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STUDIES OF GASEOUS IODINE AND BROMINE
IN THE MARINE ATMOSPHERE

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ABSTRACT

A method has been developed for the collection and analysis of atmospheric gaseous iodine and bromine. The gaseous iodine and bromine were adsorbed onto specially cleaned activated charcoal from an airstream which had been cleaned of particulate matter by electrostatic precipitation. The amounts of iodine and bromine collected by the charcoal were determined by neutron activation analysis.

Sixty gaseous iodine and bromine samples collected from a 20 m tower on the windward shore of Oahu, Hawaii during the summer of 1969 showed that the average concentration of gaseous iodine in marine air is approximately 8 ng/m^3 and that the average concentration of gaseous bromine is approximately 50 ng/m^3 . Particulate iodine and bromine samples collected simultaneously with the gaseous samples showed that the atmospheric concentration of gaseous iodine in marine air is from 2 to 4 times the concentration of particulate iodine, and that the gaseous bromine concentration is from 4 to 10 times the particulate bromine concentration. The concentration of particulate iodine appeared to be directly related to the concentration of gaseous iodine. No correlation between gaseous and particulate bromine or between gaseous iodine and gaseous bromine could be seen.

Thermodynamic calculations indicated that at the concentrations of gaseous iodine and bromine found in this investigation, sea salt particles should act as a source for gaseous bromine and as a sink for gaseous iodine. Although the mechanism of gaseous iodine introduction into the atmosphere is uncertain, indications are that a

photochemical oxidation of iodide at the sea surface may not be the major source for atmospheric iodine. It is possible that gaseous iodine is released to the atmosphere as the iodine rich organic material on sea salt particles decomposes.

Thermodynamic calculations indicated that the dissolving of gaseous iodine and bromine into cloud and rain water may at least partially explain the fact that the I/Cl and Br/Cl ratios are higher in oceanic rain than in oceanic particulate matter.

Residence time calculations indicated that gaseous iodine has a residence time in the atmosphere of 1 to 12 days, and gaseous bromine has a residence time of 5 to 10 days.

Gaseous iodine and bromine samples collected from Mauna Loa Weather Observatory on the island of Hawaii at an altitude of approximately 3500 m indicate that air above the trade wind inversion contains lower concentrations of both iodine and bromine than does air at sea level.

Gaseous and particulate samples collected from a ship at sea showed concentrations of gaseous iodine and bromine, and particulate iodine and bromine similar to those concentrations found on the windward shore of Oahu.

Samples of gaseous iodine and particulate iodine and lead collected in Cambridge, Massachusetts during September, 1969 showed no significant source of pollution iodine. There was some evidence that the particulate iodine in polluted air is controlled by a reversible adsorption of gaseous iodine to pollution particulate material.

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I. INTRODUCTION

A. Geochemistry of Iodine

Iodine, the sixty-first most abundant element in the earth's lithosphere, represents about $3 \times 10^{-5}\%$ of the earth's crust. The rather extensive studies of iodine in the earth's environment have been considered important since iodine is so critical to man's physical well-being. The study of iodine in various environmental systems dates back to the very discovery of the element itself, when in 1813 Courtiou discovered the element iodine in the residue of burnt seaweed on the shores of France. Iodine never occurs naturally in major proportions: concentrations of the element range from about one thousand parts per million in certain marine organisms down to tens of parts per billion in some igneous and sedimentary rocks. In the literature it is difficult to find an element in our environment which, while as rare as iodine, has been studied as extensively or as long.

Probably the most important reason for the great interest over the years in naturally occurring iodine is iodine's relationship to goiter. By 1820, less than ten years after the discovery of iodine, the medical community of Europe noted the effect of iodine on man's health, specifically with reference to goiter. McClendon (1939), after reviewing and tabulating the world's studies on iodine in soils and waters, and comparing the results of these studies with statistics on endemic goiter, showed indisputably that areas with a high incidence of goiter have a lower iodine content in the soil than those

areas where the incidence of goiter is low. At this time, iodine is the only element which is known to be the sole reason for the existence or nonexistence of a disease in man. Because of the great interest in goiter and iodine for the past 150 years, a considerably larger store of knowledge about the geochemistry of iodine has been gained than would have been gained had this goiter-iodine relationship not existed.

1. Iodine in Soils and Rocks

A very important aspect of the geochemistry of iodine is that iodine is enriched in soils with respect to the rocks from which the soil is derived. Vinogradov (1959) reported that there is about ten times more iodine in soils on a weight-weight percentage basis, than in the rocks from which the soils are derived. McClendon (1939) noted such an enrichment in soils and explained that this enrichment occurs because vegetation, in the process of changing rock material to soils, extracts iodine from the rocks and concentrates the iodine in these soils. The Chilean Iodine Educational Bureau (1956) explained the enrichment as envisioned by McClendon to occur in the following way. First, the iodine from the soil is extracted by the growing plants, which as they die, return the iodine to the soil in humus. The iodine at this time is probably organically bound. The iodine is then held in this humic material while the other constituents of the parent rock are carried off with ground water as the weathering process progresses. As the rock or material undergoes weathering, clay colloids are formed and these colloids are

able to adsorb and hold iodine, while the percolation of ground water through the soil carries away other constituents of the weathered rocks. The Bureau points out that the iodine enrichment of the soil is dependent upon the soil's chemical properties: its acidity and essentially its oxidative properties (i.e., the ratio of ferrous to ferric ion, manganous to manganic ion, etc.).

McClendon considered the role of atmospheric iodine originating from the sea as an important factor in the iodine enrichment in soils. Recent workers, however, have suggested that the atmospheric iodine which originates from the sea is by far the most important factor in the large iodine enrichment observed in soils. Goldschmidt (1958) has considered the enrichment of iodine in soils on the basis of atmospheric iodine originating from the sea being carried inland by the wind and air masses. Goldschmidt hypothesized that since there is some correlation between iodine in soils and distance inland, and since the iodine content in rain is also somewhat dependent on distance from the sea, these facts strongly suggest that the sea is the primary source of iodine in soils. As evidence for the theory that airborne iodine is responsible for iodine enrichment in soils, Goldschmidt advanced a relationship between the iodine content of soils and glaciation. He stated that if the iodine in the soil has an oceanic source, then soils which are far removed from the sea will require perhaps hundreds of thousands of years for a significant amount of iodine to be accumulated. On the other hand, one would not expect the iodine concentration to be

dependent on the age of the soil if the iodine in soils has a source from the parent rock. In this case, the iodine concentration would depend on soil production and not soil age.

Goldschmidt then pointed out that areas of more recent glaciation contain soils with lower iodine concentration than is present in older soils, giving strong support to the theory that iodine in soils has an oceanic origin.

Vinogradov (1959), also believing that iodine enrichment in soils is a result of oceanic airborne iodine, based his assumptions on the fact that the iodine content of the soils in the Soviet Union is very dependent on distance from the oceans, and on his own measurements of iodine in air (which he reported to be as high as ten micrograms of iodine per cubic meter of air). Vinogradov gave no details about collection technique or the physical or chemical form of the iodine he measured in the air. Other workers such as von Fellenberg (1924), Cauer (1936), and Heymann (1925), have taken the position that both the oceans and the fixing of iodine from the parent rocks are the sources of the iodine content in soils. They could not determine the extent of enrichment from each source, but concluded that in general, the oceans are at least partly responsible for the iodine enrichment in soils.

2. Iodine in Sea Water

Studies investigating the chemistry and distribution of iodine in sea water are very meager when compared to the store of information which has been documented for iodine in rocks,

soils, and inland water systems. The land studies were prompted by medical reasons, whereas there has been no similar motivating force for the study of iodine in the seas. Furthermore, iodine is a very difficult element to determine quantitatively as it exists in sea water. Examination of available literature concerning iodine in sea water shows that many questions regarding the concentration and chemistry of iodine in sea water are still unanswered. One of the most important factors evident in the literature is that organic materials and biological matter must play an important role in the chemistry and distribution of iodine in the sea and its sediments.

a. Concentration of Iodine in Sea Water

Generally, iodine concentrations in the world's oceans are accepted to be between 50 and 60 micrograms per kilogram of sea water, or 50 to 60 parts per billion (ppb). Sugawara and Terada (1957) investigated the total iodine concentration of the western Pacific Ocean, and reported that total iodine tends to decrease, as least as far as surface waters are concerned, as one moves from the Arctic south to the equator. This tendency for decreasing iodine concentration with southerly movement was by no means marked or extensive: the values reported by Sugawara and Terada ranged from around 26 to 46 ppb with an overall average of approximately 39 ppb total iodine, and considerable overlap of values reported for equatorial and northern waters. Sugawara and Terada could find no apparent variations of iodine concentration with

depth to about 900 meters, although in a number of their measurements, but not in all, there was a tendency for the iodine concentration to be slightly decreased in the surface water (in about the upper ten meters) when compared to values obtained for the deeper water. It must be pointed out that these differences were not large and there was considerable overlapping of values reported for surface and subsurface waters.

Barkley and Thompson (1960) reported that the iodine concentration in the north Pacific was 60 ppb, independent of location. They deduced that the ratio of iodine to chlorinity below 200 meters was constant, while in the 200 meter surface layer it appeared that the surface water (top one meter) had a slightly higher iodine to chlorinity ratio than the water immediately under it. At the same time the water in the 200 meter surface layer was depleted in iodine with respect to the water beneath it.

Voipio (1961), measuring the iodine in the surface water (bucket sample) and the iodine concentration at a depth of about 200 meters in the Barents Sea in the Arctic Ocean, found that the iodine concentrations varied from about 60 ppb to around 100 ppb with an average of about 71 ppb. His data indicates that the surface water samples contained less iodine in general than did the 200 meter samples. Voipio also reported in this paper that Barkley and Thompson found lower iodine concentrations in more southerly Pacific waters

than the values they reported in their 1960 paper, although no detail or elaboration other than the statement of occurrence was made. Voipio pointed out that the reported variations in iodine concentrations in the world's oceans must be investigated more thoroughly so that discrepancies might be explained, and suggested that the variations might be due to the analytical techniques employed, regional variations, or perhaps seasonal effects.

After summarizing their several years of iodine studies in the Pacific and other oceans, Sugawara and Terada (1962) concluded that there appeared to be iodine variations from one position or sea to another. Their results indicated that the total average iodine concentration of the northwestern Pacific Ocean is about 38 ppb, while the concentrations for other water bodies are significantly higher: 51 ppb in the South China Sea, 51 ppb in the Indian Ocean, and approximately 55 ppb in the West Wind Drift Zone and the Antarctic Ocean. These workers concluded that the iodine concentrations in the world's oceans are unequal but gave no reasons for their observed variations.

Tsunogai (1966) studied the iodine content with depth of the western Pacific Ocean and reported that, in general, there is a tendency for the total iodine content to increase from about 50 ppb in the surface water to about 60 ppb at one thousand meters, and to remain constant with depth below one thousand meters. Tsunogai also reported very good agreement

from station to station in these values (the standard deviation of obtained values was approximately 5% for different stations at the same depths). Furthermore, Tsunogai predicted that the values reported may be indicative of those of the Pacific Ocean as a whole and not just the areas where his samples were collected, since his analysis of one sample from Antarctic waters gave the same results as his samples from the northwest Pacific.

Revel (1969) studied the iodine concentration in surface waters on a cruise from Tahiti to the southern tip of South America, continuing across the Atlantic Ocean to France. The reported values had variations of about 20% with no trend apparent between equatorial waters and the colder northern and southern waters. Likewise, there appeared to be no significant differences between the values reported for the Atlantic and Pacific Oceans. Iodine concentration with depth was not studied in this work.

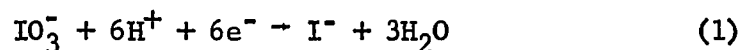
In general, the following may be said: there appear to be real variations in the iodine concentrations of the world's oceans. Some of these differences probably can be explained by the different analytical techniques employed by the various investigators. However, differences reported by the same investigator must be presumed to be real since the same technique is involved in obtaining these results. At the present time the variations with position are inadequately explained. The most recent investigations would indicate

that a general iodine depletion in warm equatorial waters with respect to the colder waters is probably not a verifiable observation. It is possible that there may be seasonal variation, or that one would have to look for some new variable to explain these variations.

b. Chemical Species of Iodine in Sea Water

Although the concentration of iodine in sea water is variable and its variation still leaves several unanswered questions, a most interesting and important aspect of iodine in sea water is its chemistry. Much of the data available on iodine concentrations in sea water has been prompted, not by an interest in concentrations per se, but by an interest in the chemical species of iodine which are present in sea water.

Sill  n (1961) considered the equation



$$K = 10^{110.1}$$

He calculated that in sea water with pH = 8.2 and pE = 12.5, the ratio of $\text{IO}_3^-/\text{I}^- = 10^{13.5}$, or that iodate is the thermodynamically stable form of iodine. Although iodate is the thermodynamically stable form it has long been known and reported that iodate is not the only form of iodine in sea water. Winkler (1916) and Blackmore (1912) reported that iodine in sea water exists as both iodate and iodide, with the iodate to iodide ratio being approximately four.

Sugawara and Terada (1957) investigated the oxidation

state of iodine in the Pacific Ocean by analyzing sea water for iodide, then reducing the oxidized iodine species to iodide and repeating the determination. These workers found that iodate and iodide were present in roughly equal amounts approximately 25 $\mu\text{g/l}$). The sum of these two determinations was reported as total iodine (previously discussed).

Although Sugawara and Terada assumed that the oxidized portion of iodine was iodate, Shaw and Cooper (1957) suggested that Sugawara and Terada were actually measuring hypiodite as the oxidized species of iodine in sea water. Shaw and Cooper did acknowledge the fact that thermodynamically, iodate should be the stable form of iodine in sea water, but envisioned the following to occur: Iodate is attacked by strong biological reducing organisms and converted to iodide. This iodide is then oxidized to the hypiodite ion by the oxygen in sea water:



Calculations from equilibrium data give a ratio of IO^-/I^- around unity under sea water conditions, and this is close to the value obtained by Sugawara and Terada for oxidized iodine to iodide. Hypiodite should disproportionate to iodate and iodide according to the equation



This reactions, however, is trimolecular and would proceed at a negligible rate at the concentrations of iodine in sea water.

Sugawara and Terada (1958) in a rebuttal to Shaw and Cooper's proposal of hypiodous acid being the oxidized form of iodine in sea water, reported that laboratory studies indicated that the disproportionation of IO^- at concentrations of sea water iodine proceeded quite rapidly, while the oxidation of iodide to hypiodite proceeded quite slowly and for all practical purposes, could be ignored. Johannesson (1958) reported that in measuring sea water samples collected near New Zealand, he could not detect the presence of the hypiodite ion although at the concentrations predicted by Shaw and Cooper the ion should be quite easy to detect. In light of the evidence offered by Sugawara and Terada along with that of Johannesson, Shaw and Cooper (1958) agreed that the oxidation states of iodine in sea water were probably iodide and iodate, although they felt that many questions about the chemistry of iodine in sea water remained unanswered.

A review of the iodide-iodate distribution in the world's oceans allows one to see that more data is needed to accurately describe iodine and its oxidation states as it exists in sea water. Sugawara and Terada (1957) studies the relationship between iodide and iodate in the western Pacific Ocean, and concluded from this study that there appeared to be no regular variation of the iodide to iodate ratio either with respect to position in the ocean or depth of the sample. The values obtained for the ratio of iodide to iodate ranged

from 0 to infinity with an average close to one.

Barkley and Thompson (1960), using independent analysis methods for iodate and total iodine, studied the relationship of iodate to total iodine in the northern Pacific Ocean, and found results quite similar to those obtained by Sugawara and Terada. Barkley and Thompson could find no regular variation of the iodate to iodine ratio with either depth or position, except in one instance, when a profile taken in the Arctic Ocean showed a very pronounced decrease in the iodate to iodine ratio in surface water as compared to the subsurface water (below 200 meters). These investigators pointed out that their work indicated that in all samples in waters below 200 meters, the iodate to total iodine ratio was quite constant and that variations (although irregular with no apparent trends) which did occur did so in the top 200 meters of water. The investigators suggested that living organisms in this surface water may be responsible for the iodate/iodine variation.

Tsunogai (1966), using the same method of analysis as did Sugawara and Terada, investigated the iodide-iodate ratio in the western Pacific Ocean and presented results which are in opposition to those reported by Sugawara and Terada, and to those reported by Barkley and Thompson. Tsunogai reported that there is a variation in the iodide to iodate ratio which is dependent upon depth, and that he observed no wide variations in this ratio with geographical position as did previous

workers. Tsunogai found that iodide ion in sea water decreased from the surface to approximately 1000 meters, from about 20% of the total iodine in the surface to 10% or less. Furthermore, he found that below about 1000 meters essentially all iodine existed as iodate. The highest iodide value Tsunogai obtained was about 35% of the total iodine (the works previously discussed reported average values of iodide to be 50% of the total iodine).

The presence of organic iodine has been suggested by several workers. Reviewing Vinogradov's (1953) documentation of the iodine concentrations in marine organisms, it is quite evident that iodine is greatly concentrated in many organisms, with at least part of this iodine existing as organic iodine and part existing in an inorganic form (elemental iodine, for example). To the present, however, no one has been able to determine an organic fraction of iodine in sea water which is significant when compared to the inorganic species present. Sugawara and Terada (1957) reported that they believe organic iodine is present in sea water, but as a very minor component. These workers reported that ashing of filter samples of particulate matter in the presence of base gave no measurable amounts of organic iodide.

From the above, it is obvious that more data is needed about iodide, iodate, organic iodine, and total iodine before definitive statements may be made on iodine behavior in the oceans. To account for the relationship between iodide,

iodate, and total iodine in sea water, one factor must be considered: the conversion processes which permit iodate to be changed to iodide and iodide to iodate. It is noted that sea water saturated with air would thermodynamically favor the formation of iodate if iodide were present; however, Barkley and Thompson, and Sugawara and Terada reported that they stored sea water samples up to a year with no change in the iodide to iodate ratio. This suggests that perhaps kinetically, the iodide to iodate oxidation goes extremely slowly under sea water conditions.

Probably the most agreed upon method of conversion between the two iodine species is the action of marine organisms. Tsunogai (1966), Sugawara and Terada (1957, 1962), Barkley and Thompson (1960), and others have suggested that marine organisms could be important for both oxidation of iodide to iodate and for the reduction of iodate to iodide. The question which must be asked, however, is how much can marine organisms affect the iodine distribution in a given area, or how much iodine can be converted from one oxidation state to another by material living in the sea.

The effect of biological material on iodine in sea water can be estimated by considering the effect of biological material on the nutrient concentration of sea water. It is known that nitrogen nutrients (nitrate, nitrite, and ammonia) will be depleted in surface waters with respect to deep water due to the utilization by biological material. Thus, in

surface waters with a very high concentration of living organisms the nitrogen nutrient concentration might be approximately 70 $\mu\text{g/l}$ (as N) while deep water will have a nitrogen nutrient content of 210 $\mu\text{g/l}$ (Stefansson, 1968). In other words, biological material is using up nutrients at such a rate that the addition of new nutrients by mixing of the surface water with deeper water results in a nutrient concentration about one-third of that found in deep water. It is possible to calculate the expected change in the iodine concentration which would accompany a change in the nutrient concentration, assuming that the organisms take up (or fix) iodine at the same rate at which they take up nitrogen. Vinogradov (1953) gave the concentration of iodine in diatoms in the ocean as 0.02 to 0.06% by dry weight; and the nitrogen concentration was given as 2 to 5%. Assuming average concentrations of iodine and nitrogen in marine organisms to equal 0.05% and 4% respectively, the N/I ratio would then be 80. In deep water the N/I ratio is approximately 4. Thus marine organisms are enriched in nitrogen 20 times with respect to iodine. This means that if nitrogen concentration (as nutrients) is decreased by a factor of three the expected change in iodine concentration would be $3/20$, or 15%. If this process is converting iodate to iodide, it is then possible that biological material can account for the iodide production in sea surface water. This calculation agrees well with the results reported by Tsunogai (1966), that iodide

concentration was higher in surface water than in deep water.

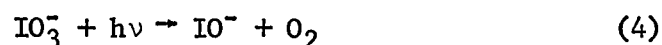
The importance of biological material on total iodine concentration can be crudely estimated in the following way: Strickland (1963) has stated that the yearly production rate of organic material in the sea is approximately 10^{16} grams. Assuming that in the process of producing this organic material the biological material of the sea also turns over 0.05% of this amount of iodine (i.e., 5×10^{12} grams), then by knowing that the total volume of the sea is 1.5×10^{24} ml (or that the sea contains 7.5×10^{16} grams of iodine) it is seen that the amount of iodine used up by biological material per year is about 0.01% of the total iodine available in the sea. Thus, if the iodide concentration of deep water is between 10 and 50% of the total iodine concentration, it would take 10^4 years or longer to produce this amount of iodide at the production rate discussed above. If biological activity is the mechanism responsible for converting iodate to iodide, the conversion of iodide to iodate must proceed extremely slowly.

Recently Tsunogai and Sase (1969) presented laboratory studies indicating that iodate can be reduced to iodide by marine bacteria which reduce nitrate. These workers indicated that this reduction of iodate is the result of the enzymatic action by the enzyme nitrate reductase. They were uncertain as to whether the iodate was reduced directly to iodide, or to elemental iodine with the subsequent

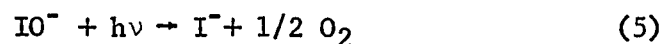
disproportionation to iodide and iodate. These workers felt, however, that the bacterial action was possibly the major source of iodide in sea water.

Another suggestion to explain iodide in sea water has been offered by Sugawara (1967b), who pointed out that the input systems to the world's oceans, the rivers, deliver iodine in the form of iodide. The total amount delivered per year, however, represents only 0.0001% of the total iodine present in the ocean. Thus, while river inputs may affect local concentrations of iodide, their effect on the iodide concentration of the oceans as a whole is negligible when compared to the effect of biological material.

Duce (1964) has suggested the possibility of iodate being reduced by ultraviolet light at the sea surface according to the equation



and followed by



or



The photoreduction of iodate to hypoiodite proceeds only with light whose wavelength is shorter than 295 m , and since this is about the value where the atmosphere cuts off incoming ultraviolet irradiation it must be presumed that this would be a very negligible way of producing iodide in the sea.

Thus it appears that of the ways in which iodate can possibly be converted to iodide in sea water, the most efficient method is presented by biological material. Workers who have investigated the uptake of iodine from sea water by marine organisms state that these organisms utilize both iodide and iodate (Tsunogai, 1966; Sugawara, 1963; and others) and the relative importance of the two iodine species in its interaction with biological material is not known.

Several suggestions have been advanced as to how iodide may be converted to iodate. These include oxidation by oxygen in sea water, the action of biological material, and a photooxidation of iodide to elemental iodine with the subsequent disproportionation to iodide and iodate. It appears, however, that the problem is not to try to explain the iodide to iodate conversion but its reverse, since iodate is the thermodynamically stable state. In summary, it seems that both iodide and iodate are stable under sea water conditions: iodate is thermodynamically stable, while iodide is kinetically stable with respect to oxidation to iodate.

3. Iodine in the Atmosphere

Studies of iodine in the atmosphere have been made for some time, and it has long been realized that iodine is considerably enriched with respect to the sodium or chlorine concentrations in the marine atmosphere. Von Fellenberg (1924, 1926, 1933) and Heymann (1925) were the first workers to note that the iodine content of the air over Europe was much higher than one would

expect if the source of this iodine were the sea. These workers found that the iodine content of the air at times exceeded 5 micrograms per cubic meter, or a concentration greater than the sodium content of the atmosphere.

Cauer (1930, 1939) measured the iodine content of European air and determined that much of the iodine being measured was a result of the iodine industry which obtained iodine by burning seaweed. The seaweed burning was very inefficient, however, and Cauer believed that approximately 10% of the iodine in seaweed escaped into the atmosphere, accounting for the very high concentrations which were previously measured over Europe. By the 1930's the world's source of iodine was shifting from seaweed to to the Chilean Nitrate deposits, and after this change was complete it was shown by Cauer that there was a marked decrease in the iodine content of the air over Europe. Since that time, numerous investigators have shown that iodine in rain and particulate matter collected in the marine atmosphere is enriched from about 100-3,000 times what would be expected based on the sodium and chlorine content on the same air mass (Jesser and Thomae, 1937, 1939, 1943; Sugawara, 1965, 1967a; Dean, 1963; Duce et al., 1963, 1965, 1967).

a. Transport of Sea Salt from the Sea to the Atmosphere

It has been well documented by Kientzler et al. (1954), Mason (1954), Woodcock (1953), Blanchard and Woodcock (1957), and Blanchard (1963), that material from the sea is transferred to the atmosphere by wind driven whitecaps over the

open sea. As these small waves break, air is entrapped in the water causing large numbers of small bubbles to be formed. These bubbles rise to the surface and break with enough energy to hurl one or more small droplets (commonly called jet droplets) of sea water into the air. Once in the atmosphere these small drops will undergo physical and chemical changes which give them properties much different from sea water.

Eriksson (1959, 1960) and Junge (1963) have summarized some of the physical changes which a jet droplet will undergo in the air. These drops will first equilibrate with the ambient relative humidity. A droplet injected into the air with a relative humidity of 96% will lose approximately half its volume of water, at 91.4% relative humidity approximately $3/4$ of the water will evaporate, and at 80% relative humidity the water evaporation will amount to about $7/8$ of the initial volume. Once the relative humidity goes below about 70%, the droplet can lose all of its water and become a dry particle of salt. A density change also accompanies this evaporation process. A change in relative humidity of air from 99% to 70% produces a change in particle density of 1.02 g/cm^3 to 1.21 g/cm^3 . The crystalline density of the particle (i.e., below 70% relative humidity) is 2.1 g/cm^3 . This loss of water means that the chemical concentration of various elements in a droplet will undergo a change (i.e., an aerosol at a relative humidity of 80% will be 8 times as

concentrated in Cl as is sea water).

In addition to these changes which result from evaporation, once a particle is airborne it can react with or dissolve gases in the air. Duce (1969, personal communication) has calculated that a sea salt particle in a marine atmosphere will have a pH of 5 to 6 due to the equilibrium between the particle and the atmospheric concentration of CO_2 , NH_3 , SO_2 , and NO_2 .

Blanchard (1963) and Mason (1957) have shown that in addition to jet droplets, droplets are also produced from the bubble film when the bubble collapses. These droplets which are much smaller than jet drops, are commonly called film drops. While jet drops have a radius from around $5\ \mu$ to as large as $50\ \mu$ when injected into the atmosphere, film drops have a radius of approximately $0.5\ \mu$ or less (Blanchard, 1963). At this time the importance of film droplets in transporting material to the atmosphere is not known.

Blanchard (1963) has shown that breaking bubbles can be an effective method of transferring surface active organic material into the atmosphere. This organic material can be carried into the air by both the film and jet droplets.

b. Suggested Sources for Atmospheric Iodine

The fact that iodine is enriched in the atmosphere with respect to chlorine means either iodine is enriched on the droplets injected into the atmosphere or that iodine is transferred to the atmosphere by a different mechanism than is the

case for chlorine and sodium. To date there are two popular explanations for the atmospheric iodine enrichment: 1) the escape of iodine gas from the sea surface, and 2) organic material on the surface of the sea is enriched in iodine and this surface active material is injected into the atmosphere with the droplets resulting from breaking bubbles.

Cauer (1939) proposed that iodine in the atmosphere was the result of volatilization of elemental iodine (I_2) at the sea surface, and suggested that I_2 would be formed by the oxidation of iodide by ozone and ultraviolet light. Eriksson (1952) reviewed Cauer's hypothesis and suggested that there are two mechanisms of iodine transport: 1) oxidation of iodide and the escape of the produced I_2 ; and 2) transfer of spray containing iodine by the normal process which results in the sodium the chlorine being ejected into the atmosphere. Eriksson also suggested that once iodine is brought inland and precipitated onto the soils, it may again be revolatilized to I_2 and return to the air by the same mechanisms of oxidation which allow its escape from sea water. Although Eriksson believes there is an industrial pollution source of iodine, he feels this is a very small source of iodine on a global scale.

Miyake and Tsunogai (1963) and Tsunogai (1966) in his dissertation, investigated the possibility of photooxidation of I^- by ultraviolet light. ^{131}I Iodine was added to sea water as iodide, iodate, and a mixture of iodide and iodate, and

the amount of iodine released was measured both in the dark and in the presence of light with wavelengths from 290 mμ to 550 mμ. These workers showed that free iodine is released when $^{131}\text{I}^-$ is present in sea water. From their experiments, these investigators also calculated the amount of iodine which would be expected to be released from the sea by such a reaction and concluded that this mechanism would account for 5×10^{11} grams of iodine being put into the earth's atmosphere yearly.

Blanchard (1963) reports that 10^{16} g of salt per year are ejected into the atmosphere, which is equivalent to 4×10^{15} g of Na, and if Miyake and Tsunogai's (1963) calculation of 5×10^{11} g of iodine is correct, the ratio of the yearly production of iodine to the yearly production of sodium is 1.5×10^{-4} , (the I/Na ratio of sea water is 5×10^{-6}). Therefore, thirty times more iodine is released to the atmosphere by a photochemical oxidation than the amount put into the atmosphere by breaking bubbles ejecting spray droplets which have the same chemical composition as sea water. The I to Na ratio which is normally measured in precipitation and particulate matter in a marine atmosphere is almost always greater than 5×10^{-4} and it appears that the most commonly reported values are 1 to 3×10^{-3} . This number is at least six times smaller than the ratio of the yearly production rate of iodine to the yearly production rate of sodium calculated by using Miyake and Tsunogai's estimate of iodine

production. If the photo mechanism proposed by Miyake and Tsunogai is indeed the correct mechanism accounting for iodine in the atmosphere and their numbers on the amount of iodine released to the atmosphere yearly are correct, the implication clearly is that the average iodine molecule has a residence time which is six or more times longer than the average residence time of a sodium ion. However, if the iodine exists as a gas and the sodium exists as particulate matter this difference in residence time may not be an unreasonable expectation.

Dean (1963) measured iodine in rain over New Zealand and reported that 40% of the iodine found was organically bound. Since the biological organisms in the sea which produce surface organic material are highly enriched in iodine, he suggested that organic material on the surface of the ocean is also enriched in iodine. Dean felt this organic material could be carried into the air by the breaking bubbles, resulting in particles enriched in iodine.

MacIntyre (1965), in a study of phosphate enrichment in sea salt particles by organic surface active material, predicted that all elements which are enriched in marine organisms would be susceptible to an enrichment mechanism similar to that which he found in the case of phosphates. Iodine was included in a group of elements which he expected to show enrichment in the atmosphere due to an organic film process.

After measuring organic material in the marine atmosphere,

Blanchard (1968) stated that organic concentration was high enough that if the organic material in the atmosphere was 0.1% iodine (0.1% iodine by weight is a value which is found in some marine organisms) this would account for the enrichment of iodine which is measured in the air. Blanchard found that the marine atmosphere contained approximately $2-3 \mu\text{g}/\text{m}^3$ of surface active organic material as particulate matter (this is approximately equal to the sodium concentration in the marine atmosphere). The average concentration of organic material in sea water is approximately 1 mg/l (or the $\text{C}(\text{org})/\text{Na}$ ratio is 10^{-4}). Thus organic material in the atmosphere is 10^4 times more than would be expected from the sea water concentration.

It appears, then, from the studies of Dean (1963), MacIntyre (1965), and Blanchard (1968), that surface active organic material could have a significant role in the transfer of iodine from the ocean to the atmosphere. At the same time, a photochemical production of I_2 may also contribute to the atmospheric concentration of iodine, as was suggested by Miyake and Tsunogai (1963) as a result of their laboratory work. Before it is possible to describe the importance of each as the source of atmospheric iodine, additional data and information would be required.

c. Concentration and Behavior of Iodine in the Atmosphere

Duce et al. (1963, 1965) studied the iodine, bromine, and chlorine concentration in particulate matter and precipitation

in Hawaiian air. They attempted to measure particulate concentrations of the halogens with respect to particle size and with respect to altitude or distance away from the sea. They also measured the halogens in rain at various altitudes, and attempted to measure the gaseous components of these elements. Many interesting and important observations were made in these studies.

Duce et al. (1963, 1965) found that in general, iodine was 2 to 3 times more enriched with respect to chlorine in precipitation than it was in sea salt particles, and that in rain, the I/Cl ratio increased with altitude (or with distance away from the sea). They also reported that iodine enrichment seemed to be dependent upon particle size, with small particles apparently having larger I/Cl ratios than large particles. However, due to collection conditions and equipment, the effect of particle size could not accurately be determined. Gaseous measurements were very uncertain due to contamination problems, but indications were that gaseous iodine could possibly be as much as two or more times the particulate iodine concentration. Duce et al. (1965) concluded that the significant amount of atmospheric iodine which exists as a gas is probably the reason for the variation in the iodine enrichment factors, and proposed that the tendency for the iodine enrichment to increase with decreasing particle size was due to an adsorption of gaseous iodine onto the surface of the particles (the surface area to mass ratio

increases with decreasing particle size, and therefore an adsorption type mechanism means higher I/Cl ratios on the smaller particles). Since the I to Cl ratio appeared to be dependent upon particle size, it was acknowledged that the I/Cl ratio could increase with distance inland because the larger particles with low I/Cl ratios could be removed from the air, and hence a higher enrichment of iodine with respect to chlorine would be observed. However, these workers felt that the reason for the tendency of the I/Cl ratio of particles to increase with altitude was that the particles would have more time for adsorption of gaseous iodine. Duce et al. (1965) explained the tendency for the I/Cl ratio in rain to increase with altitude by suggesting that there may be a loss of gaseous chlorine rather than an uptake of gaseous iodine since the I/Br ratio remains approximately constant with altitude. From the data presented it is evident that the I/Cl ratio in precipitation is higher than it is in the particles; however, this fact is not noted and no explanation is advanced for it. On the basis of diffusion calculations, Duce (1964) presented evidence which indicates that the average lifetime of an iodine molecule should be approximately 30 minutes, and that the time required for gaseous iodine adsorption on particulate matter to build the I/Cl ratio up to values normally observed in the atmosphere should also be approximately 30 minutes.

Sugawara (1965) quoted values for the enrichment factors

for iodine in air and precipitation samples collected in Japan and noted that the enrichment values obtained by Duce et al. (1963) agreed remarkably well with the Japanese results for the precipitation samples. The Japanese results, however, showed that the particulate samples were more enriched in iodine than were rain samples while Duce et al. found the opposite to occur. Sugawara pointed out that the Japanese measurements of iodine in air were obtained by bubbling air through a solution of sodium hydroxide and measuring the iodine and chlorine which were trapped. Duce et al. (1963), on the other hand, collected their samples on a cascade impactor and an aircraft aerosol sampler (which is also an impaction collection method). Although Sugawara thought that the two different collection techniques might result in the apparently contradictory values obtained by the two groups, he could not explain how different techniques might give different results. It is probable that the different values obtained were indeed due to the different sampling techniques employed: the Japanese used a technique which permitted collection of gas as well as aerosols, while Duce et al. (1963) used an impaction technique which collected only particles.

Duce et al. (1965) suggested that some of the results obtained in attempting to measure the relationship between the halogens and particle size might not be truly representative of over-the-ocean samples since they were collecting

on a beach very near the surf zone. In 1967, Duce et al. avoided this problem by collecting samples from a tower approximately 20 meters above the surf zone. Using a six stage cascade impactor which was much superior to the old four stage instrument used in the previous study, these workers showed that the enrichment of iodine with respect to chlorine was inversely proportional to particle size. They found that the I/Cl ratio increased by a factor of about 20 between particles of 5 μ radius and particles of 0.3 μ radius. ($I/Cl = 8 \times 10^{-5}$ for 5 μ radius particles and 2×10^{-3} for 0.3 μ radius particles). These workers pointed out that this was in close agreement with what would be expected if the iodine associated with particulate matter was the result of diffusion of I_2 vapor to the surface of the particles. Such a diffusion process means that the amount of iodine added to the particle is dependent upon the surface area of the particle, while the amount of chloride present is dependent upon particle volume (assuming that every particle has an equal chloride concentration). Thus, the I/Cl ratio is dependent on the particle's ratio of surface area to volume, or the reciprocal of the radius. These workers did not conclude that the iodine on sea salt particles was definitely or only the result of a surface diffusion phenomenon since MacIntyre (1965) had presented laboratory evidence that phosphate enrichment on particles was particle size dependent (although this dependency did not follow that

which is found for iodine) and quite convincingly showed that this PO_4^{3-} enrichment was the result of organic surface active material enriched in PO_4^{3-} being carried into the air by breaking bubbles.

Subsequent work by Duce and Woodcock (1970, personal communication) has shown that selection of sampling location is extremely important. These workers collected cascade impactor samples using the same location and equipment of Duce et al. (1967) and collected simultaneous samples from the base and top of a 20 meter tower. It was found that at the base of the tower, the I/Cl ratio could be 100 times smaller than the value obtained at the top of the tower. This is explained by the fact that the local surf zone does not inject particles into the air by the same process which occurs over the open oceans and thus the samples collected at the tower base are contaminated (or diluted) with bulk sea water.

Paslowska and Ostrowski (1968a) have reported that the atmospheric concentration of gaseous plus particulate iodine (collected by a K_2CO_3 bubbling system) over the Baltic Sea is about $1,000 \text{ ng/m}^3$. They also reported that the atmospheric concentration of iodine varied by a factor of about 2 between night and day and suggested that this is a result of a photochemical production of I_2 at the sea surface, as proposed by Miyake and Tsunogai (1963). Concentrations of atmospheric iodine (in rain and particulate matter) from

1-10 ng/m³ have been reported by previous workers (Duce et al., 1963, 1965, 1967; and Sugawara, 1965), yet Paslowska and Ostrowski have given no explanations for the fact that their iodine values are much higher than those reported earlier. Geographical location, analytical technique, or conditions under which samples were collected may be the cause of the differences.

Recently a new factor has emerged, generating considerable interest in environmental, and especially atmospheric, studies of iodine. This is the growing use of the fission of uranium for reactor power plants and explosive devices. ¹³¹Iodine is a very important by-product produced in high yields, its very high specific activity (due to an 8 day half life), and the fact that most living organisms concentrate iodine to a large degree, make this potentially one of the most physiologically dangerous isotopes which can be released in the lower atmosphere by a fission explosion or accident.

Chamberlain (1953, 1959, 1966), Chamberlain and Chadwick (1953), Chamberlain and Dunster (1958), Chamberlain and Wiffen (1959), Bolin (1959), Chamberlain et al. (1960), and Clough et al. (1965), have been concerned with the uptake of iodine by vegetation, and have made both laboratory and field studies using ¹³¹I to determine the behavior of iodine in the atmosphere and the interaction of this iodine with soil and vegetation and particulate matter in the air. The main concern of these workers has been how iodine is removed

from the atmosphere, and more specifically, the amount of radioactive ^{131}I which would be deposited on vegetation at various concentrations in the event of a nuclear accident. The most convenient way for these workers to obtain the information they were interested in was to measure deposition velocities of iodine onto various surfaces (mostly vegetation or vegetation-like surfaces). Therefore, they studied how various materials in the atmosphere or various surfaces exposed to the atmosphere may affect the deposition rate (or velocity) of iodine. The deposition velocity as measured in the atmosphere is given by

$$v_g = \frac{\text{wt. of I deposited (g/cm}^2\text{-sec)}}{\text{concentration of I in air (g/cm}^3\text{)}} \quad (7)$$

These workers have shown that the deposition velocities for iodine are from 0.5 to 1.0 cm/sec (some values as high as 2.8 have been reported but the accepted values, from the most recent work, are from 0.5 to 1.0 cm/sec). Their work is not directly related to the problem of iodine in a marine atmosphere, but from it, it is possible to gain information about the removal rate of iodine from the atmosphere.

Meteorologists have recently shown an interest in gaseous iodine in connection with the possible modification of our atmosphere by the formation of large concentrations of ice nuclei from air pollution products. Schaefer (1968a, 1969) has demonstrated evidence of such ice nuclei in clouds at and below inversions near large polluted cities. Schaefer (1966, 1968a, 1968b, 1969), Morgan (1967), and Hogan (1967)

have suggested that ice nuclei are formed by the reaction of elemental iodine vapor (I_2) and lead particles from automobile exhaust, and have shown that this reaction occurs in the laboratory.

Schaefer (1968a) has found that the burning of wood chips followed by the addition of auto exhaust will produce large concentrations of ice nuclei, and he has suggested that the combustion of such products releases sufficient quantities of iodine to produce ice nuclei in polluted areas. Hobbs and Locatelli (1969) have reported that ice nuclei concentrations were significantly higher downwind of a forest fire in the Cascade Mountains than they were upwind of the fire.

In addition to proposing that a pollution source for iodine may cause the formation of ice nuclei, Schaefer (1966, 1969) pointed out that in oceanic air, reported iodine concentrations of 50 to 500 ng/m^3 (Junge, 1963) would be several orders of magnitude larger than the amount of iodine required to react with the available lead particles in a polluted area if the iodine is $I_2(g)$. Schaefer (1969) suggested that quantitative measurements, both in the ambient atmosphere and in the laboratory, are required to understand how pollution is affecting the weather in our atmosphere.

From this discussion it is apparent that before a complete understanding of iodine in the maritime atmosphere (and to a lesser extent, in the terrestrial atmosphere) can be achieved,

the following must be investigated: The roles of both organic material and gaseous iodine must be investigated to determine the extent to which each of these factors are dictating the concentrations and behavior of iodine in particles and rain. Such an investigation requires that information about the source for iodine in the atmosphere be obtained. Also, information is required regarding the concentration of gaseous iodine (if any) and the possible interaction of this gaseous iodine with particles and rain as well as with various factors which may affect gaseous iodine concentration.

B. Geochemistry of Bromine

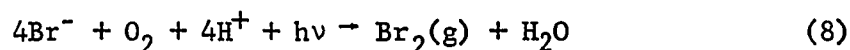
Environmental studies of bromine have not been nearly as extensive as those for iodine. The geochemical cycle of bromine appears to present none of the complex problems as does that of iodine. The bromine to chlorine ratio is very similar in almost all geochemical systems. Sugiura (1963) reported that volcanic springs and gases have a Br/Cl ratio of 1 to 4×10^{-3} , which is very close to the sea water value of the Br/Cl ratio, 3.4×10^{-3} , given by Harvey (1960). Similarly, Vinogradov (1959) reported that rocks and terrestrial water systems approximate the Br/Cl value of sea water. Vinogradov (1959) reported that bromine is concentrated in soils and ascribed this to the production of bromoorganic compounds since there is a strong correlation between bromine concentration and organic content of the soils. The bromine, however, is not nearly as concentrated with respect to chlorine as is iodine. The Br/Cl ratio in soils may be a few hundred times that of the Br/Cl ratio in sea water, while the

I/Cl ratio in soils is approximately 10^4 that of the sea water value. Vinogradov (1953) has shown that marine organisms will concentrate bromine, but again, not to the extent they concentrate iodine. Vinogradov gave bromine values in various marine organisms from about 0.05% to 0.08% by dry weight. Walters (1967) investigated the halogen content of marine sediments and found the Br/Cl ratio to be essentially the same as the sea water value.

Sill  n (1961), using thermodynamic data, has calculated that bromine in sea water will exist as bromide, and apparently this is indeed the case. Bromide is considered a major constituent of sea water with a concentration of 65 parts per million (ppm) and a Br/Cl ratio of 3.4×10^{-3} independent of depth and geographical position (Harvey, 1960; and Culkin, 1965). The fact that bromine in sea water exists only in one oxidation state and is uniformly mixed in the world's oceans probably accounts for the little scientific interest in it, compared to iodine.

Investigation of bromine in the atmosphere is meager when compared to iodine investigations. Marchand (1852) determined the bromine concentration of rain in France, and Behne (1953) analyzed rain in Germany for bromine. Dean analyzed bromine in rain and sea spray and found the Br/Cl ratios to be essentially the same as those for sea water. Duce et al. (1963, 1965, and 1967) studied the bromine concentration in rain and sea salt particles in conjunction with the iodine studies mentioned earlier, and found that the Br/Cl ratio of particles was about 2×10^{-3} which is slightly lower than the sea water value. Duce et al. (1965) suggested that a photo-

chemical oxidation of bromide was occurring and that $\text{Br}_2(\text{g})$ was released from the particles according to the following equation:



Duce et al. showed that the Br/Cl ratio in rain was equal to, or higher than the Br/Cl ratio of particles and suggested that the reason for this was that rain underwent a loss of gaseous chlorine. Investigating the Br/Cl ratio with respect to particle size, Duce et al. (1967) found that the Br/Cl ratio was variable, with a tendency for this ratio to be a minimum for particles of radius 1.2 to 0.6 μ .

Winchester et al. (1966) and Lininger et al. (1966) have shown that areas polluted by automobile exhaust contain a much higher concentration of bromine than does maritime air. This is explained by the fact that the ethyl fluid which is added to gasoline as an anti-knock agent contains lead, bromine, and chlorine in the relative weight ratios of 1:0.39:0.34. Bromine and chlorine are added to the gasoline to produce the volatile lead halides upon combustion, so that lead can be expelled from the engine. Rose (1962) reports that the lead compounds expelled in automobile exhausts are PbClBr , $2\text{NH}_4\text{Cl} \cdot \text{PbBrCl}$, and $\text{NH}_4\text{Cl} \cdot 2\text{PbBrCl}$.

Winchester et al. (1966) studied the pollution particle concentrations of lead, bromine, chlorine, and iodine in Fairbanks, Alaska (where the pollution lead particles are almost entirely the result of automobiles). They were able to determine a natural halogen background by collecting particulate samples outside of Fairbanks, at the University of Alaska in College, Alaska. Although iodine showed no significant variation in or outside of Fairbanks, particulate bromine

and chlorine were much higher in Fairbanks than in College. Examination of the lead to excess chlorine ratio (excess chlorine was that amount above the natural halogen background) showed that it was almost identical to the Pb/Cl ratio in gasoline. The lead to excess bromine ratio, however, was only about 1/2 to 1/3 the same ratio in gasoline. Oxidation of bromide to bromine by a photochemical reaction or by naturally occurring oxidants in the atmosphere such as ozone was suggested as the reason for the apparently low concentrations of particulate bromine. Loucks (1969) has shown that bromine apparently is released on very small particles upon combustion of gasoline and is then volatilized and redistributed throughout the stable aerosol particle size range. He suggested oxidation of Br^- to $\text{Br}_2(\text{g})$ by oxidants such as ozone. In a laboratory study, Pierrard (1968) has shown that PbBrCl can apparently lose $\text{Br}_2(\text{g})$ quite efficiently by exposure to ultraviolet irradiation.

The behavior of bromine in the atmosphere does not appear to be as complex and uncertain as is the case with iodine. There are, however, some questions which require answers before the complete cycle of bromine between the sea and air is known. Data is required concerning the concentration of gaseous bromine and factors (both meteorological and chemical) in the atmosphere which control this concentration.

C. Statement of the Problem

At the beginning of this work it was decided that a detailed investigation of both the role of organic material on iodine in the atmosphere, and a study of gaseous iodine concentration and the

various factors which affect it required more time and energy than was available. Thus it was decided to concentrate on the aspect of measuring gaseous iodine in the atmosphere.

While the principle interest in this work was the measurement of gaseous iodine in the atmosphere, the sampling and analytical technique eventually adopted also permitted the study of bromine, if desired. It was then decided to simultaneously measure gaseous iodine and bromine. It was hoped that in addition to gaining more detailed information about the behavior of bromine in the atmosphere, the measurement of gaseous bromine might also help to give a better understanding of the chemical and physical processes which gaseous iodine may undergo in the atmosphere. Since iodine and bromine are in the same group in the periodic table, they undergo similar chemical and physical changes. There are, however, differences in behavior which may give clues to the nature of the reactions which these elements undergo. For example, both iodine and bromine undergo similar oxidation and reduction reactions, yet iodine is more easily oxidized than is bromine. Likewise, there are differences in adsorption characteristics between I_2 and Br_2 , yet both can be adsorbed. Thus, any similarities and/or differences in the behavior of iodine and bromine in the atmosphere may permit a clue as to what chemical and/or physical processes are occurring (or not occurring) which might not be apparent if only one of these elements were being measured.

As a preliminary study, particulate samples were collected from the U. S. Coast and Geodetic Survey Ship Surveyor on a cruise from Kodiak, Alaska to Hawaii. A few investigators have reported very

high concentrations of iodine in the atmosphere, much different from those reported for Japan, Hawaii, and Alaska. Eggleton et al. (1965) have reported concentrations of iodine in the atmosphere in England ranging from 10 ng/m^3 to 1000 ng/m^3 with an average value of 100 ng/m^3 . Vinogradov (1959) reported values as high as $10,000 \text{ ng/m}^3$ in the Union of Soviet Socialist Republics. Paslawska and Ostrowski (1968a, 1968b) reported concentrations of airborne iodine to be in excess of 1000 ng/m^3 in air over the Baltic Sea. Details of the physical and chemical form of the iodine collected and of the sampling and analytical technique are unavailable. If these reported values are real, then geographical location may be a very important factor. Therefore, the reason for the Alaska to Hawaii cruise was to investigate a possible geographical dependence of particulate iodine in the atmosphere. Once the gas sampling apparatus was operational a cruise from Honolulu to Seattle aboard the U. S. Coast and Geodetic Survey Ship MacArthur was made for the same reason.

Duce et al. (1965) have been the only workers who have attempted to measure only gaseous iodine in the atmosphere. They used a bubbling device which operated in the following manner: Air was first drawn through a Millipore Filter to remove particulate matter. These workers recognized the fact that gaseous iodine might be sorbed by the filter, and therefore pretreated the filter by passing 50 m^3 of air through it prior to collecting any samples. These workers hoped that this pretreatment would saturate the filter with respect to gaseous iodine and bromine sorptions, as was known to occur for

gaseous chlorine (Junge, 1957). The air drawn through the Millipore Filter was then forced through a glass frit into a solution of K_2CO_3 . In addition to sorption of gaseous iodine on the filter the following problems were encountered: By using two bubblers in line it was found that this procedure was only about 60% efficient for gaseous iodine removal. The water from the solution evaporated rather rapidly due to the large volume of air passing through it and the workers attempted to compensate for this by periodically adding new water to the solution. In addition to the water loss by evaporation, some of the solution was lost due to the formation of spray by the violent bubbling which occurred as a sample was being collected. Although Duce et al. (1965) had spray traps mounted behind the bubbler, potassium analysis performed on the solution after the collection of a sample showed that a significant amount (approximately 15%) of potassium was still lost. Considering the problems Duce et al. (1965) encountered it was felt that some technique other than a bubbling arrangement was required. Investigation of the various possibilities of both particulate removal and of gaseous collection resulted in selecting an electrostatic precipitator as the method of particulate removal and activated charcoal as the method of gaseous collection.

