(11) Lovelock, J. E. *Nature (London)* **1975**, *256*, 193–194.
(12) Bechard, M. J.; Rayburn, W. R. *J. Phycol.* **1979**, *15*, 379–382.
(13) Rasmussen, R. A. *Tellus* **1974**, *26*, 254–259.
(14) Hill, R. B.; Anegja, V. P.; Felder, R. M. *J. Environ. Sci. Health, Part A* **1978**, *A13*, 199–225.
(15) Lovelock, J. E.; Maggs, R. J.; Rasmussen, R. A. *Nature (London)* **1972**, *237*, 452–453.
(16) Nguyen, B. G.; Caudry, A.; Bonsang, B.; Lambert, G. *Nature (London)* **1978**, *275*, 637–639.
(17) Challenger, F.; Higginbottom, C. *Biochem. J.* **1935**, *29*, 1757–1778.
(18) Challenger, F.; Taylor, P.; Taylor, B. *J. Chem. Soc.* **1942**, 48–55.
(19) Barnard, D. Ph.D. Thesis, University of Leeds, U.K., 1947.
(20) Snyder, L. J.; Bentz, J. M. *Nature (London)* **1982**, *296*, 228–229. Ahmad, I.; Chau, Y. K.; Wong, P. T. S.; Carty, A. J.; Taylor L. *Nature (London)* **1980**, *287*, 716–717.
(21) Jarvie, A. W. P.; Whitmore, A. P. *Environ. Technol. Lett.* **1981**, *2*, 197–204.
(22) Henderson, S. R.; Snyder, L. J. *Anal. Chem.* **1961**, *33*, 1172–1175.
(23) Cusack, P.; Smith, P. J.; Donaldson, J. D. *J. Chem. Soc., Dalton Trans.* **1982**, 439–444.
(24) Chow, S. T.; McAuliffe, C. A.; Sybe, B. J. *J. Inorg. Nucl. Chem.* **1973**, *35*, 4349–4354.
(25) Rapsomanikis, S. Ph.D. Thesis, Leicester Polytechnic, U.K., 1983.
(26) Gynane, M. J. S.; Lappert, M. F.; Miles, S. J.; Power, P. P. *J. Chem. Soc., Chem. Commun.* **1976**, 256–257.
(27) Gynane, M. J. S.; Lappert, M. F.; Miles, S. J.; Power, P. P. *J. Chem. Soc., Chem. Commun.* **1978**, 192–193.
(28) Wolborsky, H. M.; Arouoff, M. S. *J. Organomet. Chem.* **1973**, *51*, 31–53.
(29) Hill, E. A. *J. Organomet. Chem.* **1975**, *91*, 123–271.
(30) Huber, F.; Schmidt, Y.; Kirchmann, H. In "Organometals and Organometalloids—Occurrence and Fate in the Environment"; Brinckman, F. E.; Bellama, J. M., Eds.; American Chemical Society: Washington, DC, 1978; ACS Symp. Ser. No. 82, pp 65–82.
(31) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: London, 1978; p 284.

Received for review September 13, 1984. Accepted March 15, 1985. Funding was provided by the Science and Engineering Research Council, London (SERC).

Chemical Composition of Fogwater Collected along the California Coast

Daniel J. Jacob,† Jed M. Waldman, J. William Munger, and Michael R. Hoffmann*

Environmental Engineering Science, W. M. Keck Engineering Laboratories, California Institute of Technology, Pasadena, California 91125

■ Fogwater collected at both urban and nonurban coastal sites in California was found to be consistently acidic. Millimolar concentrations of NO_3^-, and fogwater pH values below 3, were observed at sites downwind of the Los Angeles basin. Fogwater composition at remote sites showed evidence of substantial continental and anthropogenic contributions. Acid-neutralizing capacities in coastal air were found to be very low and insufficient to neutralize even small acid inputs. Chloride loss relative to its sea salt contribution was observed at sites furthest from anthropogenic sources.

