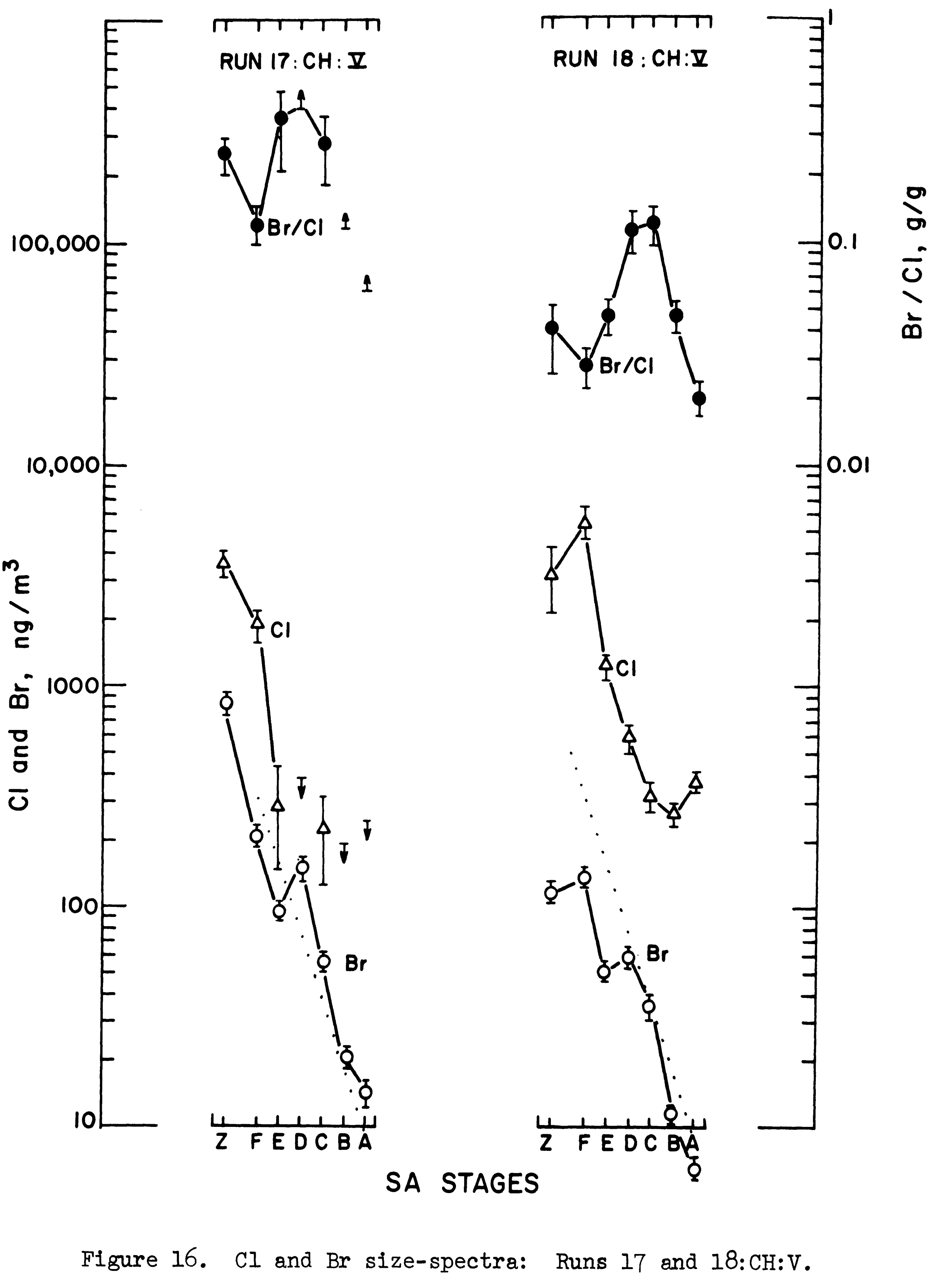

Figure 16. Cl and Br size-spectra: Runs 17 and 18:CH:V.

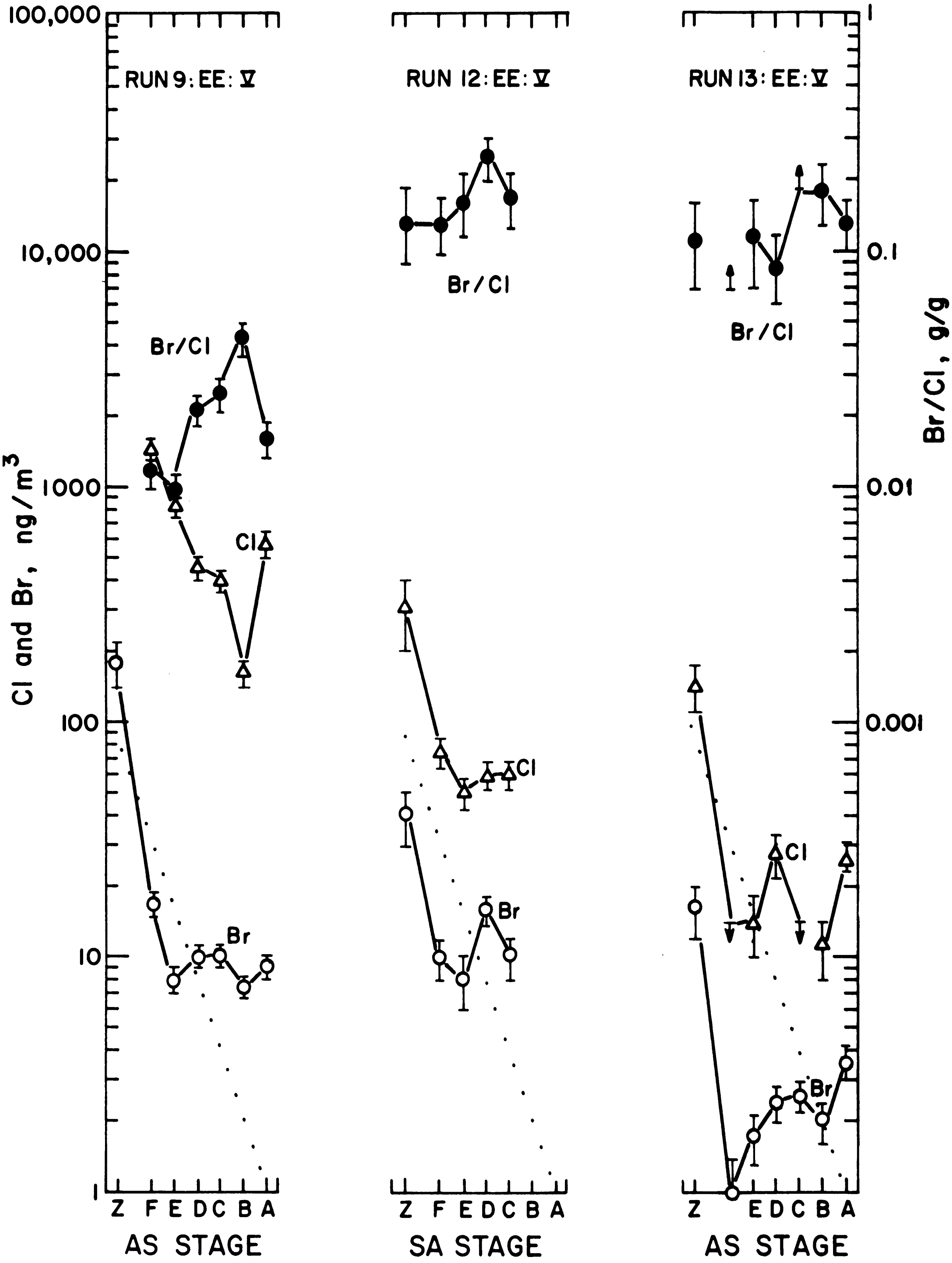

Figure 17. Cl and Br size-spectra: Runs 9, 12, and 13:EE:V.

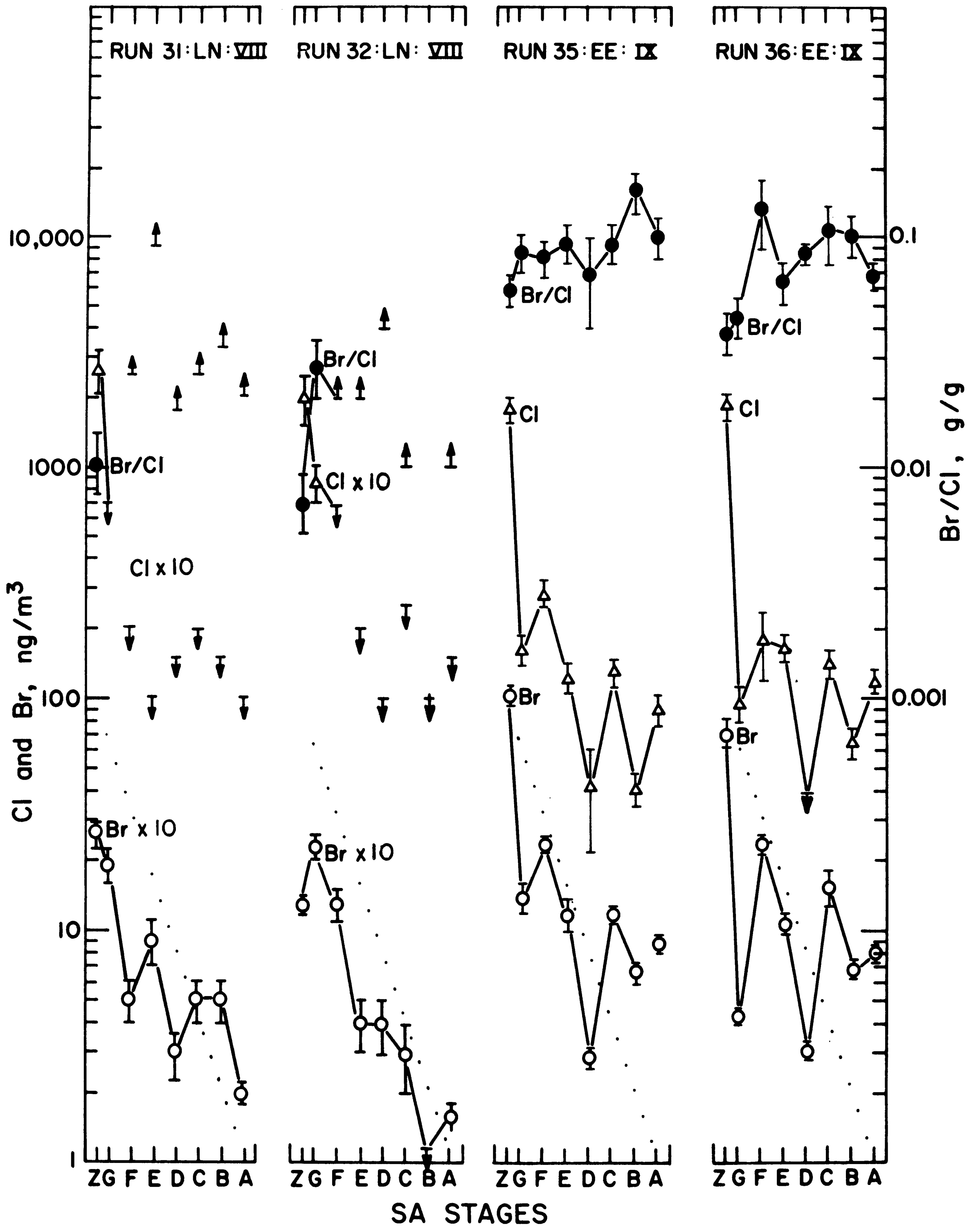

Figure 18. Cl and Br size-spectra: Runs 31 and 32:LN:VIII and 35 and 36:EE:IX.

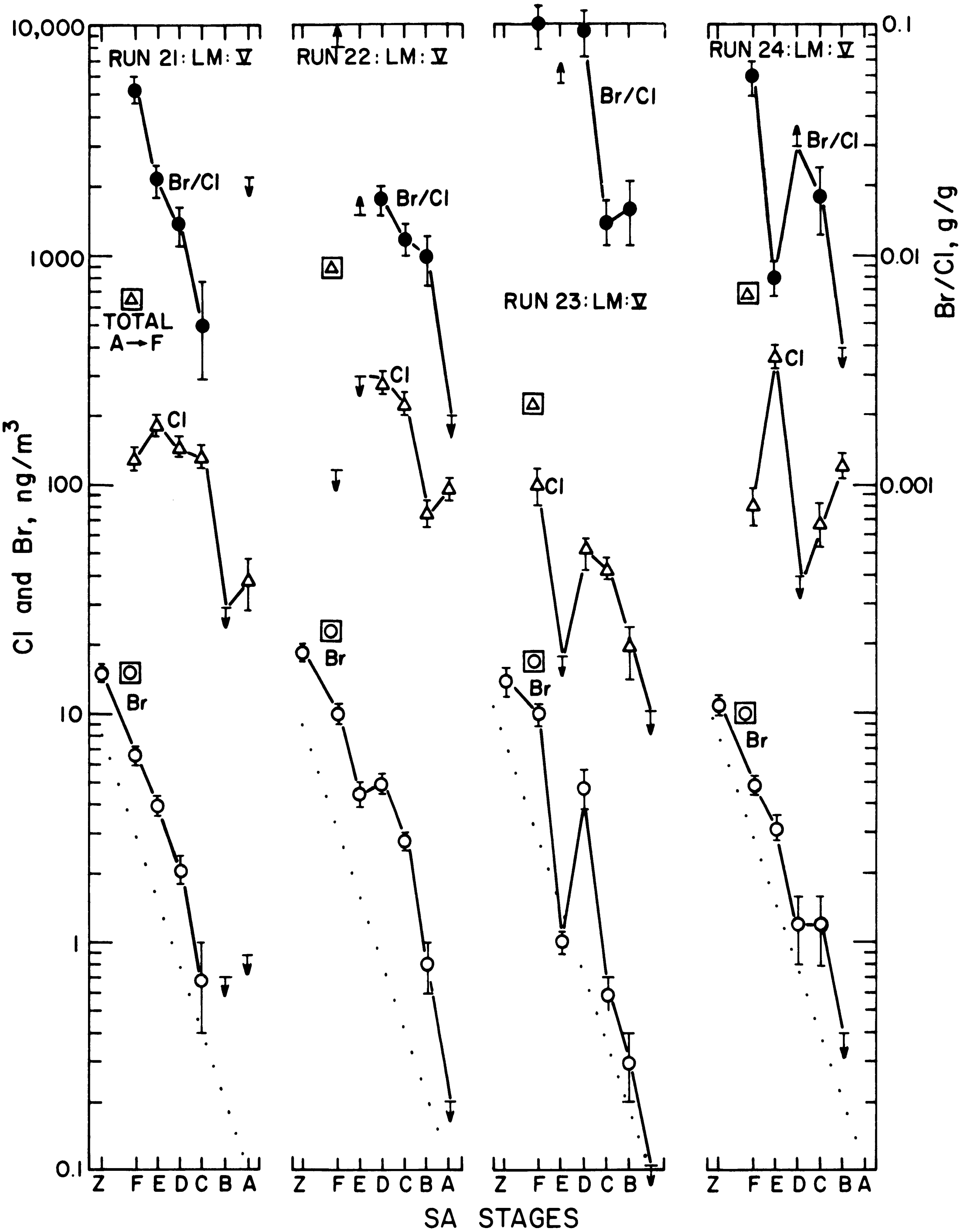

Figure 19. Cl and Br size-spectra: Runs 21, 22, 23, and 24:LM:V.

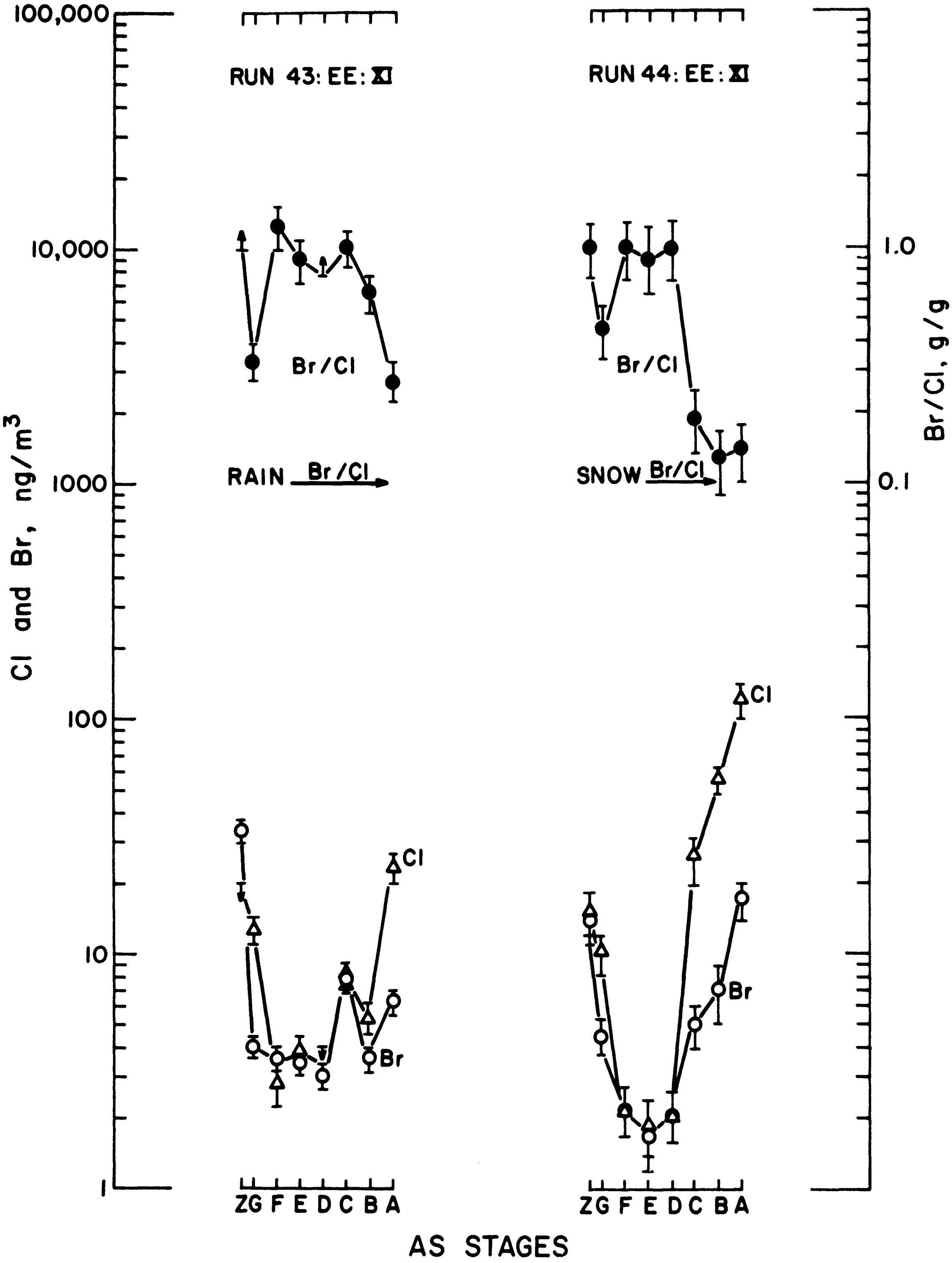

Figure 20. Cl and Br size-spectra: Runs 43:EE:XI and 44:EE:XII.

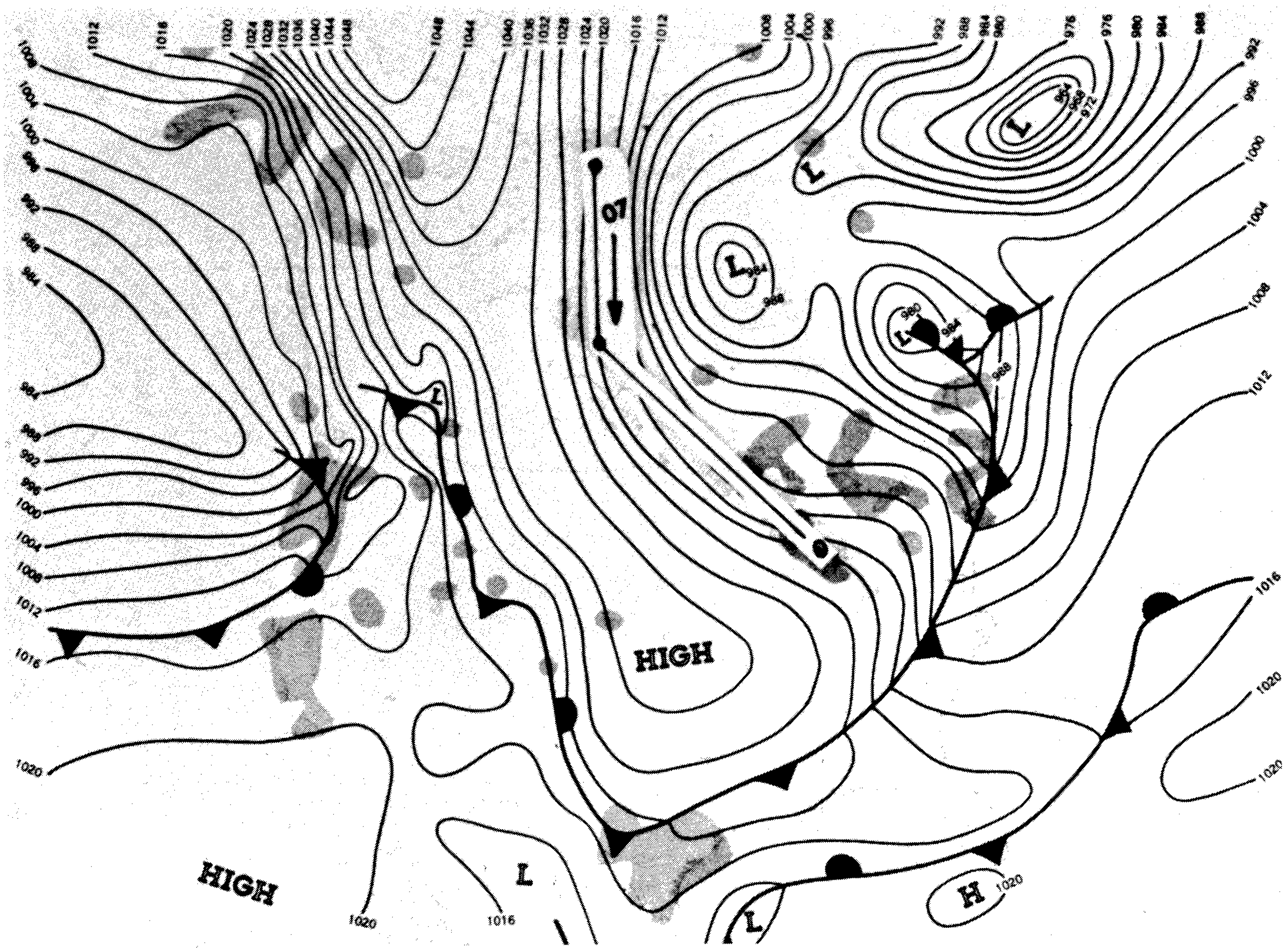

Figure 21. Run 2:GR:II. Surface weather at 1300/17/II with 850 mb geostrophic trajectory hindcast at 12-hr intervals from 0700/17/II.

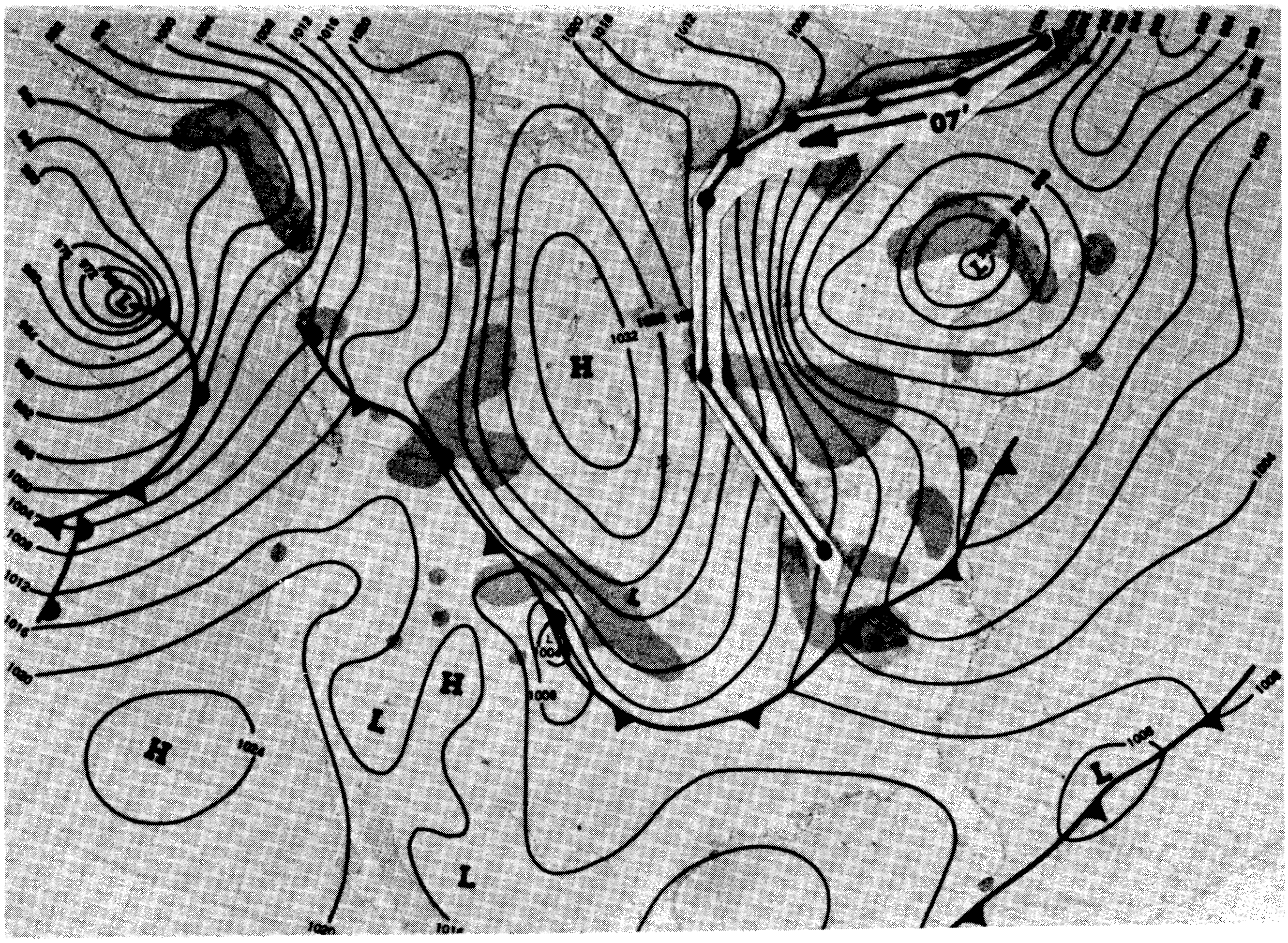

Figure 22. Run 2:GR:II. Surface weather at 1300/20/II with 850 mb geostrophic trajectory hindcast at 12-hr intervals from 0700/21/II.

