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FLUX AND PROCESSES OF DEPOSITION OF
ATMOSPHERIC SEA SALT TO THE EARTH SURFACE

BY

AZHARI F. M. AHMED

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE
IN
OCEANOGRAPHY

UNIVERSITY OF RHODE ISLAND

1978

ABSTRACT

Dry deposition of SO_2 and H_2SO_4 was measured at a coastal Rhode Island site, and sulfur isotope ratios of the sulfate were analyzed. The sulfate was analyzed for $\delta^{34}\text{S}$ and $\delta^{33}\text{S}$ in order to determine the rate and mechanism of deposition of atmospheric SO_2 . Sulfur isotope ratios of sulfate were analyzed for $\delta^{34}\text{S}$ and $\delta^{33}\text{S}$ in order to determine the rate and mechanism of deposition of atmospheric SO_2 . The sulfate was analyzed for $\delta^{34}\text{S}$ and $\delta^{33}\text{S}$ in order to determine the rate and mechanism of deposition of atmospheric SO_2 . The sulfate was analyzed for $\delta^{34}\text{S}$ and $\delta^{33}\text{S}$ in order to determine the rate and mechanism of deposition of atmospheric SO_2 .

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1978

ABSTRACT

Dry deposition, rainfall and atmospheric particulate samples collected at a coastal Rhode Island site, and aboard RV/Trident over the North West Atlantic Ocean were analysed for Na and Mg in order to understand the rate and mechanisms of removal of atmospheric sea salt. Perkin Elmer atomic absorption spectrophotometer models 303 and 360 were used for the analyses. Samples collected at the R.I. coastal site were divided into 3 different categories, namely, "marine", "land" and "mixed" samples depending on the local surface wind direction during sampling. Based upon the Mg/Na ratio, it appears that most of the Na and Mg in "marine" samples were derived from the ocean while "land" samples essentially consist of Na and Mg of crustal origin and "mixed" samples were a combination of the two.

The rate of wet removal of atmospheric Na and Mg, calculated from "marine" and "land" samples and the rate of dry deposition of sea salt calculated only from "marine" samples, appear to be proportional to the wind speed. Consideration of the Mg/Na ratios in rainfall and dry fallout samples observed from the "marine", "mixed" and "land" samples categories, suggest that rainfall scavenges sea salt Na and Mg more efficiently than crustal particles.

The annual global removal rate of atmospheric sea salt was estimated at $\sim 3.0 \times 10^{15}$ g/yr. 60% of this is removed by rainfall and the rest by dry deposition. Of the total cyclic sea salt removed annually over the globe, less than 7% is deposited over land. 90% of this is removed by rainfall and the rest by dry deposition.

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TABLE OF CONTENTS

	Page
ABSTRACT	iii
ACKNOWLEDGEMENT	iv
LIST OF TABLES	ix
LIST OF FIGURES	xi
CHAPTER I. INTRODUCTION	1
A. Removal Mechanisms of Atmospheric Sea Salt	1
B. Review of the History of Sea Salt in Rainwater ...	3
C. Mechanisms of Production of Atmospheric Sea Salt. Particles	7
D. Geochemical Cycle of Atmospheric Sea Salt	8
E. Research Objectives	11
CHAPTER II. EXPERIMENTAL METHODS	13
A. Sampling Procedures	13
1. General Considerations	13
2. The Automatic Rain-Dry Fallout Collector	14
3. Sample Handling	16
4. Testing Programs for the Sampling System	16
a. Determination of rainfall collection efficiency of 42x29x25 cm and 11x10x4 cm plastic containers	17
b. Collection efficiency of various sur- faces for dry fallout and total fallout samples	17
c. Dissolution of Na and Mg in the dry fallout samples from the bottom and sides of the plastic buckets	21

	Page
d. Efficiency of the automatic rain dry fallout collector for total deposition....	24
B. Analytical Procedures.....	27
1. Extraction of Na and Mg from Whatman 41 Filter.....	27
a. Extraction of known amounts of Na and Mg from Whatman 41 filter.....	27
b. Ultrasonic extraction versus high tem- perature ashing.....	27
c. Extraction of particulate Na and Mg from Whatman 41 filter samples using 0.1N HNO ₃ and distilled deionized water.,..	29
d. Efficiency of recovery of one extraction for particulate Na and Mg.....	36
2. Sample Analysis.....	38
a. Atomic absorption.....	38
b. Sampling and analytical precision.....	41
CHAPTER III. RESULTS.....	42
A. General Consideration.....	42
B. Classification of Samples.....	42
1. Atmospheric Concentrations and Dry Deposition..	42
a. Coastal Rhode Island.....	42
i. "Marine", "mixed" and "land" samples.....	42
ii. "Corrected-to-Marine" samples.....	47
b. Samples collected aboard RV/Trident.....	53

c. Deposition velocity for particulate

Na and Mg..... 53

2. Rainfall Samples 60

CHAPTER IV. DISCUSSION 64

A. The Rate and Processes of Removal of Atmospheric
Sea Salt..... 64

1. Dry Removal of Atmospheric Sea Salt..... 64

a. The rate of dry fallout and atmospheric
concentrations of Na and Mg for samples
collected in the "Marine", "mixed"
and "land" subenvironments of R.I.
environment..... 64b. "Mixed" samples collected within the
"010-090" wind sector 73

c. Samples collected aboard RV/Trident..... 76

d. The Mg/Na ratios..... 76

e. Deposition velocities for particulate
Na and Mg..... 78

2. Wet Removal of Atmospheric Sea Salt..... 78

a. Rainfall collected from different
wind sectors..... 78b. Selective removal of sea salt aerosol
by rainfall..... 83

B. Geochemistry of Atmospheric Sea Salt..... 84

1. Significance of Wet Removal (rain) of
sea salt Relative to Dry Deposition in
the Coastal Environment of Rhode Island..... 84

2. Sea Salt Yearly Removal Over the World Oceans...	84
3. Significance of Atmospheric Removal of Sea Salt Over the Coast of Rhode Island.....	85
4. Atmospheric Removal of Na and Mg Over Land.....	87
CHAPTER V. CONCLUSIONS	89
REFERENCES.....	91

LIST OF TABLES

Table	Page
1. Collection efficiency of rainfall by 42x29x25 cm and 11x10x4 cm plastic buckets.....	18
2. Surface collection efficiency for dry fallout and total fallout samples.....	20
3a. Dissolution of Na and Mg in the dry fallout samples from the bottom and sides of the plastic buckets.....	22
3b. Proportions of Na and Mg in the dry fallout collected on the bottom and sides of the plastic buckets.....	23
4. Efficiency of the automatic rain-dry fallout collector for total deposition.....	26
5. Extraction of known amounts of Na and Mg from a Whatman 41 filter using 0.1N HNO ₃ acid and an ultra-sonic cleaner.....	28
6. Extraction of Na and Mg from Whatman 41 filters using high temperature ashing and extraction with 0.1N HNO ₃ in an ultrasonic bath.....	30
7. Extraction of particulate Na and Mg from a Whatman 41 filter blank using 0.1N HNO ₃ and D.D. H ₂ O and an ultrasonic bath.....	32
8. Extraction of particulate Na and Mg from atmospheric particulate sample No. 14.....	34
9. Extraction of particulate Na and Mg from atmospheric particulate sample No. 15.....	35
10. Efficiency of extraction of atmospheric Na and Mg from Whatman 41 filter using ultrasonic cleaner and D.D. H ₂ O.....	37

	Page
11. Sample collection information.....	43
12. Rate of dry fallout and atmospheric concentration of Na and Mg for "marine" samples.....	48
13. Rate of dry fallout and atmospheric concentration of Na and Mg for "land" samples.....	49
14. Rate of dry fallout and atmospheric concentration of Na and Mg for "mixed" samples.....	50
15. "Corrected-to-marine" rate of dry fallout and atmos- pheric concentrations of Na and Mg for "mixed" samples....	54
16. "Marine" samples and "Corrected-to-marine" samples correlation with wind speed	55
17. Rate of dry fallout and atmospheric concentrations of Na and Mg. Wind direction 010-090°.....	56
18. Atmospheric flux of Na and Mg to the North Atlantic Ocean (R/V Trident samples).....	57
19. Deposition velocities for atmospheric Na and Mg.....	58
20. Na and Mg in "marine" rain samples.....	61
21. Na and Mg in "mixed" rain samples.....	62
22. Na and Mg in "land" rain samples.....	63
23. Summary table for rain and dry fallout samples collected in coastal Rhode Island.....	65
24. Geochemistry of cyclic sea salt.....	86

LIST OF FIGURES

Page

Figure 1.	Effects of varying wind force upon number and weight of large sea-salt particles near cloud base over sea in Hawaii area.....	9
Figure 2.	The automatic rain-dry fallout collector. Only the dry fallout half is shown (The rain half is identical).....	15
Figure 3.	A typical calibration curve of Na concentration versus absorbance, with burner head rotated at 90°.....	39
Figure 4.	A typical calibration curve of Mg concentration versus absorbance, with burner head rotated at 45°.....	40
Figure 5.	Coastal Rhode Island sampling site.....	46
Figure 6.	R/V Trident cruise #169, sampling stations.....	59
Figure 7.	Atmospheric Na and Mg concentration vs. wind speed ("marine" samples).....	67
Figure 8.	Na and Mg rate of dry fallout vs. wind speed ("marine" samples).....	68
Figure 9.	Na and Mg rate of dry fallout vs. wind speed ("land" samples).....	70
Figure 10.	Atmospheric Na and Mg concentration vs. wind speed ("marine" and "corrected-to-marine" samples).....	74
Figure 11.	Na and Mg rate of dry fallout vs. wind speed ("marine", "corrected-to-marine" and Trident samples).....	75

Figure 12. Na and Mg concentration in rain water vs. wind speed ("marine" rain).....	80
Figure 13. Na concentration in rainwater vs rain depth.	81
Figure 14. Mg concentration in rainwater vs. rain depth.....	82

I. INTRODUCTION

It appears that a Hungarian geologist named Posephny was the first person to visualize the geochemical implication of sea salt transport between the ocean, the atmosphere, and land in 1877 (Eriksson 1959). Posephny used geological evidence to conclude that chloride in river water and saline deposits must have originated in the sea and been carried inland by the atmosphere. Posephny's observation went largely without notice until 1959 when Erik Eriksson, in Sweden, made the first quantitative estimations for the removal of atmospheric sea salt by rainfall and dry deposition over the ocean and land. This will be discussed in full detail later.

A. Removal Mechanisms of Atmospheric Sea Salt

Junge (1963) classified the removal mechanisms for atmospheric aerosols as wet removal by precipitation, dry removal by sedimentation, and dry removal by impaction on obstacles on the earth surface. The third mechanism can be important in land covered with forests (Junge 1963; Madgwick and Ovington, 1959; Georgii 1962).

Wet removal comprises two distinct processes 1) rainout, which is the removal due to processes within the clouds, and 2) washout, which is the process of removal by rainfall below the clouds. During the journey of the raindrops from the cloud base downwards, in addition to the washout processes, evaporation of the raindrops also occurs. The net effect of these three processes, namely rainout, washout and evaporation, determine the concentration of any substance in rain water.

During the rainout process, atmospheric aerosols enter the cloud droplets in the following ways:

- 1) Consumption of condensation nuclei,
- 2) The attachment of aerosol particles to the cloud elements by Brownian motion,
- 3) The attachment of aerosol particles by the water vapour gradient (Fagy-effect). For atmospheric sea salt and other aerosol particles of radii $>0.1 \mu\text{m}$, the consumption of condensation nuclei is considered the primary mechanism of rainout. The other two mechanisms, 2 and 3 are important for Aitken particles (radii $< 0.1 \mu\text{m}$), (Junge 1963).

Martens, et al. (1973), observed a chemical change during the transformation of aerosols to cloud droplets on the eastern end of the island of Puerto Rico. Comparison of elemental ratios in particles and rain and of the elemental particle size distribution in and out of the clouds showed an apparent efficiency of 100% for the marine particles (Na , I , Br , Cl^-) compared to less than 25% scavenging efficiency for the terrestrial fraction of the aerosol (Al , Mn , V).

When the rain drops leave the cloud base, they scavenge aerosol particles as they fall and they begin to evaporate. Both these processes lead to an increase in the rain water concentration of dissolved substances. Washout and evaporation are both inversely proportional to the radius of the rain drop (Junge, 1963).

$$K \propto \frac{1}{r_c} \quad (1)$$

where K is the concentration of any dissolved substance in rain water due to washout and evaporation and r_c is the rain drop radius.

Although the mass of sea salt collected by a rain drop falling through air containing sea salt depends upon the volume of air swept out by

the falling drop, i.e., proportional to the cross-sectional area of the falling drop or r_c^2 , the concentration of salt in the rain drop is inversely proportional to the volume of the rain drop or $1/r_c^3$. The net salinity change would be proportional to $1/r_c$. In addition small rain drops become more saline than larger ones due to evaporation. Again, although evaporation is proportional to the surface area of the drop or r_c^2 , the salinity is proportional to $1/r_c^3$ (Turner 1955; Duce, et al., 1969). Duce et al., 1969 measured the Na^+ and Cl^- content of rain as a function of rain intensity. Large raindrops were associated with higher rainfall intensity. They found that high intensity rains were associated with low concentrations of Na^+ and Cl^- while low intensity rain showers results in rains with higher amounts of Na^+ and Cl^- . The Na^+/Cl^- ratio, however, was found to be constant, independent of evaporation, washout or the intensity of rain.

B. Review of the History of Sea Salt in Rain Water

Although the history of research on chemical compounds in rain and snow date back to 1750 (Eriksson, 1959), for a long time ammonia and nitrate nitrogen were the only compounds of interest. The first determination of sea salt in rain water was made at the beginning of the nineteenth century, when several investigators around the world measured Cl^- in rain water collected at coastal and inland locations, (Eriksson, 1952). Although the geochemical significance of atmospheric transport of sea salt between the ocean and land was suggested by Posephny as early as 1877, little was done to evaluate the processes of production and removal of atmospheric sea salt until the middle of the 20th century. During this early period in the history of atmospheric sea salt chemistry, the majority of the studies done were concerned

with measuring chloride and/or other sea salt components in rain-water collected over specified periods of time. This was undertaken in several localities around the world, including inland and marine areas. Eriksson (1952) extensively reviewed the various studies during this period. Some of this pioneer work, as quoted from Eriksson's review (1952), merits mentioning. Two points, however, should be made before proceeding further. Firstly all these reported values of sea salt in rain and in snow include dry deposition as well, because it appears that the total deposition was measured, not rainfall alone. Secondly, most of these investigations were not done under meteorologically controlled or monitored conditions, and hence the results cannot be taken as strictly representative of marine or continental environments.

Although the first determination of chloride in rain water was made at the beginning of the nineteenth century, systematic work was not published until 1851 when Arago in Paris reported monthly amounts of Cl^- in rain water for a half year period. Another systematic investigation was carried out by Smith in 1872. He analysed rain water collected at different places in the British Isles. His reported values for the chloride content of rain water showed a considerable variation with a maximum of 54.6 mg/l on the west coast of England and a minimum of 1.20 mg/l in London. Smith, however, could not determine the cause of this considerable variation (Eriksson, 1952).

In Eriksson's review tables of the Cl^- content in mg/l of rain fall collected in Europe, America, Asia, Africa, New Zealand and Australia were presented. From these data, Eriksson found that the Cl^- content

of rain water is always higher in coastal areas compared to inland places. He also noticed that the concentrations of Cl^- in rain water do not vary much in inland places whereas coastal locations show a great variation. Remarkably, high concentrations have been observed at Mt. Vernon, Iowa in the United States, although it is located inland far from both the Atlantic and Pacific oceans, (Trieschmann, 1919; Knight, 1920; Shaffer, 1921; Fries, 1923; Woehlk, 1923; Knight, 1924; Kynett, 1929; Krehl et. al., 1935). At this location one of the longest series of analyses of Cl^- in rain was carried out, covering the period 1919-1935. As there is no other likely source for the Cl^- in the rain, it must be assumed that most of it originated from the ocean and was transported inland.