In order to insure a collection of air from a source representative of the true maritime atmosphere two factors must be kept in mind. 1) It is necessary to collect samples from a position where the effects of vegetation, soil, and man (pollution) will not contribute to these samples. 2) It is also necessary to be in a position such that the air being sampled will not contain material resulting

from local surf conditions. Duce et al. (1965, 1967) have indicated that particulate samples collected in or near local surf zones can be significantly different from samples collected over the open ocean, and this is probably because the transfer of material to the atmosphere in surf zones occurs by a mechanism much different from that which occurs in the open ocean.

A tower approximately 20 meters high was constructed at Bellows Air Force Station on the windward shore of Oahu. Here, samples of air blowing from the open ocean could be collected, quite free of any contamination caused by land or man. The height of the tower was such that the material produced by the local surf zone would be carried by the wind inland and beneath the sampling platform at the top of the tower. This tower was used in conjunction with a recording anemometer which permitted one to know that the winds were onshore during the sampling period.

Samples were also collected at Hilo, Hawaii. Two gas collecting apparatus were constructed so that samples could be collected simultaneously at sea level and at various altitudes to determine the effect that altitude and distance from the sea might have on the concentration of gaseous iodine and bromine. Samples were collected in Honolulu simultaneously with those collected at Bellows Air Force Station to study the effect of distance from the sea and/or a pollution effect. Gaseous samples were collected in Cambridge, Massachusetts to investigate the possibility of a pollution source of iodine.

In addition to the gaseous samples, simultaneous cascade impactor samples were collected at Bellows Air Force Station, Oahu. These

samples were collected to study the relationship between gaseous and particulate iodine.

Thus, this work was designed to accomplish the following:

1. Develop a method which allows collection and analysis of only gaseous iodine and bromine.
2. Accurately measure the gaseous concentration of iodine and bromine in the marine atmosphere.
3. Examine this concentration of gaseous iodine and bromine with geographical position.
4. To a limited extent, measure how well the atmosphere is mixed with respect to gaseous iodine and bromine concentrations.
5. Investigate the relationship between gaseous and particulate iodine and bromine as well as any relationship between gaseous iodine and bromine and meteorological parameters.
6. Investigate the possibility of a pollution source of iodine and the relationship of gaseous iodine to the particulate matter associated with a polluted atmosphere.

From this information it was hoped that details concerning the following points might be obtained:

1. An indication of the source or sink for iodine and bromine in the atmosphere and the physical or chemical processes which give rise to this source and sink in the marine atmosphere.
2. An estimation of the length of time that iodine and bromine exist in the atmosphere, and hence, an estimation of the production rate of these elements.

3. An indication of chemical or physical interactions between gaseous iodine and pollution particles, which in turn may give an indication of the potential for weather modification.

II. EXPERIMENTAL PROCEDURE

Gaseous iodine and bromine samples were collected by passing air through an electrostatic precipitator to remove the sea salt particles, and then through precleaned activated charcoal. Particulate samples were collected by filtration and by use of a six stage cascade impactor.

A. Electrostatic Precipitator

It was realized at the beginning of this work that in order to obtain accurate measurements of gaseous iodine and bromine in the atmosphere it was necessary to first remove the particulate matter from the air which was to be sampled. Three methods of particulate removal from the air were considered: filtration, impaction, and electrostatic precipitation. Filtration was ruled out because of possible loss of gaseous iodine and bromine due to adsorption or to reaction with the filter material as the air passed through it. It was determined that any impaction system which would effectively remove all the atmospheric particulate matter would have a flowrate which was too low.

An electrostatic precipitator was chosen since such a device can be operated without exposing the air to be sampled to large surface areas which might adsorb gaseous iodine and bromine, and because higher flow rates can be used with this instrument than with an impaction instrument.

Rose and Wood (1966) have presented a detailed study of electrostatic precipitators. Basically, an electrostatic precipitator consists of two electrodes: a charging electrode and a collector

electrode. The charging electrode is a wire charged (either positively or negatively) to a voltage at which a corona discharge occurs. The corona ionizes the air molecules (N_2 and O_2) which are then attracted toward the collector electrode. The collector electrode is either grounded or charged oppositely to the charging electrode. The result of such an arrangement is a flow of ions from the charging electrode to the collecting electrode. When air containing particulate matter is passed between these electrodes, the charged ions collide with and attach themselves to the particulate matter. Thus, the particulate matter becomes charged and is attracted to the collector electrode and is removed from the airstream. The charging and collection electrodes can be arranged in a variety of ways: The charging wire can be surrounded by a tube which is the collector electrode (wire in tube type), there can be a series of charging wire separated by parallel collector plates (parallel plate type), or the charging wire can be followed by collecting plates (two stage type). Modifications of these designs are also used. For this work the wire in tube type precipitator was used since this is the simplest type to construct and the air flow through this instrument approaches streamline flow. Rose and Wood (1966) show that the efficiency with which particulate matter can be removed from an airstream by electrostatic precipitation is a function of flow rate, strength of the electric field, conductivity of the particulate matter (or the charge which the particulate matter can attain), size of the particulate matter, ion mobility in the electric field, and precipitator length and radius.

An electrostatic precipitator was constructed such that a charcoal trap could be mounted at the air exit. Figure 1 shows a schematic diagram of this instrument. The collector electrode was made from 1.35" i.d. type 304 stainless steel pipe 7" in length, which was threaded at each end. Teflon collars were constructed to mount on either end of the collection tube. The center charging wire was 0.01" diameter tungsten wire which was mounted on brass rods through the teflon collars. The brass rods also served as electrical connections to the high voltage power supply. The teflon collar at the exit end of the precipitator was machined such that a pyrex tube which contained the activated charcoal could be attached by means of an "O-ring" seal and clamp. Two such units were constructed. Additional teflon collars were prepared so that either a stainless steel 47 mm Millipore Filter holder or the cascade impactor could be attached to the precipitator.

The precipitator was operated at a positive voltage of 11,000 volts and at a current of 0.3 ma. Rose and Wood (1966) have reported that a positive discharge produces less ozone than a negative discharge. One of the major concerns was that ozone produced by the discharge might react with either gaseous iodine and bromine or react with particulate iodine and bromine resulting in the measured concentration of gaseous iodine and bromine being different from the actual air concentrations of these species. Laboratory tests (see Appendix A) showed that these reactions produced only a very minor alteration in the concentration of gaseous iodine and bromine. A portable variable high voltage power supply (Model UHP15P10, Spellman High Voltage Corporation, New York) was used to operate the precipitator.

The gaseous iodine and bromine samples were collected by pulling air through the precipitator and over the charcoal by use of a vacuum pump at a flowrate of 1.0 - 1.5 m³/hr.

B. Activated Charcoal

Activated charcoal is well known as an excellent quantitative absorbing medium for small quantities of gaseous iodine and bromine compounds. Since carbon does not form radioisotopes to any extent when irradiated with thermal neutrons, activated charcoal offers the advantage of direct neutron irradiation of iodine and bromine while they are still adsorbed to the charcoal. Thus, gaseous halogen samples collected on activated charcoal require only a minimum of handling and the chances for sample contamination are small.

The largest problem encountered in attempting to use activated charcoal for this work was obtaining activated charcoal with low enough iodine and bromine blanks to be usable. Various samples of activated charcoal from several sources were obtained and the iodine and bromine content of these samples were determined by neutron activation. Most samples contained parts per million amounts (by weight) of iodine and bromine and it was felt that these blanks were prohibitively high. One type of charcoal (coconut shell, Type AC, 8-12 mesh, Barnebey-Cheney Activated Charcoal Company, Columbus, Ohio) had iodine concentrations between 50 and 300 parts per billion and bromine concentrations between 500 and 1,000 parts per billion.

To improve the halogen blanks, several methods of cleaning the charcoal were investigated. These investigations included washing

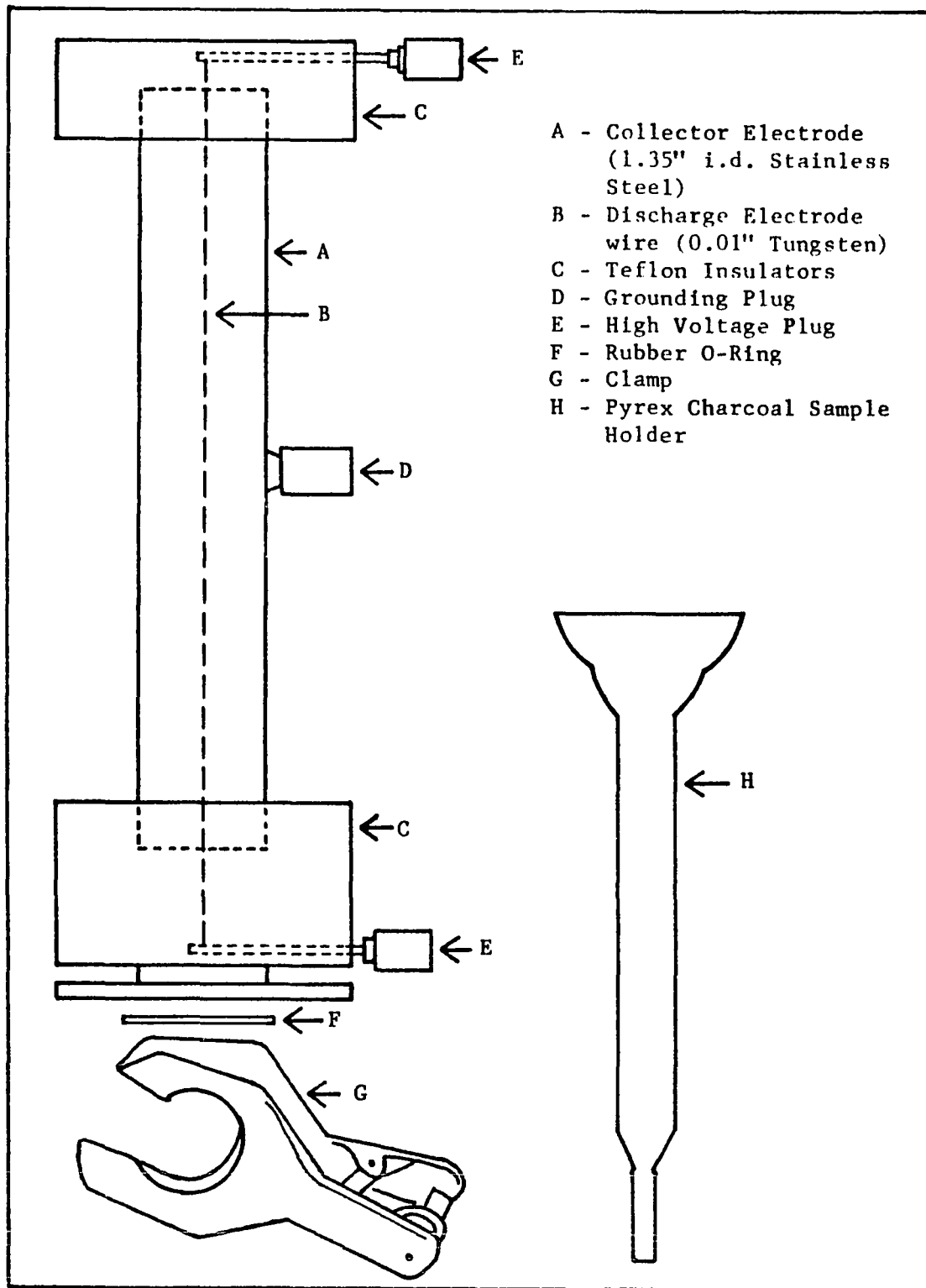


Figure 1. Schematic View of Electrostatic Precipitator

the charcoal with hot concentrated HNO_3 , washing with basic solutions, heating in an inert atmosphere, and heating under a high vacuum. All washing techniques proved either to raise the blank or show no improvement. It was found that heating the charcoal in a helium atmosphere to 600°C resulted in a reduction of the iodine and bromine blank by about a factor of two. Heating the charcoal to approximately 750°C under a high vacuum (approximately 10^{-5} cm Hg) proved to be an extremely effective method of reducing the blanks. The charcoal blanks for iodine and bromine were lowered by one to two orders of magnitude as a result of the vacuum heat treatment. Table I shows typical iodine and bromine concentrations (in units of 10^{-9} g per gram of carbon) of Barnebey-Cheney Type AC 8-12 mesh coconut shell activated charcoal both before and after the vacuum heat treatment.

The charcoal was cleaned and handled in the following manner: Approximately 100 g of activated charcoal (8-12 mesh Barnebey-Cheney Type AC) were placed in a quartz tube and attached to a high vacuum system. The pressure of the system was lowered to approximately 10^{-5} cm Hg. The temperature of the charcoal was then raised in 50° increments once a day, and heating continued until a temperature of 750°C was attained. This temperature was held for one week, and was then lowered slowly (25°C per hour) to ambient laboratory temperature. An activated charcoal trap was placed on the vacuum system before it was opened to the atmosphere. This was done to adsorb any gaseous iodine and bromine in the laboratory air before the air reached the cleaned charcoal. (A sample of the air in the laboratory used for this work showed an iodine concentration of 700 ng/m^3 and a bromine concentration of approximately

Table I

Iodine and Bromine Concentrations of Barnebey-Cheney
AC Activated Charcoal Before and After Vacuum Treatment

<u>Sample</u> [*]	<u>Iodine (10⁻⁹ g/gC)</u>	<u>Bromine (10⁻⁹ g/gC)</u>
1. Untreated	256	702
Treated	3.5	4.7
Treated (duplicate)	5.8	7.2
2. Untreated	61.2	800
Treated	6.5	11.7
3. Untreated	104	946
Treated	2.5	16.7

*

Samples listed are from different 1 pound bags of charcoal obtained from Barnebey-Cheney Activated Charcoal Company, Columbus, Ohio. Different numbered samples were treated at different times.

100 ng/m³.) After opening the vacuum system to the atmosphere the charcoal was immediately transferred to a clean vacuum desiccator (no desiccant). A vacuum was drawn on the desiccator and the charcoal was stored in this manner until it was used for sample correction. When the desiccator was opened to the atmosphere to remove the charcoal, an activated charcoal trap was placed on the air inlet to clean the air before it entered the desiccator. After removing enough charcoal for a sample, a vacuum was again drawn on the desiccator.

For this work five different batches of charcoal were prepared by the vacuum heat treatment. From each batch of charcoal one blank charcoal was packaged for analysis for every 5 to 6 samples (each batch was sufficient for approximately 25 samples). The blank concentrations of iodine and bromine for each batch are given in Table II. The blank concentrations from batch to batch vary by more than a factor of three for both the iodine and the bromine. However, the blank concentrations of samples within an individual batch are generally in good agreement.

C. Cascade Impactor

A six stage cascade impactor (Model CI-S-6, Scientific Advances Company, Columbus, Ohio) was used in this work to study the relationship between gaseous and particulate iodine and bromine. With this instrument, particles of 6 different size ranges can be collected. The cascade impactor is a successive series of six jets: each jet is smaller in area than the previous jet and each jet is followed by an impaction slide. Figure 2 shows a schematic repre-

Table II

Iodine and Bromine Concentrations of Charcoal Blanks

Batch No.	Blank No.	Iodine (10^{-9} g/gC)	Bromine (10^{-9} g/gC)
1.	B	4.1	15.9
	BB	4.0	18.1
	H2B	3.7	19.6
	H2A	5.9	13.3
	H11B	3.2	7.5
Average and Std. Dev.		4.2 ± 1.1	14.9 ± 4.8
2.	B8B	12.4	19.1
	B11B	16.2	22.7
	B28B	15.7	18.8
	B33B	9.9	8.4
	L10A	8.0	17.1
Average and Std. Dev.		12.5 ± 3.4	17.2 ± 5.3
3.	L12A	5.6	4.4
	B52B	4.2	6.9
	L14A	5.5	6.7
	B69B	5.5	6.0
Average and Std. Dev.		5.2 ± 0.7	6.2 ± 1.1
4.	B70B	3.1	6.7
	B73B	2.5	4.9
	B4A	2.3	4.8
Average and Std. Dev.		2.6 ± 0.4	5.5 ± 1.1
5.	M1B	5.6	17.7
	M13B	6.4	13.4

sentation of two of the six stages. As an airstream is pulled through the instrument by use of a vacuum pump, the velocity of the air is increased as it passes through a jet. Immediately after exiting from a jet, the air is slowed down and curves around the impaction slide as shown in Figure 2. A particle in the airstream will have momentum imparted to it by the airstream as it is accelerated through the jet. Leaving the jet, the particle will be subject to the axial momentum provided by the acceleration through the jet and the radial momentum which is provided by the airstream as the particle curves around the impaction slide. If the axial momentum (which is dependent upon the mass of the particle and the velocity of the airstream through the jet) is sufficient, the particle will bend away from the airstream enough to be impacted on the slide. If the particle is not impacted it will be carried by the airstream to the next jet which is smaller and hence supplies a greater acceleration and momentum than was the case in the previous jet. This process continues until the particle attains enough momentum to be impacted on one of the slides. Efficiency curves for each stage of the cascade impactor versus particle radius (at unit density) are reproduced in Figure 3. The impactor used in this work was constructed such that a given stage will collect particles of one-half the radius of the particle collected on the previous stage, with equal efficiency.

For this work it was necessary to realize that both the density and radius of a particle are a function of the relative humidity. Relative humidity changes, either during collection of a sample or

from sample to sample, could shift the efficiency curves shown in Figure 3. Ranz and Wong (1952) have shown that the collection efficiency for any particle is a function of the particle radius and the square root of the particle density:

$$n_j = K r \sqrt{\rho} \quad (9)$$

where

n_j = fractional efficiency of jet j for collecting particles
of radius r and density, ρ

r = radius of particle, (cm)

ρ = density of particle, (g/cm^3)

K = impactor constant ($\text{cm}^{1/2}/\text{g}^{1/2}$) which is a function of the diameter of jet j, the velocity of air through jet j, and air viscosity. It is constant when a uniform flowrate of air is used.

The density of a sea salt particle in the atmosphere will change from 1.0 g/cm^3 at 100% relative humidity to about 1.2 g/cm^3 at a relative humidity of 70% (assuming the particle is still liquid). At approximately 70% relative humidity, a particle can undergo a phase change from liquid to solid and this phase change is accompanied by a change in particle density from 1.2 to 2.2 g/cm^3 . The size of particle any jet will capture at a fractional efficiency of 1.0 at densities different from 1 g/cm^3 will then be given by:

$$r_{1.0}(\rho) = r_{1.0}(\rho=1) / \sqrt{\rho} \quad (10)$$

where

$r_{1.0}(\rho)$ = radius of particle with density ρ captured with an efficiency of 1.0, (cm)

ρ = density, (g/cm³)

$r_{1.0}(\rho=1)$ = radius of particle with unit density captured with an efficiency of 1.0 (cm) (obtained from Figure 3).

Under the sampling conditions encountered in this work, the relative humidity varied from about 90% to 60% (or the density changed from approximately 1 to 2.2). From equation (10) it is seen that the radius of particles collected on a given slide at a given fractional efficiency would change by a factor of approximately $(1/\sqrt{2.2})$, or 0.7. However, the radius of a particle also changes with changing relative humidity. Woodcock (1952) has shown that the radius of a sea salt particle will decrease by a factor of about 2.3 as it changes from a liquid drop to a solid salt particle (relative humidity less than 70%). Thus a particle collected at a relative humidity below 70% on a given stage at a given fractional efficiency will be equivalent to 1.6 times (0.7×2.3) a particle collected at unit density (from equation (10)).

Consider, for example, the shaded efficiency curve for slide D on Figure 3. It is seen that at unit density, stage D will capture particles of 1.25 μ radius with a fractional efficiency of 1.0. The radius of a dry salt particle of density 2.2 g/cm³ captured on stage D with a fractional efficiency of 1.0 will be, according to

equation (10), 0.88μ . This same dry particle of 0.88μ radius, however, would have a radius of 2.0μ (0.88×2.3) at a relative humidity of 90%. Thus, stage D will capture with a fractional efficiency of 1.0, those particles whose radii at 90% relative humidity would be between 1.25 and 2μ , depending on the relative humidity of the sampling period. Throughout this dissertation, particle sizes of different stages are referred to as those particles of unit density captured with a fractional efficiency of 1.0, as shown in Figure 3.

D. Sample Handling and Packaging

All samples and standards were prepared and packaged in Honolulu and stored in a freezer until they were taken to the Massachusetts Institute of Technology for analysis.

For the charcoal samples, approximately 2.5 g of cleaned charcoal were taken from the vacuum desiccator and were sealed in a clean polyethylene bag. This bag was carried to the sampling location and opened, and the charcoal was transferred to a pyrex sample holder which was then clamped onto the exit end of the electrostatic precipitator (see Figure 1). After completion of sample collection, the charcoal was transferred to a clean polyethylene bag, sealed, and returned to the laboratory. The charcoal was transferred to and heat sealed in a 2 dram polyethylene vial which had been previously cleaned in HNO_3 and distilled demineralized water. This vial, along with two chloride standards (flux monitors), was placed in a clean 4 dram polyethylene vial, which was heat sealed and then stored in a freezer. Charcoal blanks

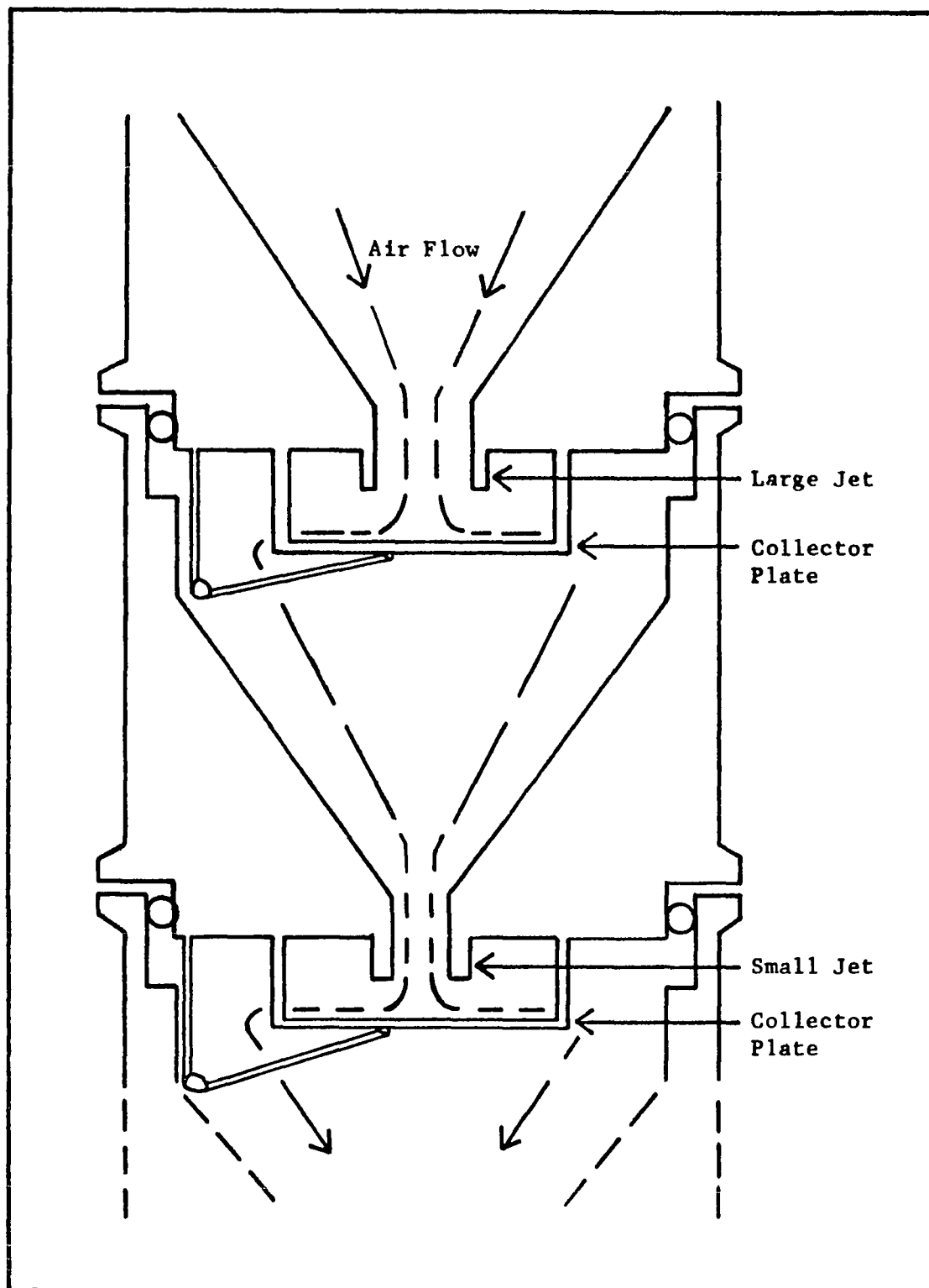


Figure 2. Schematic View of Two of the Six Stages of the Scientific Advances Inc. Cascade Impactor, Model CI-S-6

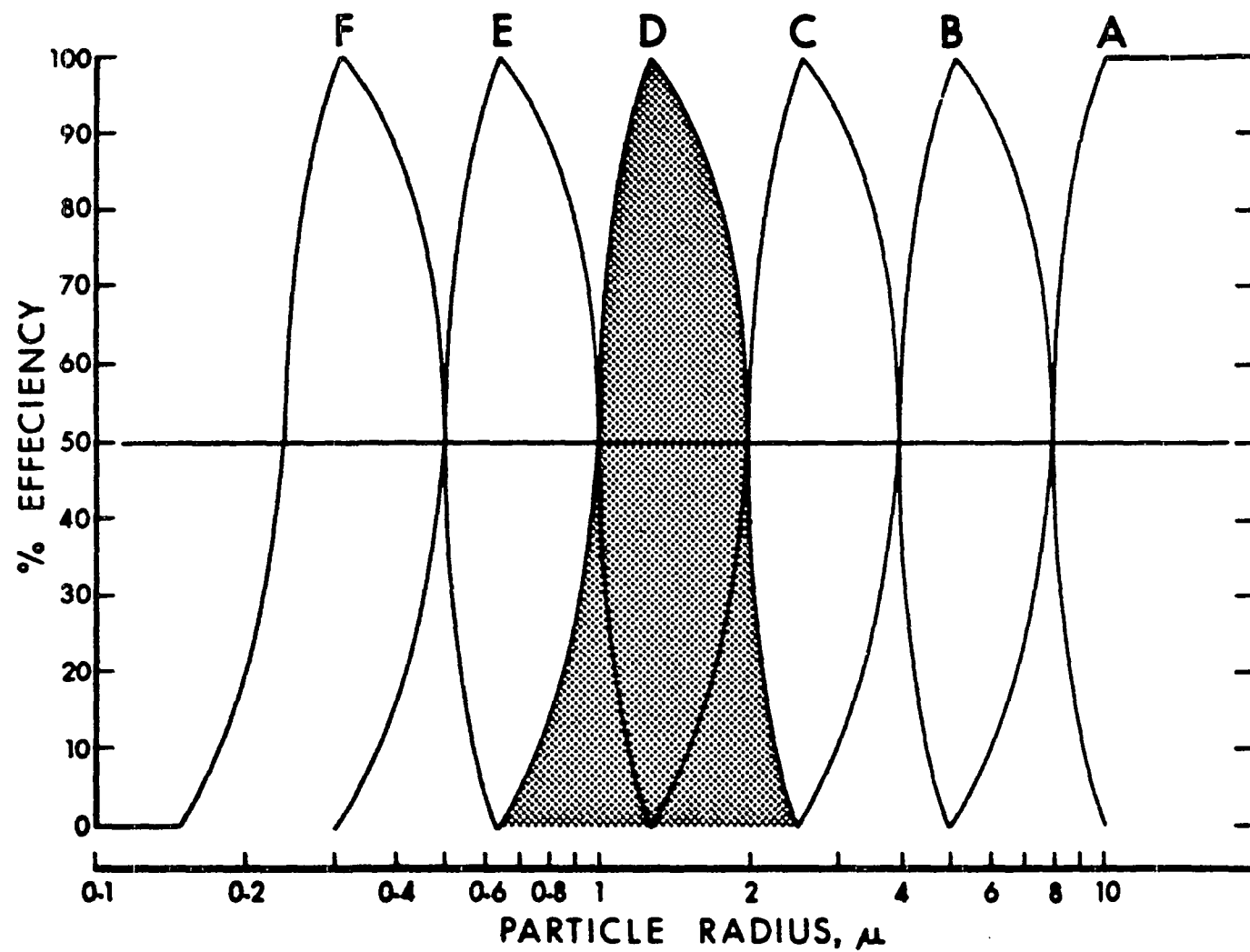


Figure 3. Collection Efficiencies of Each Stage of Scientific Advances Inc. Cascade Impactor, Model CI-S-6, for Particles of Unit Density

were prepared periodically for each batch of charcoal. The blanks were treated in exactly the same manner as were the samples (i.e., carried to the sampling location, transferred to the holder, returned to the laboratory, and sealed in a vial). Approximately one blank per five or six samples was prepared.

For the cascade impactor samples circular glass slides were used as impaction stages. The slides were cleaned in hot HNO_3 and washed with distilled demineralized H_2O . The slides were loaded in the impactor in the laboratory. The impactor was sealed from the air with clean polyethylene bags and carried to the sampling site. After completion of sample collection the impactor was again sealed in a polyethylene bag and returned to the laboratory. The slides were removed and the samples on each slide were quantitatively removed with 0.1 ml - 0.2 ml of distilled demineralized H_2O . The solution was transferred to and heat sealed in a small clean polyethylene vial (made from 0.2 cm polyethylene tubing) which was then heat sealed along with two chloride standards in a clean 4 dram polyethylene vial and stored in a freezer.

After collection of filter samples, the Millipore Filters were cut up on a clean glass slide and transferred to a 2 dram polyethylene vial which was heat sealed. This vial, along with two chloride standards, was put in a clean 4 dram polyethylene vial, which was heat sealed and stored in a freezer.

Chloride, iodide, and bromide standards were prepared by dissolving an appropriate weight of dried potassium salt in distilled demineralized water to give solutions for Cl^- , Br^- , and I^- of

1,000 ppm, 200 ppm, and 200 ppm, respectively. Small polyethylene vials made from 0.2 cm polyethylene tubing were cleaned with HNO_3 , distilled demineralized water, and rinsed with the standard which was to be packaged. One hundred to 200 μl of standard solution were heat sealed in the small vial.

E. Analytical Procedure

All halogen samples were analyzed by thermal neutron activation analysis using the reactor facilities at the Massachusetts Institute of Technology in Cambridge, Massachusetts. Neutron activation analysis is an extremely sensitive technique for the quantitative determination of chlorine, bromine, and iodine. The sensitivities of these elements are given by:

$$w = MD / \phi \sigma A F (1 - e^{-\lambda t}) \quad (11)$$

where

w = weight of halogen

M = atomic weight of halogen

D = disintegration rate, (dps)

ϕ = thermal neutron flux, ($\text{n cm}^{-2} \text{ sec}^{-1}$)

σ = halogen cross section for thermal neutron capture, (cm^2)

A = Avogadro's number

F = fractional abundance of halogen species undergoing
neutron capture

λ = decay constant, (min^{-1})

t = irradiation time, (min)

The M.I.T. reactor has a flux of $2.3 \times 10^{13} \text{ n cm}^{-2} \text{ sec}^{-1}$. The irradiation time for this work was 20 minutes, and if it is assumed that the minimum activity which can be measured is 10 dps, then the halogen sensitivities for this work, according to equation (11) are:

$$^{38}\text{Cl} = 6.1 \times 10^{-10} \text{ grams } (\beta, \gamma, t_{1/2} = 37.3 \text{ minutes})$$

$$^{80}\text{Br} = 0.25 \times 10^{-10} \text{ grams } (\beta, \gamma, t_{1/2} = 18 \text{ minutes})$$

$$^{80\text{m}}\text{Br} = 8.7 \times 10^{-10} \text{ grams } (\beta, \gamma, t_{1/2} = 4.5 \text{ hours})$$

$$^{128}\text{I} = 0.33 \times 10^{-10} \text{ grams } (\beta, \gamma, t_{1/2} = 25 \text{ minutes})$$

(Also listed above are the radioactive isotopes produced, the modes of decay, and half-lives.)

For the liquid samples (i.e., cascade impactor samples) the procedure used was that reported by Duce and Winchester (1965). The irradiation vial was opened immediately after irradiation and the Cl, Br, and I were separated by using selective oxidizing and reducing agents, solvent extraction, and precipitation. The purified halogens were then counted along with a chloride standard (or flux monitor) for gross beta activity on a low background, anticoincidence, gas flow proportional counter in conjunction with an automatic sample changer and timer.

For the charcoal samples, Duce and Winchester's (1965) procedure was modified slightly. Duce and Winchester used bromide and iodide carriers to separate the radioisotopes of bromine and iodine. To facilitate chemical exchange between the inactive carrier and the radioactive sample halogen, they oxidized the carrier bromide and iodide to bromate and periodate, and then

reduced the oxidized species back to bromide and iodide. In this work, it was found that iodide and bromide are difficult to oxidize while in the presence of charcoal, and it was necessary to use bromate and periodate as the carriers.

Immediately after irradiation the vial containing the charcoal was cut open and the charcoal was quantitatively transferred to a hot solution of 5 ml 1 M NaOH containing IO_3^- and BrO_3^- carriers (AgI and AgBr equivalents of 50.00 mg each) and one or two drops of 5% NaClO. The solution was allowed to digest for 1 to 2 minutes on a hot plate; distilled H_2O was added periodically to prevent the solution from boiling too vigorously. The flask was then removed from the hot plate and allowed to cool for 1-2 minutes. The solution was acidified to phenolphthalein with 16 M HNO_3 , and while still in the presence of the charcoal, the periodate and bromate were reduced to iodide and bromide with the dropwise addition of 0.05 M $\text{Na}_2\text{S}_2\text{O}_5$. The solution was then filtered through a 24 mm Millipore Filter (Type HA) and made basic to phenolphthalein with 12 M NaOH. It is important to filter the solution while acidic. If the solution is basic, the Millipore Filter (Type HA) is saponified and, under these conditions the solution is filtered extremely slowly. The pH was then adjusted to 4 with the addition of approximately 2 ml of acetic acid and the solution was transferred to a separatory funnel containing 20 ml of CCl_4 . From this point, the procedure followed is that described by Duce and Winchester (1965).

Millipore Filter samples were irradiated while still on the filter. After completion of irradiation the vial was opened and

the Filter was transferred to a 125 ml Erlenmeyer flask containing 10 ml of I^- and Br^- carrier. The flask was heated slightly, swirled, and the contents were filtered through a 25 mm glass fiber filter. From this point, the I, Br, and Cl separations were carried out according to the procedure of Duce and Winchester (1965).

F. Estimation of Errors

The atmospheric concentrations of halogens reported in this work generally have uncertainties of about $\pm 10\%$. The concentration uncertainties are the result of four separate uncertainties which are encountered in the course of collecting and analyzing the samples. These uncertainties are:

1. Analytical error which includes transferring, pipetting, and filtering of samples during sample analysis.
2. Counting statistics error, which is equal to the square root of the number of counts obtained for each sample.
3. Blank correction error, which is the uncertainty of the blank correction which has to be made for each sample.
4. Flow volume error, which is a result of the uncertainty of the reading of flowrates on the vacuum pumps used for sample collection.

Duce and Winchester (1965) reported that the analytical error in the procedure used for sample analysis for this work was about $\pm 4\%$. In general, counting errors contributed very slightly to the overall concentration uncertainty in this work. Both the Millipore Filter samples and charcoal samples had counting rates corresponding to an uncertainty of 0.5% or less. Some of the

cascade impactor samples had low counting rates and for these samples the counting uncertainty could be as high as 6-7%. Blank correction errors were variable (depending on the amount of sample collected), but generally were approximately 5%. Again, for some of the cascade impactor samples the blank uncertainty could be as high as 50-75%. A flowrate uncertainty of $\pm 5\%$ was assigned to all samples reported in this work.

III. RESULTS

The data obtained in this study are given in Tables III to XI. Figures 4-6 show sampling locations and Figures 8-33 show the relationships (or lack of relationships) noted in this work.

All concentrations reported in the tables of data are $\pm 10\%$ unless otherwise indicated. Concentration ratios are $\pm 15\%$ except where the individual concentrations making up the ratio have an uncertainty greater than 10% . The ratio uncertainty is obtained by the following.

$$\text{If } R = x/y \quad (12)$$

$$\text{then } U_R = \% \text{ uncertainty of ratio} = \sqrt{U_x^2 + U_y^2} \quad (13)$$

where

$$U_x \text{ and } U_y = \% \text{ uncertainties of } x \text{ and } y \text{ respectively.}$$

Table XI gives a summary of the averages and standards deviations of gaseous iodine and bromine concentrations obtained at various locations and times.

Table XII is a summary of averages, standard deviations, standard error of least square regression lines, and correlations coefficients of the various graphs which are presented. All graphs are presented with the best fit least square regression line included for consistency, although in many cases the correlation coefficients do not warrant the addition of this line.

The statistical data for the various figures presented in Table XII have been obtained for linear least square analysis using the IBM 360-65 computer in conjunction with the IBM 1401 computer and "Cal-Com plotter" at the University of Hawaii. The program for the

calculations and the plotting of data is presented in Appendix B.

The formulae and notations used to obtain the statistical data in

Table XII are (Mills, 1955):

$$\bar{x} = \text{average value of } x = \Sigma x/n \quad (14)$$

where n = number of observations

$$\sigma_x = \text{standard deviation of } \bar{x} = \sqrt{\Sigma(x-\bar{x})^2/(n-1)} \quad (15)$$

$$\bar{y} = \text{average value of } Y = \Sigma y/n \quad (16)$$

$$\sigma_y = \text{standard deviation of } \bar{y} = \sqrt{\Sigma(y-\bar{y})^2/(n-1)} \quad (17)$$

A best fit regression line of the form

$$y = a + bx \quad (18)$$

where a = y intercept

and b = slope of the line

is obtained. For this the simultaneous equations

$$\Sigma(y) = na + b\Sigma(x) \quad (19)$$

$$\text{and } \Sigma(xy) = a\Sigma(x) + b\Sigma(x^2) \quad (20)$$

are solved. In all plots presented in this dissertation, x is arbitrarily defined as the independent variable and y as the dependent variable. The standard error of estimate of the regression line, $s_{y.x}$, (analogous to the standard deviation of the regression line) is given by

$$s_{y.x} = \sqrt{\Sigma(y^2) - a\Sigma(y) - b\Sigma(xy)}/n \quad (21)$$

The correlation coefficient, $r_{y.x}$, is then obtained according to:

$$r_{y.x} = \sqrt{1 - s_y^2/s_{y.x}^2} \quad (22)$$

$$\text{where } s_y^2 = \sqrt{(y-\bar{y})^2/n}$$

By convention $r_{y.x}$ is assigned the same sign (i.e., + or -) as the slope of the regression line, b . According to equation (22), $r_{y.x}$

will have a value between 0 and 1.0, and the degree of correlation between x and y improves as $r_{y.x}$ approaches unity. In this dissertation the following definitions have been arbitrarily assigned:

1) when $r < 0.6$, no correlation exists between x and y; 2) when $0.6 < r < 0.7$, the correlation is questionable; and 3) when $r > 0.7$, a correlation between x and y is strongly suggested.

A. Bellows Air Force Station, Oahu Samples

1. Gas Samples

The data for the tower samples collected at Bellows Air Force Station on the windward side of Oahu are presented in Table III. Also reported in this table are the atmospheric particulate sodium concentrations, which were determined in a study independent of this work (Hoffman, 1970). The samples used for sodium analysis were collected of 8" x 10" Delbag filters (Type 99/97 Micro-sorban, manufactured by Delbag Luftfilter, GmbH., Berlin) using a high volume Hurricane Air Sampler (Model 16003, manufactured by Gelman Instrument Co.) at the same location as were the gaseous iodine and bromine samples. Sodium analyses were performed by atomic absorption spectrophotometry using a Perkin-Elmer 303 Atomic Absorption Spectrophotometer. Details of the sodium analyses are given by Hoffman (1970). Table III is constructed such that the numbers in parentheses are the average concentrations of gaseous iodine and bromine which would have been obtained if a single sample had been collected during the same sampling period as the sodium samples. These averages are not the arithmetic means of the reported values for the individual samples.

Two factors cause this deviation from the arithmetic mean:

1) there are small fluctuations in flow rates of individual samples and 2) the collection times for the individual samples vary. There are two possible methods of obtaining the average concentrations: 1) simply average the individual concentrations; 2) sum the total amount of iodine or bromine collected in each sample and divide by the sum of the total volume of air sampled. In case 1), since the individual samples were not collected for the same period of time, the calculated average will be different from the real average. In case 2) flow rate fluctuations between individual samples will result in the calculated average differing from the real average. To compensate for these factors the average concentrations for iodine and bromine (in parentheses in Table III) were obtained in the following way:

let C_1 and C_2 = concentration of iodine (or bromine) for samples 1 and 2, respectively;

and T_1 and T_2 = collection time of samples 1 and 2, respectively;

and if $\bar{C}$ = concentration of iodine (or bromine) for the time period T_1 and T_2 ;

then

$$\bar{C} = \frac{C_1 T_1 + C_2 T_2}{T_1 + T_2} \quad (24)$$

and in the general case of more than two samples the average concentration, $\bar{C}$, is given by:

$$\bar{C} = \frac{\sum_{i=1}^n (C_i T_i)}{\sum_{i=1}^n (T_i)} \quad (24a)$$

where n is the number of individual samples. Use of equation (24) eliminates the variations between real and calculated concentrations due to flow rate fluctuations and to sampling time differences.

Samples B12B to B51B have uncertainties of $\pm 15\%$ for the iodine concentrations unless otherwise indicated. The larger uncertainties in these samples are due to the fact that this particular batch of charcoal had a higher iodine blank than that found for the other batches used in this work.

Figure 8 shows the day to day variation of gaseous iodine and bromine concentrations. Examination of the data shows that gaseous iodine and bromine do not appear to be correlated. This is seen in Figure 9 which shows a plot of gaseous iodine concentration versus gaseous bromine concentration, with a correlation coefficient of 0.18, as given in Table XII. However, this lack of correlation may be misleading, since sample to sample fluctuations in the gaseous iodine and bromine concentrations tend to be similar. Examination of Table III shows there is a tendency for the bromine concentration to rise and fall as the iodine concentration rises and falls. Admittedly, the degree to which the bromine concentration changes as the iodine concentration changes is highly variable. However, the fact that the iodine and bromine concentrations change in the same way (although the degree to which each is affected is inconsistent) may indicate

more correlation between gaseous iodine and bromine than Figure 9 suggests. The relationship of gaseous iodine and gaseous bromine over two periods of time can be examined in Figures 10 and 11. Figure 10 shows the concentration of gaseous iodine versus the gaseous bromine concentration from July 4, 1969 to July 25, 1969, while Figure 11 is a similar plot for the time period July 26, 1969 to August 9, 1969. Figures 10 and 11, along with the statistical data in Table XII show the interesting fact that there is a significant difference in the average bromine concentrations between the two time periods (the average iodine concentrations are approximately equal). For the time period July 4, 1969 to July 25, 1969, the average bromine concentration $38.1 \pm 9.1 \text{ ng/m}^3$ and for the time period July 26, 1969, the concentration is $55.0 \pm 11.3 \text{ ng/m}^3$. There is also an indication that the correlation between gaseous iodine and gaseous bromine concentration is improved (at least for Figure 10 where $r_{y.x} = 0.58$) when one does not look at the data as a whole. These facts may suggest that both gaseous iodine and bromine are affected in approximately the same manner by short term (i.e., day to day) meteorological variations. In addition to these short term fluctuations in gaseous iodine and bromine concentrations, it appears that the gaseous bromine concentration in the atmosphere undergoes gradual, or long term variations which are not evident for gaseous iodine. It is uncertain why this should occur, but differences in residence time for gaseous bromine and iodine may at least partially account for these changes. If, for

example, gaseous bromine has a longer residence time than does gaseous iodine, it might then be expected that when conditions in the atmosphere favored a decrease of gaseous iodine and bromine concentrations, the bromine would be removed at a slower rate than would iodine (due to bromine's longer residence time, which is also a measure of either the atmospheric removal or addition rate).

Figures 12 and 13 are plots of gaseous iodine and bromine concentrations versus particulate sodium concentration. The particulate sodium concentration should be a monitor of the total mass of sea salt in the atmosphere, and graphs of gaseous iodine and bromine versus particulate sodium will show if there is a correlation between gaseous iodine and bromine and the weight of sea salt particles in the atmosphere. Such a correlation might be expected if the sea salt particles are either a source or a sink for gaseous iodine and bromine. Figures 12 and 13 show that neither gaseous iodine nor bromine appear to be dependent on the sodium concentration; the correlation coefficients from Table XII are -0.08 and -0.17 for Figures 12 and 13, respectively. This indicates that if the sea salt particles are either a source or a sink for gaseous iodine and bromine, the interaction (at least on a short-term scale) between gas and particle is so small that any interdependence cannot be seen.

Table III includes local wind data which was obtained by using a recording anemometer (Kahlsico Mechanical Anemograph Model 02Am100 manufactured by Kahl Scientific Instrument

Corporation). It was hoped that these measurements along with data from daily surface weather maps might provide information on how various meteorological factors (i.e., wind speed, wind direction, and trajectory) could affect the gaseous iodine and bromine concentrations. Daily weather charts of the northern Pacific Ocean were obtained from the U. S. Weather Bureau in Honolulu. Figure 7 shows the average weather pattern for the northern Pacific Ocean for the month of July. In addition to the information on Figure 7, daily charts show positions of ships which report wind speed and direction. Four charts per day are prepared in six hour intervals for 0000, 0600, 1200, and 1800 hours, Greenwich Meridian Time. These charts were examined in the following way: A semicircle of radius 600 miles with Oahu as the center, was drawn to the windward direction of Oahu (when normal trades are blowing, this is northeast of Oahu). All ship reports of wind speed and direction were recorded for each six hour map. All wind speeds reported by all ships during each sampling interval were summed and averaged. Statistical calculations as described previously were performed for wind speed versus concentration of gaseous iodine (and bromine). These calculations showed no correlations between wind speed and gaseous halogen concentrations. In addition to recording wind data from the surface weather maps, notations were also made of wind trajectory (i.e., where the wind came from and the path it took). This was done to see whether air from different parts of the Pacific would have different gaseous iodine and bromine

concentrations. The trajectories, however, were quite consistent over the entire sampling period, and therefore, nothing can be said about trajectory and gaseous halogen concentration. These trajectories were essentially the same as those seen in Figure 7 where the winds came from about 50°N along the western coast of North America to about 25°N, and then turned west toward Oahu.

No difference in gaseous iodine and bromine concentration could be detected between those samples collected during the day and those collected at night. This implies that if a photochemical oxidation is responsible for the gaseous iodine and/or bromine, the amount supplied to the atmosphere daily is small compared to the total amount present in the atmosphere.

2. Cascade Impactor Samples

Cascade impactor samples were collected simultaneously with gaseous iodine and bromine samples at Bellows Air Force Station, Oahu. Table IV gives the results for the individual cascade impactor samples and Table V presents the average values of the I, Br, and Cl concentrations and the I/Cl, Br/Cl, and I/Br ratios along with their standard deviations. These average values are graphically illustrated in Figures 14 and 15. From these figures, the following points can be noted: Both Br and Cl have the highest mass on slides C and D, which collect particles of radius 2.5 μ and 1.25 μ , respectively. Iodine, however, is most concentrated on slides D and E, or particles of radius 1.25 μ and 0.62 μ . The Br/Cl ratio changes very little with particle size (Figure 15), but both the I/Br ratio and I/Cl ratio increase

by more than one order of magnitude between particles of radius 5.0 μ and 0.3 μ (slides B to F). These facts are in excellent agreement with the results published by Duce et al. (1967).

The most significant information obtained for the cascade impactor studies concerns the relationship between the gaseous iodine concentration and the iodine concentration of the various size particles. Statistical calculations for the relationships between gaseous iodine concentration and particulate iodine, particulate I/Cl ratio, and particulate I/Br ratio show that the gaseous iodine is correlated with these parameters for the middle stages of the cascade impactor and also for the impactor totals.

Figures 16 to 27 are graphs of gaseous iodine versus particulate iodine, particulate I/Cl ratio, and particulate I/Br ratio on the various cascade impactor stages where correlations were obtained. Stages where no graphs are presented are those for which no correlations could be seen.

Figures 16 to 20, along with the statistical data of Table XII, show the relationship between gaseous iodine and particulate iodine for the impactor stages C to F plus the total concentration represented by all six stages. Particulate iodine on stages A and B showed no significant correlation with gaseous iodine as was indicated by correlation coefficients of -0.20 and -0.11, respectively. Stage C (Figure 16) shows a fairly good correlation ($r_{y.x} = 0.87$) while stages D, E, and F (Figures 17, 18, and 19) indicate the possibility of correlation ($r_{y.x} = 0.59, 0.61, \text{ and } 0.58$, respectively). Figure 20, a graph of

total particulate iodine (as represented by the sum of particulate iodine for all six impactor stages) versus gaseous iodine, shows a relatively good correlation ($r_{y.x} = 0.89$). The fact that particulate iodine on stages A and B shows no correlation with gaseous iodine might perhaps be explained by the fact that these stages contain the smallest mass of iodine and therefore have very large analytical uncertainties.

Figures 21 and 22 are plots of gaseous iodine concentration versus the I/Cl ratio observed on cascade impactor stages C and D. Figure 23 is a plot of gaseous iodine concentration versus the ratio of the iodine total of all six stages to the chlorine total of all six stages. Table XII shows that the correlation coefficients for Figures 21-23 are 0.93, 0.84, and 0.90, respectively.