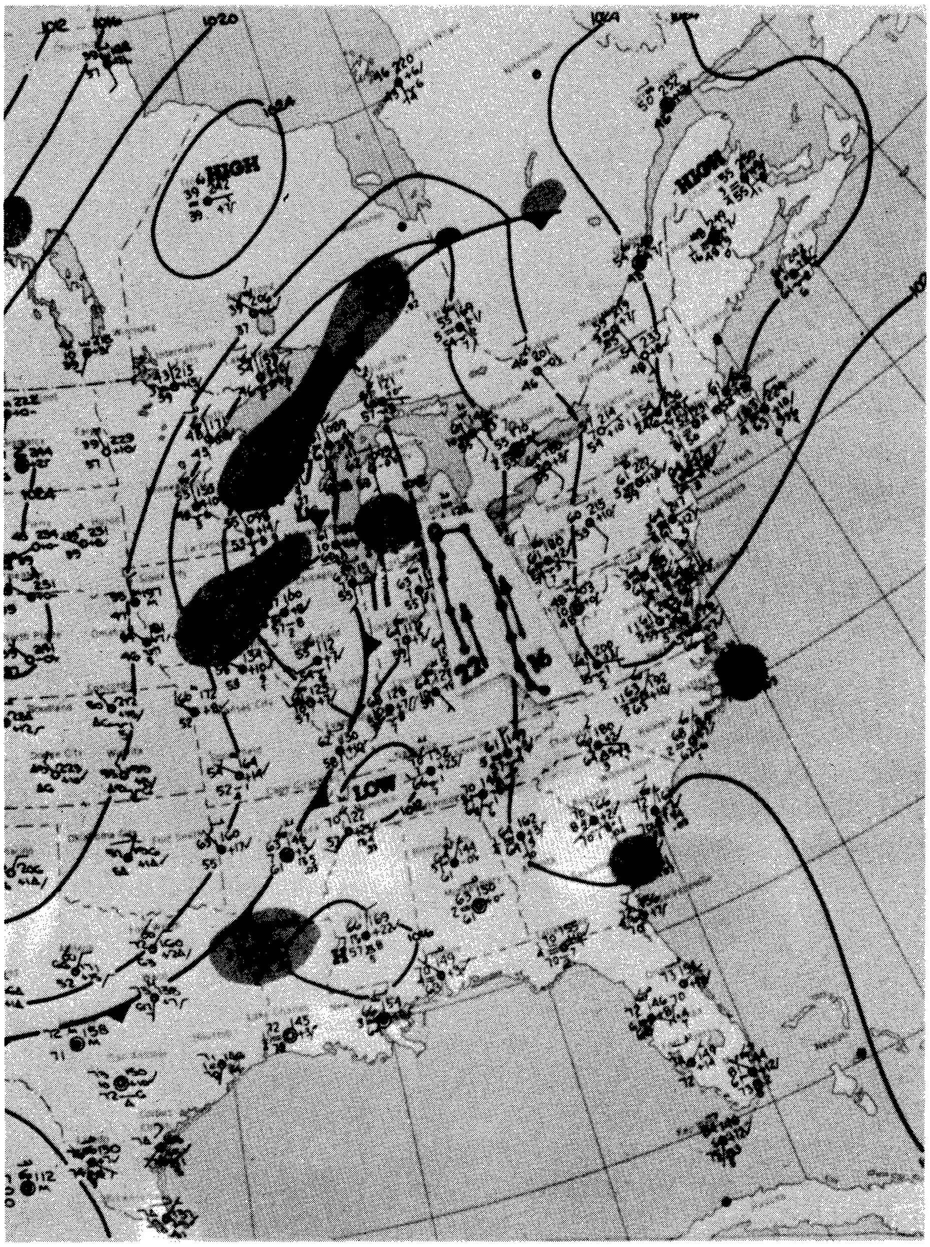

Figure 23. Runs 35 and 36:EE:IX. Surface weather at 0700/9/IX with surface level trajectories hindcast at 3-hr intervals from 1600 and 2200/9/IX.

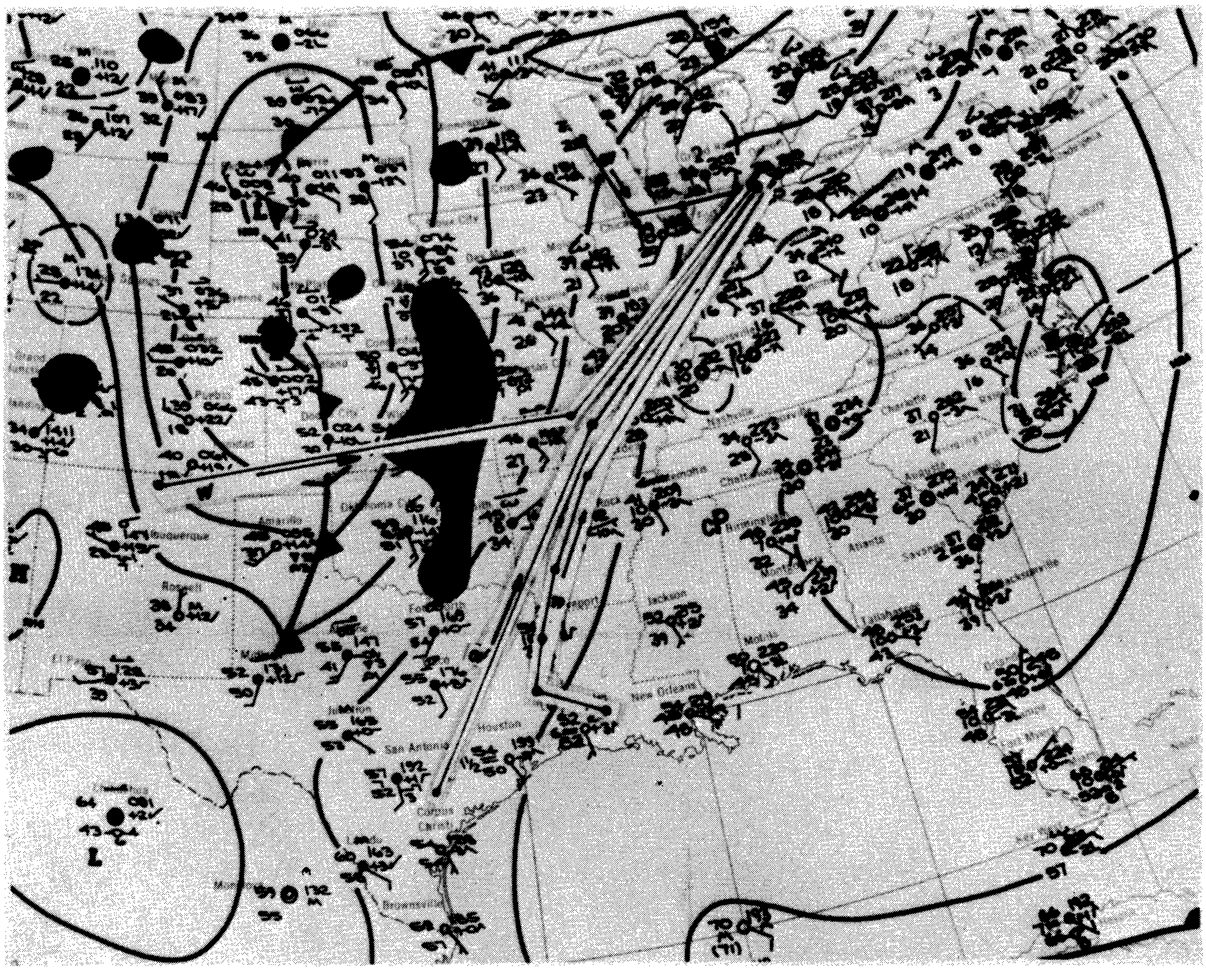

Figure 24. Runs 3 and 4:EE:III. Surface weather at 0100/8/III with 850 mb geostrophic trajectories hindcast at 12-hr intervals from 0700/7/III, 1900/7/III, 0700/8/III, and 1900/8/III.

Figure 25. Run 5:EE:III. Surface weather at 0100/12/III with surface level geostrophic trajectories hindcast at 3-hr intervals from 1900/11/III, 0100/12/III, and 1000/12/III.

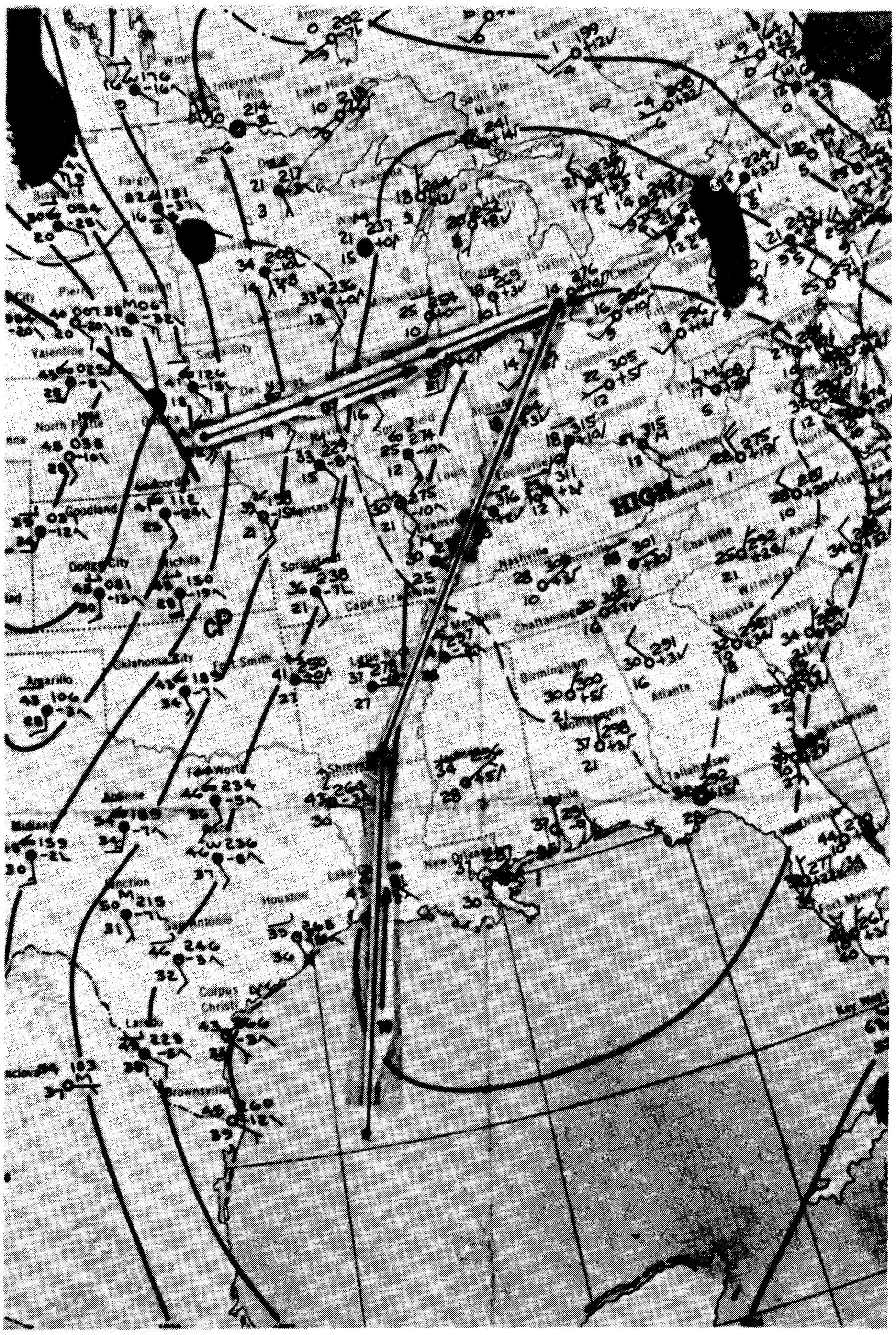

Figure 26. Run 6:EE:III. Surface weather at 0100/14/III with 850 mb geostrophic trajectories hindcast at 12-hr intervals from 0700/14/III and 1900/14/III.

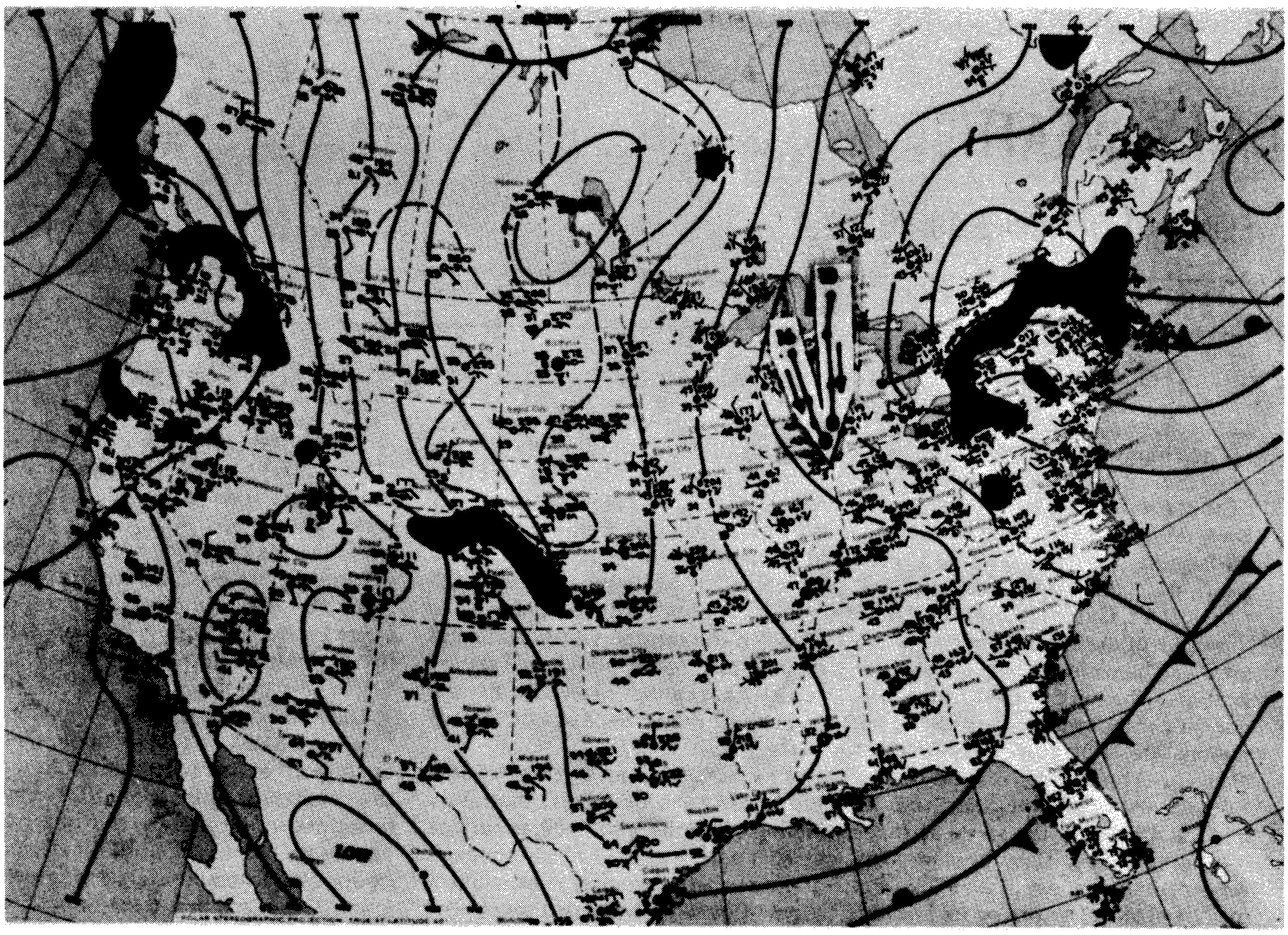

Figure 27. Runs 15 and 16:LM:V,17 and 18:CH:V and 19:LM:V. Surface weather at 0700/20/V with surface level geostrophic trajectories hindcast at 3-hr intervals from 1000/20/V and 1600/20/V.

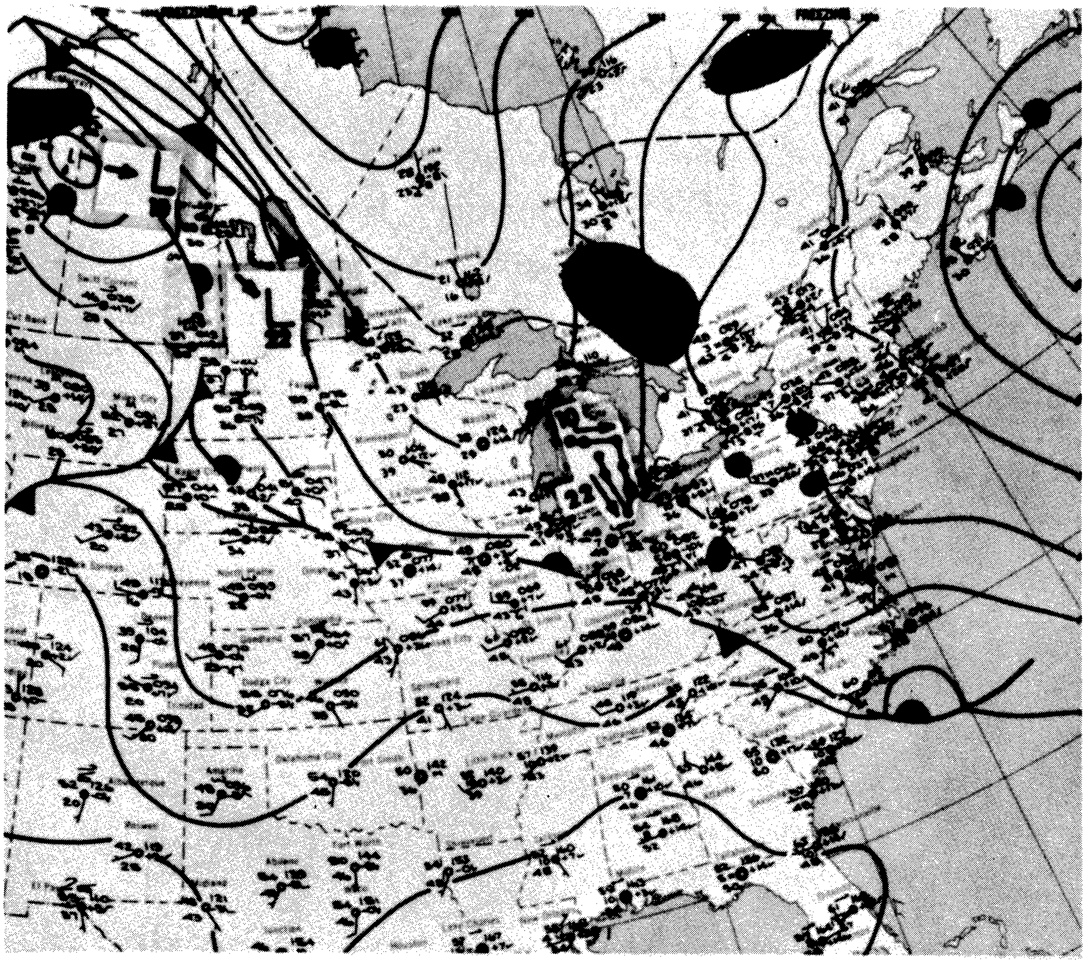

Figure 28. Run 9:EE:V. Surface weather at 0700/1/V with surface level trajectories hindcast at 3-hr intervals from 1000/1/V and 2200/1/V.

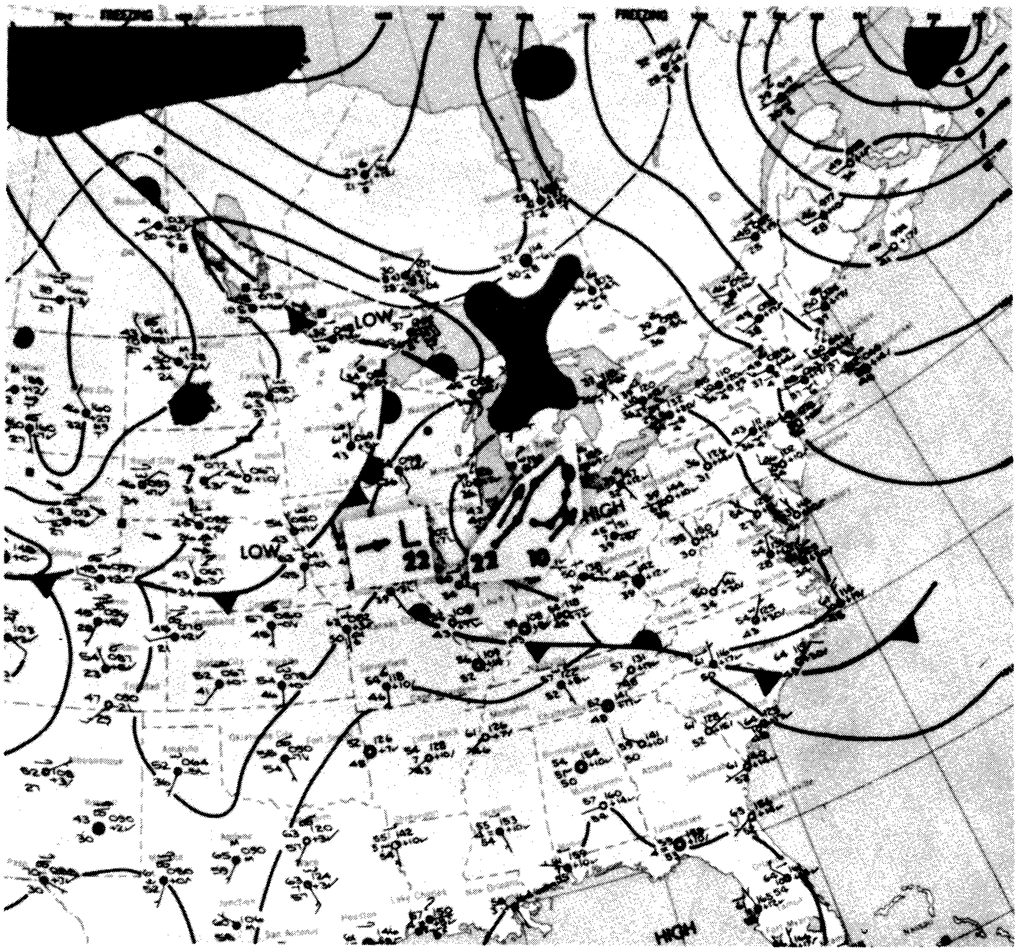

Figure 29. Run 12:EE:V. Surface weather at 0700/2/V with surface level trajectories hindcast at 3-hr intervals from 1000/2/V and 2200/2/V.

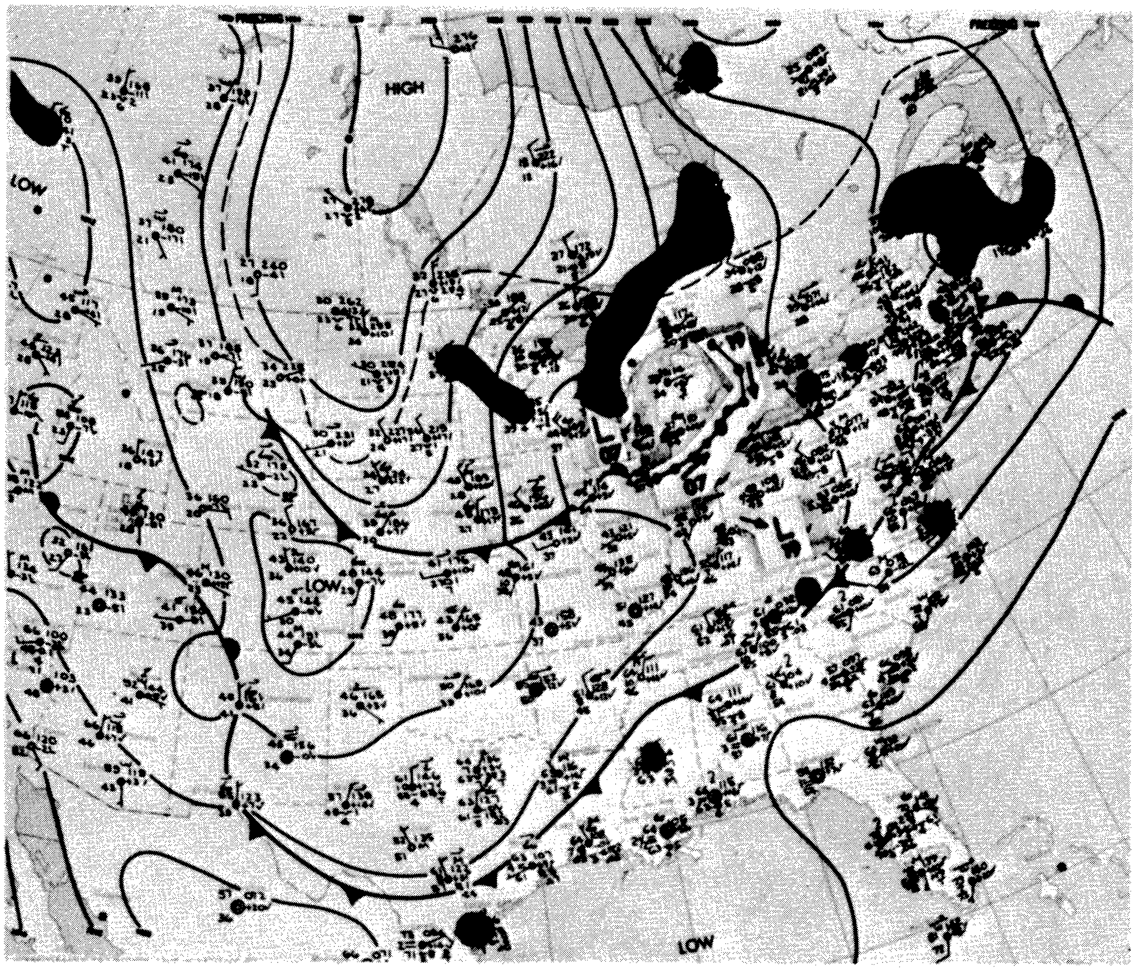

Figure 30. Run 13:EE:V. Surface weather at 0700/4/V with surface level trajectories hindcast at 3-hr intervals from 0700/4/V and 1900/4/V.

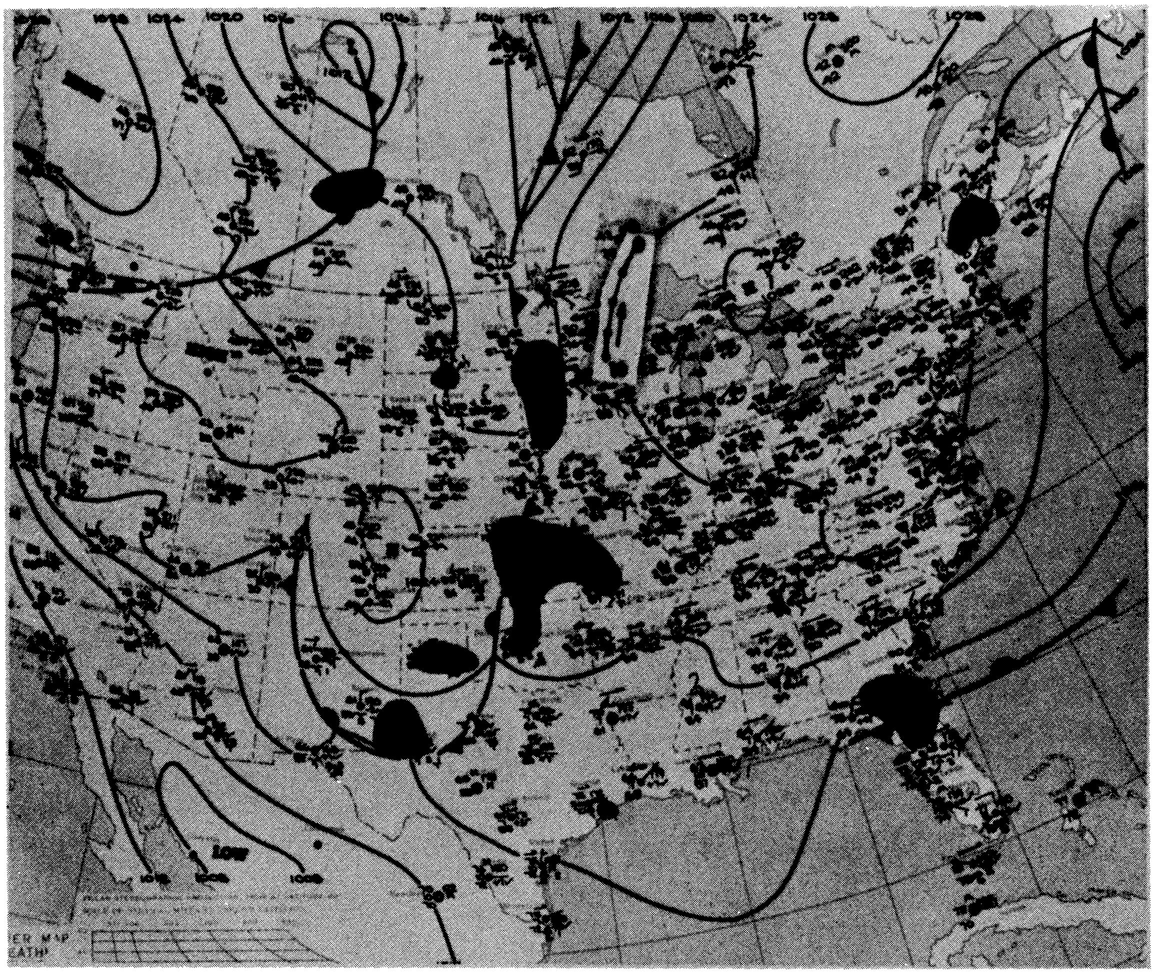

Figure 31. Runs 31 and 32:LN:VIII. Surface weather at 0700/30/VIII with the surface level geostrophic trajectory hindcast at 3-hr intervals from 1600/30/VIII.