Extremely high amounts of salt falling with rain and snow were also reported in central Russia (see for example Krivopalova, 1971; Yushkevich, 1971; Kashtanov, 1968). They measured Na^+ , Mg^{++} , K^+ , Ca^{++} , Cl^- , SO_4^{--} , CO_3^{--} . Although it is possible that a fraction of these ions in the rain and snow originated in the sea and was carried inland by the atmosphere, it appears that most of them were crustal since the ionic ratios in these samples approached the crustal values. Zverev, et. al., (1973) determined the average chemical composition of atmospheric precipitation for 10 climatic zones of the USSR. He found that the mean concentrations for the USSR were:

Na = 3.14 mg/l

Mg = 0.70 "

Ca = 3.37 "

K = 0.645 "

Cl^- = 3.89 "

Contrary to the previous Russian data, these values suggest that much of the Na^+ and Cl^- in rainfall in USSR may be of oceanic origin, as the Na/Cl ratio of 0.81 approaches that of sea water, 0.55. This data, however does not give typical sea salt ratios for cations. It is likely that the deviations are due to the inclusion of crustal material containing these metals.

Francesco Palmieri (1966) studied the salt content of rainfall in Caserta, on the southern coast of Italy. He determined a total depth of rainfall of 63 cm/year. He calculated a yearly total deposition for Na of $347 \mu\text{g}/\text{cm}^2$; Mg, $61.9 \mu\text{g}/\text{cm}^2$; K, $121 \mu\text{g}/\text{cm}^2$, and Ca, $33.8 \mu\text{g}/\text{cm}^2$. Although his data gives a Mg/Na ratio of 0.18 compared with a sea salt ratio of 0.12, the K/Na and Ca/Na ratios are very high compared to their sea water ratios, which are: K/Na = 0.038, Ca/Na = 0.038 (Riley and Chester, 1971). Since Caserta is on the coast it seems that the deviations in the K/Na and Ca/Na ratios (as well as the Mg/Na ratio) are due to the addition of crustal K and Ca to the samples.

Zhavoronkina, (1958) in Russia observed that the salt content of rain increased in winter and decreased in summer in coastal areas. He explained the salt increase in winter as being due to winter storms over the ocean. Girenko, (1959) made a more detailed investigation of the effect of weather on the total mineral content of rain and snow. He concluded from his study of an annual cycle that the maximum mineral content in rain corresponds to the lowest amounts of precipitation, the largest period of drought between rainfall, and the most frequent strong winds during the corresponding month.

Mather (1960) reviewed and summarized results of chloride analyses in rain water from different places around the world. Based on Mather's

and Eriksson's reviews (1952) the following can be deduced.

1. The ocean is the major source of airborne salt. This is clearly shown by the higher salt content of rain in coastal areas compared to inland zones.

2. The concentration of sea salt in precipitation shows an annual and geographic variation.

3. The composition of salt in precipitation deviates from the characteristic sea water ratios as one goes inland.

C. Mechanisms of Production of Atmospheric Sea Salt Particles:

It is generally believed that sea salt particle with atmospheric residence time longer than a few minutes are produced by bubbles bursting at the sea surface. Blanchard and Woodcock (1957) investigated the various processes for bubble production at the sea surface. They found that breaking waves, or white caps are the most important mechanism for bubble formation. Sea salt particles are produced and injected in the atmosphere when these bubbles burst. (Boyce, 1951). Kientzler et al. (1954) showed that immediately after a bubble bursts on the ocean surface, it forms a bubble jet which ejects 2 to 5 droplets into the air. The diameter of the jet droplet is usually $\sim 10\%$ of the bubble diameter from which they form (Blanchard, 1963). Mason (1957) and Blanchard (1963) found that when the bubbles burst, other droplets were also formed due to the shattering of the bubble film cap. Little is known about the size and number distribution of these film drops.

In addition little is known about the size and number of bubbles in the open ocean under various wind speed conditions. Blanchard and Woodcock (1957) studied the distribution of bubbles between $75 \mu\text{m}$ and $750 \mu\text{m}$ diameter in waves breaking on a beach. Their experimental set up did not allow them to measure larger size bubbles.

Medwin (1970, 1977) used acoustic attenuation measurements to study bubbles size distribution and densities in coastal waters. He investigated bubbles of radius of 15-300 μm at depth of 3-36 meters. He found relationships between the bubble size or densities and the season, time of day, wind speed and presence or absence of sea slicks. He postulated that micro bubbles are entrained by aerosols as they fall into the ocean as well as produced by biological activity. Blanchard (1963) estimated that at any moment $\sim 3\%$ of the ocean surface is covered by white caps.

D. Geochemical cycle of Atmospheric Sea Salt

The size distribution of sea salt particles in the marine atmosphere was investigated by Woodcock and coworkers. Woodcock (1953) determined the size distribution of sea salt below the cloud base (500 m) over Hawaii and other marine and continental areas. He did this for several wind forces (Fig. 1). He found that the number and size of particles or airborne sea salt increase with increasing wind force and with decreasing altitude above the sea.

Using the size distribution of Woodcock (1953, Fig. 1), and assuming a mean wind speed of 12 knots, Eriksson (1959), utilized Stokes Law to calculate the flux of sea salt particles that would be expected to fall through the surface laminar boundary layer into the sea. In the steady state this output should be equal to the total rate of production of sea salt particles in the area of the whitecap, from the ocean surface. Eriksson calculated the rate of dry fallout over Hawaii, the Caribbean and Florida. He deduced an average dry deposition rate of $5.5 \times 10^{-12} \text{ gm cm}^{-2} \text{ sec}^{-1}$ of sea salt. The rate of removal over the entire ocean surface is then $5.4 \times 10^{14} \text{ g}$ per year. He used rain and river runoff Cl^- data

Figure 1. Effects of varying Beaufort wind force upon number and weight of large sea/salt particles near cloud base over sea in Hawaii area. After Woodcock (1953).

from Scandinavia. He found that the ratio of Cl^- concentration in rain water relative to Cl^- concentration in river runoff was 0.3. He concluded that over land dry deposition was twice as important as rain in transporting sea salt from the atmosphere to land. This led him to believe that over the ocean probably as much sea salt is removed by precipitation as by dry fallout. Thus he suggested the total amount of sea salt removed annually was approximately 10^{15} g. He estimated that 90% of this amount is deposited over the ocean while the rest is removed over land as the cyclic salt subsequently carried by rivers, streams, and groundwater.

In 1963 Blanchard made a similar calculation but arrived at a yearly removal of 10^{16} g/yr of sea salt. Blanchard's calculation seems to be more refined because he made more realistic estimates of the mean wind speed over various parts of the world's ocean, not relying on a global average speed of 12 Kts. From an assumed annual oceanic rainfall of 89 cm for the Hawaiian area, and an estimated salinity of 3.4 mg/l in the rain, he calculated the flux of sea salt by rain as 9.60×10^{-12} gm cm⁻² sec⁻¹. He compared this figure to the amount of sea salt fallout by sedimentation, which he computed as 5.1×10^{-12} gm cm⁻² sec⁻¹ at a wind speed of 12 Kts, the average wind speed in Hawaii.

The ratio of the two fluxes led Blanchard to conclude that rainfall is twice as important as dry deposition as a removal mechanism of atmospheric sea salt to the ocean surface. If one accepts Eriksson's figure of 10% of the total sea salt deposited on land, Blanchard's estimate of total sea salt production of 10^{16} gm/yr results in an estimated amount of cyclic sea salt deposited over land of $\sim 10^{15}$ g/yr. Livingstone (1963) calculated that the annual global input of cyclic sea salt from river runoff into the ocean is approximately 3×10^{14} g/yr, in between the estimates of Blanchard and Eriksson.

Cawse et. al. (1972, 1974) made a two year analytical study of trace elements in the atmospheric environment in the United Kingdom. They measured the concentration of 30 trace elements in airborne dust, rain water, and dry deposition at several localities. From these measurements they calculated a dry deposition velocity for each element. The deposition velocity, in cm/sec, was defined as the rate of dry deposition in $\mu\text{g cm}^{-2} \text{sec}^{-1}$ divided by the concentration in air in $\mu\text{g/cm}^3$. They calculated the ratio of dry deposition to total deposition for Na^+ and for Cl^- as 5%, i.e. rainfall was by far the major removal pathway.

Tsunogai (1975) investigated sea salt transport to land in Japan. He found that the share of dry sedimentation was only 20% of the total removal over the various parts of Japan. Most of this 20% was transported during discrete events such as Summer typhoons.

E. Research Objectives

It can be seen that rainfall and dry fallout are the two main routes by which atmospheric sea salt is transported back to the ocean and to the land. As mentioned earlier, the total amount of atmospheric sea salt particles produced by the ocean is apparently in the range of $10^{15} \text{ g/yr} - 10^{16} \text{ g/yr}$. The primary objectives of this present investigation are to:

1. Test the validity of the two estimates of annual production of atmospheric sea salt particle.
2. Investigate and determine by chemical analyses the rate of dry and wet removal (rain) of atmospheric sea salt (Na and Mg) from the marine and near shore Rhode Island atmosphere to the earth surface, and to establish empirically the relationship between the rate of dry

and wet removal (rain) and wind speed and direction on the Rhode Island coast.

3. Assess the role of dry fallout in comparison to wet removal (rain) of sea salt from the marine and coastal Rhode Island atmosphere.

4. Calculate atmospheric deposition velocities to the earth surface in the coastal Rhode Island environment for particulate Na and Mg.

Dry deposition velocity V_g has been defined (Chamberlain, 1960) as:

$$V_g \text{ (cm sec}^{-1}\text{)} = \frac{\text{rate of dry deposition } (\mu\text{g cm}^{-2} \text{ sec}^{-1})}{\text{concentration in air } (\mu\text{g cm}^{-3})}$$

EXPERIMENTAL METHODS

A. Sampling Procedures:

1. General Considerations:

Rainfall, dry fallout, total deposition and atmospheric particulate samples were collected at the Narragansett Bay campus of the University of Rhode Island in southern R.I. The roof of a mobile trailer, which was approximately 2.5 meters above the ground, was used as an atmospheric sampling station. The station is approximately 150 meters west of the west coast of Narragansett Bay and 15 meters above sea level. A field recording wind system (model R.M. Young, 1973), was installed on the sampling station to provide a continuous record of wind speed and direction. Also a standard plastic rain gauge was used to record the amounts of rainfall.

Seventeen rainfall samples, 55 dry fallout samples and 28 atmospheric particulate samples were collected. The majority of these samples were collected during 24 hour periods continually from April 15 to June 28, 1976. A few rainfall and dry fallout samples were collected during December 1975. Duplicates of seven dry fallout samples were collected aboard RV/Trident, Cruise #169, Narragansett to Bermuda to Narragansett during July, 1975. These samples were collected manually on top of the wet laboratory.

The majority of the rainfall and dry fallout samples were collected in duplicate and a few in triplicate. Acid cleaned 11x10x4 cm and/or 42x29x25 cm plastic containers were used for this purpose. The atmospheric samples were collected on double Whatman 41 filters using a high volume pump. These filters are reported to be 90% efficient for removing particles ≥ 0.26 μm in diameter for air (Stafford and Ettinger, 1972). Also the blank content of Na and Mg in these filters is low (Cawse et al., 1972; Dams et al., 1972).

Out of the total number of dry fallout and rainfall samples, 34 dry fallout and 7 rain samples were collected using the automatic rain-dry fallout sampler (Fig. 2), while the rest were collected manually. Manual rain samples were obtained by sampling the rain shower beginning immediately after the start of the shower and ending as soon as the rain stopped. Dry fallout samples were collected during dry periods. Whenever rainfall was collected with dry fallout samples, as was the case sometimes at inconvenient hours, the collected samples were considered as total fallout samples.

2. The Automatic Rain-Dry Fallout Collector (AEC)

This automatic collector is a modification of a device designed and built by Dr. Herbert Volchok of the Health and Safety Laboratory, ERDA, N.Y., N.Y. The system as shown (Fig. 2) consists of a two polyethylene bucket collector controlled by a printed circuit board rain sensor. Each collector was designed to house precisely a polyethylene bucket of a size 42x29x25 cm. This way only single samples could be collected by the collector. In order to collect dry fallout replicate samples using the automatic collector, the system was modified as follows: a wooden platform wrapped with polyethylene sheets and having the same size as the plastic buckets was placed in the collector instead of the dry fallout bucket. This platform was designed to house as many as 4 polyethylene buckets of a size 11x10x4 cm. During rainfall one vessel is exposed and collects rain while the dry fallout vessel (or vessels) is covered. When it is not raining the dry fallout collector(s) is exposed and the rain collector is covered. A heater is attached to the sensor to assure activation during cold periods and to dry the sensor so that a quick shut-off will occur at the end of precipitation.

Figure 2. The automatic rain-dry fallout collector. Only the dry fallout half is shown. (The rain half is identical).

3. Sample Handling

Dry fallout samples were obtained by washing the bottom and sides of the plastic buckets with distilled deionized water after sampling. Samples were stored in acid cleaned polyethylene bottles and kept in a freezer. Blanks were obtained twice for every sample. The first blanks were taken from the clean plastic collection container before sampling using distilled deionized water. The second blanks were taken from the distilled deionized water used to wash out the dry fallout samples.

Total fallout and rainfall samples were also stored in acid cleaned polyethylene bottles, kept in a freezer. For those samples of large volumes only aliquots were retained and the rest of the sample was disposed of after determining the total volume.

Whatman 41 filter blanks were obtained periodically for the atmospheric particulate samples by treating filter blanks exactly as sample filters, except no air was drawn through them. Sample filters and blanks were sealed in polyethylene bags and stored in a freezer prior to analysis.

4. Testing Programs for the Sampling Systems

To determine the optimum conditions for sample collection, several tests were conducted prior to the start of the sampling program for this project. These tests, discussed in full below, included the following: determination of the collection efficiency of two types of plastic buckets for rainfall and dry fallout, collected manually and automatically; investigation of the collection efficiency of 3 type of surfaces for dry fallout collection; and determination of the collection reliability of the automatic rain-dry fallout sampler.

- a. Determination of rainfall collection efficiency of 42x29x24 cm and 11x10x4 cm plastic containers.

The total volume of 13 rain showers collected in 42x29x25 cm (1233cm^2 bottom area) and 11x10x4 cm (110cm^2 bottom area) plastic buckets was measured. Seven of these rain shower samples were collected manually and 6 of them were collected using the automatic rain dry fallout sampler. Manual samples were collected in duplicate and triplicate. During rain shower number 5, two sets of samples, 5I and 5II were collected.

The collection efficiency of the two types of plastic containers and collection methods were calculated relative to the total rainfall measurements obtained from the standard plastic rain gauge. The results, shown in Table (1) indicate that the two types of collectors and collection efficiency for each of the two sized of plastic containers was 98%. The mean collection efficiency for the automatic collector which used the larger bucket, was also 98%, with sample number 12 not included. The overall efficiency for all collectors was also 98%.

- b. Collection efficiency of various surfaces for dry fallout and total fallout samples.

Seven experiments were conducted to determine what type of collection surface should be utilized to collect dry fallout samples. Three types of surfaces were investigated.

1. A dry plastic bucket surface

2. A water surface,

where distilled deionized water was added to the bucket to make a thin film of water at the bottom of the bucket.