Gaseous iodine concentration versus the I/Br ratio on stages B, C, D, and the impactor total for the I/Br ratio is shown in Figures 24 to 27. These relationships are very similar to those found in the previous sets, with slides B, C, D, and the ratio of total particulate iodine to total particulate bromine showing correlation coefficients of 0.79, 0.85, 0.79, and 0.93, respectively, with gaseous iodine.

The fact that correlations often are not exceedingly good is not surprising even ignoring the large analytical uncertainties on slides A and F. It was mentioned in the introduction that organic material may be contributing to the high iodine concentration of sea salt particles. If a significant mass of organically

bound iodine is injected into the atmosphere with the sea salt droplets, the particles in the air may then have concentrations of iodine only partially dependent on the gaseous concentration of iodine. Even if organic material is not responsible for enriching iodine with respect to chlorine in atmospheric particles, it might affect the interaction of gaseous iodine with the particles. Blanchard (1968) has shown that a large concentration ($>1 \mu\text{g}/\text{m}^3$) of organic material is present in the marine atmosphere. The relationship between amount of organic material and sea salt particle size is not known but if organic material is associated predominantly with one size of particle (either large or small), then any particle highly enriched in organic material might show a different behavior toward gaseous iodine than would particles containing lesser amounts of organic material.

Caution is necessary in interpreting the significance of the correlation coefficients obtained for Figures 16-27. Examination of these figures shows one disconcerting feature: there is a group of data points which shows only a small variation in gaseous iodine concentration and in the impactor parameter being examined, and, in addition to this group of points there is a single point which has a high gaseous iodine concentration and also a high value for the cascade impactor parameter. If, for example, the graph of gaseous iodine versus total particulate I/Cl (Figure 23) is examined, it is seen that eight points have gaseous iodine concentrations between 4 and 8 ng/m^3 and these same points have an I/Cl ratio between 0.3×10^{-3} and 0.75×10^{-3} .

In addition to these eight points there is one point with a gaseous iodine concentration of 12 ng/m^3 and an I/Cl ratio of 1.2×10^{-3} . The correlation coefficient for Figure 23 is 0.90, but removing the point where the gaseous iodine concentration is equal to 12.1 ng/m^3 and recalculating the correlation coefficient results in a value of 0.74. Although the correlation is somewhat lowered, it is still high enough to indicate that a correlation exists between gaseous iodine and total particulate I/Cl ratio. Therefore, if on all graphs mentioned, the data point corresponding to a gaseous iodine concentration of 12.1 ng/m^3 is removed, then all correlation coefficients quoted earlier are lowered.

The fact that a correlation between gaseous iodine concentration and particulate iodine concentration appears to exist suggests one of two possible occurrences. 1) If particulate iodine is the source of gaseous iodine, the rate of gaseous iodine release must then be fast enough so that an increase (or decrease) in both the particulate and gaseous iodine concentration can be measured simultaneously. It is unlikely that this is the case since the concentration of gaseous iodine is so much larger than that for particulate iodine (i.e., the amount of iodine available to be released from the particles is so small, it is doubtful that a resulting change in the gaseous iodine concentration could be seen). 2) The second possibility is that gaseous iodine controls the particulate iodine concentration (or the sea salt particles are a sink for gaseous iodine). This

proposal seems more likely than the first since the gaseous iodine concentration is so much larger (3-4 times) than the total particulate iodine concentration. The fact that it is possible to monitor a simultaneous change in the gaseous and particulate iodine concentration may indicate that the gaseous iodine is controlling the amount of particulate iodine present in the marine atmosphere.

Statistical calculations for the relationship between gaseous bromine concentration and particulate bromine, particulate Br/Cl ratio, and particulate I/Br ratio indicated no correlations existed.

The fact that the particulate bromine concentration is not related to the gaseous bromine concentration is consistent with the fact that the gaseous bromine concentration is not related to the mass of sea salt particles in the atmosphere (as was shown to be the case when gaseous bromine was compared to the particulate sodium concentration). This again suggests that if the bromine associated with the sea salt population in the atmosphere is the source for gaseous bromine, the production rate of gaseous bromine from sea salt particles is small when compared to the total amount of bromine in the atmosphere.

B. Ship Samples

Table VI presents the analytical results obtained for particulate samples collected on 47 mm Type EH Millipore Filters aboard the U. S. Coast and Geodetic Survey Ship Surveyor on a cruise from Kodiak, Alaska to Honolulu, Hawaii in September 1967. Table VII shows the

results of the analyses of gaseous iodine and bromine samples collected on the U. S. Coast and Geodetic Survey Ship MacArthur in May, 1969 on a cruise from Honolulu, Hawaii to Seattle, Washington. The locations reported in these two tables are those at the midpoint of the sampling period. Figure 5 shows the positions of these samples with respect to Honolulu, Alaska, and the west coast of North America. Previously it was noted that one might expect to find the iodine concentration varying with geographical position if iodine in the atmosphere is a consequence of organic material in sea water, since biological productivity in the sea is a function of geographical position. Examination of the filter sample data showed that enrichment of iodine with respect to chlorine does not appear to vary between the samples collected in northern waters and those collected in more southerly waters. At the beginning of the Kodiak to Honolulu cruise it was hoped that many more samples could be taken so that a large number of samples might show small differences in the I/Cl ratio, something not possible with a small number of samples. Bad weather during this cruise forced collection of considerably fewer samples than was desired. Thus, from the data obtained, it can only be said that the I/Cl ratio in air over southern waters does not appear to differ from the I/Cl ratio found in the atmosphere over more productive northern waters, although many more samples must be collected to ascertain this. Small differences in the I/Cl ratio with geographical position may exist.

The number of gaseous iodine and bromine samples collected on the MacArthur was again much smaller than was desired due to inclement

weather. After this cruise it was concluded that the collection of air samples from a ship is very risky indeed. To collect air samples from a ship one must be very certain that the ship is not contaminating the samples: thus it is standard procedure to only collect in a position where the wind will blow any dirt or gases from the ship's stacks or decks away from the sampling equipment (i.e., collections are always made upwind of the ship's stacks). On this cruise, a portable condensation nuclei counter (Small Particles Detector Type CN, manufactured by Gardner Associates, Incorporated) was used to measure the "purity" of the air being sampled. The only place on the ship where one could be fairly certain of no contamination was at the very bow of the ship several feet above the deck. Every other position on the ship showed that although the sampling apparatus was upwind from the stacks, the air was contaminated due to eddy currents around the ship picking up dust from the deck and stack. It is thought that this is why sample S1A (in Table VII) was contaminated, for it was not collected on the bow of the ship but on the flying bridge. All remaining samples were collected on the bow of the ship approximately seven feet above the deck. The gaseous iodine concentrations found on this cruise are consistent with the values found at Bellows Air Force Station on Oahu. Although the bromine values are somewhat lower than the average values found at Bellows, they are in the range of those numbers. As with particulate iodine, no large differences in gaseous iodine and bromine concentration appear with geographical position.

C. Island of Hawaii Samples

The data for the gaseous halogen samples collected on the island of Hawaii, which is located about 200 miles southeast of Honolulu, are given in Table VIII. Figure 6 indicates the sampling locations and the direction of the normal trade winds.

Inspection of the data from the Hawaii samples collected at the University of Hawaii Hilo Campus (U.H.H.C.) shows strong diurnal variations of gaseous iodine and bromine concentrations. From Figure 28 and Table XI it is seen that the daytime samples have a concentration equal to two to three times that of the nighttime samples. Figure 29 shows the relationship between gaseous I and Br. Based on the statistical data from Table XII ($r_{y.x} = 0.57$), it is questionable whether or not a relationship between iodine and bromine exists. Previously it was noted that if iodine in the air is being produced by photochemical oxidation at the sea surface, a difference in the iodine concentration of the air between those samples collected during the day and those collected at night might be observed. However, examination of the data for samples collected at Bellows Air Force Station shows no such diurnal variation of iodine concentration. For this reason, it is felt that the diurnal variation of iodine concentration observed on the island of Hawaii may be explained by meteorological conditions rather than as a result of a production mechanism.

The island of Hawaii is dominated by two large volcanoes, Mauna Loa and Mauna Kea, which cause the meteorology of this island to be somewhat different than that of the other islands in the Hawaiian

chain. It is well known that these mountains generate a nighttime wind which blows from the heights of the mountains down the slopes in all directions and out to sea. Such land breezes (commonly called downslope winds) occur in the evening and night when the land cools more rapidly than the sea, and the air over the mountains, cooler (and therefore heavier) than the air over the sea, sinks under the warmer air over the ocean. Thus, during the night, the downslope winds on the east side of the island are opposed to the normal trade winds which blow during the day. The importance of such an occurrence is that the mountains are high enough (greater than 4,000 meters) that much of the sinking air may come from above the trade wind inversion (generally 2,000 to 2,500 meters). The air above the trade wind inversion is an entirely different air mass than that below the inversion. These two air masses do not mix rapidly and air from above the inversion is air which has not been in contact with the sea surface for a relatively long period of time. Thus it is felt that the diurnal variation observed at the University of Hawaii Hilo Campus is a result of measuring two different air masses: in the daytime the air sampled is that carried inland from the sea by the normal trade winds, whereas at night the samples are collected from a mixture of above-inversion and below-inversion air.

It is very interesting to note that the U.H.H.C. samples have concentrations of iodine much higher than any other samples collected. There may be several reasons for this high iodine content in the air. Hilo could have a pollution source of iodine although this appears to be inconsistent with the results obtained for Honolulu and Boston

samples (see Table XI). Pollution source, as used in this dissertation, is defined as the addition of material to the atmosphere as a result of man's industrial action. Such a definition would include the use of machinery or the burning of fuel or vegetation (which occurs in Hilo because of the sugar industry).

The sampling equipment of the U.H.H.C. samples was set up on the northeast side of Wentworth Hall, such that the charcoal and precipitator were about two meters away from the building. The vacuum pump and high voltage power supply were in a laboratory with connections to the collecting apparatus passing through a window. It is possible that the samples were contaminated by laboratory air as it diffused through the open window. The laboratory was not being used at the time these samples were collected, but it is possible that the laboratory could have an iodine source from previous lab work. However, it is possible to argue against such contamination. It is difficult to imagine that if the laboratory air were contaminating the samples, such a marked change in the iodine concentration would be observed between night and day. Since the collector was on the northeast side of the laboratory and the trade winds during the day were from the northeast, it might be argued that there should be less contamination of the samples during the day. At night the downslope winds are from the southwest, which means that the laboratory was placed between the sampling apparatus and the wind to be sampled, and therefore, contamination would seem more likely. However since the sampling apparatus was so close to the building, the normal daytime trade winds might have blown

into the lab forcing lab air out the window, resulting in a contamination of the samples.

Another possible explanation of the high iodine concentrations obtained in Hilo is that the soil and/or vegetation may be a source of iodine. Von Fellenberg (1926) reported that under certain conditions the soil and vegetation could release iodine to the atmosphere. More recently, Bolin (1959) has estimated that the net flux of iodine from the air to the soil is much smaller than the total iodine exchanged between the two media. It is certain that there is a net flux of iodine from the atmosphere to the land, but in localized areas it may be possible for the opposite effect to occur. One possible explanation for a localized flux of iodine from ground to air may be the decomposition of vegetation which is known to be rich in iodine. Vegetation can contain as much as 1 ppm iodine (Chilean Iodine Educational Bureau, 1950), and it is quite possible that vegetation can release iodine vapor when decomposing. The U.H.H.C. samples were collected in an area with considerable yard grass which was frequently mowed and the decaying grass might account for the high iodine values observed in the daytime samples. The downslope winds at night are not blowing over a large yard area and one might perhaps expect that the values would not be as high. Due to the uncertainty of the source of the gaseous iodine concentrations measured at Hilo, it is impossible to accurately state the reasons for the high concentrations of gaseous iodine measured there. A study of the exchange of iodine between the atmosphere and vegetation would be a very important future investigation.

It was mentioned in the Introduction that gaseous bromine will probably have a pollution source from the burning of gasoline in automobiles and this fact must be kept in mind when reviewing the gaseous bromine result obtained at U.H.H.C., since automobiles have access to the areas near the location of the sampling equipment. The values obtained for bromine concentrations during the daytime at U.H.H.C. are quite consistent with the values obtained at Bellows Air Force Station. While the possibility of a bromine pollution source cannot be eliminated, it appears that the samples probably are not contaminated to a large extent with pollution bromine.

Samples H8B and H10B were collected at an altitude of 900 meters on the Kulani Road (position 2 on Figure 6). These samples show that the concentration of iodine is much lower than the values obtained at U.H.H.C., while the bromine concentration is quite similar to the U.H.H.C. values. Both the iodine and bromine values for H8B and H10B are consistent with the results obtained at Bellows Air Force Station. The Kulani Road samples were collected in a grassy area surrounded by woods, away from the road so that local traffic would not affect the samples. If the high iodine values obtained at U.H.H.C. were a result of soil or vegetation, this source must be very limited since high iodine values were not observed in the rural Kulani Road samples. It must be pointed out that the soil and vegetation in the immediate vicinity of the Kulani Road sampling site is much different from the neatly trimmed grass and well fertilized soil at the University of Hawaii Hilo Campus, and because of

these differences, the possibility of the soil and/or vegetation being the source of the gaseous iodine concentrations which were measured at U.H.H.C. still cannot be eliminated.

Samples H5B, H6B, and H7B were collected from the Mauna Loa Weather Observatory. For H5B and H6B, it is seen that both iodine and bromine concentrations are much lower than the values found in either Hilo or Bellows Air Force Station samples. This would indicate that the air above the inversion has an iodine concentration $1/2$ to $1/3$ the values found in "clean" air below the trade wind inversion. The fact that samples H7B has iodine and bromine concentrations comparable to samples collected in "clean marine air" at Bellows is somewhat unexpected. There is evidence, however, that the air being sampled in this case was not truly representative of above-inversion air. It was noted during collection of this sample that clouds were rising to an altitude equal to that of the sampling location (about 3,500 meters). In fact, the sampling area was in and out of this cloud for much of the sampling period. This same effect was noted during the collection of sample H5B, but not to the extent observed during collection of sample H7B. There is CO_2 evidence given by Pales and Keeling (1965) that in the daytime during the period of maximum land surface heating, air below the inversion can be carried through the inversion layer as high as, or higher than the Mauna Loa Observatory where the gaseous iodine and bromine samples were collected. It is felt that sample H6B is the only sample which is truly representative of above-inversion air. At night the cooling of the mountains generates the downslope winds

and it is assumed that this action tends to inhibit the flux of below-inversion air up the mountain. Indeed, the opposite effect occurs and above-inversion air is carried down the mountain. Although it is extremely dangerous to make statements based on only one or two samples, it appears that there is a significant difference in the iodine and bromine concentrations above the inversion when compared to iodine and bromine concentrations for below-inversion air. However, this difference is not nearly as great for iodine as that observed for particulate concentration. Junge (1957) has estimated that "sea salt" particulates are as much as 4 orders of magnitude lower in mass in above-inversion air than in below-inversion air. This indicates that gaseous iodine's residence time in the atmosphere must be longer than the particulate residence time.

D. Honolulu Samples

Table IX presents the concentrations of gaseous iodine and bromine which were measured on the roof of Bilger Hall at the University of Hawaii (Manoa Campus) in Honolulu. Here it is seen that the iodine concentrations tend to be slightly higher than the values obtained at Bellows Air Force Station: in some cases, as much as 3 times the concentrations found at Bellows during the same sampling period. Figure 30 and the correlation coefficient of 0.61 indicate that there is a question as to whether or not a correlation exists between gaseous iodine concentration and gaseous bromine concentration for the samples collected at the University of Hawaii in Honolulu.

During the same sampling period, the bromine concentrations in some samples are about 3 to 4 times the values found at Bellows Air

Force Station, while in other samples the values are approximately equal. Ray (1969) has shown that the particulate bromine concentration in Honolulu is controlled to a large degree by a pollution source (i.e., automobiles). Almost certainly, the high bromine values at Bilger Hall are due to an automobile pollution source, and the samples which give similar results to those found at Bellows are probably only slightly contaminated by pollution.

It is interesting to note that when the bromine concentrations at Bilger Hall are high, the iodine values are not necessarily high. This probably indicates that either the high iodine concentrations are not the result of a pollution source, or that if there is a pollution source for iodine, it is different than that for bromine.

E. Cambridge, Massachusetts Samples

Samples of gaseous iodine and bromine as well as particulate iodine and lead were collected simultaneously in Cambridge, Massachusetts. The particulate samples were collected on 47 mm Millipore Filters (Type EH and HA). The results of the analyses for gaseous iodine concentration, particulate iodine concentration, and particulate lead concentration are presented in Table X. The gaseous bromine concentrations are not presented here since many questions must still be answered regarding the release of Br^- by the oxidants produced in the electrostatic precipitator. These questions will be studied in the near future and the bromine results and the implications of these results will be presented elsewhere. For comparison with other locations, the average and range of gaseous bromine concentrations observed in Cambridge, Massachusetts are

included in Table XI, although the reliability of these values may be questionable. The lead samples were analyzed by atomic absorption spectrophotometry, using Jernigan's (1969) method.

The sampling period was characterized by two types of weather situations. Samples M1B to M5B were collected during predominantly hazy days with weak westerly winds (i.e., winds blowing from the land). Samples M6B to M12B were collected during days of clear, cool weather and easterly winds (i.e., sea breezes). The marked difference in the lead concentrations during the two meteorological situations can be seen in Figure 31 which shows the variation of lead as well as particulate and gaseous iodine concentrations with date of collection. The values shown for the lead concentrations are within the range of values reported by the U. S. Public Health Service (1962, 1968) for the Cambridge-Boston area.

The gaseous iodine concentrations show two interesting characteristics. First, the concentration of gaseous iodine is much more constant with varying meteorological conditions than lead and particulate iodine. Second, the concentration of gaseous iodine averages approximately $13.9 \pm 2.8 \text{ ng/m}^3$, less than twice the average value and within the range of values observed in the unpolluted marine atmosphere. This indicates that, at least in this study, if a pollution source exists for iodine, this source is adding very little iodine to the atmosphere relative to that coming from the sea. The most commonly suggested pollution sources of iodine are fossil fuel oils and coal, and it is possible that the amount of pollution iodine is seasonally dependent with more iodine added to the air in

winter and less in summer.

The comparison of cascade impactor samples and gas samples gives a ratio of particulate to gaseous iodine in the unpolluted marine atmosphere of 0.25 to 0.50. In Cambridge it was found that the samples collected during the period characterized by easterly winds and low lead concentrations had a particulate to gaseous iodine ratio which ranged between 0.2 and 0.8 while during the period of westerly winds and high lead content the ratio was 0.5 to 0.9. Clough et al. (1965) have suggested that adsorption of iodine on particles from combustion processes is largely a reversible adsorption and presented the empirical relationship that the particulate to gaseous iodine ratio should be equal to approximately 1.5×10^3 times the mass of particulate matter in the air (g/m^3) and should be independent of gaseous iodine concentration at $10^{-7} \text{ g}/\text{m}^3$ and smaller. This value was obtained by studying the adsorption of I_2 vapor (using ^{131}I) onto particles produced from the combustion of coal at various particulate matter and gaseous iodine concentrations. Thus, at a total particulate mass of $100 \text{ } \mu\text{g}/\text{m}^3$ the ratio of particulate to gaseous iodine would be approximately 0.15 while at a particulate mass of $1000 \text{ } \mu\text{g}/\text{m}^3$ the ratio would be about 1.5. The average weight of total particulate material in Boston-Cambridge air as given by the Bureau of Environmental Sanitation, Department of Public Health, Commonwealth of Massachusetts (1968) is approximately $90 \text{ } \mu\text{g}/\text{m}^3$. According to the U. S. Public Health Service (1968) the average lead concentration in the Boston-Cambridge area is about $1 \text{ } \mu\text{g}/\text{m}^3$, and this implies that lead represents about one percent of the total

suspended particulate matter in Boston-Cambridge air. Using Clough's et al. (1965) empirical formula, it would be expected that the particulate to gaseous iodine ratio would be 0.15 when the lead concentration was $1 \mu\text{g}/\text{m}^3$. Figure 32 shows a plot of particulate lead versus the ratio of particulate to gaseous iodine; and the correlation coefficient for this figure is 0.80 which would indicate that particulate matter does control the ratio of particulate to gaseous iodine concentration (if lead is assumed to be a monitor of the total particulate mass in the air). If it is assumed that the lead concentration is approximately equal to 1% of the total particulate mass concentration, then from the "best fit" line in Figure 32, the particulate iodine to gaseous iodine ratio can be expressed by:

$$R = 2.1 \times 10^3 m - 0.04 \quad (25)$$

where

R = particulate iodine to gaseous iodine ratio

m = mass concentration (g/m^3) of total particulate matter in the air

Equation (25) is in very good agreement with the relationship of

$R = 1.5 \times 10^3 m$ suggested by Clough et al. (1965).

The relationship between particulate iodine and particulate lead is also shown in Figure 33, which has a correlation coefficient of 0.82. Statistical calculations indicate that there is no correlation between gaseous iodine and particulate lead.

Table III
Gaseous Iodine and Bromine and Particulate Sodium Concentrations
Measured at Bellows Air Force Station, Oahu, Hawaii

Sample Number	Date	Time (HST)	Wind (m/sec)	Ppt (in)	Remarks	Gaseous I ng/m ³	Gaseous Br ng/m ³	Na μg/m ³
B1B	7/4/69	1215-1925	4.3	0	Clear weather; NE trade winds	20.2 (19.2)	66.3 (52.9)	2.0
B2B	7/4/69	1925-0845	6.3	0.02	"	18.5	45.8	
B3B	7/5/69	0845-1745	9.2	0	"	16.9 (14.8)	46.0 (40.0)	---
B4B	7/5/69	1745-0930	7.4	0	"	13.6	36.9	
B7B	7/7/69	0845-1830	7.5	0	"	9.7 (11.1)	35.9 (45.2)	3.8
B9B	7/7/69	1830-0850	7.9	0	"	12.3	53.1	
B10B	7/8/69	0850-1850	7.5	0	"	13.1 (9.3)	28.1 (30.6)	2.4
B12B	7/8/69	1850-0850	7.4	0	"	6.7	32.8	
B13B	7/9/69	0850-1850	7.5	Tr	"	10.5 (8.0)	50.1 (34.4)	3.6
B14B	7/9/69	1850-0835	6.5	Tr	"	6.1	23.1	
B15B	7/10/69	0840-1900	6.3	0	"	10.1 (8.7)	26.7 (30.5)	3.9
B16B	7/10/69	1000-0840	8.0	0	"	7.7	33.3	

Table III (Continued)
Gaseous Iodine and Bromine and Particulate Sodium Concentrations
Measured at Bellows Air Force Station, Oahu, Hawaii

Sample Number	Date	Time (HST)	Wind (m/sec)	Ppt (in)	Remarks	Gaseous I ng/m ³	Gaseous Br ng/m ³	Na μg/m ³
B17B	7/11/69	0840-1940	9.5	0	Clear weather; NE trade winds	6.2	32.8	---
B20B	7/15/69	0900-1840	6.7	0	"	6.5 (5.8)	39.7 (33.2)	3.4
B21B	7/15/69	1840-						
	7/16/69	0930	7.8	Tr	"	5.2	28.4	
B22B	7/16/69	0930-1910	6.2	0.02	"	5.3 (5.1)	38.0 (35.3)	2.9
B23B	7/16/69	1910-						
	7/17/69	0640	6.1	0	"	4.9	32.4	
B24B	7/17/69	0640-1920	6.2	0	"	6.1 (9.3)	39.3 (37.9)	2.1
B25B	7/17/69	1920-						
	7/18/69	0645	5.7	0	"	12.9	36.4	
B26B	7/18/69	0645-1850	6.2	Tr	"	9.0 (8.4)	37.5 (35.6)	2.5
B27B	7/18/69	1850-						
	7/19/69	0720	6.8	0	"	7.9	34.1	
B30B	7/20/69	0820-1920	8.1	0	"	6.1 (6.9)	47.6 (39.4)	3.1
B31B	7/20/69	1920-						
	7/21/69	0700	7.7	0.03	"	7.6	31.6	

Table III (Continued)
Gaseous Iodine and Bromine and Particulate Sodium Concentrations
Measured at Bellows Air Force Station, Oahu, Hawaii

Sample Number	Date	Time (HST)	Wind (m/sec)	Ppt (in)	Remarks	Gaseous I ng/m ³	Gaseous Br ng/m ³	Na μg/m ³
B32B	7/21/69	0700-1920	7.7	0	Clear weather; NE trade winds	4.7 (4.2)	30.2 (29.0)	2.2
B34B	7/21/69 7/22/69	1920-0800	7.1	0.01	"	3.7	27.9	
B35B	7/22/69	0800-1900	6.3	0	"	8.9 (7.7)	45.4 (44.8)	2.9
B36B	7/22/69 7/23/69	1900-0655	6.6	0.05	"	6.4	44.1	
B37B	7/23/69	0655-1910	6.1	0	"	9.4 (7.8)	42.3 (41.2)	1.5
B38B	7/23/69 7/24/69	1910-0600	6.4	0	"	5.9	40.1	
B39B	7/24/69	0600-1915	6.0	0	"	7.2 (6.5)	39.6 (40.4)	2.5
B40B	7/24/69 7/25/69	1915-0600	6.1	0	"	5.7	41.2	
B42B	7/26/69	0730-1920	2.3*	Tr	Overcast South winds	5.0 (4.2)	63.4 (53.5)	3.1
B43B	7/26/69 7/27/69	1920-0730	1.8*	Tr	"	3.5	43.6	

Table III (Continued)
Gaseous Iodine and Bromine and Particulate Sodium Concentrations
Measured at Bellows Air Force Station, Oahu, Hawaii

Sample Number	Date	Time (HST)	Wind (m/sec)	Ppt (in)	Remarks	Gaseous I ng/m ³	Gaseous Br ng/m ³	Na μg/m ³
B44B	7/27/69	0730-1920	3.4*	0	Partly overcast, variable winds	5.9 (5.8)	63.0 (50.6)	3.2
B45B	7/27/69	1920-						
	7/28/69	0700	3.4*	0	"	5.6	38.2	
B46B	7/28/69	0700-1910	5.4	0	Clear weather; NE trade winds	5.6 (6.4)	39.4 (46.4)	1.5
B47B	7/28/69	1910-						
	7/29/69	0700	5.8	0	"	7.3	51.8	
B48B	7/29/69	0700-						
	7/30/69	0120	7.2	0	"	7.9	51.7	2.1
B49B	7/30/69	0720-1925	7.8	0	"	7.7 (6.1)	54.2 (49.7)	
B50B	7/30/69	1925-						
	7/31/69	0715	7.9	0	"	4.4 ± 1.0	45.4	
B51B	7/31/69	0715-1945	7.2	0	"	10.3 (9.5)	90.5 (75.4)	
B53B	7/31/69	1945-						
	8/1/69	0720	7.0	0.01	"	8.6	59.1	
B54B	8/1/69	0720-1930	7.4	Tr	"	6.8	51.0	2.4

Table III (Continued)
Gaseous Iodine and Bromine and Particulate Sodium Concentrations
Measured at Bellows Air Force Station, Oahu, Hawaii

Sample Number	Date	Time (HST)	Wind (m/sec)	Ppt (in)	Remarks	Gaseous I ng/m ³	Gaseous Br ng/m ³	Na μg/m ³
B56B	8/2/69	1200-1900	7.1	0	Clear weather; NE trade winds	4.4 ± 1.2 (6.0)	56.8 (54.7)	2.7
B57B	8/3/69	1900-0815	7.1	0	"	5.6 ± 1.0	57.7	
B58B	8/3/69	0815-2115	5.7	0	"	7.2	49.0	
B59B	8/3/69 8/4/69	2115-1000	8.5	0	"	6.7 (7.1)	56.2 (59.9)	2.0
B60B	8/4/69	1000-1800	6.9	0.01	"	7.6	65.9	
B61B	8/4/69 8/5/69	1800-0700	6.9	0	"	7.0 (6.2)	60.4 (56.2)	2.2
B62B	8/5/69	0700-1615	6.5	0.01	"	5.0	50.4	
B63B	8/5/69 8/6/69	1615-0830	7.3	0	"	5.1 ± 1.0 (6.8)	60.3 (55.1)	3.0
B64B	8/6/69	0830-1500	6.9	0	"	11.1	42.0	

Table III (Continued)
Gaseous Iodine and Bromine and Particulate Sodium Concentrations
Measured at Bellows Air Force Station, Oahu, Hawaii

Sample Number	Date	Time (HST)	Wind (m/sec)	Ppt (in)	Remarks	Gaseous I ng/m ³	Gaseous Br ng/m ³	Na μg/m ³
B65B	8/6/69	1500-2215	6.9	0	Clear weather; NE trade winds	8.0 (6.8)	66.6 (61.0)	2.2
B66B	8/6/69	2215-						
	8/7/69	0715	6.7	0	"	5.7	56.3	
B67B	8/7/69	0715-						
		1300	5.1	0	"	8.1	59.4	
B71B	8/8/69	2020-						
	8/9/69	1400	5.9	0	"	10.2 (10.6)	42.6 (48.4)	2.3
B72B	8/9/69	1400-1900	6.9	0	"	12.1	68.8	
B1A	8/5/69	1615-			Duplicate of			
	8/6/69	0830	7.3	0	B63B	4.9 ± 1.2	63.9	---
B2A	8/6/69	1500-2215	6.9	0	Duplicate of B65B	6.5 ± 1.0	58.0	---

* Wind blowing from the land.

Table IV
Particulate Iodine, Bromine, and Chlorine Concentrations Using Cascade Impactor
Bellows Air Force Station, Oahu, Hawaii.

Sample Number	Date	Time	Remarks	Stage	Cl $\mu\text{g}/\text{m}^3$	Br ng/m^3	I ng/m^3	I/Cl $\times 10^3$	Br/Cl $\times 10^3$	I/Br
C2	8/1/69 8/2/69	2030- 1215		A	0.10 ± 0.03	0.34 ± 0.09	0.02 ± 0.01	0.16	3.4	0.048
				B	0.75	2.52	0.05 ± 0.01	0.07	3.4	0.021
				C	2.13	3.86	0.22	0.10	1.8	0.057
				D	0.99	1.61	0.35	0.35	1.6	0.21
				E	0.70	0.84	0.61	0.88	1.2	0.73
				F	0.11	-	0.38 ± 0.08	3.5	-	-
				Total	4.76	>9.21	1.62	0.35	>1.94	>0.18
C3	8/2/69	1240- 1900	Collected at same time as B56B	A	0.39	0.42 ± 0.06	0.02 ± 0.01	0.04	1.1	0.04
				B	0.74	1.74	0.06 ± 0.01	0.08	2.4	0.04
				C	1.32	3.06	0.16 ± 0.03	0.12	2.3	0.05
				D	1.34	1.80	0.59	0.42	1.3	0.32
				E	0.49	0.56	0.58	1.20	1.2	1.0
				F	0.34	-	-	-	-	-
				Total	4.31	>7.58	>1.41	>0.33	>1.76	-

Table IV (Continued)

Particulate Iodine, Bromine, and Chlorine Concentrations Using Cascade Impactor
Bellows Air Force Station, Oahu, Hawaii.

Sample Number	Date	Time	Remarks	Stage	Cl $\mu\text{g}/\text{m}^3$	Br ng/m^3	I ng/m^3	I/Cl $\times 10^3$	Br/Cl $\times 10^3$	I/Br
C4	8/2/69 8/3/69	1930- 0815	Collected at same time as B57B	A	0.41	0.59	0.02 ± 0.01	0.04	1.4	0.03
				B	0.82	2.33	0.09 ± 0.01	0.11	2.8	0.04
				C	1.56	3.56	0.29	0.19	2.3	0.082
				D	1.90	3.28	0.92	0.48	1.7	0.28
				E	0.46	0.62	1.13	2.5	1.4	1.8
				F	0.08	0.11	0.44	5.8	1.5	3.8
				Total	5.22	10.5	2.88	0.55	2.0	0.27
C5	8/3/69	0850- 2115	Collected at same time as B58B	A	-	-	-	-	-	-
				B	0.77	1.87	0.04 ± 0.01	0.057	2.4	0.03
				C	1.72	2.98	0.32	0.19	1.7	0.11
				D	1.21	1.13	1.14	0.94	0.93	1.0
				E	0.37	0.29	0.96	2.41	0.77	3.1
				F	0.08	0.46	0.26	3.24	5.68	0.57
				Total	>4.11	>6.71	>3.05	<0.74	1.6	0.45

Table IV (Continued)
 Particulate Iodine, Bromine, and Chlorine Concentrations Using Cascade Impactor
 Bellows Air Force Station, Oahu, Hawaii.

Sample Number	Date	Time	Remarks	Stage	Cl $\mu\text{g}/\text{m}^3$	Br ng/m^3	I ng/m^3	I/Cl $\times 10^3$	Br/Cl $\times 10^3$	I/Br
C6	8/3/69	2145-	Collected at same time as B59B	A	0.13	0.43	0.05 ± 0.02	0.41	3.2	0.13
				B	0.62	1.86	0.13 ± 0.04	0.23	3.0	0.07
				C	1.22	2.92	0.14	0.12	2.4	0.05
				D	3.58	7.38	1.68	0.47	2.1	0.23
				E	0.61	1.18	0.20	0.29	1.8	0.16
				F	0.095	0.24	0.14	1.47	2.6	0.58
				Total	6.32	14.1	2.35	0.37	2.2	0.17
C8	8/4/69 8/5/69	1900- 0700	Collected at same time as B61B	A	0.08	0.36 ± 0.10	0.01 ± 0.01	0.13	3.7	0.04
				B	0.54	1.56	0.03	0.06	2.9	0.02
				C	1.42	2.80	0.24	0.17	2.0	0.09
				D	1.12	1.84	0.86	0.77	1.6	0.47
				E	0.26	0.35	0.90	3.09	1.4	2.3
				F	0.08	0.18 ± 0.04	0.19	2.27	2.1	1.1
				Total	3.51	7.02	2.44	0.69	2.0	0.35

Table IV (Continued)

Particulate Iodine, Bromine, and Chlorine Concentrations Using Cascade Impactor
Bellows Air Force Station, Oahu, Hawaii.

Sample Number	Date	Time	Remarks	Stage	Cl $\mu\text{g}/\text{m}^3$	Br ng/m^3	I ng/m^3	I/Cl $\times 10^3$	Br/Cl $\times 10^3$	I/Br
C9	8/5/69	0730- 1615	Collected at same time as B62B	A	0.14	0.50	0.04 ± 0.02	0.26	2.7	0.08
				B	0.89	2.74	0.10 ± 0.02	0.11	3.1	0.04
				C	1.48	3.29	0.23	0.15	2.2	0.07
				D	1.11	1.49	0.50	0.42	1.3	0.33
				E	0.53	0.43	1.44	2.7	0.83	3.3
				F	0.24	0.24 ± 0.06	0.24	1.0	1.0	1.0
				Total	4.39	8.69	2.53	0.58	1.98	0.29
C10	8/5/69 8/6/69	1700- 0830	Collected at same time as B63B	A	0.40	1.55	0.08 ± 0.04	0.02	3.9	0.05
				B	1.59	2.56	0.03 ± 0.02	0.02	1.6	0.01
				C	2.93	7.27	0.30	0.10	2.5	0.04
				D	1.21	1.59	0.80	0.66	1.3	0.51
				E	0.57	0.63	1.13	2.0	1.1	1.79
				F	0.11	0.11	0.22	2.2	1.0	2.0
				Total	7.01	-13.7	2.55	0.35	2.0	0.18

Table IV (Continued)
 Particulate Iodine, Bromine, and Chlorine Concentration Using Cascade Impactor
 Bellows Air Force Station, Oahu, Hawaii.

Sample Number	Date	Time	Remarks	Stage	Cl $\mu\text{g}/\text{m}^3$	Br ng/m^3	I ng/m^3	I/Cl $\times 10^3$	Br/Cl $\times 10^3$	I/Br
C11	8/6/69 8/7/69	2215- 0715	Collected at same time as B66B	A	0.02 ± 0.01	0.06 ± 0.02	0.01 ± 0.01	0.65	4.2	0.16
				B	0.05 ± 0.01	0.27	0.005 ± 0.01	0.11	5.4	0.01
				C	1.17	1.76	0.20	0.17	1.5	0.11
				D	0.69	1.86	0.25	0.36	2.7	0.14
				E	0.35	1.43	0.88	2.54	4.1	0.62
				F	0.03 ± 0.01	0.10	0.18	5.60	3.0	1.8
				Total	2.31	5.45	1.52	0.66	2.4	0.28
C12	8/7/69	0740- 1300	Collected at same time as B67B	A	-	-	-	-	-	-
				B	-	-	-	-	-	-
				C	1.09	6.02	0.28 ± 0.06	0.25	5.6	0.05
				D	1.32	-	0.93 ± 0.30	0.70	-	-
				E	0.38	0.25	0.94	2.5	0.65	3.8
				F	0.11	0.09 ± 0.03	0.14 ± 0.06	1.2	0.81	1.6
				Total	-	-	>2.3	-	-	-

Table IV (Continued)
 Particulate Iodine, Bromine, and Chlorine Concentration Using Cascade Impactor
 Bellows Air Force Station, Oahu, Hawaii.

Sample Number	Date	Time	Remarks	Stage	Cl $\mu\text{g}/\text{m}^3$	Br ng/m^3	I ng/m^3	I/Cl $\times 10^3$	Br/Cl $\times 10^3$	I/Br
C17	8/9/69	1430- 1900	Collected at same time as B52B	A	0.35 ± 0.06	0.40 ± 0.07	0.02 ± 0.01	0.06	1.2	0.05
				B	0.34	0.42 ± 0.07	0.05 ± 0.01	0.13	1.2	0.11
				C	1.41	2.17	0.88	0.62	1.5	0.41
				D	1.19	1.16	1.39	1.17	0.98	1.2
				E	0.68	1.00	2.28	3.35	1.5	2.3
				F	0.32	0.62 ± 0.10	0.56 ± 0.10	1.73	1.9	0.90
				Total	4.29	5.76	5.17	1.20	1.3	0.90
C19	8/10/69	0030- 2100		A	0.08	0.30	0.02 ± 0.01	0.25	4.0	0.06
				B	1.06	1.95	0.14 ± 0.02	0.14	1.9	0.07
				C	1.32	2.54	0.25	0.19	1.9	0.10
				D	1.08	1.21	0.70	0.65	1.1	0.58
				E	0.48	0.38	0.75	1.56	0.8	2.0
				F	-	-	-	-	-	-
				Total	>3.97	>6.38	>2.05	-	-	-

Table V
Average Values and Standard Deviations of Cascade Impactor Samples

Stage	Cl, $\mu\text{g}/\text{m}^3$	Br, ng/m^3	I, ng/m^3	I/Cl $\times 10^3$	Br/Cl $\times 10^3$	I/Br
A	0.19 ± 0.15	0.49 ± 0.38	0.029 ± 0.022	0.20 ± 0.18	3.00 ± 1.28	0.069 ± 0.040
B	0.76 ± 0.36	1.82 ± 0.73	0.070 ± 0.038	0.10 ± 0.05	2.73 ± 1.04	0.042 ± 0.029
C	1.55 ± 0.47	3.52 ± 1.58	0.29 ± 0.18	0.20 ± 0.13	2.31 ± 1.04	0.10 ± 0.096
D	1.42 ± 0.69	2.53 ± 1.91	0.84 ± 0.40	0.62 ± 0.24	1.52 ± 0.49	0.48 ± 0.32
E	0.51 ± 0.14	0.68 ± 0.35	0.98 ± 0.49	2.08 ± 0.89	1.37 ± 0.92	1.93 ± 1.17
F	0.11 ± 0.08	0.23 ± 0.16	0.28 ± 0.14	2.87 ± 1.73	2.00 ± 1.00	1.43 ± 1.00
Total	4.51 ± 1.12	8.62 ± 2.82	2.50 ± 0.94	0.57 ± 0.24	1.95 ± 0.23	0.36 ± 0.20

Table VI
Particulate Iodine, Bromine, and Chlorine Concentrations Using Millipore Filters
Kodiak, Alaska to Honolulu, Hawaii.

Sample Number	Date	Time (HST)	Location	Remarks	Cl $\mu\text{g}/\text{m}^3$	Br ng/m^3	I ng/m^3	I/Cl $\times 10^3$	Br/Cl $\times 10^3$	I/Br
1	9/13/67	0830-1940	53° 40' N 163° 20' W	Sample collected intermittently due to RW	8.02	28.9	8.9	1.11	3.60	0.308
2	9/14/67	0830-1725	52° 15' N 161° 20' W	Off and on	12.8	12.7	5.4	0.417	0.98	0.425
3	9/14/67	1800-2145	51° 44' N 161° 08' W	Continuous sample	6.43	17.0	6.2	0.962	2.64	0.365
4	9/19/67	1025-1845	46° 15' N 160° 29' W	RW - caused sample to be stopped - spray	294*	727*	2.4*	-	-	-
5	9/20/67	0800-1500	43° 10' N 160° 20' W	Continuous sample	25.8*	51.1*	0.683*	-	-	-
6	9/21/67	1725-2310	39° 20' N 160° 17' W	Continuous sample	30.4*	23.4*	2.24*	-	-	-
7	9/23/67	0925-1533	34° 58' N 160° 22' W	Continuous sample	1.73	2.75	1.37	0.791	1.59	0.497
8	9/23/67	1555-1930	34° 50' N 160° 15' W	RW - shut sample off	25.2*	21.9*	1.50*	-	-	-

Table VI (Continued)
 Particulate Iodine, Bromine, and Chlorine Concentrations Using Millipore Filters
 Kodiak, Alaska to Honolulu, Hawaii.

Sample Number	Date	Time (HST)	Location	Remarks	Cl $\mu\text{g}/\text{m}^3$	Br ng/m^3	I ng/m^3	I/Cl $\times 10^3$	Br/Cl $\times 10^3$	I/Br
9	9/25/67	1110- 1800	31° 15' N 160° 10' W	RW - at 1200- 1300 and sample off	2.80	2.63	1.48	0.529	0.72	0.730
10	9/26/67	0640- 1700	28° 10' N 160° 00' W	Off 0800-0950	6.81*	-	30.3*	-	-	-
11	9/27/67	1405- 2040	26° 05' N 159° 45' W	Continuous sample	2.62	2.12	6.45	2.46 ⁺	0.807	3.05 ⁺
12	9/28/67 9/29/67	0845- 1157	25° 50' N 160° 00' W	Off 1630- 0950	1.20	0.63	1.23	1.01	0.524	1.93
13	9/29/67 9/30/67	1200- 1130	24° 20' N 160° 00' W	RW Off 1620-0940	3.84	1.90	1.34	0.349	0.494	0.706
14	9/30/67	1130- 2150	22° 55' N 160° 00' W	RW - 1700 Sample off for 10 min.	9.74	6.37	1.69	0.173	0.652	0.265

* Sample contaminated by sea spray.

⁺ $\pm 50\%$

RW - Rain shower

Table VII
Gaseous Iodine and Bromine Concentrations Measured
Between Honolulu, Hawaii and Seattle, Washington

Sample Number	Date	Time (HST)	Location	Remarks	I ng/m ³	Br ng/m ³
S1A	5/20/69	1330- 1825	24° 45' N 157° 40' W	Calm seas, clear skies light trades	32.9*	28.0*
S2A	5/21/69	1115- 1445	27° 00' N 157° 40' W	Calm seas, clear skies, light trades	12.4	18.7
S3A	5/22/69	1200- 1845	30° 50' N 154° 10' W	Calm seas, partly overcast slicks visible on sea surface Trades	12.3	38.8
S4A	5/23/69	1050- 1845	33° 30' N 151° 10' W	Partly overcast - trades Seas slightly rougher than previous samples - no rain	9.6	30.7
S5A	5/23/69	1130- 1615	42° 20' N 138° 45' W	Intermittent rain, seas choppy, some spray	7.8	32.6

* Contaminated sample

Table VIII

Gaseous Iodine and Bromine Concentrations Measured on the Island of Hawaii

Sample Number	Date	Time (HST)	Location	Remarks	I ng/m ³	Br ng/m ³
H1A	6/26/69	1320-1845	UHHC*	Partly overcast. Trade winds.	54.8	39.0
H3A	6/27/69	1900-0920	UHHC	Down slope winds; rain during night	19.3	23.2
H4A	6/27/69	1015-1915	UHHC	Trade winds	37.6	39.4
H5A	6/28/69	1930-0850	UHHC	Down slope winds; many RW	11.8	12.1
H6A	6/28/69	1005-1920	UHHC	Trade winds	31.7	41.2
H7A	6/29/69	1920-0855	UHHC	Down slope winds. RW 0800	17.0	18.0
H8A	6/29/69	0855-2000	UHHC	Trade winds. RW from 0900-1400	30.9	21.6
H9A	6/30/69	2000-0855	UHHC	Downslope winds; many RW	11.6	20.3
H10A	6/30/69	0855-2045	UHHC	Trade winds	21.9	34.7
H11A	7/1/69	2050-0830	UHHC	Downslope winds	13.8	42.3
H12A	7/1/69	0830-1745	UHHC	Trade winds	34.8	47.4

Table VIII (Continued)

Gaseous Iodine and Bromine Concentrations Measured on the Island of Hawaii

Sample Number	Date	Time (HST)	Location	Remarks	I ng/m ³	Br ng/m ³
H3B	6/26/69 6/27/69	1900-0920	UHC	Duplicate of H3A	19.8	27.0
H5B	6/27/69	1700-2345	MLO ⁺	Clear weather	4.1 ± 1.5	6.9 ± 3.0
H6B	6/27/69 6/28/69	2345-0800	MLO	Clear weather	2.5 ± 1.2	<5.0
H7B	6/28/69	0800-1510	MLO	Cloud tops at the sampling site	8.5	20.2
H8B	6/30/69	1040-1720	KR [#]	Overcast - many RW	10.2	31.0
H9B	6/30/69 7/1/69	2100-0830	UHC	Duplicate of H11A	15.2	39.3
H10B	7/1/69		KR	Overcast - No RW	9.1	34.3

* UHC - University of Hawaii, Hilo Campus, Wentworth Hall

⁺ MLO - Mauna Loa Observatory, (3,500 m above sea level)

[#] KR - Kulani Road, (900 m above sea level)

RW - Rain showers

Table IX

Gaseous Iodine and Bromine Concentrations
Measured at the University of Hawaii, Honolulu, Oahu, Hawaii

Sample Number	Date	Time (HST)	I ng/m ³	Br ng/m ³
	7/27/69			
L2A	7/28/69	2230-0815	20.6	168.0
L3A	7/28/69	0815-1615	19.9	171.0
L7A	7/30/69	0830-1615	14.9	181.0
L8A	7/30/69	1630-2330	10.9	63.0
	7/30/69			
L9A	7/31/69	2330-0800	14.1	39.1
L11A	7/31/69	0830-1605	19.7	79.9
L15A	7/31/69			
	8/1/69	1605-0030	12.2	85.3
L16A	8/1/69	0030-0845	11.9	55.1

Table X
Gaseous Iodine and Particulate Lead and Iodine Collected in Cambridge, Massachusetts

Sample No.	Date	Time EDT	Gaseous Iodine ng/m ³	Particulate Iodine ng/m ³	Particulate Lead ng/m ³
M1B	9/2/69	1100-1900	-	-	2.04
M2B	9/3/69	0730-1230	17.8	9.9	2.31
M3B	9/4/69	0745-1245	11.0	9.6	3.32
M4B	9/4/69	1300-1730	18.5	15.4	3.70
M5B	9/4/69- 9/5/69	1745-0630	12.7	7.2	3.30
M6B	9/5/69	0630-1645	13.7	3.2	0.68 ± 0.10
M7B	9/15/69	1340-2000	-	1.9	1.33
M8B	9/15/69- 9/16/69	2000-0650	14.4	2.8	0.45 ± 0.10
M9B	9/16/69	0650-1720	12.5	3.9	1.84
M10B	9/16/69- 9/17/69	1720-0040	10.2	8.0	1.66 ± 0.2
M11B	9/17/69	0040-0640	14.7	-	0.39 ± 0.10

Table XI
Means, Standard Deviations, and Ranges
of Gaseous Iodine and Bromine Concentrations at Various Locations

Location	Iodine, ng/m ³		Bromine, ng/m ³	
	Mean $\pm$ SD	Range	Mean $\pm$ SD	Range
Bellows Air Force Station, Oahu (TOTAL)	8.1 $\pm$ 3.5	3.5 - 20.2	46.1 $\pm$ 13.2	23.1 - 90.5
Bellows Air Force Station, Oahu 7/4/69 - 7/25/69	9.0 $\pm$ 4.2	3.7 - 20.2	38.2 $\pm$ 9.1	23.1 - 66.3
Bellows Air Force Station, Oahu 7/26/69 - 8/10/69	7.0 $\pm$ 2.1	3.5 - 12.1	55.0 $\pm$ 11.3	38.2 - 90.5
Honolulu	15.5 $\pm$ 4.0	10.9 - 20.6	105.0 $\pm$ 58.0	39.1 - 181.
Hilo, UHHC (Day)	35.3 $\pm$ 10.9	21.9 - 54.8	37.2 $\pm$ 8.7	21.6 - 47.4
Hilo, UHHC (Night)	14.7 $\pm$ 3.4	11.6 - 19.3	23.2 $\pm$ 11.4	12.1 - 42.3
Hilo, Kulani Road	2 samples only	9.1 - 10.2	N/A	31.0 - 34.3
Mauna Loa Weather Observatory, Hawaii	3 samples only	2.5 - 8.5	N/A	<5.0 - 20.2
U.S.C.G.S.S. MacArthur, at sea	4 samples only	7.8 - 12.4	N/A	18.7 - 38.8
Cambridge, Massachusetts	14.0 $\pm$ 2.8	10.2 - 18.5	214.0 $\pm$ 100.0	122.0 - 450.