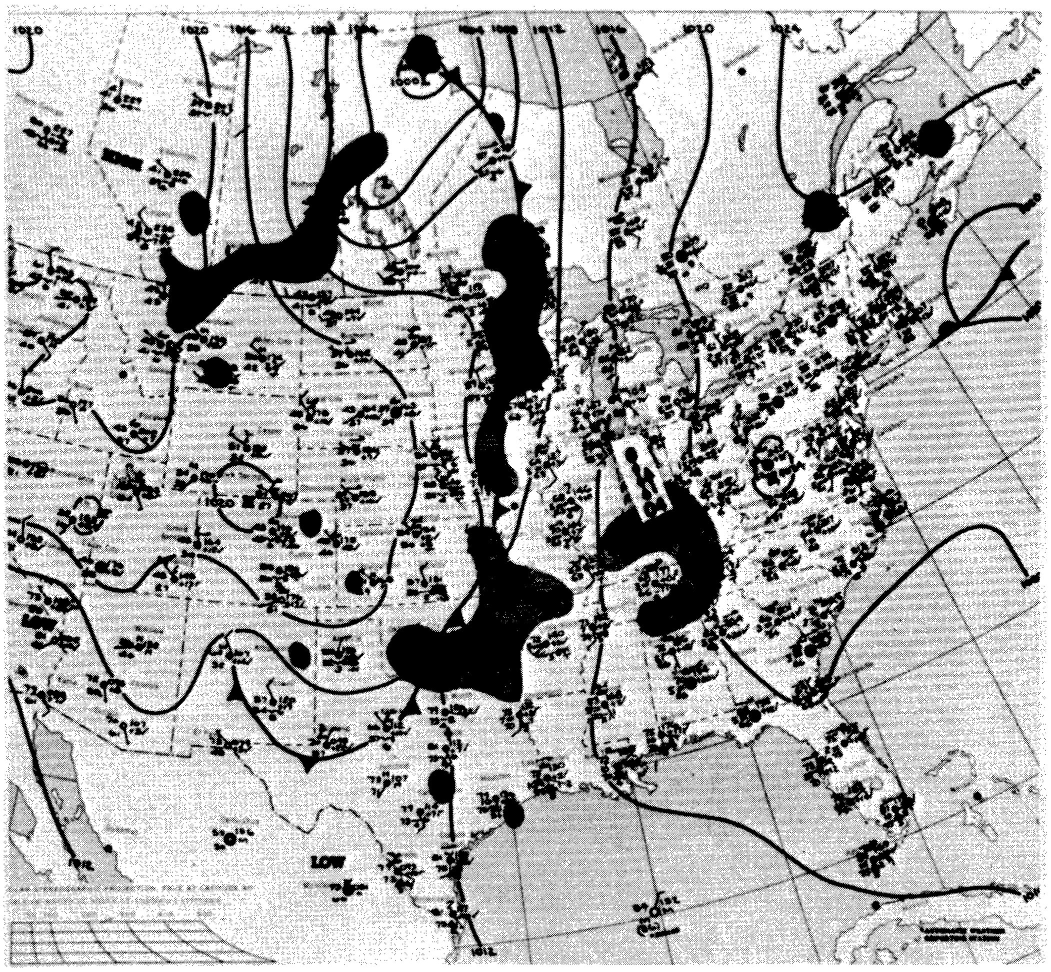

Figure 32. Run 33:LP:IX. Surface weather at 0700/4/IX with surface level trajectory hindcast at 3-hr intervals from 0400/4/IX.

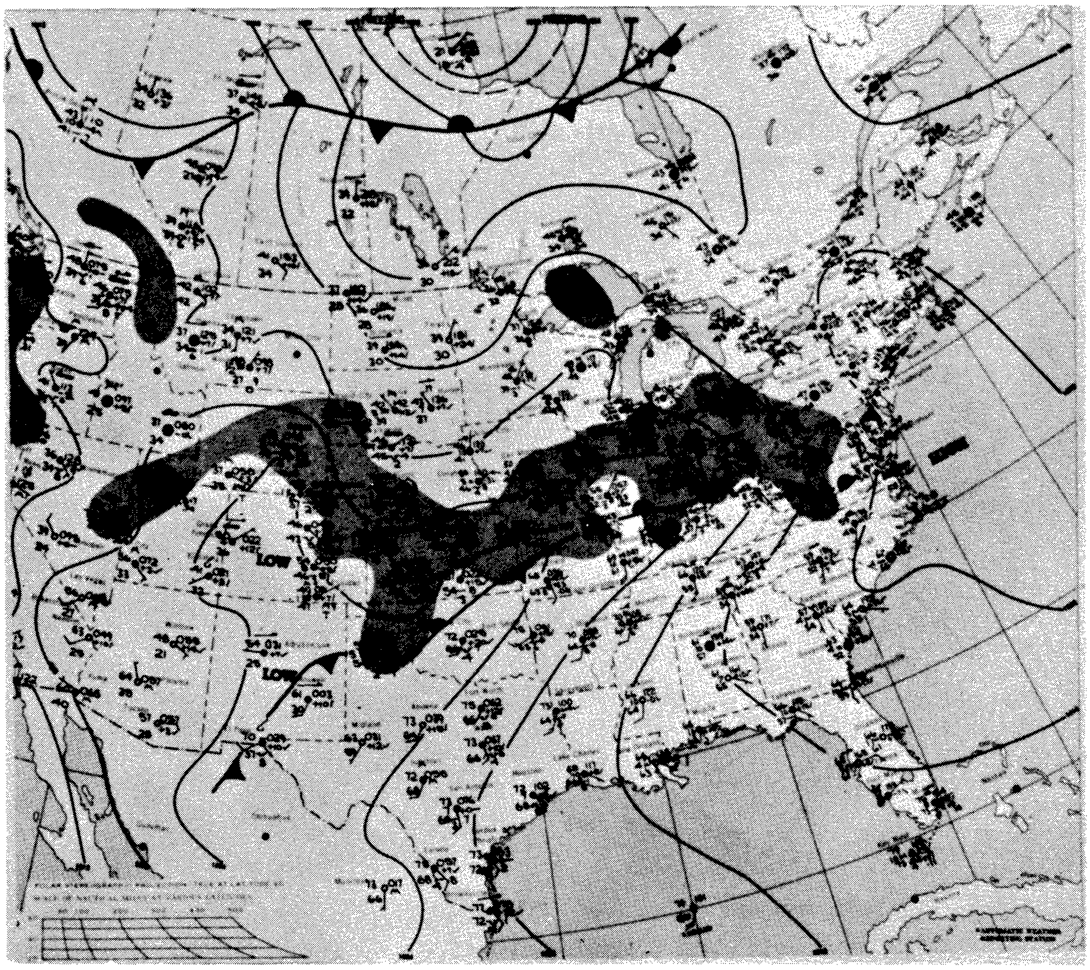

Figure 33. Runs 21, 22, 23, and 24:LM:V. Surface weather at 0700/23/V.

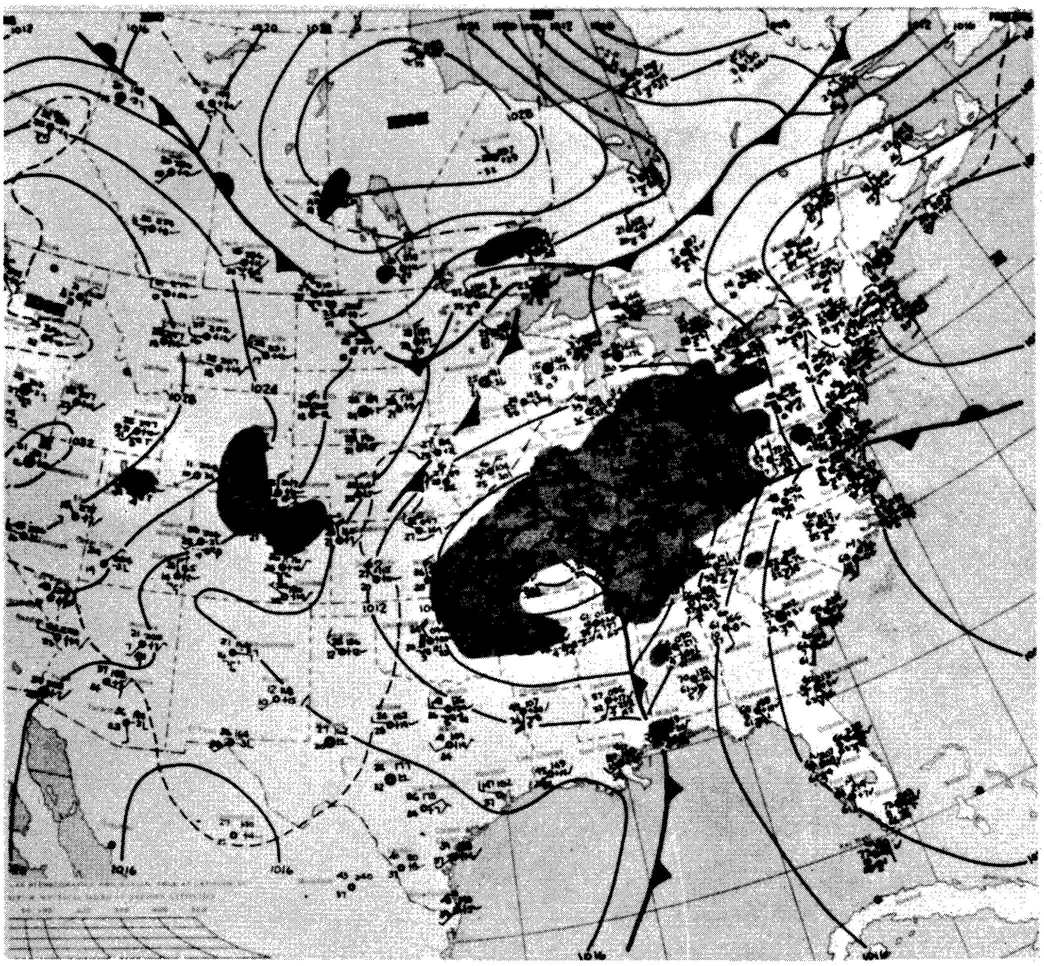

Figure 34. Run 43:EE:XI. Surface weather at 0700/28/XI.

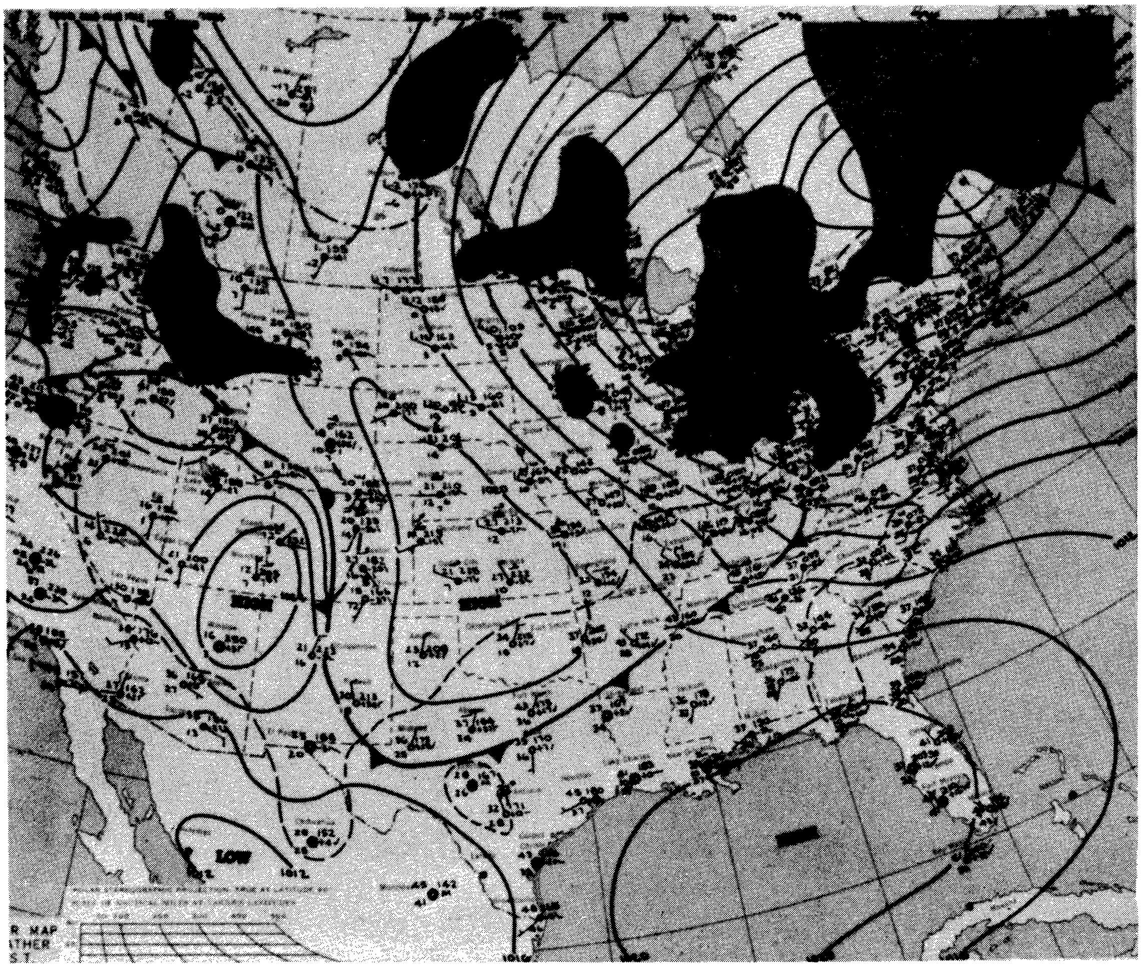

Figure 35. Run 44:EE:XII. Surface weather at 0700/5/XII.

CHAPTER IV

INTERPRETATION

A. INTRODUCTION

When the inland aerosol Cl and Br distributions (Figures 11 to 20) are compared with the suite of corresponding results for marine aerosols (Figures 9 and 10, after Duce et al., 1967), the contrast between the variability of the inland data and the uniformity of the Hawaii data is striking. This variability inland undoubtedly arises by interaction of the several source aerosols and atmospheric processes. However, with the intricacies of the aerosols revealed to the extent that they are through size-fraction analysis, these data can be interpreted with consistency. Thus they are valuable first as guides to the sources and processes important in the environment and then as indicators of promising directions for relevant controlled experiments.

Although the patterns are complex, the features of the data do combine to suggest a behavioral scheme or model for aerosol Br and Cl in the atmosphere. This model is portrayed schematically in Figure 36. The detailed explanation of the model will be developed piecemeal below but it can easily be seen from Figure 36 that, given the source for an aerosol halogen subpopulation, one can find a description of the resulting aerosol and a flow pattern indicating the modifying atmospheric processes in which that subpopulation is likely to be involved.

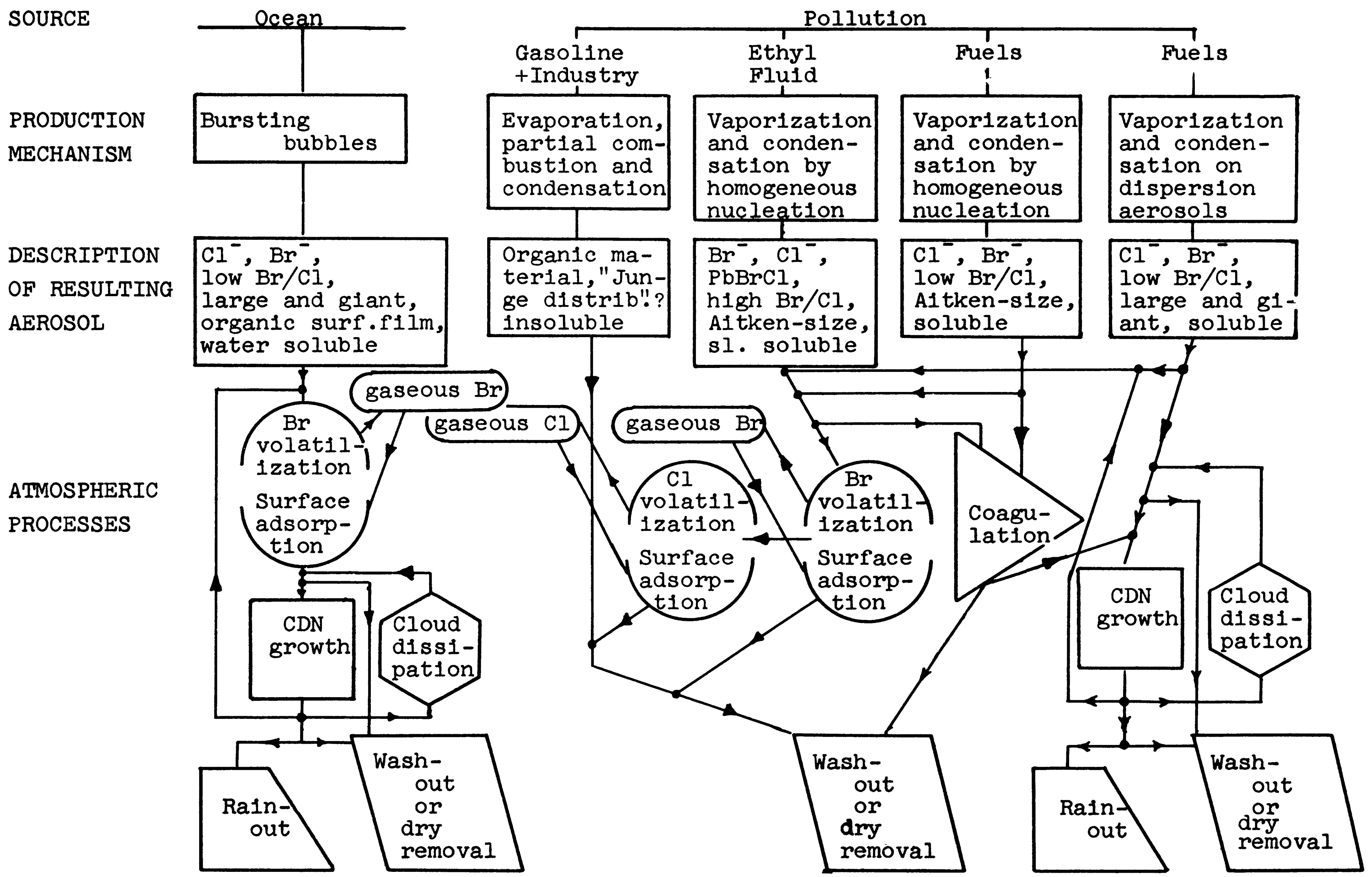

Figure 36. Flow chart depicting a model for the behavior of atmospheric Cl- and Br-rich particles.

B. THE DATA AND THE MODEL

1. The Sources

From Chapter I and Appendix D, we recall the following source characteristics. The ocean produces small numbers of large and giant particles and constitutes a strong source for Cl (as Cl^-) and a weak source for Br (as Br^-). Combustion processes are expected to produce large numbers of Aitken-sized particles (condensation aerosols) as well possibly, as dispersion aerosols (large- and giant-sized). The combustion of coal releases large amounts of aerosol Cl. The combustion of leaded gasoline is a major source for aerosol Br. In addition we consider the possibility that an aerosol subpopulation composed in part of organic material (e.g., evaporated or incompletely burned fuel) and distributed in the "Junge universal distribution" may be produced by dispersion or condensation of organic substances (Figure 36).

2. The Atmospheric Processes

The aerosol halogen data can be interpreted by relating the data to the sources of the aerosol and to the atmospheric processes which may have modified the aerosol. Figure 37 portrays the data classified, to the extent possible, by source and age. The chemical data together with the trajectory analyses have suggested the source and history of the aerosols collected. Many subsidiary pieces of information have also been invoked during the development from identification of the likely source (Figure 37) to a model for the roles of aerosol Br and Cl in the atmosphere (Figure 36). The reader is urged to take 10 min and compare the individual patterns shown in Figures 11-20 with

SOURCES / AEROSOL AGE		OCEAN →	MIXTURE ←	POLLUTION		
				AUTOMOBILE EXHAUST →	MIXTURE ←	INDUSTRY
0 to 0.3 HOURS				38:AG:IX 39:AG:IX		
↑ TRANSITION ↓		8:HAWAII		17:CH:V 18:CH:V		
0.3 to 3 HOURS	NOT CLEARLY EXHIBITING CDN.			40:AG:IX 41:AG:IX	12:EE:V 35:EE:IX 36:EE:IX	
	CDN CLEARLY EXHIBITED			37:AG:IX	13; EE:V	
↑ TRANSITION ↓					33:LP:IX	
>3 HOURS	NOT CLEARLY EXHIBITING CDN		15:LM:V		9:EE:V 16:LM:V 19:LM:V 21:LM:V 24:LM:V 31:LN:VIII 32:LN:VIII	
	CDN CLEARLY EXHIBITED	2:GR:II	3:EE:III 4:EE:III 5:EE:III 6:EE:III		22:LM:V 23:LM:V 43:EE:XI 44:EE:XII	

Figure 37. Classification of sampling runs according to inferred aerosol source and age.

the classification in Figure 37 and refer as needed to the individual run descriptions in the previous chapter.

*Run 8:HAWAII (Figure 11)

This marine aerosol, produced at the sea surface by the bursting bubble mechanism, has the ratio, Br/Cl, approximately equal to the value in sea water. Therefore the Br and Cl may be distributed throughout the bulk of each particle as sea salt. Modification in the atmosphere has probably not been extensive, although the variations in Br/Cl are believed to be real; the aerosol is judged to be fresh. (The accompanying data for aerosol iodine (Duce et al., 1967) have the ratio, I/Cl, exceeding the sea water value and increasing with decreasing particle size. Thus iodine is not distributed throughout the bulk of each particle as in sea salt.)

*Run 2:GR:II (Figure 11)

From the trajectory of the air sample, one sees that although there was possible exposure to some pollution over northwestern Michigan, the remainder of the path was over the Canadian Sub-Arctic, Arctic, and then the sea; thus the sea may be the major source for these aerosols. Furthermore, the air was sampled less than three days after leaving the North Atlantic and along the route precipitation was sporadic and light.

The Cl distribution, compared to that for Run 8:HAWAII, shows a shift to larger particles; some redistribution may have occurred over land. The Br distribution is similar to that of Run 8:HAWAII. Two opposing effects may be

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*Sections marked (*) are of special importance.

operative: (1) Br volatilization may reduce Br especially in the large and giant particles (discussed below) while (2) cloud-droplet nucleation (CDN) acts to transfer Br and Cl to the larger size ranges.

The relatively low value of the ratio Br/Cl ($Br/Cl_{totals} = 0.004$), being close to the value in sea water, is strong additional evidence that this aerosol is of marine origin.

*Runs 3, 4, 5, and 6:EE:III (Figure 12)

For Runs 3, 4, and 6:EE:III, the air trajectory was directly from the Gulf of Mexico to Michigan. Extensive rainout had not occurred. The arrival of southern maritime air was accompanied by increases in dry bulb and dew point temperature but not in relative humidity.

The giant particles have high concentrations of Cl and Br/Cl ratios close to that of sea water. These characteristics, coupled with the favorable meteorological conditions, suggest that the giant particles are of marine origin. It is then implied, as for Run 2:GR:II, that redistribution of Cl occurred in the atmosphere. The data suggest that the sea salt nuclei encountered relative humidities high enough to allow cloud-droplet nucleation and droplet growth by condensation and coalescence but that before extensive rainout could occur lower relative humidities and cloud dissipation were experienced. The droplets then evaporated leaving solid giant sea salt nuclei to be collected at the relative humidities of less than 70% which prevailed in Michigan.

The small particles seem more likely to be predominantly of pollution origin. Pollution sources produce small (as well as large) particles and Br is a common pollutant. The rather high Br/Cl ratios on the small particles strongly suggest their pollution origin.

We have attributed the giant Cl-rich particles to sea salt. However, the possibility that these particles originated from the rock salt (NaCl) which is spread on highways to melt ice or to reduce dust was also considered—and rejected for the following reason. The distinctive Cl distribution, concentrated in the giant particles, occurs only with rapid influx of maritime air (e.g., Runs 2:GR:II, 3, 4, 5, and 6:EE:III). Moreover, in Run 5:EE:III, only 15% of the air sampled would have had recent injection of marine aerosols and the Cl concentration in the giant particles was correspondingly reduced in comparison with Runs 3, 4, and 6:EE:III (Figure 12).

Byers _et_ _al_. (1957) have found giant sea salt particles similarly size distributed in fresh tropical air at altitudes of from 1 to 2 km over Illinois. They measured the numbers of particles in several size ranges; conversion to mass of Cl indicates concentrations on the order of 0.5 $\mu g/m^3$. Run 3:EE:III shows a total Cl concentration of 3 $\mu g/m^3$; Run 6:EE:III shows 1 $\mu g/m^3$. These results afford opportunity for an order of magnitude check of the estimated ocean source strength (200 g Cl/(km^2-hr), Chapter I) as follows: Assuming uniform mixing to an altitude of 2 km and an exposure time of 100 hr, then the estimated concentration of marine aerosol Cl is 10 $\mu g/m^3$. The correspondence with the measurements is satisfactory.

Runs 15, 16, and 19:LM:V (Figure 13)

These runs, made in southern Lake Michigan during a northwesterly breeze, are interpreted to have sampled aerosols of a distant pollution source. Concentrations of Br are highest on the small-sized fractions and Br/Cl values are well above that for sea water. Nonetheless, for Run 15:LM:V, the meteorological circumstances and, to a degree, the chemical data leave open the possibility that the giant particles include a sea salt component.

*Runs 37, 38, 39, 40, and 41:AG:IX (Figure 14)

Cl and Br are added to gasoline to remove Pb from the engine as a volatile salt, PbBrCl. Thus the Br and Cl, freshly emitted, are expected to be in their reduced (Br^-, Cl^-) rather than in their oxidized states (e.g., Br_2, Cl_2). The automobile garage series provides strong evidence that Br^- is lost rapidly, and preferentially to Cl^-, from aerosols freshly produced by combustion of leaded gasoline and exposed only to weak daylight.

In addition, a substantial amount of iodine was found in the fresh automobile exhaust aerosol. The data (Appendix B) suggest that, subsequently, the iodine was lost from the aerosol at least as rapidly as bromine. Schaefer (1966) found that ice nuclei could be produced from exposure of automobile exhaust to iodine vapor. Schaefer (1968) observed extensive ice crystal plumes over and downwind of several large cities in winter. There is a need for study of the sources and roles of iodine in the atmosphere.

The gap and peak in the Cl and Br spectra of Run 37:AG:IX, a sampling of ambient air taken prior to carrying out the automobile experiment, resemble those in the size distribution sketched by Junge (and reproduced as Figure 2, Chapter I) showing the effect of cloud-droplet nucleation.

*Runs 17 and 18:CH:V (Figure 16)

In explanation of why Br/Cl ratios are lower for Run 18:CH:V than for Run 17:CH:V, we point out that in the evening hours (Run 17) both automobile (Br and Cl) and industry (Cl) sources will have been in operation but, in the early morning (Run 18), traffic density will have decreased while industry continued in operation.

The Br and Cl spectral shapes of Runs 17 and 18:CH:V stimulated an hypothesis worthy of consideration. It was noticed, in a key observation, that the spectral shapes are similar and fall off approximately twofold for each twofold increase in radius (a step of one impactor stage). The hypothesis is that the r^{-1} dependence in these Br and Cl spectra may be related to the r^{-1} dependence of the "Junge surface area distribution" which was discussed in Chapter I. (A dotted guideline with r^{-1} dependence is included in the plots of Cl and Br size distributions.) The extent to which the halogen distributions have r^{-1} dependence is the extent to which a relationship is implied between halogen mass and aerosol surface area. (Aerosol mass in the "Junge distribution" is invariant with radius if density variations are small. Therefore, as an important example, Br, if surface-distributed on a "Junge aerosol," would vary as (surface area)/mass $\cong r^{-1}$. In marine aerosols, Cl mass and aerosol mass will have the same variation with radius because sea salt is the bulk of the aerosol. If Br were surface-distributed, Br/Cl would have r^{-1} dependence.) The Br and Cl distributions of Runs 17 and 18:CH:V do show approximate r^{-1} dependence. Moreover, the many industrial and vehicular sources of Calumet Harbor could very likely produce a "Junge distributed aerosol" because these are the conditions under which it is observed (Junge, 1963 and Clark and Whitby, 1967). In addition, the meteorological circumstances were such that the aerosol distribution would be only slightly perturbed by cloud-droplet nucleation. The interpretation which follows naturally is that Cl and Br, in gaseous form, are being adsorbed onto the surfaces of particles distributed according to the average distribution recognized by Junge.