3. A Whatman 41 filter surface.

Table 1. Collection efficiency of rainfall by 42x29x25cm and 11x10x4 cm plastic buckets

Rain Sample #	Date	Bucket Bottom Area (cm ²)	Total Rain Volume (cm ³)	Calculated Rain Depth (cm)	Rain Gauge Depth (cm)	Efficiency (%)
1	12/30/75	110	182	1.65	1.50	110
		110	190	1.70	1.50	113
		110	189	1.70	1.50	113
		1233	1810	1.50	1.50	100
		1233	1880	1.50	1.50	100
2.	12/31/75	110	89	0.51	0.83	98
		110	93	0.85	0.83	102
		110	91	0.83	0.83	100
		110	92	0.84	0.83	101
		110	92	0.84	0.83	101
		1233	1000	0.81	0.83	98
		1233	1010	0.82	0.83	99
		110	422	3.80	3.80	100
3.	1/6/76	110	418	3.80	3.80	100
		110	425	3.90	3.80	103
		110	422	3.80	3.80	100
		110	115	1.05	1.00	105
4.	4/24/76	110	105	0.95	1.00	95
		110	108	0.98	1.00	98
		110	255	2.30	2.60	88
5I	5/1/76	110	265	2.40	2.60	92
		110	260	2.40	2.60	92
		110	235	2.14	2.50	86
5II	5/1/76	110	240	2.20	2.50	88
		110	245	2.20	2.50	88
		110	96	0.87	0.90	97
6.	5/11/76	110	97	0.88	0.90	98
		110	181	1.65	1.75	94
		110	189	1.70	1.75	97
7.	5/16/76	110	213	1.90	1.75	109
		110	170	1.60	1.75	91
		1233	2160	1.75	1.75	100
		110	35	0.32	0.35	91
		110	36	0.33	0.35	94
8.	5/18/76	1233	405	0.33	0.35	94
		1233	690	0.56	0.53	105
9.*	5/21/76	1233	52	0.04	0.04	100
10.*	5/27/76	1233	1650	1.34	1.45	92
11.*	6/1/76	1233	400	0.32	0.40	80
12.*	6/19/76	1233				
Mean of the samples -		-	-	-	-	98±7

* Samples collected using the automatic rain-dry fallout sampler. The rest of the samples were collected manually.

mean collection efficiency for 110 cm² plastic buckets = 98 ± 7

mean collection efficiency for 1233 cm² plastic buckets = 98 ± 7

In one experiment a 20 mesh plastic screen was placed over one of the buckets. The purpose of this screen was to determine the extent of contamination, if any, of the samples by insects.

The results of these studies, shown in Table 2, indicate that dry and wet bucket surfaces collect about the same quantities of either Na or Mg. The amount of sea salt fallout collected by these two surfaces are always higher than the amount collected by the Whatman 41 filter. In the experiment where a plastic screen was used, the results show that the bucket with the screen cover collected almost twice as much as either the dry or wet buckets. These findings may be explained as follows: the wet surface was chosen in attempt to simulate the ocean surface. The fact that dry and wet plastic bucket surfaces have approximately the same collection efficiency for sea salt may be due to the hygroscopic nature of sea salt particles which exist as droplets at relative humidity over 70%. It is possible that sea salt particles falling on a dry bucket surface adhere to the side and bottom of the bucket just as well as they when they strike on a wet surface.

Although there is only one datum point for the experiment where a screen cover was used, the higher collection efficiency of the screen surface may be real. This may be because the screen itself acts as an impaction surface or as a filter. As a result of these experiments the choice of a collection surface for dry deposition was limited to a wet or dry plastic bucket surface. However, due to convenience and generally lower blanks, the dry plastic bucket surface was chosen over the wet surface. Also it was noticed that contamination by insects was far less for the dry surface compared to the wet surface.

Table 2. Surface collection efficiency for dry fallout and total fallout samples

Experiment Number	Sample Type	Surface	Area (cm ²)	Na $\mu\text{g}/\text{cm}^2$	Mg $\mu\text{g}/\text{cm}^2$	Na Mean $\mu\text{g}/\text{cm}^2$	Mg $\mu\text{g}/\text{cm}^2$	Na % Efficiency relative to Deposition on Dry Surface	Mg % Efficiency relative to Deposition on Dry Surface
3.	Total ^a	Dry	1233	0.092	0.015	0.092	0.015		
		Wet	1233	0.094	0.025	0.094	0.025	102	166
4.	Total ^a	Dry	1233	1.05	0.136	1.05	0.136		
		Wet	110	1.00	0.144				
5.	m.d.f. ^b	"	110	1.06	0.149	1.03	0.147	98	108
		Dry	1233	0.060	0.005				
		"	110	0.063	0.007	0.062	0.006		
		Wet	110	0.070	0.006				
		"	1233	0.063	0.005	0.067	0.006	108	100
7I	Total ^a	Dry	110	2.51	0.173	2.51	0.173		
		Wet	110	2.79	0.195				
		"	1233	2.38	0.161	2.59	0.178	103	103
7II 10	m.d.f. ^b	Dry	110	0.982	0.095	0.982	0.095		
		"	110	0.177	0.038				
		"	110	0.165	0.039				
		"	110	0.196	0.046	0.179	0.041		
		Wet	110	0.170	0.037				
		"	110	0.155	0.034				
		"	110	0.204	0.046	0.176	0.039	98	95
		W41 ^c	64	0.093	0.020				
		"	64	0.136	0.027				
		"	64	0.132	0.028	0.120	0.025	67	61
		Screen	960	0.314	0.068	0.314	0.068	175	166
11	m.d.f.	Dry	110	0.045	0.028				
		"	110	0.041	0.024	0.043	0.026		
		Wet	110	0.046	0.029				
		"	110	0.045	0.029	0.046	0.029	107	112
		W41 ^c	90	0.036	0.032				
		"	90	0.033	0.033	0.035	0.033	81	127

Mean EFF.% wet/dry = 102 ± 4 Na" " " = 111 ± 24 MgMean EFF.% W41/dry = 74 ± 10 Na" " " = 94 ± 47 Mg

a = Total fallout (rain and dry fallout).

b = Manually collected dry fallout.

c = Whatman 41 filter.

d = Samples collected in plastic buckets were obtained by washing the bottom and sides of these buckets.

- c. Dissolution of Na and Mg in the dry fallout samples from the bottom and sides of the plastic buckets

This experiment was conducted to determine the number of washes required to wash out Na and Mg in the dry fallout samples collected by the plastic buckets. The experiment was also intended to estimate the amounts of Na and Mg collected on the sides of the plastic buckets as compared to the bottoms.

Distilled deionized water was used to wash out 4 samples of dry fallout collected in 42x29x25 cm plastic buckets. The bottoms and the sides of these buckets were washed 3 times each using a wash bottle, only the bottoms of the buckets were carefully washed at first. To avoid washing out some of the Na and Mg collected on the sides of the buckets, an acid cleaned pipette was used to transfer the 3 washes from the bottoms of the buckets. After that, sea salt collected on the sides of the buckets was washed down to the bottoms and transferred from the buckets. Again 3 washes were used. The amounts of Na and Mg in each wash was determined (Table 3a and 3b). Of the total Na and Mg collected on the bottoms of the buckets, 97% and 89% respectively were obtained in the first washes. 86% of the total Na and 66% of the total Mg collected on the sides of the buckets were obtained in the first washes, (Table 3b). Essentially all the rest of the Na on the bottoms and sides of the buckets was removed in the second washes of the buckets. For Mg, three washes were generally required.

Of the total amounts of Na and Mg in the fallout samples, $88 \pm 7\%$ of the Na and $78 \pm 5\%$ of the Mg were collected on the bottoms of the plastic buckets (Table 3a and b). A student t-test showed that these numbers are statistically different at a confidence level of 96%. This suggests that particles falling on the sides of the buckets are relatively enriched in

Table 3a. Dissolution of Na and Mg in the 'dry fallout samples from the bottom

sides of the plastic buckets

# Bucket		Samp B ₁ (ug)	Samp B ₂ (ug)	Samp B ₃ (ug)	T _B (ug)	Samp S ₁ (ug)	Samp S ₂ (ug)	Samp S ₃ (ug)	T _S	Total	T _B /Tot. %
1 11W ^a	Na	74.6	1.40	1.90	77.9	7.19	14.1	1.90	23.2	101	77
	Mg	6.12	0.460	0.300	6.88	1.06	1.39	0.460	2.91	9.79	70
2 18D ^b	Na	26.3	0.00	0.00	26.3	1.40	1.00	0.00	2.40	28.7	92
	Mg	9.92	0.250	0.066	10.2	1.40	0.940	0.00	2.34	12.5	81
3 34DT ^c	Na	90.1	9.28	0.00	99.4	13.3	0.00	0.00	13.3	113	88
	Mg	10.7	2.52	0.530	13.8	3.65	0.500	0.00	4.15	18.0	77
4. 35WT ^d	Na	108	0.00	0.00	108	8.12	0.00	0.00	8.12	116	93
	Mg	24.7	0.660	0.400	25.7	4.26	0.820	0.400	5.48	31.2	82
Mean	Na	-	-	-	-	-	-	-	-	-	88±7
	Mg	-	-	-	-	-	-	-	-	-	78±5

a = wet bucket

b = dry bucket

c = dry bucket collected total fallout

d = wet bucket collected total fallout

B₁, B₂, B₃ = bottom of the bucket first wash, second wash, etc.S₁, S₂, S₃ = first wash of the sides of the bucket, second wash of the sides of the buckets, etc.T_B = B₁+B₂+B₃T_S = S₁+S₂+S₃T_B/Tot. = ratio of T_B to (T_B+T_S) x 100 (percentage)

Table 3b. Proportions of Na and Mg in the dry fallout collected on the bottom and sides of the plastic buckets

Expt. No.	%Na		%Mg	
	B_1/T_B	S_1/T_S	B_1/T_B	S_1/T_B
1	96.	31.	89.	36.
2	100.	58.	97.	60.
3	91.	100.	76.	88.
4	100	100	96	78
Mean	97 ± 4	86 ± 24	89 ± 10	66 ± 23

B_1/T_B = Ratio of the amount of Na or Mg obtained from the first wash of the bottom of the plastic buckets relative to the total amount of Na or Mg collected by the bottom of the plastic buckets.

S_1/T_S = Ratio of the amount of Na or Mg obtained from the first wash of the sides of the buckets relative to the total amount of Na or Mg collected by the sides of the buckets.

Mg compared with those falling on the bottoms of the buckets. It is possible that some segregation of the falling aerosol particles occurs when they reach the sampling container. Perhaps a higher proportion of the aerosol particles of crustal origin, with their smaller size and higher Mg/Na ratio, are preferentially deposited on the sides of the buckets. Aerosol particles of crustal origin are known to be enriched in Mg relative to Na as compared to marine aerosols, (Junge, 1963; Riley and Chester, 1971).

In the previous experiment where the collection efficiencies of various surfaces for dry fallout were tested, a Whatman 41 filter surface collected only 74% as much Na and 95% as much Mg as the dry plastic bucket surface. If we consider that the Whatman 41 filter surface is equivalent only to the bottom of the plastic bucket, one would expect that the Whatman 41 filter would collect about 88% of the Na and about 78% of the Mg collected by the plastic bucket, assuming the two surfaces had equal collection efficiency. Since these values are approximately equivalent to the actual relative amounts collected by Whatman 41 filter, it seems therefore, the relatively poor collection efficiency of the Whatman 41 filter must be due to the geometry of the collection vessel and not the nature of the filter surface.

d) Efficiency of the automatic rain-dry fallout collector for total deposition

A description of the instrument and the collection efficiency of the containers used in it for rainfall were given earlier in this chapter.

The efficiency of the automatic rain-dry fallout collector for total deposition is defined in percent as equal to (total amount of Na or Mg in an automatic collector dry fallout sample + total amount of Na or Mg in an automatic collector rainfall sample) divided by the total amount of

Na or Mg in a manual total fallout sample, all times 100. Four experiments were conducted for this purpose. Replicates of rainfall and dry fallout samples were collected using the automatic rain-dry fallout collector while, during the same period of time, total fallout samples were collected manually using the plastic buckets. The collection efficiency of the automatic samples for total deposition was calculated for Na and Mg, (Table 4). In experiment 3 and 4, collected during the same rain shower, dry fallout and total fallout samples were collected over two different intervals.

The mean total deposition efficiency was $92 \pm 6\%$ for Na and $96 \pm 3\%$ for Mg. This high efficiency combined with the high collection efficiency for rainfall samples (Table 1), make the automatic rain-dry fallout collector an acceptable instrument for convenient and reliable sampling of rainfall and dry fallout samples. Galloway et al. (1976), investigated the collector reliability for rain and dry fallout of several bulk and automated collectors. They found that the automatic rain-dry fallout collector, better known as the U.S. Atomic Energy Commission Collector, was the most reliable of all the automatic collectors investigated.

4. Efficiency of the automatic rain-Dry fallout collector for total deposition

Exp. No.	Automatic Rain		Automatic dry fallout		Manual total fallout		Automatic Collector Efficiency for Total Deposition	
	Na ($\mu\text{g}/110 \text{ cm}^2$)	Mg	Na ($\mu\text{g}/110 \text{ cm}^2$)	Mg	Na ($\mu\text{g}/110 \text{ cm}^2$)	Mg	Na	Mg
1	35.8	9.50	16.0	10.6	65.5	22.5		
	-	-	-	11.0	55.0	21.1		
	-	-	15.0	10.3	59.0	20.4		
	-	-	16.0	10.2	-	-		
mean for 1	35.8 $\pm$ 10.	9.50 $\pm$ 0.95	15.7 $\pm$ 5.8	10.5 $\pm$ 3.6	59.7 $\pm$ 5.0	21.3 $\pm$ 1.7	86	94
2	125	19.7	13.8	3.00	154	22.8		
	-	-	17.7	3.00	-	22.7		
mean for 2	125 $\pm$ 13	19.7 $\pm$ 1.97	15.8 $\pm$ 2.8	3.00 $\pm$ 0.0	154 $\pm$ 15	22.8 $\pm$ 0.1	92	100
3	54.2	9.04	43.	8.20	113	18.3		
	-	-	73.5	8.00	-	-		
mean for 3	54.2 $\pm$ 5.4	9.04 $\pm$ 0.90	58.3 $\pm$ 22	8.10 $\pm$ 0.14	113 $\pm$ 20	18.3 $\pm$ 25	100	94
4	54.2 $\pm$ 5.4	9.04 $\pm$ 0.90	75.0 $\pm$ 7.5	11.8 $\pm$ 1.2	145 $\pm$ 15	22.3 $\pm$ 2.2	90	94
							92 $\pm$ 6	96 $\pm$ 3

B. Analytical Procedures

1. Extraction of Na and Mg from Whatman 41 Filter

As mentioned previously, atmospheric particulate Na and Mg were collected on 20x25 cm double Whatman 41 cellulose filters. The filter holder and housing were constructed of polyvinyl chloride (PVC). Samples were collected over a period of 24 hours.

