NOTES

Measurements of Transformations in the Physical and Chemical Properties of Clouds Associated with Onshore Flow in Washington State[1]

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ABSTRACT

Preliminary measurements of several physical and chemical parameters associated with clouds in two cases of onshore flow over western Washington suggest that the physical and chemical properties of maritime, cloudy air passing over this region change over relatively small spatial and temporal scales (~100–200 km, and 5–15 h, respectively). These scales are similar to those for changes in precipitation chemistry in this region. This tentative conclusion concerning the scales for air mass changes differs from the assumption usually made concerning air mass characteristics and transport distances in the eastern United States.

1. Introduction

The problems of acid deposition and long-range transport of potentially acidic pollutants have heightened interest in the chemical transformations that take place in clouds and air masses as they pass through pollutant source regions (e.g., Pack, 1979). The chemical composition of precipitation has been shown to depend on the previous trajectory of the air mass, and, in particular, whether or not it has passed over any major sources of pollution (Miller *et al.*, 1978; Wilson *et al.*, 1982). Here we are concerned with the temporal and spatial scales over which the physical and chemical properties of relatively clean maritime air masses are converted into those that are more typical of polluted continental air. We also address the question: Is the spatial scale over which the composition of cloud water is modified similar to that for the chemical modification of precipitation, or is precipitation more strongly influenced by the composition of the boundary layer? While definitive answers to questions such as this will require large-scale field studies, we have recently undertaken some preliminary field measurements that provide some information on the time and spatial scales for the chemical modification of clouds and air masses as they move eastward from the Pacific Ocean into the western portion of Washington State.

2. Instrumentation and experimental procedures

All of the measurements to be described were obtained from the University of Washington's B-23 research aircraft. The instrumentation aboard this aircraft has been described by Hobbs *et al.* (1976), Hegg and Hobbs (1980) and Radke (1982).

The measurements relevant to the present studies were particulate Cl^-, NO_3^- and $SO_4^=$ concentrations in the air (derived from ion chromatographic analysis of filter samples exposed from the aircraft), cloud condensation nucleus (CCN) activation spectra, particle size distributions, cloud droplet size distributions, and the concentrations of Cl^-, NO_3^- and $SO_4^=$ in cloud water samples collected from the aircraft.

The procedure was to sample clouds and clear air from just off the Pacific Coast of Washington State through the Puget Sound Basin of Washington during onshore flow. Two such studies were undertaken. In the first, the aircraft sampled air and clouds offshore and then, by means of doppler wind measurements aboard the aircraft and real-time analysis of synoptic data relayed to the aircraft from the University of Washington, the trajectory of this parcel of air was determined and the aircraft continued to sample it at selected intervals as it passed over western Washington. This constitutes Lagrangian-type sampling. In the second case, air and cloud sampling was carried out at selected points successively farther inland during a prolonged period of relatively steady on-shore flow in western Washington. This constituted a hybrid Lagrangian–Eulerian type sampling procedure, since the aircraft proceeded from one sample point to the next much faster than the motion of an air parcel but obviously not instantaneously. From the point of view of studying physical and chemical transformations, such a sampling procedure can only be justified under the assumption of steady-state flow. The windflow patterns for the two cases are shown in Figs. 1 and 2.