Approximate r^{-1} dependence is observed for Cl only in Runs 17 and 18:CH:V; however, it is observed for Br in Runs 2:GR:II, 3:EE:III, 17 and 18:CH:V, 21, 22 and 24:LM:V, 32:LN:VIII and 33:LP:IX. Surface adsorption or condensation of bromine from the gaseous phase is implied. Two series of processes can be envisaged: (1) condensation of high temperature halide vapors onto "Junge distributed" particles through physical adsorption or (2) low temperature volatilization of aerosol halogens followed by uptake onto "Junge distributed" particles through chemical reaction. The observational criteria which must be satisfied are: (1) Surface adsorption or condensation occurs. The r^{-1} dependence implies a surface layer distribution. (2) Volatilization occurs. This is a prerequisite for surface adsorption or condensation and is observed for Br at least. (3) Br is carried through the series preferentially to Cl. Br exhibits r^{-1} dependence even where Cl does not. The alternative processes are to be tested against these observational criteria; however, it will be useful to make the following definitions beforehand.

A dispersion aerosol (Fletcher, 1962) is a population of particles formed by dispersion of material e.g., by grinding a large piece into smaller pieces, by ejecting droplets or by burning to produce a residue of nonvolatile airborne particles. Dispersion aerosols are distributed, often log-normally, in the large and giant size ranges.

A condensation aerosol is produced in combustion. Volatile components are raised to high vapor pressures by the high temperatures. When they are rapidly cooled, the exhaust gases reach such high supersaturations that homogeneous nucleation occurs. Because of the curvature effect on vapor pressure, the droplets produced may remain small (less than 0.1μ). (The small droplets have high curvature and can survive in equilibrium with the high vapor pressure.)

The first series of processes suggested above involves condensation of high temperature halide vapors onto "Junge distributed" particles through physical adsorption. Combustion temperatures (1500-2500°C., Taylor and Taylor (1962) and Trinks and Mawhinney (1961)) exceed the boiling points of most halide salts. Some representative boiling points are the following:

Halide Salt	Boiling Point (°C)
NH_4Br	235
NH_4Cl	315
$PbBr_2$	918
$PbCl_2$	945
$MnCl_2$	1190
$MgCl_2$	1412
NaBr	1390
NaCl	1413
$CaBr_2$	810
$CaCl_2$	> 1600

However other implications of the hypothesis are less probable. The halides would be required to condense on the surfaces of pre-existing "Junge distributed" particles. A "Junge distribution" would not likely be formed in a single combustion source (Junge, 1969). Moreover the halides fresh from a source, viz., Run 38:AG:IX, suggest an Aitken-sized condensation aerosol rather than r^{-1} dependence.

The second series of processes suggested involves the formation of a condensation aerosol in the exhaust gases and, subsequently in the atmosphere, the volatilization (for the second time) of the halogens followed by adsorption from the gaseous phase onto the surfaces of particles. The volatilization observed in the automobile garage series, where Br/Cl decreased tenfold in about an hour, may be an example of this second volatilization. The criterion that Br be preferentially volatilized is shown below to be satisfied if volatilization occurs by oxidation of the halides to Br_2(gas) and Cl_2(gas).

If the original condensation, dispersion, or mixed aerosol contains aqueous Br^- or Cl^-, then, by the analysis of Appendix C, it is probable that the Br^- will be preferentially oxidized to Br_2(gas) by atmospheric oxidants such as ozone. The reaction may be

$$2Br^-(aq) + O_3(g) + 2H^+ \;=\; O_2(g) + Br_2(g) + H_2O \quad K_{eq} \;=\; 10^{+33.0} \;.$$

The corresponding reaction for Cl^- and ozone has $K_{eq} = 10^{+24.1}$. The implication is that ozone will attack Br^- more strongly than Cl^- in a droplet; the reaction is aided by acidic conditions such as are found in pollution H_2SO_4 aerosols. It is shown in Appendix C that the Br^- will be completely oxidized before any Cl^- in the droplet is oxidized if chemical equilibrium is maintained within the droplet. If the original aerosol contains solid Br^- and Cl^-, the results of Pierrard (1969) indicate, for PbBrCl at least, that gaseous Br is produced by photo-oxidation at twice the rate for gaseous Cl. Finally, if gaseous HCl or HBr exist, the oxidation, by ozone, of HBr to produce Br_2 proceeds much more rapidly than that of HCl producing Cl_2 (Lewis and Feitknecht, 1932). Our adopted hypothesis is that low temperature volatilization occurs through oxidation to the free halogen gas, a process in which Br is preferred over Cl.

Free halogen gases (Br_2 and Cl_2) are suggested to become incorporated into the surface layers of organic matter on certain particles by "halogenation" reactions, especially those common reactions in which the halogen gas adds, at the double bond, to an olefinic or unsaturated hydrocarbon (alkene) e.g.,

$$Br_2 + H_2C{=}CH_2 \rightarrow (CH_2\,Br)_2 \ .$$

"Addition of halogens is a characteristic reaction of the alkene linkage" (Royals, 1954). A commonly used test for the presence of this linkage is that a solution of bromine in CCl_4 will discolor instantly without evolution of HBr.

Alkenes are present in polluted air; they constitute 10 to 30%, by weight, of automobile exhaust. However, bromination does not occur in the gas phase (Royals, 1954) and the alkenes which are liquid at atmospheric temperatures may only be present in amounts of a few percent in automobile exhaust (U.S. Department Health, Education, and Welfare, 1962 report, Motor Vehicles, Air Pollution and Health). Nonetheless, those alkenes which are liquid at atmospheric temperatures may be constituents of "Junge distributed" aerosols. Boiling points of some alkenes are listed below (Luder *et al.*, 1959).

Formula	Name	Boiling Point (°C)
$CH_2{=}CH2$	Ethylene	-103.8
$CH_3CH{=}CH_2$	Propylene	- 47.0
$CH_3CH_2CH{=}CH_2$	1-Butene	- 6.7
$CH_3(CH_2)_2CH{=}CH_2$	1-Pentene	+ 40.0
$CH_3(CH_2)_3CH{=}CH_2$	1-Hexene	64.1
$CH_3(CH_2)_4CH{=}CH_2$	1-Heptene	99.0

The suggestion of preferential oxidation of Br^- to Br_2 was made by Duce et al. (1965). It is suggested here in addition that subsequent adsorption by unsaturated organic material in background aerosols is a mechanism for achieving rapid surface distribution of Br from the Aitken range throughout the large and giant size ranges. These processes are included in Figure 36, the flow chart for the model; they satisfy the observational criteria—volatilization, surface adsorption and preference for Br over Cl.

Finally, Runs 17 and 18:CH:V are interpreted to include relatively fresh aerosols from the combustion of ethyl fluid and fuels such as coal. The concentration of oxidants in the atmosphere is suggested to have been sufficiently high to oxidize Br and Cl to gaseous forms which were later adsorbed on the surfaces of "Junge distributed" particles containing unsaturated hydrocarbons.

A short digression is made here to show how many of the above ideas may be woven into an interpretation of some features of the Hawaiian aerosol data of Duce et al. (1967). Whereas in continental aerosols the "Junge distribution" is the best estimate for aerosol mass, in fresh marine aerosols the Cl distribution should reflect the distribution of (sea salt) aerosol mass. In continental or pollution aerosols, Br_2 has been suggested often to be surface adsorbed by unsaturated hydrocarbons. This leads to an r^{-1} dependence for Br because the ratio of surface area to mass has this dependence and mass is constant. In marine aerosols iodine may be surface distributed because I/Cl has dependence r^{-b}, $1 \leq b \leq 2$, which is close to the r^{-1} dependence of (surface area)/mass, and Cl is proportional to mass.

Iodine is likely concentrated in organic sea-surface films. Dawson (1966) reports that algae may concentrate iodine up to 30,000 times its concentration in sea water; surface-active algal material probably accumulates at the sea surface. Blanchard (1964) has found surface-active material in the aerosol downwind from Hawaiian surf. He calculated the area of surface-active material, at zero surface pressure, to be from four to eleven times the total surface area of the aerosol droplets. This suggested that the droplets carry a compressed surface film. Therefore the proposition is advanced that iodine-rich, organic, surface-active material is surface distributed on marine aerosols. This is consistent with the results (Duce et al., 1967) that I/Cl in the aerosol exceeds the sea water ratio for all particle sizes and that I/Cl (or surface area/mass) decreases at least as rapidly as r^{-1} for increasing particle radius.

*Runs 43:EE:XI and 44:EE:XII (Figure 20)

These aerosols were collected in air masses with overland trajectories along which they spawned precipitation for many hours. These circumstances together with the high values for Br/Cl which were observed suggest the aerosol to be of pollution origin (Figure 37).

One marked feature of these Cl and Br spectra is the deep gap indicating the relative depletion of Cl- and Br-rich particles with radii between 0.1 and 1μ. This gap corresponds with the cloud-droplet nucleating behavior of continental aerosols as envisaged by Mordy (1959), Neiburger and Chien (1960) and, in our Figure 2, by Junge (1963). The fact that these runs were made during periods of precipitation supports the possibility of cloud-droplet nucleation but strong evidence in support is also afforded by the observed preferential depletion of Cl relative to Br.

Particles of the same size, Cl-rich or Br-rich, would be expected to be removed with equal efficiency if washout by falling raindrops were the only process operative. The fact that particulate Cl is preferentially removed is established below; this implies that the particles richest in Cl are more actively involved in the precipitation process and suggests that these, more readily than Br-rich particles, are activated as cloud-droplet nuclei and removed by rainout.

We shall now proceed to establish that Cl-rich particles are preferentially removed by precipitation; then an explanation will be offered. The mass ratios, Br/Cl, on impactor stages D to Z (Runs 43 and 44) are extremely high ($\cong 1$). Since automobile exhaust is the major source of Br and since, in fresh exhaust (Run 38:AG:IX), the Stage Z ratio was only 0.35, then these high Br/Cl ratios must arise, not only by accumulation of Br, but also by depletion of Cl-rich particles. The data also suggest that this occurs by cloud-droplet nucleation. The gap in the Br and Cl spectra has been noted. This should separate the activated from the unactivated particles. Examination shows the small particles in and below the gap (Figure 20) to be Br-rich while the giant, activated particles to the right are increasingly Cl-rich with increasing size—up to raindrops and snowflakes. Thus the Cl-rich particles, preferentially, are involved in cloud-droplet nucleation, droplet growth and rainout, leaving the remnant aerosol Br-rich.

(The possibility has been pointed out that the nucleation may occur, not in the atmosphere, but in the cascade impactor. This can be ruled out by cases as clear as Run 43:EE:XI. A full discussion is given in Appendix A, however, concisely, the logic is that since the observed chemical differentiation between Br and Cl is consistent in the results for impactor samples and precipitation, the nucleation must have occurred in the atmosphere.)

The explanation offered for the preferential involvement of Cl-rich particles in cloud-droplet nucleation is that the Cl-rich particles are more soluble than Br-rich particles. Soluble particles were shown in Chapter I to be more readily activated as cloud-droplet nuclei. A list of the solubilities of several halogen compounds is given below.

Compound	Molality at Saturation (0°C)
C_4H_9Br	insoluble*
C_4H_9Cl	0.0071
$C_5H_{10}Br_2$	insoluble
$C_5H_{10}Cl_2$	insoluble
$C_5H_{11}Br$	insoluble
$C_5H_{11}Cl$	insoluble
$PbBr_2$	0.0124**
$PbCl_2$	0.0242
NH_4Br	6.10
NH_4Cl	5.55
$FeBr_2$	4.9
$FeCl_2$	4.74
$MgBr_2$	4.99
$MgCl_2$	5.50
$MnBr_2$	5.8
$MnCl_2$	5.04
NaBr	7.71
NaCl	6.10
$CaBr_2$	6.2
$CaCl_2$	5.35

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*Handbook of Chemistry and Physics, 42nd ed. 1960. The Chemical Rubber Publishing Co., Cleveland, Ohio.

**International Critical Tables, 1928. McGraw-Hill, New York.

(The molality at saturation is proportional to the mole fraction of solute and, by Raoult's law, to the decrease in vapor pressure over the solution. This decrease in vapor pressure facilitates condensation toward solution droplets and is important for cloud-droplet growth.)

These data show that particles fresh from the major Br source, automobile exhaust, are only slightly soluble. Also particles made Br-rich through volatilization and adsorption in surface organic materials are insoluble. Therefore the majority of Br-rich particles, fresh from the source or arising from atmospheric processes, are only slightly soluble. Common halogen compounds, other than lead halides and organics, are generally quite soluble in water; therefore Cl-rich particles which are produced largely as compounds other than lead halides and which are not so likely to be volatilized and combined with organics, tend to be soluble in water. This difference in solubilities is suggested to be an explanation for the preferential involvement of Cl-rich particles in cloud-droplet nucleation. It also implies that particles from different sources do not rapidly form conglomerations but rather that the (Cl- and Br-rich) subpopulations remain distinguishable for hours at least. Thus in our model, Figure 36, the preferred process for Br, volatilization and adsorption, is to a degree independent of the preferred process for Cl particles, cloud-droplet nucleation.

Runs 9, 12, and 13:EE:V (Figure 17)

For Run 9:EE:V, the slow movement of air through the Great Lakes region, absence of rain, presence of haze and high concentrations of Cl and Br establish the aerosol as being of pollution origin. Br volatilization over many hours is suggested to have produced the moderate Br/Cl values. For Run 12:EE:V trace precipitation, giving preferential Cl depletion, and decreased atmospheric stability, giving dilution by mixing, may explain why the Br concentration was not increased while Cl was decreased although trajectories passed over industrial areas of Illinois and Indiana. (Georgii and Weber, 1960 (cited in Junge, 1963) report Cl and other constituents to be more concentrated in unit volumes of trace than of heavy precipitation.) Run 13:EE:V was collected during a frontal passage. Because the Br/Cl values were not further increased compared to those of Run 12:EE:V, although Br and Cl concentrations were reduced, dilution (in the atmosphere and in the impactor by mixing air masses) as well as rainout is suggested to have occurred. The absence of r^{-1} dependence in Run 9:EE:V cannot readily be explained from the available data but we suggest that the processes of coagulation or cloud-droplet nucleation, if operative, could perturb the "Junge distribution," e.g., Figure 2. Alternatively, the substrate aerosol in Run 9:EE:V may, for some unspecified reason, have a distribution deviating of its own accord from the "Junge distribution."

The spectra of Runs 12 and 13:EE:V are likely distorted by cloud-droplet nucleation.

Runs 31 and 32:LN:VIII, 33:LP:IX, 35 and 36:EE:IX (Figures 13 and 18)

This group of runs bears resemblance to the group just previously discussed. The Lake Nipigon aerosols are probably aged pollution particles. The trajectory from the United States, the absence of rain, low concentrations of Br and Cl, the spectral shapes and the moderately low Br/Cl ratios all support this view.

The La Porte sample may consist of somewhat fresher pollution aerosol acquired by the air mass after rainout in the southern U.S. The spectrum shapes are continental in character; concentrations and Br/Cl ratios are higher than at Lake Nipigon.

Approximate r^{-1} dependence of Br is exhibited by Runs 32:LN:VIII and 33:LP:IX. This is consistent with the absence of cloud-droplet nucleation.

During Runs 35 and 36:EE:IX (which were taken simultaneously and provide a useful test of reproducibility of sample collection and analysis) the passage of a cold front led to thundershowers and winds from southerly to easterly which may have transported relatively fresh pollutants from Toledo, Ohio, or Detroit. The total measured Cl and Br concentrations in the aerosol, 2600 ± 200 ng Cl/m^3 and 190 ± 12 ng Br/m^3, afford an opportunity for comparison with the pollution input estimated (Chapter I) for a city such as Detroit. A trajectory involving 3 hr exposure to the pollution from a city like Detroit would result in the acquisition by the air of an estimated 1800 ng Cl/m^3 and 300 ng Br/m^3. Although Br volatilization and some Cl depletion by rainout are expected to have occurred, it is judged that the above estimates are roughly correct and, therefore, that the correspondence with measured values is satisfactory.

The Br/Cl ratios are relatively high implying fresh pollution, rainout or both. The spectral shapes from the two impactors agree, implying that the particles were wet. The spectral shapes for Br and Cl correspond, suggesting that the Br-rich particles are not completely excluded from cloud-droplet nucleation. However, because of complications in radiochemistry (Appendix A), the matched spectral shapes should be confirmed by additional observations. The matched spectral shapes and relatively constant Br/Cl ratio may have been caused by cloud-droplet nucleation, then agglomeration of the aerosol subpopulations by droplet coalescence and, finally, cloud dissipation giving reduction in particle size.

*Runs 21, 22, 23 and 24:LM:V (Figure 19)

During this sequence of runs, haze, fog, rain, and then clearing were experienced. The winds and chemical data (spectral shapes and Br/Cl ratios) suggest the aerosols to have been of pollution origin. The Br, and not the Cl, spectra have r^{-1} dependence but show a pronounced gap and peak during the rain (Run 23:LM:V). The resemblance to the evolution envisaged for cloud-droplet nucleation by Junge (1963) (Figure 2) is striking. The concentration of Cl, totalled over the impactor stages, shows a distinct reduction (by a factor of about 3) during the rain. The concentration of Br, similarly totalled, shows much less reduction (by a factor of about 1.3). The interpretation may be that cloud-droplet nucleation occurred with the Cl subpopulation being activated and rained out more than twice as effectively as the Br subpopulation.

3. Interpretation from Other Aspects

r^{-1} dependence

If the distribution of continental aerosol mass is perturbed by cloud-droplet nucleation and no longer invariant with log radius, then the Br distribution will no longer show the r^{-1} dependence. This is because surface distributed Br corresponds to the ratio (surface area)/mass only when mass is invariant with log radius. Consistent with this, approximate r^{-1} dependence is found for Br and Cl in the following runs where cloud-droplet nucleation (CDN) probably did not occur; Runs 17 and 18:CH:V, 31 and 32:LN:VIII. Where CDN may have occurred to a slight degree, the Br, but not the Cl, distribution is found to preserve r^{-1} dependence; e.g., Runs 19:LM:V, 21, 22 and 24:LM:V and 33:LP:IX. In aerosols exposed to extensive rain formation, both Cl and Br distributions are distorted; e.g., Runs 12:EE:V, 23:LM:V, 35:EE:IX, 37:AG:IX, 43:EE:XI and 44:EE:XII.

We will now make another short digression to consider a related situation in Hawaii. Duce et al. (1965), in samples of rain from orographic rain clouds, found concentrations of Cl to decrease more rapidly than Br or I (iodine) with increasing altitude on Mauna Loa. In addition, Seto et al. (1969), have found the ratio Na/Cl to increase only slightly compared to the previously measured increase of Br/Cl and I/Cl with altitude. The key difference here from the case of continental aerosols is that there is initially only one aerosol population, the marine aerosol, with its volume-distributed Cl and Br and surface-distributed organic material and I. (The continental aerosols are comprised of many subpopulations; among these are Cl and Br condensation aerosols, Cl dispersion aerosol and a background aerosol with organic constituents.) The hypotheses developed for continental aerosols mesh with those of the above authors for the Hawaiian aerosols and are the following: (1) For iodine, because giant particles become more depleted and supersaturations increase with altitude, progressively smaller particles become activated and rained out. These smaller particles have higher surface/mass and I/Cl ratios and so, therefore, will the rains have higher I/Cl. (2) For Br a surface area mechanism is attractive because then the fact that the variations of I/Cl and Br/Cl with altitude have the same slope could be explained. We suggest that much of the aerosol Br is volatilized by photons or atmospheric oxidants and subsequently adsorbed in the droplets' organic surface film. This interpretation could be tested by making cascade impactor collections at many altitudes in Hawaii (with some above cloud base). According to the interpretation offered, both Br/Cl and I/Cl should have r^{-1} dependence. (This r^{-1} dependence would not be distorted by cloud-droplet nucleation because Br/Cl and I/Cl would always correspond to the ratio, surface/mass.)

It may be noted in the flow chart of the model (Figure 36) that only in the case of marine aerosols is a particle with Br adsorbed by surface organic material subsequently considered a potential cloud-droplet nucleus. Marine aerosols do nucleate cloud droplets, probably while carrying an organic surface film. However, this film is expected to be small in amount and partly soluble, whereas in pollution aerosols the organic material is likely insoluble and present in relatively large amounts in certain subpopulations. These pollution particles would be inefficient cloud droplet nuclei.

Br/Cl ratio

In Figure 38, the Cl and Br concentrations, totalled within the impactor (Table B-4, Appendix B), are plotted (and the point identified by abbreviated run number) on a background of Br/Cl isopleths. The plotted points range from the fresh marine aerosol (Run 8:HAWAII) with low Br/Cl to the pollution aerosols with high Br/Cl, either fresh (Run 17:CH:V), rained out (Runs 12 and 13:EE:V, 23:LM:V, 43:EE:XI and 44:EE:XII), or both (Runs 35and 36:EE:IX).

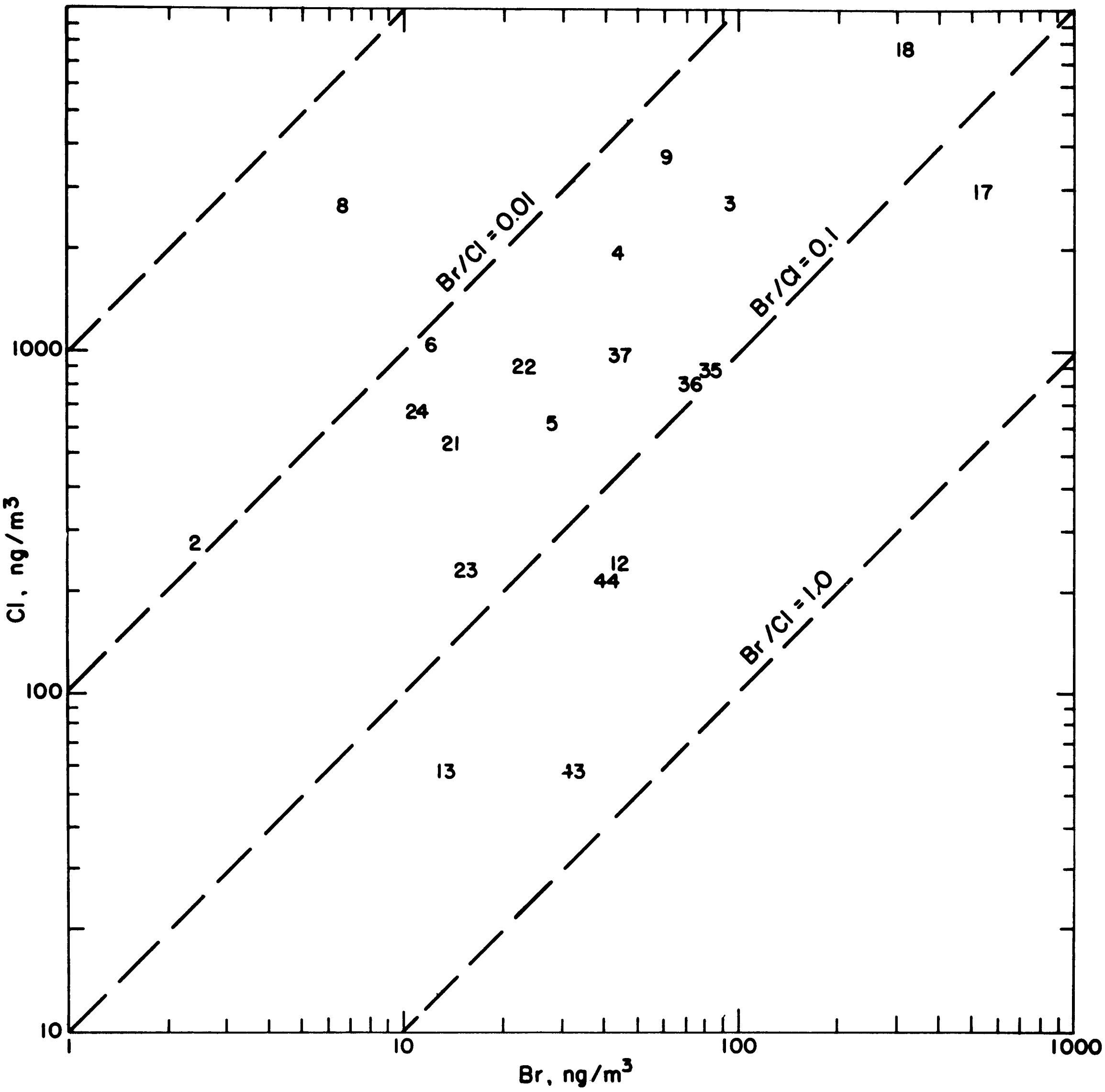

Figure 38. Run numbers arrayed according to Br and Cl concentrations totaled within the impactor (excluding the filter).

The other runs have Br/Cl ratios intermediate between these extremes.

With Figure 38 as an introduction, more can be perceived from Figure 39 which differs only in that the result for each impactor stage of several runs is plotted, Cl versus Br. One feature is that the values for Run 8:HAWAII occupy an elongated region aligned along an isopleth of Br/Cl; this ratio is consistently low for size-fractions of fresh marine aerosols. Similarly, Runs 12 and 13:EE:V and 35:EE:IX show Br/Cl to be consistently high in size-fractions of fresh pollution aerosols. In contrast, Runs 2:GR:II, 3, 5 and 6:EE:III occupy regions perpendicular to isopleths of Br/Cl. These runs have their giant particles in the marine aerosol region and their small particles in the pollution aerosol region as previously suggested.

The highest values for Br/Cl are found, not in fresh pollution aerosols of high Br and Cl concentration, but in those stages in the spectral valleys of Runs 43:EE:XI and 44:EE:XII. The Br/Cl values there are very high, even equalling that of pure ethyl fluid in one case, and must arise through Cl depletion as a result of cloud-droplet nucleation and rainout.

C. SUGGESTIONS FOR FURTHER STUDY

1. Confirmation of Present Results

There are several features of the model presented above which should be further tested by field observations and controlled experiments. Field observations might be made in an industrial area to test for the occurrence of the "Junge distribution" and for surface adsorption of Br. Measurements of the numbers of particles as well as the mass of halogens, in size distribution,

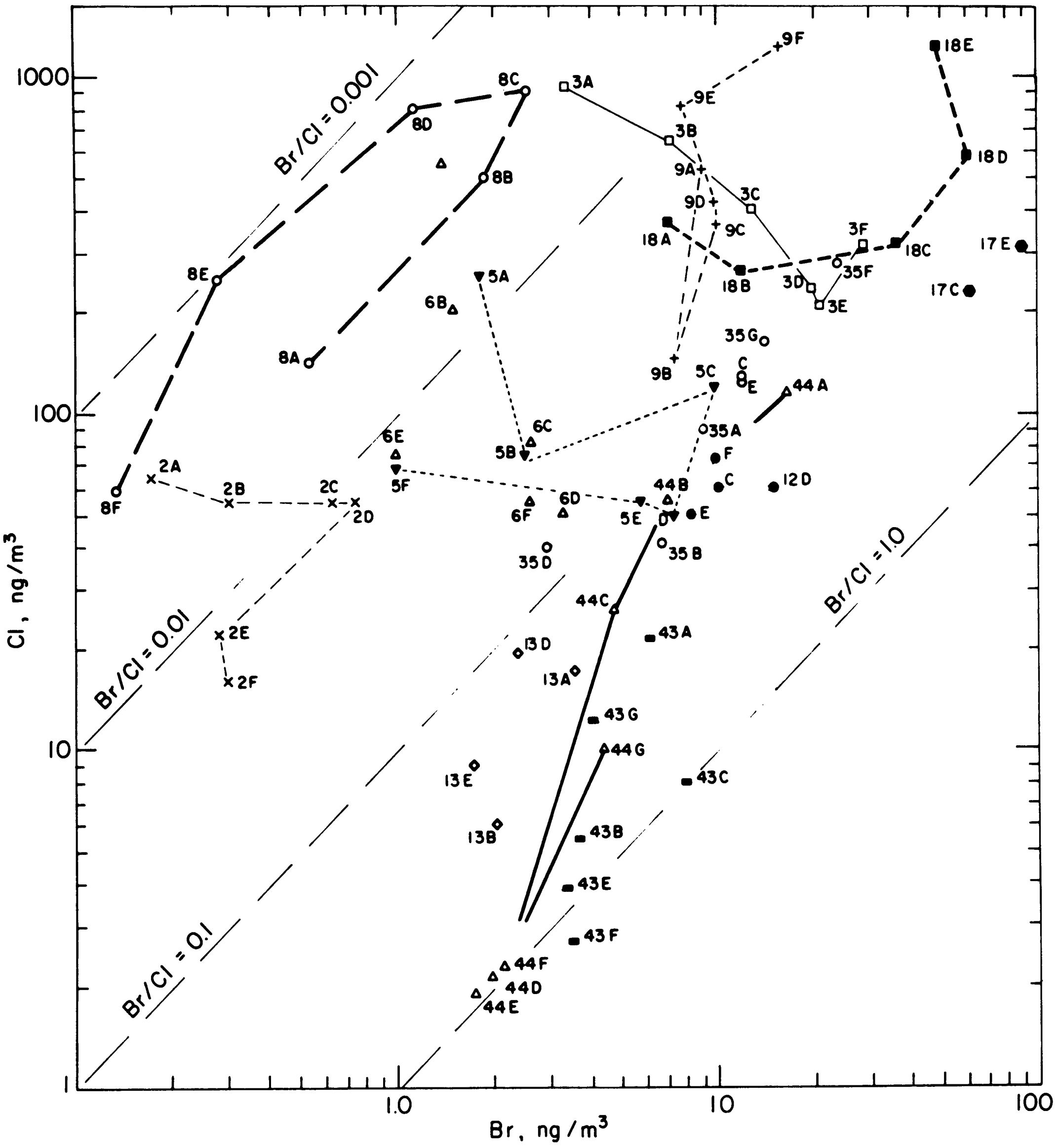

Figure 39. Impactor stage designations for various runs arrayed according to Br and Cl concentrations.

would be necessary. The number-size distribution might be measured by electrical or optical particle counters (Clark and Whitby, 1967). The cascade impactor might again be used for the halogen mass-size distribution.