Table XII

Statistical Index of Figures

Figure No.	X-Axis	Y-Axis	$\bar{X}$	σ_x	$\bar{Y}$	σ_y	$s_{y.x}$	$r_{y.x}$
9	I(G)	Br(G)	8.1	3.5	46.1	13.2	12.9	0.14
10	I(G)	Br(G)	9.0	4.2	38.2	9.1	7.3	0.58
11	I(G)	Br(G)	7.0	2.1	55.0	11.3	10.4	0.34
12	Na(P)	I(G)	2.6	0.6	7.9	3.0	2.8	-0.08
13	Na(P)	Br(G)	2.6	0.6	45.9	11.1	10.7	0.08
16	I(G)	I(P)	6.7	2.2	0.30	0.20	0.10	0.87
17	I(G)	I(P)	6.7	2.2	0.90	0.41	0.32	0.59
18	I(G)	I(P)	6.7	2.2	1.03	0.52	0.41	0.61
19	I(G)	I(P)	6.7	2.2	0.27	0.14	0.11	0.57
20	I(G)	I(P)	6.7	2.2	2.56	1.08	0.46	0.89
21	I(G)	I/Cl(P)	6.7	2.2	0.20*	0.14*	0.05*	0.93
22	I(G)	I/Cl(P)	6.7	2.2	0.62*	0.25*	0.13*	0.84

Table XII (Continued)

Statistical Index of Figures

Figure No.	X-Axis	Y-Axis	$\bar{X}$	σ_x	$\bar{Y}$	σ_y	$s_{y.x}$	$r_{y.x}$
23	I(G)	I/Cl(P)	6.7	2.2	0.58*	0.27*	0.26*	0.90
24	I(G)	I/Br(P)	6.7	2.2	0.04	0.03	0.02	0.79
25	I(G)	I/Br(P)	6.7	2.2	0.10	0.10	0.05	0.85
26	I(G)	I/Br(P)	6.7	2.2	0.48	0.34	0.21	0.79
27	I(G)	I/Br(P)	6.7	2.2	0.37	0.22	0.08	0.93
29	I(G)	Br(G)	25.9	13.4	30.80	12.00	9.40	0.57
30	I(G)	Br(G)	15.5	4.0	105.00	58.10	43.00	0.61
32	I(P)/I(G)	Pb(P)	0.54	0.27	1.9	1.2	0.69	0.80
33	I(P)	Pb(P)	6.9	4.4	1.9	1.2	0.63	0.82

(P) - Particulate

(G) - Gaseous

* - 10^{-3} I and Br values are in ng/m^3 Na and Pb values are in $\mu\text{g/m}^3$

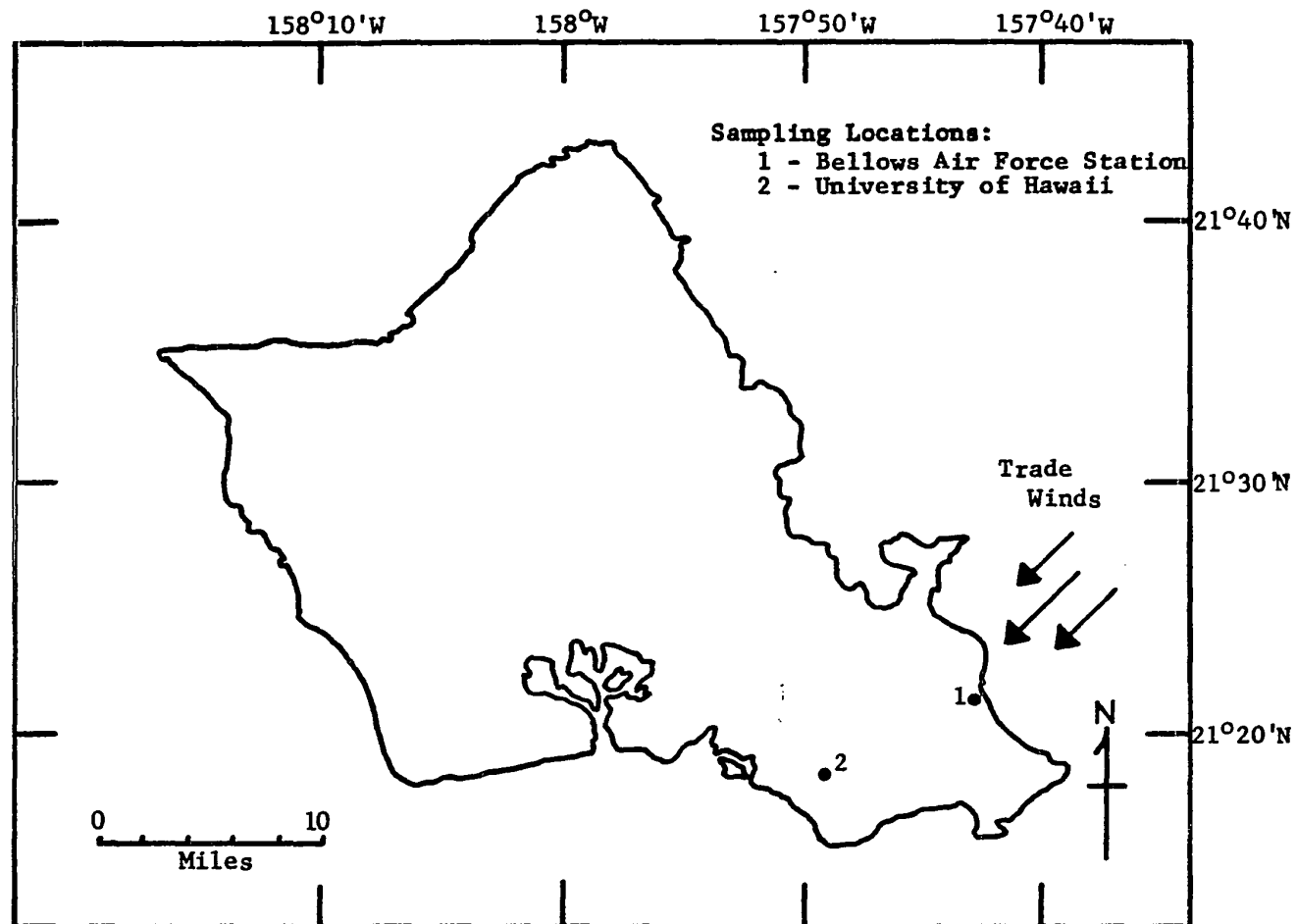


Figure 4. Island of Oahu

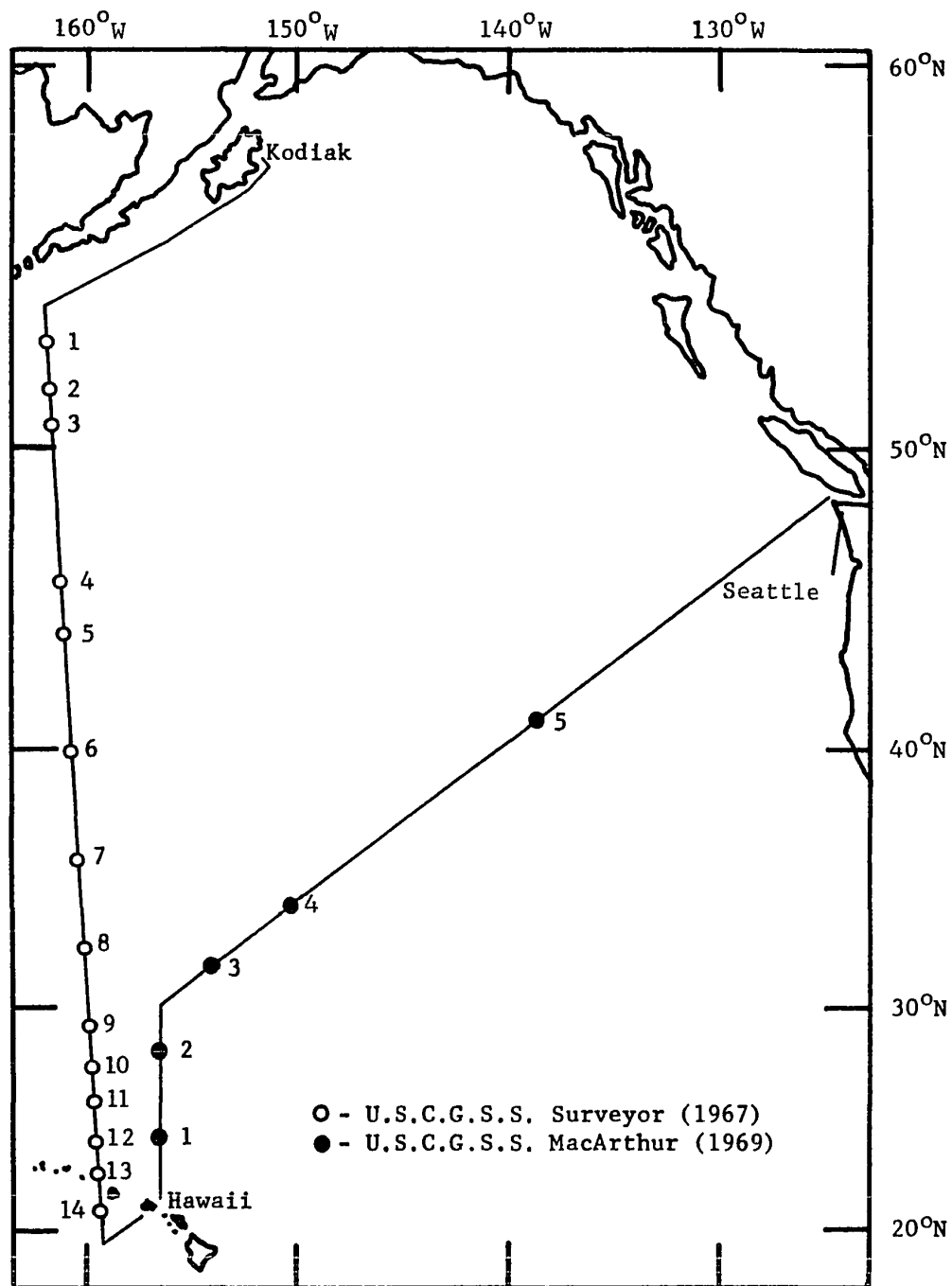


Figure 5. Northeast Pacific Ocean

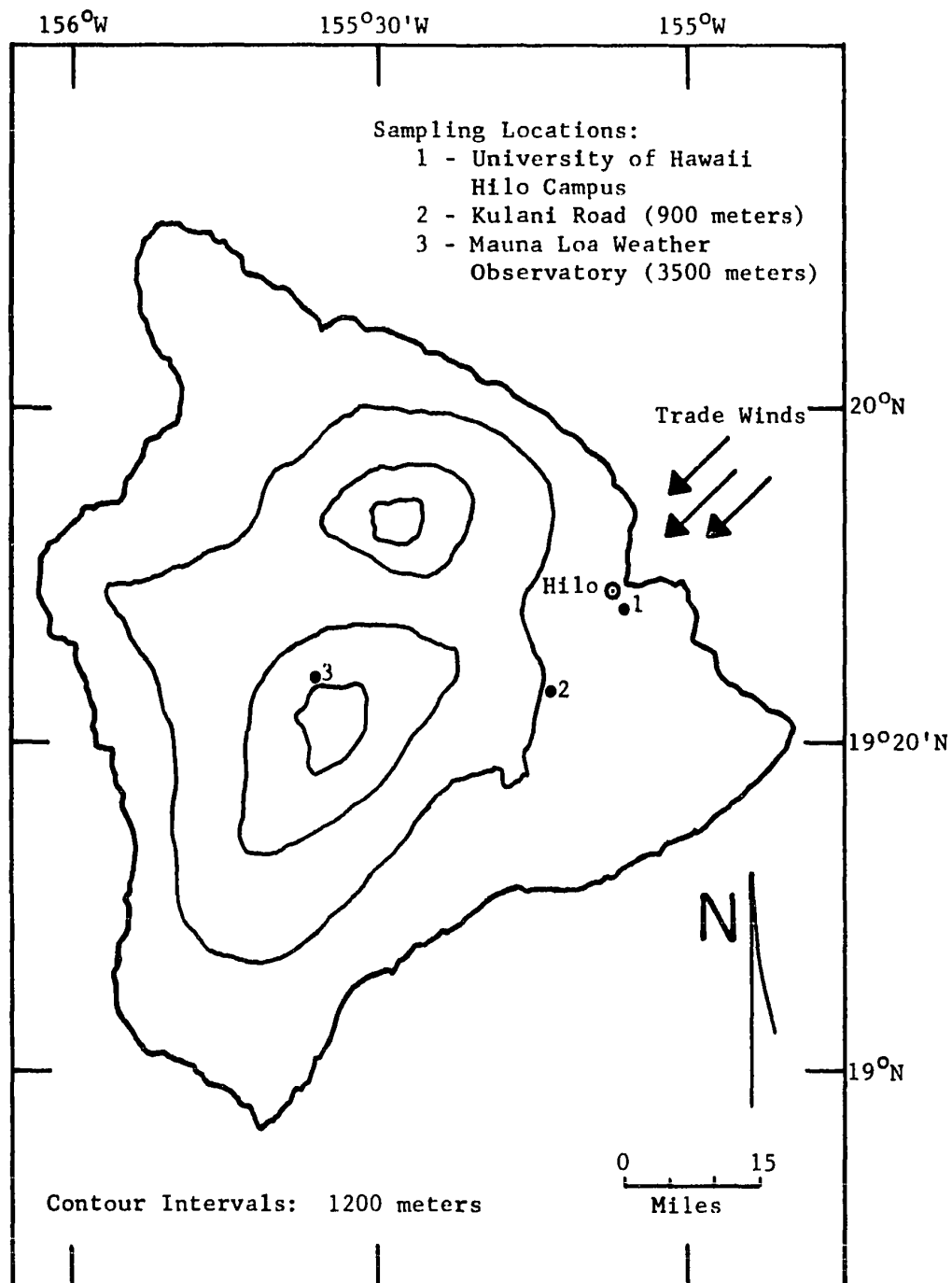


Figure 6. Island of Hawaii

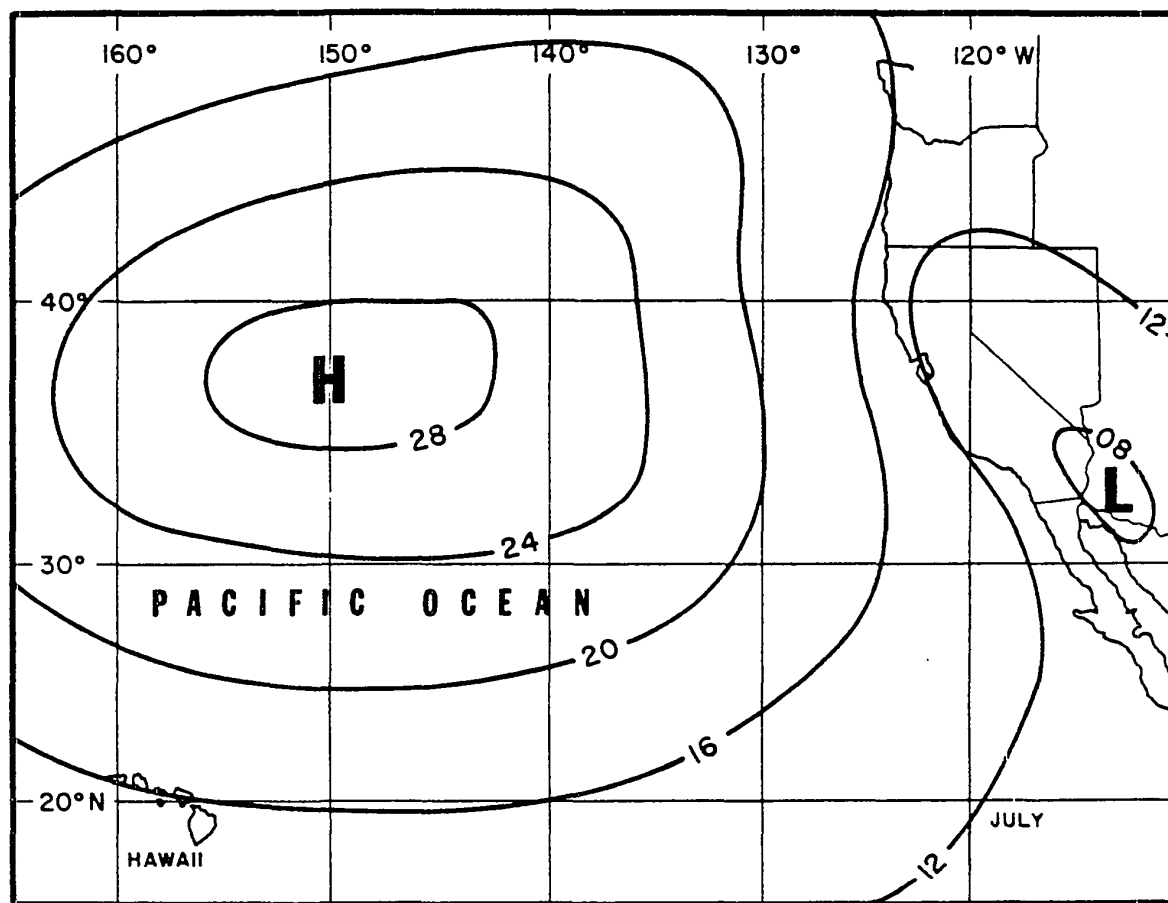


Figure 7. Average Surface Weather Map for the Month of July

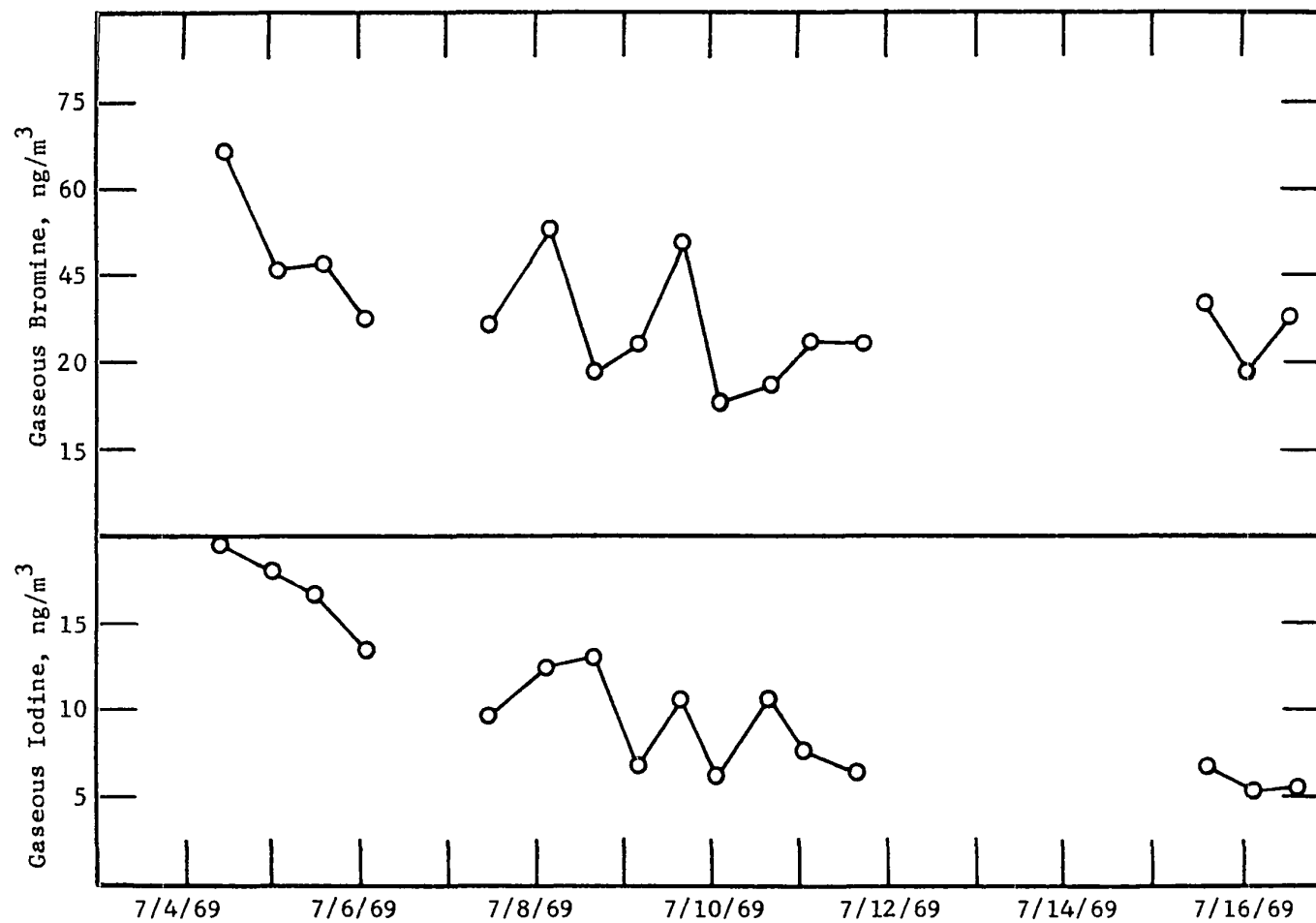


Figure 8. Daily Concentrations of Gaseous Iodine and Bromine; Bellows Air Force Station, Oahu

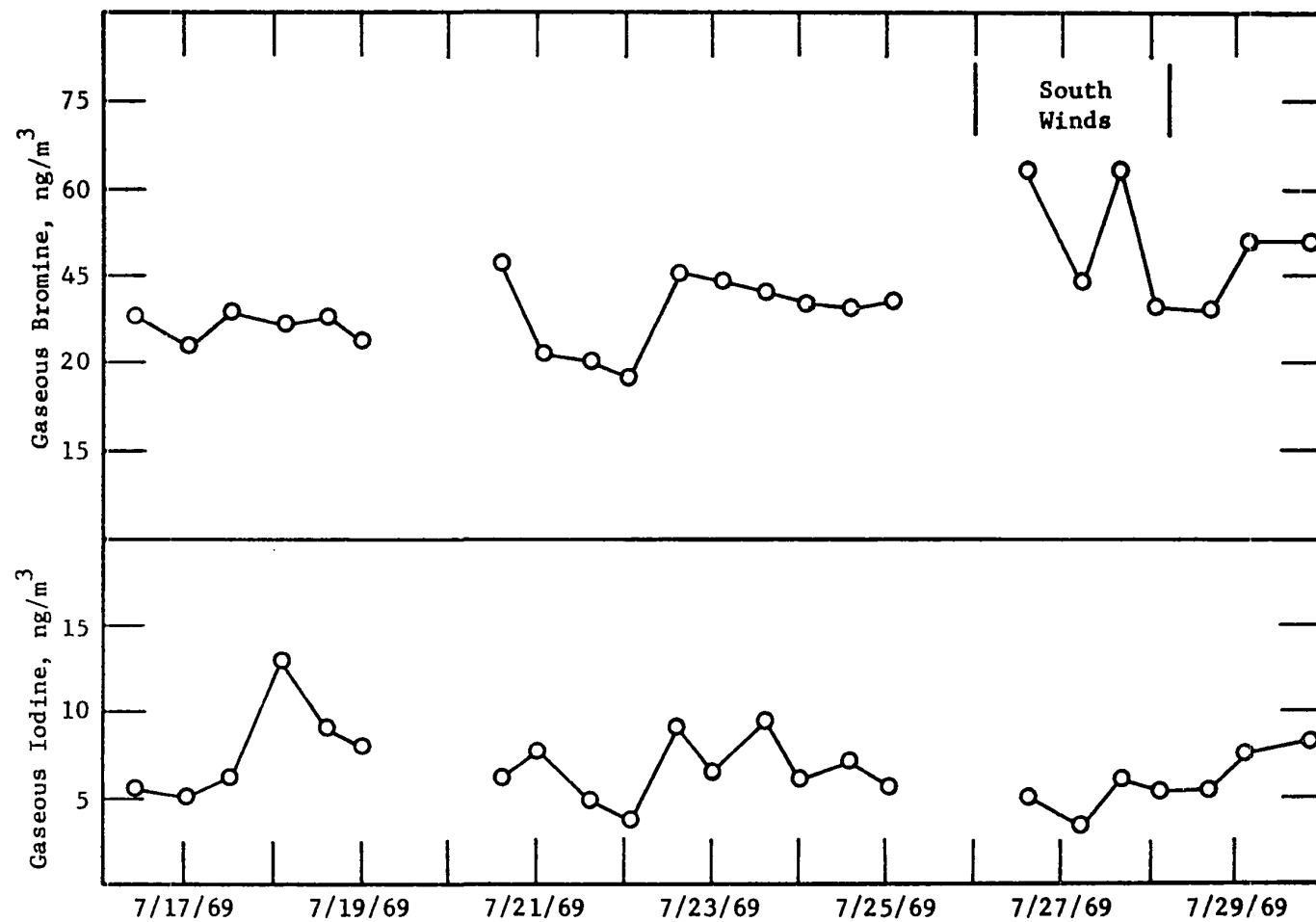


Figure 8 (cont.). Daily Concentrations of Gaseous Iodine and Bromine; Bellows Air Force Station, Oahu

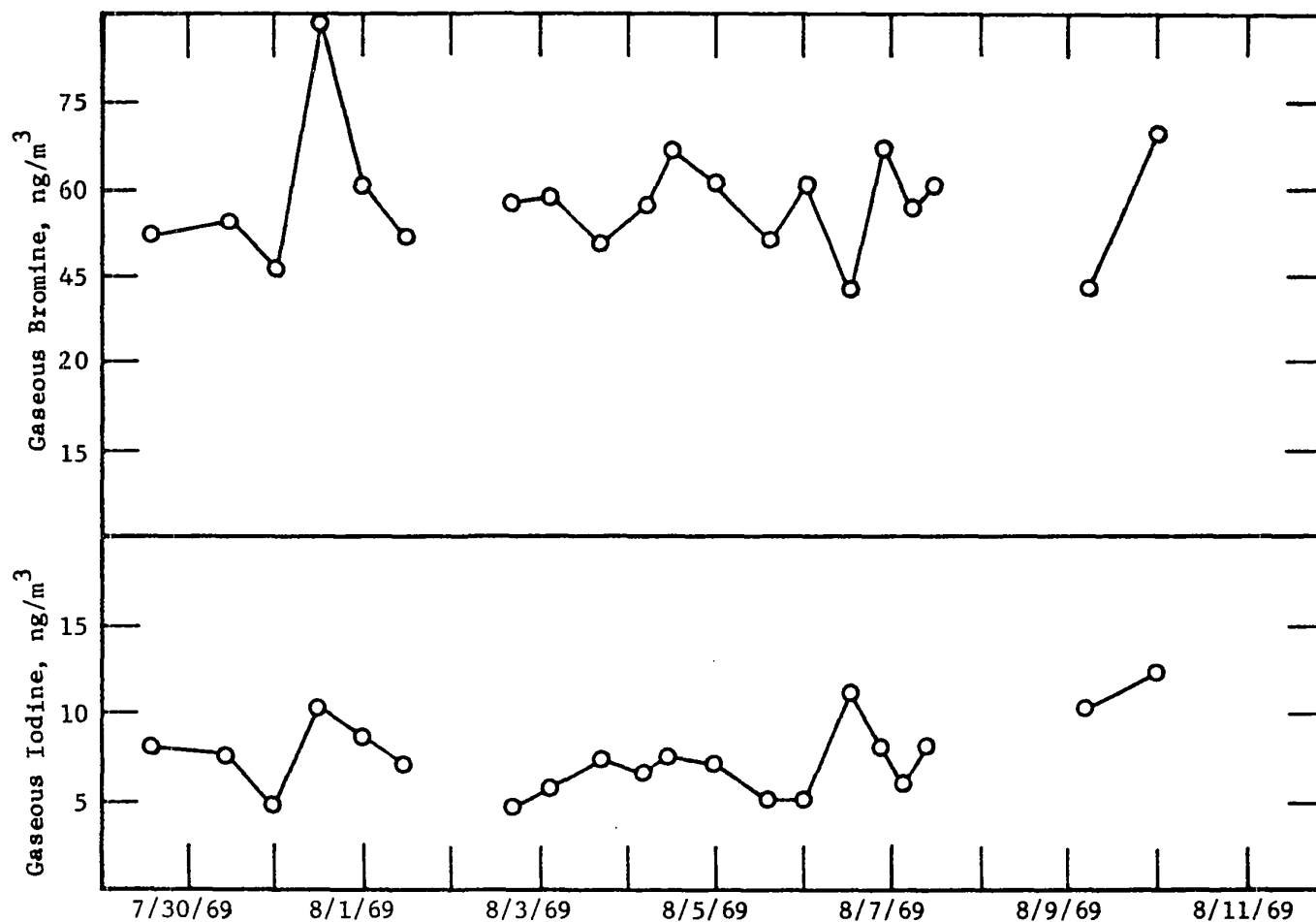


Figure 8 (cont.). Daily Concentrations of Gaseous Iodine and Bromine; Bellows Air Force Station, Oahu

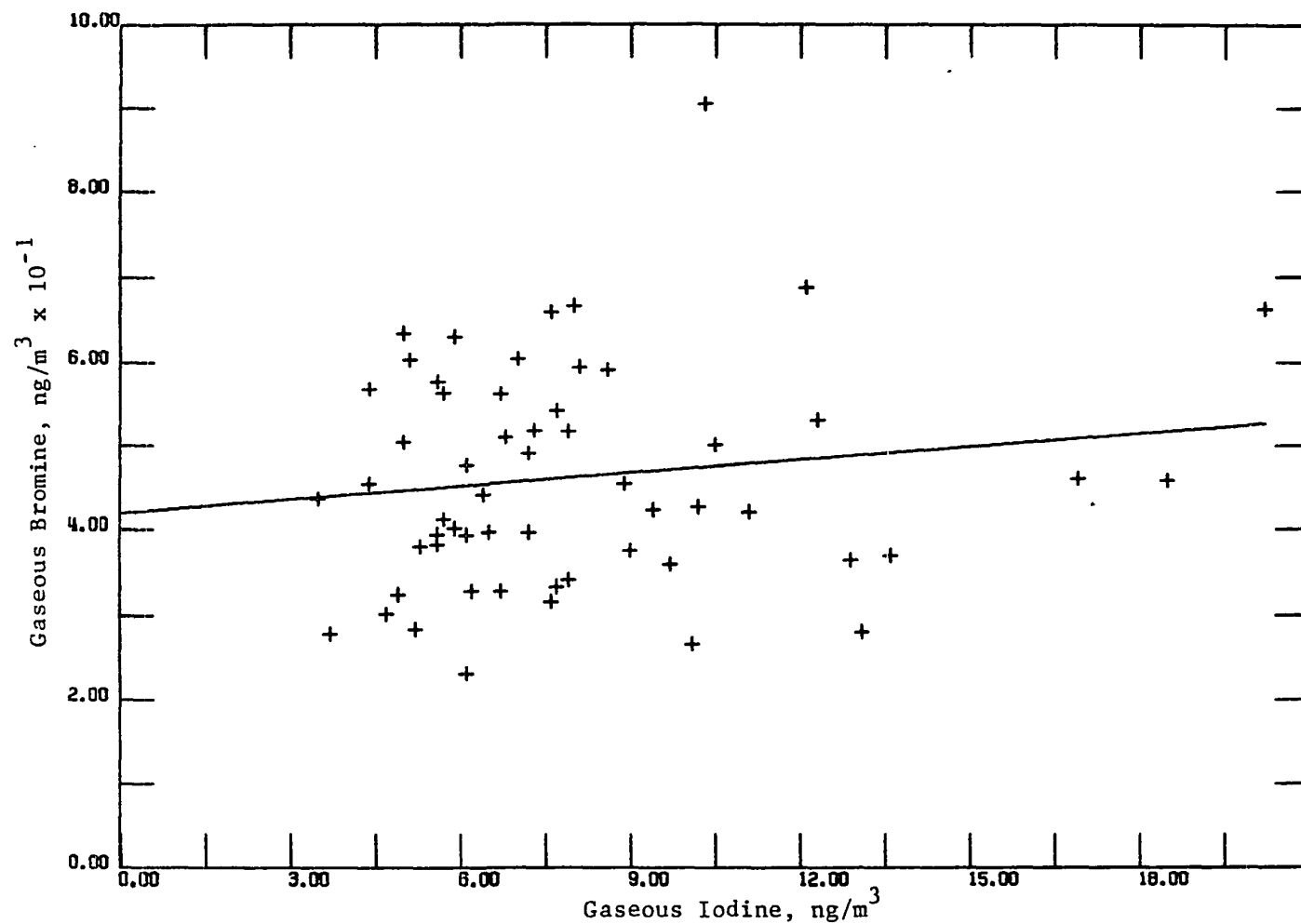


Figure 9. Gaseous Iodine Concentration vs. Gaseous Bromine Concentration; Bellows Air Force Station, 7/4/69-8/10/69

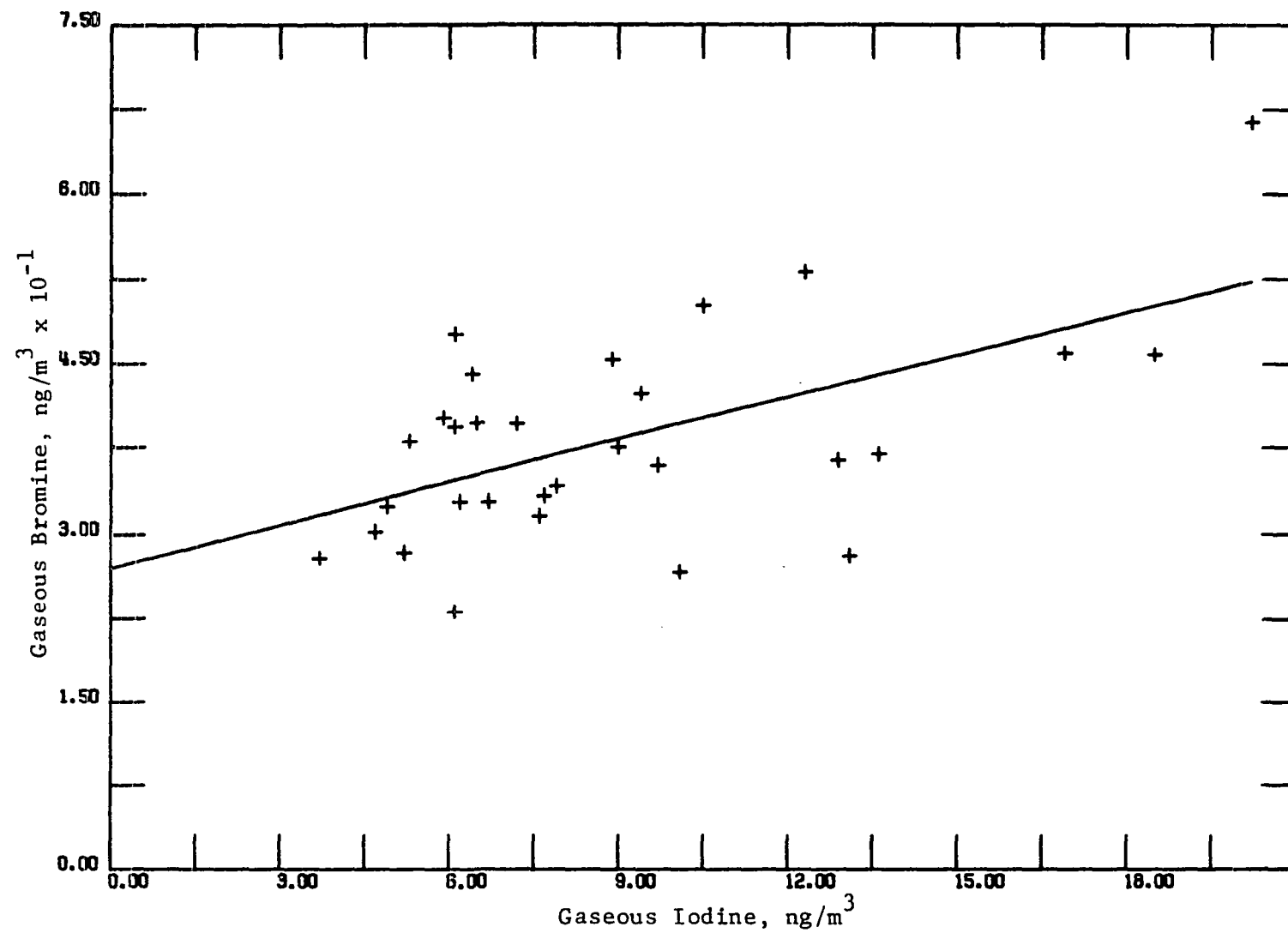


Figure 10. Gaseous Iodine Concentration vs. Gaseous Bromine Concentration; Bellows Air Force Station, 7/4/69-7/25/69

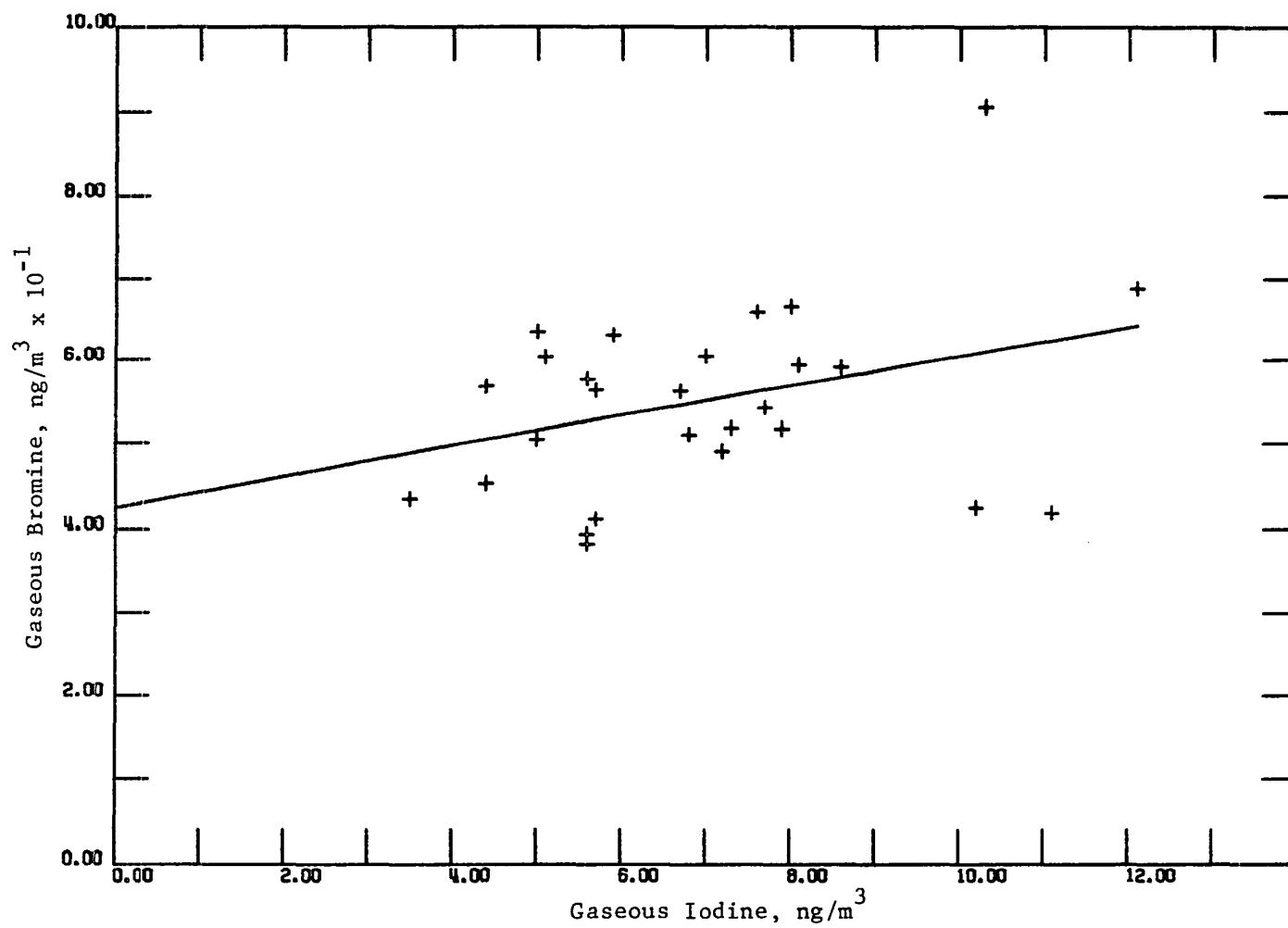


Figure 11. Gaseous Iodine Concentration vs. Gaseous Bromine Concentration; Bellows Air Force Station, 7/26/69-8/10/69

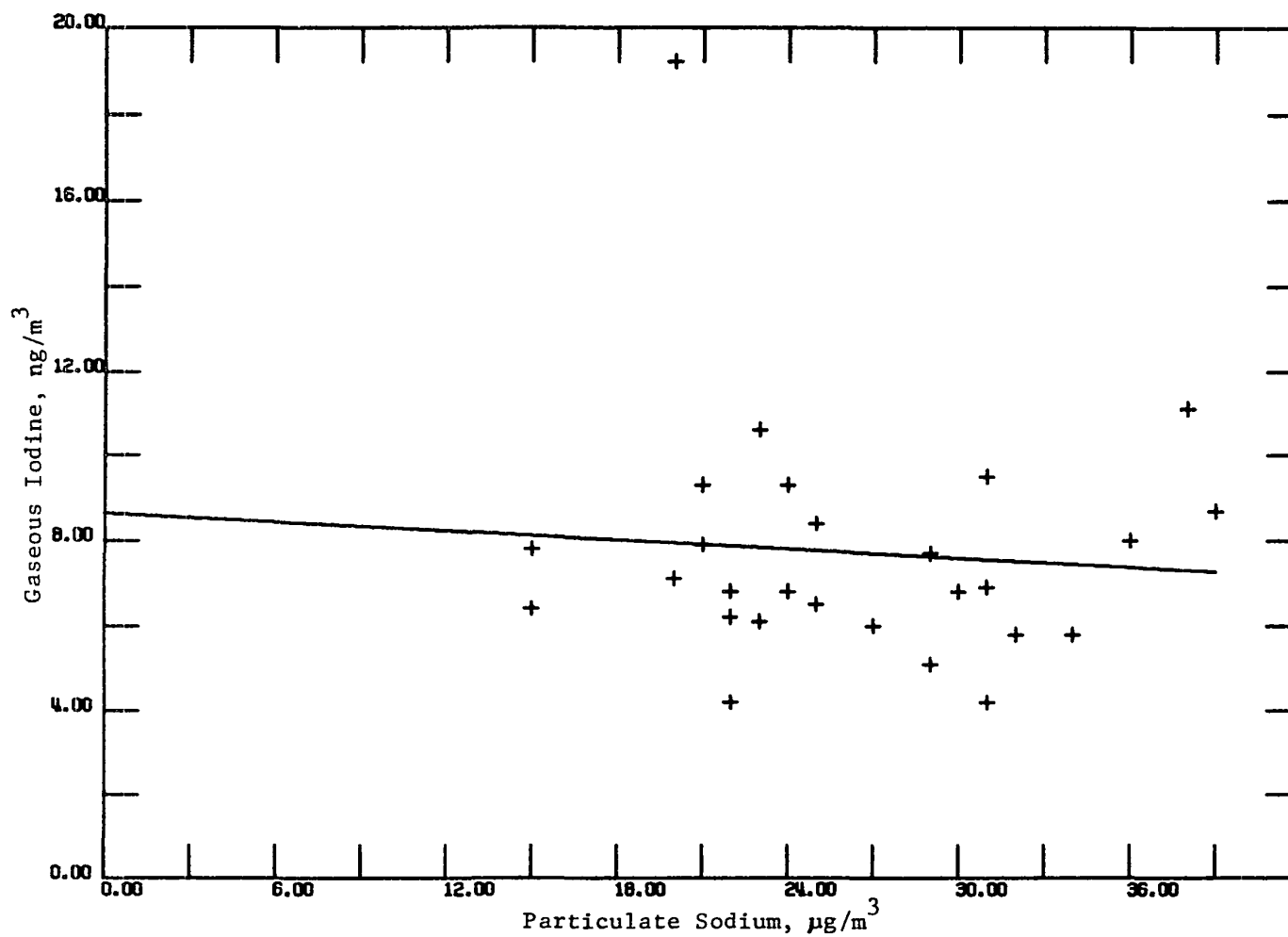


Figure 12. Gaseous Iodine Concentration vs. Particulate Sodium Concentration;
Bellows Air Force Station

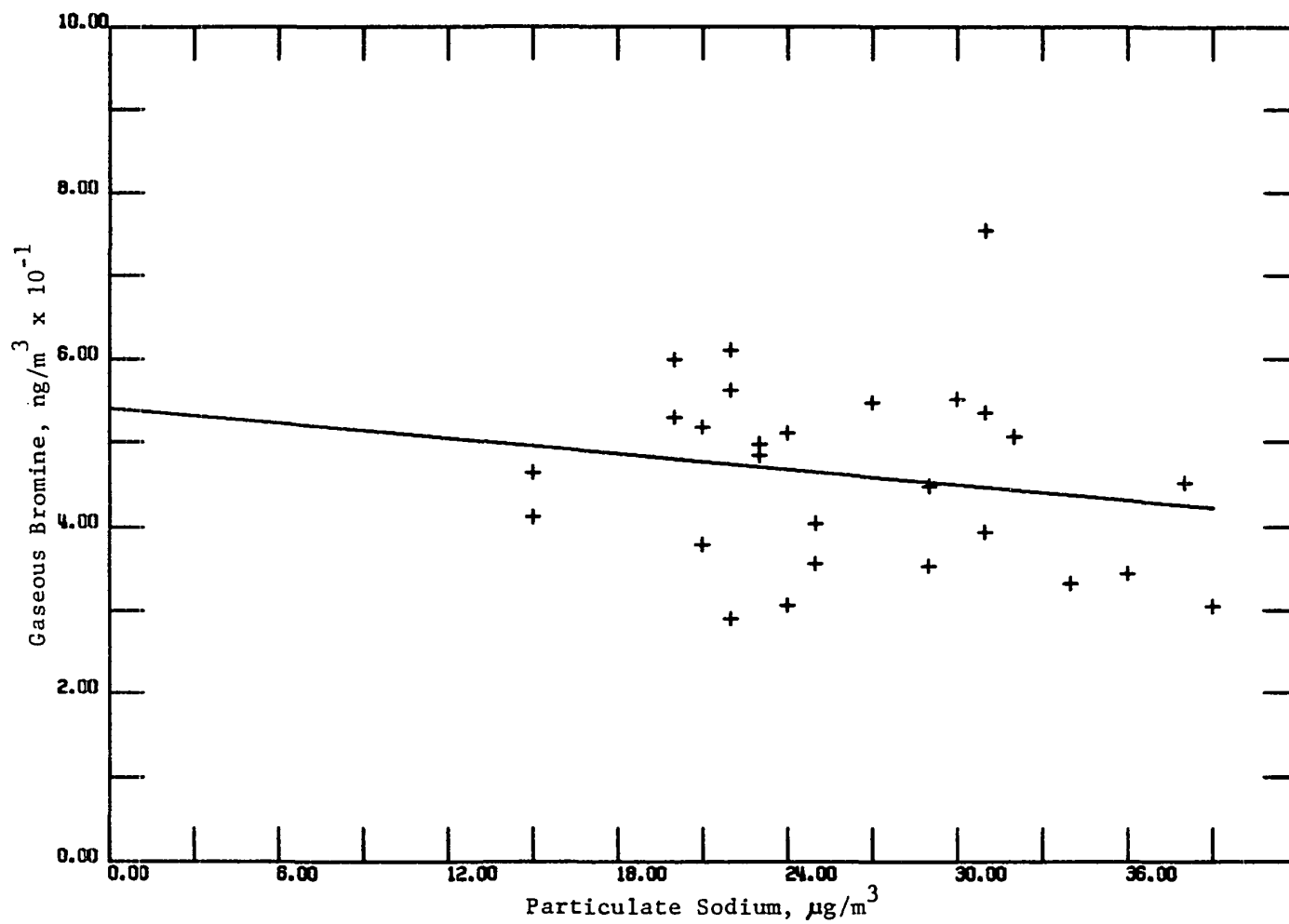


Figure 13. Gaseous Bromine Concentration vs. Particulate Sodium Concentration;
Bellows Air Force Station

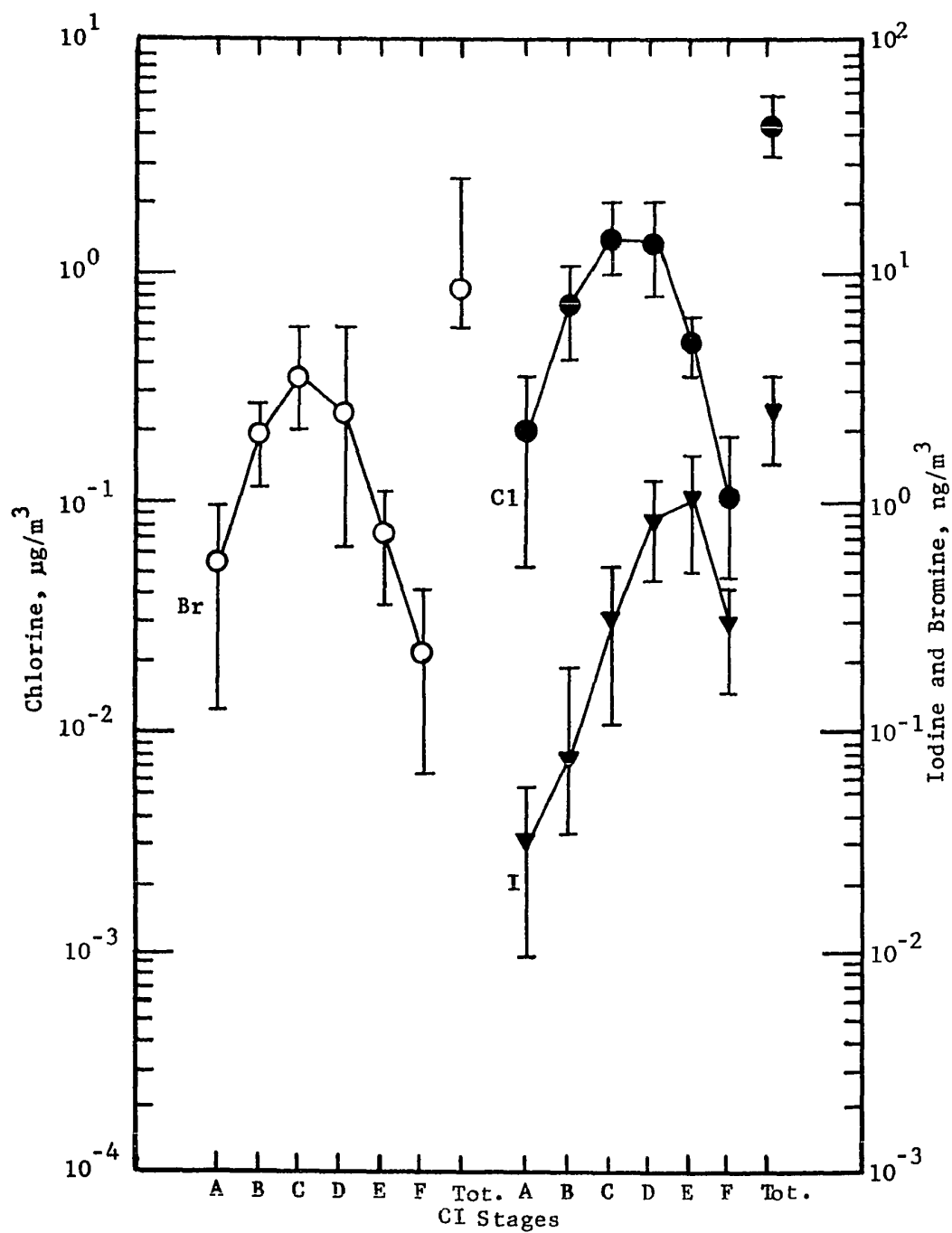


Figure 14. Average Size Spectra for Iodine, Bromine, and Chlorine Concentrations of Sea Salt Particles