In order to dissolve the particulate Na and Mg collected on Whatman 41 filters, 3 different procedures were considered. These were 1) sample elution using distilled deionized water or 0.1 N HNO_3 in an ultra-sonic bath; 2) high temperature ashing of the filter at 450-500°C using a muffle furnace 3) low temperature ashing of the filter using a LFE model LTA505 low temperature asher. The three techniques were compared as follows:

a. Extraction of known amounts of Na and Mg from Whatman 41 filter

Using Copenhagen standard sea water, known amounts of Na and Mg were added to 3 Whatman 41 filters placed in acid cleaned polyethylene containers. The three filters and two filter blanks were then extracted using 25 ml of 0.1N HNO_3 in an ultrasonic cleaner for 5 minutes. Results, shown in Table 5, indicate that the ultrasonic extraction procedure was 100% efficient in recovering soluble Na and Mg. The extractable blank for Whatman 41 filters was $0.091 \mu\text{g Na/cm}^2$ and $0.014 \mu\text{g Mg/cm}^2$.

b. Ultrasonic extraction versus high temperature ashing

To compare the efficiency of the ultrasonic extraction technique to the high temperature ashing method, 3 dry fallout samples collected on Whatman 41 filters and one filter blank were studied. Using clean stainless-steel surgical scissors and a laminar flow clean bench, each of the 4 filters were cut into 2 equal halves. Disposable polyethylene

Table 5. Extraction of known amounts of Na and Mg from a Whatman 41 filter using 0.1 N HNO_3 acid and an ultrasonic cleaner

Sample	ug Na added	ug Na added	ug Na found	ug Mg added	% EFF. Na	% EFF. Mg
131	Blank	Blank	0.091 cm^{-2}	0.014 cm^{-2}	-	-
132	"	"	0.091 cm^{-2}	0.014 cm^{-2}	-	-
134	8.62	1.04	8.70	1.08	101	104
135	4.31	0.52	4.45	0.53	103	102
136	2.59	0.31	2.58	0.50	100	161*

*Possible Mg contamination

Na and Mg blanks were subtracted from samples 134, 135 and 136.

gloves were worn during the cutting and handling of the filters. One half of each filter was then extracted using 0.1 N HNO_3 in an ultrasonic bath while the other half was ashed at 450-500°C in a muffle furnace for 15 hours. A clean 100 ml pyrex beaker with a watch glass was used for this purpose. After ashing, the contents of the beaker were dissolved with a combination of suprapur HCl and HNO_3 , of concentrations 12N and 16N respectively. The results (Table 6), show that the amount of Na and Mg obtained by the two dissolution procedures are comparable in the three samples analysed. The differences are within the analytical error. If we consider that the Na and Mg blanks obtained by high temperature ashing represent the total blank values and the ones obtained by ultra-sonic extraction represent only the extractable blanks in Whatman 41 filter, then it appears that the extractable Na blank amounts to only 1/3 of the total Na blank and the extractable Mg blank is equivalent to about 3/4 of the total Mg blank. Hoffman et al. (1972) compared dry ashing with extraction techniques for atmospheric particulate Na collected on Delbag polystyrene filters. They found that the two techniques have essentially the same dissolution efficiency.

c. Extraction of particulate Na and Mg from Whatman 41 filter samples using 0.1N HNO_3 and distilled deionized water.

Hoffman (1969) used 0.1 N HNO_3 and 3N HNO_3 to extract particulate Pb from equal portions of glass fiber filters. She found that filters extracted ultrasonically with 3N HNO_3 contained more Pb than those extracted with 0.1 N HNO_3 . That was due to the higher blanks of the glass fiber filters when eluted with 3N HNO_3 . She also found that the ultrasonic cleaner reached a maximum efficiency after 5 minutes.

Table 6. Extraction of Na and Mg from Whatman 41 filters using high temperature ashing and extraction with 0.1N HNO_3 in an ultrasonic bath.

Sample No.	ugNa/cm^2	ugMg/cm^2	ugNa/cm^2	ugMg/cm^2
	Ultrasonic Extraction		High Temperature Ashing	
*B ₁	0.088	0.009	0.272	0.012
+S ₁	0.467	0.023	0.483	0.030
+S ₂	1.05	0.037	0.710	0.027
+S ₃	0.029	0.010	0.027	0.013

* Whatman 41 filter blank

+ Dry fallout samples, blank subtracted

In the present study distilled deionized water was compared to 0.1N HNO_3 as solvent for ultrasonic extraction of particulate Na and Mg from Whatman 41 filters. Extractions were carried out for different time intervals to determine the time required before the ultrasonic cleaner reached the maximum efficiency.

In this experiment a 20x25 cm double Whatman 41 filter blank and two atmospheric particulate samples, #14 and 15, were each cut diagonally into 8 equal sections. Selected alternatively, 4 sections of the filter blank and of each of the two samples were extracted with distilled deionized water in an ultrasonic cleaner for different time intervals. The same procedure was repeated with the other 4 sections using 0.1 N HNO_3 acid. After being extracted, 2 sections of the filter blank and 4 sections of each of the two sample filters were then low temperature ashed to determine the efficiency of the ultrasonic extraction. The filters were ashed at an oxygen flow of 50 cc/min and a radio-frequency (RF) power of 50 watts for 24 hours. The residue was then taken up in 0.5 ml of concentrated Suprapur HF acid to which was added 0.5 ml of concentrated, distilled HNO_3 acid. The solution was then transferred to a precleaned 7ml polyethylene vial. The vial was left to stand for 2 weeks and prior to analysis 5 ml of distilled deionized H_2O was added to make the acid content $\sim 1.6\text{N } \text{HNO}_3$ and 2N HF.

The results of the blank filter study, shown in Table 7, indicate that there may be some tendency for the extractable Na blank to increase with increase in extraction time interval. This trend was more obvious when distilled deionized water was used as a solvent. At an extraction time interval of 7 minutes the Na blank was almost twice the one obtained

Table 7. Extraction of particulate Na and Mg from a Whatman 41 filter blank using 0.1 N HNO_3 and D.D. H_2O and an ultrasonic bath.

Whatman Blank	Section No.	Solvent	Time Min	g Na cm^{-2} Extracted	g Mg cm^{-2} Extracted	g Na cm^{-2} Ashed(L.T.A.)	μg Mg cm^{-2} After Extraction
	1	0.1N HNO_3	1	0.055	0.010	-	-
	3	"	3	0.049	0.008	-	-
	5	"	5	0.105	0.008	0.280	0.162
	7	"	7	0.080	0.008	-	-
Mean	-	-	-	0.072 ± 0.026	0.009 ± 0.001	0.280 ± 0.03	0.162 ± 0.02
	2	D.D. H_2O	1	0.043	0.006	-	-
	4	"	3	0.049	0.005	0.139	0.002
	6	"	5	0.075	0.006	-	-
	8	"	7	0.087	0.008	-	-
Mean	-	-	-	0.064 ± 0.021	0.006 ± 0.001	0.139 ± 0.01	0.002
mean (H_2O)	-	-	-	0.068	0.008	0.139	0.002
+0.1 N HNO_3)	-	-	-	± 0.022	± 0.002	± 0.01	

at 1 minute time interval. This trend was not observed for the Mg blank. It appears that the extractable Mg blank is independent of the extraction time intervals for the two solvents used. This suggests that the ultrasonic cleaner reaches a maximum efficiency after only one minute in the case of Mg blank.

If we add the mean of extractable blank to the mean of the ashed blank (Table 7), the total blank for Whatman 41 filter becomes $0.207 \mu\text{g Na/cm}^2$ and $0.010 \mu\text{g Mg/cm}^2$. These blank values are comparable to the values obtained by high temperature ashing alone (Table 6).

Dams et al. (1972) obtained $0.150 \mu\text{g Na/cm}^2$ and $\sim 0.08 \mu\text{g Mg/cm}^2$ blank values for Whatman 41 filters. This last figure is considerably higher than found here. E. Hoffman (personal communication) found that the Mg blank in Whatman 41 filter was $\sim 0.018 \mu\text{g/cm}^2$.

As seen from the data in Table 7, 8 and 9, the extractable Na and Mg blanks amount to only 8% and 4% respectively of the extractable Na and Mg collected by sample filter 14, while for sample 15 they comprise only 3% of the total extractable Na or Mg. Since these figures are within the sampling and analytical error it was not possible to observe any effect of increased extraction time on the amount of Na recovered in sample 14 and 15. The results also confirm that distilled deionized water is as efficient a solvent as 0.1 N HNO_3 for dissolving sea salt collected on Whatman 41 cellulose filters.

Out of the 50 ml of H_2O used to extract particulate Na and Mg from Whatman 41 filters, approximately 88% is recovered, the rest remaining in the filter. Taking this into consideration and using the mean amount of Na and Mg recovered from sample filters #14 and 15 the data in Tables

Table 8. Extraction of particulate Na and Mg from atmospheric particulate sample
 No. 14. (Blank subtracted)

Sample No. 14	Section No.	Solvent	Time Min	$\mu\text{g Na/cm}^2$ Extracted	$\mu\text{g Mg/cm}^2$ Extracted	$\mu\text{g Na/cm}^2$ Ashed(L.T.A.)	$\mu\text{g Mg/cm}^2$ After Extraction
	1	0.1N HNO_3	1	0.795	0.190	-	-
	3	"	3	0.872	0.215	0.250	0.232
	5	"	5	0.770	0.193		
	7	"	7	0.790	0.205	0.180	0.232
	Mean	-		0.807	0.201	0.215	0.232
				± 0.045	± 0.012	± 0.049	± 0.023
	2	DD H_2O	1	0.787	0.178	0.165	0.236
	4	"	3	0.800	0.203	-	
	6	"	5	0.824	0.185	0.404*	0.418*
	8	"	7	0.816	0.192	-	-
	Mean	-		0.807	0.190	0.165	0.236
				± 0.017	± 0.011	± 0.017	± 0.024
	mean (H_2O)			0.807	0.195	0.198	0.233
	+0.1 N HNO_3)			± 0.03	± 0.01	± 0.05	± 0.002

* Possible contamination. Values not used when means calculated.

Table 9. Extraction of particulate Na and Mg from atmospheric particulate sample

No. 15 (Blank subtracted)

Sample No. 15	Section No.	Solvent	Time Min	$\mu\text{g Na cm}^{-2}$ Extracted	$\mu\text{g Mg cm}^{-2}$ Extracted	$\mu\text{g Na cm}^{-2}$ Ashed (LTA) after	$\mu\text{g Mg cm}^{-2}$ Extraction
	1	0.1N HNO_3	1	2.22	0.289	0.207	0.210
	3	"	3	2.25	0.290	-	-
	5	"	5	2.06	0.273	0.194	0.160
	7	"	7	2.20	0.290		
	Mean	-		2.18 ± 0.084	0.286 ± 0.008	0.201 ± 0.009	0.185 ± 0.035
	2	DD H_2O	1	2.04	0.177	-	-
	4	"	3	2.11	0.263	0.207	0.316
	6	"	5	2.33	0.293	-	
	8	"	7	2.21	0.284	0.207	0.199
	Mean			2.17 ± 0.126	0.254 ± 0.053	0.207 ± 0.021	0.258 ± 0.083
Mean ($\text{H}_2\text{O} +$ 0.1N HNO_3)		-		2.18 ± 0.10	0.270 ± 0.04	0.204 ± 0.01	0.222 ± 0.07

8 and 9 indicate that ultrasonic extraction is essentially 100% efficient for removing Na but only 50-60% efficient for Mg.

Meteorological data compiled during sampling indicate that sample 14 and 15 are "mixed" samples, i.e. winds shifted from marine to land during the sampling periods. Sample 15 has a greater marine fraction in it than sample 14. Considering the above, it is likely the poor extraction of Mg is due to a significant fraction of Mg of crustal origin. These alumino-silicate matrix particles are much less soluble in water and 0.1N HNO_3 than sea salt particles. This also explains why a lower percentage of Mg was extracted from sample 14.

d. Efficiency of recovery of one extraction for particulate Na and Mg

To determine whether a second extraction might solublize more of the crustal Mg(and Na)left in the Whatman 41 filters the following experiment was conducted.

Fifty ml of distilled deionized water, measured volumetrically, was used to extract particulate Na and Mg from 3 Whatman 41 filter blanks and duplicates of 4 atmospheric samples. The blanks and sample were quarters of 20x25 cm double Whatman 41 cellulose filters. The extraction was carried out for 2 minutes using an ultrasonic cleaner. The volume of extract recovered was determined by weight. Then another 10 ml of distilled deionized water was used to re-extract the filters in order to determine the efficiency of the first extraction. Again the volume recovered was determined by weight. The results (Table 10), were presented as percent recovery of the volume of solvent used and of the Na and Mg recovered from the first extraction. As shown, the percentage of

Table 10. Efficiency of extraction of atmospheric Na and Mg from
Whatman 41 filter using an ultrasonic cleaner and DD H₂O.

Sample No.	% of total H ₂ O recovered on first extract	% of total Na recovered on first extract	% of total Mg recovered on first extract
Blank 500	87	77	73
" 501	85	79	-
" 502	84	77	68
mean (blank)	85±1.5	78±1.2	71±3.5
23A	88	87	84
23B	87	87	83
24A	88	87	82
24B	88	86	82
26A	88	86	83
26B	88	86	83
27A	91	91	90
27B	91	89	88
mean	89±1.5	87±1.8	84±3.0

the Na and Mg recovered is very close to the percentage of the volume of water recovered after the first extraction. This result suggests that one extraction is sufficient to obtain all the soluble Na and Mg collected on the Whatman 41 filters, if the volume of water remaining in the filter after extraction taken into consideration.

Atmospheric particulate samples collected on Whatman 41 filters for this project were therefore extracted ultrasonically only once using 50 ml of distilled deionized water. The amounts of Na and Mg recovered were calculated on the basis of the total volume of solvent used.

2. Sample Analysis

a. Atomic absorption

Dry fallout, rainfall and total fallout samples were analysed for Na and Mg using Perkin Elmer Atomic Absorption Spectrophotometer Models 360 and 303. Acetylene-air flame atomic absorption procedures were used. Depending on the concentration range of samples, burner heads of sizes 1", 2" and 4" with one or three slots were used. Burner heads were sometimes turned at 45° or 90°, depending on the concentration of the samples, so as to remain within the linear region of atomic absorption. Perkin-Elmer Intensitron lamps were used, and wavelengths of 589 nm for Na and 285 nm for Mg were utilized. During analysis standards were prepared every other day from Copenhagen standard sea water, of salinity equal to 35⁰/oo. This corresponds to a Na concentration of 10772 ppm and a Mg concentration equal to 1297 ppm (R. Pytkowicz and D. R. Kester 1971).

Typical calibration curves for Na and Mg are given in Figures 3-4. Calibration curves used in determining unknown concentrations were computed

Figure 3. A typical calibration curve of Na aconcentration versus absorbance, with burner head rotated at 90°.

Figure 4. A typical calibration curve of Mg concentration versus absorbance, with burner head rotated at 45°.

TYPICAL Mg Std. Curve
 A.A. 365
 Burner head rotated at 45°

ABSORBANCE

Mg (mg/L)

using a Texas Instrument SR-51-II Electronic Calculator programmed for a standard least squares, linear regression analysis. The computed slope and intercept from the program were used to determine unknown concentrations. In general, the use of this calibration curve was restricted to correlation coefficient values ≥ 0.996 . Standards were run at the beginning, at the end and in between sample analyses.

b. Sampling and analytical precision

Since in this work, in general, duplicates and triplicates of samples were collected, the overall analytical plus sampling precision in % were calculated from the standard deviation and mean of these replicate analyses. The analytical precision for Na and Mg analyses were 5.7% and 5.4% respectively.

III. RESULTS

A. General Considerations

The results of the analyses of dry fallout, rain and atmospheric particulate samples collected in this study are given in Table 12-22. Except for samples 3,4,5,6 and 10 and samples collected aboard RV/Trident (Table 18), all samples were collected over a 24 hour period continually from April 15 to June 28, 1976. Samples collection information is shown on Table II.