In such a sampling program, care might be taken to accurately identify the source or sources in order to see whether the "Junge distribution" is found in aerosols from a single smoke stack or whether it is the resultant only of a blending (without heterogeneous coagulation) of aerosol subpopulations.

As a controlled experiment, one might fruitfully repeat the automobile exhaust sampling. Larger samples, to overcome blank levels, would be desirable. This could best be arranged by passing the exhaust through delay pipes in order that aging might occur while sampling went on continuously.

The processes of oxidation and surface adsorption of Br could also be made operative under controlled experimental conditions. Again it would be desirable to measure particle sizes, numbers, and halogen masses as well as concentrations of oxidants and organic materials.

The process of cloud-droplet nucleation might be studied by measuring particle sizes, numbers and halogen content before and after passage of an air sample through a cloud chamber. The size-shifts due to CDN would be detectable. The cloud droplets can be sized and counted by collecting them on impactor slides coated with a pure gelatin film and viewing the small stains with a phase-contrast microscope (May, 1959). In addition, one ought to be able to size and count ice nuclei by subjecting the impactor slides to low temperatures, water vapor saturation, and ice detecting solution (of water and sugar) (Bigg *et al.*, 1963). This latter technique would be useful in the study of the role of iodine in ice nuclei from pollution aerosols.

Through such observations and experiments, one might approach an understanding of the following questions: Are the Cl-rich nuclei a majority of the cloud-droplet nuclei population? Are the Cl compounds the active agents in cloud-droplet nucleation? What are the concentrations and composition of ice nuclei from pollution sources?

2. Extension of the Present Results and Techniques

We wish to introduce two further proposals. The first may be most simply described by reference to Figure 40 from Jiusto (1967). The objective would be to determine those regions on such a diagram where fog and rain formation could be expected. That is, one would like to establish, by field observations over a range of supersaturations, what numbers and quality of cloud-droplet nuclei can be present with concomitant rain or fog. The normal situation in clear air at low supersaturations is that there are too many nuclei sharing the available liquid water to allow many of them to grow into large cloud droplets. During uplift and cooling, enough liquid water may become available so that the efficient cloud-droplet nuclei are unimpeded in their growth into large cloud droplets. However, if the numbers of these nuclei were increased, by pollution for example, individual droplet growth would again be inhibited (Gunn, 1957). It is thus possible that pollution aerosols are influencing rainfall patterns. One can imagine that a shift which caused a larger fraction of rain in the Great Lakes Basin to fall over land rather than on the Lakes themselves would be significant because much of the rain falling on land may be

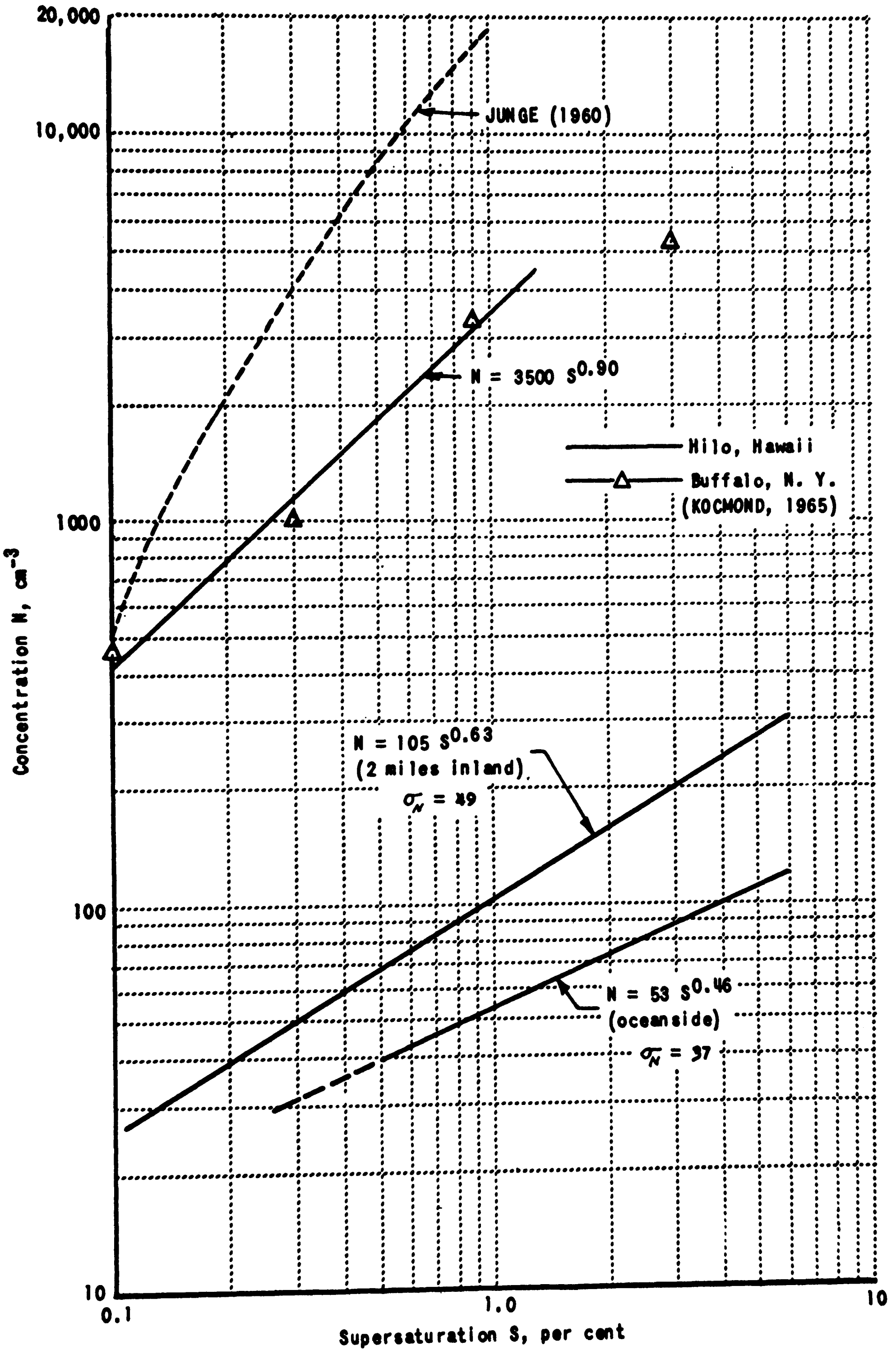

Figure 40. Concentrations of cloud nuclei at Hilo, Hawaii and Buffalo, New York (after Jiusto, 1967).

evaporated and transported out of the Basin.

Measurements of cloud nuclei numbers at various supersaturations, cloud droplet numbers and sizes and halogen masses, made from lake tower and land stations during periods of clear air, rain and especially fog, would lead to knowledge of the extent, if any, to which pollution nuclei are raising the supersaturations prerequisite for rain.

Another proposal is to test the hypothesis that Niagara Falls influences water quality by the formation of bubbles which cause surface active material to collect at the surface (Jarvis, 1967) and be, in part, transferred to the atmosphere as ejected droplets (Blanchard and Woodcock (1957) and MacIntyre (1965)). The necessary instruments would include a surface film sampler (Garrett, 1965) and cascade impactor. One might analyze for phosphate, iodine and organics.

CHAPTER V

CONCLUSIONS

Measurements of Cl and Br in aerosols have been extended to a mid-continent region, the Great Lakes Basin, in an attempt to identify the sources and modifying atmospheric processes important in this environment. The data from analysis of size-fractions of aerosols for Cl and Br proved valuable for uncovering some of the complex interrelationships which prevail. (For example, our identification of aerosol source and our recognition of (Br) surface adsorption and (Cl) cloud-droplet nucleation all depended on characteristics of the halogen mass size distribution.) The present data, coupled with the findings of previous investigators, permit the formulation of a model for the roles of aerosol Br and Cl in the atmosphere. The model reflects our present understanding of the situation in nature and may be summarized as follows.

(1) The ocean seems to generate one halogen aerosol population. This consists of small numbers of large and giant particles rich in Cl. The characteristics of this aerosol seem consistent even for different times and places. Pollution sources appear to produce three halogen aerosol populations directly (Cl-rich dispersion aerosol (fly-ash), Cl-rich condensation aerosol (coal and fuel oil combustion), Br-rich condensation aerosol (leaded gasoline)) and a fourth indirectly (Br-rich, surface distributed). These particles are produced in large numbers.

(2) Inland aerosols may arise from the ocean source, the pollution sources,

or both. Marine aerosols may be transported inland by fast moving weather systems; however, rain en route will significantly reduce their concentration because the giant sea-salt particles are readily activated as cloud-droplet nuclei. The inland location is most suitable for the study of aerosol Br and Cl because the ocean source is reduced to an effective strength comparable with that of a strong pollution source for Cl while Br, mainly from the combustion of leaded gasoline and a good indicator of pollution, is often prominent, allowing comparison of its roles with those of natural and pollution Cl.

(3) The Cl-rich particles tend to be soluble while the Br-rich particles tend to be only slightly soluble in water. Since solubility, hygroscopicity, and efficiency for cloud-droplet nucleation are directly related, the Cl-rich particles, more so than the Br-rich particles, are active in cloud-droplet nucleation. Of the Cl-rich particles, those of pollution origin, by their greater numbers and despite their smaller size, provide more cloud-droplet nuclei inland than those of natural origin.

(4) Br, initially on particles in the Aitken size range, may become distributed throughout the stable aerosol range by being first volatilized and then surface adsorbed. Br^- is oxidized to Br_2 (gas) preferentially to Cl^- by atmospheric oxidants such as ozone. This process is aided by acidic conditions such as may be found in pollution aerosol droplets. The Br_2 (gas) may, by the common reaction of adding at the double bond of an unsaturated hydrocarbon, become distributed

on the surface of particles containing organic material and "Junge distributed." These new Br-rich particles would also be insoluble, in all probability. Cl would be less likely to be similarly surface distributed but might still be present on large and giant particles as a result of condensation on refractory dispersion aerosols or of droplet growth following cloud-droplet nucleation.

(5) The variability of the inland aerosol halogens results primarily because a number of distinguishable subpopulations may be present. Moreover the various subpopulations are affected by particular atmospheric conditions. A swift flow of air from the ocean, without extensive rainout, will bring marine aerosols inland. A slow-moving high pressure area will permit pollution aerosol concentrations to build up. High oxidant concentrations will favor the volatilization of Br. High relative humidity will lead to cloud-droplet nucleation and reduced residence time for the hygroscopic Cl-rich particles.

In the marine environment, the same atmospheric processes are suggested to be operative, but they operate on only one halogen aerosol population. Moreover atmospheric conditions are held relatively constant by the influence of the sea. Therefore the observed variations are small in comparison with those which occur inland.

(6) The implication that subpopulations of aerosols mainly from different sources (e.g., Cl-rich and Br-rich) remain distinguishable for hours at least, coupled with the indirect implication from Calumet Harbor (Runs 17 and 18:CH:V) that those subpopulations, singly and/or in

sum, exhibit the "Junge distribution" although they are fresh from many independent sources, provides support for the hypothesis advanced by Junge (1969). He suggests that the "Junge distribution" arises from the blending of many broad log-normal-volume aerosol subpopulations produced by independent sources rather than from equilibrium between the atmospheric processes of heterogeneous coagulation (agglomeration) and sedimentation (fallout).

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APPENDIX A

SUPPLEMENT TO CHAPTER II—THE EXPERIMENTAL TECHNIQUES

1. THE CASCADE IMPACTORS

a. Condensation

The question to be discussed is this: Had CDN and the growth by condensation occurred naturally before sampling or unnaturally due to the expansions in the jets of the cascade impactor? A decisive experiment would seem to require humidity control and then perhaps the use of identical impactor stages in series to determine whether condensation, evaporation or neither were occurring. Such an experiment may be performed here in the future; for the present, there exists some information for consideration.

Ranz and Wong (1952) comment that "...To prevent excessive cooling and the possibility of moisture condensation when the impactor is classifying a certain particle size, there is a considerable advantage in operating a small [sic] [large] jet at less than half sonic velocity rather than a large [sic] [small] jet at sonic velocity. Under these circumstances the jet temperature is effectively equal to the ambient temperature...". May (1962) characterizes the flow as near isothermal because of the metal walls. He concludes for the Casella impactor that evaporation occurs—even in the final stages. The above comments are consistent—velocities much below sonic allow more heat transfer and approach to isothermal flow; isothermal flow through a jet involves expansion and reduction of vapor pressure and relative humidity. My calculations, assuming isothermal conditions, show jet velocities to be less than half sonic in the first four stages of both SA and AS impactors (and less than velocities in the Casella impactor). On these grounds condensation within the first four stages is unlikely, yet it is here that the excess signal is found in those cases interpreted to exhibit CDN.

Another piece of evidence supporting CDN in the atmosphere is the depletion of Cl in preference to Br. The more logical sequence of events is not that chemical differentiation within the impactor allows Cl aerosol to pass but rather that Cl aerosol—with more facility than Br aerosol—nucleates cloud-droplets (in the atmosphere) which grow to rain droplets and are excluded from the impactor by its rain-shield or shelter.

It is concluded that condensation within the impactors cannot have masked the character of those runs which are judged to clearly indicate natural CDN.

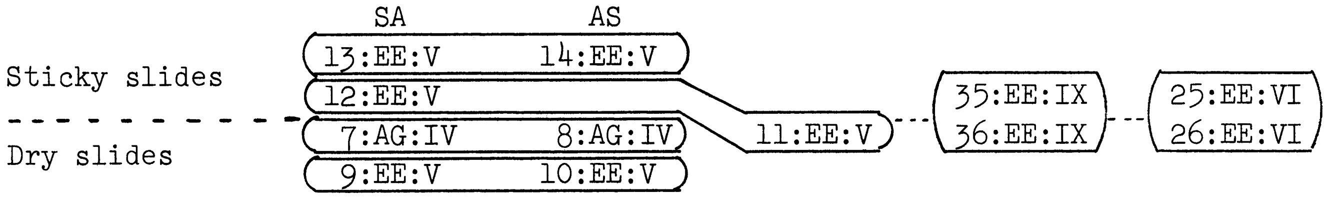
b. Comparisons of SA and AS With and Without Sticky Slides

Attempts were made to determine the effect of sticky slides on collection efficiency. Of course the most stringent test would involve low relative humidities. (Otherwise droplets are present which will remain on a dry or sticky surface, e.g., the correspondence between results of Runs 35 and 36:EE:IX.) The tests were not conclusive but suggested that stickiness was desirable. Therefore the procedural step of coating collecting surfaces with glycerol was adopted. Others have reached this conclusion, e.g., Gillespie (1955), Laskin (1952), Lundgren (1967), Mercer (1963).

In Table A-1 the comparative runs are listed. The one effective comparison of SA and AS instruments is the pair, 13 and 14:EE:V. These agree approximately (Table B-3). (The effective cut-off radius for a stage differs from SA to AS and must be taken into account.)

TABLE A-1

COMPARATIVE IMPACTOR RUNS



2. COLLECTION OF SAMPLES

a. Glass Slides

For Runs 1, 2, 9, and 10, aerosol particles were collected directly on dry glass slides. In preparation the slide was first washed in warm concentrated nitric acid, washed again in triple-distilled water and then shaken dry. A rinse of 500 ml distilled water was worked around on the slide with the tip of the pipette and collected in a washed vial for analysis as a blank. The slide was then installed in the impactor and exposed to the impinging particles of tens of cubic meters of air. The sample was rinsed off in two washes similar to the blank wash. Although the radiochemistry went smoothly, the low sample-to-blank ratio and the labor required in analyzing three washes per sample led us to look for an improved impactor slide technique.

b. Polyethylene Discs as Slide Covers

Discs of polyethylene sheeting (0.1 mm thick) were placed over the glass slides. The aerosol was collected on the disc. There were two advantages: (1) the disc with sample intact could be irradiated directly, and (2) the disc could be cut to provide portions of the sample for different analyses.

The discs were prepared for use by washing in warm nitric acid, rinsing in distilled water and shaking dry. On occasion high blanks were still a problem—being due perhaps to residues from droplets of water which had remained on the disc; but, in general, blanks were consistent and signal-to-blank ratios were greater than five.

3. ANALYSIS

For the bulk of the data the β-technique was employed, and some problems were recognized. During the course of the work the facilities for γ-analysis became easily available. With Mr. K. A. Rahn an adaptation of the procedure suitable for γ-analysis was worked out. The greater selectivity of this technique allowed us to identify Mn and Na as interfering species in the β-analysis. Later the two methods were compared directly. This led to the identification and correction of two lesser problems in the β-technique—over-oxidation of Br and under-evaporation of Br (in separate aliquots). Finally, Drs. J. W. Winchester and J. A. Robbins pointed out a possible error in the γ-technique which is discussed below under the heading, "Double-escape peak."

a. Mn and Na Interference

Mn and Na are common constituents of aerosols. Tests have shown the aerosol Mn to be largely insoluble, even after irradiation. (However aerosol Cl and Br are soluble, at least after irradiation.) The status of Na is not certain. Insoluble Mn interferes with the determination of Cl because, in this branch of the procedure, there are no solvent extractions by means of which insoluble fractions can be eliminated. Before this diagnosis, extra steps of decantation, redissolution and reprecipitation were carried out with partial success. A correction procedure was devised which extracted a Cl estimate from the composite decay curve—if this was reasonably close to the Cl decay curve. This procedure turned on the facts that the half-lives of 2.58h ^{56}Mn and 15.0h ^{24}Na are large compared to that of 37m ^{38}Cl and that ^{38}Cl is the only neutron activation product with half-life between 10 min and 1 hr which is common in aerosols (with the exceptions, 18m ^{80}Br and 25m ^{128}I, which activities are evaporated off with efficiencies of about 80 and 100%, respectively). The procedure is illustrated in Figure A-1. The composite decay curve was split into a slowly-decaying fraction and a fraction decaying with half-life, 37 m. If this Cl fraction amounted to less than half the total activity, we listed only an upper bound for the Cl component (Figure A-1(b)). If, however, the adjustment between the composite and the Cl decay curves was less, the Cl estimate was accepted with a standard deviation half as large as the adjustment (Figure A-1(a)). Those samples where the adjustment amounted to between 25 and 50% are marked in Table B-3 with an asterisk (e.g. A*). Runs 2:GR:II and 21:LM:V are affected more than any others.

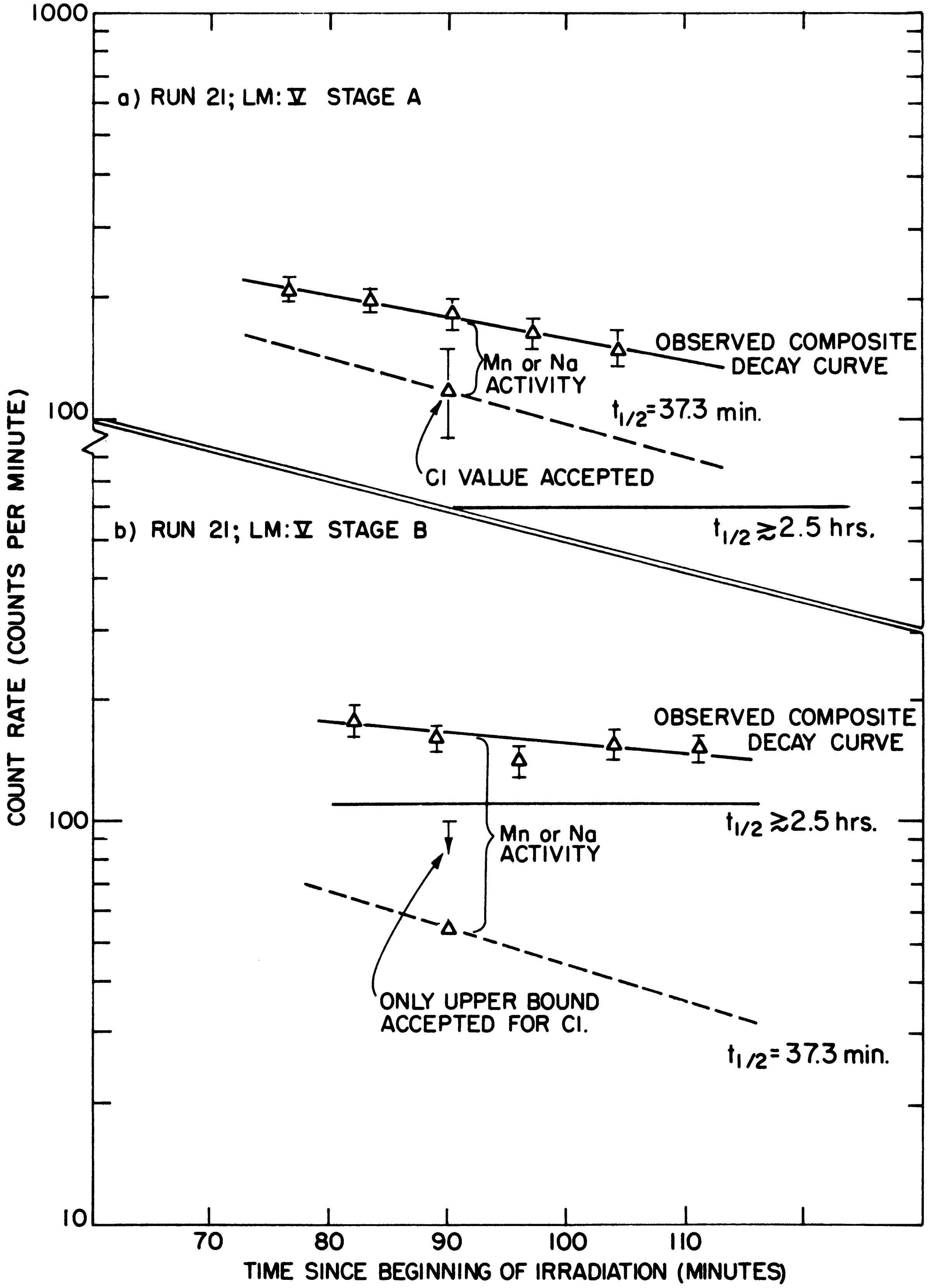


Figure A-1. Illustration of correction for Mn and Na interference.

b. Br Over-Oxidation

At one stage in the β-procedure, Br^- is oxidized to Br_2 to separate it from the Cl activity. In the presence of HNO_3, the reaction is

$$6Br^- + 2MnO_4 + 8H^+ \rightarrow 3Br_2 + 2MnO_2 + 4H_2O.$$

There is Cl from NaClO present at this stage as well as radioactive aerosol Cl. By adding too much HNO_3 in the extraction, Cl^- as well as Br^- is oxidized. The positive Br error was detected through comparison with γ-analysis: however, when the β-data were reexamined, the sign was there—yields of silver halide precipitate from the Br aliquot were unusually large. The expected yield was substituted in the calculations and verified to give reasonable results by comparison with those from γ-analysis. The samples for which the adjustment exceeded two standard deviations are marked in Table B-3 by a colon (e.g., A:). Runs 35 and 36:EE:IX were significantly affected.

c. Br Under-Evaporation

The Br/Cl values for inland aerosols are relatively high. Therefore interference by radioactive Br and I in the counting of the Cl fraction was reduced by oxidation and evaporation of Br_2 and I_2 using dilute nitric acid and heat. Specifically, the Cl aliquot, in an erlenmeyer flask, was placed on a hot plate; three drops each of ~ 0.1M KBr and KI carrier solution and ten drops of concentrated nitric acid were added. The solution was heated and swirled until, by the lack of color, the Br and I could be said to have been evaporated off. The process was then repeated. Tests have shown the process to remove 80 ± 20% of the Br activity. The Cl values have been corrected for Br under-evaporation; however, the correction was significant only where the Br/Cl ratio was large. Those few samples adjusted by two standard deviations or more are marked in Table B-3 by a slash (e.g., A/).

There are five reasons why the data retain their value in spite of the problems encountered. (1) The analyses were done in production line style; therefore corrections could be derived systematically. (2) The corrections were significant in relatively few cases. (3) The corrections were checked by an independent method—γ-analysis. (4) The corrections, even where significant, were small compared to the range of concentrations in the size distribution. (5) The results where sticky slides were used or where relative humidities were high were reproducible to within ± 2 standard deviations; otherwise, to within ± 3 standard deviations.

d. Double-Escape Peak (NaI Detector)

By chance the energy of the double-escape peak associated with the 1.60 mev γ-ray of ^{38}Cl is very close to 0.617 mev, the energy of that γ-ray of ^{80}Br which was used for measurement. Error could be incurred in the γ-measurement of Br if this interference were appreciable. As it happens it is not; γ-ray abundances and detection efficiencies indicate the interference to be small. Experiment indicates the interference to be negligible with the NaI detector for Br/Cl > 0.005. Runs 37 to 44 were analyzed via the γ-procedure and have Br concentrations easily able to dominate the double-escape peak interference.

e. Estimation of Uncertainty

Each piece of chemical data in Table B-3 (other than upper bounds) has associated with it a standard deviation estimate of its uncertainty. Standard deviations (hereafter abbreviated SD) arise naturally from the statistical nature of the radioactive counting data. The basic uncertainty comes from four factors, each with SD approximately equal to 5%. These uncertainties, in count rate of sample, count rate of blank, count rate of standards, and volume of air sampled, combine to yield an estimate of approximately 10% uncertainty (SD). This estimate is increased if the signal-to-blank ratio is as low as three or two or if significant correction is required for any of the reasons discussed above in sections 3a, 3b, and 3c. The uncertainty estimate, SD, is gauged to insure that the limits, ± 2 SD, encompass the probable deviations.