Introduction

Recent investigations of fogwater chemical composition in the Los Angeles basin (*1*, *2*) have revealed high concentrations of SO_4^{2-} and NO_3^-, usually associated with very high acidities (pH values typically in the range 2–4). Comparable acidities have been observed in low stratus clouds collected by aircraft over the basin (*3*) and sampled on the slopes of the surrounding mountains (*4*). These high acidities have raised concern regarding potential damage to materials, vegetation (*5*), crops (*6*), and public health (*7*). Laboratory studies have shown that aqueous-phase oxidation of S(IV) to S(VI) can proceed rapidly under the conditions found in fog droplets (*8*) and in the precursor aerosol at high humidities (*9*). Field data suggest that aqueous aerosols are important sites for the conversion of SO_2 to H_2SO_4 in the atmosphere (*10–13*).

Fogs are frequent seasonal occurrences along the California coast. During the summer, coastal stations may report over 50% foggy days (*14*). These fogs are often coupled with land breeze/sea breeze systems, which recirculate the same air parcels several times across the shoreline (*12*). Tracer studies in the Santa Barbara Channel (*15*) have shown that emissions from offshore and coastal sources may reside several days along the coast. These humid, poorly ventilated conditions favor pollutant accumulation and H_2SO_4 production.

As part of an extensive fog sampling program in California, we have collected fogwater at a number of coastal sites. Coastal fogs may be a major cause of sulfate pollution episodes in southern California (*13*). Furthermore, impaction of fog droplets can be an important source of water and chemical loading to the coastal vegetation (*16*); in some cases, fogwater has important local implications for acid deposition. Recent interest in these problems has been stirred by federal plans to encourage oil exploration and production in the outer continental shelf off California (*17*).

Sampling Sites and Methods

Fogwater was sampled at eight coastal sites and one island site (Figure 1). The sites, and meteorological conditions during sampling, are described in Table I. Samples were collected with a rotating arm collector over intervals ranging from 30 min to 2 h. The rotating arm collector, which has been described in detail previously (*18*), collects fog droplets by impaction on a slotted rod rotating at high velocity. Droplets impacting inside the slots flow by centrifugal force to bottles mounted at the ends of the rod. In this way, impacted droplets are immediately sheltered in a quiescent environment, and sample evaporation is prevented (*18*). The rotating arm collector samples air at a rate of 5 m^3 min^{-1}. Model-scale laboratory calibration has indicated a lower size cut (50% collection efficiency) of 20-μm diameter.

A recent intercomparison of fogwater collectors (*19*) has established that our rotating arm collector provides samples that are representative of ambient fogwater. In that study, no significant differences in ionic concentrations were observed between samples collected concurrently with the rotating arm collector and with a jet impactor devel-

†Present address: Center for Earth and Planetary Physics, Harvard University, Cambridge, MA.

0013-936X/85/0919-0730$01.50/0

730-736

Table I. Description of Sampling Sites

site		Conditions during sampling: inversion base,[a] m MSL	temp,[b] °C	surface wind,[b] m s^{-1}
Del Mar	coastal lagoon, residential area, 800 m from shore	surface	11	moderate NW shifting to moderate E
Corona del Mar	residential area; collector set on pier	260	11	calm
Long Beach Harbor	industrial area, ships; collector set on dock, 10 m from water	220	10	calm
Lennox	industrial and residential area; Los Angeles Int'l Airport is 2 km NW, major freeway is 500 m E; ocean is 4 km W; collector set on roof of 1-story building	surface	12 (Dec 7, 1981)	1 NE
		surface	14 (Dec 18, 1981)	1 SE
		220	10 (Jan 7, 1983)	calm
San Nicholas Island	U.S. Navy base, 100 km offshore; no impact from local sources; collector set at 50 m elevation, 400 m from shore	150	14	5 NNW
San Marcos Pass	mountain pass in coastal range, 700-m elevation; no nearby sources	1800	8–15	2 S
Morro Bay	rural town at the base of major power plant; agriculture, ranches; some local traffic; collector set 500 m from shore, on roof of 1-story building	450	11	0–2 SW
Mt. Sutro	250-m elevation hill above San Francisco; radio towers, no local traffic; ocean is 5 km W	570	12	1 W
Pt. Reyes	National Seashore, no nearby sources; collector set at tip of peninsula, 10-m elevation, 50 m from shore	600	12 (Aug 9, 1982)	10–15 N
		420	11–12 (Aug 10, 1982)	10–15 N
		1800	12–14 (Aug 11, 1982)	10–15 N
		240	11–14 (Aug 12, 1982)	2 SE

[a] Base of temperature inversion, measured at San Diego, Los Angeles, Vandenberg AFB, or Oakland. [b] Measured at the site.