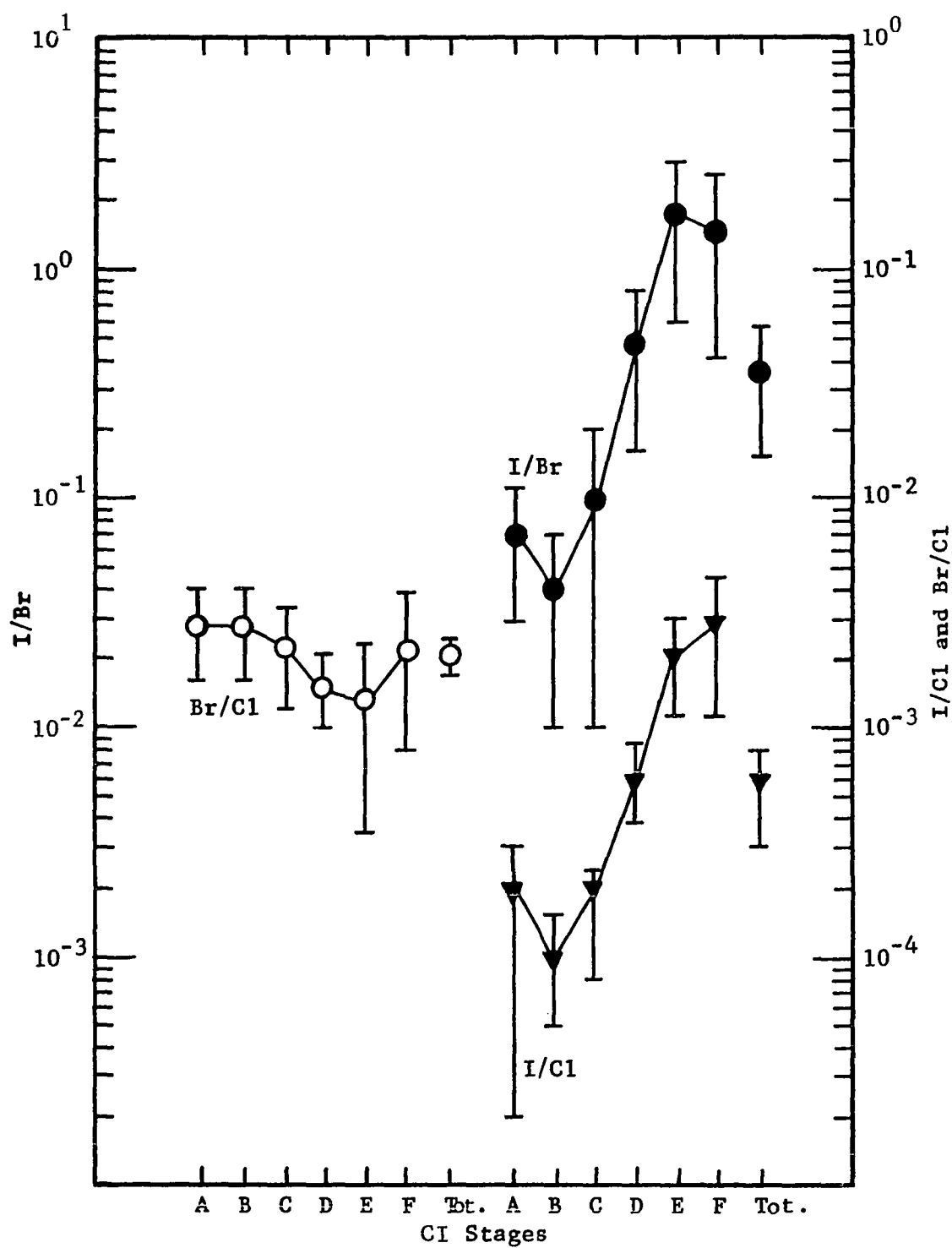


Figure 15. Average Size Spectra of I/Cl, Br/Cl, and I/Br Sea Salt Particles

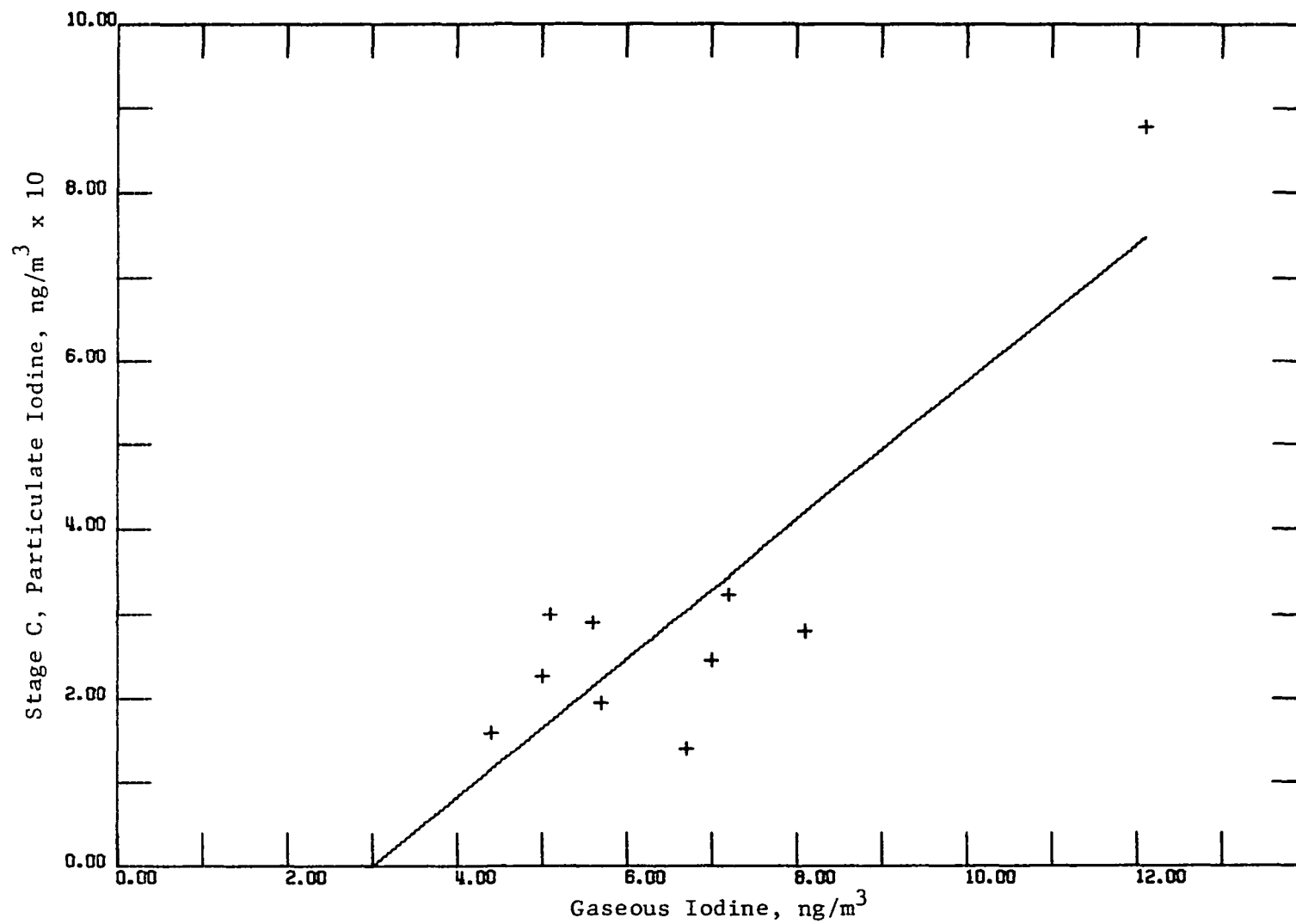


Figure 16. Gaseous Iodine Concentration vs. Particulate Iodine Concentration, Cascade Impactor Stage C

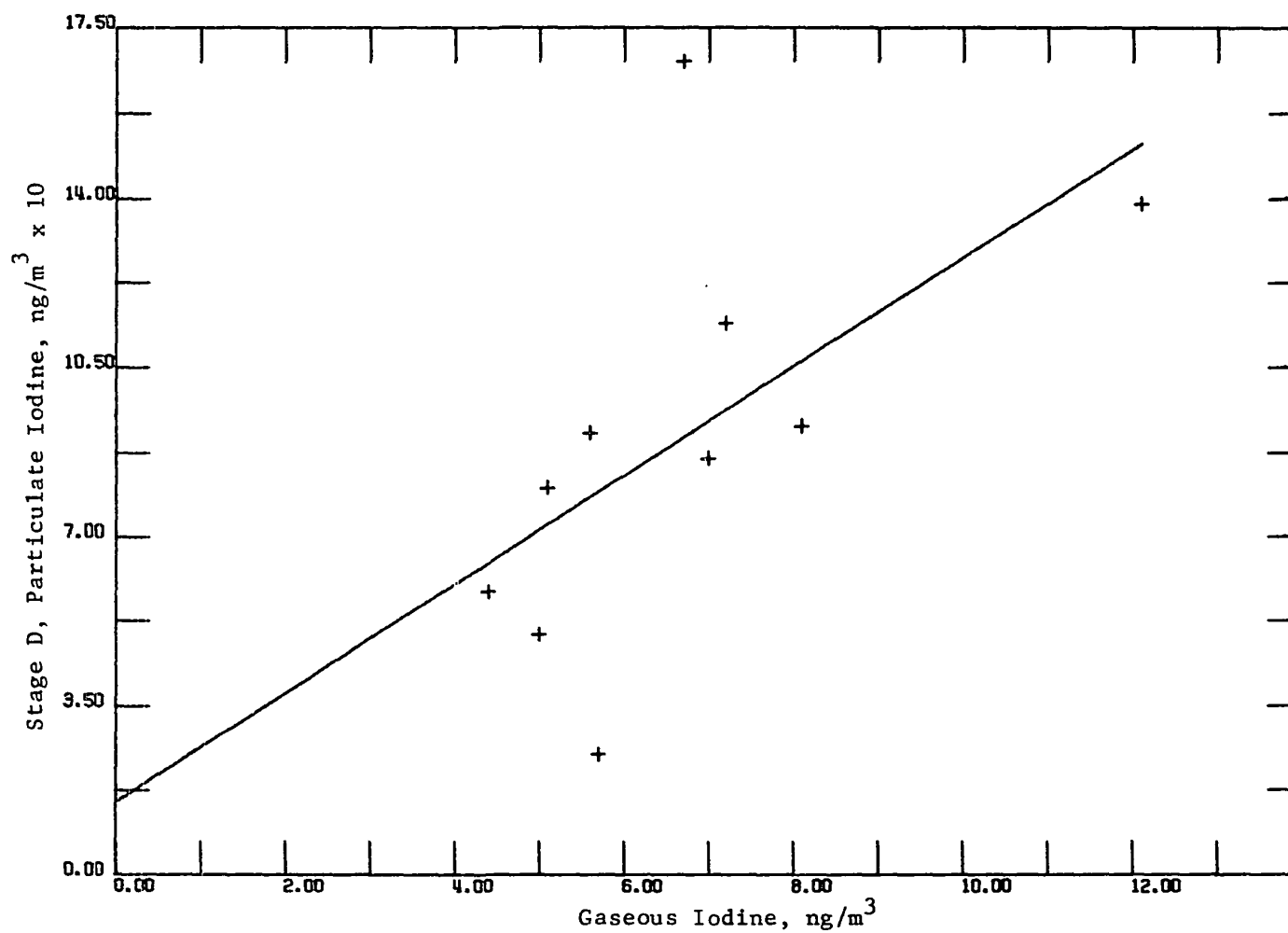


Figure 17. Gaseous Iodine Concentration vs. Particulate Iodine Concentration, Cascade Impactor Stage D

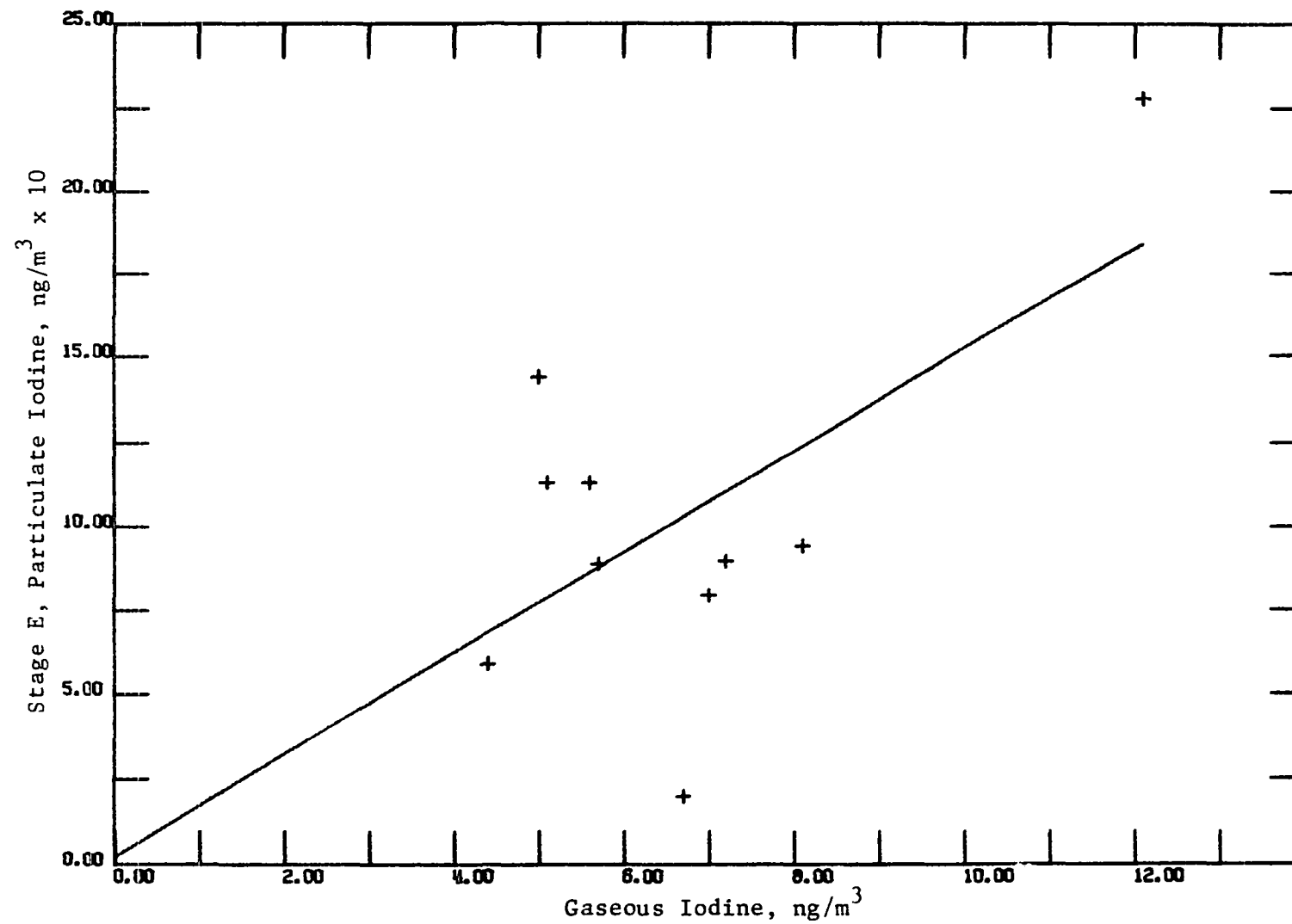


Figure 18. Gaseous Iodine Concentration vs. Particulate Iodine Concentration, Cascade Impactor Stage E

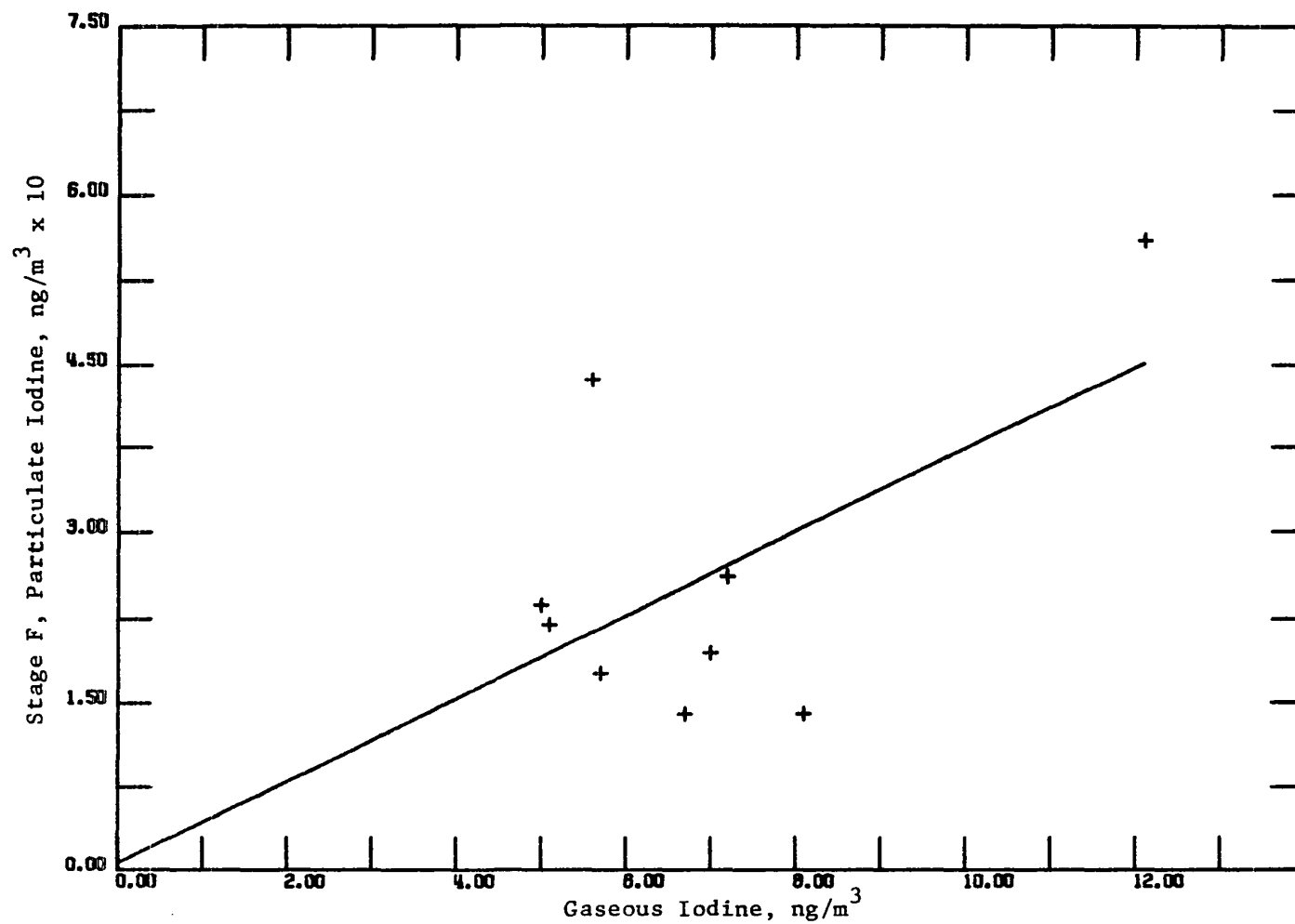


Figure 19. Gaseous Iodine Concentration vs. Particulate Iodine Concentration, Cascade Impactor Stage F

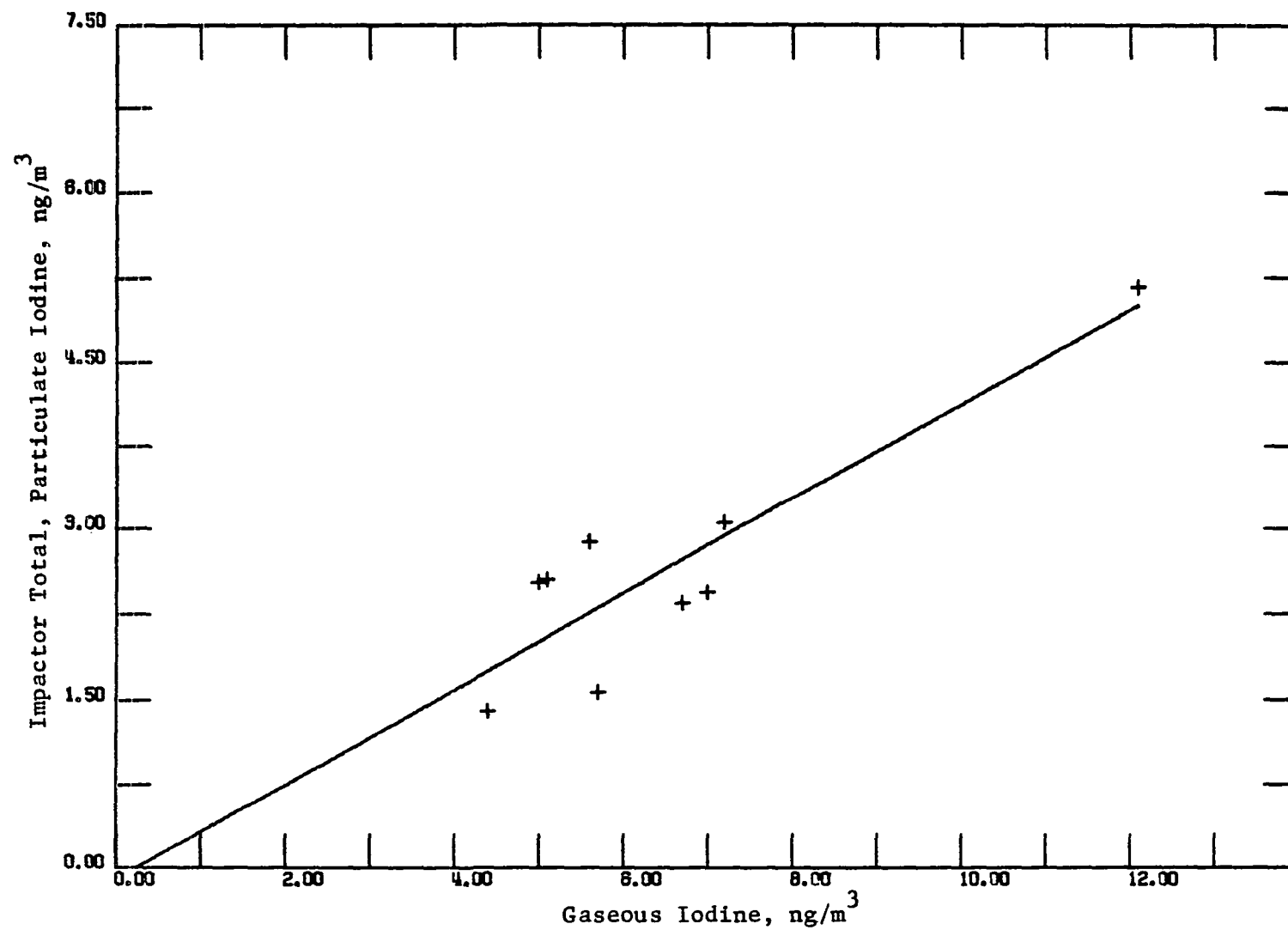


Figure 20. Gaseous Iodine Concentration vs. Particulate Iodine Concentration, Cascade Impactor Total

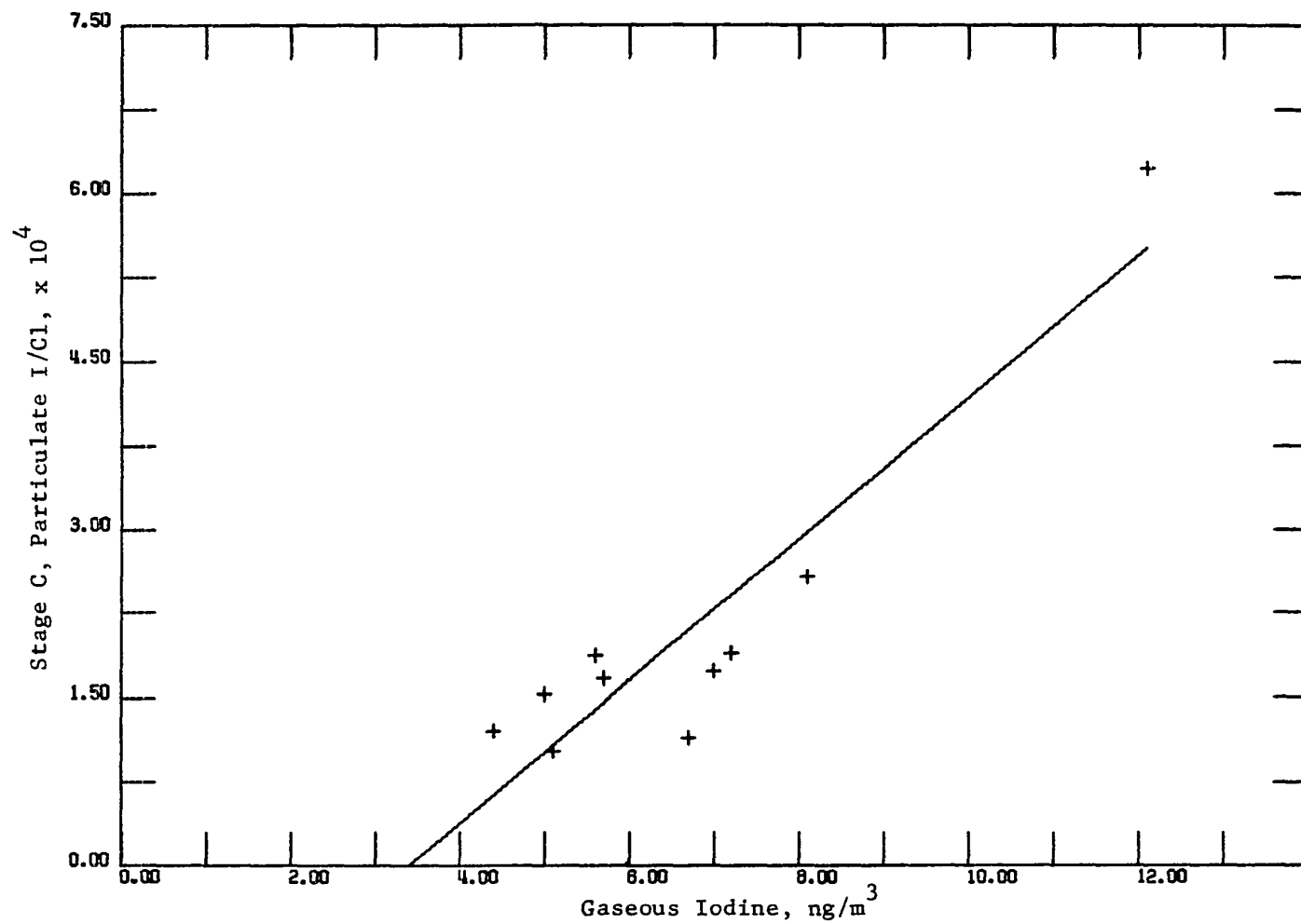


Figure 21. Gaseous Iodine Concentration vs. Particulate I/Cl Ratio, Cascade Impactor Stage C

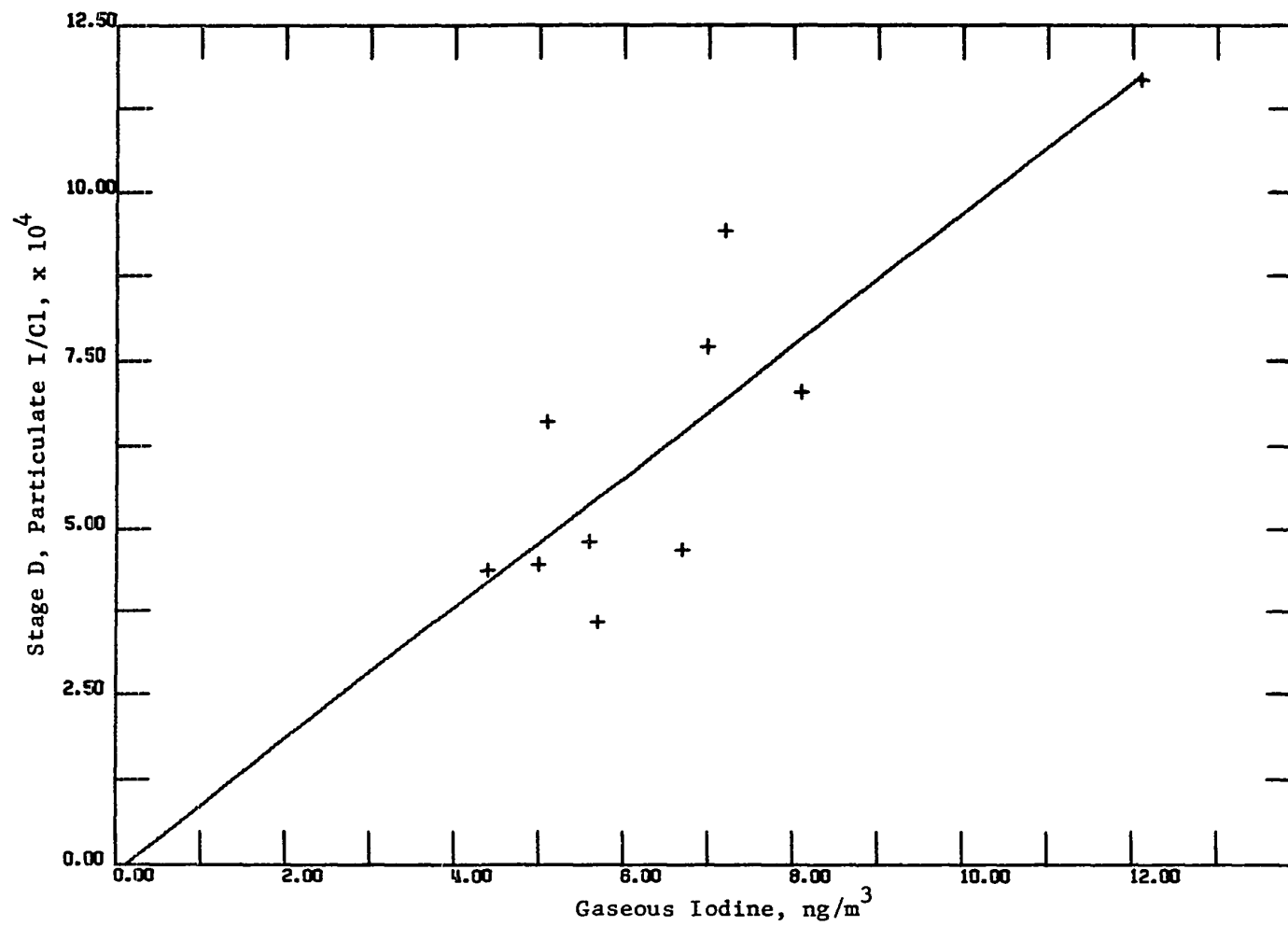


Figure 22. Gaseous Iodine Concentration vs. Particulate I/Cl Ratio, Cascade Impactor Stage D

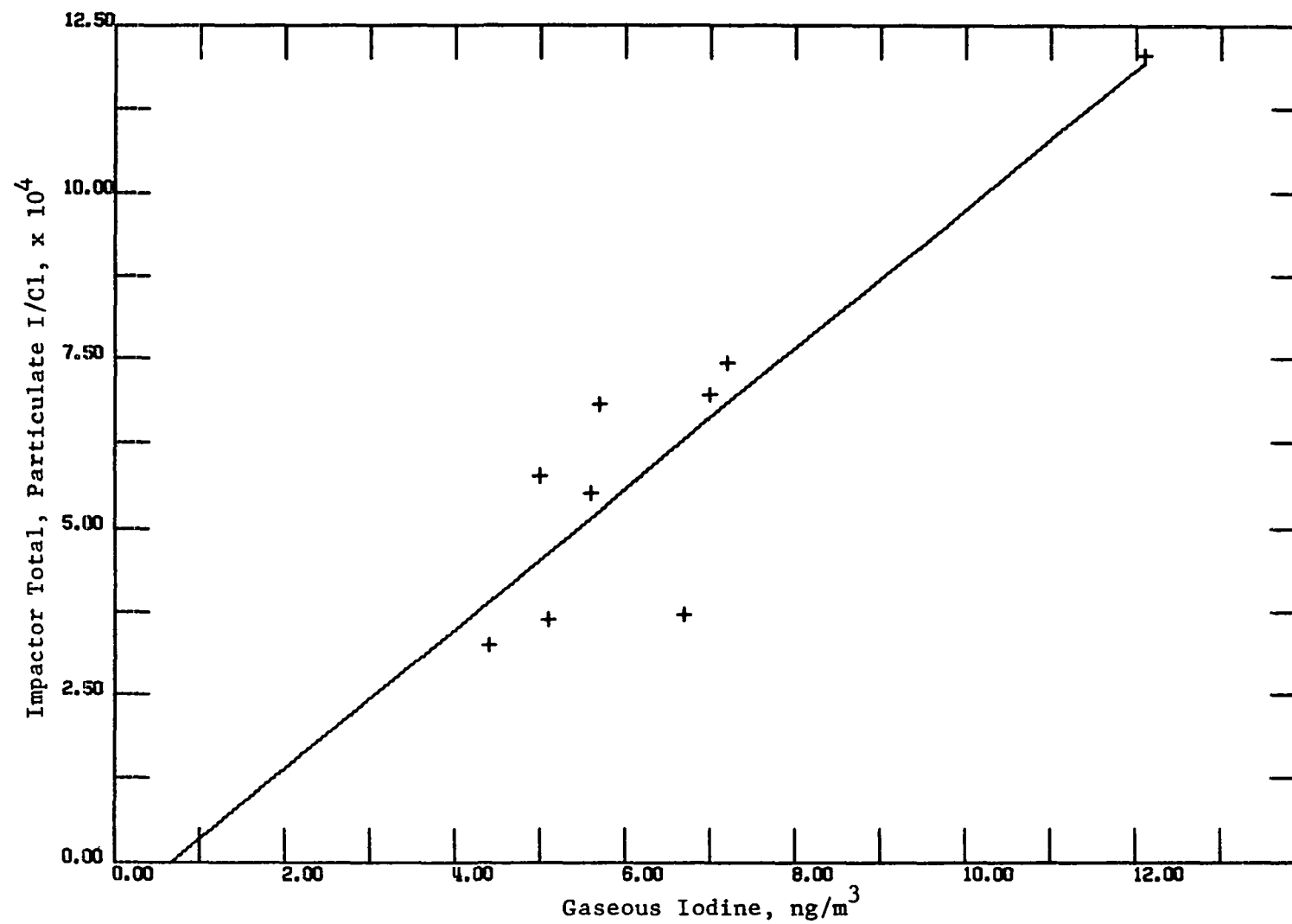


Figure 23. Gaseous Iodine Concentration vs. Particulate I/Cl Ratio, Cascade Impactor Total

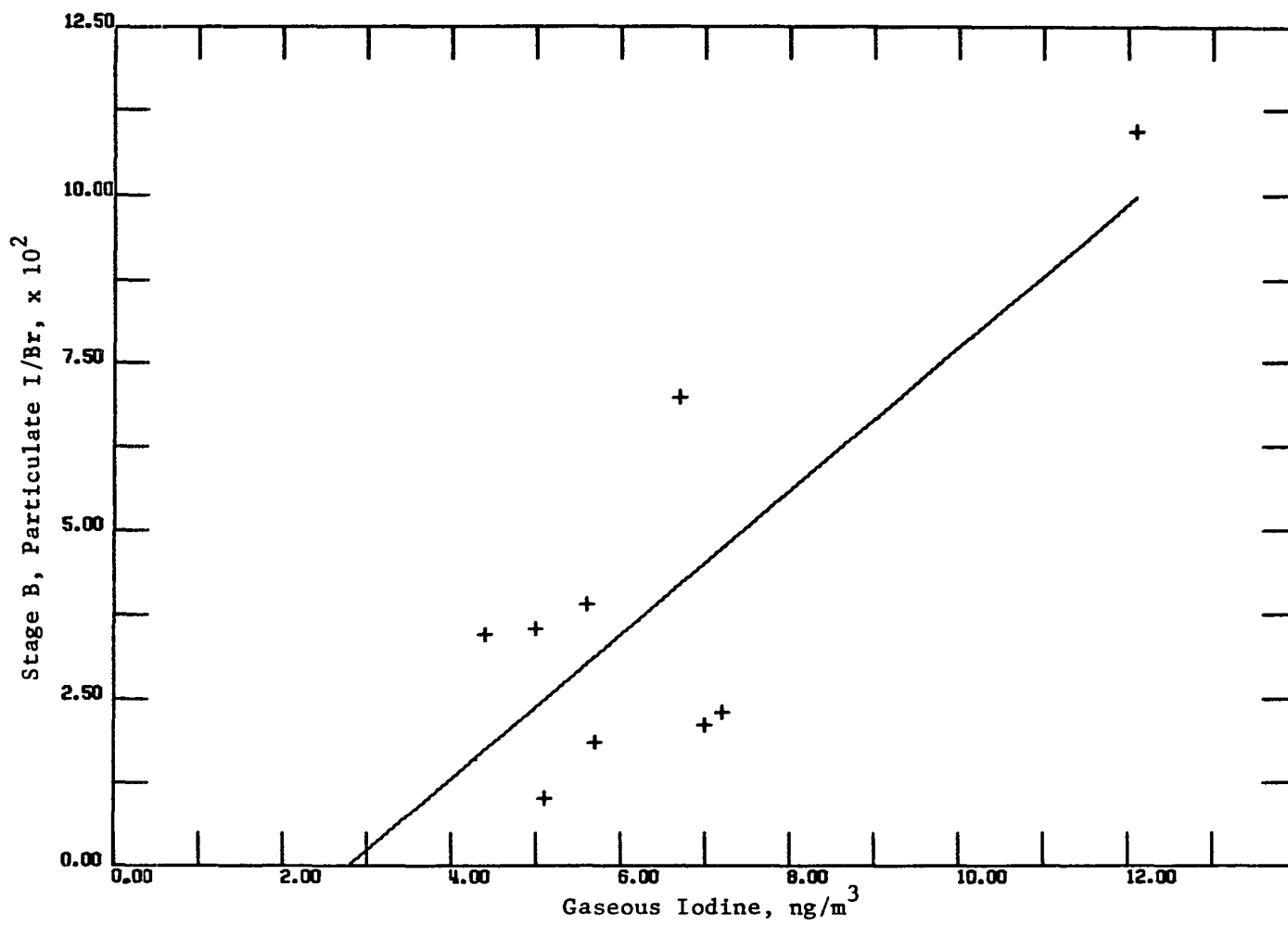


Figure 24. Gaseous Iodine Concentration vs. Particulate I/Br Ratio, Cascade Impactor Stage B

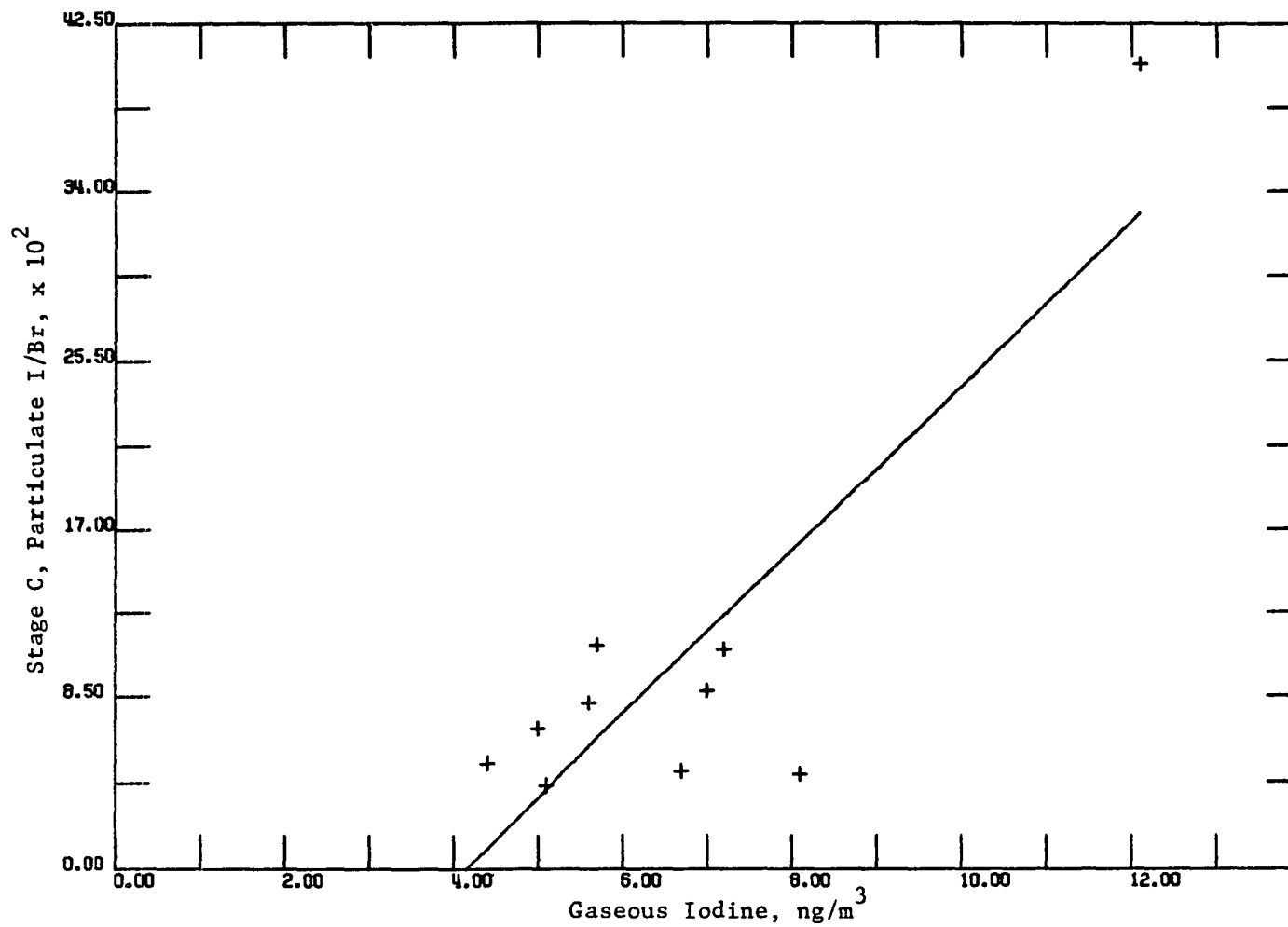


Figure 25. Gaseous Iodine Concentration vs. Particulate I/Br Ratio, Cascade Impactor Stage C

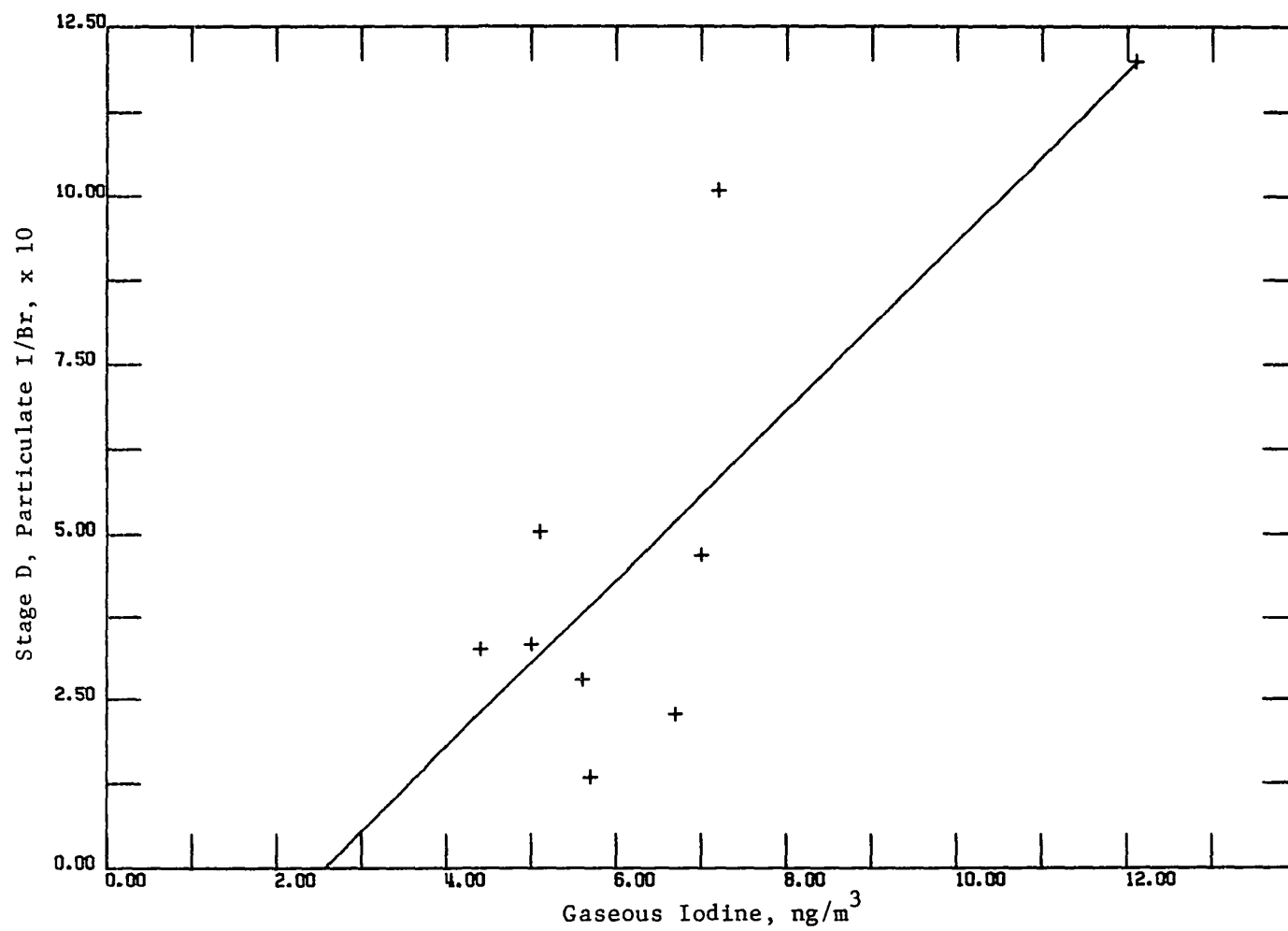


Figure 26. Gaseous Iodine Concentration vs. Particulate I/Br Ratio, Cascade Impactor Stage D

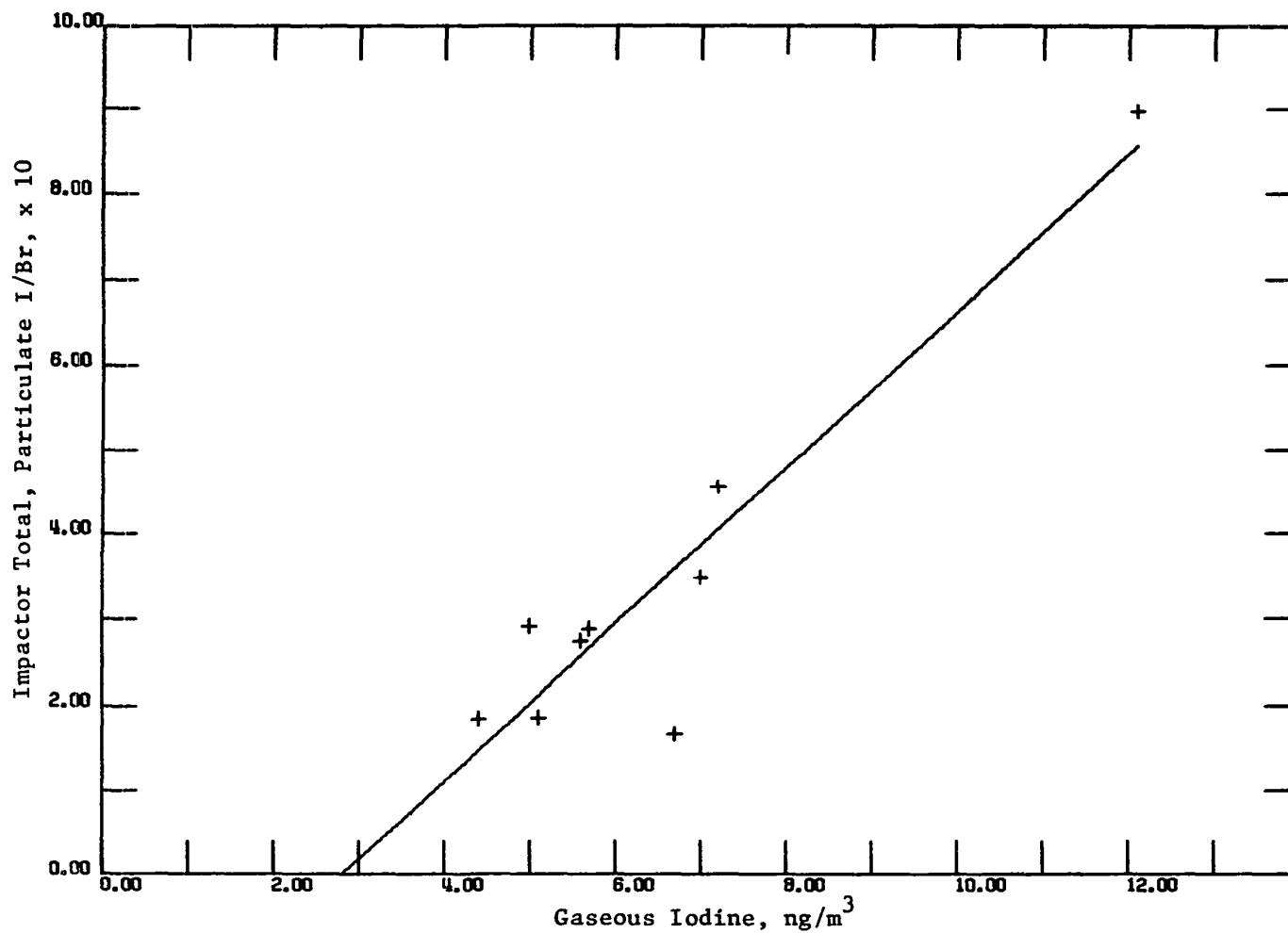


Figure 27. Gaseous Iodine Concentration vs. Particulate I/Br Ratio, Cascade Impactor Total