APPENDIX B

TABULATION OF DATA

TABLE B-1

DETAILS OF THE CASCADE IMPACTOR RUNS

RUN #	START-STOP TIMES HOUR/DAY (EST)	AIR VOL. (M**3)	IMPACTOR USED	FILTER?	STICKY SLIDES?
1:GR:II	1756/4¬1617/6	36	SA	NO	NO
2;GR;II	1115/16¬1235/21	91	SA	NO	NO
3;EE;III	1158/7¬0830/8	15	SA	NO	NO
4;EE;III	0907/8¬1527/8	4.8	SA	NO	NO
5;EE;III	0907/11¬1232/12	21	SA	NO	NO
6;EE;III	1239/14¬1627/14	2.9	SA	NO	NO
7;AG;IV	0751/11¬0841/12	42	AS	NO	NO
8;AG;IV	0751/11¬0841/12	19	SA	NO	NO
8;HAWAII			SA	NO	NO
9;EE;V	0921/1¬0739/2	38	AS	YES	NO
10;EE;V	0921/1¬0739/2	17	SA	YES	NO
11;EE;V	0840/2¬0525/3	35	AS	YES	NO
12;EE;V	0840/2¬0525/3	16	SA	YES	YES
13;EE;V	0648/4¬0457/5	37	AS	YES	YES
14;EE;V	0648/4¬0457/5	17	SA	YES	YES
15;LM;V	0722/20¬1156/20	3.4	SA	YES	NO
16;LM;V	1225/20¬1606/20	2.8	SA	YES	NO
17;CH;V	1652/20¬0224/21	7.1	SA	YES	NO
18;CH;V	0307/21¬0559/21	2.2	SA	YES	NO
19;LM;V	0640/21¬1102/21	3.3	SA	YES	NO
20;LM;V	1124/21¬1450/21	2.6	SA	YES	NO
21;LM;V	0633/22¬1033/22	3.0	SA	YES	NO
22;LM;V	1102/22¬1912/22	6.1	SA	YES	NO
23;LM;V	1940/22¬0614/23	7.9	SA	YES	NO
24;LM;V	0650/23¬0952/23	2.3	SA	YES	NO

TABLE B-1 (Concluded)

25:EE:VI	1146/19¬0616/20	31	AS	NO	NO
26:EE:VI	1146/19¬0616/20	31	AS	NO	YES
31:LN:VIII	1317/29¬0100/30	19	AS	YES	YES
32:LN:VIII	1734/30¬0720/31	23	AS	YES	YES
33:LP:IX	1928/3¬0638/4	16	AS	YES	YES
34:LP:IX	2309/5¬0606/5	12	AS	YES	YES
35:EE:IX	1522/9¬1104/10	26	AS	YES	YES
36:EE:IX	1522/9¬1104/10	23	AS	YES	NO
37:AG:IX	0909/11¬1322/11	9.6	AS	YES	YES
38:AG:IX	1345/11¬1355/11	.3	AS	YES	YES
39:AG:IX	1355/11¬1405/11	.3	AS	YES	YES
40:AG:IX	1425¬35&1440¬1500/11	.9	AS	YES	YES
41:AG:IX	1515¬25&1530¬1620/11	1.8	AS	YES	YES
43:EE:XI	0530/28¬1450/30	80	AS	YES	YES
44:EE:XII	1050/4¬0850/7	100	AS	YES	YES

TABLE B-2

METEOROLOGICAL CONDITIONS FOR THE CASCADE IMPACTOR RUNS

RUN NUMBER :	WIND EXTREMES	:	TEMP. :	REL-HUM. :	WEATHER
	DRCTN.	SPEED M/SEC	EXTREMES DEG. C	EXTREMES %	
1:GR:II	N¬W	2¬ 6	-8¬ 9	20¬65	CLEAR, STNRY. HIGH
2:GR:II	/SW¬N	3¬12	-14¬ 3	20¬75	SNOW SHOWERS
3:EE:III	SE¬SW	1¬ 7	-3¬ 7	30¬75	SMOKE,HAZE
4:EE:III	SW	3¬ 7	-3¬13	60¬30	RAIN IMMINENT
5:EE:III	N¬E	4¬10	6¬-4	35¬70	SNOW IMMINENT
6:EE:III	SW¬S	4¬ 7	-7¬ 1	50	CLEAR
9 & 10:EE:V	NE¬S	1¬ 7	2¬16	30¬80	SMOKE, HAZE
11 & 12:EE:V	SW¬N	1¬ 8	2¬22	25¬80	RAIN IMMINENT
13 & 14:EE:V	NW¬NE	2¬ 7	3¬12	55¬80	THUNDER SHOWERS
15:LM:V	NW	5	6	85	4/8 CLOUD
17:CH:V	NNW	3	13¬ 8	70¬85	CLEAR
18:CH:V	W	5	8	95	CLEAR
21:LM:V	SSE	2	6	100¬95	7/8 CLOUD
22:LM:V	SSE	3	6¬14	100¬70	FOG
23:LM:V	VARIABLE	3	8¬ 5	80¬100	RAIN
24:LM:V	ENE	4	6¬10	100¬90	OVERCAST
25,26:EE:VI	W¬N	2¬ 7	34¬10	40¬80	CLEAR
32:LN:VIII	S	7¬ 2	18¬13	70¬90	HAZE
33:LP:IX	S¬SE	2	26¬13	70¬95	HAZE
34:LP:IX	S¬W	1¬ 4	20¬17	100¬90	FINE RAIN ENDING
35, 36:EE:IX	S¬E	2¬ 6	18¬22	75¬100	THUNDER SHOWERS
37:AG:IX			13	80	INTERMIT. LT. RAIN
43:EE:XI	W	3¬ 8	1¬10	100¬60	HEAVY RAIN, CLEARING
44:EE:XII	W¬NW	3¬12		80¬60	COLD SECTOR, SNOW

TABLE B-3

CONCENTRATIONS, STANDARD DEVIATIONS, AND RATIOS OF CHLORINE, BROMINE, IODINE, AND LEAD, IN NANOGRAMS PER CUBIC METER, FROM CASCADE IMPACTOR SAMPLES

1:GR:II 1756/4¬1617/6

SA STAGE:	CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
A	7	2	.3	.1	.05	.02	40	70	2		
B	12	3	.10	.02	<.01		8	<10	.5		
C	<20		.12	.04	<.01		>6				
D	14	5	.4	.1	<.01		30	<10	.2		
E	6	2	.9	.2	.08	.02	150	130	.9		
F	63	7	6.2	.6	.21	.02	100	33	.3		

2;GR;II 1115/16¬1235/21

SA STAGE:	CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
A*	65	20	.17	.02	.008	.002	3	1	.5		
B*	55	20	.30	.03	.013	.003	5	2	.4		
C*	55	20	.63	.06	.011	.003	11	2	.2		
D*	55	20	.73	.07	.006	.002	13	1	.1		
E*	22	5	.28	.03	.008	.002	13	4	.3		
F*	16	5	.30	.03	.023	.005	19	14	.7		

3;EE;III 1158/7¬0830/8

SA STAGE:	CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
A	940	95	3.4	.3	.10	.02	4	1	.3		
B	645	70	7.1	.7	.08	.02	11	1	.1		
C	405	45	13	1	.04	.01	30	1	.03		
D	240	35	20	2	.08	.02	80	3	.04		
E	210	30	21	2	.08	.02	100	4	.04		
F	325	50	29	3	.04	.01	90	1	.01		

4;EE:III 0907/8¬1527/8

SA STAGE:	CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
A	940	100	3.5	.3			4				
B	550	60	3.7	.4			7				
C	180	20	9	1			50				
D	140	20	7	1			50				
E:	60	20	10	1			170				
F:/	95	10	11	1			115				

5;EE;III 0907/11¬1232/12

SA STAGE:	CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
A	255	25	1.8	.3	<.01		7				
B	75	10	2.5	.4	<.03		30				
C/	120	20	10	1	<.08		80				
D/	50	10	7.2	.7	<.02		140				
E	55	10	5.9	.6	<.03		110				
F*	70	30	1.0	.1	.03	.01	14	4	.3		

TABLE B-3 (Continued)

6;EE;III 1239/14¬1627/14

SA STAGE:	CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
A	575	80	1.4	.2			2				
B	205	30	1.5	.3			7				
C*	80	20	2.6	.5			30				
D	50	10	3.3	.3			60				
E	75	15	1.0	.3			13				
F	55	20	2.6	.4			50				

7;AG;IV 0751/11¬0841/12

AS STAGE:	CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
A											
B			6.4	.6							
C			13	2							
D:			5	1							
E			8.5	.8							
F			6	1							

8;AG;IV 0751/11¬0841/12

SA STAGE:	CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
A											
B			1.8	.3							
C			3.3	.3							
D:			11	2							
E			7.6	.8							
F			13	1							

8;HAWAII

SA STAGE:	CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
A	140	20	.53	.05	<.01		4				
B	500	40	1.9	.4	<.01		4				
C	920	60	2.6	.3	.12	.02	3	1	.5		
D	820	50	1.1	.1	.46	.04	1	6	4		
E	250	30	.27	.05	.46	.04	1	18	17		
F	55	5	.13	.02	.14	.01	2	25	11		

9;EE;V 0921/1¬0739/2

AS STAGE:	CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
A	535	60	9	1	.25	.04	15	5	.2		
B	145	15	7.4	.7	.40	.04	50	25	.4		
C	375	40	10	1	1.1	.1	25	30	1		
D	425	45	10	1	.5	.1	25	12	.5		
E	810	85	7.9	.8	.30	.03	10	4	.3		
F	1400	150	17	2	1.2	.1	12	9	.7		
Z			180	40	3.0	.6			.2		

TABLE B-3 (Continued)

10;EE;V 0921/1¬0739/2

SA							3	4			
STAGE:CL		SD:	BR	SD:	I	SD:10	*BR/CL:10	*I/CL:	10*I/BR	: PB	SD:
A	120	15	2.4	.2	<.1		20				
B	170	20	2.6	.3	.20	.04	15	12	.7		
C	255	30	8.8	.9	.30	.05	35	12	.3		
D	250	30	9.0	.9	.30	.05	35	12	.3		
E	545	60	9.3	.9	.10	.04	16	2	.1		
F	825	90	10	1	.20	.04	12	2	.2		
Z			220	25	7	1			.3		

11;EE;V 0840/2¬0525/3

AS							3	4			
STAGE:CL		SD:	BR	SD:	I	SD:10	*BR/CL:10	*I/CL:	10*I/BR	: PB	SD:
A											
B											
C	190	11	7.0	.7			80				
D	20	4	6.0	.6			300				
E/	55	8	6	3			100				
F	80	15	3.0	.5			25				
Z	450	100	60	15			130				

12:EE;V 0840/2¬0525/3

SA							3	4			
STAGE:CL		SD:	BR	SD:	I	SD:10	*BR/CL:10	*I/CL:	10*I/BR	: PB	SD:
C	60	8	10	2			170				
D	60	8	16	2			250				
E	50	8	8	2			160				
F	75	10	10	2			130				
Z	300	100	40	10	.3	.	130	10	.1		

13;EE;V 0648/4¬0457/5

AS							3	4			
STAGE:CL		SD:	BR	SD:	I	SD:10	*BR/CL:10	*I/CL:	10*I/BR	: PB	SD:
A	17	6	3.6	.6			200				
B	6	3	2.0	.4			300				
C	<14		2.6	.4			>180				
D	20	6	2.4	.4			120				
E	9	4	1.7	.4			200				
F	<14		1.0	.4			>70				
Z	100	30	16	4			160				

14;EE;V 0648/4¬0457/5

SA							3	4			
STAGE:CL		SD:	BR	SD:	I	SD:10	*BR/CL:10	*I/CL:	10*I/BR	: PB	SD:
A	40	5	1.6	.2			40				
B	19	3	1.6	.2			80				
C	9	4	3.2	.3			350				
D	28	7	4.3	.4			150				
E	<11		<8								
F/	6	2	1.5	.2			300				
Z	135	30	11	3			80				

TABLE B-3 (Continued)

15;LM;V 0722/20¬1156/20

SA STAGE:	CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
A	60	12	<.6		.3	.2	<10	50	>6	40	5
B*	30	15	<.8		<.2		<30	<70		40	5
C	60	20	.8	.4	.5	.2	13	80	6	20	5
D*	45	20	<.4		1.3	.3	<9	290	>3	20	5
E	<45		<1		.9	.2				20	5
F	<40		.8	.4	<.3		>20		<4	100	20
Z	<400		29	4	5	1	>70		2	40	6

16;LM;V 1225/20¬1606/20

SA STAGE:	CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
A	<30		<.8		<.2					60	6
B	<30		<.7		<.3					40	5
C	<27		1.5	.2	<.2		>55			80	10
D	<30		1.0	.1	<.2		>30			40	5
E*	43	6	.7	.2	.4	.2	16	100	6	60	6
F*	53	10	2.8	.2	<.3		50			160	30
Z	<1000		8	3	.7	.4			.9	300	45

17;CH;V 1652/20¬0224/21

SA STAGE:	CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
A	<250		15	2	.4	.1	>60	>16	.2	120	20
B	<200		22	2	<.1		>110			30	5
C*	230	100	60	6	<.2		250			80	10
D	<400		160	20	.5	.1	>390			170	20
E*	300	150	100	10	.4	.1	330	10	.04	40	5
F	1900	300	218	22	2.1	.2	115	10	.1	40	5
Z/	3600	500	850	85	3.8	.4	240	10	.05	2000	200

18;CH;V 0307/21¬0559/21

SA STAGE:	CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
A	370	40	7	1	<.3		19			100	20
B	270	30	12	1	<.6		44			60	10
C	320	50	37	5	<.3		115			20	5
D	580	90	62	7	<.2		110			20	5
E	1200	150	50	6	<.3		44			200	30
F	5200	600	140	15	1.2	.3	27	2	.08	1600	200
Z/	3100	1500	120	12	.7	.4	40	2	.06	2000	200

19;LM;V 0640/21¬1102/21

SA STAGE:	CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
A										20	5
B	<40		<.6		<.1					20	5
C	<30		.7	.3	<.3		>20			<10	
D	38	10	1.2	.3	<.1		30				
E	<30		.6	.3	<.2		>20			20	5
F*	110	20	8.6	.9	<.3		80			180	30
Z	<600		11	2	<.4					240	40

TABLE B-3 (Continued)

20;LM;V 1124/21¬1450/21

SA

STAGE:CL		SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
A	45	7	<1		<.3					20	5
B	<20		1.0		1.0	.1			10	30	5
C	35	5	<.3		.09	.02	<10	30		<10	
D	<30		<1		<.2					<10	
E*	50	15	.6	.1	.09	.02	12	15	2	<10	
F	40	5	<.8		<.2		<20	<50		65	10
Z	<600		7	1	2.0	.3			3	50	10

21;LM;V 0633/22¬1033/22

SA

STAGE:CL		SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
A*	38	10	<.9		<.1		<22			20	5
B	<30		<.7		<.1					30	5
C*	135	15	.7	.3	<.1		5				
D*	150	15	2.1	.3	<.1		14			10	2
E*	185	20	4.0	.5	<.1		22			35	6
F*	130	15	6.7	.6	<.1		52			160	30
Z	<1000		15	1	1.0	.2	>15		.7	100	20

22;LM;V 1102/22¬1912/22

SA

STAGE:CL		SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
A	95	10	<.2		<.2		<2			15	3
B*	75	10	.8	.2	<.2		10			15	3
C*	230	24	2.8	.2	<2		12			50	10
D*	285	30	5.0		<3		18	500	3	10	2
E	<300		4.5	.5	.2	.1	>15		.5	40	8
F	<120		10	1	1.1	.1	>85		1	90	15
Z	<1400		19	1	.6	.2	>13		.3	50	10

23;LM;V 1940/22¬0614/23

SA

STAGE:CL		SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
A	<10		<.1		<.05					20	3
B	20	5	.3	.1	<.05		15			15	2
C	44	4	.6	.1	.07	.0	14	14	1	15	2
D*	50	8	4.8	1.0	.08	.02	95	20	.2	35	4
E	<18		1.0	.1	.05	.02	>55		.5	35	4
F	100	15	10	1	.5	.1	100	50	.5	200	40
Z	<1000		14	2	.4	.1	>14		.3	380	50

24;LM:V 0650/23¬0952/23

SA

STAGE:CL		SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
A											
B	123	15	<.4		<.2		<4				
C	68	15	1.2	.4	<.3		18				
D	<40		1.2	.4	<.3		>30				
E	370	40	3.2	.4			8				
F*	82	15	4.9	.4	<.2		60				
Z	<1000		11	1	.7	.3	>11				

TABLE B-3 (Continued)

25;EE;VI 1146/19¬0616/20

AS

STAGE:	CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
C	20	2	1.9	.2			100				
D	<10		1.5	.2			350				
F	<10		.5	.1	.23	.02	120	500	4		
G	<10		1.5	.2	.19	.02	>300		1		

26;EE;VI 1146/19¬0616/20

AS

STAGE:	CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
C	35	5	6.3	.6			180				
D	12	2	3.1	.3			260				
F	36	4	3.0	.3	.26	.03	85	70	.9		

31;LN;VIII 1317/29¬0100/30

SA

STAGE:	CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
A	<10		.26	.03	<.1						
B	<15		.6	.1	<.1						
C	<20		.5	.1	<.1						
D	<15		.3	.1							
E	<10		.9	.2	.2	.1			2		
F	<20		.6	.1	<.1						
G	<70		2.5	.3	<.2		>230				
Z	250	50	2.6	.3	<.1		10				

32;LN;VIII 1734/30¬0720/31

AS

STAGE:	CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
A	<15		.23	.04	<.1						
B	<10		<.1		<.1						
C	<25		.4	.1	<.1						
D	<10		.4	.1	<.1						
E	<20		.4	.1	<.2						
F	<70		1.6	.3	<.3						
G	80	15	3.1	.5	<.1		40				
Z*	200	50	1.3	.1	.12	.05	7	6	.9		

33;LP;IX 1928/3¬0638/4

AS

STAGE:	CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
A	<70		<.4		<.05						
B	<45		<.3		<.1						
C	<40		<.4		<.1						
D	<40		<.3		<.05						
E	<80		1.3	.6	<.1						
F	50	10	5.7	.8	<.1		110				
G	30	10	6.5	.7	.20	.06	200	60	.3		
Z*	500	100	21	3	<.1		40				

TABLE B-3 (Continued)

34;LP;IX 2309/5¬0606/5

AS STAGE:CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
A <40		<.4		<.1						
B <40		<.3		<.1						
C <50		<.3		<.1						
D <30		<.3								
E <20		5.7	.7	<.2						
F <40		1.5	.5	<.1						
G <40		<1		.2	.1					
Z* 580	100	2.2	.3	<.1		4				

35;EE;IX 1522/9¬1104/10

AS STAGE:CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
A: 90	12	9.0	.5	<.1		100				
B: 41	7	6.7	.7	<.1		160				
C 130	18	12	1	.14	.04	90	14	1		
D* 40	20	2.9	.3	<.1		70				
E 125	18	12	2	<.11		100				
F 285	35	24	2	<.08		85				
G 165	22	14	2	.10	.04	85	7	.1		
Z: 1750	200	105	10	.5	.1	60	3			

36;EE;IX 1522/9¬1104/10

AS STAGE:CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
A: 120	15	8.1	.5	<.1		70				
B: 66	10	6.9	.7	<.1		105				
C 144	18	16	3	<.05		110				
D: <40		3.1	.3	<.1		>75				
E 170	20	11	1	<.08		65				
F 180	60	24	2	<.1		130				
G 100	15	4.4	.3	<.16		45				
Z 1860	250	70	10	.3	.1	40	2	.05		

37;AG;IX 0909/11¬1322/11

AS STAGE:CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
A <30		<2		<3						
B 52	12	<2		<3		<40				
C <60		<2		<2						
D 120	10	3	1	<3		25				
E 250	25	6	2	<2		25				
F <70		<2		<2						
G <70		<3		<3					108	20
Z 1000	100	45	5			45				

38;AG;IX 1345/11¬1355/11

AS STAGE:CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR :	PB	SD:
A 860	350	<40		<70		<45				
B <1400		<40								
C <1700		<40								
D <1500		<40								
E <1800		<40								
F <1700		<40		<70						
G <1000		75	30	100	10	>75			7200	1000
Z 40000	4000	15000	1000			370				

TABLE B-3 (Concluded)

39:AG:IX 1355/11¬1405/11

AS

STAGE:	CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR	: PB	SD:
A	<1000		<40		<50						
B	<700		60	25	150	30	>80		25		
C	<500		<50		<60						
D	<1000		<50		60	25					
E	<1200		<50		50	10					
F	<600		<50		<50						
G	600	200	<50		70	15	<80			5200	1000
Z	16000	2000	3200	300			200				

40:AG;IX 1425¬35&1440¬1500/11

AS

STAGE:	CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR	: PB	SD:
A	<100		<8		<15						
B	<300		25	8			>80				
C	<200		<8								
D	<400		<20		<20						
E	<150		<10		<15						
F	<250		<20		<10						
G	<300		<20		20	10					
Z	5000	1000	80	15			15				

41:AG;IX 1515¬25&1530¬1620/11

AS

STAGE:	CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR	: PB	SD:
A	<110										
A	<100		<10								
B	<130		<10								
C	<220		<10								
D	<200		<5		<10						
E	<200		<5		<10						
F	<80		<10								
G	<150		<10							180	35
Z	1500	200	26	5			17				

43:EE;XI 0430/28¬1350/30

AS

STAGE:	CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR	: PB	SD:
A	23	3	6.3	.6			270				
B	5.4	.8	3.5	.4			650				
C	8	1	8.0	.8			1000				
D	<4		3.0	.3			>750				
E	3.9	.6	3.5	.4			900				
F	2.7	.5	3.6	.4			1300				
G	12.5	1.5	4.1	.4			330				
Z	<20		33	3			>1600				

44:EE:XII 0950/4¬0750/7

AS

STAGE:	CL	SD:	BR	SD:	I	SD:	10^3*BR/CL:	10^4*I/CL:	10*I/BR	: PB	SD:
A	120	20	17	3			140				
B	55	7	7	2			130				
C	26	5	5	1			190				
D	2.1	.5	2.0	.5			1000				
E	1.9	.5	1.7	.5			900				
F	2.2	.5	2.3	.5			1000				
G	10	2	4.5	.7			450				
Z	15	3	14	3			1000				

TABLE B-4

TOTAL CONCENTRATIONS, STANDARD DEVIATIONS, AND RATIOS OF CHLORINE, BROMINE, AND IODINE, IN NANOGRAMS PER CUBIC METER, FROM CASCADE IMPACTOR SAMPLES

RUN #	STAGES	CL	SD:	BR	SD:	I	SD:	1000*BR/CL:	10000*I/CL:	10*I/BR:
1:GR:II	A¬F	110	10	8.0	.7	.35	.05	70	30	.4
2:GR:II	A¬F	270	35	2.4	.1	.07	.01	9	3	.3
3:EE:III	A¬F	2760	150	93	5	.40	.04	34	1	.04
4;EE:III	A¬F	1970	110	44	2			22		
5:EE:III	A¬F	625	45	28	2			45		
6:EE:III	A¬F	1040	90	12	1			12		
7:AG:IV	A¬F			35	2					
8;AG:IV	A¬F			37	3					
8;HAWAII	A¬F	2700	95	6.5	.5	1.2	.1	2	4	2
9;EE:V	A¬F	3700	200	61	3	3.8	.2	17	10	.6
	Z			180	40	3.0	.6			.2
10;EE:V	A¬F	2160	120	42	1	1.1	.5	20	5	.3
	Z			220	25	7	1			.3
11:EE:V	C¬F	310	20	22	3			70		
	Z	450	100	60	15			130		
12:EE:V	C¬F	240	16	44	3			180		
	Z	300	100	40	10	.3	.1	130	10	.1
13:EE:V	A¬F	66	13	13.3	1.2			200		
	Z	100	30	16	4			160		
14:EE:V	A¬F	110	12	16	4			150		
	Z	135	30	11	3			80		
15:LM:V	A¬F	240	45			3.2	.5		130	
	Z			29	4	5	1			2
16:LM;V	A¬F			7	1					
	Z			8	3	.7	.4			.9
17:CH:V	A¬F			570	30	3.5	.3			.06
	Z	3600	500	850	85	3.8	.4	240	10	.05
18:CH;V	A¬F	7940	700	310	18			40		
	Z	3100	1500	120	12	.7	.4	40	2	.06
19:LM:V	B¬F			11.4	.4					
	Z			11	2					

TABLE B-4 (Concluded)

RUN #	STAGES	CL	SD:	BR	SD:	I	SD:	1000*BR/CL:	10000*I/CL:	10*I/BR:
20:LM:V	A¬F	200	25							
	Z			7	1	2.0	.3			3
21:LM:V	A¬F	550	40	14	1			25		
	Z			15	1	1.0	.2			.7
22:LM:V	A¬F	900	200	23	1	4	2	25	45	1.8
	Z			19	1	.6	.2			.3
23:LM:V	A¬F	230	25	15.5	1.3	.6	.1	70	25	.4
	Z			14	2	.4	.1			.3
24:LM:V	B¬F	660	50	11	1			17		
	Z			11	1	.7	.3			.6
31:LN:VIII	A¬G			5.7	1.4					
	Z	250	50	2.6	.3			10		
32:LN:VIII	A¬G			6.2	1.4					
	Z	200	50	1.3	.1	.12	.05	7	6	.9
33:LP:IX	A¬G			14	2					
	Z	500	100	21	3			40		
34:LP:IX	A¬G			9	2					
	Z	580	100	2.2	.3			4		
35:EE:IX	A¬G	870	50	83	4			95		
	Z	1750	200	105	10	.5	.1	60	3	
36:EE:IX	A¬G	800	75	73	4			90		
	Z	1860	250	70	10	.3	.1	40	2	.05
37:AG:IX	Z	1000	100	45	5			45		
38:AG:IX	Z	40000	4000	15000	1000			370		
39:AG:IX	Z	16000	2000	3200	300			200		
40:AG:IX	Z	5000	1000	80	15			15		
41:AG:IX	Z	1500	200	26	5			17		
43:EE:XI	A¬G	57	5	32	2			550		
	Z			33	3					
44:EE:XII	A¬G	215	22	40	4			180		
	Z	15	3	14	3			1000		

APPENDIX C

OXIDATION REACTIONS

The atmosphere contains both oxidizing and reducing agents and is not an equilibrium mixture. For example, molecular oxygen and ozone are oxidizing agents while hydrocarbons and sulphur dioxide are reducing agents; pollution oxidizing and reducing agents are continually reacting. Nevertheless, for many inorganic reactions where aqueous solution reaction rates are rapid, it is probable that equilibrium prevails within the aerosol droplet although not between the droplet and the air at large. Therefore equilibrium constants for a variety of oxidation-reduction reactions have been calculated and are interpreted as gauges of their likelihood within aerosol droplets.

The calculation of equilibrium constants is accomplished through use of the Nernst equation (Daniels and Alberty, 1966). For the general reaction,

$$qQ + rR = sS + tT,$$

in which q moles of Q and r moles of R react to give s moles of S and t moles of T, the Nernst equation is

$$E = E^{o} - \frac{RT}{n\mathfrak{F}} \ln \frac{a_S^{s} a_T^{t}}{a_Q^{q} a_R^{r}}$$

where E is the potential for the reaction (and is zero at equilibrium); E^{o} is the potential when the activities, a (which are proportional to molar concentrations in dilute solutions), are each equal to unity; n is the number of electrons transferred per molecule and $\mathfrak{F}$ is the faraday constant. At 25°C, the equation becomes

$$E = E^o - \frac{0.059}{n} \log \frac{a_S^s a_T^t}{a_Q^q a_R^r} = E^o - \frac{0.059}{n} \log Q$$

At equilibrium, E = 0 and Q = K, the equilibrium constant.

1. OXIDATION OF Cl^- BY O_2

$$4Cl^-(aq) \rightarrow 2Cl_2(g) + 4e^- \qquad E^o = -1.3595 \text{ volts*}$$

$$4H^+ + O_2 + 4e^- \rightarrow 2H_2O \qquad E^o = 1.229$$

$$4H^+ + 4Cl^-(aq) + O_2 \rightarrow 2Cl_2(g) + 2H_2O \qquad -0.130$$

At equilibrium, E = 0 and therefore

$$K = 10^{nE^o/0.059} = 10^{4(-0.130)/0.059} = 10^{-8.8} = \frac{P^2_{Cl_2(g)} a^2_{H_2O}}{\left(a^4_{H^+}\right)\left(a^4_{Cl^-}\right)\left(P_{O_2(g)}\right)} .$$

If $a_{H_2O} = 1$ and $P_{O_2} = 0.21$ atmospheres, then the variation of $P_{Cl_2(g)}$ with pH is

$$\log P_{Cl_2(g)} = -4.7 - 2\text{ pH} + 2 \log a_{Cl^-} .$$

This relationship is plotted in Figure C-1.

---

*Standard potentials are taken from Latimer (1952).

2. OXIDATION OF Br^- BY O_2

$$
\begin{array}{ll}
4Br^-(aq) \rightarrow 2Br_2(aq) + 4e^- & E^o = -1.087 \\
\underline{4H^+ + O_2 + 4e^- \rightarrow 2H_2O} & \underline{E^o = 1.229} \\
4H^+ + 4Br^-(aq) + O_2 \rightarrow 2Br_2(aq) + 2H_2O & +0.142
\end{array}
$$

At equilibrium,

$$\log 10^{4(0.142)/0.059} = 9.6 = \log\left[\frac{a^2_{Br_2}(aq)a^2_{H_2O}}{\left(a^4_{H^+}\right)\left(a^4_{Cl^-}\right)\left(P_{O_2(g)}\right)}\right]$$

We again assume $a_{H_2O} = 1$ and $P_{O_2(g)} = 0.21$ atm. Also, from Latimer (1952)

$$\frac{P_{Br_2(g)}}{a_{Br_2(aq)}} = 10^{-0.166}.$$

Therefore,

$$\log\left[\frac{P^2_{Br_2(g)}a^2_{H_2O}}{\left(a^4_{H^+}\right)\left(a^4_{Cl^-}\right)P_{O_2(g)}}\right] = 9.6 - 0.3 = 9.3$$

and

$$K = 10^{9.3}$$

while

$$\log P_{Br_2(g)} = 4.3 - 2\text{ pH} + 2\log a_{Cl^-}$$

(Figure C-2).

