A Study of the Composition of Marine Atmospheres

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Abstract

Data on trace substances in air, obtained in mid-Pacific during two summers, are summarized. Particulate matter was analyzed for chloride, sulfate and nitrate; tests were performed for ozone, nitrogen dioxide, sulfur dioxide and carbon monoxide. The results give information concerning the composition of marine air which can assist in evaluating possible natural contributions to urban pollution on the West Coast of the United States during the summer months, in addition to the geochemical value of the work.

1. Introduction

In spite of a substantial effort presently under way in determining the composition of polluted atmospheres in cities, little effort has been expended on the study of natural levels of pollutants in influent air, or on the contribution of nature to the overall pollution complex of cities. The state of our knowledge with regard to gaseous pollutants of natural origin has recently been reviewed by ALTSHULLER (1958). Studies of the composition of marine aerosol have been made, among others, by WOODCOCK (1949, 1950, 1952, 1953), JUNGE (1953, 1954, 1956, 1957), TWOMEY (1954), LODGE (1955), and by BYERS, SIEVERS, and TUFTS (1957). These, however, were made for special purposes, and do not contain the information necessary, in most cases, to evaluate the specific contribution of marine aerosols to urban pollution. Probably the most useful studies in this connection have been made by the group in Sweden (EGNÉR AND ERIKSSON, 1955, and quarterly reports by a variety of authors in *Tellus*), who have analyzed both precipitation and air for a number of substances using samples from a dense network of stations covering the Scandanavian peninsula and extending into contiguous portions of Europe and Britain. It may be questioned, however, to what extent these stations ever sample unpolluted air. The National Air Sampling Network (Public Health Service, 1958) now provides particulate analyses from a number of nonurban sites, but these are subject to the same doubt.

In 1956, the U. S. Public Health Service and the Department of Public Health, State of California, undertook a series of joint studies of the composition of air at coastal sites in the State of California (HOLZWORTH, 1959; HARRISON and LODGE, 1959). Even at these sites, considerable evidence was obtained of man-made contamination. Accordingly, plans were made to take measurements from Weather Station November, the weather ship maintained by the U. S. Weather Bureau and the Coast Guard at

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Table 1. Techniques used in air quality measurements in mid-ocean.

Substance	Technique		Reference
	1957	1958	
Oxidant (ozone)	20 % KI (a)		Hagen-Smit, private communication
		Phenolphthalin	McCabe, 1953
		Rubber cracking	Bradley and Haagen-Smit, 1951
		Brewer-Mast ozone recorder	A. W. Brewer, unpublished work
Nitrogen dioxide	Modified Griess reagent	Modified Griess reagent	Saltzman, 1954
Sulfur dioxide	Tetrachloromercurate method	Tetrachloromercurate method	West and Gaeke, 1956
Carbon monoxide		Indicator tubes (Mine Saftey Appliances)	Shepherd, 1947
Particulate matter	"High-Volume" sampler wiht glass filter	"High-Volume" sampler with both cellulose and glass filters	Public Health Service, 1958

(a) Data invalidated by photolysis of reagent.

a position approximately midway between San Francisco and Honolulu (latitude 30°N, longitude 140°W).

Two separate series of measurements were made. The first set spanned the period from 27 July to 13 August 1957, during which time the station was manned by the USCGC Gresham. The second set of samples was taken during the duty period of the USCGC Taney, from 31 July to 28 August 1958. Measurements were made of oxidant, nitrogen dioxide, sulfur dioxide, carbon monoxide and of particulate chloride, sulfate, nitrate and organic material.

2. Experimental

Some different techniques were used during the two seasons of operation. The sampling sites were in general on boat deck level; they were moved as necessary to avoid contamination from stacks, ventilators, etc. Table I outlines the basic techniques used in the two years. The analytical methods for gases were checked, and the reagents were prepared and calibrated by the Air and Industrial Hygiene Laboratory, Department of Public Health, State of California. The particulate analyses were performed in part by that laboratory and in part by the laboratories of the National Air Sampling Network, Air Pollution Engineering Research, U. S Public Health Service. The analytical methods used at both laboratories were in the main those of the National Air Sampling Network (Public Health Service, 1958). The Air and Industrial Hygiene Laboratory also performed the interpretation of the rubber cracking determinations.

3. Results

Nitrogen dioxide levels were found to be below the limit of detection (0.1 pphm) of the method used 94 percent of the time. Only a single value above 0.5 part per a hundred million (pphm) was measured. Only five of the 32 carbon monoxide measurements (16 percent) showed any detectable reaction, and these were estimated to correspond to values below 1 part per million (ppm). Though determinations of carbon monoxide in this concentration range are highly inaccurate, it is estimated that concentrations above 0.2 ppm can be detected. Detectable amounts of sulfur dioxide (>0.01 pphm) were found in 42 percent of the samples, though 91 percent lay below 0.5 pphm. Seven values were above 1 pphm, with a maximum value of 4.6 pphm. The occasional high values of the first two gases are almost certainly traceable to contamination from the ships. It is less certain that the sulfur dioxide levels measured are entirely caused by local sources. JUNGE (1957) measured concentrations of sulfur dioxide of the order of 0.03 pphm in marine air; the bulk of the non-zero values lay in this range.