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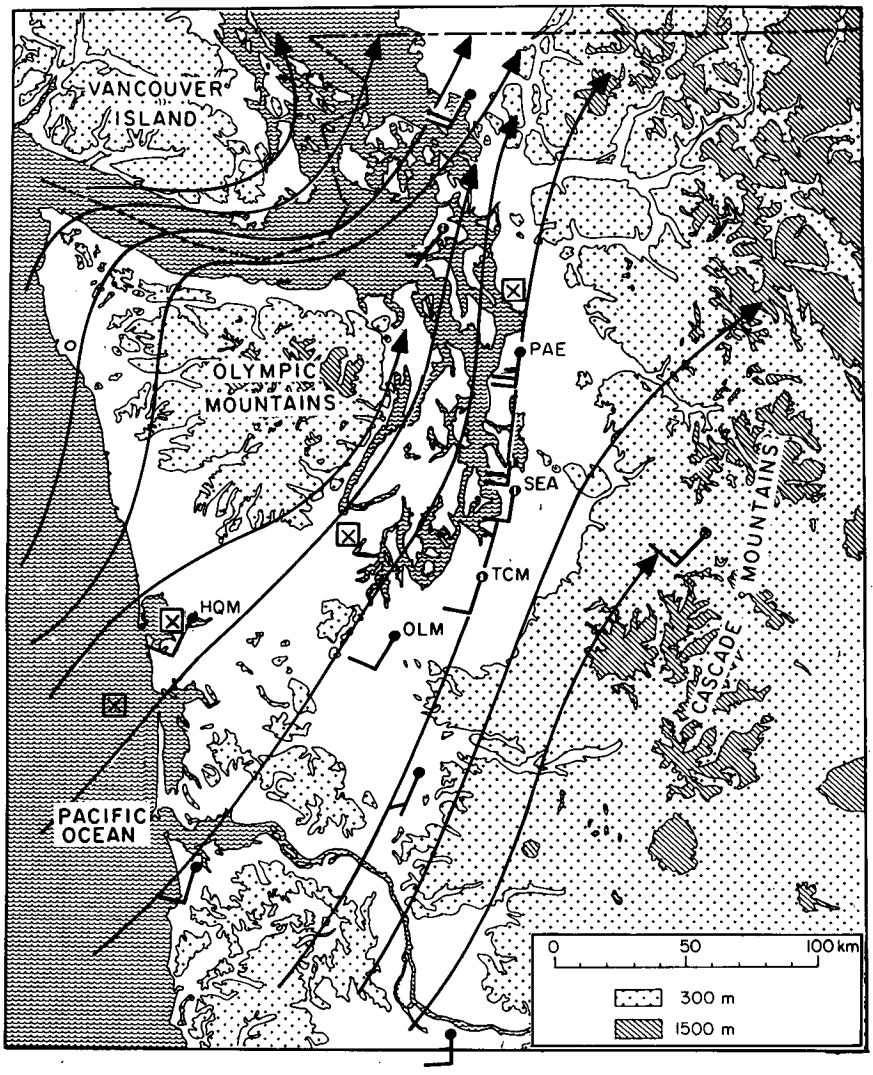

FIG. 1. Windflow field (streamlines) during the flight of 10 March 1983. The synoptic wind observations at 1000 LST are shown. Points at which the air and clouds were sampled from the aircraft are indicated by crosses within squares. In consecutive order from left to right, the sampling locations were: Offshore, Hoquiam, Shelton and Everett. The windbarbs on the chart represent windspeeds of 5 and 2.5 m s^{-1} for full and half-barbs, respectively.

3. Results and discussion

a. Physical measurements

Since we are primarily interested in the changes in the properties of clouds that might affect precipitation, we examine here the evolutions of the cloud condensation nucleus (CCN) spectra and the cloud droplet size distributions as a function of distance inland from the Pacific Coast of Washington.

The measurements of CCN spectra were fitted to an expression of the form (Twomey, 1959):

$$N = cS^k, \tag{1}$$

where N is the number concentration of CCN active at a supersaturation S (%) and c and k are fitted parameters. The results are shown in Table 1. The parameters indicate that for the case of 10 March 1983 the CCN spectrum changed from that typical of maritime air to that more typical of continental air (Twomey, 1959) by the time the air parcel had reached Shelton, some 90 km (and roughly 5 h travel time for an air parcel) from the Pacific coast. The CCN spectrum measured at Everett (near the center of the Puget Sound urban-industrial area) has a k value that is typical not merely of continental air but of polluted air.