3. OXIDATION OF Cl^- BY O_3

$$\begin{array}{lrcl}
2Cl^-(aq) \rightarrow Cl_2(g) + 2e^- & E^o & = & -\ 1.36 \text{ volts} \\
\underline{O_3(g) + 2H^+ + 2e^- \rightarrow O_2(g) + H_2O} & \underline{E^o} & \underline{=} & \underline{2.07} \\
2H^+ + 2Cl^-(aq) + O_3(g) \rightarrow Cl_2(g) + O_2(g) + H_2O & & & +\ 0.71
\end{array}$$

At equilibrium,

$$\log 10^{2(0.71)/0.059} = 24.1 = \log \frac{P_{Cl_2(g)} P_{O_2(g)} a_{H_2O}}{a^2_{H^+} a^2_{Cl^-(aq)} P_{O_3(g)}} = \log K \ .$$

Then if $a_{H_2O} = 1$, $P_{O_2} = 0.21$ atm. and $P_{O_3} = 10^{-8}$ atm.,

$$\begin{array}{rcl}
\log P_{Cl_2(g)} & = & 24.1 + 0.7 - 8 - 2\ pH + 2 \log a_{Cl^-(aq)} \\
 & & \uparrow \qquad \uparrow \qquad \uparrow \\
\text{from:} & & E^o, \quad O_2, \quad O_3 \\
 & = & 16.8 - 2\ pH + 2 \log a_{Cl^-(aq)}
\end{array}$$

(Figure C-3).

4. OXIDATION OF Br^- BY O_3

$$\begin{array}{lrcl}
2Br^-(aq) \rightarrow Br_2(aq) + 2e^- & E^o & = & -\ 1.09 \\
\underline{O_3(g) + 2H^+ + 2e^- \rightarrow O_2(g) + H_2O} & \underline{E^o} & \underline{=} & \underline{2.07} \\
2H^+ + 2Br^-(aq) + O_3(g) \rightarrow Br_2(aq) + O_2(g) + H_2O & & & 0.98
\end{array}$$

Since

$$\frac{P_{Br_2(g)}}{a_{Br_2(aq)}} = 10^{-0.166} ,$$

then

$$\log \frac{P_{Br_2(g)} P_{O_2(g)} a_{H_2O}}{a_{H^+}^2 a_{Br^-(aq)}^2 P_{O_3(g)}} = \frac{2(0.98)}{0.059} - 0.2 = 33.2 - 0.2 = 33.0 .$$

If we assume $a_{H_2O} = 1$, $P_{O_2} = 0.21$ atm. and $P_{O_3} = 10^{-8}$ atm., then

$$\begin{array}{rcl} \log P_{Br_2(g)} & = & 33.0 + 0.7 - 8 - 2\ \mathrm{pH} + 2 \log a_{Br^-(aq)} \\ & & \uparrow \qquad \uparrow \qquad \uparrow \\ \text{from:} & & E_0, \quad O_2, \quad O_3 \\ & = & 25.7 - 2\ \mathrm{pH} + 2 \log a_{Br^-(aq)} \end{array}$$

(Figure C-4).

5. OXIDATION OF Br^- BY Cl_2

$$\begin{array}{ll} 2Br^-(aq) \rightarrow Br_2(aq) + 2e^- & E^o = -1.09 \\ \underline{Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)} & \underline{E^o = +1.36} \\ Cl_2(g) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq) & \qquad\quad 0.27 \end{array}$$

Then

$$\log \frac{P_{Br_2(g)} a_{Cl^-(aq)}^2}{P_{Cl_2(g)} a_{Br^-(aq)}^2} = \frac{2(0.27)}{0.059} - 0.2 = 9.2 - 0.2 = 9.0 = \log K$$

and

$$\log P_{Br_2(g)} = \log P_{Cl_2(g)} + 2 \log a_{Br^-(aq)} - 2 \log a_{Cl^-(aq)} \; .$$

The above results show that Br tends to be oxidized preferentially to Cl in a droplet, that the oxidation is favored at low pH and that ozone is much more effective than oxygen as the oxidizing agent.

The rate at which $Br_2(g)$ is produced from typical pollution concentrations of PbBrCl by irradiation was calculated by Pierrard (1969) to be 1-2 x 10^{-10} hr^{-1} with respect to unit mass of air at 25°C. In the somewhat extreme conditions of our automobile garage experiment, Br was lost from the aerosol at a rate of about 10^{-8} hr^{-1}. This $Br_2(g)$ has been suggested to add at the multiple bonds of unsaturated hydrocarbons. These reactions must compete with those between ozone and unsaturated hydrocarbons (e.g., Cadle and Shadt, 1953) which are important in the formation of photochemical smog and produce aldehydes, organic acids and oxides at a typical rate of 2-20 x 10^{-8} hr^{-1} (Leighton, 1961).

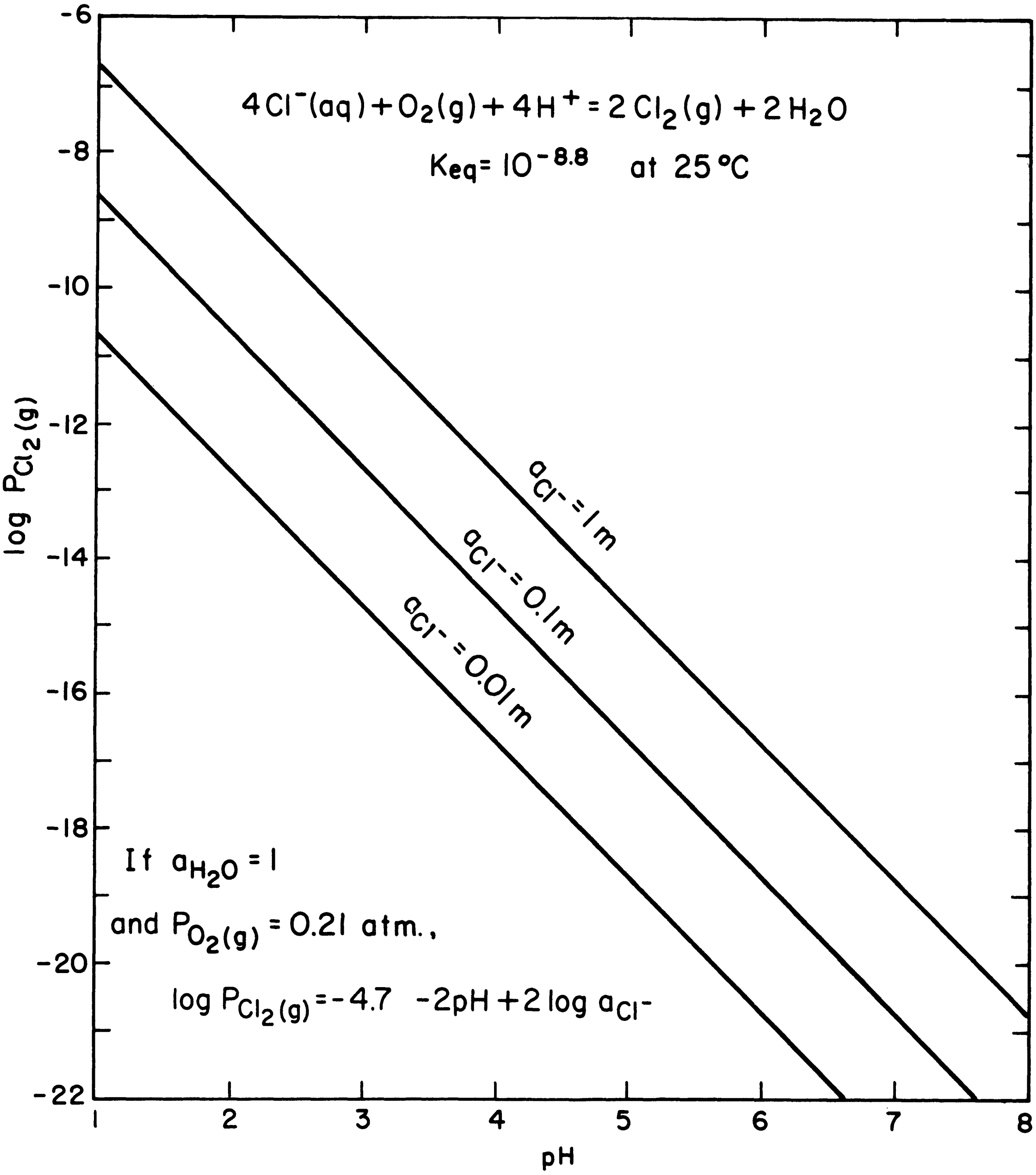


Figure C-1. The dependence on a_{Cl^-} and pH of Cl_2 concentration through oxidation by oxygen (at equilibrium).

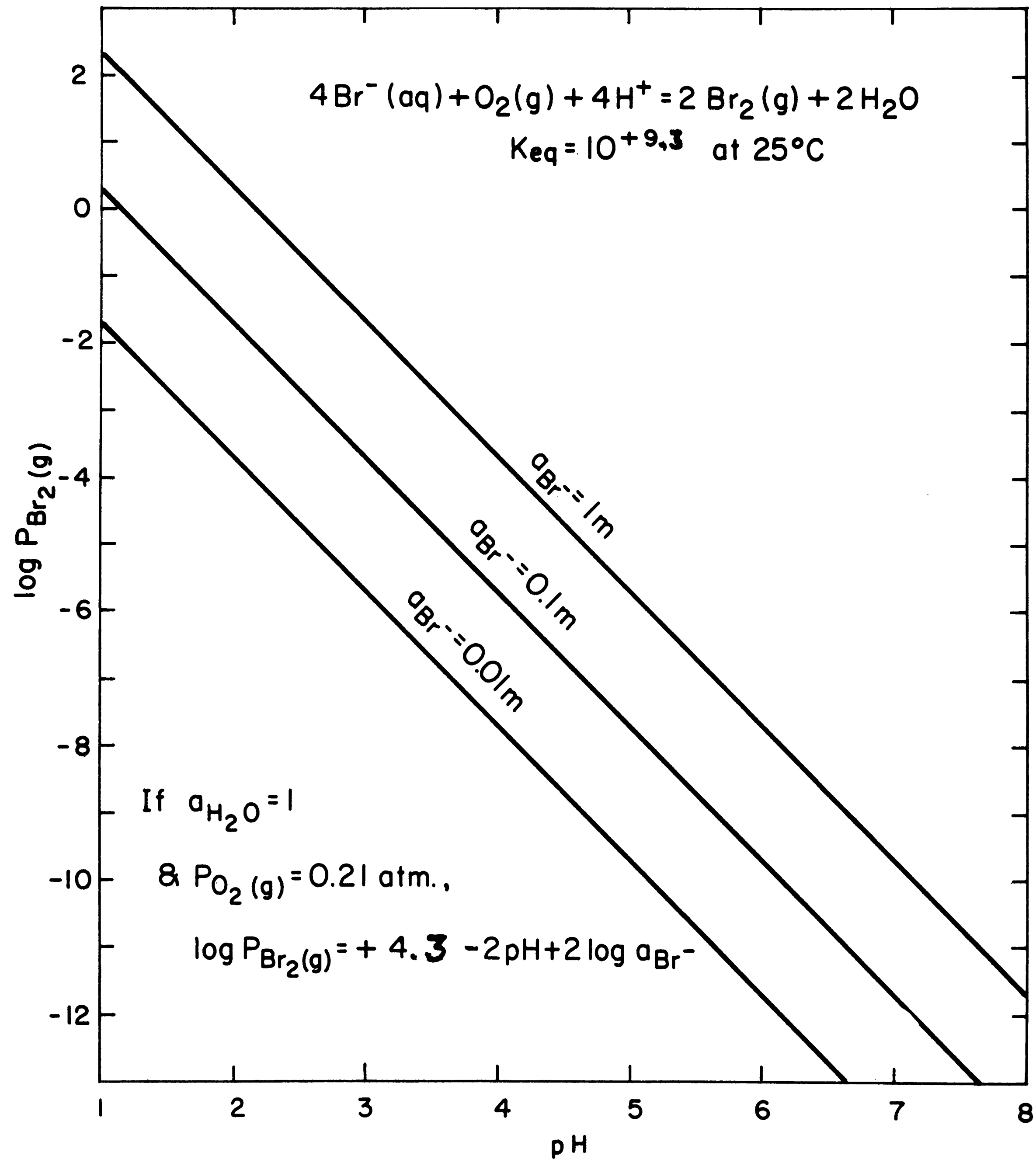


Figure C-2. The dependence on a_{Br^-} and pH of Br_2 concentration through oxidation by oxygen (at equilibrium).

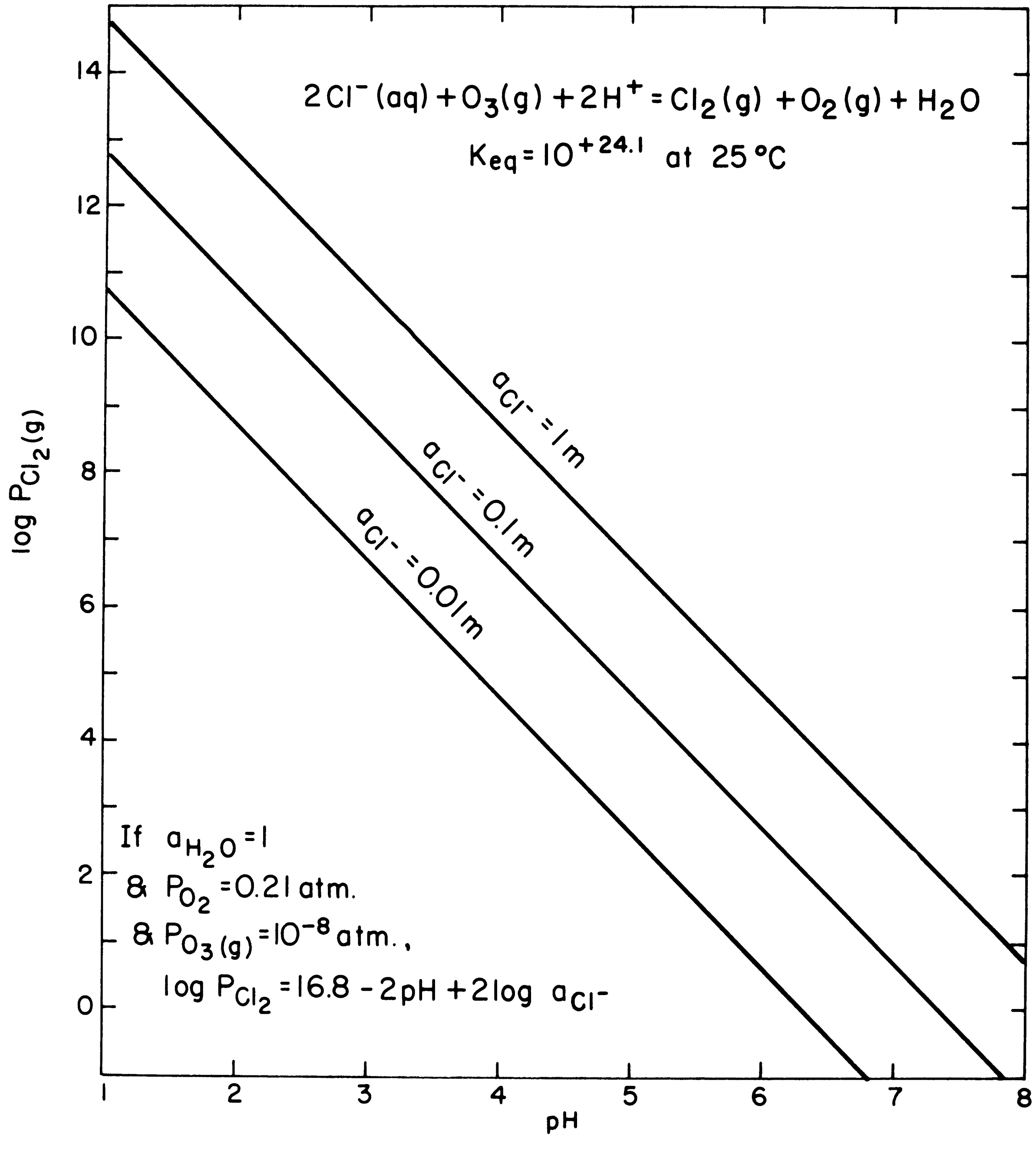


Figure C-3. The dependence on a_{Cl^-} and pH of Cl_2 concentration through oxidation by ozone (at equilibrium).

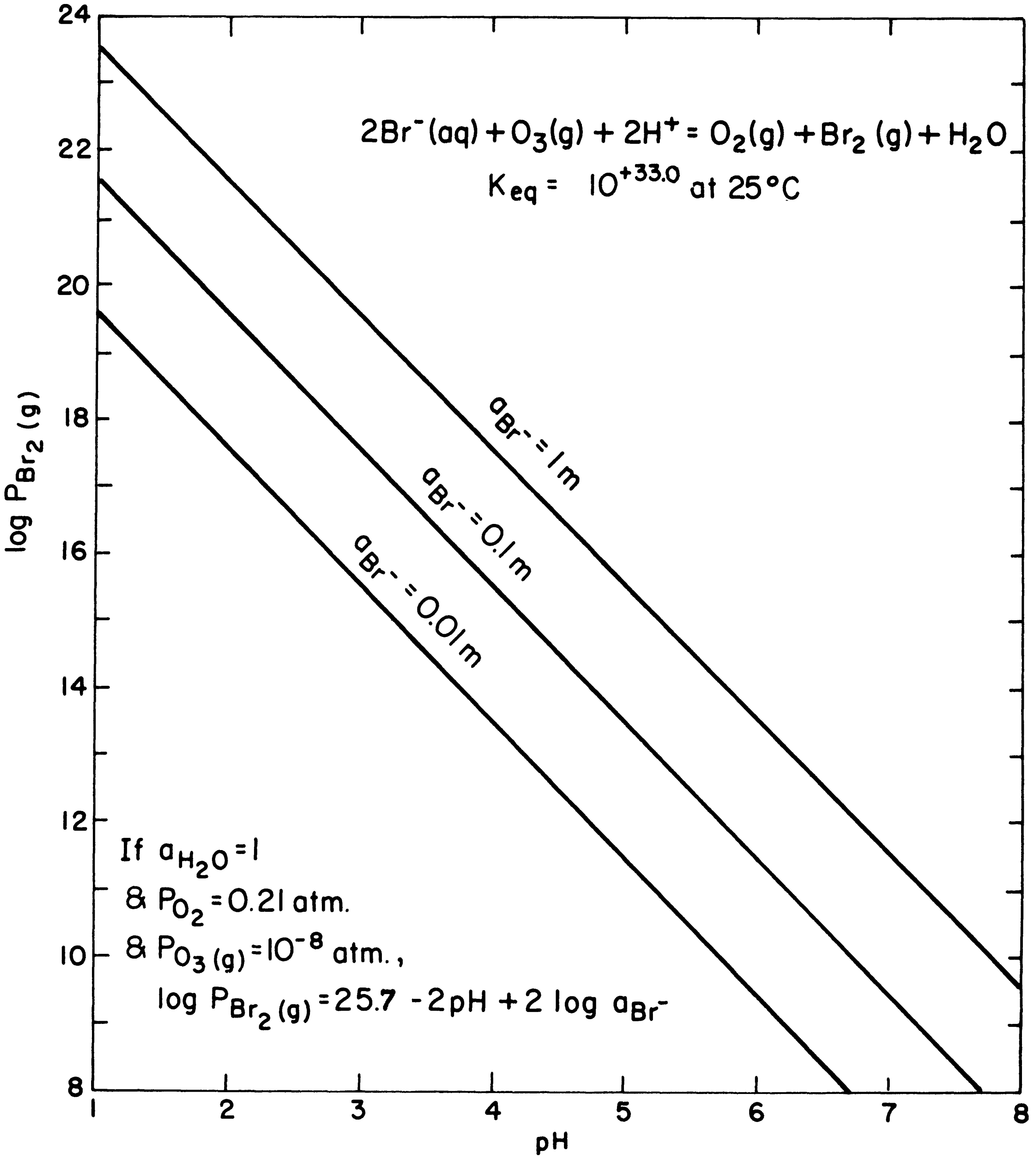


Figure C-4. The dependence on a_{Br^-} and pH of Br_2 concentration through oxidation by ozone (at equilibrium).

APPENDIX D

TRACE SUBSTANCES IN ENVIRONMENTAL HEALTH-III

Proceedings of Third Annual Conference

June 24, 1969

University of Missouri, Columbia, Missouri

Invited Paper

POLLUTION CONTRIBUTIONS TO THE ATMOSPHERIC INVENTORY OF CHLORINE AND BROMINE IN AEROSOLS OVER CONTINENTAL U.S.A.

by

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ABSTRACT

Continental aerosols in the U.S.A. contain halogens derived from both pollution and natural sources. Particle size distributions of Cl and Br in continental aerosols, determined by sampling with cascade impactors and analyzing by neutron activation, show marked differences from fresh marine aerosols. An inventory of major sources shows most of the Cl in continental aerosols to come from the sea, but most of the Br appears to be derived from the combustion of ethyl fluid. About 95% of total U. S. bromine production, about 100,000 metric tons of Br per year, is converted to ethylene dibromide and burned with tetraethyl lead. Most of the Br contained in the lead halide aerosol appears to be volatilized in the atmosphere and may react further, e.g., by bromination of organic materials. The toxicological significance of these reactions is not yet known.

1. INTRODUCTION

The halogen elements are especially useful objects for investigation in the field of air and water pollution because both natural and pollution sources may be significant. Thus, a detailed comparison of the abundances of Cl and Br in environmental samples and a knowledge of natural sources may lead to quantitative estimates of the prevalence and dispersion characteristics of pollution substances. Furthermore, the halogens are not without important environmental chemical properties of their own. For example, chloride and bromide are highly water soluble and tend to be conservative properties of water bodies. In the atmosphere heterogeneous gas-particle chemical reactions of the halogens may cause transfer of the elements from one group of particles to another. Cloud droplet nucleation may operate more effectively with some particle substrates than with others, and halogens may prove to be convenient tracers for details of this process. Overall atmospheric residence times and removal efficiencies of pollution and natural aerosols produced near the earth's surface may be estimated from data on the halogen composition of aerosols and precipitation. With these possibilities in mind, we have begun an investigation of bromine and chlorine occurrences in aerosols from the Great Lakes Basin where pollution sources are large and the oceanic source is remote.

Some typical particle size distributions of Br and Cl are presented in Figure D-1. Aerosol particles are collected by cascade impactor of either of two designs, Andersen Sampler (AS) or Scientific Advances (SA), and the horizontal scale of impactor stage ranges from largest particles (Stage A) to smallest particles (Stage F, G, or in-line backup filter, Z). Particle sizes collected on each stage depend on the inertia of the particles, and smaller and smaller particles are caused to impact on successive stages because the linear air flow is increased as the air is passed through smaller and smaller orifices in the device. Particle size, shape, and density determine the stage on which a particle will impact if the device is operated at a carefully controlled flow rate, but one often speaks of equivalent particle radius for spheres of unit density. Within these limitations, the effective particle radius ranges represented by the data of Figure D-1 are given in Table D-1 (2,9,19).

TABLE D-1

RANGES OF EFFECTIVE RADII FOR PARTICLE COLLECTION BY CASCADE IMPACTOR STAGES

Stage	Effective Radius Range, microns	
	SA Impactor	AS Impactor
A	$r > 8$	$r > 4.6$
B	$8 > r > 4$	$4.6 > r > 2.9$
C	$4 > r > 2$	$2.9 > r > 1.6$
D	$2 > r > 1$	$1.6 > r > 0.9$
E	$1 > r > 0.5$	$0.9 > r > 0.5$
F	$0.5 > r > 0.25$	$0.5 > r > 0.3$
G		$0.3 > r > 0.1$
Z		$0.1 > r$

Neutron activation analysis is used to analyze each stage of the cascade impactor for Cl and Br. Normally the impaction surface is a 95 mm disk of thin polyethylene or Mylar plastic to which adhere particles of the appropriate size range. For example, the Andersen Sampler, which has a large number of orifices per stage, operates at a flow rate of 1 cfm (2 m^3/hr) and usually in a few hours dark spots of particulate material are visible below each orifice. The disk is removed and packaged in a capsule for neutron irradiation after which the induced radioactivity is leached from the surface and counted, usually following a radiochemical separation step (5). In Figure D-1, the total amount of Cl and Br found on particles of each impactor stage, expressed as concentration in the air mass sampled, is plotted against impactor stage, i.e., particle size. Because particle radii differ by approximately a factor of 2 for successive impactor stages, the figure is essentially a plot of mass of the element on a logarithmic scale versus logarithm of particle radius for aerosols containing the element. It would also be of interest to know the concentration of the element in the particles themselves, but, owing to the experimental difficulty of determining total mass of particulate material on each stage, this has not been attempted in the present investigation. Because of the great sensitivity of neutron activation analysis for certain elements but not others, it is actually easier to measure individual elements than total mass of particles. Nevertheless, it is sometimes possible to make inferences about composition of the particles themselves from the systematics of elemental distribution among the size fractions collected by the cascade impactor.

The data in Figure D-1 illustrate the contrasts which are found between

Cl and Br size spectra characteristic of aerosols fresh from the sea and those of inland localities. Duce et al. (7), found aerosols of the Hawaiian marine atmosphere to carry most of the Cl and Br in particles of a few microns radius but most of the I on much smaller particles. The ratio Br/Cl, however, showed significant variation around the sea water value, as can be seen on the left side of Figure D-1.

The center and right-hand portions of Figure D-1 show two of the Cl and Br spectra we determined in samples of aerosols collected in the Great Lakes Basin near Ann Arbor, Michigan. These inland data, collected under different meteorological circumstances, reflect the variability which we find to be typical far from the sea. For Run 2:GR:II, from a rural area in southeastern Michigan, the winds were from the northwest and trajectory analysis indicates the air to have traveled from the North Atlantic around Hudson Bay. The implication is that a major source upwind was the ocean. However, the data of Run 2:GR:II differ from those of Run 8:HAWAII in several respects. Concentrations, especially of Cl, are reduced in Run 2:GR:II and the Cl distribution is shifted toward giant ($r > 1\mu$) particles. The mass ratio Br/Cl does have approximately the sea water value on Stages A and B but rises far above this in the smaller particles.

For Run 35:EE:IX, from the roof-top of the East Engineering Building in the city of Ann Arbor, the winds were from southerly to easterly and the major sources upwind probably included important air pollution components. The tendency of the Br/Cl ratios of Run 2:GR:II to exceed the sea water ratio is strengthened in Run 35:EE:IX where Br/Cl ratios are uniformly high. The Cl distribution tends to be weighted toward the small particles in contrast to Run 8:HAWAII, although the Cl concentrations in these two runs are comparable. The Br distribution in Run 35:EE:IX has a shape similar to the Cl distribution, and the Br concentrations vastly exceed those in the other two runs.

In this paper we wish to develop a perspective over-view of the sources and modifying atmospheric processes for aerosol Cl and Br in order to account for some of the contrasts illustrated by Figure D-1. (A discussion of intricacies of the complete set of inland Cl and Br aerosol distributions will be presented elsewhere (17).) We shall begin by analysis of the sources and removal processes for atmospheric Cl and Br guided both by information in the literature and by the present data.

2. SOURCES OF AEROSOL Cl AND Br

a. OCEAN

The ocean is the greatest natural source for aerosol Cl and Br although in arid areas salt crystals from the soil may also become airborne (8). The production mechanism for oceanic aerosols involves breaking waves giving rise to air bubbles in the water; the airborne sea spray particles are produced as droplets ejected by the breaking bubbles (3). On the average, the particles produced have a mass ratio, Br/Cl, approximately equal to the sea water ratio, 0.0034 (7). Most of the aerosol mass is found in the large particle ($0.1 < r$ 2 1μ) and giant particle ($1 < r < 10\mu$) size ranges (7). Aitken particles ($r < 0.1\mu$), though they have not been analyzed for Cl and Br, are judged not to include a significant sea salt component (14).

b. ETHYL FLUID

Ethyl fluid, the automobile gasoline additive containing tetraethyl lead, also contains ethylene dibromide and ethylene dichloride with the mass ratio Br/Cl = 1.15 and a ratio Br/Pb = 0.39. Upon combustion the halogens form PbBrCl which is relatively volatile. This salt is dispelled in the exhaust and thus Pb, Br, and Cl are scavenged from the combustion chamber and added to the atmosphere. Stipp (24) reports that 95% of Br produced in the U. S. is used in ethyl fluid. The circumstances of combustion of ethyl fluid satisfy the requirements for formation of a condensation aerosol (10). The volatile halide salt is heated to high temperature and then rapidly cooled in the exhaust conduits. High supersaturation leading to the formation of small ($r < 0.1\mu$) particles is expected. Subsequently coagulation would probably transfer some of this material to larger particle sizes (14).