The first year's oxidant data were rejected when it was shown that they were confounded by photolysis of the reagent during the sampling

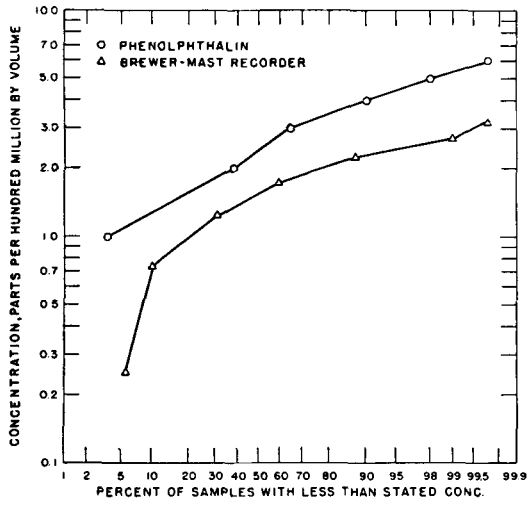

Fig. 1. Cumulative frequency distributions of oxidant in mid-Pacific by two methods, August 1958.

period. Data for the second year are summarized in Figure 1. Roughly the expected ratio was found between the values given by the Brewer-Mast recorder, a potassium iodide instrument, and the phenolphthalin method (RENZETTI and ROMANOVSKY, 1956). While no attempt has been made to prove the logarithmico-normal distributions suggested by Figure 1, it is clear that the two measures give very similar distributions of values. It will also be noted that no concentrations were obtained in excess of 7 pphm by phenolphthalin. The absence of any higher values, while not conclusive, makes it seem likely that the high levels measured on offshore islands by HARRISON and LODGE (1959) were caused by urban sources, or at least by the influence of land.

Rubber cracking determinations were inconclusive. There was no clear correlation between measured crack rates and ozone level as measured by either technique. It appears that the uncertainty in the cracking measurements exceeds the total span of measured ozone levels. The mean rate of cracking for samples exposed for 24 hours was 0.245 mm $hr.^{-1}$.

The particulate analyses are summarized in Figure 2. Separate plots of the two years' data showed them to have similar dispersion, so they have been lumped. Nitrates were measured only on the 1958 samples. Several points are noteworthy. Nitrates were in general an order of magnitude less than chloride, in accordance with the findings of JUNGE (1956). Rather more surprising is the fact that sulfate levels tend to be higher than chloride, in contrast to the roughly seven-fold excess of chloride over sulfate in sea water. ERIKSSON (1959) has noted that the total cyclic sulfate must be of the same order of magnitude as the chloride, and suggests that the "excess" sulfur may escape from the sea as gaseous hydrogen sulfide. While these data give no direct evidence in this matter, they should substantially exclude urban sources as major contributors to the overall sulfate levels measured.

Benzene soluble organic compounds were determined on a few samples. The mean level was approximately 1.6 $\mu g/m^{-3}$. A rough calculation shows that this loading could be accounted for by assuming a monolayer of organic matter on the surface of the sea at the point of formation of the aerosol.

4. Conclusions

All gases measured, except ozone and possibly sulfur dioxide, have in nature normal levels below the limit of detection by the present instrumentation. Ozone levels in mid-ocean are variable; during the period under study, they ranged from 1 to 7 pphm by phenolphthalin or

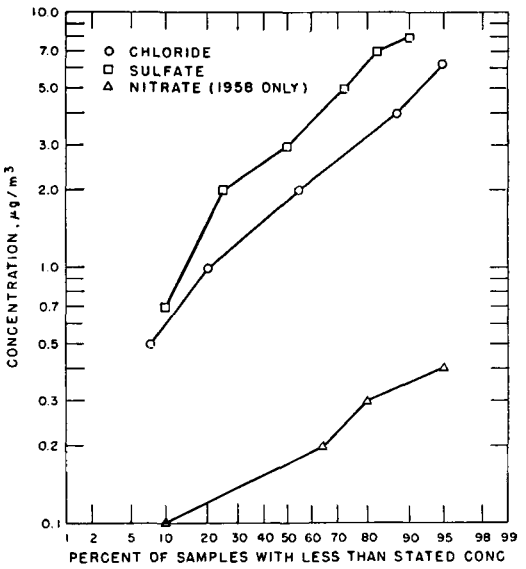

Fig. 2. Cumulative frequency distributions of particulate species.

from 0.25 to somewhat over 3 pphm by potassium iodide. No regular diurnal variation was apparent.

In the particulate state, sulfate levels were somewhat higher than chloride, and nitrate was an order of magnitude less. Organics were low, at a concentration which could be accounted for by the pickup of a monolayer on sea-spray droplets.

A reasonably good measure of natural levels of "pollutants" was obtained for the summer season in mid-Pacific. Further work will be necessary to determine whether there is any marked seasonal variation.

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