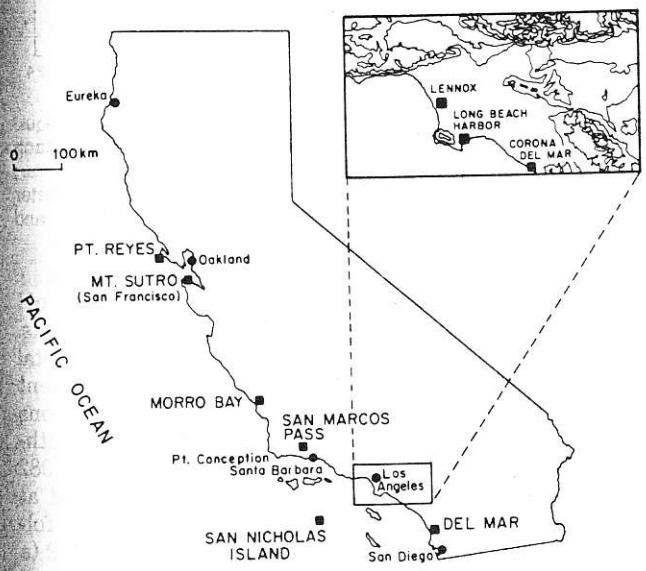


Figure 1. Fogwater sampling sites (■).

oper by the Desert Research Institute, Reno, NV (*20*). Moreover, it was shown that the rotating arm collector provides chemically reproducible samples; no significant differences in ionic concentrations were found between samples collected by two rotating arm collectors set side by side.

Fogwater pH was measured within 10 min of sample collection with a Radiometer PHM 82 meter and Radiometer GK2320C combination electrode. The pH meter was calibrated before each measurement with pH 1.68, 4, and 7 standards. The pH readings were very stable, as would be expected in view of the high ionic strengths of the samples. Major ions and metals were analyzed in our laboratory following previously described protocol (*1*). The standard errors on chemical analyses were about 5% and the detection limits, 1 μequiv L^{-1}, for all ions reported. Detection limits for metals were 1 μg L^{-1}. When the ionic concentrations to be determined were larger than 150 μequiv L^{-1}, the samples had to be quantitatively diluted to bring them within analytical range. Concentrations of Na^+, K^+, Ca^{2+}, and Mg^{2+} were determined by atomic absorption spectroscopy on filtered aliquots; at some sites (Del Mar, Long Beach, Lennox, and Morro Bay), we analyzed both filtered and unfiltered aliquots and did not observe significant differences in concentrations. In samples collected at some urban sites, Cl^- determinations by ion chromatography were subject to positive interference from unidentified peaks eluting just before Cl^-. The interference was substantial when Cl^- concentrations were low; Cl^- concentrations reported are then an upper bound of true Cl^- concentrations and are identified as such. The unidentified peaks were likely due to organic acids (*21*). Formate and acetate at concentrations near 10^{-4} M have been observed by us in inland fogs.

Liquid water content in fog was estimated from the collection rate of the rotating arm collector, assuming that the instrument collects 60% of the incident water. This empirical correction factor of 60%, which is justifiable by the experimental lower size cut of the instrument, leads to liquid water content estimates that are in reasonable agreement (within a factor of 2) with those determined by laser transmissometer and Hi-Vol filter methods (*18*, *19*, *22*). It must be stressed that there is at this time no widely accepted method for measuring liquid water content in fog, and discrepancies by a factor of 2 are commonly observed between different methods (*22*). Estimate of liquid water content from the collection rate of the sampling device presents the advantage of coinciding in time and space with the chemical characterization of fogwater.