The measurements obtained on 1 June 1983 are more ambiguous. While the CCN spectrum shifted from maritime to continental in character between Cosmopolis and Olympia (110 km from coast and ~12 h travel time for an air parcel from coast), the

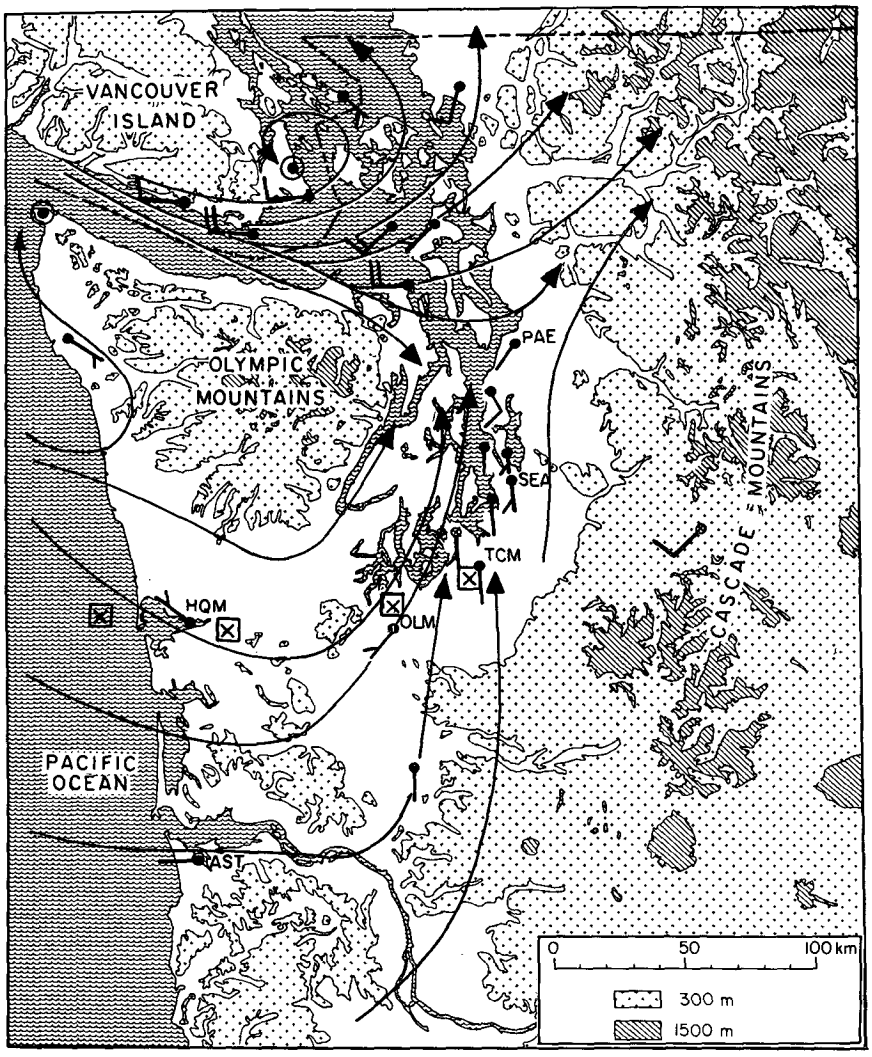

FIG. 2. Windflow field (streamlines) during the flight of 1 June 1983. The synoptic wind observations at 0800 LST are shown. Points at which the air and clouds are samples from the aircraft are indicated by crosses within squares. In consecutive order from left to right, the sampling locations were: Offshore, Cosmopolis, Olympia and McChord AFB. Wind barbs as in Fig. 1.

spectrum measured even farther inland over McChord AFB (140 km and ~15 h travel time) was less continental in character than that measured over Olympia. This anomaly may have been due to cloud processing and precipitation scavenging of the air sampled near McChord, since showers were present. Also, since the flow pattern on 1 June was not as well defined as that on 10 March, the air parcel sampled at McChord on 1 June could have had a substantially different history from that sampled at Olympia. Indeed, it is quite conceivable that the travel time from the coast to the sampling site was less for the McChord parcel than for the Olympia parcel. In any case, the McChord site (with its ostensibly larger travel time from the coast) has been selected for comparison with the marine measurements since we wish for a conservative estimate of the minimum travel time and distance scale for significant transformation of the marine air mass.