The aerosol particles from automobile exhaust have Br/Cl ranging from 0.1 to 0.9 initially but decreasing with time due to preferential volatilization of Br (26). Figure D-2 shows the results of an experiment designed to test the hypothesis of selective volatilization of Br from lead halide pollution aerosols, formulated on the basis of our earlier analyses of environmental samples. The ratio Br/Cl found in the smallest aerosol particles, viz., those which are caught on the Z filter stage after passing through seven impaction stages of the Andersen Sampler, are plotted against time during the experiment. For a 2-hr period ambient air was sampled in Ann Arbor in an open garage. Then the garage was closed, an automobile engine was run for 10 min, and the Andersen Sampler was operated in the garage simultaneously. Immediately after the engine was stopped another Andersen sample was taken for 10 min to sample aerosols which ranged in "age" from 0 to 20 min. A third Andersen sample was taken from 30 to 65 min after stopping the engine and a fourth was taken from 80 to 145 min after the end of engine operation and aerosol generation. The Br/Cl ratios in the finest particles are plotted in Figure D-2 against aerosol age and show a marked decrease in Br relative to Cl in the first half hour but thereafter a constant low value some 50 times lower than the ethyl fluid ratio. The somewhat higher ratio observed before the experiment started we attribute to nearby automobile traffic and the possibility of some aerosols less than a half hour in age being sampled in the open garage. The selective loss of Br we believe to be due to selective oxidation of bromide ion, compared to the more stable chloride ion, by oxidants in the atmosphere, and the reaction apparently proceeds readily in the low light intensities of our garage experiment. Evidence in hand (17) suggests that the volatile product, perhaps Br_2, may be reactive and combine with unsaturated organic matter contained in other aerosol particles. It is important to note that the Br and Cl were detected only on the Z filter stage of the garage experiment (e.g., Z-stage Br > 98% of total Br during engine operation), indicating that the combustion product is very fine particles.

c. FUEL OIL

In fuel oil Cl is present in trace amounts. While a small sized condensation aerosol with a Cl component would be expected to be produced on combustion, fly-ash or dispersion aerosol would not be expected. The Br/Cl ratio is taken to be that of sea water (23).

d. COAL

Coal contains a few parts per thousand of Cl and the Br/Cl ratio may be near the sea water ratio, 0.0034 (23). On combustion, a small sized condensation aerosol would be expected. In addition, condensation onto less volatile constituents, mechanically dispersed by combustion, would produce a Cl component in fly-ash and dust-fall. Thus it is likely that Cl-rich particles of all aerosol size ranges, from Aitken ($r < 0.1\mu$) to giant ($r > 1\mu$) are produced.

3. ESTIMATION OF Cl AND Br AEROSOL SOURCE STRENGTHS

Useful upper and lower bounds on the masses of Cl and Br from the major sources contributing to inland aerosols can be estimated.

a. THE OCEAN

For the upper bound we note that Eriksson (8) reports an estimate of 5.4 kg of sea salts, or 3 kg Cl, transported per day across each meter of windward Hawaiian sea coast in projection perpendicular to the wind. This result is based on measurements of Amman (1) and Woodcock (27). It is consistent with results of Duce _et_ _al_. (7), who find approximately 3 μg Cl/m^3 at a few meters altitude. Assuming uniform mixing to an altitude of 2 km and an average wind speed of 10 m/sec, this is equivalent to a resultant transport of 5 kg Cl/(m-day). As both these estimates may underestimate storm conditions which enhance sea salt transport inland, we choose 1.5 times Eriksson's estimated flux of chloride and apply it along a projected windward coastline of 4000 km to obtain 7 x 10^{12} g Cl/yr as an upper bound for the annual natural Cl input over the continental United States. Taking Br/Cl = 0.0034, an upper bound for the annual natural Br input is 2 x 10^{10} g Br/yr.

For the lower bounds, Eriksson (8), using Woodcock's data, finds the rate of salt transport at Pompano Beach, Florida, and at various places in the Caribbean to be as little as half the rate found for Hawaii. If, in addition, the transport extends over as little as 1000 km of projected coastline then a lower bound for natural Cl input is 1/8 the values calculated above, viz., 8 x 10^{11} g Cl/yr. For Br the lower bound estimate is 3 x 10^{9} g Br/yr.

b. ETHYL FLUID

For the upper bound, May (18) reports the bromine sold by primary producers in the U. S. in 1967 to amount to 133 x 10^{6} kg. If 95% of this is used as ethylene dibromide in ethyl fluid (24), then 12.5 x 10^{7} kg of Br was so consumed in 1967. From data presented by Hirschler et al. (12), we infer that up to 100% of the lead halides being consumed might be emitted and of these 75% might remain airborne during country driving. Therefore the annual Br input from automobile exhaust might be as high as 9 x 10^{10} g Br/yr.

With Br/Cl = 1.15, the annual Cl input from this source, as an upper bound, is 0.8 x 10^{11} g Cl/yr.

For a lower bound, Hirschler et al. (12), suggest that in city driving only about 40% of the lead halide material may be emitted of which 50% remains airborne. Consequently, lower bounds on inputs from the automobile source are 2.5 x 10^{10} g Br/yr and 2 x 10^{10} g Cl/yr.

c. FUEL OIL

For the upper bound, Kirby and Moore (16) report that 6.75×10^{11} kg of fuel oil were consumed in the U.S.A. in 1967. Smith (21) finds from 1 to 5 g of particles produced by the firing of 1 kg of oil. Moreover in the only analysis reported, the particles were found to be 0.5% Cl (21). We estimate as an upper limit for Cl input from the combustion of fuel oil 2×10^{10} g Cl/yr. Assuming Br/Cl = 0.0034, we estimate as an upper limit 6×10^{7} g Br/yr.

For the lower bound, we suggest the particulate production to be 1 g/kg of fuel oil fired and the Cl content of the particulates to be only 0.05%. Consequently we find at least 4×10^{8} g Cl/yr and 1×10^{6} g Br/yr to be emitted by fuel oil combustion.

d. COAL

Young and Gallagher (29) report the consumption of coal in the U.S.A. during 1967 to be 5×10^{11} kg. Smith and Gruber (22) find the Cl content of several American coals to lie between 0.5% and 0.01% and Cuffe and Gerstle (4) find between 3% and 25% of the fly-ash to escape collection and be emitted to the atmosphere while Jones (13) reports electrostatic precipitators to be approximately equally efficient in the collection of particles of all size ranges. Therefore let us assume that equal masses of fly-ash and smaller particles are produced and emitted. These particles should include the Cl component because it is not rapidly oxidized by combustion. The upper bounds for Cl and Br aerosol production (assuming Br/Cl = 0.0034) are 6×10^{11} g Cl/yr and 2×10^{9} g Br/yr. The corresponding lower bounds are 1.5×10^{9} g Cl/yr and 5×10^{6} g Br/yr.

Table D-2 summarizes the calculations of upper and lower bounds for Cl and Br inputs to the atmosphere from the major natural and pollution sources. Quite clearly Cl which is deposited over the U.S.A. comes overwhelmingly from the ocean, although local exceptions may be observed in highly polluted areas. However, for Br the situation is quite different. Although the Br contained naturally in fuel oil and coal contributes only in a minor way, the Br originating from ethyl fluid combustion appears to be the major source, exceeding oceanic Br probably manyfold.

TABLE D-2

ESTIMATED ATMOSPHERIC Cl AND Br INPUTS TO CONTINENTAL U.S.A.

Source	Cl, 10^9 g/yr		Br, 10^9 g/yr	
	Maximum	Minimum	Maximum	Minimum
Ocean	7000	800	20	3
Ethyl Fluid	80	20	100	20
Fuel Oil	20	0.4	0.06	0.001
Coal	600	1.5	2	0.005

4. NUMBERS OF AEROSOL PARTICLES GENERATED

In meteorology the number of particles produced by a source may be more important than total particulate mass. Visibility through haze is reduced by particle-scattering and depends upon the number as well as the sizes of the particles (14). Rain drops and ice crystals are formed around nucleating particles (20). Size, solubility, and numbers of particles are important factors in nucleation. Human intake of atmospheric aerosols depends on particle size; e.g., larger aerosols may be deposited in the respiratory tree but smaller aerosols may enter in the alveoli and be retained (28). In spite of the practical importance of knowing the sizes of particles which contain different chemical elements and compounds and the numerical abundance of these particles, most air pollution measurements are of total particle mass without distinction as to particle size distribution.

Any serious attempt to estimate the total number of particles generated by all important processes operating in the U.S.A. is met with formidable difficulties mainly because of the scarcity of information on sizes of particles generated. Nevertheless, it is informative to make the attempt based on our data for Cl to at least deepen our appreciation for the difficulties of the task. Beginning with the source strength estimates of the previous section, we may estimate numbers of particles if we make certain assumptions for particle size, density, and fractional content of Cl in the particles.

For sea salt, average particle radii range from 0.5 to 5μ (7), density is close to 2 g/cm^3 (NaCl) and the Cl fraction is 0.6. For ethyl fluid, particle radii may range from 0.05 to 0.5μ (28), density may be 6 g/cm^3 (PbClBr), and the Cl fraction, 0.1 (26). For fuel oil, the condensation aerosol particles are expected to range in radius from 0.05 to 0.5μ with density about 1 g/cm^3 and Cl content, 0.05 (21). For coal, the condensation aerosol particles with radius range from 0.05 to 0.5μ may be most important numerically. Their density may be about 1 g/cm^3 and Cl content, 0.5 (taking Smith and Gruber's (22) 0.5% Cl in coal and assuming 1% ash).

Now the Cl mass strength, M g Cl/yr, particle radius, r cm, particle density, ρ g/cm^3, and fractional Cl content, f, can be combined as

$$\frac{M}{4/3\ \pi r^3 \rho f} = N \text{ particles/yr}$$

where the upper bound for M (Table D-2) and lower bound for r give an upper bound for N and vice versa. The numbers of particles generated, so estimated, are listed in Table D-3.

Particle concentrations may be estimated only after we have knowledge of dilution volumes. Very crudely, we may view the 7.8×10^6 km^2 area of continental U.S.A. as covered with air uniformly mixed to an altitude of 2 km and replenished with "clean" air 10 to 100 times per year. By dividing the particle generation rate by the air replenishment rate, $10^{8.2}$ to $10^{9.2}$ km^3/yr, we arrive at an estimate of steady state particle concentration for the different sources. These results are also shown in Table D-3.

TABLE D-3

NUMBERS OF AEROSOL PARTICLES GENERATED AS INFERRED FROM ESTIMATED CHLORIDE INPUTS

Source	Log (particles/yr)		Log (particles/cm^3)	
	Maximum	Minimum	Maximum	Minimum
Ocean	25	21	1.8	- 3.2
Ethyl Fluid	26.3	22.8	3.1	- 1.4
Fuel Oil	27.8	23	4.6	- 1.2
Coal	27	21.3	3.8	- 2.9

The results of Table D-4 were inferred from cascade impactor data. Estimates of numbers of particles were obtained by assuming the average density and fractional Cl content to be $\rho = 2\ g/cm^3$ and $f = 0.5$, respectively, for marine aerosols and $\rho = 3\ g/cm^3$ and $f = 0.1$, respectively, for pollution aerosols. However, the Cl concentration was measured over several hours rather than estimated for continental U.S.A. over a year.

TABLE D-4

CONCENTRATIONS OF AEROSOL PARTICLES AS INFERRED FROM MEASUREMENTS OF Cl (17)

Location	Approximate Particle Radius (μ)	Log (particles/cm^3)	
		Maximum	Minimum
Hawaii (7) (ocean, 1 case)		0.5	
S. E. Michigan			
(probable ocean aerosol, 3 cases)	4	- 3.7	- 4.7
(high concentration pollution, 5 cases)	0.05	+ 3.9	+ 3.0
S. Chicago (high concentration pollution, 2 cases)	0.05	+ 4.3	+ 4.2

Comparison of Tables D-4 with Table D-3 shows those aerosols probably of marine origin to have numbers comparable to the average in Hawaii (1 run) (7) and to be in low abundance inland compared to the average, while the pollution particles may exceed the average concentration. These conclusions are consistent and suggest that, in spite of the crude estimation and resulting wide separation, the limits (Table D-3) do encompass the true average particle concentration due to each major Cl source.

The results suggest that a substantially greater concentration of particles on the average over the U.S.A. arise from pollution sources than from the ocean. The calculations of Table D-3 consider only particles containing Cl, a major component of marine aerosols but a component not common to all pollution aerosols. Additional pollution aerosols may exist, and the relative importance of pollution sources of particles may be greater than shown in Table D-3.

5. ATMOSPHERIC REMOVAL PROCESSES

The cycle of halogens in aerosols is closed by their return to the earth's surface by wet or dry fallout. Eriksson (8) has made an especially valuable analysis of data taken by Junge and Werby (15) on the Cl content of rains primarily due to sea salt, which portrays the extent of transport of marine aerosols inland. Figure D-3 shows that Cl deposition in kg/hectare-yr diminishes with increasing distance from the sea coast and enables us to estimate the mean Cl deposition velocity for the U.S.A. Since the contours are logarithmically spaced, we can estimate the mean travel distance of aerosol Cl to be about 200 km near the coast to 1000 km far from the coast. If air masses move 400 km/day (5 m/sec), an atmospheric residence time of (4-20) x 10^4 sec is implied. A single mean deposition velocity of 1 cm/sec would account for this range of residence times if the mean altitude for atmospheric Cl varied from

400 m near the coast to 2000 m inland. Eriksson (8) cites other evidence indicating that 1 cm/sec is not an unreasonable deposition velocity for sea salt aerosols.

By inspection of Figure D-3, the mean deposition may lie in the range 1-4 kg Cl/hectare-yr by wet precipitation. Eriksson (8) argues that dry deposition may exceed wet precipitation by twofold, i.e., 2-8 kg Cl/hectare-yr, and total deposition becomes 3-12 kg Cl/hectare-yr or (1-4) x 10^{-12} g Cl/cm^2 sec. Over the 7.8 x 10^8 hectares of continental U.S.A., deposition totals (2-10) x 10^{12} g Cl/yr. This value is not in disagreement with the source strength estimate given in Table D-2.

A further check may be made by calculating the product of total Cl found in Run 2:GR:II (Figure D-1), about 0.3 μg Cl/m^3, and deposition velocity, 1 cm/sec. This result, 0.3 x 10^{-12} g Cl/cm^2sec, is not far from the above estimate based on Eriksson's analysis.

Deposition of natural Br can be estimated from the ratios Br/Cl = 0.0034 for sea water, and Br/Cl = 0.01 for uncontaminated surface waters near Lake Superior (25). Assuming the higher ratio is typical far from the sea (6), wet removal of Br may be 10-14 g Br/hectare-yr. Dry deposition of Br may not be as efficient as that for Cl owing to the small particle size for inland Br found in this work. Accordingly, the range 10-40 g Br/hectare-yr or (8-30) x 10^9 g Br/yr over the U.S.A. for total wet and dry deposition of natural Br is our best estimate. This result agrees with Table D-2.

Locally much greater ratios Br/Cl have been observed in rain water as well as aerosols by ourselves and others (11). If the removal characteristics of pollution aerosols resemble those of natural aerosols, such that mean transport distances are much shorter than continental dimensions, then the total removal of pollution Br and Cl is approximated by the pollution generation rate. Consequently the total input rates presented in Table D-2 also represent reasonable estimates of removal rates.

6. SUMMARY AND CONCLUSIONS

Several broad perspectives emerge from the foregoing discussion. The ocean is the strongest source for mass of aerosol Cl over the continental U.S.A. and exceeds the strength of pollution sources. Combustion of ethyl fluid as a source for mass of aerosol Br is stronger than the natural source. While the natural aerosol has a Br/Cl ratio of approximately 0.003, the pollution aerosol has a much greater Br/Cl ratio, sometimes 0.1 or larger. The pollution sources considered, combustion of ethyl fluid, fuel oil and coal, exceed the oceanic production for numbers of overland particles. The estimated inputs of aerosol Cl and Br generally agree with the outputs due to wet and dry precipitation.

Finally, some interpretation of the data in Figure D-1 is feasible. While Run 8:HAWAII (7), our reference for marine aerosols, has the size distributions of a dispersion aerosol and Br/Cl values approximately equal to the ratio in sea water, Run 35:EE:IX, collected in Ann Arbor, Michigan, during a period of southeasterly winds and thundershowers, has Br and Cl mass concentrated in small particles (condensation aerosol) and Br/Cl thirty times greater than the sea water ratio. The total Cl concentrations in Runs 8:HAWAII and 35:EE:IX are comparable but the total Br concentration is greater in Run 35:EE:IX. These features all suggest that the aerosol sampled in Run 35:EE:IX was of pollution origin.

Run 2:GR:II, collected in southeastern Michigan during an intrusion of Arctic and Atlantic Ocean air, shows some characteristics intermediate between the extremes of the other two runs. The Br distribution and Br/Cl values suggest the giant particles to be of marine origin and the smaller particles of pollution origin. Precipitation en route from the Arctic may have been responsible for reducing the concentration and modifying the size distribution of the Cl-rich aerosols of Run 2:GR:II (17).

Both natural and pollution aerosols may be transported and modified in the atmosphere. Thus, depending upon meteorological conditions, the prevalence inland of one or the other of these classes leads to wide variations in the characteristics of the aerosols observed there.

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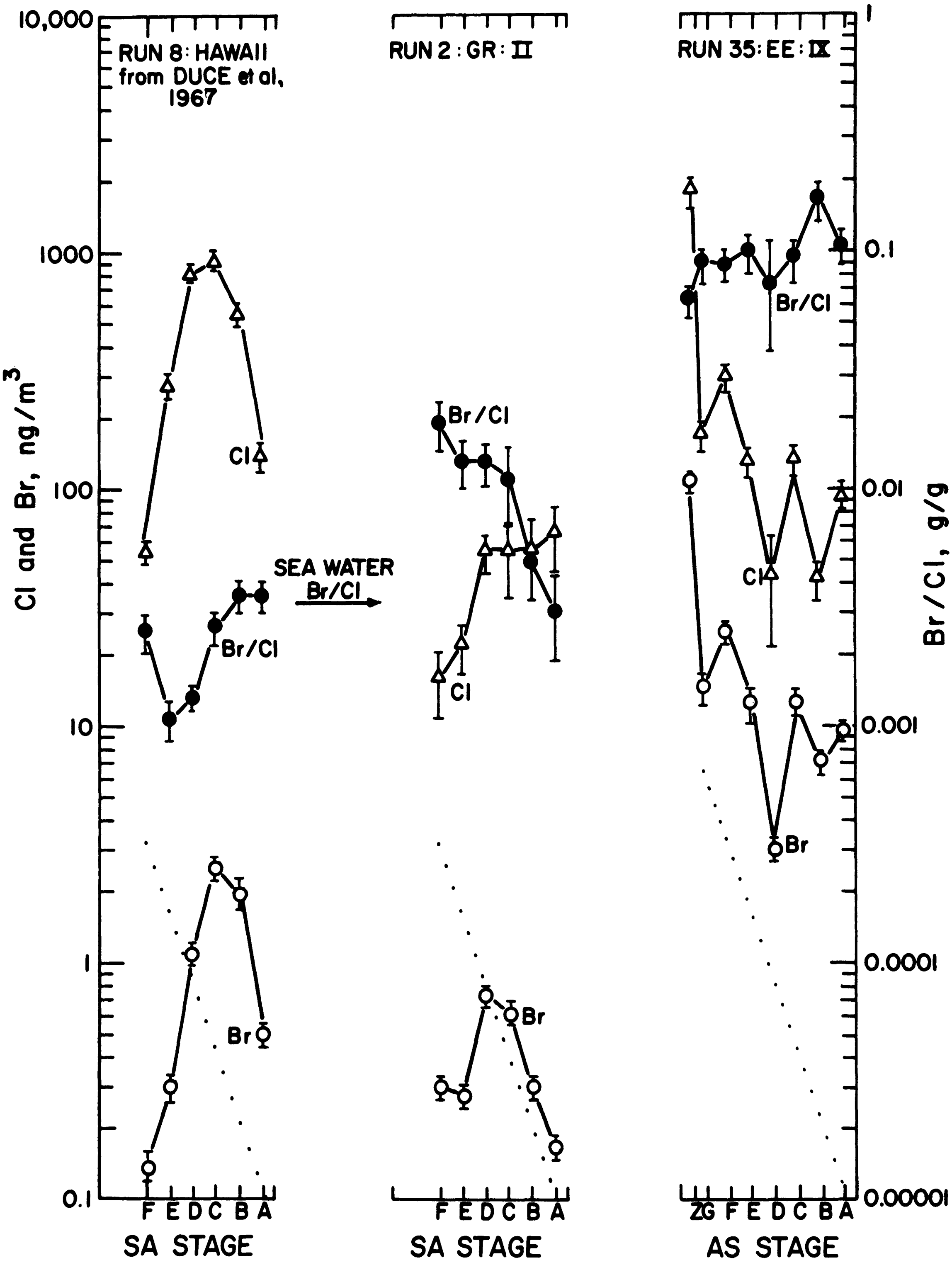

Figure D-1. Size distribution of aerosol Cl and Br from Hawaii (1 run) and Michigan (2 runs).

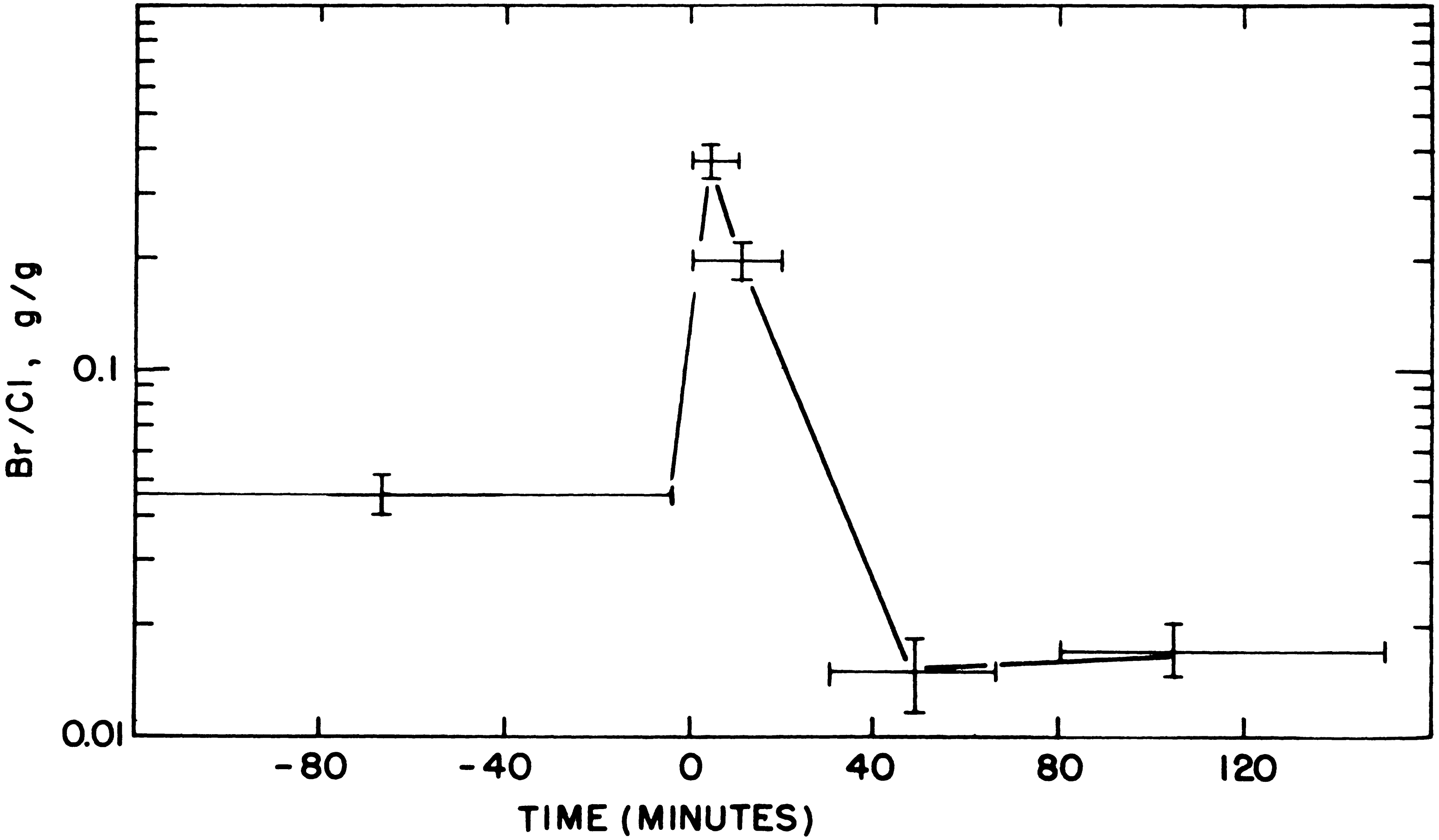

Figure D-2. The time variation of the Br/Cl ratio in very small automobile exhaust particles introduced fresh at time zero.

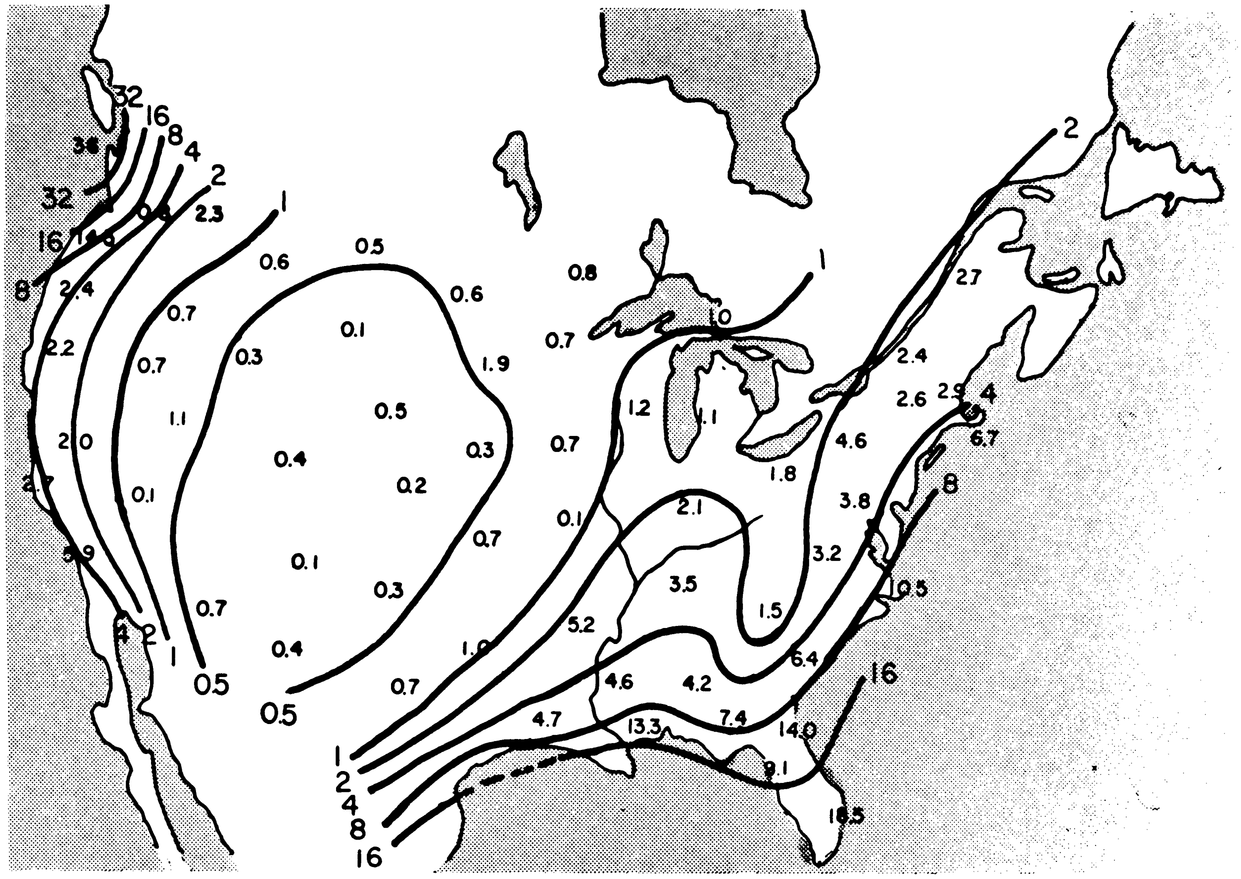

Figure D-3. Chloride in precipitation over the U.S.A. in kg/(hectare-yr), computed from concentrations of chloride in precipitation (Junge and Werby, (15)) and rainfall data (from Eriksson, (8)).