B. Classification of Samples

After studying the meteorological data compiled during sampling, dry fallout, rainfall and atmospheric samples were divided into 3 different categories depending on the local surface wind direction during the sampling period (Fig. 5). Samples collected while the wind direction was between 090° and 230° were considered "marine" samples and were designated S. Samples collected within the sector 230° - 010° were considered "land" samples and were designated L. Samples collected while the wind was blowing from near the boundary between the land and marine sectors and/or where the wind direction shifted from the marine to the land sector or vice versa were considered "mixed" samples and were designated S/L. To this category, samples collected within the sector 010° - 090° were also included. These 3 different sets of samples could be considered to represent 3 different meteorological subenvironments of the coastal Rhode Island environment depending on the local wind conditions

1. Atmospheric Concentrations and Dry Deposition

a. Coastal Rhode Island

i) "Marine", "Mixed" and "Land" Samples

The rate of dry fallout for Na and Mg, the Mg/Na ratios, the

Table 11. Samples collection information

Experiment No.	Sample No.	Sample type	Date of collection	Collection time(hours)	Volume ⁺ of air (m ³)
3	S3	(Marine)m.r.	12/15/75	-	-
4	L4	(Land)m.r.	12/17/75	-	-
5	S/L5	(Mixed)m.d.f.	12/29-30/75	23.3	-
6	S6	(Marine)m.r.	12/30-31/75	-	-
10	S/L10	(Mixed)m.d.f.	2/24-26/76	45.3	-
13	L13	(Land)a.d.f.	4/15-19/76	93.5	-
14	178,179	(Mixed)a.d.f.	4/20-21/76	24.0	-
"	17a,14b	(")atmospheric	"	"	1752
15	190,191	(Mixed)a.d.f.	4/21-22/76	23.3	-
"	15a,15b	(")atmospheric	"	"	1742
16	200,201,202	(Land)m.r.	4/22-23/76	-	-
17	204,205	(")m.d.f.	4/23-24/76	22.5	-
"	17a,17b	(")atmospheric	"	"	1651
18	208,209,210	(Mixed)m.r.	4/24-26/76	-	-
19	211,212,213	(Land)m.r.	4/26-27/76	-	-
20	215,217,219	(")m.r.	4/27-28/76	-	-
21	221,222,223	(")m.d.f.	4/28-29/76	23.5	-
"	21a,21b	(")atmospheric	"	"	1763
22	224,225,226	(")m.d.f.	4/29-30/76	24.0	-
"	22a,22b	(")atmospheric	"	"	1764
23	227,228,229	(Marine)m.r.	5/1-2/76	-	-
24	233,234,235	(Marine)m.d.f.	5/2-3/76	23.5	-
"	24a,24b	(")atmospheric	"	"	1716
25	23,237	(Land)m.d.f.	5/3-4/76	24.0	-
"	25a,25b	(")atmospheric	"	"	1752
26	238,239	(Mixed)m.d.f.	5/4-5/76	23.0	-
"	26a,26b	(")atmospheric	"	"	1691
27	240,241	(Marine)m.d.f.	5/5-6/76	25.0	-
"	27a,27b	(")atmospheric	"	"	1825
28	244,245	(Marine)m.r.	5/7/76	-	-
29	249,250	(Land)m.d.f.	5/8-9/76	22.5	-
"	29a,29b	(")atmospheric	"	"	1530
30	251,252,253	(Mixed)m.d.f.	5/9-10/76	22.5	-
"	30a,30b	(")atmospheric	"	"	1688
31	254,255	(Mixed)m.d.f.	5/10-11/76	22.75	-
"	31a,31b	(")atmospheric	"	15	1010
32	256,257	(Marine)m.r.	5/11-12/76	-	-
33	258,259	(Mixed)m.d.f.	5/12-13/76	25.0	-
"	33a,33b	(")atmospheric	"	"	1675

Table 11 (Continued)

Experiment No.	Sample No.	Sample Type	Date of collection (hours)	Collection time(hours)	Volume of air (m ³)
34	260,261	(Marine)m.d.f.	5/13-14/76	21.5	-
"	342,34b	(")atmospheric	"	"	1570
35	262,263,265	(Mixed)a.d.f.	5/14-15/76	23.0	-
"	352,35b	(")atmospheric	"	"	1564
36	267,268	(Marine)a.d.f.	5/15-16/76	25.25	-
"	36a,36b	(")atmospheric	"	"	1793
37	266	(Marine)a.r.	5/17/76	-	-
38	274*,277*,278*	(Marine)a.d.f.	5/17-18/76	20.25	-
"	38a,38b	(")atmospheric	"	"	1377
39	275,276	(Marine)a.d.f.	5/18-19/76	26.0	-
"	392,39b	(")atmospheric	"	"	1742
39	273	(Marine)rainfall	5/19/76	-	-
40	282*,283*	(Mixed)a.d.f.	5/19-20/76	20.5	-
"	40a,40b	(")atmospheric	"	"	1456
41	284,285	(Mixed)dry fallout	5/20-21/76	24.0	-
"	41a,41b	(")atmospheric	"	"	1584
41	281	(Mixed)a.r.	5/21/76	-	-
42	286*,287*	(Land)a.d.f.	5/21-22/76	24.7	-
"	42a,42b	(Land)atmospheric	"	"	1778
43	288,289	(Land)a.d.f.	5/22-23/76	23.3	-
"	42,43b	(")atmospheric	"	"	1584
44	291*,292*	(Land)a.d.f.	5/23-24/76	24.8	-
"	44a,44b	(")atmospheric	"	"	1637
45	293,294	(Mixed)a.d.f.	5/24-25/76	21.2	-
"	452,45b	(")atmospheric	"	"	1442
46	297,298*	(Mixed)a.d.f.	5/25-26/76	23.5	-
"	46a,46b	(Mixed)atmospheric	"	"	1598
47	299,300	(Mixed)a.d.f.	5/26-27/76	22.5	-
"	47a,47b	(")atmospheric	"	"	1485
"	296	(Land)a.r.	5/27/76	-	-
48	400*,401*	(Mixed)a.d.f.	5/27-28/76	21.0	-
"	48a,48b	(")atmospheric	"	"	1323
49	402,403	(Mixed)a.d.f.	5/28-29/76	25.0	-
"	49a,49b	(")atmospheric	"	"	1525
50	306*,307*	(Mixed)a.d.f.	5/29-30/76	23.0	-
51	308,309	(Marine)a.d.f.	5/30-31/76	25.0	-
52	311*,312*	(Mixed)a.d.f.	5/31-6/1/76	20.75	-
53	313,314	(Marine)a.d.f.	6/1-2/76	27.25	-

Table 11 (Continued)

Experi- ment No.	Sample No.	Sample type	Date of collection (hours)	Collection time(hours)	Volume+ of air (m ³)
53	310	(Mixed)a.r.	6/1-2/76	-	-
54	315*,316*	(Land)a.d.f.	6/2-3/76	22.0	-
55	317,318	(Mixed)a.d.f.	6/3-5/76	46.0	-
56	319,320	(Mixed)a.d.f.	6/5-8/76	71.5	-
57	321*,322*	(Mixed)a.d.f.	6/8-9/76	25.0	-
58	323,324	(Mixed)a.d.f.	6/9-11/76	44.5	-
59	325,326	(Mixed)a.d.f.	6/11-13/76	52.2	-
60	327,328	(Marine)a.d.f.	6/13-15/76	44.8	-
61	329,330	(Marine)a.d.f.	6/15-17/76	48.3	-
62	333*,334*	(Mixed)a.d.f.	6/17-18/76	22.0	-
63	335,336	(Marine)a.d.f.	6/18-21/76	73.3	-
"	332	(Marine)a.r.	6/19-20/76	-	-
64	337,338	(Mixed)a.d.f.	6/21-23/76	44.7	-
65	340,341	(Land)a.d.f.	6/23-25/76	48.8	-
66	340,341	(Mixed)a.d.f.	6/25-28/76	72.0	-

*The rates of dry fallout were arrived at by subtracting values obtained from the samples below, since these samples actually represent a total of the two.

+ Pump mean flow rate = $70 \pm 3. (\text{m}^3/\text{h})$

m.r. =manually collected rain

a.r. =automatically collected rain

m.d.f.=manually collected dry fallout

a.d.f.=automatically collected dry fallout

Figure 5. Coastal Rhode Island Sampling Site.

$$R = \frac{1}{2} \left(\frac{1}{\rho} \frac{d\rho}{dt} + \frac{1}{\rho} \frac{d\rho}{dx} \right) \quad (2)$$

atmospheric concentrations of particulate Na and Mg and the mean wind speed for each sample were calculated and are presented in Tables 12-14. Least-squares linear regression analysis was used, for each category of samples, to evaluate the relationship between the wind speed and both the rate of dry fallout and the atmospheric concentrations of particulate Na and Mg. Intercepts, slopes and correlation coefficients calculated from these regression analyses were obtained and are also presented in Table 12-14.

ii. "Corrected to Marine" samples

Since over 50% of the total number of dry fallout and atmospheric samples were "mixed" samples, an attempt was made to recalculate the rates of dry fallout and atmospheric concentrations for the marine fraction of Na and Mg in these samples. Only "mixed" samples where the wind shifted from marine to land sectors or vice versa were chosen for this calculation. These constituted the majority of the "mixed" samples category. Calculations were made using the following parameters determined for each samples: a) the time intervals during which the local surface wind was blowing off the ocean and off land; b) the rate of dry fallout for the land fraction of the samples. This rate was assumed to be a constant, not varying with wind speed and equal to the mean rate of dry fallout calculated from the "land" subenvironment of the R.I. coastal environment. ($0.260 \times 10^{-12} \text{ gNa/cm}^2 \cdot \text{sec}$ and $0.215 \times 10^{-12} \text{ gMg/cm}^2 \cdot \text{sec}$). The Na and Mg rate of dry fallout for the marine fraction was then calculated as follows:

$$F_{CM} = \frac{F_{ML} t_{ML} - F_L t_L}{t_M} \quad (2)$$

Table 12. Rate of dry fallout and atmospheric concentration of Na and Mg for "marine" samples

Sample #	Rate of Dry Fallout		Mg/Na	Atmospheric Concentration		Mg/Na	Wind	
	Na 10^{-12} g	Mg $\text{cm}^{-2} \text{sec}^{-1}$		Na ($\mu\text{g}/\text{m}^3$)	Mg		Direction (degrees)	Speed miles/hour
S24	4.60 ± 0.481	0.690 ± 0.086	0.13	0.700 ± 0.040	0.120 ± 0.006	0.17	150-180	13.9
S27	7.73 ± 1.31	1.23 ± 0.157	0.16	2.84 ± 0.015	0.370 ± 0.020	0.13	220-230	24.
S34	1.61 ± 0.092	0.380 ± 0.021	0.23	1.51	0.205 ± 0.011	0.13	180-230	8.50
S36	1.31 ± 0.325	0.183 ± 0.045	0.14	0.590 ± 0.086	0.105 ± 0.005	0.18	100-170	7.4
S38	2.09 ± 0.209	0.460 ± 0.046	0.22	0.310 ± 0.050	0.086 ± 0.005	0.28	140-190	9.0
S39	5.66 ± 1.48	0.792 ± 0.043	0.14	1.50 ± 0.086	0.173 ± 0.009	0.12	150-230	14.0
S51	1.68 ± 0.121	0.220 ± 0.021	0.13	-	-	-	140-230	7.0
S53	3.87 ± 0.387	0.580 ± 0.059	0.15	-	-	-	40-90	13.3
S60	2.95 ± 0.243	0.530 ± 0.074	0.18	-	-	-	200-230	13.6
S61	2.67 ± 0.152	0.454 ± 0.022	0.17	-	-	-	190-230	13.7
S63	5.25 ± 0.299	0.787 ± 0.042	0.15	-	-	-	160-230	11.9
Mean	3.58 ± 2.04	0.573 ± 0.297	0.16 ± 0.03	1.24 ± 0.925	0.177 ± 0.105	0.17 ± 0.060	-	12.4 ± 4.74
Slope	2.04 ± 0.370	14.6 ± 2.18	-	5.50 ± 1.89	49.5 ± 16.0	-	-	-
int.	5.07 ± 1.51	4.05 ± 1.39	-	5.98 ± 2.83	4.07 ± 3.21	-	-	-
Corr. Coeff.	0.88	0.91	-	0.82	0.84	-	-	-

Form of regression equation:

wind = slope X (rate of dry fallout or atmospheric concentration) + intercept

Table 13. Rate of dry fallout and atmospheric concentration of Na and Mg for "land" samples

Sample #	Rate of Dry Fallout Mg/Na			Atmospheric Concentration		Mg/Na	Wind	
	Na $10^{-12} \text{ g cm}^{-2} \text{ sec}^{-1}$	Mg		Na ($\mu\text{g/m}^3$)	Mg		Direction (degrees)	Speed miles/hour
L13	0.420 ± 0.024	0.285 ± 0.015	0.68	-	-	-	230-270	13.0
L17	0.220 ± 0.022	0.210 ± 0.011	0.95	0.043 ± 0.008	0.044 ± 0.002	1.0	300-320	12.0
L21	0.240 ± 0.027	0.280 ± 0.016	1.2	0.059 ± 0.004	0.034 ± 0.002	0.58	300-360	12.0
L22	0.180 ± 0.020	0.360 ± 0.019	2.0	0.098 ± 0.005	0.074 ± 0.004	0.76	260-300	11.0
L25	0.370 ± 0.037	0.200 ± 0.016	0.54	0.008 ± 0.002	0.005 ± 0.001	0.63	240-320	12.0
L29	0.280 ± 0.016	0.260 ± 0.017	0.93	0.085 ± 0.005	0.054 ± 0.003	0.64	270-300	12.6
L42	0.188 ± 0.019	0.109 ± 0.015	0.58	0.068 ± 0.004	0.051 ± 0.003	0.75	300-310	8.20
L43	0.176 ± 0.010	0.138 ± 0.007	0.78	0.024 ± 0.001	0.029 ± 0.001	1.2	300-310	12
L44*	0.110 ± 0.050	0.064 ± 0.007	0.57	0.110 ± 0.006	0.043 ± 0.002	0.39	280-360	8.80
L54	0.031 ± 0.003	0.090 0.009	2.9	-	-	-	310-360	8.6
L65	0.493 ± 0.028	0.222 ± 0.012	0.45	-	-	-	230-280	13.2
Mean	0.260 ± 0.129	0.215 ± 0.012	1.1 ± 0.73	0.055 ± 0.030	0.042 ± 0.020	0.79 ± 0.21	-	11.5 ± 1.64
Slope	9.57	12.1	-	-11.9	21.3	-	-	-
int.	8.98	8.85	-	12.1	12.3	-	-	-
Corr. Coeff.	0.75	0.60	-	-0.26	- 0.31	-	-	-

*Not included in calculation of mean, slope, int and corr. coeff.