The cloud droplet size spectra measured just off the Pacific Coast and at Shelton on 10 March 1983 are shown in Fig. 3. The Shelton site was selected for comparison because it was the site closest to the coast at which the CCN spectrum became markedly continental. Comparison of the two spectra reveal that the total droplet concentrations increased (from 40 to 130 cm^{-3}) and the mean droplet diameter decreased during the passage of the air parcel inland. This is consistent with the CCN spectra. It shows that the cloud microstructures had become fully continental in character after roughly 5 h of travel inland from the coast.

Similar modifications occurred on 1 June (Fig. 4), although, as previously noted, the time scale in this

TABLE 1. Values of c and k fitted to Eq. (1) at various sampling points over western Washington. The locations where the samples were taken are shown in Figs. 1 and 2.

Date (1983)	Location	Distance from coast* (km)	Altitude (km)	c**	k**	Correlation coefficient (r^2) for fit to Eq. (1)
10 March	Over ocean	20	0.33	82	0.74	0.89
10 March	Hoquiam	5	0.33	599	0.76	0.93
10 March	Shelton	90	0.49	569	1.34	0.85
10 March	Everett	185	1.05	892	3.45	0.84
1 June	Cosmopolis***	10	0.30	177	0.78	0.97
1 June	Olympia	110	0.60	670	1.64	0.48
1 June	McChord AFB	140	0.53	513	0.78	0.99

* Along the airflow trajectories.
** The supersaturation range over which c and k were determined was 0.1 to 2.0%. Four points were used for each fit.
*** Due to an instrument malfunction, an offshore CCN spectrum was not obtained on this flight. However, the Cosmopolis spectrum should be quite similar to an entirely marine spectrum.

case was considerably longer and less certain than for 10 March.

The important point revealed by these measurements is that the modification of several physical parameters relevant to cloud microstructures and precipitation formation, occur over relatively short spatial and temporal scales as clouds move from the ocean over land.

b. *Chemical measurements*

Feeley and Liljestrand (1983) and Liljestrand and Morgan (1981) noted systematic increases in the ratio of NO_3^- to $SO_4^=$ and NO_3^- to Cl^- in rainwater collected at the ground at inland sites compared to coastal locations on the Texas Gulf Coast and the Los Angeles Basin, respectively. The increase in the ratio NO_3^-/Cl^- can reflect not only a gain of (essentially anthropogenic) NO_3^- relative to background levels but also a loss of Cl^- due to incorporation of either $SO_4^=$ or the NO_3^- itself into aerosol particles or cloud droplets (Robbins *et al.*, 1959; Martens *et al.*, 1973, Hitchcock *et al.*, 1980). Thus, the $NO_3^-/SO_4^=$ ratio is probably a more reliable indicator of changes in chemical composition associated with air mass modification. The magnitude of this change should be a strong function of the strength and density of the sources of nitrogen and sulfur over which the air mass is moving. For example, the data of Feeley and Liljestrand reveal an increase in the mass ratio of $NO_3^-/SO_4^=$ in rain of less