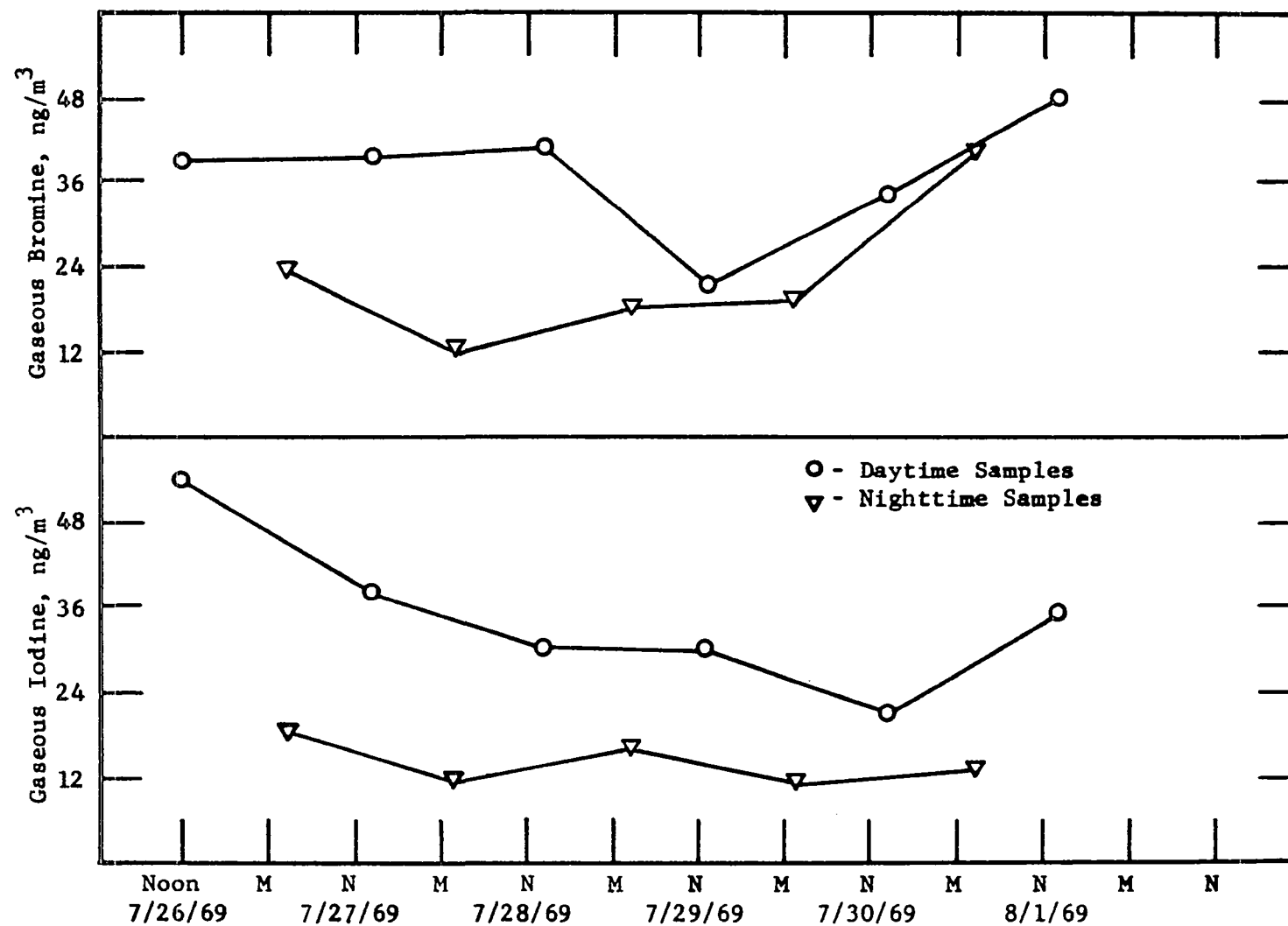


Figure 28. Variation of Gaseous Bromine and Iodine Between Night and Day;
 University of Hawaii Hilo Campus, Hilo, Hawaii

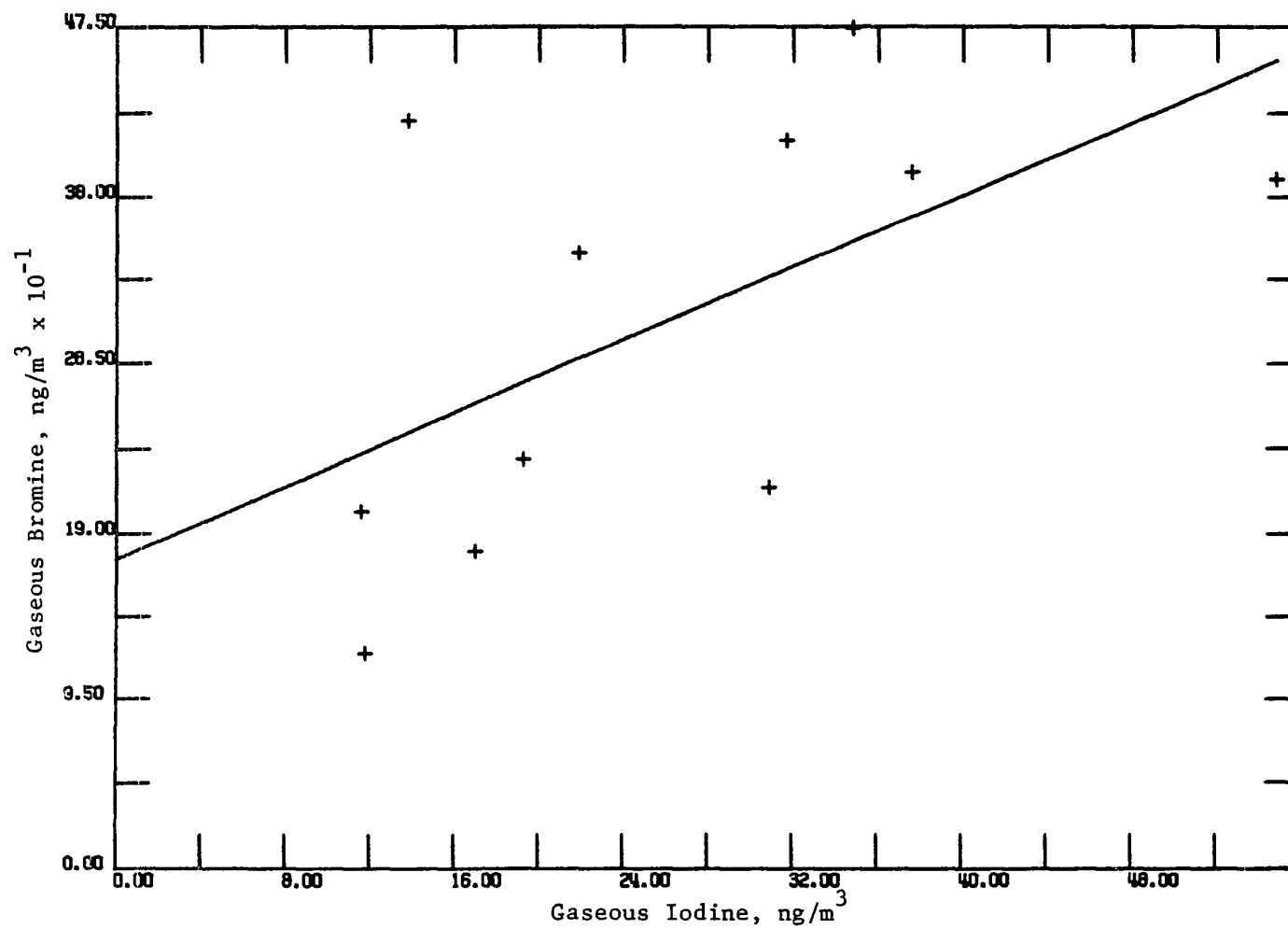


Figure 29. Gaseous Iodine Concentration vs. Gaseous Bromine Concentration; U.H.H.C.

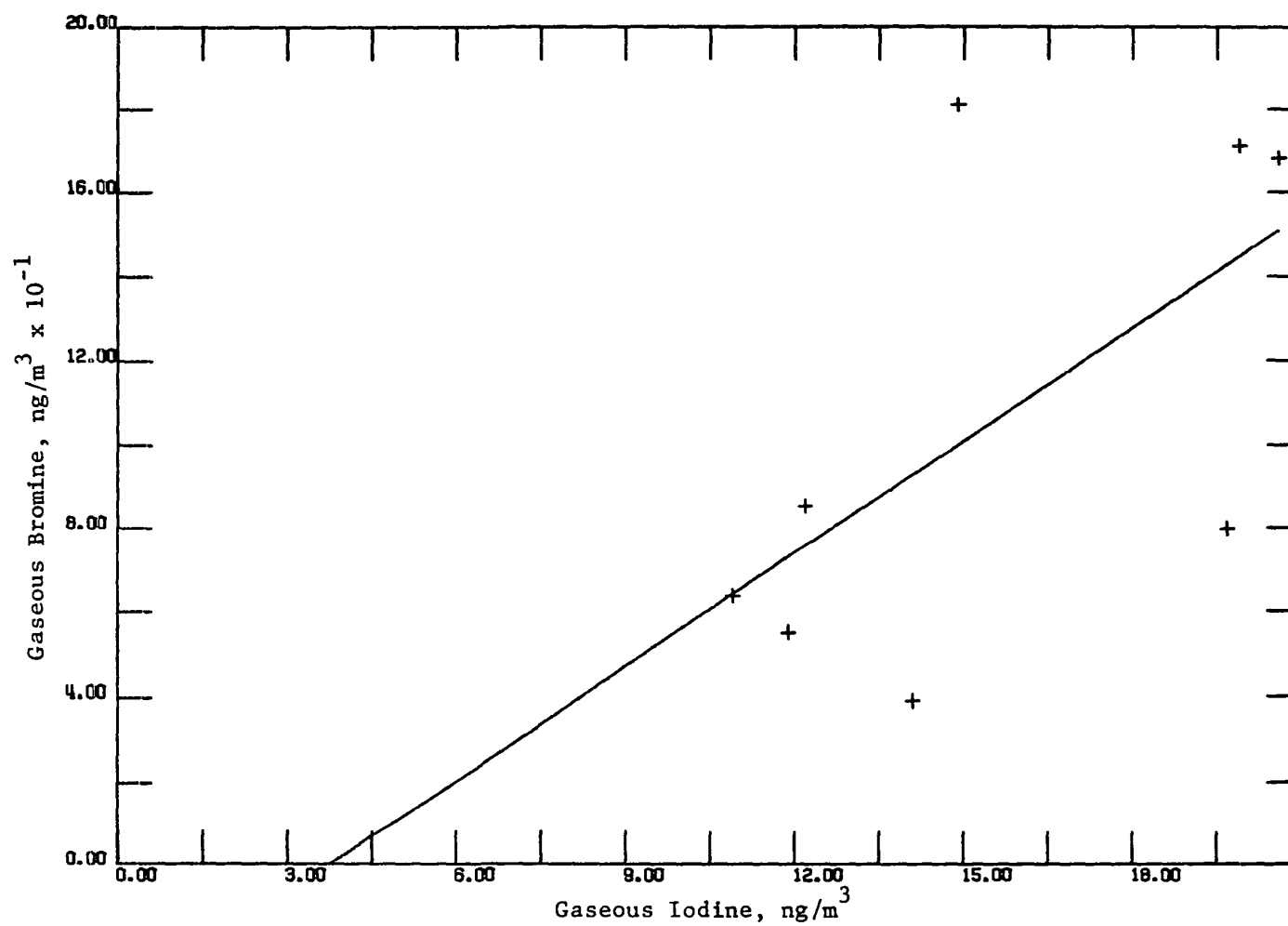


Figure 30. Gaseous Iodine Concentration vs. Gaseous Bromine Concentration, Honolulu

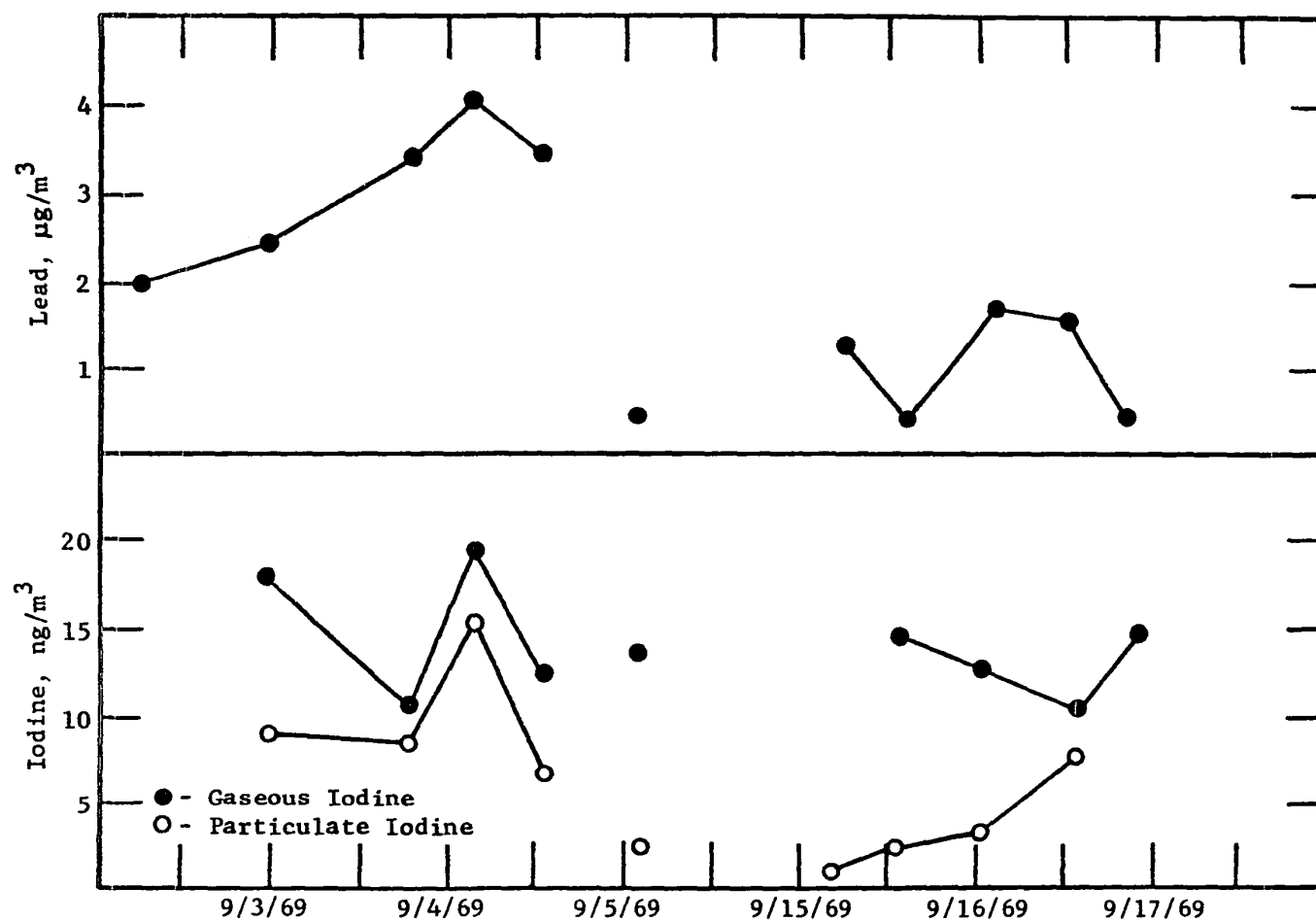


Figure 31. Daily Concentrations of Gaseous Iodine and Particulate Lead and Iodine in Cambridge, Massachusetts

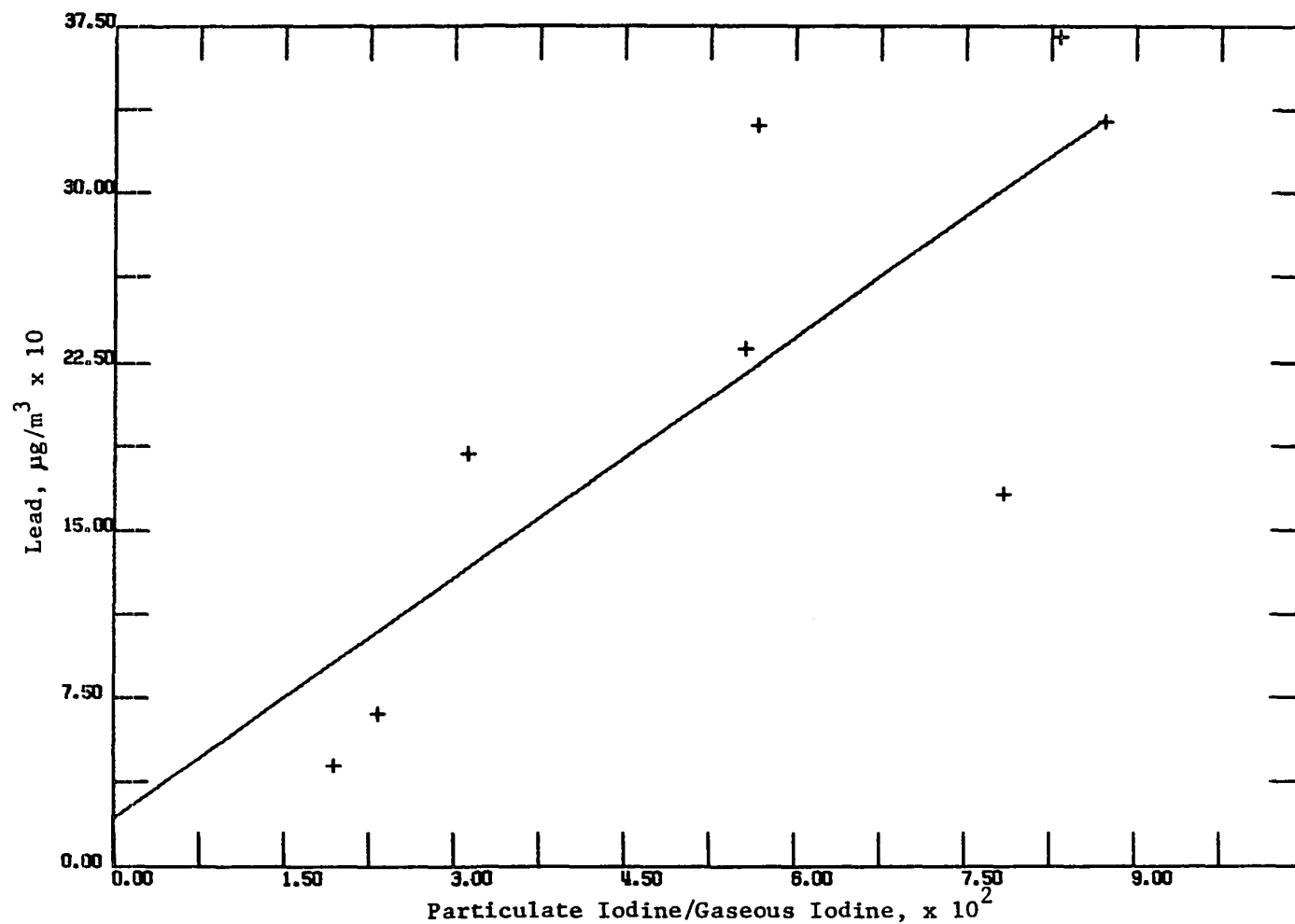


Figure 32. Particulate Iodine/Gaseous Iodine Ratio vs. Particulate Lead Concentration; Cambridge, Massachusetts

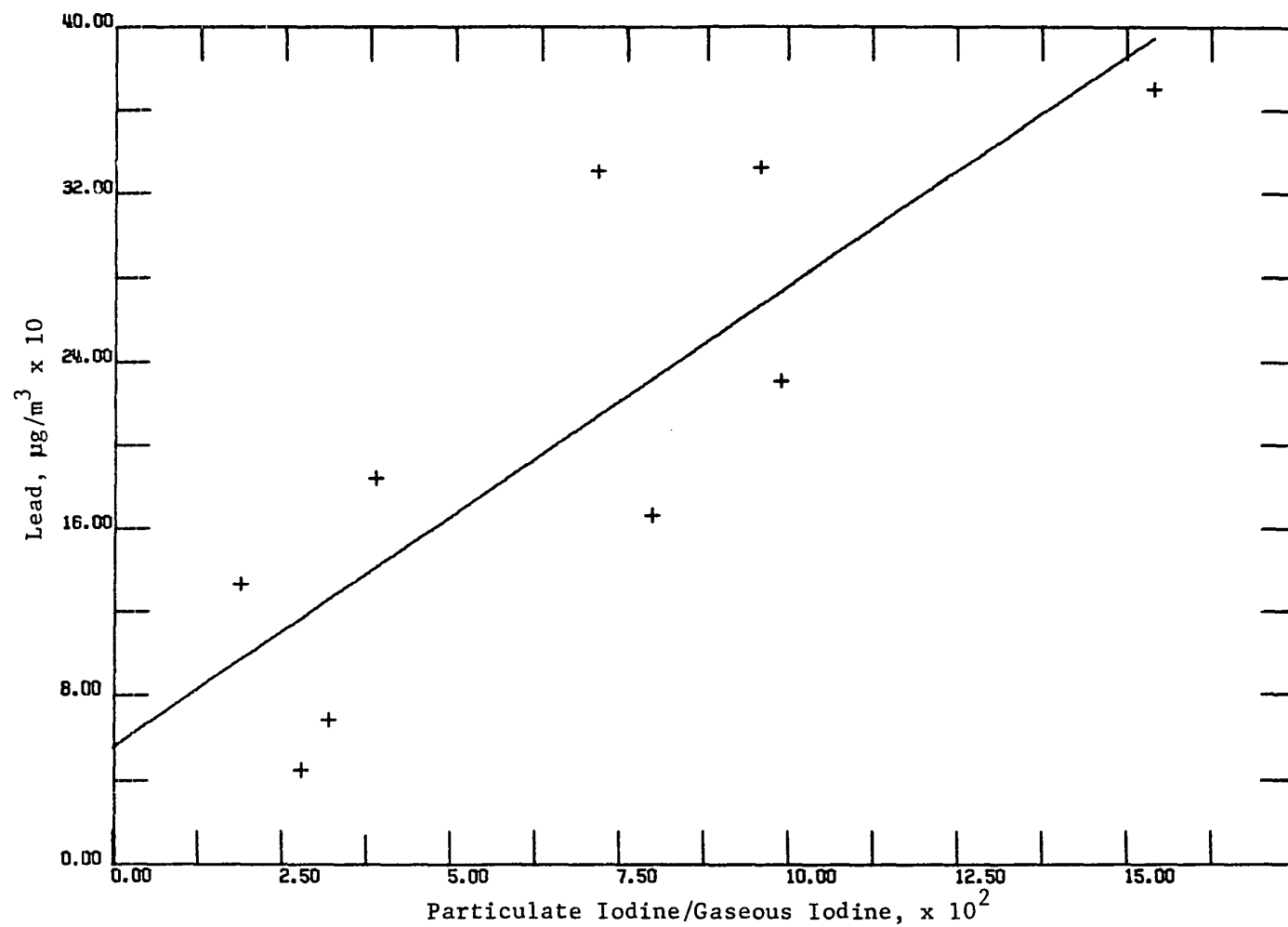


Figure 33. Particulate Iodine Concentration vs. Particulate Lead Concentration;
Cambridge, Massachusetts

IV. DISCUSSION

From these results it appears probable that the gaseous concentration of iodine in the air is related in some way to the particulate iodine concentration; and it is also likely that this interaction is not extremely simple. This interaction may be complicated because there are several possible mechanisms affecting the concentration of gaseous and particulate iodine in the atmosphere. These mechanisms can include the role of organic material (as mentioned in the Introduction and the Results), a photochemical process occurring both in the sea and on sea salt particles (which also could include organic material), and the direct interactions of gas and particulate matter in the atmosphere. The interaction of gaseous iodine and sea salt particles could include the release of gaseous iodine from the particle, or the uptake of gaseous iodine via adsorption, or the gas going into solution. It is clear that this study cannot distinguish between all of these interactions. However a few possibilities can be presented which are not inconsistent with the results which were obtained.

A. Interaction of Sea Salt Particles and Rain with Gaseous Iodine and Bromine

The first reliable measurements of the concentration of gaseous iodine and bromine in the marine atmosphere have been presented in this dissertation, and it is now possible to examine the interaction of this gaseous iodine with sea salt particles and rain or cloud droplets using equilibria data to see whether some light may be shed on the iodine and bromine concentrations which are normally observed

in rain and particulate samples. Assuming that the gaseous iodine and bromine are I_2 and Br_2 , respectively, the role which gaseous iodine and bromine will have on the iodine and bromine concentrations of the particulate matter in the air can be investigated using the thermodynamic data of Table XIII. If the following are assumed: 1) that the average $I_2(g)$ concentration is 10^{-12} atm (10 ng/m^3) and the $Br_2(g)$ concentration is $10^{-11.1}$ atm (50 ng/m^3), approximating that found in this investigation; 2) that sea salt particles are liquid droplets (which is true at relative humidities greater than 70%); and 3) that the best estimate for the pH of these particles and rain is approximately 5-6 (Duce, 1969, personal communication; and Eriksson, 1957), the following calculations can then be made.

1. Iodine

a. Interaction of Gaseous Iodine with Sea Salt Particles

At an $I_2(g)$ concentration of 10^{-12} atm the $I_2(aq)$ concentration on sea salt particles at equilibrium will be given by

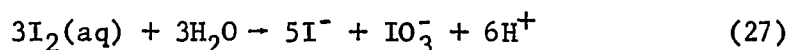


$$\Delta G^\circ = -0.70 \text{ Kcal}$$

$$K = 10^{0.51}$$

$$\text{or } [I_2(aq)] = K[I_2(g)] = 10^{0.51} \cdot 10^{-12} = 3 \times 10^{-12} \text{ M.}$$

However, $I_2(aq)$ disproportionates according to the following equation:



$$\Delta G^\circ = 64.56 \text{ Kcal}$$

$$K = 10^{-47.6}$$

Such a disproportionation would result in $[IO_3^-] = [I^-]/5$.

Table XIII
Thermodynamic Data for
Iodine and Bromine Reactions

$I_2(g) \longrightarrow I_2(aq)$	$\Delta G^\circ = -0.70 \text{ Kcal}$
$I_2(s) \longrightarrow I_2(aq)$	$\Delta G^\circ = 3.93 \text{ Kcal}$
$I_2(s) \longrightarrow I_2(g)$	$\Delta G^\circ = 4.63 \text{ Kcal}$
$\frac{1}{2}I_2(s) + e^- \longrightarrow I^-(aq)$	$\Delta G^\circ = -12.35 \text{ Kcal}$
$\frac{1}{2}I_2(s) + 3H_2O(l) \longrightarrow 6H^+ + IO_3^- + 5e^-$	$\Delta G^\circ = 138.10 \text{ Kcal}^*$
$\frac{1}{2}O_2(g) + 2H^+ \longrightarrow H_2O(l)$	$\Delta G^\circ = -56.69 \text{ Kcal}$
$I_2(s) + I^-(aq) \longrightarrow I_3^-(aq)$	$\Delta G^\circ = -12.31 \text{ Kcal}$
$Br_2(l) \longrightarrow Br_2(aq)$	$\Delta G^\circ = 0.977 \text{ Kcal}$
$Br_2(l) \longrightarrow Br_2(g)$	$\Delta G^\circ = 0.751 \text{ Kcal}$
$Br_2(g) \longrightarrow Br_2(aq)$	$\Delta G^\circ = 0.226 \text{ Kcal}$
$\frac{1}{2}Br_2(s) + e^- \longrightarrow Br^-(aq)$	$\Delta G^\circ = -24.574 \text{ Kcal}$
$\frac{1}{2}Br_2(l) + 3H_2O(l) \longrightarrow 6H^+ + BrO_3^- + 5e^-$	$\Delta G^\circ = 172.0 \text{ Kcal}^*$
$Br_2(l) + H_2O(l) \longrightarrow HBrO + H^+ + Br^-$	$\Delta G^\circ = -19.90 \text{ Kcal}$

Sources: Latimer (1952)

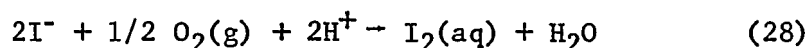
*Randall (1930)

Using a $\text{pH} = 5$ and $[\text{I}_2(\text{aq})] = 3 \times 10^{-12} \text{ M}$, the resulting concentration of the two iodine species on sea salt particles would be

$$[\text{I}^-] = 4 \times 10^{-9} \text{ M}$$

$$\text{and } [\text{IO}_3^-] = 8 \times 10^{-10} \text{ M}$$

However, these two iodine species will not necessarily exist in this 1:5 ratio since other reactions such as oxidation of I^- and $\text{I}_2(\text{aq})$ by O_2 are taking place. The equilibria between I^- and atmospheric oxygen is given by equation (28):

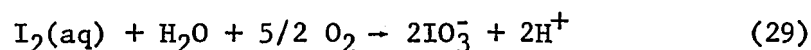


$$\Delta G^\circ = -28.06 \text{ Kcal}$$

$$K = 10^{20.6}$$

At an $\text{O}_2(\text{g})$ concentration of 0.2 atmospheres, a pH of 5, and $\text{I}_2(\text{aq}) = 3 \times 10^{-12} \text{ M}$, the concentration of I^- at equilibrium would be $1.2 \times 10^{-11} \text{ M}$. If this concentration of I^- is used in equation (27), the IO_3^- concentration at equilibrium on sea salt particles would then be $2.5 \times 10^2 \text{ M}$.

It is also possible to examine the equilibrium between $\text{I}_2(\text{aq})$, O_2 , and IO_3^- , which is given according to equation (29):



$$\Delta G^\circ = -11.18$$

$$K = 10^{8.2}$$

Using the same concentrations for $\text{I}_2(\text{aq})$, $\text{O}_2(\text{g})$, and H^+ which were used previously give an IO_3^- concentration of $2.5 \times 10^2 \text{ M}$ which is in agreement with the previous value

obtained. This is as it should be, since combining equations (28) and (29) results in equation (27). However, equation (29) is included to show that it is possible to build up IO_3^- by two separate paths: 1) oxidation of I^- to $\text{I}_2(\text{g})$ with the subsequent disproportionation of $\text{I}_2(\text{aq})$ to $1/6 \text{IO}_3^-$ and $5/6 \text{I}^-$ (each I^- will form $1/12 \text{IO}_3^-$), and 2) the oxidation of $\text{I}_2(\text{aq})$ directly to IO_3^- as shown in equation (29). Both of these mechanisms may be occurring on sea salt particles. At a pH of 6 the equilibrium concentrations of I^- , IO_3^- , and $\text{I}_2(\text{aq})$ according to equations (26)-(29) will be:

$$\text{I}^- = 1.2 \times 10^{-10} \text{ M}$$

$$\text{IO}_3^- = 2.5 \times 10^3 \text{ M}$$

$$\text{I}_2(\text{aq}) = 3 \times 10^{-12} \text{ M}$$

Calculations for the interhalogen complexes (i.e., I_3^- , ICl_2^- , etc.) associated with sea salt particles show that these species will be unimportant in terms of the amount of species present.

These calculations indicate that because of the extremely large equilibrium concentration of IO_3^- , sea salt particles should act as a perfect sink for $\text{I}_2(\text{g})$ in the atmosphere. There are other considerations, however, the most important being whether or not equilibrium is actually attained. In the Introduction it was indicated that equilibrium between I^- and O_2 is apparently not attained in sea water and this may be true in the atmosphere as well. It is obvious that total equilibrium between all iodine species and O_2 is not attained

since this would result in an iodine concentration (as IO_3^-) several times that of Cl^- (in particles Cl^- varies from 0.5 M to about 5.0 M). It may be that equilibrium between I^- , IO_3^- , and I_2 , according to equations (26) and (27), is established rather rapidly, perhaps within a few hours. Duce (1964) has presented diffusion calculations which indicate that at a gaseous iodine concentration similar to that found in this study, the average time required for a molecule of gaseous I_2 to interact with a sea salt particle is approximately 30 minutes. The attainment of equilibrium between O_2 and I^- and/or $\text{I}_2(\text{aq})$ according to equations (28) and/or (29) (which would act to increase IO_3^- concentration if equilibrium according to equation (27) is maintained) may be the rate controlling step(s) which dictates the amount of iodine which will be associated with sea salt particles. It may be that the oxidation of I^- by O_2 is too slow to be of importance and the oxidation of $\text{I}_2(\text{aq})$ by atmospheric O_2 to form IO_3^- is the rate controlling step. Presumably this reaction between I^- and O_2 (which is dependent on pH) will proceed more rapidly on the particles than in sea water since H^+ concentration is probably about two to three orders of magnitude higher in sea salt particles than in sea water. In either case, the fact that the I/Cl ratio increases on particles of decreasing size may be a result of the slowness of the oxidation of I^- and/or $\text{I}_2(\text{aq})$ by O_2 , since smaller particles have a longer residence time in the air than larger

sea salt particles.

Figure 34 gives a comparison of the average I/Cl ratios (and their standard deviations) of the 30 cascade impactor samples collected by workers in this laboratory over the past 3 years along with residence times of various size sea salt particles which have been reported by Toba (1965) and Eriksson (1959). In this figure the I/Cl ratios and residence times (γ) are plotted as a function of cascade impactor stage. At relative humidities of 70% and greater (the density of the sea salt particles is approximately 1) slide F collects particles with an average radius of approximately 0.3μ ; slides E, D, C, and B collect particles with average radii of 0.6μ , 1.2μ , 2.5μ and 5μ , respectively. The average size of the particles collected on slide A is indeterminate since this slide collected all particles of 10μ radius and greater with an efficiency of 100%. The values for residence times were given by Toba (1965) and Eriksson (1959) for particles with radii of 9μ , 6μ , 3μ , and 1μ (RH = 80%). These values are plotted near the corresponding cascade impactor stage in Figure 34 (i.e., 9μ is plotted just less than slide A and so on). It can be seen in Figure 34 that the I/Cl ratio for slides B, C, and D follows Eriksson's estimate of residence time based on sea salt particle production rate quite well. Unfortunately, Eriksson's data does not permit calculation of residence times for particles with radii smaller than 1μ . Eriksson states that

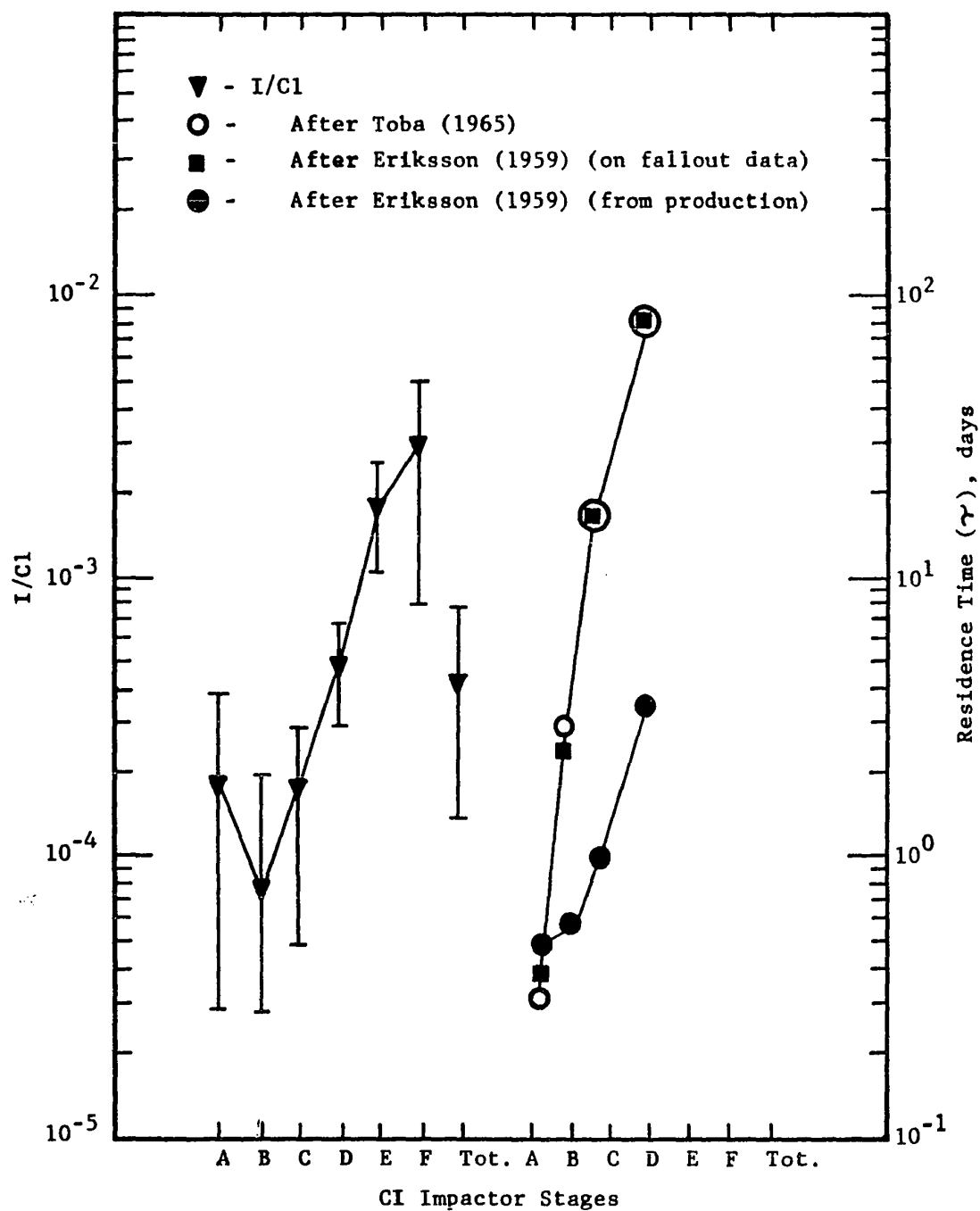


Figure 34. Comparison of the Change in I/C1 Ratio with Particle Size to the Change in Residence Time with Particle Size

the residence times based on production data are more reasonable than the times calculated from fallout data, since the fallout residence time appears to be inconsistent with the amounts of particulate matter observed in the air. Assuming that Eriksson's residence times based on production rate approximate the true values, it would appear that the I/Cl ratio could be a result of the slow increase of IO_3^- due to a slow oxidation of I^- or $\text{I}_2(\text{aq})$. Toba (1965) calculated residence times for sea salt particles based on the distribution of particles present in the marine air as a function of particle weight and altitude, and obtained values very close to those presented by Eriksson (1959) for fallout data (this is seen in Figure 34). Toba felt his numbers were representative of the true residence time in the atmosphere. Regardless of which estimate of residence time is correct, the I/Cl ratio parallels both fairly closely. The important fact is that the slopes of the I/Cl ratio and residence time versus particle size are similar.

For the I/Cl ratios on particulate matter, Duce et al. (1965, 1967) proposed a surface adsorption of I_2 gas since the change in the I/Cl ratio with particle size agreed well with the change in the surface area/volume ratio with particle size. It will be shown, however, that the surface area/volume ratio may not be the controlling factor. According to equation (27), IO_3^- in the presence of acid will oxidize I^- to I_2 , and according to Latimer (1951) this reaction

proceeds rapidly (when acidic) and equilibria is attained. The concentration of iodine in sea water is approximately $[\text{IO}_3^-] = 2 \times 10^{-7} \text{ M} = [\text{I}^-]$ (Sugawara and Terada, 1957; Barkley and Thompson, 1960). At this concentration of iodate and iodide, and with the pH of sea water equal to 8.3, calculations from equation (27) show that the $\text{I}_2(\text{aq})$ concentration would be $10^{-14.7} \text{ M}$. Thus, if the partial pressure of $\text{I}_2(\text{g})$ in the air over the sea is 10^{-12} atmospheres, then according to equations (26) and (27) the ocean should act as a sink, and not a source for $\text{I}_2(\text{g})$. If the sea salt particles are injected into the air with iodine concentrations equal to that in bulk sea water, then changes will occur which do favor the release of $\text{I}_2(\text{g})$. It was previously noted that injection of a droplet of sea water in the the air at a relative humidity of 80% will cause the pH of the solution to be lowered to about 5-6 and approximately 7/8 of the water will evaporate. This leaves a droplet of water with IO_3^- and I^- concentrations about eight times larger than the sea water concentrations, or $[\text{IO}_3^-] = 1.6 \times 10^{-6} \text{ M} = [\text{I}^-]$. Calculations from equation (27) show that at these concentrations of iodate and iodide, $[\text{I}_2(\text{aq})] = 10^{-6.1} \text{ M}$ at a pH of 5 and $[\text{I}_2(\text{aq})] = 10^{-8.1} \text{ M}$ at a pH of 6. The concentration of $\text{I}_2(\text{g})$ in equilibrium with this concentration of $\text{I}_2(\text{aq})$, as determined from equation (26) would be $10^{-6.5}$ atmospheres at a pH of 5 and $10^{-8.6}$ atmospheres at a pH of 6. Since this is from 10^3 to 10^5 times the gaseous iodine

concentration observed in the atmosphere, it is apparent that soon after injection of a sea salt droplet into the atmosphere there should be an initial release of gaseous I_2 (this should occur approximately as rapidly as the water evaporates and the pH is lowered). This might then be followed by a slow increase in the IO_3^- concentration of the particle due to oxidation of I^- and/or $I_2(aq)$ by O_2 (such that the equilibrium between the I^- - IO_3^- couple is maintained). In a mechanism such as this the I/Cl ratio would be independent of the surface area/volume ratio and would depend only on the length of time a particle remains airborne. In other words, the I/Cl ratio observed in particulate matter in the marine atmosphere may be controlled by chemical processes (due to thermodynamic and kinetic consideration) and not by physical processes such as diffusion and adsorption.

Thus, a chronological chemical history of iodine association with a sea salt particle may be at least similar to the following: A small droplet of sea water injected into the atmosphere will release $I_2(g)$ as the water evaporates and the pH is lowered. This $I_2(g)$ is formed as a result of the high iodide concentrations present which becomes unstable with respect to oxidation by iodate as the pH is lowered. At this time the particle equilibrates with the atmosphere with respect of pH and water content, and it should also be in equilibrium with respect to $I_2(aq)$ and the gaseous concentration of I_2 in the atmosphere. This is followed by the slow

oxidation of I^- or $I_2(aq)$ by atmospheric oxygen which will increase the IO_3^- concentration. The increase in IO_3^- concentration should continue until the particle is removed from the atmosphere.

b. Interaction of Gaseous Iodine and Rain Water

Woodcock et al. (1970) have noted that the I/Cl ratio of rain collected from showers on the island of Hawaii (20 km from shore and at an altitude of approximately 900 m) is higher than the ratio of total particulate iodine to total particulate chlorine. The I/Cl ratio of rain samples collected by these workers was found to be approximately 3×10^{-3} or roughly equal to the I/Cl ratio of particles between 0.6 μ and 0.3 μ (as shown in Figure 34). Woodcock et al. (1970) have suggested that this high I/Cl ratio in rain water may be due to a mechanism of rain formation in which only the smaller sea salt particles with their high I/Cl ratio are the raindrop formation nuclei, and/or that gaseous iodine is dissolving in cloud water resulting in rain with a higher concentration of iodine than would be expected if only sea salt particles (of all sizes) were supplying iodine to rain water.

The calculations presented for the interaction of gaseous iodine with sea salt particles should also be applicable to rain and cloud water. Eriksson (1957) has reported pH values for oceanic rain consistent with the pH values assumed for the calculations of gaseous iodine interactions with sea salt

particles. In the case of gaseous iodine reactions with cloud water, however, the time factor becomes extremely important. Woodcock et al. (1970) generally collected rain from clouds which formed close to the island of Hawaii, due to the rising of the trade winds as they blew up the mountains of the island. Such a process of cloud formation means that time between condensation of water and raining is short (approximately 1 hour or less) and therefore, the time available for interaction of gaseous iodine and cloud water is short when compared to the time available for gaseous iodine interactions with sea salt particles (which have an average life time of one-half to perhaps several days (Figure 34)). Thus, it is probable that the build up of IO_3^- due to the oxidation of I^- and $\text{I}_2(\text{aq})$ according to equations (28) and (29) does not occur to an appreciable extent. If it is assumed that equilibrium is attained in the cloud droplets with respect to $\text{I}_2(\text{aq})$ and $\text{I}_2(\text{g})$ and also with respect to disproportionation of $\text{I}_2(\text{aq})$ to IO_3^- and I^- , then, according to the calculation from equations (26) and (27), the total iodine concentration would be approximately $5 \times 10^{-9} \text{ M I}$ ($\text{IO}_3^- + \text{I}^-$), which is equivalent to $0.6 \times 10^{-6} \text{ g I/l}$ in the cloud water. If the particles around which rain droplets form are particles of all sizes, the I/Cl ratio in rain as a result of these particles should be approximately 4×10^{-4} (i.e., the average I/Cl ratio for particles of all sizes from Figure 34). Both Duce et al. (1965) and Seto (1967) have

reported that the average Cl^- concentration at an altitude of 900 meters is 2.5×10^{-3} g/l. If the particles have an I/Cl ratio of 4×10^{-4} , the contribution of iodine to rain from sea salt particles would then be 1.0×10^{-6} g/l. This would mean that establishment of equilibria between $\text{I}_2(\text{g})$, $\text{I}_2(\text{aq})$, IO_3^- , and I^- , according to equations (26) and (27), would result in rain having an iodine concentration of 1.6×10^{-6} g/l (0.6×10^{-6} g/l from gaseous iodine and 1.0×10^{-6} g/l from particulate iodine), and an I/Cl ratio of 0.65×10^{-3} (if Cl^- is equal to 2.5 ppm). This is approximately one-fifth the value of 3×10^{-3} observed in rain by Woodcock et al. (1970). If these same calculations are repeated using a pH of 6 rather than 5, then the total iodine concentration in rain would be 7×10^{-6} g/l (6×10^{-6} g/l from gaseous iodine and 1×10^{-6} g/l from particulate iodine), and the resulting I/Cl ratio is 2.8×10^{-3} which is very close to the value of 3×10^{-3} found by Woodcock et al.

These calculations have used the average I/Cl ratio (or total iodine to total chlorine of sea salt particles) found for sea salt particles collected at sea level (20 m tower) near the sea shore. Woodcock et al. (1970) made their rain measurements at an altitude of 900 m on the island of Hawaii (approximately 20 km from the sea shore). Duce et al. (1965) have presented some evidence that the I/Cl ratio on particulate matter might increase with distance from the sea (or with altitude). If the I/Cl

ratio of particulate matter does increase with distance from the sea or with altitude, then the sea salt contribution of iodine relative to chlorine in rain water will also increase with distance from the sea, which in turn means a higher I/Cl ratio will be observed in rain.

In the calculations for the dissolution and hydrolysis of $I_2(g)$, it was assumed that $I_2(g)$ would be supplied to the cloud from the air surrounding the cloud at such a rate that the dissolution of $I_2(g)$ would not change the concentration of $I_2(g)$ within the cloud (i.e., an infinite source of $I_2(g)$ has been assumed). If these calculations are repeated assuming that the cloud is a closed system and only the $I_2(g)$ contained in the air in the cloud is available for dissolution and hydrolysis, the gaseous contribution of $I_2(g)$ to the iodine concentration in rain will be one-half the values previously listed. This means that in a closed cloud system (i.e., only the material within the volume of the cloud is available for incorporation into the cloud and rain water) the dissolution and hydrolysis of $I_2(g)$ plus the iodine supplied by particulate matter of all sizes would give an I/Cl ratio in rain of 0.5×10^{-3} when the pH is 5 and 1.8×10^{-3} when the pH is 6.

In any case, it is seen that even by completely ignoring the oxidation of I^- and/or $I_2(aq)$, it is possible to at least partially account for the observed I/Cl ratio by considering the dissolution of the gaseous iodine into the rain (or cloud)

water, plus the iodine already present on the salt particle. Any oxidation of I^- and/or $I_2(aq)$ would build up the IO_3^- concentration and the I/Cl ratio would be raised even higher.