Form of regression equation:

wind = slope X (rate of dry fallout or atmospheric concentration) + intercept

Table 14. Rate of dry fallout and atmospheric concentration of Na and Mg for "mixed" samples

Sample #	Rate of Dry Fallout			Atmospheric Concentration		Mg/Na	Wind	
	Na $10^{-12} \text{ g cm}^{-2} \text{ sec}^{-1}$	Mg $10^{-12} \text{ g cm}^{-2} \text{ sec}^{-1}$	Mg/Na	Na $(\mu\text{g/m}^3)$	Mg $(\mu\text{g/m}^3)$		Direction (degrees)	Speed miles/hour
S/L 5	0.801 ± 0.060	0.072 ± 0.012	0.09	-	-	-	260-360+ 160-180	4.0
S/L10	1.11 ± 0.105	0.246 ± 0.031	0.22	-	-	-	200-300	12.0
S/L14 ^a	0.780 ± 0.044	0.550 ± 0.062	0.70	0.450 ± 0.026	0.105 0.007	0.24	230-300 30-60	13.7
S/L15	2.20 ± 0.161	0.320 0.016	0.15	1.24 ± 0.071	0.160 ± 0.009	0.13	69-90 180-220	123
S/L26	1.65 ± 0.094	0.590 ± 0.032	0.35	0.615 ± 0.035	0.130 ± 0.007	0.21	240-290 220-230	14.8
S/L30	0.540 ± 0.036	0.330 ± 0.028	0.60	0.640 ± 0.036	0.145 ± 0.008	0.23	250-270 160-190	12.8
S/L31	2.04 ± 0.172	0.430 ± 0.039	0.20	2.16 ± 0.123	0.428 ± 0.088	0.20	230 160-200	15.7
S/L33	0.650 ± 0.076	0.340 ± 0.018	0.52	0.235 ± 0.013	0.080 ± 0.004	0.34	280-310	7.3
S/L35	1.20 ± 0.068	0.330 ± 0.018	0.27	0.760 ± 0.043	0.120 ± 0.006	0.16	220-240	15.5
S/L40	2.53 ± 0.370	0.455 ± 0.072	0.18	0.557 ± 0.032	0.108 ± 0.006	0.19	220-250 280-300	17.7
S/L41	0.943 ± 0.125	0.330 ± 0.018	0.35	1.06 ± 0.060	0.175 ± 0.009	0.17	250-300 300-50	7.0
S/L45 ^a	1.83 ± 0.131	0.329 ± 0.045	0.18	0.723 ± 0.041	0.133 ± 0.007	0.18	30-70	20.6
S/L46 ^a	1.14 ± 0.383	0.227 ± 0.047	0.20	1.28 ± 0.073	0.195 ± 0.011	0.15	360-60	10.9
S/L47	0.659 ± 0.250	0.152 ± 0.008	0.23	0.606 ± 0.035	0.116 ± 0.006	0.19	220-230 270-340	8.3
S/L48	0.219 ± 0.075	0.624 ± 0.057	2.9 ^a	0.280 ± 0.016	0.109 ± 0.006	0.39	250-360 160-260	7.3
S/L49	0.636 ± 0.036	0.146 ± 0.008	0.23	0.393 ± 0.022	0.109 ± 0.006	0.27	230-260 160-230	8.4
S/L50	1.57 ± 0.089	0.315 ± 0.017	0.20	-	-	-	120-160 360-80	4.8
S/L52	0.886 ± 0.090	0.195 ± 0.020	0.22	-	-	-	180-240 290-80	7.0

Table 14. (Continued)

S/L55	0.349 ±0.091	0.122 ±0.018	0.35	-	-	-	120-360	8.3
S/L56	0.624 ±0.062	0.256 ±0.016	0.41	-	-	-	180-300	16.6
S/L57	0.586 ±0.060	0.234 ±0.030	0.40	-	-	-	230-240 230-270	7.7
S/L58	1.20 ±0.068	0.540 ±0.048	0.45	-	-	-	160-220 230-250	5.9
S/L59	0.849 ±0.048	0.297 ±0.040	0.35	-	-	-	230-360 200-230	14.0
S/L62	1.85 ±0.020	0.462 ±0.050	0.25	-	-	-	160-240 230-29	9.9
S/L64	1.74 ±0.170	0.261 ±0.014	0.15	-	-	-	180-240	11.1
S/L66	0.347 ±0.020	0.108 ±0.006	0.31	-	-	-	270-300 170-230	8.6
Mean	1.11 ±0.627	0.318 ±0.151	0.30 ±0.15	0.786 ±0.510	0.151 ±0.085	0.22 ±0.07	-	10.6 ±4.10
Slope	3.50	8.82	-	2.15	10.8	-		
int.	6.77	7.87	-	10.6	10.7	-		
Corr. Coeff.	0.53	0.32		0.26	0.21	-		

^anot included in calculating the mean of Mg/Na.

Form of regression equation:

wind = slope X (rate of dry fallout or atmospheric concentration) + intercept

where F_{CM} = corrected rate of dry fallout in $g \times 10^{-12} cm^{-2} sec^{-1}$
for Na or Mg.

F_{ML} = rate of dry fallout for a "mixed" sample in $g \times 10^{-12} cm^{-2} sec^{-1}$ for Na or Mg.

F_L = assumed rate of dry fallout for "land" fraction
 $= 0.260 \times 10^{-12} gNa/cm^2/sec$
 $= 0.215 \times 10^{-12} gMg/cm^2/sec$

t_{ML} = total sampling period in seconds for a "mixed" sample.

t_L = time in seconds where wind was blowing off the land.

t_M = time in seconds where wind was blowing off the ocean.

Using a similar approach the atmospheric concentrations of particulate Na and Mg for the marine fraction of "mixed" atmospheric samples were calculated as follows:

$$C_{CM} = \frac{C_{ML} t_{ML} - C_L t_L}{t_M} \quad (3)$$

where C_{CM} = corrected atmospheric concentration of Na or Mg in Mg/m^3 .

C_{ML} = concentrations of atmospheric particulate Na or Mg in ug/m^3 for a "mixed" sample.

C_L = assumed concentration of Na or Mg in ug/m^3 for the land fraction of the sample = $0.055 ugNa/m^3$;
 $0.042 ugMg/m^3$ (mean concentrations of particulate Na and Mg calculated from land subenvironments of R.I. coastal environment (Table 12)).

t_{ML}, t_L, t_M = as described previously.

The "corrected-to-marine" rates of dry fallout, and atmospheric concentrations for particulate Na and Mg, the corrected Mg/Na ratios, and the wind speeds during sampling of the marine fractions of the "mixed" samples are given in Table 15. Correlation between these values and wind speed as well as slopes and intercepts from linear least square regression analysis are also tabulated in Table 15. These same parameters were recalculated for the total sample population after the "marine" samples were combined with the "corrected to marine" samples (Table 16).

Since "mixed" samples collected within the wind sector 010-090° showed a different trend from the rest of "mixed" samples, they were listed separately in Table 17. Since sample 14 has a continental fraction, it was corrected to the 010-090° sector.

b. Samples collected aboard RV/Trident

Dry fallout samples were collected during cruise #169 from Narragansett to Bermuda to Narragansett in June-July 1975. The rates of Na and Mg dry fallout were calculated for the samples and are reported along with surface wind speed, in Table 18. Fig. 6 shows the stations where these samples were collected.

c. Deposition velocity for particulate Na and Mg

The deposition velocity was defined earlier in Chapter I. Na and Mg deposition velocities in cm/sec calculated for samples collected in the three sampling categories ("marine", "land", and "mixed") and for the "corrected to marine" samples are given in Table 19. The mean Na and Mg deposition velocities for each subenvironment and the overall mean for the R.I. coastal environment are also presented in Table 19.

Table 15. Corrected-to-Marine rate of dry fallout and atmospheric concentrations of Na and Mg for "mixed" samples

Sample #	Rate of Dry Fallout		Mg/Na	Atmospheric Concentration		Mg/Na	Wind	
	Na	Mg		Na	Mg		Direction (degrees)	Speed miles/hour
	10^{-12}	$\text{gcm}^{-2} \text{sec}^{-1}$		$\mu\text{g/m}^3$				
C10	3.52 ± 0.333	0.590 ± 0.074	0.17	-	-		200-230	12.0
C26	6.65 ± 0.379	1.94 ± 0.105	0.29	2.63 ± 0.150	0.447 ± 0.024	0.17	220-230	24.0
C31	5.02 ± 0.423	0.790 ± 0.072	0.16	5.69 ± 0.324	1.08 ± 0.222	0.19	160-200	21.0
C35	4.80 ± 0.274	0.526 ± 0.028	0.11	2.82 ± 0.161	0.441 ± 0.024	0.16	220-230	17.3
C40	4.10 ± 0.600	0.625 ± 0.099	0.15	0.913 ± 0.052	0.155 ± 0.008	0.17	220-230	15.0
C47	1.54 ± 0.584	0.013 ^{a+} ± 0.001	0.01	1.83 ± 0.104	0.280 ± 0.015	0.15	220-230	7.0
C49	0.886 ± 0.051	0.104 ± 0.006	0.12	0.600 ± 0.034	0.150 ± 0.008	0.25	160-230	9.5
C52	1.70 ± 0.173	0.203 ± 0.021	0.12	-	-	-	180-230	8.4
C56	1.12 ± 0.064	0.297 ± 0.019	0.27	-	-	-	180-230	11.6
C58	1.61 ± 0.092	0.682 ± 0.061	0.42	-	-	-	160-220	8.0
C59	1.66 ± 0.095	0.410 ± 0.055	0.25	-	-	-	200-230	8.50
C62	2.15 ± 0.232	0.509 ± 0.055	0.24	-	-	-	160-230	11.0
C64	2.04 ± 0.204	0.279 ± 0.014	0.13	-	-	-	180-230	11.1
Cmean	2.83 ± 1.80	0.579 ± 0.476	0.20 ± 0.099	2.41 ± 1.83	0.426 ± 0.346	-	-	12.6 ± 5.25
Slope	2.72 ± 0.311	8.55 ± 2.15	-	2.21 ± 1.40	11.4 ± 7.54	-	-	-
int.	4.94 ± 1.03	8.17 ± 1.58	-	10.3 ± 4.11	10.8 ± 3.99	-	-	-
Corr. Coeff.	0.94	0.78		0.62	0.60			

a+ is not included in the calculation of the mean, std deviation, slope, intercept, and the correlation coefficient.

Form of regression equation:

$$\text{wind} = \text{slope} \times (\text{rate of dry fallout or atmospheric concentration}) + \text{intercept}$$

Table 16. "Marine" samples and "Corrected-to-marine" samples -
Correlation with wind speed

	Dry Fallout		Atmospheric Concentration	
	Na	Mg	Na	Mg
# of samples	24	23	12	12
Mean Wind Speed miles/hour	12.6	12.7	14.4	14.4
Mean Rate of dry fallout or Atmospheric concentration	3.18×10^{-12} gmcm ⁻² sec ⁻¹	0.576×10^{-12} gmcm ⁻² sec ⁻¹	1.83 μg/m ³	0.301 μg/m ³
Slope	2.20±0.24	10.1±1.5	2.80±0.96	14.0±5.6
intercept	5.4±0.9	7.1±1.0	9.1±2.2	10.0±2.3
Correlation Coefficient	0.88	0.80	0.68	0.62

Form of regression equation:

wind = slope X (rate of dry fallout or atmospheric concentration) + intercept

Table 17. Rate of dry fallout and atmospheric concentrations of Na and Mg. Wind direction 010°-090°

Sample No.	Rate of dry fallout		Mg/Na	Atmospheric		Mg/Na	Wind Speed miles/hour
	Na 10 ⁻¹²	Mg gm/cm ² /sec		Na (µg/m ³)	Mg		
14	1.30	0.885	0.68 ^a	0.845	0.168	0.20	13.7
45	1.83	0.329	0.18	0.723	0.133	0.18	20.6
46	1.14	0.227	0.20	1.28	0.195	0.15	10.9
50	1.57	0.315	0.20	-	-	-	4.8
mean	1.46	0.439	0.19	0.946	0.165	0.18	12.5

^aNot included in calculating the mean because there is a possible error while adjusting the rate to the 010-090° sector.

Table 18. Atmospheric flux of Na and Mg to the North Atlantic Ocean
(R/V Trident samples)

Station No.	Samples	Date	Location	Flux		Mg/Na	Wind Speed miles/hour
				Na ^c ($\text{g} \times 10^{-12}$)	Mg ^c ($\text{cm}^{-2} \text{sec}^{-1}$)		
1	TR1-TR2	6/24-25/75	37.46N-69.24W 35.27.7N-67.3W	53.6	6.81	0.13	27.0
2	TR3-TR4	6/25-27/75	35.2N-67.2W 31.54N-64.51W	5.65	0.632	0.11	16.0
3	TR5-TR6	6/27-29/75	32.03.6-67.2W 32.10.6N-64.4W	3.80	0.513	0.14	12.0
4	TR10	7/3-6/75	28.38N-64.3W 29.42N-64.55W	3.40 [*]	0.408	0.12 [*]	13.0
5	TR11	7/6-8/75	30.18:9N-65.32W 33.46N-66.56W	35.4 [*]	4.25	0.12 [*]	10+25 ^b
6	TR13 ^a	7/10-11/75	38.39N-69.40W 41.19N-71.18W	52.6 [*]	6.31	0.12 [*]	22.0
7	TR14	7/10-11/75	" "	51.6 [*]	6.20	0.12 [*]	22.0

a-0.025 cm rain shower collected. Sample represents a total fallout.

b-Within the last 24 hour of experiment the mean wind speed reached 25 m/h.

*-Na calculated from the Mg data using the 0.12 Mg/Na ratio

c-Precision is $\pm 20\%$.

Table 19. Deposition velocities for atmospheric Na and Mg

Sample	V_g, Na cmsec ⁻¹	V_g, Mg cmsec ⁻¹	Wind Speed miles/hour	Sample	V_g, Na cmsec ⁻¹	V_g, Mg cmsec ⁻¹	Wind Speed miles/hour
L17	5.1	4.8	12.0	S/L 30	0.84	2.3	12.8
L21	4.1	8.2	12.0	S/L 31	0.94	1.0	15.7
L22	1.8	4.9	11.0	S/L 33	2.8	4.2	7.3
L25	-	-	12.0	S/L 35	1.6	2.8	15.5
L29	3.3	4.8	12.6	S/L 40	4.5	4.2	17.7
L42	2.8	2.1	8.2	S/L 41	0.89	1.9	7.0
L43	7.3	4.8	12.0	S/L 45	2.5	2.5	20.6
L44	1.0	1.5	8.8	S/L 46	0.89	1.2	10.9
Mean _L	3.6	4.4	-	S/L 47	1.1	1.3	8.3
	±2.1	±2.1		S/L 48	0.78	-	7.3
				S/L 49	1.6	1.3	8.4
S24	6.6	5.8	13.9	Mean _{S/L}	1.8	2.6	-
S27	2.7	3.3	26.0		±1.1	±1.4	
S34	1.1	1.9	8.5	C 26	2.5	4.3	14.8
S36	2.2	1.7	7.4	C 31	0.88	0.73	15.7
S38	6.7	5.3	9.0	C 35	1.7	1.2	15.5
S39	3.8	4.6	14.0	C 40	4.5	4.0	15.0
Mean _S	3.9	3.8	-	C 47	0.84	-	7.0
	±2.3	±1.7		C 49	1.5	0.69	9.5
S/L14	1.7	5.2	13.7	Mean _C	2.0	2.2	-
S/L15	1.8	2.0	12.3		±1.4	±1.8	
				Mean	2.4	3.0	-
				L+S+S/L+C	±1.6	±1.6	

where:

L = "land" samples

S = "marine" samples

S/L = "mixed" samples

C = "corrected-to-marine" samples

R/V TRIDENT
CRUISE #169
6/22 - 7/11, 1979

Figure 6. R/V Trident Cruise #169, sampling stations.

2. Rainfall Samples

Similar to dry fallout and atmospheric samples, rainfall data were categorized into 3 different classes designated (S) "marine", (S/L) "mixed" and (L) "land" samples depending on the wind direction during sampling. The rain depth in cm, the concentration of Na and Mg in mg/l, the total deposition in $\mu\text{g}/\text{cm}^2$, the Mg/Na ratio and the mean wind speed for each rainfall sample and for each category of rain samples were given in Table 20-22. Intercepts, slopes and correlation coefficients obtained from least square linear regression analysis used for each category of samples, to evaluate the relationship between wind speed and the concentration of Na and Mg in rain water, are also given (Table 20-22).

Table 20. Na and Mg in "marine" rain samples

Sample	Date	Sample Type	h cm	Na mg/l	Mg	Na Total deposition/ μg/cm ² . rain	Mg deposition/ μg/cm ² . rain	Mg/Na	Wind Miles/hour
S3	12/15/75	TM	0.25	3.28 ±0.328	0.370 ±0.037	0.819 ±0.082	0.098 ±0.01	0.12	7.60
S6	12/30-31/75	TM	1.4	0.613 ±0.086	0.074 ±0.023	1.02 ±0.109	0.125 ±0.013	0.12	5.50
S23	5/12/76	TM	2.7	2.82 ±0.460	0.379 ±0.039	6.02 ±0.982	0.809 ±0.089		
S28	5/7/	TM	0.45	1.75 ±0.050	0.300 ±0.00	0.795 ±0.033	0.136 ±0.00	0.17	11.7
S32	5/11/12/76	TM	0.87	0.920 ±0.092	0.133 ±0.010	0.801 ±0.080	0.116 ±0.009	0.14	10.5
S37	5/17/76	RA	1.8	0.600 ±0.060	0.100 ±0.010	1.05 ±0.105	0.179 ±0.018	0.17	9.10
S39	5/19/76	RA	0.35	1.50 ±0.500	0.250 ±0.025	0.493 ±0.175	0.082 ±0.009	0.17	9.00
S63	6/19/20/76	RA*	0.43	3.00 ±0.300	0.410 ±0.041	0.974 ±0.097	0.133 ±0.013	0.14	11.9
Mean	-	-	1.1 ±0.88	1.62 ±0.77	0.238 ±0.140	1.70 ±2.07	0.248 ±0.294	0.15 ±0.018	10.0± 2.42
Slope	-	-	-	1.87±0.70	14.3±4.7	-	-	-	-
Int.	-	-	-	7.04±1.29	6.66±1.26	-	-	-	-
Corr. Coeff.	-	-	-	0.77	0.81	0.46	0.48	-	-

T = Total fallout, R = Rainfall

M = Manually collected sample; A = samples collected using the automatic rain dry fallout collector

* Thunderstorm

Sample 53 was not included in the calculation of the mean and regression analysis.