The marine, continental, and anthropogenic contributions to the fogwater composition were determined from a source apportionment matrix for primary California aerosol (*23*) (Table II). Because of the relatively small number of elements analyzed and the large spread in elemental concentrations, a stepwise apportionment approach was used instead of the usual least-squares fitting procedure. First, contributions from automobile exhaust and fuel oil fly ash were determined from the concentrations of the Pb and V, which originate almost exclusively from these two sources, respectively. The sea salt con-

Table II. Source Concentrations of Particulate Matter[a]

	% mass				
	sea salt	soil dust	cement dust	fuel oil fly ash	automobile exhaust
Na	30.6	2.5	0.4	5	x[b]
S	2.6	0.1[b]	0.1[b]	15[b]	2[b]
Ca	1.16	1.5	46.0	1.3	0.02[b]
Mg	3.7	1.4	0.48	0.06	x
K	1.1	1.5	0.53	0.2	x[b]
V	10^{-6}[c]	0.006	x[d]	7	x
Fe	10^{-5}[c]	3.2	1.09	6	0.4
Pb	10^{-6}[c]	0.02	x	0.07	40

[a] Data from ref 23 unless otherwise specified. [b] Ref 24. [c] Ref 25. [d] x, negligible.

tribution was then determined from the remaining Na, and from there the cement dust and soil dust contributions were determined from the remaining Ca and Fe. The calculation was iterated if necessary until observed Na and Ca were accounted for to within 5%. No such constraint was placed on the fit to Fe because of the variability of Fe concentrations in soils (*26*); it must be kept in mind that, depending on the actual Fe fraction in soil dust, the determined soil contributions may be substantially off. Similarly, fluctuations of the V content of fuel oil will correspondingly alter the fuel oil fly ash contribution from that given in Table IV. The contribution of secondary SO_4^{2-} was calculated by subtraction of primary contributions from the total SO_4^{2-} concentration. All NO_3^- was assumed to be of secondary origin.

Results and Discussion

Fogwater Concentrations. Table III gives liquid water weighted average fogwater concentrations for each event; the detailed data set is available elsewhere (*27*). Results of the source apportionment are given in Table IV in terms of fogwater loadings, which we define as the mass of material in fogwater per cubic meter of air. Fogwater loadings were obtained by multiplying the fogwater concentrations by the liquid water content of the fog.

In Table V elemental ratios in fogwater are compared to those for sea salt. The observed Na/Mg ratios were close to that for sea salt; exceptions were the Long Beach, Lennox, and San Marcos sites, where sea salt constituted only a small fraction of the total loading and significant soil dust contributions of Na and Mg were apparent. Calcium and sulfate were partly of marine origin but usually had larger contributions from dust (calcium) and secondary production (sulfate). The K/Na ratios were close to that for sea salt at Del Mar, San Nicholas Island, and Pt. Reyes; soil dust was an important source of K at other sites.

The sites in and around the Los Angeles basin were by far the most affected by anthropogenic sources (Table IV). The large contribution from automobile exhaust in the fog samples collected at Lennox can be attributed to the nearby freeway and airport traffic. Fogwater collected at Long Beach Harbor on Jan 6, 1983, had the same NO_3^- loading as fogwater collected at Lennox on the same night, but SO_4^{2-} loadings at Long Beach Harbor were 6 times higher than at Lennox. The SO_4^{2-}/NO_3^- equivalent ratio was 1.9 in fogwater at Long Beach Harbor, compared to 0.2–0.5 values usually observed in the Los Angeles basin (*1*, *2*). Cass (*10*) has shown that SO_4^{2-} concentrations in the Los Angeles basin peak in Long Beach Harbor because of residual oil burning by ships.

The fogs of Dec 7 and Dec 18, 1981, at Lennox and Dec 7, 1983, at Corona del Mar occurred during severe sulfate