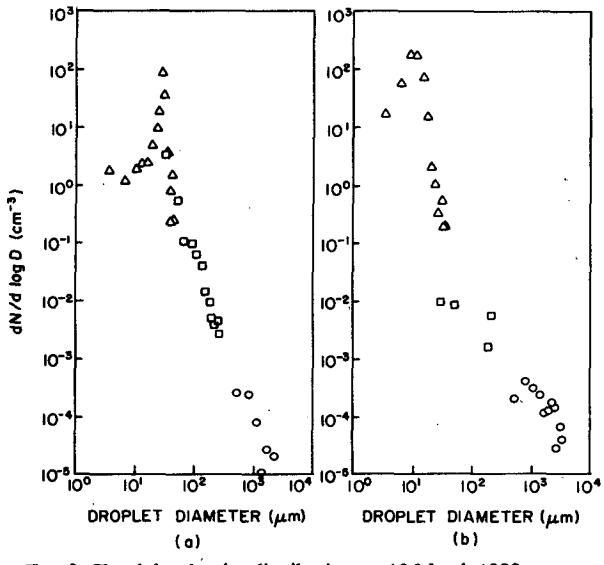

FIG. 3. Cloud droplet size distribution on 10 March 1983 measured (a) offshore over the Pacific Ocean, and (b) 90 km inland from the coast (over Shelton) on 10 March 1983. The clouds were cumuliform. The square data points were obtained with a PMS FSSP, the triangles with a PMS OAP-200X, and the circles with a PMS OAP-200Y.

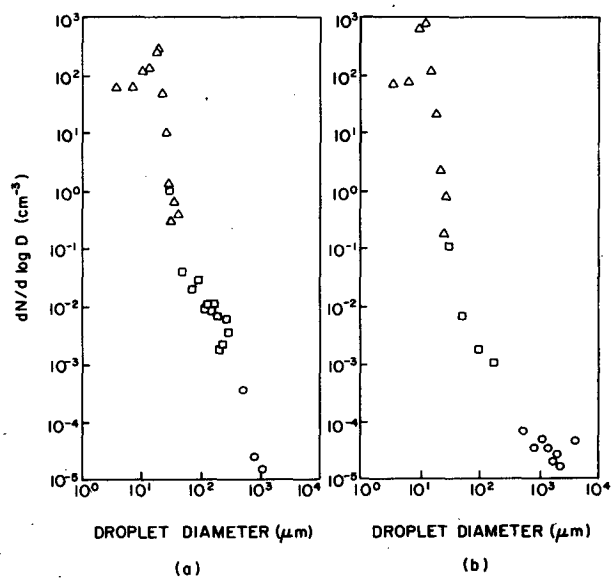

FIG. 4. Cloud droplet size distribution measured on 1 June 1983 (a) in an offshore stratus cloud (10 km offshore) and (b) in a stratus cloud 140 km inland from the ocean (over McChord AFB). Symbols as in Fig. 3.

than a factor of 3 over the roughly 190 km trajectory between the Gulf Coast and Austin, Texas. On the other hand, the Liljestrand and Morgan data reveal an increase in the same ratio of approximately a factor of 7 over the 130 km distance from the Pacific Coast to Big Bear (at the easterly end of the Los Angeles Basin). Nevertheless, marine and continental air masses show distinct values of the ratio $NO_2^-/SO_4^=$. Data from Amsterdam and the Bermuda Islands (Galloway *et al.*, 1982) and for the Catalina and Santa Maria Islands (Liljestrand and Morgan, 1981) show $NO_3^-/SO_4^=$ in rain ratios that are generally <0.25. On the other hand, even remote continental sites, such as Poker Flat, Alaska, (Galloway *et al.*, 1982) or the Amazon Basin (Stallard and Edmond, 1981), show rain $NO_3^-/SO_4^=$ > 0.3. As for more polluted areas, data from the Northeastern United States show this ratio to be >1 (Pack, 1980). Recent measurements taken in clouds at White Face Mountain (New York) show this trend to be true for a particular site experiencing passage of various air masses (R. Pueschel, private communication, 1983). The limited data available for western Washington State support this trend. Measurements taken on the Hoh River, near the Washington Coast, show a $NO_3^-/SO_4^=$ ratio of 0.22, whereas, in and downwind of Seattle the ratio is 0.4 to 0.5 (Vong and Waggoner, 1983).

Of course, all of the ratios cited here are based on long-term (annual or greater) averaged data and thus are long-term means. Considerable deviation from these means can obviously be expected on shorter time scales. However, the data of Liljestrand and his colleagues point out the essentially systematic, geographic variation in the $NO_3^-/SO_4^=$ ratio and it is this systematic variation for which we shall be examining our data.