Form of regression equation:

$$\text{wind} = (\text{slope} \times \text{rain concentration}) + \text{intercept}$$

Table 21. Na and Mg in "mixed" rain samples

Sample	Date	Sample Type	h cm	Na mg/l	Mg	Na Total deposition $\mu\text{g}/\text{cm}^2$ rain	Mg Total deposition $\mu\text{g}/\text{cm}^2$ rain	Mg/ Na	Wind Miles/hour
S/L18	4/24-26 76	TM	1.03	1.23 ± 0.057	0.224 ± 0.000	1.19 ± 0.059	0.216 ± 0.00	0.18	20
S/L41 ^a	5/21/ 76	RA*	0.520	0.900 ± 0.100	0.200 ± 0.020	0.504 ± 0.056	0.112 ± 0.011	0.22	11
S/L53	6/1-2/ 76	RA*	1.45	0.380 ± 0.040	0.060 ± 0.006	0.509 ± 0.051	0.080 ± 0.008	0.16	13.3
Mean	-	-	1.0 ± 0.466	0.837 ± 0.429	0.161 ± 0.089	0.759 ± 0.437	0.141 ± 0.079	0.19 ± 0.03	14.8 ± 4.68
Slope	-	-		6.78	21.1	-	-	-	-
Int.	-	-		9.09	11.4	-	-	-	-
Corr. Coeff.	-	-		0.621	0.400	-	-	-	-

T = Total fallout, R = Rain

M = Manually collected sample; A = Sample collected using the automatic rain dry fallout collector

* Thunderstorm

a Thundershower occurred within one hour (15:00-16:00) on 5/21.

Table 22. Na and Mg in "land" rain samples

Sample	Date	Sample Type	h cm	Na mg/l	Mg	Na Total deposition ug/cm ² rain	Mg	Mg/ Na	Wind Miles/hour
L4	12/17/ 75	TM	1.4	1.92 ±0.010	0.260 ±0.010	1.03 ±0.043	0.143 ±0.003	0.14	14.0
L13	4/16/ 76	RA	0.25	0.650 ±0.065	0.350 ±0.035	0.163 ±0.016	0.086 ±0.009	0.53	12.0
L16	4/22 - 23/76	RM	0.35	1.00 ±0.060	0.300 ±0.010	0.350 ±0.021	0.105 ±0.004	0.30	13.3
L19	4/26-27 76	RM	0.08	0.380 ±0.040	0.200 ±0.020	0.029 ±0.003	0.015 ±0.002	0.52	15.0
L20	4/27-28 76	RM	0.30	0.250 ±0.046	0.046 ±0.003	0.075 ±0.014	0.014 ±0.001	0.18	13.4
L47	5/27/ 76	RA*	0.04	2.00 ±0.200	0.440 ±0.044	0.085 ±0.009	0.019 ±0.002	0.22	8.0
Mean	-	-	0.40 ±0.50	1.03 ±0.763	0.266 ±0.135	0.289 ±0.380	0.064 ±0.055	0.315 ±0.171	12.6 ±2.46
Slope				-1.79	-12.8	-	-	-	-
Int.				14.5	16.0	-	-	-	-
Corr. Coeff.	-	-	-	-0.553	-0.703	0.277	0.257	-	-

T = Total fallout

R = Rainfall

M = Manually collected samples

A = Samples collected using the automatic rain-dry fallout sample

* Thunderstorm occurred only within 5 minutes.

Form of regression equation:

$$\text{wind} = (\text{slope} \times \text{rain concentration}) + \text{intercept}$$

IV. DISCUSSION

A. The Rate and Processes of Removal of Atmospheric Sea Salt

1. Dry Removal of Atmospheric Sea Salt

- a. The rate of dry fallout and atmospheric concentrations of Na and Mg for samples collected in the "marine", "mixed" and "land" subenvironments of the Coastal R.I. environment

The means of the rates of dry fallout in $\text{gx}10^{-12}/\text{cm}^2/\text{sec}$ and atmospheric concentration in ug/m^3 for Na and Mg collected in the 3 subenvironments of coastal R.I. environment are shown in Table 23.

Values obtained from "corrected to marine" samples are also included. As expected, these data indicates clearly that the ocean is the major source of atmospheric Na and Mg in coastal Rhode Island.

Sea salt particles produced by bubbles bursting at the ocean surface are carried by the prevailing winds in the atmosphere. Since they have residence

Table 23. Summary table for rain and dry fallout samples collected in coastal Rhode Island*

Sample Type	Mean Rate of dry fallout		Mean Mg/Na	Mean Mean Atmospheric conc.		Mean Mg/Na	Mean conc. of rainfall		Mean Mg/Na
	Na ($\text{gm} \times 10^{-12} / \text{cm}^2 \text{sec}$)	Mg		Na ($\mu\text{g} / \text{m}^3$)	Mg		Na (mg / l)	Mg	
Marine	3.58	0.573	0.16	1.24	0.177	0.17	1.62	0.238	0.15
Corrected-to-marine	2.83	0.579	0.20	2.41	0.426	0.18	-	-	
Mixed	1.11	0.318	0.30	0.786	0.151	0.22	0.837	0.161	0.19
Land	0.260	0.215	1.1	0.055	0.042	0.79	1.03	0.266	0.32

* For standard deviations of the mean see individual data tables.

times of a few minutes to a few days depending upon their size, (Junge, 1963), they are ultimately removed from the atmosphere by dry fallout and rainfall to the ocean surface, coastal areas and some smaller fraction to inland zones. The higher dry removal rates and atmospheric concentrations shown for "mixed" samples compared to "land" samples is due to the marine fractions in these samples. This is clearly demonstrated by the fact that "corrected-to-marine" samples show values comparable to marine samples.

The correlation coefficients for the rates of dry fallout or atmospheric concentration for Na or Mg versus wind speed are above 0.80 for the "marine" samples category (Table 12). These are significant correlations at the 1% level, i.e. a 99% probability that a real correlation exists between these variables (Fisher 1958). A plot of wind speed versus the atmospheric concentrations and wind speed versus the rate of dry fallout for Na and Mg are shown in Fig. 7-8 respectively. The regression equations for the resulting lines obtained in Fig. 7 and Fig. 8 are:

Atmospheric concentrations ($\mu\text{g}/\text{m}^3$) versus wind speed (miles/ hour)

$$\text{Wind}_{(S)} = 5.5 \times \text{Na} + 6.0 \quad (4)$$

$$\text{Wind}_{(S)} = 50 \times \text{Mg} + 4.1 \quad (5)$$

Rate of dry fallout ($10^{-12} \text{gcm}^{-2} \text{sec}^{-1}$) versus wind speed (miles/hour)

$$\text{Wind}_{(S)} = 2.0 \times \text{Na} + 5.1 \quad (6)$$

$$\text{Wind}_{(S)} = 15 \times \text{Mg} + 4.1 \quad (7)$$

The intercepts in these equations represent the wind speed in miles/hour at which Na and Mg rate of dry fallout or atmospheric concentration are equal to zero. This zero Na or Mg intercept may be explained as the minimum wind speed above which white caps (which produce the atmos-

Figure 7. Atmospheric Na and Mg concentration vs. wind speed ("marine" samples).

Figure 8. Na and Mg rate of dry fallout vs. wind speed ("marine" samples).

pheric sea salt) are formed on the ocean surface. However, the approximate speed of 5 miles/hour (2.2 meters/sec) calculated from equations 4-7 appears too low for this. According to the Beaufort wind scale white caps begin to form at wind speeds of 8-12 miles/hour.

G. Hoffman (1971) measured the concentrations of atmospheric particulate Na as a function of wind speed over the ocean in Hawaii. He determined a zero atmospheric Na intercept of ~ 5.5 miles/hour. Hoffman explained the low value of the intercept as due to the presence of residual atmospheric sea salt caused by the "lag time" associated with the production and/or the removal of maritime sea salt at a given wind speed. He pointed out that sea salt present in the marine atmosphere, at any time, at wind speed less than 8-12 miles/hour is residual sea salt produced previously at a higher wind speed.

Blanchard (1963) discussed the problem of attaining a steady state of atmospheric sea salt particles at a given wind speed. A steady state for a given wind force will be attained only if the wind blows at the same speed for a period of time equal or exceeding the average residence time for the smallest particle in the air-borne sea salt size spectrum.

The correlation coefficients for the Na and Mg rate of dry fallout versus wind speed for "land" samples are 0.75 and 0.60 respectively. These correlation coefficients are significant at the 2% and 5% level respectively (Fisher, 1958). Fig. 9 shows the plot of the Na and Mg rate of dry fallout versus wind speed for "land" samples. Since the Na and Mg in these samples are primarily of crustal origin ($Mg/Na = 1.1$; Mg/Na in the earth's crust = 1.0, (Riley and Chester 1971), it is likely that the higher the wind force over land the more crustal

Figure 9. Na and Mg rate of dry fallout vs. wind speed ("land samples").

Na and Mg particles become suspended in the atmosphere. The regression equations for the resulting straight lines shown in Fig. 9 are:

Dry fallout (10^{-12} g/cm²sec) versus wind speed (miles per hour)

$$\text{Wind}_{(L)} = 9.6 \times \text{Na} + 9.0 \quad (8)$$

$$\text{Wind}_{(L)} = 12 \times \text{Mg} + 9.0 \quad (9)$$

The zero Na and Mg intercepts in these two equations at 9 miles/hour may be interpreted as the minimum wind speed above which significant quantities of soil and crustal weathering particles are lifted into the atmosphere by the wind. Since we do not know the particle size and residence time of these particles, it is not possible to determine accurately whether the question of "lag time" discussed earlier is also involved here. However, since the Beaufort scale indicates that wind raises dust on land at speeds of 13-18 miles/hour, the low intercepts may also be due to "lag time" and equilibria between production and/or removal of these particles and the wind speed.

As indicated in Table 13 no significant correlation was observed between the atmospheric Na or Mg in "land" samples and the wind speed. This is probably because there are no atmospheric concentration samples available for the sampling periods which have the two highest rates of dry fallout and wind speeds.

As expected, "mixed" samples showed intermediate values between "marine" and "land" samples for the mean rates of dry fallout and atmospheric concentrations of Na and Mg and for the Mg/Na ratios (Table 14). It is apparent that the bulk of Mg and Na in these samples is derived from the ocean with the rest primarily contributed by the crustal weathering products. Linear least square regression analysis for this category of samples showed that the only significant

correlation (1%) was between Na dry fallout and wind speed. The correlation coefficient between Mg dry fallout and wind speed is significant at only the 10% level i.e. (90% probability that a real correlation exists, Fisher 1958).

In an attempt to look at these marine fractions of "mixed" samples, the "mixed" samples were "corrected-to-marine" as described in Chapter III (Table 15). Linear least square regression analysis showed that correlations between the corrected rates of dry fallout, corrected atmospheric Na and Mg with corrected wind speeds were very significant (1% level). The linear regression equations for wind speed versus the Na and Mg rate of dry fallout and atmospheric concentrations can be derived from the slopes and intercepts given in Table 15.

For atmospheric concentrations ($\mu\text{g}/\text{m}^3$) versus wind speed (miles/hour)

$$\text{Wind}_{(C)} = 2.2 \times \text{Na} + 10. \quad (10)$$

$$\text{Wind}_{(C)} = 11 \times \text{Mg} + 11 \quad (11)$$

For the rates of dry fallout ($10^{-12} \text{g}/\text{cm}^2 \text{sec}$) versus wind speed (miles/hour)

$$\text{Wind}_{(C)} = 2.7 \times \text{Na} + 4.9 \quad (12)$$

$$\text{Wind}_{(C)} = 8.6 \times \text{Mg} + 8.2 \quad (13)$$

If we compare these equations with equations 6,7,8 and 9 derived for "marine" samples, it seems that only the Na/wind equations are comparable to each other. It is interesting, however, to observe that for the combined "marine" and "corrected-to-marine" samples significant correlations were observed between both dry fallout and atmospheric concentrations versus wind speed for both Na and Mg (see Table 16). This suggests that the assumptions behind the calculation of the "corrected-to-marine" rates of dry fallout and atmospheric concentration

for Na and perhaps Mg may be valid. A plot of wind speed versus the atmospheric concentrations and wind speed versus the rate of dry fallout for Na and Mg in the "marine" plus "corrected-to-marine" sample populations combined are shown in Figs. 10-11.

b. "Mixed" samples collected within the 010-090° wind sector

Although samples collected within the wind sector 010-090° are essentially "mixed" samples, they appear to show a different trend than the rest of the samples. Since they merit special discussion they are listed separately in Table 17. As shown, it seems that the rates of dry fallout and atmospheric concentrations of Na and Mg in these samples are not related to wind speed. Although the wind speeds recorded while sampling these samples were quite variable, the differences in the rate of dry removal and atmospheric concentrations are negligible. As can be seen from the map of sampling sectors (Fig. 5), wind blowing within the sector 010-090° can be considered to bring marine air masses which have travelled over land for ~150 kilometers (100 miles). The constancy of the rate of dry fallout and atmospheric concentration of Na and Mg and their non-dependence on wind speed may suggest that the decrease in the rate of dry removal and atmospheric concentrations of sea salt as we go inland is not continually linear. It is likely that most of the sea salt produced by the ocean is removed very rapidly and is primarily deposited in the coastal zones. Sea salt particles of smaller size and longer residence time are possibly carried further inland. As shown in Table 17, the mean rate of Na dry fallout for samples collected in this sector is $\sim 1.5 \times 10^{-12} \text{ g/cm}^2 \text{ sec}$ at a mean wind speed of 12.5 miles/hour. If

Figure 10. Atmospheric Na and Mg concentration vs. wind speed ("marine" and "corrected-to-marine" samples).