There are questions, however, which must be answered before the extent to which gaseous iodine controls the iodine concentration of rain can be determined. If the average I/Cl ratio of all particles in a cloud is the same as the I/Cl ratio of all particles collected near the sea surface, and if the pH of rain and cloud water is close to 5, then the dissolution of gaseous iodine may not account for the I/Cl ratio of the rain samples measured by Woodcock et al. (1970), and there may be a mechanism of rain formation whereby raindrops selectively form around small particles (with high I/Cl ratios). On the other hand, if the average I/Cl ratio of all particles in a rain cloud is higher than the average I/Cl ratio of all particles near the sea surface, and (or) if the pH is close to 6, it may then be that the mechanism of raindrop formation is not particle size selective.

Two interesting studies which would do much to determine the role of gaseous iodine in contributing to the iodine concentration of rain are suggested by the calculations in this dissertation. The first would be to simultaneously measure the particulate I/Cl ratio and the ratio of I/Cl in rain. Since the gaseous iodine contribution to the iodine dissolved in the cloud water would be expected to be the same for all the cloud droplets, a comparison of the I/Cl ratio to Cl

concentration in the rain within an individual shower might indicate what effect gaseous iodine has on the iodine concentration of rain. Duce et al. (1969) has shown that the Cl^- and Na^+ concentrations vary widely within an individual rain shower. Thus, if the I/Cl ratio increased with decreasing concentrations of Cl this would be strong evidence that the iodine gas is causing the high I/Cl ratio observed. Actually, it would be better to compare the I/Na ratio with Na^+ concentration in the rain since Junge (1957), Duce et al. (1965), and others have presented evidence of a gaseous chlorine component in the atmosphere. If the excess iodine in rain (calculated by assuming an I/Na or I/Cl ratio consistent with that observed in particulate matter, and determining from this the I contributed to the rain by particulate matter) is constant within an individual shower this would suggest that gaseous iodine causes the high I/Cl ratio which is observed in rain. Second, one could measure the pH of rain and compare pH changes with the iodine (or excess iodine) concentration of rain. At the present time, however, it is possible to only say that based upon these calculations, it is probable that gaseous iodine is a large contributing factor to the high I/Cl concentration which is observed in rain water.

2. Bromine

Calculations can be made for expected concentrations of bromine in particles and rain based on the gaseous bromine

concentration, in the same manner as for iodine.

a. Interaction of Gaseous Bromine with Sea Salt Particles

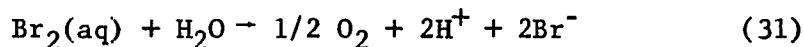
Assuming a gaseous bromine concentration in the atmosphere to be 8×10^{-12} atmospheres (which is equivalent to 50 ng/m^3), the interaction of $\text{Br}_2(\text{g})$ with liquid sea salt particles at a pH of 5-6 would be given by equation (30):



$$\Delta G^\circ = 0.226 \text{ Kcal}$$

$$K = 10^{-0.17}$$

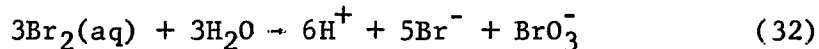
Then, at a $\text{Br}_2(\text{g})$ concentration of $10^{-11.1}$ atmospheres, the $\text{Br}_2(\text{aq})$ concentration will be $5 \times 10^{-12} \text{ M}$. The concentration of bromide which would be expected at this concentration of $\text{Br}_2(\text{aq})$ is given by equation (31):



$$\Delta G^\circ = -6.57 \text{ Kcal}$$

$$K = 10^{-4.85}$$

At a pH of 5, $\text{Br}^- = 1.2 \times 10^{-3} \text{ M}$ and at a pH of 6, $\text{Br}^- = 1.2 \times 10^{-2} \text{ M}$. Equation (32) shows that the formation of BrO_3^- will be insignificant:



$$\Delta G^\circ = 46.2 \text{ Kcal}$$

$$K = 10^{-34.1}$$

At a pH of 5, the equilibrium concentration of bromate on sea salt particles would be approximately $2 \times 10^{-24} \text{ M}$, and at a pH of 6 the bromate concentration would be $2 \times 10^{-23} \text{ M}$.

The concentration of Br^- in sea water is $60 \text{ } \mu\text{g/ml}$ or

0.75×10^{-3} M. Thus, when a droplet of water is injected into the atmosphere at a relative humidity of 80%, the resulting Br^- concentration of this droplet will be approximately eight times the sea water value or 6×10^{-3} M. At a pH of 5, according to equations (31) and (30), the equilibrium concentration of $\text{Br}_2(\text{g})$ at a Br^- concentration of 6×10^{-3} would be 1.2×10^{-10} atmospheres. At a pH of 6, according to the same calculations, the equilibrium partial pressure of $\text{Br}_2(\text{g})$ would be 1.2×10^{-12} atmospheres. Thus if the pH is close to 5, thermodynamics favors the formation of $\text{Br}_2(\text{aq})$ and the release of $\text{Br}_2(\text{g})$ from sea salt particles due to the oxidation of Br^- by O_2 according to equations (30) and (31) (if the pH were 6, however, this would not be true). In a sea salt particle in the air with a relative humidity of 80%, the Cl^- concentration is approximately 4.0 M, or 150 g/l. The average Br/Cl ratio obtained is 2×10^{-3} (which is lower than the sea water value of 3.4×10^{-3}), which gives a bromide concentration in sea salt particles of 0.3 g/l (when $\text{Cl}^- = 4$ M). This is equivalent to a bromide concentration of 4×10^{-3} M, which is slightly higher than the equilibrium concentration of 1.2×10^{-3} calculated for a pH of 5, but lower than the pH 6 equilibrium concentration. Examination of Figure 15 shows that the ratio of Br/Cl is nearly constant on particles of all sizes (this indicates the bromine concentration is constant on particles of all sizes). These calculations, as well as the actual atmospheric measurements, would

suggest that bromine gas is released from the particles and the gaseous release is fast when compared to the residence time of the particles.

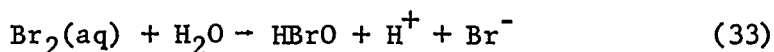
Comparing the calculations for gaseous bromine interaction with sea salt particles to those same calculations for gaseous iodine, the following facts can be seen. Initially after injection into the atmosphere, thermodynamic data should favor the release of both $I_2(g)$ and $Br_2(g)$. After this initial release the sea salt particle should be an excellent sink for iodine gas but not for bromine gas. This difference is the result of the fact that thermodynamically, iodate is the stable oxidation state of iodine associated with a sea salt particle, while the thermodynamically stable form of bromine is bromide and not bromate.

b. Interaction of Gaseous Bromine with Rain Water

As in the case of gaseous iodine (i.e., dissolution of iodine gas followed by the hydrolysis of $I_2(aq)$), the same type of mechanism will be considered for the interaction of bromine gas with rain or cloud water. Thus, considering only equations (30) and (32), the gaseous contribution of bromine to rain water, according to equation (30) would be $Br_2(aq) = 5 \times 10^{-12}$ M (when $Br_2(g) = 8 \times 10^{-12}$ atmospheres), and according to equation (32) this concentration of $Br_2(aq)$ will result in an approximate equilibrium concentration of $Br^- = 5 \times 10^{-7}$ M and $BrO_3^- = 1 \times 10^{-7}$ which is equivalent to 4.8×10^{-5} g/l of total bromine when the pH is 5. At a pH

of 6 the total gaseous bromine contribution to rain would be 4.8×10^{-4} g/l (as Br^- and BrO_3^-). At a chlorine concentration in rain of 2.5×10^{-3} g/l as used in the iodine calculations, the Br/Cl ratio of rain predicted by equation (32) would be approximately 2×10^{-2} when the pH is 5, and 2×10^{-1} at a pH of 6.

$\text{Br}_2(\text{aq})$ can undergo a hydrolysis reaction different from that of equation (32) and this reaction occurs according to equation (33):



$$\Delta G^\circ = 11.2 \text{ Kcal}$$

$$K = 10^{-8.2}$$

At a pH of 5, and $\text{Br}_2(\text{aq}) = 5 \times 10^{-12}$ M, the resulting equilibrium concentration of HBrO and Br^- would be 6×10^{-8} M or the total bromine concentration would be approximately 10^{-5} grams. And, if $[\text{Cl}^-] = 2.5 \times 10^{-3}$ g/l, then the Br/Cl ratio would be 4×10^{-3} . At a pH of 6 the gaseous bromine contribution to rain would be 2.5×10^{-5} grams total bromine with a resulting Br/Cl ratio of 10^{-2} . Cotton and Wilkinson (1962) report that in basic solutions, hydrolysis of $\text{Br}_2(\text{aq})$ will occur according to equation (32), and in acidic solutions according to equation (33). Duce et al. (1965) have shown that the average Br/Cl ratio of rain is approximately 6×10^{-3} g/l. This would indicate that if dissolution of gaseous bromine is the cause of the Br/Cl ratio in rain being higher than the same ratio in sea salt particles, the

hydrolysis of $\text{Br}_2(\text{aq})$ occurs as shown in equation (33), or if the hydrolysis occurs according to equation (32), then equilibrium apparently is not established.

Thus, it appears that the interaction of gaseous bromine with rain and cloud water can account for the fact that the Br/Cl ratio is higher in rain than it is in particles.

3. Uncertainties Regarding Equilibria Calculations

It is necessary to mention various factors which may cause the calculations for gaseous iodine and bromine interactions with sea salt particles and rain water to be different from this presentation. All oxidation calculations in this dissertation are based on oxidation by atmospheric oxygen. Ozone, at the concentration present in the atmosphere, is an even stronger oxidizing agent than oxygen and will force all of the oxidation reactions which were considered (i.e., equations (28), (29), and (31) more toward the oxidized species than oxygen. In addition to ozone, exposure to ultraviolet radiation may cause the reactions involving oxygen to be more favorable and to proceed at a more rapid rate. Thus, the calculations presented in this discussion might be considered the minimum oxidation properties of the atmosphere with respect to the thermodynamically stable concentrations of the various oxidation states of iodine and bromine.

A very important factor, mentioned in the Introduction and again in the Discussion of iodine equilibria with sea salt particles, is the possible presence of organic material associated

with the particles (and to a lesser extent in rain water).

The presence of organic material on sea salt particles could make the various interactions which were considered much different from those suggested in this Discussion.

Throughout this Discussion, the use of activity coefficients has been ignored. In most cases the equilibrium concentrations which were obtained were low enough that for all practical purposes, the activity coefficients could be assumed to be unity. The exceptions to an activity coefficient of unity are the equilibrium concentrations of iodate and bromide associated with sea salt particles. In these cases, it was chosen not to introduce activity coefficients because the concentration uncertainties which result from a pH uncertainty overshadow any improvements which might be made by considering activity coefficients. To be correct, the equilibrium concentrations of iodate and bromide calculated from equations (27) and (31), respectively, (when an assumption of $I_2(g)$ and $Br_2(g)$ concentrations is made) should be referred to as the activity of iodate and bromide and not as the concentration.

Regardless of the many uncertainties present in these calculations, it is felt that these calculations, while probably not extremely accurate, do allow explanation of many of the naturally observed phenomena, and do allow a more complete understanding of the cycle of bromine and iodine in the atmosphere.

B. Atmospheric Residence Times for Iodine and Bromine

It would be extremely valuable to calculate a residence time for

iodine in the atmosphere. Knowledge of the iodine residence time would aid greatly in ascertaining the extent of the danger resulting from a large release of ^{131}I due to a nuclear accident or fission explosion in the lower atmosphere. A value for the iodine residence time would also allow estimation of the extent to which a pollution source for iodine might affect the world's atmospheric iodine concentration.

Unfortunately, not all the parameters required for such a calculation are known. It is possible, however, to make an estimate of this iodine residence time by using the known parameters and making some assumptions about those less well known or unknown.

The definition of residence time is given by

$$\tau(a) = \frac{n(a)}{dn(a)/dt} \quad (34)$$

where $\tau(a)$ = residence time of substance a in days

$n(a)$ = amount of substance a (grams) present in atmosphere

at any one time

$dn(a)/dt$ = the amount of substance a removed (or added) to the atmosphere per unit time (g/day)

First, maximum and minimum values for $n(a)$ and $dn(a)/dt$ will be calculated; then using these values it will be possible to calculate both a maximum and minimum residence time. Calculations will be made for both gaseous iodine and total iodine in the atmosphere.

1. Iodine

a. Mass of Iodine in the Atmosphere

The total amount of gaseous iodine in the atmosphere at any one time $n(a)$ can be estimated in the following way. The

mass of the atmosphere as given by Krauskoph (1967) is 5.1×10^{21} grams. Air has a "molecular weight" of about 29 g/mole, and thus the volume of the atmosphere is approximately 4×10^{18} standard cubic meters (SCM). With an average gaseous iodine concentration of about 8 ng/SCM as was found in this work, the total gaseous iodine present in the atmosphere would be 3.2×10^{10} grams. This value is based on the assumption that the atmosphere is homogeneously mixed with respect to iodine concentration and should represent the maximum value in the atmosphere. If the sea is the major source of gaseous iodine, it would be expected that the continental atmospheric gaseous iodine concentration would be equal to or less than the concentration of the gaseous iodine in the marine atmosphere. In this work it was found that the marine atmospheric particulate iodine concentration was equal to about 1/3 the gaseous iodine concentration in the marine atmosphere. This means the total iodine concentration in the atmosphere would be 10.5 ng/m^3 (2.5 ng/m^3 particulate iodine and 8 ng/m^3 gaseous iodine). Using the value cited previously (4×10^{18} SCM) as the volume of the atmosphere, this means the total amount of iodine in the air is 4.2×10^{10} g assuming the atmosphere is homogeneously mixed with respect to total iodine concentration.

It is possible, however, that the atmosphere is not homogeneously mixed with respect to either gaseous iodine concentration or total iodine concentration. Considering the former

possibility, the results of the limited number of samples collected at the Mauna Loa Weather Observatory indicate that the concentration of gaseous iodine in the atmosphere may be dependent on altitude (or distance away from the sea). Certainly, the air below about 2500 m over the ocean is homogeneously mixed with respect to gaseous iodine (concentration equals 8 ng/m^3). This represents about 2/9 of the world's atmosphere (with respect to weight). If the remaining 7/9 of the atmosphere has a gaseous iodine concentration of about 3 ng/m^3 (the minimum concentration measured at the Mauna Loa Weather Observatory, elevation 2500 meters) then the total amount of iodine in the atmosphere would be about one-half the value of $3.2 \times 10^{10} \text{ g}$ cited previously. Thus it would seem that the estimation of total gaseous iodine in the atmosphere is at most a factor of 2 too high. For total iodine concentration, it is probable there will be an even larger difference than for gaseous iodine. Junge (1957) has shown that the mass concentration of sea salt particles below the trade wind inversion may be as much as four orders of magnitude larger than the mass concentration above the inversion. Junge and Werby (1958) have shown that the mass concentration of sea salt particles over the center of the United States is about 1/10 the value found over the ocean. This would mean that essentially all of the sea salt particles in the atmosphere are contained in the air below about 2500 meters and most of this mass is in the air over the

ocean. The total amount of particulate iodine in the atmosphere would then be about 0.2×10^{10} g (using the same type of calculation as in the case of gaseous iodine in a heterogeneously mixed atmosphere). This then means the minimum amount of total iodine in the atmosphere would be 1.8×10^{10} g (0.2×10^{10} g of particulate iodine and 1.6×10^{10} g of gaseous iodine).

b. Removal Rate of Iodine from the Atmosphere

1) Possible Sources and Sinks for Iodine

If a maximum and minimum residence time for gaseous iodine is to be calculated, it will be necessary to calculate a minimum and maximum removal rate. To do this it is necessary to examine in detail the possible sinks and sources for gaseous iodine in the marine atmosphere. (It is assumed that land is a sink only, and not a source.)

Miyake and Tsunogai (1963) have suggested the release of $I_2(g)$ at the surface of the ocean as the source of iodine in the atmosphere. These workers considered sources other than the sea surface and concluded that none of these sources are important when compared to the sea for the amount of iodine it can deliver. These sources included pollution (an estimated, not a measured amount), volcanism, and the decomposition of biological material (also estimated). Table XIV shows the amounts of iodine Miyake and Tsunogai calculated would be

Table XIV

Annual Rate of Supply of Iodine to the Atmosphere
(after Miyake and Tsunogai, 1963).

Source	Iodine, g/year
Volcanic acitivity	1.2×10^9
Decay of organic matter	1.0×10^8
Combustion of fossil fuels	5×10^9
Sea spray	5×10^9 (1.8×10^{10}) ^a
Evaporation from ocean (as $I_2(g)$)	5×10^{11}

^a This is an estimate of the sea spray contribution to the atmosphere assuming that the sea droplets when injected into the air have the same I/Cl ratio as does sea water, and using Blanchard's (1963) value of 10^{16} g of salt injected into the atmosphere annually.

Miyake and Tsunogai's estimate is based on calculating a yearly removal rate of sea salt, assuming that the I/Cl ratio of this sea salt is equal to the I/Cl ratio of sea water.

delivered to the atmosphere by each of these sources. These workers calculated that the photochemical oxidation of I^- at the sea surface would result in 5×10^{11} g of iodine being released annually from the surface of the ocean. However, upon examination of the total amount of sea salt cycled through the atmosphere annually, a discrepancy between annual production of iodine and annual removal becomes evident. Blanchard (1963) has estimated that 10^{16} g of sea salt (or 6×10^{15} g of chloride) are injected into the atmosphere annually. Earlier, it was shown that the average I/Cl ratio of all particles in the atmosphere is approximately 0.4×10^{-3} . If the annual production rate of sea salt particles is equivalent to the annual removal rate then the total amount of iodine removed from the atmosphere yearly (by precipitation and dry fallout) with sea salt particles is 2.4×10^{12} g. Thus, even ignoring the interaction of gaseous iodine with rain, continental particles, and land and vegetation, there exists a large discrepancy between removal and production rate. It is then apparent that either Miyake and Tsunogai's production estimate is too low or there must be a source of gaseous iodine other than the sea surface. It is probable that Miyake and Tsunogai's estimate of production rate, if in error, is high rather than low. These workers drew air over the surface of sea water containing ^{131}I , then

collected and counted the iodine released. From the amount of iodine released they calculated a production rate of this release. However, an accurate production rate is not possible unless the concentration of $I_2(g)$ in the air is known. The closer the $I_2(aq)$, $I_2(g)$ system approaches equilibrium, the slower will be the release of iodine from the sea surface. If air with an $I_2(g)$ concentration much lower than is present in the atmosphere is used, then laboratory production rates will be inflated with respect to production rates actually occurring at the sea surface in the ambient atmosphere. It is impossible to know the concentration of gaseous iodine in the air Miyake and Tsunogai used. They did, however, pass the air through a column of silica gel before drawing it across the sea water, and Mantell (1951) reported that silica gel will adsorb iodine. Thus, it might be expected that the air used for this experiment was relatively iodine free.

With respect to the transfer of gaseous iodine between the atmosphere and ocean, three possible situations can exist. 1) There can be an equilibrium between the $I_2(g)$ in the atmosphere and $I_2(aq)$ at the sea surface. If this were the case then there would be no need to consider the dissolution of atmospheric gaseous iodine into the sea when calculating a removal rate for iodine since there is no net transfer of gaseous iodine between the sea and

atmosphere. 2) Equilibrium is not established and the sea surface concentration of $I_2(aq)$ is higher than the equilibrium calculation would predict, based on the concentration of $I_2(g)$ in the atmosphere. Miyake and Tsunogai (1963) have suggested this possibility occurs via a photochemical oxidation of iodide. If this is the case, then the dissolution of atmospheric $I_2(g)$ at the sea surface does not have to be considered. 3) Finally, equilibrium between $I_2(g)$ in the atmosphere and the $I_2(aq)$ concentration of sea water is not established and the sea surface concentration of $I_2(aq)$ is less than would be predicted at equilibrium from the concentration of $I_2(g)$ in the atmosphere. If this is the case, then it may be necessary to consider dissolution of $I_2(g)$ at the sea surface in calculating a removal rate from the atmosphere.

Since Miyake and Tsunogai's (1967) estimate of gaseous production rate is possibly in error, it is possible that any one of the three situations mentioned concerning $I_2(g)$ in the atmosphere and $I_2(aq)$ at the sea surface can exist. Thus, calculating a removal rate of iodine from the atmosphere requires that the possibility of $I_2(g)$ dissolving into the sea be considered when calculating both the gaseous iodine and total iodine removal rate. If $I_2(g)$ does dissolve in the sea then $I_2(g)$ release from the sea surface cannot be the source of iodine in the

atmosphere. The only other possible source of gaseous iodine in the atmosphere would be particles injected into the atmosphere which have been enriched in iodine (with respect to sea water) and have lost this iodine (or part of it) to the gaseous phase. If gaseous iodine is released from the sea salt particles then it is possible that these particles are not a sink at all for the gaseous iodine in the atmosphere. Thus a removal rate calculation of gaseous iodine requires that two extreme possibilities be considered: 1) the I/Cl ratio observed on sea salt particles in the atmosphere is entirely the result of interaction with gaseous iodine; and 2) the I/Cl ratio observed on sea salt particles in the atmosphere is inherent on these particles as they are injected into the atmosphere and gaseous iodine does not affect I/Cl ratio at all (sea salt particles are ignored when calculating a gaseous iodine removal rate). It is quite probable that actual conditions lie somewhere between the two extremes just mentioned, yet, further work and data are needed in this field before one can say what the exact role actually is between gaseous iodine and sea salt particles.

With these facts in mind a removal rate can be calculated. The removal rate calculation must be divided into two parts: both the flux of iodine (gaseous and total) from the atmosphere to the land and the flux of iodine

from the atmosphere to sea must be considered.

2) Iodine Removal Rate over Land

A calculation for iodine deposition on land is more complicated than the calculation for oceanic deposition and is therefore more uncertain. Based on studies made by Chamberlain (1953, 1959, 1966), Bolin (1959), Chamberlain et al. (1953, 1958, 1959, 1960), and Clough et al. (1965), it is possible to estimate the amount of iodine deposited on land and foliage by using the deposition velocity for iodine (from ^{131}I data) that these workers have measured. This deposition velocity is obtained by measuring the total iodine concentration of air (particulate plus gaseous iodine) and measuring the rate at which iodine is taken up by the land and vegetation surfaces. The deposition velocity is given by:

$$V_g = \frac{\text{wt. of I deposited (g/cm}^2\text{-sec)}}{\text{concentration of I in air (g/cm}^3\text{)}} \quad (7)$$

Thus, V_g indicates the rate at which iodine is carried to land and foliage surfaces. Measurements of deposition for iodine velocities have ranged from 0.5 to about 2.5 cm/sec. The most recent work by Chamberlain (1966) and Clough et al. (1965) would indicate that the deposition velocity for iodine is from 0.5 to 1.0 cm/sec. From equation (7) the amount of iodine deposited on land per year by dry deposition can be calculated. Using a value of $V_g = 0.5$ cm/sec, assuming the average concentration of total iodine is 10.5 ng/m^3 or $1.05 \times 10^{-14} \text{ g/cm}^3$, and using

a value of $1.5 \times 10^8 \text{ cm}^2$ as the area of the world's continents (Krauskopf, 1967), then the total amount of iodine deposited per year by dry deposition would be $8 \times 10^3 \text{ g/sec}$ or $2.5 \times 10^{11} \text{ g}$ per year. In this calculation it is necessary to use the total concentration of iodine in the air since the deposition rates are a measure of both particulate and gaseous iodine which are deposited on land and foliage surfaces. The 10.5 ng/m^3 is based on gaseous iodine and particulate iodine contributions of 8 ng/m^3 and 2.5 ng/m^3 , respectively. For the marine atmosphere, the gaseous iodine concentration found in this work was equivalent to approximately 3 times the particulate iodine concentration. In Cambridge, Massachusetts, it was found that on relatively pollution free days the ratio of particulate to gaseous iodine was essentially equal to that of the marine atmosphere. The value of 10.5 ng/m^3 as the total iodine concentration of continental air may be somewhat in error, but until inland iodine measurements are available, a more accurate number cannot be obtained.

If the maximum deposition velocity is 1 cm/sec , then the maximum removal rate by dry deposition over land would be $5.0 \times 10^{11} \text{ g/year}$.

Reports of the concentration of iodine in continental precipitation are scarce. Duce et al. (1966) reported that iodine concentrations of Barrow, Alaska snow range

from 0.5 to about 3 g/l. Winchester and Duce (1966) reported the concentration of iodine in freshly fallen snow in Antarctica to be approximately 1 $\mu\text{g/l}$. Tsunogai (1966) reported iodine concentrations in rain at the top of Mount Fuji in Japan to be 1 to 3 $\mu\text{g/l}$. If 1 $\mu\text{g/l}$ is used as a conservative estimate of the iodine concentration in continental precipitation, and it is assumed that 10^{17} l of water are precipitated onto the continents per annum (Sellers, 1965) then 10^{11} g of iodine will be deposited onto the world's land area per annum, and this should be close to a minimum value. If an iodine concentration of 3 $\mu\text{g/l}$ is used, then the maximum amount of iodine delivered by rain and snow to the land area of the world would be approximately 3×10^{11} g/year. Thus, the minimum and maximum amounts of total iodine delivered to the surface of the land per annum would be 0.35×10^{12} g/year and 0.8×10^{12} g/year, respectively. These removal rates will be used for the calculations of both gaseous iodine and total iodine residence times since it is assumed that all over-continent iodine has a gaseous source from the ocean (either from the sea surface, or from sea salt particles, or both).

3) Iodine Removal Rate over the Ocean

To determine the removal rate of gaseous iodine over the ocean it is necessary to calculate the gaseous iodine removed from the atmosphere by three mechanisms: 1) dry

deposition of sea salt particles; 2) rain and snow over the ocean; and 3) the amount of gaseous iodine which will dissolve in the ocean. For dry deposition the following are used: Blanchard's (1963) estimate of 6×10^{15} g of chloride delivered to the atmosphere per year, Eriksson's (1959) estimate that 90% of the sea salt injected into the atmosphere falls back into the ocean (50% in the form of rain and 50% in the form of dry fallout), and the average I/Cl ratio of all particles in the atmosphere which is approximately 0.4×10^{-3} . These numbers then result in a value of 1.1×10^{12} g of iodine returned to the sea surface annually by dry deposition of sea salt particles. In the case of iodine deposition by rain and snow two possible mechanisms must be considered to account for the I/Cl ratio observed in rain. 1) Rain formation over the sea proceeds by a mechanism in which the formation of raindrops involves a selective process for small particles, i.e., it is assumed that the dissolving of gaseous iodine in cloud and rain water is negligible. 2) The dissolution of gaseous iodine in rain is important and the amount dissolved in rain and cloud water must be estimated. The first case will be used to calculate a minimum removal rate of gaseous and total iodine. The second case will be used to calculate the maximum removal rate of gaseous and total iodine. By using the data of Duce et al. (1965), an estimate may be made of the amount

of gaseous iodine which may dissolve in marine rain annually. These workers have reported the average iodine concentration of marine rain to be approximately 10 $\mu\text{g/l}$ and Sellers (1965) has estimated that 4×10^{17} l of rain fall onto the surface of the ocean per annum. Using these values, 4×10^{12} g of iodine will be delivered to the ocean's surface per annum in the form of rain. If one-half of the sea salt particles is returned to the ocean by rain per year, this corresponds to 1.1×10^{12} g/year and the remaining iodine (2.9×10^{12} g/year) in the rain will be that dissolved from the gaseous phase. Eriksson's (1959) estimate of 0.87 cm/sec for the deposition velocity of gaseous components from the atmosphere to the sea surface is used for the dissolution of gaseous iodine into the ocean. This deposition velocity is a measure of the rate with which gaseous iodine from the air is brought into immediate contact with the sea surface. Assuming that the $\text{I}_2(\text{aq})$ concentration of sea water is less than the equilibrium value predicted by the $\text{I}_2(\text{g})$ concentration of the atmosphere (which is the only time when gaseous dissolution must be considered), then it can also be assumed that essentially all gaseous iodine brought into immediate contact with the ocean surface will dissolve. Knowing that the surface of the ocean is $3.6 \times 10^{18} \text{ cm}^2$ (Krauskopf, 1967), that the gaseous iodine concentration is 8 ng/m^3 ($8 \times 10^{-15} \text{ g/cm}^3$), and using a

Value of $V_g = 0.87$ cm/sec, the amount of iodine which can dissolve in the ocean per annum according to equation (7) is 0.7×10^{12} grams.

With these numbers it is possible to estimate a minimum and a maximum removal rate for gaseous and total iodine over the ocean. For gaseous iodine the minimum removal rate will be that resulting, assuming the sea salt particles are the source for gaseous iodine in the atmosphere, and assuming a rain formation mechanism selective for small particles (dissolution of gaseous iodine in rain is not considered). Thus, only that amount of gaseous iodine dissolved in the ocean from the gaseous phase per annum, or 0.7×10^{12} g/year will be removed. The maximum removal rate will occur when gaseous iodine is delivered to the ocean by both wet and dry deposition, and assuming the dissolution of gaseous iodine into rain and cloud water does occur (or assuming the sea surface is the source of gaseous iodine in the atmosphere), this number would then be 5.1×10^{12} g/year (1.1×10^{12} g from dry fallout and 4×10^{12} g from rain and snow). For total iodine delivered from the atmosphere to the sea, the minimum value will be that amount deposited by wet and dry precipitation (again assuming gaseous iodine does not dissolve in rain and cloud water and assuming that gaseous iodine does not dissolve in the sea surface), or 2.2×10^{12} g/year (1.1×10^{12} g by dry fallout,

1.1×10^{12} g by rain and snow). The maximum amount of iodine delivered from the atmosphere to the sea per year would be that amount delivered to the ocean by total precipitation, assuming gaseous iodine does dissolve in rain and cloud water (5.1×10^2 g/year), plus 0.7×10^{12} g/year delivered by dissolution of gaseous iodine into the sea surface, giving a total of 5.8×10^{12} g/year.

c. Iodine Residence Times

By combining the minimum and maximum values of iodine deposition onto land and surfaces and by using the maximum and minimum estimates of total iodine in the atmosphere, a maximum and minimum residence time for gaseous and total iodine in the atmosphere can be calculated. The minimum annual removal of gaseous iodine from the atmosphere according to these calculations and assumptions would be 1.0×10^{12} g/year (0.3×10^{12} g delivered to the continents and 0.7×10^{12} g delivered to the oceans). The maximum amount of gaseous iodine removed from the atmosphere would be 5.9×10^{12} g/year (0.8×10^{12} g delivered to the continents and 5.1×10^{12} g delivered to the oceans). The minimum and maximum amounts of total iodine removed from the atmosphere annually would be 2.5×10^{12} g/year (0.3×10^{12} g delivered to the continents and 2.2×10^{12} g delivered to the oceans) and 6.6×10^{12} g/year (0.8×10^{12} g delivered to the continents and 5.8×10^{12} g delivered to the oceans), respectively.

Using equation (34) and the maximum amount of gaseous

iodine in the atmosphere (3.2×10^{10} g) and the minimum gaseous iodine removal rate (1.0×10^{12} g) results in a maximum residence time of about 12 days. The minimum residence time of gaseous iodine in the atmosphere is 1.0 days, given by equation (34), using the minimum amount of gaseous iodine in the atmosphere (1.6×10^{10} g), and the maximum removal rate of gaseous iodine from the atmosphere (5.8×10^{12} g/year). For total iodine, the maximum value of the residence time as obtained from equation (34) is about 6 days, using the maximum amount of total iodine in the atmosphere (4.2×10^{10} g) and the minimum rate of total iodine removal from the atmosphere (2.5×10^{12} g/year). Use of the minimum amount of total iodine in the air (1.8×10^{10} g), the maximum removal rate of total iodine from the atmosphere (6.6×10^{12} g/year) and equation (34) gives a minimum residence time of about 1.0 days for total iodine in the atmosphere. Table XV presents a summary of these numbers.

Comparing the above values for iodine residence time to those which are obtained by using Miyake and Tsunogai's (1963) estimate of production rate, it is again seen that a large discrepancy exists between removal and production rates. The calculation using removal rates gives a residence time of about 1 to 6 days for total iodine, while a similar calculation based on Miyake and Tsunogai's production estimate results in a residence time for total iodine in the atmosphere of 13 to 31 days. This again serves to point out that loss

of gaseous iodine from the surface of the ocean may not be the major source (and may even be a sink) for iodine in the atmosphere.

If the sea is the source of iodine in the atmosphere (apparently no other source can account for the quantities observed in the atmosphere), and if the loss of gaseous iodine from the surface of the sea cannot account for this atmospheric iodine, then the implication is that the source of iodine (gaseous and particulate) in the atmosphere must be the sea salt particles. In the discussion concerning the interaction of gaseous iodine, it was indicated that if a particle were injected into the atmosphere with the sea water concentrations of iodide and iodate, conditions should favor the release of $I_2(g)$ due to the oxidation of iodide by iodate. Using Blanchard's (1963) estimate of 6×10^{15} g as the yearly oceanic production rate of atmospheric chloride, and the sea water value for the I^-/Cl^- ratio (1.6×10^{-6}), then the yearly production rate of $I_2(g)$ from this source would be only 10^{10} g, which is much smaller than the annual removal rate of gaseous iodine from the atmosphere (minimum value for removal is 1.1×10^{12} g/year). This means that in order for the sea salt particles to be a major source for gaseous iodine in the atmosphere they must be enriched in iodine when they are injected into the atmosphere.

Dean (1963) has suggested the possibility that surface active material at the sea surface is enriched in iodine, and

the particles which are injected into the atmosphere carry this surface active material with them and might thus be enriched in iodine. Blanchard (1968) has reported very high concentrations of organic surface active material in the marine atmosphere ($>1 \mu\text{g}/\text{m}^3$). If sea salt particles are enriched in iodine by this process (i.e., organic iodine), then it is possible that this organic iodine associated with sea salt particles is the source of atmospheric gaseous iodine. Goetz (1966) has shown that organic material in the atmosphere is readily decomposed by exposure to ultraviolet irradiation. The suggestion then may be that organic surface active material enriched in iodine is injected into the atmosphere with the sea salt particles, and these particles then release $\text{I}_2(\text{g})$ as the organic material decomposes.

It is important to point out that if sea salt particles are a source for gaseous iodine, they still also can be a sink. Based on previous discussion, it seems quite probable that sea salt particles are both a source and a sink for gaseous iodine. The total interaction of sea salt particles and gaseous iodine may be similar to the following: Sea salt particles are injected into the atmosphere carrying surface active organic material enriched in iodine which releases $\text{I}_2(\text{g})$ as the organic material decomposes. This is followed by the slow uptake of iodine (as iodate) as equilibrium between $\text{I}_2(\text{g})$, $\text{I}_2(\text{aq})$, I^- , and IO_3^- is approached according to thermodynamic calculations previously presented.

2. Bromine

Residence times for gaseous and total bromine can also be estimated. An estimate of bromine residence times is much easier to calculate and probably is more accurate than the values for iodine, since it is almost certain that sea salt particles are the only source of bromine in the marine atmosphere. By using the Br/Cl ratio of sea salt particles and sea water, along with estimates of the amounts of gaseous and total bromine in the atmosphere, calculations of production rates and residence times by use of equation (34) are quite readily obtained.

2. Mass of Bromine in the Atmosphere

The amount of gaseous and total bromine in the atmosphere can be estimated by the same method that was used for the iodine calculation. The amount of gaseous bromine in the atmosphere will be 2×10^{11} g if the bromine concentration is 50 ng/m^3 and the atmosphere is homogeneously mixed with respect to gaseous bromine concentration. Assuming a heterogeneous mixture of bromine in the atmosphere such that the amount of gaseous bromine is equal to $1/2$ that amount estimated for a homogeneously mixed atmosphere as was suggested in the iodine calculation, then the amount of gaseous bromine in the atmosphere would be 1.0×10^{11} g. The total bromine content of the atmosphere can be calculated by the same argument that was used above, and also for iodine. If the total bromine concentration of the atmosphere is about 60 ng/m^3 (50 ng/m^3 gaseous bromine and 10 ng/m^3 particulate

bromine) then the maximum bromine content of the air would be 2.4×10^{11} g and the minimum bromine content of the atmosphere would be about 1.2×10^{11} g.

b. Production Rate of Bromine in the Atmosphere

The average value of the Br/Cl ratio for sea salt particles found in this study was approximately 2×10^{-3} (see Figure 16 and Table V). The Br/Cl ratio of sea water is 3.4×10^{-3} . From these two values of the Br/Cl ratio the production rate of total and gaseous bromine can be calculated assuming that sea salt particles are initially injected into the atmosphere with the sea water value of the Br/Cl ratio. Using Blanchard's (1963) value of 6×10^{15} g of chloride injected into the atmosphere from the sea annually and the sea water value for the Br/Cl ratio, gives a total bromine production rate of about 2×10^{13} g/year ($6 \times 10^{15} \cdot 3.4 \times 10^{-3}$). If the difference between the Br/Cl ratio observed on sea salt particles (2×10^{-3}) and the same ratio in sea water (3.4×10^{-3}) is the result of loss of $\text{Br}_2(\text{g})$, then the production rate of $\text{Br}_2(\text{g})$ is 8.4×10^{12} g/year ($6 \times 10^{15} \cdot 1.4 \times 10^{-3}$).

It is well known that there is a pollution source for bromine from leaded gasoline which is used in the internal combustion engine. Ethyl fluid, added as an antiknock agent to gasoline, contains lead, bromine, and chlorine in the relative weight ratios of 1:0.39:0.34. Recently, Zoller et al. (1970) have indicated that leaded gasoline can release

bromine gas either during the combustion process or from the particulate matter produced by the combustion process.

Murozumi et al. (1969) report that the amount of lead added to gasoline per year is 3.1×10^{11} g. Assuming the ethyl fluid weight ratio for Br/Pb to be 0.39, the maximum amount of bromine which can be delivered to the atmosphere is about 10^{11} g/year. This assumes that all the bromine present in gasoline will eventually become gaseous bromine in the atmosphere. This quantity of gaseous bromine is not important when compared to the amount of gaseous bromine released from sea salt particles per annum (8.4×10^{12} g) and can be ignored.

c. Bromine Residence Times

By use of equation (34), the production rates for gaseous and total bromine, and maximum and minimum amounts of bromine in the atmosphere, the maximum and minimum residence time for gaseous and total bromine in the atmosphere can be calculated. The maximum residence time of gaseous bromine in the atmosphere, as given by equation (34), is approximately 9 days, using the maximum amount of gaseous bromine in the atmosphere (2×10^{11} g), and a production rate of 8.4×10^{12} g/year. The minimum residence time for gaseous bromine in the atmosphere as given by equation (34) is approximately 5 days, using the minimum amount of gaseous bromine in the atmosphere (1.0×10^{11} g) and a production rate of 8.4×10^{12} g/year.

For total bromine, the maximum residence time in the atmosphere as given by equation (34) is 4.4 days, using the maximum amount of total bromine in the atmosphere (2.4×10^{11} g), and an annual production rate of 2×10^{13} g. The minimum residence time of total bromine in the atmosphere as given by equation (34) would be approximately 2.2 days, using the minimum amount of bromine in the atmosphere (1.2×10^{11} g), and a production rate of 2×10^{13} g/year. These values are summarized in Table XV.

If atmospheric gaseous bromine has a source from sea salt particles, then the sink for gaseous bromine must be dissolving in rain and cloud water, dissolving into the surface of the sea, and adsorbing on or reacting with land surfaces (which would include vegetation and airborne continental particulate matter).

From the range of values obtained for the bromine and iodine residence times it may appear that both gaseous and total bromine have a longer residence time than do gaseous and total iodine. This may not be true, however, since the uncertainties present concerning the sources and sinks for atmospheric iodine make the uncertainties for the residence times much larger than is the case for bromine. When data which would allow a more precise determination of the role of sea salt particles as a source and/or a sink for gaseous iodine in the atmosphere becomes available, it should then be possible to better compare the residence times of bromine

and iodine than can be done at this time. However, if sea salt particles do act at least as a partial sink for iodine as has been suggested earlier, then one would expect the gaseous iodine to have a shorter residence time in the atmosphere than bromine since gaseous iodine would have more sinks available to it. In comparing the residence time of two gases, a longer atmospheric residence time means that the ratio of gaseous components being produced (or removed) per unit time to total gas in the air is smaller than the same ratio for the gaseous component with the shorter atmospheric residence time. In turn, this implies that if conditions in the atmosphere change to allow higher (or smaller) concentrations of gaseous species to be present (such changes might include the mixing of relatively gas free air with the air over the ocean, changes in relative humidity, the number and mass of sea salt particles in the air, and probably a host of other meteorological parameters) the gaseous component with the longer residence time will require more time to reach a steady state concentration. A residence time in the atmosphere for gaseous bromine longer than that for gaseous iodine would explain the results which showed a tendency for the gaseous bromine concentration to gradually increase in the air with time at Bellows Air Force Station whereas the gaseous iodine concentration showed no such tendency.

Table XV
Atmospheric Residence Times for Iodine and Bromine

	Iodine		Bromine	
	Maximum	Minimum	Maximum	Minimum
n(g) (grams)	3.2×10^{10}	1.6×10^{10}	2×10^{11}	1.0×10^{11}
n(t) (grams)	4.2×10^{10}	1.8×10^{10}	2.4×10^{11}	1.2×10^{11}
dn(g)/dt (g/year)	5.8×10^{12}	1.0×10^{12}	8.4×10^{12}	8.4×10^{12}
dn(t)/dt (g/year)	6.6×10^{12}	2.5×10^{12}	2×10^{13}	2×10^{13}
τ (g) (days)	12	1.0	9	4.4
τ (t) (days)	6	1.0	5	2.2

n(g) = weight of gaseous iodine (bromine in the atmosphere

n(t) = weight of total iodine (bromine) in the atmosphere

dn(g)/dt = atmospheric removal rate of gaseous iodine, atmospheric
production rate of gaseous bromine

dn(t)/dt = atmospheric removal rate of total iodine, atmospheric
production rate of total bromine

τ (g) = atmospheric residence time of gaseous iodine (bromine)

τ (t) = atmospheric residence time of total iodine (bromine)

$$\tau = \frac{n}{dn/dt}$$

C. Interaction of Gaseous Iodine with Pollution Particulate Material

The data and discussion presented in the Results section permit a few rather generalized statements concerning the potential weather modification properties resulting from the interaction of gaseous iodine and lead containing pollution particulate material.

Schaefer (1966) has estimated that air polluted by automobile exhausts can contain approximately 10^9 particles per cubic meter which will act as ice nuclei when exposed to I_2 vapor. In the free atmosphere, however, ice nuclei normally range for 10^1 to 10^4 m^{-3} . In a later study of ice nuclei formed by lead particles when activated by I_2 vapor, Schaefer (1966) estimated that one gram of I_2 vapor would be sufficient to activate 10^{18} lead containing particles from automobile exhaust. Thus from the two previous statements it would appear that 1 ng/m^3 of iodine in polluted air should activate all the lead particles in this air.

Measurements in Cambridge, Massachusetts showed an average gaseous iodine concentration of about 13.5 ng/m^3 , and this number apparently was independent of the degree to which the air was polluted. This amount of iodine, if it is I_2 , should be sufficient to activate all potential ice nuclei contained in automobile-polluted air. Polluted air, however, does not generally show a large concentration of ice nuclei until additional iodine is added in the laboratory. Schaefer (1969) and others have pointed out that there should be sufficient iodine in polluted air to activate the lead particles present to ice nuclei, but no one has reconciled the fact that with these quantities of iodine and lead present, the

corresponding quantity of ice nuclei are not observed. Schaefer (1966) reported that surface air normally contains 10 to 1000 ice nuclei per cubic meter of air. There may be several explanations for this. 1) The gaseous iodine observed in the atmosphere may not be elemental iodine, I_2 . 2) The carbonaceous material and non-lead inorganic materials in pollution particles may "shield" the lead from reaction with iodine. 3) At the concentration of gaseous iodine and/or lead particles present in a polluted atmosphere, the kinetics of the reaction may not be highly favorable.

The discussion of gaseous iodine in the marine atmosphere indicates that gaseous iodine exhibits various relationships which can be explained quite well by assuming that this gas is I_2 . If the sea is the major source of gaseous iodine in Cambridge, it would seem almost certain that at least part of this gaseous iodine will be elemental iodine (I_2).

The reversibility of the adsorption as reported by Clough et al. (1965) fits well with these observations, suggesting that the iodine is present as I_2 vapor. The fact that Schaefer has not observed ice nuclei in the near surface polluted air, but has observed large concentrations of these nuclei at altitudes of around 5000 feet over and down wind from polluted cities (1968) may indicate that a fairly long period of time is required for ice nuclei formation.

It is believed that large quantities of ice nuclei are normally not observed in polluted air due to the fact that the reaction of gaseous iodine with lead containing particles probably proceeds rather slowly. This slowness of reaction is probably due to the competition

for iodine adsorption with lead and other particulate surfaces, plus the fact that the reaction rates for the lead-iodine reaction at this concentration of reactants may be slow.

Lead is emitted from the automobile exhaust system as extremely small particles and these particles rapidly coalesce with each other and other small particles until they reach a size of approximately 0.1μ radius. This type of growth mechanism undoubtedly results in particles with mixed amounts of organic and inorganic material. The fact that carbonaceous material is an excellent adsorbing media for gaseous compounds such as iodine (Mantell, 1951) may mean that the carbonaceous material may act as an agent which "shields" the lead from reaction with iodine.

Schaefer (1966) has shown that when air from automobile exhausts is exposed to air with "a trace of iodine vapor" present, large concentrations of ice nuclei (10^8 m^{-3} or greater) are formed in a matter of seconds. In a typical experiment Schaefer added 80 l of automobile exhaust to a 100 l cold chamber and then added approximately 0.1 l of air from a bottle containing iodine crystals at a temperature of 25°C . In such an experiment Schaefer (1966) reported that 10^6 or more ice nuclei will form within 20 seconds. The vapor pressure of solid I_2 at 25°C is approximately 0.4 mm, and therefore, this air at 25°C has a partial pressure of $\text{I}_2(\text{g})$ equal to about 5×10^{-4} atm when saturated. Thus, 0.1 l of such air would contain 5×10^{-4} g of iodine, and when diluted to 100 l in a cold chamber the resulting iodine concentration in this chamber would then be $5 \times 10^{-3} \text{ g/m}^3$ or more than 5 orders of magnitude higher than the

concentration of gaseous iodine in the free air. Automobile exhaust directly from a car certainly has a concentration of lead particles much higher than that in even the most polluted atmosphere. Thus, if the reaction rates for this reaction are important, the time required to form measurable numbers of ice nuclei may be much longer, (perhaps days) than the times required under the laboratory conditions just described. Such a slower reaction rate would explain the fact that surface concentrations of ice nuclei are low, while at an altitude of 5,000 feet above a polluted city, larger concentrations of ice nuclei are frequently observed (Schaefer, 1969), since the time required for transport of particles from surface air to an altitude of 5,000 feet may be sufficient for the reaction between lead and iodine to proceed to the point where an increase in the number of ice nuclei can be observed.

If this argument is valid, then a reaction between atmospheric gaseous iodine and pollution lead aerosols may indeed cause a modification of the atmosphere. Also, the degree to which such a modification actually occurs will be very dependent upon the extent to which automobiles are permitted to dump lead into the atmosphere. Even more important, perhaps, would be a pollution source of iodine which would significantly raise the gaseous iodine concentration in areas of heavy automobile pollution. Thus, far, no evidence of serious iodine pollution has been detected. However, more measurements are required to ascertain this.

V. SUMMARY AND CONCLUSIONS

A method for the simultaneous determination of the gaseous concentrations of iodine and bromine in the atmosphere has been developed. This method employed an electrostatic precipitator to remove particulate matter from the air being sampled. The gaseous iodine and bromine in the particulate free air were adsorbed onto specially cleaned activated charcoal. While still on the charcoal, the trapped iodine and bromine were activated by thermal neutrons to form the radioactive isotopes ^{128}I and ^{80}Br , respectively. After irradiation the iodine and bromine were removed from the charcoal, isolated and counted to determine the amount present.

Using this method of collection and analysis the first reliable measurements of gaseous iodine and bromine concentrations in the marine atmosphere have been obtained. Approximately 60 gaseous iodine and bromine samples collected from a 20 meter tower on the windward shore of Oahu, Hawaii showed that the average sea level concentration of gaseous iodine is approximately 8 ng/m^3 and that the average concentration of gaseous bromine is approximately 50 ng/m^3 . Collection of particulate iodine and bromine and simultaneous gaseous iodine and bromine samples showed the particulate iodine concentration is 25 to 50% of the gaseous iodine concentration and the particulate bromine concentration is about 10 to 20% of the gaseous bromine concentration. There was an apparent correlation between particulate and gaseous iodine concentrations, but no such correlation was observed between particulate and gaseous bromine concentration. No correlation was

detected between total particulate matter in the marine atmosphere and either the gaseous iodine concentration or the gaseous bromine concentration. In addition, no correlation was found between wind force and the concentrations of gaseous iodine and bromine in the marine atmosphere.

Assuming that gaseous iodine and bromine exist in the marine atmosphere as $I_2(g)$ and $Br_2(g)$, respectively, it is possible to explain their presence and the particulate iodine and bromine concentrations which are found on sea salt particles solely on thermodynamic considerations. Thermodynamic calculations also show that at the gaseous iodine and bromine concentrations found in this work, the fact that the I/Cl and Br/Cl ratios are generally higher in rain than the same ratios for sea salt particles may be at least partially accounted for by the dissolution of $I_2(g)$ and $Br_2(g)$ in rain and cloud water.

The mechanism of gaseous iodine production in the marine atmosphere is uncertain, but apparently a photochemical oxidation of iodide at the sea surface is not the major source of atmospheric gaseous iodine. It is possible that iodine rich organic material from the sea surface is injected into the air and decomposes to release gaseous iodine to the atmosphere. Oxidation of sea salt particulate bromide to release $Br_2(g)$ is almost certainly the source of atmospheric gaseous bromine. Using the concentrations of gaseous iodine and bromine obtained in this work, calculations would indicate that atmospheric gaseous iodine has a residence time of between 1.0 and 12 days, and that atmospheric

gaseous bromine has a residence time between 5 and 10 days. The residence time of total iodine in the atmosphere is probably between 1.0 and 6 days and the residence time for the total bromine in the atmosphere is between about 2 and 4 days.