We turn now to our airborne measurements in western Washington. Values of the mass ratios of $NO_3^-/SO_4^=$ and NO_3^-/Cl^- in cloud water and in clear air and the pH values of the cloud water are shown in Table 2 for the flights of 10 March 1983 and 1 June 1983. The cloud water pH shows relatively small change with distance inland from the coast. Indeed, for the case of 1 June, the pH between the coast (Cosmopolis) and McChord AFB did not change at all, although the overall anionic composition changed markedly. Clearly, neutralizing cations, as well as acidic anions, were incorporated into the cloud water as it passed over the land, although we did not directly measure such cations. Asman *et al.* (1982) have shown that precipitation from maritime and continental air can exhibit concurrent increases in both acidic anions and neutralizing cations.

For the case of 10 March, the $NO_3^-/SO_4^=$ ratio of the cloud water initially decreased with the passage of the air mass onshore. We attribute this to relatively high levels of biogenic sulfur from the extensive tidal flats of Grays Harbor (Hitchcock *et al.*, 1980). Subsequently the ratio increased, and at Everett it was substantially higher than the ratio of $NO_3^-/SO_4^=$ (0.5) for precipitation at ground level in Everett (Vong and Waggoner, 1983).

On 1 June 1983, the $NO_3^-/SO_4^=$ mass ratio increased monotonically with distance in land from the coast but it did not reach the annual average values for precipitation in the Puget Sound Basin.

Perhaps the most important point illustrated by the trends shown in Table 2 is that the chemical composition of the cloud water shifted from that characteristic of maritime air to that characteristic of continental air over the same spatial (~100/~200 km) and temporal (~5–15 h) scales as the chemical composition of precipitation changes with distance inland from the Pacific Coast.

4. Conclusions

This preliminary investigation suggests that certain physical and chemical characteristics of cloudy, mar-

TABLE 2. Mass ratios of $NO_3^-/SO_4^=$ and NO_3^-/Cl^- in cloud water and clear air for samples collected in western Washington on 10 March 1983 and 1 June 1983.

Date (1983)	Location*	pH of cloud water	NO_3^- cloud water (ppm)	Content of NO_3^-/Cl^-** for cloud water	Content of $NO_3^-/SO_4^=$** for cloud water	$NO_3^-/SO_4^=$** for clear air
10 March	Offshore	~4.0	0.35	0.31	0.24	0.50
10 March	Hoquiam	4.1	1.2	0.12	0.16	—
10 March	Shelton	4.4	1.3	0.15	0.26	—
10 March	Everett	4.3	2.2	0.38	0.96	—
1 June	Offshore	4.0	2.2	0.20	0.14	0.22
1 June	Cosmopolis	4.5	2.8	0.30	0.20	0.36
1 June	Olympia	4.5	1.3	0.24	0.33	—
1 June	McChord AFB	4.5	4.3	0.86	0.34	—

* See Table 1 for distance from coast and altitude of measurements.
** The uncertainty associated with each ratio is estimated to be ±10%.

itime air moving across western Washington, change on the same temporal and spatial scales, and that these scales are similar to those previously reported for the changes in the chemical composition of precipitation at the ground in this locale. We estimate these spatial and temporal scales to be on the order of ~100–200 km and ~5–15 h, respectively. These relatively rapid transitions suggest that, at least for coastal regions with substantial precipitation and moderate sources of pollution, such as western Washington, air masses "equilibrate" rather quickly with land sources of pollution, rather than preserving their maritime properties over scales characteristic of long-range transport (the synoptic scale). This tentative conclusion (based on a limited data set) differs from the assumption of long-range transport and air mass compositional stability which is usually made for the eastern United States (Pack, 1979).

Finally, we note that the coincidence of the scales for the chemical modification of clouds and precipitation suggest that cloud processes can, in large part, account for the chemical characteristics of precipitation in western Washington.

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