Figure 11. Na and Mg rate of dry fallout vs. wind speed ("marine", "corrected-to-marine" and Trident samples).

we use equation 6 to calculate the rate of Na dry fallout at the coast at this wind speed ($\sim 3 \times 10^{-12} \text{ g/cm}^2 \text{ sec}$), it appears that the rate of Na dry fallout has dropped by a factor of ~ 2 within the 150 Km (100 miles) distance from the coast. If we assume that the wind did not change speed and the air masses were not modified meteorologically during their travel from the coast to the sampling site, the mean lifetime of the larger sea salt particles may be estimated very roughly as ~ 8 hours or less.

c. Samples collected aboard R/VTrident

Out of the total number of samples collected aboard R/VTrident over the northwest Atlantic, dry fallout rates calculated for 4 samples were $\sim 50 \times 10^{-12} \text{ gNa/cm}^2 \text{ sec}$ and for 3 samples were $\sim 3-6 \times 10^{-12} \text{ gNa/cm}^2 \text{ sec}$ (see Table 18). The former group of samples were collected at a mean wind speed of 24 miles/hour, while the latter set of samples were collected at a wind speed between 12-16 miles/hour. It appears, however, that the high flux values obtained from the first set of samples were due to contamination with bow generated sea spray. Since these samples were collected while the ship was moving, sea spray contamination was unavoidable, especially near the bow of the ship where the samples were collected. During the collection of the second group of samples, the sea surface was not as rough. Since the rate of dry fallout calculated from these latter samples agree well with those calculated from "marine" samples collected at the coastal Rhode Island site, it appears that the relationship established between the rate of dry fallout and wind speed for "marine" and "corrected-to- marine" samples collected at the Narragansett Bay Campus of U.R.I. also holds true for the open North Atlantic ocean and possibly the world's oceans.

d. The Mg/Na ratios

The mean Mg/Na ratio of 0.16 for "marine" samples approaches the

sea water ratio of 0.12. The excess Mg is possibly due to vertical mixing of the air masses with consequent addition of crustal Mg from continental sources. This probably happens when the marine air masses enter coastal areas. This explanation is further supported by the Mg/Na ratios observed for samples collected aboard R/VTrident over the North Atlantic Ocean (Table 18). The mean Mg/Na ratio calculated from 3 samples where both Mg and Na were analysed was found to be 0.126, very close to the sea water ratio of 0.12. On the other hand "land" samples showed a mean Mg/Na ratio of 1.1 for the dry fallout and 0.79 for the atmospheric samples (Table 13). This is almost identical to the 1.0 Mg/Na ratio in the earth crust (Riley and Chester 1971). This suggests that the major fraction of the Mg and Na in these samples is of crustal origin.

As expected "mixed" samples showed an intermediate Mg/Na ratio ($\sim 0.2-0.3$) between the "marine" and "land" samples. Since this is considerably closer to the sea water Mg/Na ratio than the crustal Mg/Na ratio, it suggests that the source of the main bulk of the Na and Mg in these samples is the ocean.

As described earlier the mean Mg/Na ratio observed for samples collected aboard R/VTrident was found to be almost identical to the sea salt ratio. Since these samples were collected at a mid-ocean location, where contamination of the marine aerosol with crustal particles is minimal, this suggests that there is little chemical fractionation of sea salt Mg in the marine environment. Several investigators have reported that the Mg and other alkali and alkaline earth metals are enriched relative to Na in sea salt aerosols due to chemical fractionation of these particles when they are produced by bubbles

bursting at the sea surface (eg. see Sugawara et al. 1949; Koyama and Sugawara 1953, Oddie 1960, Komabayasi 1962, Chesselet et al., 1972, Buat-Menard et al., 1974). This subject was reviewed recently by Duce and Hoffman (1976); Hoffman et al., (1977). Observed enrichment of Mg and other alkali and alkaline earth metals relative to Na in environmental samples was found to result from the addition of non-sea salt particles, particularly crustal particles to these samples.

e. Deposition velocities for particulate Na and Mg

The mean deposition velocities (V_g) calculated from the 3 different subenvironments of Rhode Island coast and "corrected-to-marine" samples are 2.4 ± 1.6 cm/sec for Na and 3.0 ± 1.6 cm/sec for Mg (Table 19). Cawse et al. (1972, 1974) determined V_g for Na to range from 0.21-3.4 cm/sec.

2. Wet Removal of Atmospheric Sea Salt

a. Rainfall collected from different wind sectors

Out of the 17 rain showers collected during this project, 8 were classified as "marine", 6 were "land" and 3 were "mixed", depending on the wind direction during the rainfall. The mean concentrations of Na and Mg in rain water and the mean amounts of Na and Mg deposited in $\mu\text{g}/\text{cm}^2$ for each subenvironment are given in Tables 20, 21, 22 and summary Table 23. As shown by these data most of the Na and Mg removed by rainfall originated in the ocean (see Tables 20, 21, 22). When the Na concentration and the total amount of rainfall are considered, more sea salt is removed by "marine" and "mixed" rain than by rain occurring when the wind is blowing off land. As would be expected linear least square regression analysis between wind speeds and concentrations of Na and Mg in rainfall showed significant correlations

for "marine" rains and no significant correlation for "land" and "mixed" rain showers. A plot of wind speed versus Na and Mg concentrations in "marine" rain is shown in Fig. 12 . The regression equations for the resulting lines are:

$$\text{Wind}_{(R)} = 1.9 \times \text{Na} + 7.0 \quad (14)$$

$$\text{Wind}_{(R)} = 14 \times \text{Mg} + 7.0 \quad (15)$$

Since these rains are marine in origin the 7 miles/hour intercepts may again be considered as the minimum wind speed above which sea salt production occurs at the ocean surface. Since white caps are formed at wind speed between 8-12 miles/hour, in the open ocean, the low intercept of 7 miles/hour may be a result of the "lag time" between production and removal of atmospheric sea salt. This concept was discussed earlier for atmospheric particulate Na and Mg concentrations and dry fallout.

The Na or Mg concentration in "marine" and "mixed" rains in mg/l, showed an inverse relationship with the rain depth in cm (Fig. 13-14). Since this relationship appears to be logarithmic, it appears washout processes may occur at the very beginning of the rain shower and may be completed very rapidly. After the completion of washout, the effect of rain is essentially dilution. This relationship was not noticed for "land" rain.

The depth of rainfall (Table 20-22), h , in cm, is measured by a standard plastic rain gauge. The amounts of rain represented by h are sometimes higher than the amounts collected by the plastic buckets. This is apparently due to evaporation of the rain water in the latter collectors. The mean depth of rainfall for "marine" and "mixed" rain

Figure 12. Na and Mg concentration in rainwater vs. wind speed ("marine" rain).

Figure 13. Na concentration in rainwater vs. rain depth.

samples was about 1.0cm, while the mean was only 0.4 cm for land rainfall. This is likely due to the higher quantities of moisture associated with "marine" air.

b) Selective removal of sea salt aerosol by rainfall

Table 23 presents the mean Mg/Na ratios calculated for rainfalls collected for each of the 3 meteorological subenvironments on the Rhode Island coast. Also shown are the mean Mg/Na ratios observed for dry fallout samples collected within these subenvironments. The mean Mg/Na ratio in "marine" rainfall samples is 0.15, similar to the Mg/Na ratio observed for "marine" dry fallout samples. These values approach the sea salt ratio of 0.12. The small quantity of excess Mg is possibly due to the inclusion of Mg of crustal origin. It is interesting, however, to note that the Mg/Na ratios in "mixed" and "land" rain samples, 0.19; 0.32, are lower than their counter parts in dry fallout samples, 0.30 and 1.1 respectively. This may suggest preferential wet removal or washout of sea salt Na and Mg relative to crustal Na or Mg. However, if we assume that during rainout Mg and Na are selectively consumed in the sea salt ratio (Martens et al., 1973), and that dry fallout samples are equivalent only to the fraction of Na and Mg collected by raindrops during washout, then the net Mg/Na ratio in rain water (a result of rainout and washout processes) must be lower than its counterpart of dry fallout in the "mixed" and "land" subenvironments.

B. Geochemistry of Atmospheric Sea Salt

1. Significance of Wet Removal (rain) of Sea Salt Relative to Dry Deposition in the Coastal Environment of Rhode Island

The mean rate of dry fallout and the mean rate of rainfall removal for Na and Mg were calculated from the total population of samples collected at the coastal Rhode Island site between 4/15/76 and 6/28/76 (Table 24). As shown, if we compare the mean rate of wet removal (rain) of Na and Mg to the mean rate of dry removal during that period of time, it appears that equivalent amounts of Mg were removed by rainfall and dry fallout and 1.3 as much Na was removed by rainfall. Since some of the manually collected rainfall samples, especially those collected at inconvenient times, possibly contained a small fraction of dry fallout, the ratio of wet removal (rain) to dry removal of atmospheric Na and perhaps sea salt is possibly close to one in the coastal environment of Rhode Island. Although this ratio was calculated from samples collected during only one quarter of the year, we will assume for subsequent calculations that the same ratio holds for the entire year. Although only 10.6 cm of rain fell on the Rhode Island coast during the sampling period between 4/15/76 - 6/28/76, lower by a factor of two than the amount expected from the mean annual rain depth of 107 cm (National Weather Service Station, Warwick), it is possible that these rains contained higher sea salt concentrations than the average rains. As shown in Fig. 13-14, the concentrations of Na or Mg in rain water are inversely proportional to the depth (or volume) of rain.

2. Sea Salt Yearly Removal Over the World Oceans

In order to estimate the rates of wet and dry removal and the annual removal rates of sea salt over the world's oceans, the mean

rates of dry fallout and rainfall were calculated from the "marine" and "corrected-to-marine" samples as well as samples collected aboard RV/Trident (Table 24). The mean wind speed at which all these samples were collected is approximately 13 miles/hour (5.5 m/sec.) (Table 16). Assuming an annual oceanic rain depth of 100 cm (Baumgartner and Reichel, 1975) and a mean Na concentration of 1.6 mg/l, (Table 20), the rate of Na wet (rain) removal from the atmosphere is $5.1 \times 10^{-12} \text{ g/cm}^2 \text{ sec}$, equivalent to $17 \times 10^{-12} \text{ g sea salt/cm}^2 \text{ sec}$. If we compare this figure to the mean rate of dry fallout of $3.3 \times 10^{-12} \text{ gNa/cm}^2 \text{ sec}$ or $11 \times 10^{-12} \text{ g sea salt/cm}^2 \text{ sec}$, it appears that, over the ocean, approximately two thirds of the atmospheric seasalt returns to the ocean in precipitation and approximately one third as dry fallout (Table 24).

If we use the sea salt dry and wet removal rates and integrate over the entire area of the world's oceans, then the total annual removal rate of cyclic sea salt at a mean wind speed of $\sim 20 \text{ Km/hour}$ is approximately $30 \times 10^{14} \text{ g/yr}$. Approximately 2/3 of this is removed by rainfall and the rest by dry fallout (Table 24). The $30 \times 10^{14} \text{ g sea salt/yr}$ removal rate determined is higher by a factor of 3 than the estimates made by Eriksson (1959) and is approximately one third the value obtained by Blanchard (1963) (Table 24).

3. Significance of Atmospheric Removal of Sea Salt Over the Coast of Rhode Island

If we compare the mean rate of Na wet and dry removal on the coast of Rhode Island for all sampling conditions with those for the marine environment (i.e. "marine" samples only) (Table 24), it appears that the amounts of sea salt deposited by rainfall and dry fallout per unit area on the coast of Rhode Island is approximately

Table 24. Geochemistry of Cyclic Sea Salt
Na and Mg

Location	Mean Rate of Dry Fallout $\text{gx}10^{-12}/\text{cm}^2\text{sec}$	Mean Rate of Wet (rain) Removal $\text{gx}10^{-12}/\text{cm}^2\text{sec}$	Wet Removal Dry	Estimated Reference Global Removal Rate(sea salt) $\text{gx}10^{14}/\text{yr}$	
"Land" (R.I.)	0.26 (Na)	2.45 (Na)	9		This work (1978)
"Marine" (R.I.)	3.30 ± 1.86 (Na) 0.57 ± 0.37 (Mg)	5.1 ± 2.4 (Na) 0.76 ± 0.44 (Mg)	1.5 ± 1.1 1.3 ± 1.2		"
All Samples (R.I.)	1.5 ± 1.6 (Na) 0.36 ± 0.22 (Mg)	2.0 ± 1.4 (Na) 0.40 ± 0.21 (Mg)	1.3 ± 1.7 1.1 ± 0.9		"
<hr/>					
<u>Sea Salt!</u>					
"Marine" (R.I.)	11 ± 6	17 ± 8	~ 1.5	30	This work (1978)
Florida, Caribbean Hawaii*	5.5	5.5	~ 1	10	Eriksson (1959)
Hawaii*	5.1	9.6	~ 2	100	Blanchard (1963)
Continents	-	-	-	3	Livingstone (1963)
Continents (R.I.)	0.85	8.0	9	2.2	This work (1978)

* calculated for the open ocean

! sea salt calculated from Na by multiplying by 3.25

40% as much as the amounts, per unit area, removed over the ocean.

4. Atmospheric Removal of Na and Mg Over Land

The Na and Mg analysed in "land" samples collected in coastal Rhode Island are essentially of crustal origin as shown by their Mg/Na ratios discussed earlier. Although the wind direction was off land during the collection of these samples it is possible that a fraction of the Na and Mg in these samples originated in the sea. In this respect these samples resemble the aerosol at inland and continental environments, where a small fraction of the aerosol Na and Mg is of oceanic origin, and the main bulk originated in the earth's crust. This small fraction of sea salt particles reaching mid-continent area are usually of smaller size and have longer residence times than the salt particles over the ocean.

Taking all this into consideration one can attempt to estimate tentatively the yearly removal rate of Na and Mg over the continents. The rate of dry and wet removal of Na over land is given in Table 24. The rate of Na wet removal was calculated from a mean "land" rain concentration of 1.03 mg/l and an annual rain depth of 75 cm (Baumgartner and Reichel, 1975). If we compare these rates of removal to the rates of removal over the oceans and take into consideration the fact that land area constitute only 25% of the earth's surface, it seems that only 2% of the total sea salt removed by dry fallout over the earth, is deposited on land and 12% of the total sea salt removed by rainfall is deposited over land. The total amount of salt, calculated from the Na data removed over land would be $\sim 2.2 \times 10^{14}$ g/yr. This is $\sim 8\%$ of the yearly global removal rate. Since a fraction of the Na and Mg in "land" samples is of crustal origin, and because the Rhode Island

coast is not really representative of mid-continent areas, even when the surface winds are not off the ocean, this estimate of 2.2×10^{14} g/yr represents a maximum value for the amount of sea salt removed annually over land. Livingstone (1963) calculated that the annual global input of cyclic salt Na from river runoff into the ocean is approximately 10^{14} g/yr, equivalent to a total salt content of $\sim 3 \times 10^{14}$ g/yr, near the estimate above.

V. CONCLUSIONS

The rates and processes of removal of atmospheric sea salt from the marine and Rhode Island coastal atmosphere to the earth surface have been investigated. Samples collected at a Rhode Island coastal site appear to represent 3 meteorologically different subenvironments depending on the surface wind direction during sampling. These 3 subenvironments, which when superimposed represent the coastal environment of Rhode Island have been designated "marine", "land", and "mixed", the latter a mixture of the first two.

Dry fallout, rainfall and atmospheric particulate samples collected in this study were analysed for Na and Mg using atomic absorption spectrophotometry. The rate of dry fallout and wet (rain) removal of atmospheric sea salt from the coastal Rhode Island "marine" subenvironment, showed a direct relationship with wind speed. Also the rate of Na dry fallout for samples collected while the wind was off land appears to be dependent on the magnitude of wind speed. Dry fallout samples collected aboard R/VTrident over the North West Atlantic Ocean gave Na and Mg rates of dry removal comparable to the values obtained from "marine" samples collected at the coastal R.I. site. Dry deposition velocities for particulate Na and Mg, calculated from samples collected on the Rhode Island coast, were 2.4 ± 1.6 cm/sec for Na and 3.0 ± 1.6 cm/sec for Mg.

The Na or Mg concentration in "marine" and "mixed" rains showed an inverse logarithmic relationship with the rain depth in cm. Comparison between the mean Mg/Na ratios in dry fallout samples with rainfall samples collected in the 3 subenvironments of coastal R.I. indicate that rainfall more efficiently removes sea salt aerosols relative to

crustal particles.

Rainfall and dry deposition are the major processes for global atmospheric removal of cyclic sea salt. The annual global removal rate of atmospheric sea salt was estimated as $\sim 3.0 \times 10^{15}$ g/yr, higher by a factor of 3 than an estimate made by Eriksson (1959), and lower by a factor of 3 than the value calculated by Blanchard (1963). It is estimated that $\sim 2/3$ of the total cyclic sea salt is removed by rainfall and the rest by dry deposition. Less than 2.2×10^{14} g/yr of cyclic sea salt ($\sim 7\%$ of the total) is removed over land by rainfall and dry deposition. Rainfall is 9 times as important as dry deposition over land.

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