Samples of gaseous iodine and bromine collected above the trade wind inversion at an elevation of 3,500 meters on the island of Hawaii may indicate that air above the inversion contains a smaller concentration of gaseous iodine and bromine than does air below the inversion. Samples collected at Hilo, Hawaii show much higher concentrations of gaseous iodine than do the samples collected in all other locations; and the reason for this high iodine concentration in Hilo, Hawaii is uncertain. A diurnal variation of gaseous iodine and bromine concentration was noted in Hilo, Hawaii and it is suggested that that is the result of air from above the trade wind inversion, which has a low concentration of gaseous iodine and bromine, mixing with below inversion air during the night.

No evidence of variation in either gaseous iodine and bromine concentration or particulate iodine and bromine concentration with geographical position was found. Samples of particulate iodine and bromine collected aboard a ship on a cruise from Kodiak, Alaska to Honolulu, Hawaii showed the same concentrations of iodine and bromine and the same values for the I/Cl and Br/Cl ratios which are found in Hawaii. Gaseous iodine and bromine samples collected from a ship between Honolulu, Hawaii and Seattle, Washington showed similar concentrations of gaseous iodine and bromine as is found in "clean" air in Hawaii.

Samples of gaseous iodine collected at Cambridge, Massachusetts indicated no significant source of iodine pollution is evident during the summer there. The average gaseous iodine concentrations of Cambridge, Massachusetts air was about twice the value found for marine air but within the same range of values found in "clean" marine air. There is an apparent relationship between total particulate material and the ratio of particulate to gaseous iodine in Cambridge, Massachusetts, which is consistent with laboratory observations of $I_2(g)$ adsorption onto combustion aerosols reported by other investigators.

In the marine atmosphere the following studies and data may do much to eliminate many of the uncertainties regarding the sinks and sources for gaseous iodine in the atmosphere. Needed are data concerning the iodine content of sea surface active organic material and studies to see whether such material can be injected into the air efficiently. The iodine concentration of sea salt particles immediately after injection into the atmosphere would be especially useful in attempting to determine the extent to which sea salt particles may act as a source for gaseous iodine in the atmosphere. Further studies are also required concerning the dissolution of gaseous iodine into rain and cloud water. New studies are required to determine if the sea surface is a source or sink for gaseous iodine.

Further studies of gaseous iodine in the non-marine atmosphere are also required. These studies would include the role that vegetation might play in affecting local concentrations of airborne gaseous iodine, and additional studies of polluted atmospheres to

see whether there is or can be a significant pollution source
for gaseous iodine.

APPENDIX A

Laboratory Studies of Collection Procedure and Equipment

It is known that an electrostatic precipitators' collection efficiency for particles is a function of particle size and flow rate of the airstream through the precipitator (Ranz and Wong, 1952). By using the electrostatic precipitator followed by the cascade impactor it was possible to determine the effect of both particle size and flowrate on the collection efficiency of the precipitator used for this work.

In addition to the six stages of the cascade impactor described in the Experimental section of this dissertation, it was possible to place a filter immediately behind the sixth stage to collect particles smaller than those collected on the sixth stage. In this manner it was possible to examine collection efficiencies of 7 ranges of particle size. Since the cascade impactor has an orifice after the sixth stage which limits the flow rate through the impactor to $0.75 \text{ m}^3/\text{hr}$, the changes in flow rate were obtained by the following method. Efficiencies for the various size particles were first obtained by using the cascade impactor at a flow rate of 0.75 m^3 . The limiting orifice was then removed and the tests were repeated with the jet for the sixth stage then being the limiting orifice. Under these conditions the flowrate was about $1.1 \text{ m}^3/\text{hour}$. Removal of the sixth stage allowed efficiency tests at a flowrate of about $2 \text{ m}^3/\text{hour}$.

When the flow rate is changed, the collection efficiency for the various particle sizes is also changed for the different stages of the cascade impactor. New collection efficiencies for each stage may be calculated by use of equation (35) (Ranz and Wong, 1952):

$$C_j \propto (\mu D_j / \rho V_j)^{\frac{1}{2}} \quad (35)$$

where

C_j = particle radius (cm) for particles collected with a fractional efficiency of 1.0 on jet j

μ = viscosity of air (dyne-sec/cm²)

D_j = diameter of jet j (cm)

ρ = density of particle (g/cm³)

V_j = gas velocity through jet j (cm/sec)

All terms remain constant when the flow rate is changed

except V_j and C_j .

But,

$$V_j = R/D_j \quad (36)$$

where R = flowrate (cm³/sec).

Therefore,
$$C_j \propto \frac{1}{R^{\frac{1}{2}}}$$

Since the collection efficiencies of each stage of 0.75 m³/hr are known (see Figure 3), the collection efficiencies at flow rates different from 0.75 m³/hr will be given by

$$C_{j(R)} = C_{j(0.75)} \sqrt{0.75/R} \quad (37)$$

where

$C_j(R)$ = particle radius (cm) of jet j collected at a
flowrate R, with fractional efficiency 1.0

$C_j(0.75)$ = particle radius (cm) of jet j collected at a
flowrate of $0.75\text{m}^3/\text{hr}$, with fractional
efficiency 1.0

R = flow rate (cm^3/sec)

To duplicate as nearly as possible the spectrum of particles produced over the open ocean, the particles produced for this work were made in the following manner: A solution of sea water spiked with a large amount of radioactive ^{22}Na was placed in a fine sintered glass filter tower. Air was then forced through the frit producing bubbles in the solution which rose to the surface and broke, thus ejecting saline particles into the air. These particles were then drawn through the precipitator and into the cascade impactor by means of a vacuum pump. The ^{22}Na activities for each stage and the filter were then γ -counted using a sodium iodide well detector and single channel analyzer (Versa/Matic II Spectrometer SC-81, Tracerlab, Inc.). Thus, by comparing the ^{22}Na activity on the different stages of the impactor with the precipitator running and with it not running, the precipitator efficiency for each stage could be calculated. This was done several times under various conditions (e.g., varying flow rate, varying collection periods, and varying ^{22}Na concentration). Table XVI gives an example of the results obtained. In all cases the efficiency was high enough that no activity could be detected on the samples

Table XVI
Electrostatic Precipitator Efficiencies

Sample Number	Stage Number	Size of particle collected at 100% efficiency	Flowrate	Na Concentration(cpm)		Efficiency (%)
				Precipitator off	Precipitator on	
1	A	10.0 μ	0.75 m ³ /hr	600	0	>99.3
	B	5.0 μ	0.75 m ³ /hr	2,031	0	>98.8
	C	2.5 μ	0.75 m ³ /hr	6,820	0	>99.9
	D	1.2 μ	0.75 m ³ /hr	6,004	0	>99.9
	E	0.6 μ	0.75 m ³ /hr	1,481	0	>99.5
	F	0.3 μ	0.75 m ³ /hr	212	0	>96
	*Filter	0.05 μ	0.75 m ³ /hr	209	0	>90
2	A	8.4 μ	1.1 m ³ /hr	750	0	>99.4
	B	4.2 μ	1.1 m ³ /hr	3,335	0	>99.8
	C	2.1 μ	1.1 m ³ /hr	14,699	0	>99.9
	D	1.05 μ	1.1 m ³ /hr	8,001	0	>99.9
	E	0.5 μ	1.1 m ³ /hr	1,006	0	>99.5
	F	0.25 μ	1.1 m ³ /hr	104	0	>95
	*Filter	0.05 μ	1.1 m ³ /hr	50	0	>90
3	A	6.4 μ	1.9 m ³ /hr	38,905	0	>99.9
	B	3.2 μ	1.9 m ³ /hr	39,137	0	>99.9
	C	1.6 μ	1.9 m ³ /hr	27,762	0	>99.9
	D	0.8 μ	1.9 m ³ /hr	5,987	0	>99.7
	E	0.4 μ	1.9 m ³ /hr	730	0	>98
	*Filter	0.05 μ	1.9 m ³ /hr	529	0	>97
4	*Filter	0.05 μ	2.1 m ³ /hr	730,000	6 $\pm$ 3	>99.9
	0.45 μ					

* Filter collects all particles greater than 0.05 μ with an efficiency equal to or greater than 90%.

collected with the precipitator running. The efficiency, therefore, could be calculated only as greater than the minimum activity which could statistically be observed. Because the maximum amount of ^{22}Na which could be used economically and safely gave no activity on the impactor stages with the precipitator on, it was decided to collect a bulk sample on a filter where several hundred thousand counts of sodium could be collected and a number for total particulate removal might be obtained. To do this a 0.45 μ HA Millipore Filter was used in place of the impactor. This filter will collect all particles of radius 0.45 μ or greater, and about 90 percent of the particles down to a radius of 0.05 μ (see Table XVI). It can be seen that by using the filter, all particulate matter was again removed from the airstream. These results indicated that essentially all particulate matter in the size range of interest was removed by the precipitator. Since the spectrum of particle size produced by this method was in close agreement with that found in the marine atmosphere, it was decided that this was an acceptable way of removing particulate matter from the air to be sampled.

An efficiency test for the electrostatic precipitator was also performed during actual sample collection. This was done by running two cascade impactors side by side. One of the cascade impactors had an electrostatic precipitator mounted in front of its entrance, the other cascade impactor was operated in the normal manner. Samples were collected for 22 hours to insure collection of enough particulate material. The sample on each stage of the cascade impactors was packaged as described in the

Experimental section of this dissertation, and analyzed for chlorine, bromine, and iodine at M.I.T. A blank problem was encountered, however, and no Cl, Br, or I could be seen above the blank. The blanks were such that for slides A, E, and F the efficiency must be equal to or greater than 95% and equal to or greater than 99% for slides B, C, and D.

It was also necessary to study the effect of the electrostatic precipitator on both particulate and gaseous iodine in an airstream. For gaseous iodine, carrier free ^{131}I was generated as $\text{I}_{2(g)}$. Air was drawn over one-half ml of a 0.01 N HNO_3 solution containing various concentrations of $^{131}\text{I}^-$. This air was passed through the electrostatic precipitator and then over a bed of activated charcoal. It was found that $\text{I}_{2(g)}$ generation under these conditions was slow and quite constant. At the end of the sampling period the iodine activity remaining in the flask and the iodine activity on the activated charcoal were γ -counted using a sodium iodide well detector and a single channel analyzer. For 20 samples analyzed in this manner with the precipitator not operating, it was found that 92-94% of the calculated activity (based on a known amount of ^{131}I activity added to the flask and the amount remaining in the flask after completion of sampling) was found on the charcoal. It was assumed that the remaining activity was lost due to incomplete washing of the flask and the adsorption of the gaseous iodine onto the glass tubing which directed the airstream from the generator flask to the electrostatic precipitator. Washing the precipitator with a solution

of 0.5 M $\text{Na}_2\text{S}_2\text{O}_5^=$ and then counting this solution showed that apparently less than 5% of the total activity generated was adsorbed to the walls of the precipitator. The precipitator was then turned on (11 KV, 0.3 ma) and the same procedure was followed (actually, the procedure was to run the samples alternately with and without the precipitator operating). In the case of the 20 samples collected with the precipitator running, it was found that 88-90% of the calculated activity was collected by the charcoal. Thus, from these experiments it appeared that the precipitator while operating would cause approximately 5% of the gaseous iodine in the airstream to be lost (presumably due to ionization of $\text{I}_2(\text{g})$ with subsequent precipitation onto the walls of the precipitator). Although gaseous bromine was not studied in this manner, it would be expected that gaseous bromine loss would be equal to or less than the iodine loss since gaseous bromine should not be ionized as easily by the precipitator as gaseous iodine (the precipitator is operated by positive charging).

Tests were also performed to determine if either gaseous iodine and bromine would be released from particulate matter as a result of the gaseous oxidants produced by the discharging wire (ozone is produced in relatively large quantities by a corona discharge). A teflon collar was constructed for the precipitator which allowed a 0.47 mm stainless steel Millipore Filter holder to be attached to the exit end of the precipitator. With this equipment it was possible to test the effect of the precipitator on particulate iodine in the following manner: Particles were

generated in the same manner as was described for the precipitator efficiency tests from a solution of sea water containing ^{131}I as I^- . The generated particles were pulled through the precipitator by means of a vacuum pump. A 47 mm HA Millipore Filter ($0.45\ \mu$) was placed at the exit end of the electrostatic precipitator, and the filter was followed by an activated charcoal trap. Samples were collected on both the filter and the charcoal. Collecting samples without the precipitator operating allowed an estimate of particulate iodine production rate (by measuring activity collected by the filter) and a production rate of gaseous iodine (activity on charcoal). Collecting samples with the precipitator operating allowed an estimate of the degree to which gaseous iodine production rate was affected by the corona discharge. Tests were performed to check the retentivity of the filter for iodine vapor. It was found that the HA 47 mm $0.45\ \mu$ Millipore Filter would retain approximately 25% of the $\text{I}_2(\text{g})$ passed through it, and this number was reasonably reproducible if the flowrates were not changed and if the filters all came from the same box. By collecting samples with and without the precipitator operating it was determined that statistically, no difference in the production rate of $\text{I}_2(\text{g})$ could be detected between these two groups of samples.

Tests for $\text{Br}_2(\text{g})$ release from particles were conducted in exactly the same manner as for $\text{I}_2(\text{g})$ by using 36 hour ^{82}Br as Br^- in seawater. For the bromine tests it was found that there is a substantial release of gaseous bromine when the precipitator

is operating. Table XVII summarizes the results. With the precipitator not operating these results would indicate that 2-3% of the particulate bromine was lost to the gaseous phase. With the precipitator operating, approximately 20-25% of the particulate bromine was released as gaseous bromine. If it is possible to extrapolate these results to the ambient marine atmosphere, it would then be expected that sampling of air containing 10 ng/m^3 of particulate bromine would result in a sample showing a gaseous bromine concentration of 2 ng/m^3 greater than the true gaseous bromine concentration, assuming the Br in the particle is present as Br^- . In the case of air containing particulate bromine and gaseous bromine in the relative proportions found for clean marine air in this study, the effect of the precipitator on the gaseous bromine concentration of the air being sampled is small since the gaseous bromine concentration is approximately 6 to 10 times higher than the particulate bromine concentration. This means that if 20% of the particulate bromine is released to the gaseous phase, the measured concentration of gaseous bromine would be only 2-3% higher than the true gaseous bromine concentration.

The charcoal was tested for adsorption efficiency for $\text{I}_2(\text{g})$ and $\text{Br}_2(\text{g})$ by placing two charcoal traps in tandem. $\text{I}_2(\text{g})$ was generated from a 0.01 N solution of HNO_3 containing $^{131}\text{I}^-$ as described previously. $\text{Br}_2(\text{g})$ was generated from a solution of 1 N HNO_3 and approximately 0.01 N KMnO_4 containing $^{82}\text{Br}^-$. The activity on the two charcoal traps was measured by γ -counting, and for both $\text{I}_2(\text{g})$ and $\text{Br}_2(\text{g})$, and 100% of the activity was

Table XVII
The Effect of the Electrostatic Precipitator
on the Rate of Release of Br₂(g) from Sea Salt Particles

Sample	Precipitator Status	Collecting Time	Particulate* Br Activity (cpm)	Total*** Gaseous activity (cpm)	Rate of Gaseous Bromine Release (cpm/hr)	% Br ₂ (g) released from particles (Br ₂ (g)/total Br) x 100
1	off	1 hr	7,800	220	220	2.7%
2	on	1 hr	Average of 1 and 3	2,300	2,300	23.5%
3	off	1 hr	6,950	170	170	2.4%
4	on	1 hr	Average of 3 and 5	1,900	1,900	21.2%
5	off	1 hr	7,150	250	250	3.5%
6	on	1 hr	Average of 5 and 8	2,370	2,370	23.7%
7	on	2 hr	Average of 5 and 8	4,180	2,090	21.6%
8	off	1 hr	8,100	1,120	1,120**	12.2%**
9	on	1 hr	Average of 8 and 10	2,280	2,280	22.4%
10	off	1 hr	7,680	280	280	3.4%

* Corrected for amount of gaseous Br adsorbed to filter.

** High gaseous bromine activity for sample 8 due to release of HNO₃ fumes in the laboratory.

*** Including amount adsorbed to filter.

All activities standardized with 0.1 ml of parent solution and counted with each sample to correct for decay of ⁸⁰Br.

found to be retained on the first trap. Flow rates and mass of charcoal used were the same as used to collect the marine air samples.

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APPENDIX B

KCKUA

COMPUTER PROGRAM FOR STATISTICAL CALCULATION AND PLOTTING OF DATA

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EACH SET OF DATA NEEDS 8 CONTROL CARDS FOLLOWED
BY THE DATA
UP TO 97 DATA POINTS PERMITTED IN EACH SET
UP TO 20 SETS OF DATA PERMITTED INCLUDING RATIOS
UP TO 10 RATIOS PERMITTED
UP TO 40 NORMAL PLOTS AND 20 TIME PLOTS POSSIBLE
FOR EACH SET

REAL*8 VABS,VCRD,SAME(20)
INTEGER CALC
INTEGER COUNT
INTEGER S,CONT(80)
DIMENSION ITEM(20)
DIMENSION ERROR(20,100),RCAR(20),YER(100),XER(100)
DIMENSION X(100),Y(100)
DIMENSION IRAT(20)
DIMENSION DUM(100)
DIMENSION BUFFER(1000),DATA(20,100)
COMMON DATA,NEL,NSAM,SAME,X,Y,MMSAM,NNSAM,LEAST
COMMON A,VABS,VORD,B
DATA SIGN/'G/CM'/
N = 1

C
C
C

CARD TO SAY HOW MANY DIFFERENT SETS OF DATA

101
102

READ (5,101) IHOW
FORMAT (I1)
S = 1
T = 1

C
C
C

REQUIRED BY PLOTTER TO SET UP TAPE

```

      CALL PLOTS (BUFFER(1),1000)
C
C   NAME OF EACH COLUMN OF DATA -- NEEDS TWO CARDS
C
      READ (5,8) SAME
      FORMAT (10A8)
C
C   CONCENTRATION SYMBOLS FOR EACH COLUMN NANA-45,
C   MICRO-34,MILLE-40
C
      READ (5,22) ITEM
      FORMAT (20I2)
C
C   CONTROL ARRAY WHICH COLUMN OF DATA TO PLOT VS.
C   WHICH -- NEEDS TWO CARDS
C
      READ (5,4) CONT
      FORMAT (40I2)
C
C   NEL = HOW MANY COLUMNS OF DATA
C   NSAM = HOW MANY POINTS IN EACH COLUMN
C   VAR - NO. OF SIGMA FROM LINE FOR DATA REJECTION
C   IFER PUT 99 IF DATA INCLUDES ERRORS
C   LEAST = PUT 99 IF WANT REGRESSION LINE PLOTTED
C   ITIME - PUT 99 IF WANT DATA VS TIME PLOTS
C   CALC - MAKE 99 IF NO PLOTS JUST CALCULATIONS
C   DESIRED
C   THESI - PUT 99 IF FOR THESIS
C   IFLOG - PUT 99 IF YOU WANT SEMI LOG PLOT
C   LLOG - PUT 99 IF WANT LOG LOG PLOT
C   IRAT - WHICH RATIOS DESIRED IRAT(1)/IRAT(2)
C   UP TO 20 NUMBERS, 10 RATIOS
C
      READ (5,1) NEL,NSAM,VAR,IFER,LEAST,ITIME,CALC,
1    THESI,IFLOG,LLOG,IRAT
      FORMAT (2I3,F4.3,27I2)
      NNEL = NEL
C
C   READS DATA POINTS
C
      IF (IFER) 103,103,104
104    READ 107,ROAR
107    FORMAT (20F4.2)
      DO 105 JK = 1,NSAM
      READ (5,106)(DATA(KK,JK),ERROR(KK,JK),KK=1,NEL)
105    CONTINUE
106    FORMAT (8(F6.2,F4.3))
      DO 85 KK = 1,NEL
      DO 85 JK = 1,NSAM
      IF (ERROR(KK,JK))87,87,85
87    ERROR(KK,JK) = ROAR(KK)*DATA(KK,JK)*.01

```

```

85      CONTINUE
      GO TO 18
103     DO 2 JK = 1,NSAM
      READ (5,3)(DATA(KK,JK),KK=1,NEL)
2       CONTINUE
3       FORMAT (13F6.2)
C
C       IF NOT ZERO, CALCULATES RATIOS
C
18      IF (IRAT(T))16,112,16
16      NEL = NEL + 1
      LL = IRAT(T)
      MM = IRAT(T+1)
      DO 17 JK = 1,NSAM
      IF (DATA(MM,JK))47,46,47
46      DATA(NEL,JK) = 0.
      ERROR(NEL,JK) = 0.
      GO TO 17
47      DATA(NEL,JK)= DATA(LL,JK)/DATA(MM,JK)
      ERROR(NEL,JK) = SQRT((ERROR(LL,JK)/DATA(LL,JK))
1      **2+(ERROR(MM,JK)/DATA(MM,JK))**2)
17      CONTINUE
      T = T + 2
      GO TO 18
C
C       CALCULATES AVERAGE AND STANDARD DEVIATION OF
C       EACH COLUMN OF DATA
C
112     PRINT 95
95      FORMAT (1H1)
      DO 72 KK = 1,NEL
      TOT = 0.
      COUNT = 0
      DO 70 JK = 1,NSAM
      IF (DATA(KK,JK))70,70,71
71      TOT = TOT + DATA(KK,JK)
      COUNT = COUNT + 1
70      CONTINUE
      SUM = 0.
      AVE = TOT/COUNT
      DO 73 JK = 1,NSAM
      IF (DATA(KK,JK)) 73,73,74
74      SUM = SUM + (AVE-DATA(KK,JK))**2
73      CONTINUE
      STAN = SQRT(SUM/(COUNT-1))
      PRINT 75, SAME(KK),AVE,STAN
75      FORMAT (' AVERAGE OF 'A8,' DATA IS 'F8.3,' STAND'
1      'ARD DEVIATION SIGMA IS 'F10.4)
72      CONTINUE
C
C       PRINTS DATA WITH NAMES

```

```

C
50   IF (IFER) 200,200,201
201   IF (NEL-10) 202,202,203
202   LM = NEL
      GO TO 204
203   LM = 10
204   PRINT 205,(SAME(KK),KK=1,LM)
205   FORMAT (//10(5X,A8))
      DO 206 JK = 1,NSAM
206   PRINT 207,(DATA(KK,JK),ERROR(KK,JK),KK=1,LM)
207   FORMAT (10(1X,F6.3,1X,F5.3))
      IF (NEL-10) 56,56,208
208   PRINT 205,(SAME(KK),KK=11,NEL)
      DO 210 JK = 1,NSAM
210   PRINT 207,(DATA(KK,JK),ERROR(KK,JK),KK=11,NEL)
200   IF (NEL-10) 54,54,55
54   LM = NEL
      GO TO 59
55   LM = 10
59   PRINT 52,(SAME(KK),KK=1,LM)
52   FORMAT (//10(2X,A8))
      DO 53 JK = 1,NSAM
53   PRINT 13,(DATA(KK,JK),KK=1,LM)
13   FORMAT (10(3X,F7.3))
      IF (NEL-10) 56,56,57
57   PRINT 52,(SAME(KK),KK=11,NEL)
      DO 58 JK = 1,NSAM
58   PRINT 13,(DATA(KK,JK),KK=11,NEL)
C
C   CALLS TIME SUBROUTINE IF ASKED FOR
C
56   PRINT 150,VAR
150   FORMAT (///' NUMBER OF ST DEV FOR REJECTION OF'
1, ' DATA ' F5.3)
      IF (ITIME) 51,7,51
51   CALL TIME
C
C   SETS UP INDEX FOR PLOTS
C
7    IF (CONT(S)) 5,100,5
5    LL = CONT(S)
      MM = CONT(S+1)
      VABS = SAME(LL)
      VORD = SAME(MM)
      PRINT 68,VABS,VORD
68   FORMAT (///' *****CALCULATIONS FOR DATA SET '
1, ' OF ' A8,2X,A8,' *****')
      KOUNT = 0
C
C   INSURES PLOT STARTING AT ZERO
C

```

```

X(1) = .001
Y(1) = .001
KK = 2

C
C   REMOVES DATA OF ZERO
C
DO 6 JK = 1, NSAM
X(KK) = DATA(LL, JK)
Y(KK) = DATA(MM, JK)
XER(KK) = ERRCR(LL, JK)
YER(KK) = ERRCR(MM, JK)
IF (X(KK)) 10, 6, 10
10 IF (Y(KK)) 11, 6, 11
11 KK = KK + 1
6   CONTINUE
NNSAM = KK - 1
IF (LLOG) 500, 500, 501

C
C   DETERMINES LARGEST AND SMALLEST X
C
501 BIGX = 0.
    SMALLX = 1000.
    DO 502 JK = 2, NNSAM
    IF (X(JK) - BIGX) 504, 504, 503
503 BIGX = X(JK)
504 IF (X(JK) - SMALLX) 505, 502, 502
505 SMALLX = X(JK)
502 CONTINUE
    BEG = 1000.
553 IF (SMALLX - BEG) 551, 552, 552
551 BEG = BEG / 10.
    GO TO 553

C
C   MAKES ALL DATA GREATER THAN 1 AND FINDS LOG OF X
C   LOGS ARE POSITIVE
C
552 GOOFX = 1./BEG
    SMALLX = SMALLX * GOOFX
    BIGX = BIGX * GOOFX
    DO 550 JK = 2, NNSAM
550 X(JK) = ALOG10(X(JK)*GOOFX)
    PRINT 305, (X(JK), JK=2, NNSAM)
    GO TO 300
500 IF (IFLOG) 299, 299, 300

C
C   FINDS LARGEST AND SMALLEST Y
C
300 TBIG = 0.
    SMALL = 1000.
    DO 301 JK = 2, NNSAM
    IF (Y(JK) - TBIG) 303, 303, 302

```

```

302  TBIG = Y(JK)
303  IF (Y(JK)-SMALL) 304,301,301
304  SMALL = Y(JK)
301  CONTINUE
    BEG = 1000.
353  IF (SMALL-BEG) 351,352,352
351  BEG = BEG / 10.
    GO TO 353

C
C  MAKES Y DATA GREATER THAN 1  -- TAKES LOGS
C
352  GCOF = 1./BEG
    SMALL = SMALL * GCOF
    TBIG = TBIG * GCOF
    DO 350 JK = 2,NNSAM
350  Y(JK) = ALCG10(Y(JK)*GCOF)
    PRINT 305, (Y(JK),JK=2,NNSAM)
305  FORMAT (10F10.5)
C
C  CALCULATES LEAST SQUARES
C
299  IF (LEAST) 27,26,27
27  XY = 0.
    YY = 0.
    XX = 0.
    YS = 0.
    XS = 0.
    MMSAM = NNSAM - 1
    LEAST = 99
    DO 28 JK = 2,NNSAM
    XY = XY + X(JK)*Y(JK)
    YY = YY + Y(JK)*Y(JK)
    XX = XX + X(JK)*X(JK)
    YS = YS + Y(JK)
    XS = XS + X(JK)
28  A = (MMSAM*XY-XS*YS)/(MMSAM*XX-XS*XS)
    B = (YS-A*XS)/MMSAM
    PRINT 29,A,B
29  FORMAT (///' COEFF OF X = 'F12.5,/' CONSTANT = '
1 F12.5)
    KOUNT = KOUNT + 1
    YBAR = YS/MMSAM
    SUM = 0.
    DO 60 JK = 2,NNSAM
60  SUM = SUM + (Y(JK)-YBAR)**2
    SIGMA = SQRT(SUM/MMSAM)
    KODE = 69
    SYX = SQRT((YY-B*YS-A*XY)/MMSAM)
    RYX = SQRT(1.-(SYX**2/SIGMA**2))
    PRINT 65, YBAR,SIGMA,SYX
65  FORMAT (///' AVERAGE CF Y VALUES 'F10.4,/' STANDAR'

```

```

1, 'D DEVIATION OF Y VALUES 'F10.4,/'STANDARD DEVI'
2, 'ATION OF REGRESSION LINE ' F10.4)
  PRINT 66,RYX
66  FORMAT (///' COEFFICIENT OF CORRELATION R IS '
1 F10.4//)
  IF (RYX-.500)76,76,77
76  PRINT 78
78  FORMAT (///' CORRELATION COEFFICIENT IS RIDICULOUS'
1, 'LY LOW AND NO DATA POINTS WILL BE REJECTED')
  IF (RYX-0.10) 79,79,67
79  PRINT 81
81  FORMAT (///' *****YOUR DATA IS OF SUCH LOW '
1, 'QUALITY THAT IT HAS BEEN GARNISHEED *****')
  GO TO 67
77  CONTINUE
  DO 61 JK = 2,NNSAM
  DUM(JK) = X(JK)*A + B
C
C  MULTIPLYER OF SYX GIVES NUMBER OF SIGMA FOR BAD
C  POINT REMOVAL (2.56 = 99 PERCENT ASSURDNESS)
C
  IF (ABS(DUM(JK)-Y(JK))-VAR*SYX) 61,61,62
62  PRINT 63,X(JK),Y(JK)
63  FORMAT (' DATA POINT IN ERROR'2F7.3)
  X(JK) = 0.
  Y(JK) = 0.
  KODE = -69
61  CONTINUE
  IF (KODE) 69,69,67
69  IF (KOUNT-10) 64,67,67
C
C  REMOVES BAD DATA POINTS
C
64  K = 1
  DO 80 I = 2,NNSAM
  IF (Y(I)) 80,80,82
82  K = K + 1
  Y(K) = Y(I)
  X(K) = X(I)
  YER(K) = YER(I)
  XER(K) = XER(I)
80  CONTINUE
  NNSAM = K
  GO TO 27
67  IF (CALC) 90,90,91
C
C  SETS BEGINNING AND END POINTS OF REGRESSION LINE
C
90  D = B
  E = 0.
  IF (B) 31,30,30

```

```

31      C = -B/A
      E = C
      D = 0.
      IF (C) 32,30,30
32      PRINT 33
33      FORMAT (' ERROR IN EQUATION ')
      LEAST = 0
      GO TO 26
30      BIG = 0.
      DO 35 JK = 2,NNSAM
      IF (X(JK)-BIG) 35,35,36
36      BIG = X(JK)
35      CONTINUE
      Y(NNSAM+2) = BIG*A + B
      X(NNSAM+2) = BIG
      Y(NNSAM+1) = D
      X(NNSAM+1) = E
      NNSAM = NNSAM + 2
26      JK = NNSAM-3
      PRINT 15,JK
15      FORMAT (' NUMBER OF DATA POINTS = 'I3)
C
C      SCALES DATA TO INCHES
C
      IF (THESI) 211,211,212
212     CALL THESIS
      GO TO 91
211     IF (IFLOG) 213,213,306
306     CALL SLOG(TBIG,SMALL,GOOF)
      GO TO 91
213     IF (LLOG) 520,520,521
521     CALL LOGLOG (TBIG,SMALL,GOOF,BIGX,SMALLX,GOOFX)
      GO TO 91
520     CALL SCALE (X,12.,NNSAM,XMIN,DX,1,10.)
      CALL SCALE (Y,9.0,NNSAM,YMIN,DY,1,10.)
C
C      DRAWS AXIS
C
      CALL AXIS (0.0,0.0,VABS,-8,12.,0.0,XMIN,DX,10.)
      CALL AXIS (0.,0.,VORD,8,9.,90.,YMIN,DY,10.)
      CALL PLOT (0.0,9.0,3)
      DO 84 JK = 1,12
      V = JK
      CALL PLOT (V,9.0,2)
      CALL PLOT (V,8.8,2)
      CALL PLOT (V,9.0,2)
84     CONTINUE
      V = 8.
      DO 83 JK = 1,9
      CALL PLOT (12.0,V,2)
      CALL PLOT (11.8,V,2)

```

```

      CALL PLOT (12.0,V,2)
      V = V - 1.
83    CONTINUE
      C
      C    PLOTS CONCENTRATION SYMBOLS
      C
      IF (LL-NNEL) 40,40,41
40    CONTINUE
      IF (ITEM(LL)-40) 21,19,21
19    ANG = 180.
      GO TO 20
21    ANG = 0.
20    CALL SYMBOL (7.0,-.4,.14,ITEM(LL),ANG,-1)
      CALL SYMBCL (7.3,-.4,.14,SIGN,0.0,4)
41    IF (MM-NNEL) 42,42,43
42    CONTINUE
      IF (ITEM(MM)-40) 25,23,25
23    ANG = 180.
      GO TO 24
25    ANG = 0.
24    CALL SYMBOL (-.4,5.,.14,ITEM(MM),ANG+90.,-1)
      CALL SYMBOL (-.4,5.3,.14,SIGN,90.0,4)
43    CONTINUE
      C
      C    PLOTS DATA POINTS
      C
      IF (IFER-99) 109,108,109
109   CALL LINE(X(2),Y(2),MMSAM,1,-1,3,XMIN,YMIN,DX,DY)
      GO TO 110
108   KK = 1+ MMSAM
      DO 88 JK = 2, KK
      Y(JK) = (Y(JK)-YMIN)/DY
      YER(JK) = ((YER(JK)-YMIN)/DY)/2.
      XER(JK) = ((XER(JK)-XMIN)/DX)/2.
88    X(JK) = (X(JK)-XMIN)/DX
      DO 89 JK = 2, KK
      CALL PLOT (X(JK),Y(JK)+YER(JK),3)
      CALL PLOT (X(JK),Y(JK)-YER(JK),2)
      CALL PLOT (X(JK)-XER(JK),Y(JK),3)
      CALL PLOT (X(JK)+XER(JK),Y(JK),2)
89    CONTINUE
      C
      C    DRAWS REGRESSION LINE IF DESIRED
      C
      IF (LEAST) 37,37,39
39    CALL LINE (X(NNSAM-1),Y(NNSAM-1),2,1,0,3,XMIN,
1 YMIN,DX,DY)
      C
      C    MOVES PEN AND ZERO POINT PAST PLOT READY FOR NEXT
      C
37    CALL PLOT (15.,0.,-3)

```

```

91      S = S + 2
      GC TO 7
C
C      TESTS IF LAST BATCH OF DAT FINISHED
C
100     N = N + 1
      IF (N-IHCW) 102,102,111
C
C      SIGNALS END TO PLOTTER TAPE
C
111     CALL PLOT (0.,0.,999)
      CALL EXIT
      END
C
C
C
C
C
C      PLOTS CONCENTRATION OF ANY ELEMENT OR RATIO OF
C      ELEMENTS VS. TIME
C
      SUBROUTINE TIME
      REAL*8 SAME(20)
      INTEGER WHICH(20),S
      DIMENSION X(100),Y(100)
      DIMENSION DATA(20,100)
      COMMON DATA,NEL,NSAM,SAME
      S = 1
C
C      SETS UP X (TIME) ARRAY
C
      X(1) = .25
      DO 3 JK = 2,100
3        X(JK) = X(JK-1) + .25
C
C      READS WHICH DATA IS TO BE PLOTTED VERSUS TIME
C      UP TO 20 ALLOWED
C
      READ (5,1) WHICH
1        FORMAT (20I2)
14       IF (WHICH(S)) 9,20,9
9        LL = WHICH(S)
      PRINT 17,LL
17       FORMAT (I5)
C
C      PUTS NEST DATA INTO Y ARRAY
C
      DO 2 JK = 1,NSAM
2        Y(JK) = DATA(LL,JK)
C
C      FIGURES SCALE FOR Y

```

```

C      CALL SCALE(Y,9.0,NSAM,YMIN,DY,1,10.)
      PRINT 16,YMIN,DY
16     FCRMAT (2F10.4)
C
C      CHANGES DATA TO INCHES
C
      DO 18 JK = 1,NSAM
18     Y(JK) = (Y(JK)-YMIN)/DY
      PRINT 19,(Y(JK),JK=1,NSAM)
19     FCRMAT (10F10.4)
C
C      DRAWS AXIS
C
      CALL AXIS (0.,0.,SAME(LL),8,9.,90.,YMIN,DY,10.)
      CALL PLOT (0.,0.,3)
      KK = NSAM + 5
      DO 4 JK = 1,KK
      CALL PLOT (X(JK),0.,2)
      CALL PLOT (X(JK),-.1,2)
4     CALL PLOT (X(JK),0.,2)
C
C      PUTS NUMBERS ON X AXIS
C
      T = 0.
      TT = 0.
      KK = KK/5 + 1
      DO 5 JK = 1,KK
      CALL NUMBER (1,-.25,.14,TT,0.,-1)
      T = T + 1.25
5     TT = TT + 5.
C
C      PLOTS DATA
C
      CALL PLOT (0.,0.,3)
      KCDE = 69
      JK = 1
7     IF (Y(JK)) 6,6,8
6     JK = JK + 1
      KCDE = 69
      IF (JK-NSAM) 7,7,13
8     IF (KCDE) 11,11,10
10    CALL SYMBCL (X(JK),Y(JK),.14,5,0.,-1)
12    KCDE = -69
      JK = JK + 1
      IF (JK-NSAM) 7,7,13
11    CALL SYMBCL (X(JK),Y(JK),.14,5,0.,-2)
      GO TO 12
C
C      FINISHED THIS PLOT - FIX PLOTTER FOR NEXT
C

```

```

13      S = S + 1
        CALL PLOT (.25*NSAM+3.,0.,-3)
        GO TO 14
20      RETURN
        END

C
C
C
C

        SUBROUTINE THESIS
        REAL*8 SAME(20)
        DIMENSION DATA(20,100),X(100),Y(100)
        COMMON DATA,NEL,NSAM,SAME,X,Y,MMSAM,NNSAM,LEAST
        CALL PLOT (0,2.,-3)

C
C      SCALES DATA - CALCULATES MINIMUM VALUE AND
C      UNITS OF DATA PER INCH
C

        YMIN = 0.
        XMIN = 0.
        MM = 1
        BIG = 0.
        DO 7 JK = 2,NNSAM
          IF (BIG-X(JK))8,7,7
8          BIG = X(JK)
7          CONTINUE
          BIG = BIG/7.0
          PRINT 22,BIG
20         FACT = 1.
15         IF (BIG-1.)10,9,9
9          IF (BIG-10.)11,16,16
10         FACT = FACT * 10.
          BIG = BIG * 10.
          GO TO 15
16         FACT = FACT * .1
          BIG = BIG / 10.
          GO TO 15
11         I = BIG
          S = BIG - I
          PRINT 22,BIG,S
          IF (S-.5) 12,13,13
12         T = I + .5
          GO TO 14
13         T = I + 1.
14         T = T / FACT
          IF (MM-1) 17,17,21
17         DX = T
          BX = T * FACT
          PRINT 22,BIG,DX
          BIG = 0.
          DO 18 JK = 2,NNSAM

```

```

      IF (BIG-Y(JK))19,18,18
19    BIG = Y(JK)
18    CONTINUE
      BIG = BIG / 5.
      PRINT 22,BIG
      MM = 2
      GO TO 20
21    DY = T
      BY = T * FACT
      PRINT 22,DX,DY
22    FORMAT (2F12.4)
C
C    DRAWS AXIS
C
      V = .5
      DO 1 JK = 1,10
      CALL PLOT (0.,V,2)
      CALL PLOT (.2,V,2)
      CALL PLOT (.0,V,2)
1    V = V + .5
      V = .5
      DO 2 JK = 1,14
      CALL PLOT (V,5.0,2)
      CALL PLOT (V,4.8,2)
      CALL PLOT (V,5.0,2)
2    V = V + .5
      V = 4.5
      DO 3 JK = 1,10
      CALL PLOT (7.0,V,2)
      CALL PLOT (6.8,V,2)
      CALL PLOT (7.0,V,2)
3    V = V - .5
      V = 6.5
      DO 4 JK = 1,14
      CALL PLOT (V,0.,2)
      CALL PLOT (V,.2,2)
      CALL PLOT (V,0.,2)
4    V = V - .5
C
C    NUMBERS AXIS
C
      BY = BY/1.0
      R = 0.
      YY = 0.
      DO 30 JK = 1,6
      CALL NUMBER (-.3,YY,.07,R,0.,2)
      R = R + BY
30    YY = YY + 1.
      BX = BX/1.0
      R = 0.
      XX = 0.

```

```

      DC 31 JK = 1,7
      CALL NUMBER (XX,-.1,.07,R,0.0,2)
      R = R + BX
31    XX = XX + 1.
      C
      C
      C    PLOTS DATA
      C
      C    CALL LINE(X(2),Y(2),MMSAM,1,-1,3,XMIN,YMIN,DX,DY)
      C
      C    PLOTS REGRESSION LINE
      C
      C    IF (LEAST)5,5,6
6      CALL LINE (X(NNSAM-1),Y(NNSAM-1),2,1,0,3,XMIN,
1 YMIN,DX,DY)
      C
      C    RETURNS PEN FOR NEXT PLOT
      C
      C
5      CALL PLOT (10.,-2.,-3)
      RETURN
      END
      C
      C
      C
      C
      C    SUBROUTINE SLCG(BIG,SMALL,GCOF)
      REAL*8 VABS,VORD,SAME(20)
      DIMENSION DATA(20,100),X(100),Y(100)
      COMMON DATA,NEL,NSAM,SAME,X,Y,MMSAM,NNSAM,LEAST
      COMMON A,VABS,VORD,B
      C
      C    SETS UP SCALE OF Y AXIS DATA
      C
      END = 1
      BEG = 1000
7      IF (SMALL-BEG) 6,5,5
6      BEG = BEG / 10.
      GO TO 7
5      IF (BIG-END) 8,9,9
9      END = END * 10.
      GO TO 5
8      YMIN = ALOG10(BEG)
      DY = (ALOG10(END)-ALOG10(BEG))/9.
      NN = ALOG10(END) - ALCG10(BEG)
      C
      C    SCALES X AXIS DATA
      C
      CALL SCALE (X,12.,NNSAM,XMIN,DX,1,10.)
      C
      C    DRAWS Y AXIS
      C
      CALL PLOT (0.0,0.0,3)

```

```

RX = 0.
T = .2
13 DO 10 JK = 1,NN
   KK = JK - 1
   FACT = (10**KK)* BEG
   R = (ALOG10(FACT)-YMIN)/DY
   CALL PLOT (RX,R,2)
   CALL PLOT (RX+2.*T,R,2)
   CALL PLOT (RX,R,2)
   DO 11 MM = 2,9
   RS = MM
   R = (ALOG10(RS*FACT)-YMIN)/DY
   CALL PLOT (RX,R,2)
   CALL PLOT (RX+T,R,2)
11 CALL PLOT (RX,R,2)
10 CONTINUE
   R = (ALOG10(10.*FACT)-YMIN)/DY
   CALL PLOT (RX,R,2)
   IF (RX)14,12,14
12 RX = 12.
   T = -.2
   CALL PLOT (12.,0.,3)
   GO TO 13

C
C   DRAWS X AXIS
C
14 CALL AXIS (0.,0.,VABS,-8,12.,0.,XMIN,DX,10.)
   CALL PLOT (0.,9.,3)
   DO 15 JK = 1,12
   V = JK
   CALL PLOT (V,9.0,2)
   CALL PLOT (V,8.8,2)
15 CALL PLOT (V,9.0,2)
C
C   LABELS Y AXIS
C
   CALL SYMBGL (-.5,2.,.28,VORD,90.,8)
C
C   WRITES NUMBERS ON LOG AXIS
C
   DO 16 JK = 1,NN
   KK = JK - 1
   FACT = (10**KK)* BEG
   R = (ALOG10(FACT)-YMIN)/DY
   SNUM = FACT/GCOF
   IF (SNUM-1)17,18,18
17 ND = 2
   GO TO 19
18 ND = -1
19 CALL NUMBER (-.4,R,.07,SNUM,0.,ND)
   DO 20 MM = 2,5

```

```

      RS = MM
      SNUM = (RS*FACT)/GOOF
      R = (ALOG10(RS*FACT)-YMIN)/DY
20  CALL NUMBER (-.4,R,.07,SNUM,0.,ND)
16  CONTINUE
      SNUM = (10.*FACT)/GOOF
      R = (ALOG10(10.*FACT)-YMIN)/DY
      CALL NUMBER (-.4,R,.07,SNUM,0.,ND)

C
C   PLOTS DATA
C
      CALL LINE (X(2),Y(2),MMSAM,1,-1,3,XMIN,YMIN,DX,
1  DY)

C
C   DRAWS REGRESSION LINE
      IF (LEAST) 21,21,22
22  CONTINUE
      I = NNSAM-1
      IF (Y(I)-9.*DY) 30,30,31
31  Y(I) = 9.*DY
      X(I) = (Y(I)-B)/A
30  CALL LINE (X(I),Y(I),2,1,0,3,XMIN,YMIN,DX,DY)
21  CALL PLOT (15.,0.,-3)
      RETURN
      END

C
C
C
C
      SUBROUTINE LOGLOG(BIG,SMALL,GOOF,BIBX,SMALLX,
1  GOOFX)
      REAL*8 VABS,VORD,SAME(20)
      DIMENSION DATA(20,100),X(100),Y(100)
      COMMON DATA,NEL,NSAM,SAME,X,Y,MMSAM,NNSAM,LEAST
      COMMON A,VABS,VORD,B

C
C   SETS UP SCALE OF Y AXIS DATA
C
      END = 1
      BEG = 1000
      IF (SMALL-BEG) 6,5,5
7   BEG = BEG / 10.
6   GO TO 7
      IF (BIG-END) 8,9,9
9   END = END * 10.
      GO TO 5
8   YMIN = ALOG10(BEG)
      DY = (ALOG10(END)-ALOG10(BEG))/9.
      NN = ALOG10(END) - ALOG10(BEG)

C
C   DRAWS Y AXIS

```

```

C      CALL PLOT (0.0,-10.,-3)
      CALL PLOT (0.0,1.,-3)
      RX = 0.
      T = .2
13     DO 10 JK = 1,NN
      KK = JK - 1
      FACT = (10**KK)* BEG
      R = (ALOG10(FACT)-YMIN)/DY
      CALL PLOT (RX,R,2)
      CALL PLOT (RX+2.*T,R,2)
      CALL PLOT (RX,R,2)
      DO 11 MM = 2,9
      RS = MM
      R = (ALOG10(RS*FACT)-YMIN)/DY
      CALL PLOT (RX,R,2)
      CALL PLOT (RX+T,R,2)
11     CALL PLOT (RX,R,2)
10     CONTINUE
      R = (ALOG10(10.*FACT)-YMIN)/DY
      CALL PLOT (RX,R,2)
      IF (RX)14,12,14
12     RX = 12.
      T = -.2
      CALL PLOT (12.,0.,3)
      GO TO 13

C
C      LABELS Y AXIS
C
14     CALL SYMBOL (-.5,3.,.28,VORD,90.,8)
C
C      SETS UP SCALE OF X AXIS DATA
C
      END = 1
      BEGX = 1000
47     IF (SMALLX-BEGX) 46,45,45
46     BEGX = BEGX / 10.
      GO TO 47
45     IF (BIGX-END)48,49,49
49     END = END * 10.
      GO TO 45
48     XMIN = ALOG10(BEGX)
      DX = (ALOG10(END)-ALOG10(BEGX))/12.
      NNX = ALOG10(END) - ALOG10(BEGX)
      CALL PLOT(0.0,9.0,3)
      RX = 9.

C
C      DRAWS X AXIS
C
53     DO 50 JK = 1,NNX
      KK = JK - 1

```

```

FACT = (10**KK) * BEGX
R = (ALOG10(FACT)-XMIN)/DX
CALL PLOT (R,RX,2)
CALL PLOT (R,RX+T*2.,2)
CALL PLOT (R,RX,2)
DO 51 MM = 2,9
RS = MM
R = (ALOG10(RS*FACT)-XMIN)/DX
CALL PLOT (R,RX,2)
CALL PLOT (R,RX+T,2)
51 CALL PLOT (R,RX,2)
50 CONTINUE
R = (ALOG10(10.*FACT)-XMIN)/DX
CALL PLOT (R,RX,2)
IF (RX) 52,54,52
52 RX = 0.
T = .2
CALL PLOT (0.0,0.0,3)
GO TO 53

C
C   NUMBERS Y AXIS
C
54 DO 16 JK = 1,NN
KK = JK - 1
FACT = (10**KK)* BEG
R = (ALOG10(FACT)-YMIN)/DY
SNUM = FACT/GOOF
IF (SNUM-1)17,18,18
17 ND = 2
GO TO 19
18 ND = -1
19 CALL NUMBER (-.4,R,.07,SNUM,0.,ND)
DO 20 MM = 2,5
RS = MM
SNUM =(RS*FACT)/GOOF
R = (ALOG10(RS*FACT)-YMIN)/DY
20 CALL NUMBER (-.4,R,.07,SNUM,0.,ND)
16 CONTINUE
SNUM = (10.*FACT)/GOOF
R = (ALOG10(10.*FACT)-YMIN)/DY
CALL NUMBER (-.4,R,.07,SNUM,0.,ND)

C
C   NUMBERS X AXIS
C
DO 56 JK = 1,NNX
KK = JK - 1
FACT = (10**KK) * BEGX
R = (ALOG10(FACT)-XMIN)/DX
SNUM = FACT/GOOFX
IF (SNUM-1) 57,58,58
57 ND = 2

```

```

GC TO 59
58 ND = -1
59 CALL NUMBER (R,-.3,.07,SNUM,90.,ND)
DC 60 MM = 2,5
RS = MM
SNUM = (RS*FACT)/GOCFX
R = (ALOG10(RS*FACT)-XMIN)/DX
60 CALL NUMBER (R,-.3,.07,SNUM,90.,ND)
56 CONTINUE
SNUM = (10.*FACT)/GOCFX
R = (ALOG10(10.*FACT)-XMIN)/DX
CALL NUMBER (R,-.3,.07,SNUM,90.,ND)

C
C LABELS X AXIS
C
CALL SYMBCL (4.,-.7,.21,VABS,0.,8)

C
C PLOTS DATA
C
CALL LINE (X(2),Y(2),MMSAM,1,-1,3,XMIN,YMIN,DX,
1 DY)

C
C DRAWS REGRESSION LINE
IF (LEAST) 21,21,22
22 I = NNSAM - 1
IF (Y(I)-9.*DY) 30,30,31
31 Y(I) = 9.*DY
X(I) = (Y(I)-B)/A
30 CALL LINE (X(I),Y(I),2,1,0,3,XMIN,YMIN,DX,DY)

C
C RETURNS PEN FOR NEXT PLOT
C
21 CALL PLOT (15.,0.,-3)
RETURN
END

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