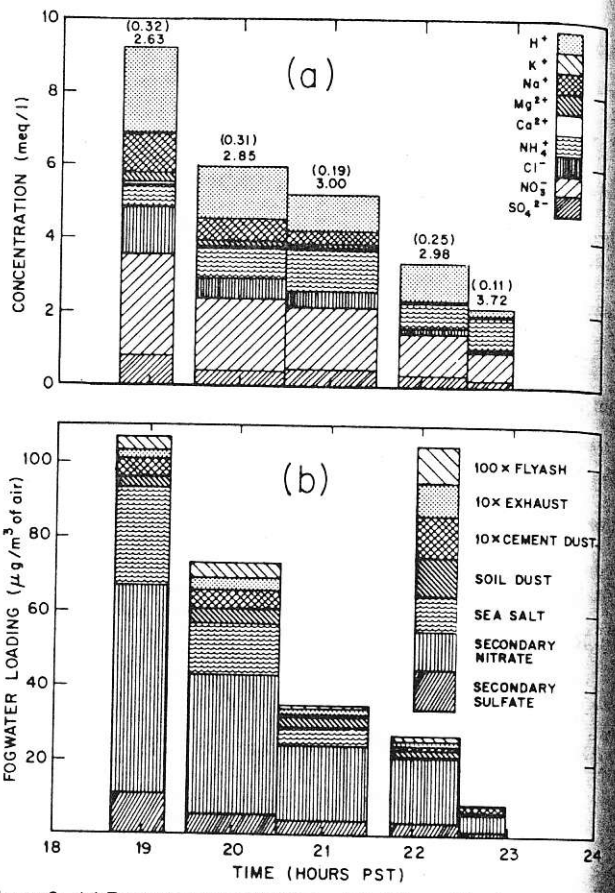


Figure 2. (a) Fogwater concentrations at Del Mar. pH values and liquid water contents (g m^{-3}; in parentheses) are indicated on top of each data bar. (b) Source contributions to the fogwater loading at Del Mar; the fogwater loading is defined as the mass of material in fogwater per cubic meter of air. Contributions from soil dust, fly ash, and exhaust were not determined for the last sample.

pollution episodes in the Los Angeles basin. Fogwater pH values below 3 were consistently observed on those nights. On the day following the Corona del Mar event, all coastal stations of the South Coast Air Quality Management District recorded their highest 24-h SO_4^{2-} concentrations for 1982, ranging from 23 to 37 μg m^{-3}. Prevailing southward transport of pollutants on the night of Dec 6–7, 1982 (*28*), explains the extremely high acidities observed at Corona del Mar; a second sample (1 mL) collected following the first as the fog dissipated had a pH of 1.69 (a value which was later confirmed in the laboratory).

High ionic concentrations and acidities were also found in samples collected at Del Mar on Jan 8, 1983 (Figure 2). NW winds over Del Mar at the beginning of the sampling period carried pollutants from the Los Angeles basin, which had been transported offshore by weak NE winds the previous morning (*29*). Flow was reversed by a developing land breeze between 1900 and 2000 Pacific standard time, and inland air from suburban San Diego County was advected over the site. Sea salt concentrations dropped considerably as the land breeze developed; contributions from anthropogenic sources, and acidities, also decreased as the Los Angeles air was replaced by less polluted air.

Fogwater collected at San Marcos Pass (low stratus), Morro Bay, Mt. Sutro, and Pt. Reyes contained much less NO_3^-, secondary SO_4^{2-}, and automobile exhaust than fogwater collected in the Los Angeles basin or downwind. However, except at Morro Bay, all samples were acidic; fogwater pH ranged from 4.21 to 4.69 at San Marcos Pass and from 3.60 to 5.00 at Pt. Reyes. Significant concen-

Table III. Liquid Water Weighted Average Fogwater Concentrations

site	date[a]	n	L^b	pH	μequiv L^{-1}									n'^c	$\mu g\ L^{-1}$					
					H^+	Na^+	K^+	NH_4^+	Ca^{2+}	Mg^{2+}	Cl^-	NO_3^-	SO_4^{2-}		Fe	Mn	Pb	Cu	Ni	V
Del Mar	Jan 9, 1983, 1840–2300	5	0.24	2.85	1410	511	9	781	49	130	614[d]	1850	469	4	354	36	310	NA	111	6
Corona del Mar	Dec 7, 1982, 2100–2300	1	0.11	2.16	6920	725	71	2860	197	188	1050	7900	1290	0	NA[g]	NA	NA	NA	NA	NA
Long Beach	Jan 6, 1983, 0400–0500	2	0.25	4.90	12.7	62	12	759	45	26	221[d]	252	487	2	96	22	152	NA	17	1
Lennox[e]	Dec 7, 1981, 2305–0840	8	0.30	2.96	1100	65	12	1610	111	42	178[d]	2210	926	8	1440	37	1180	34	10	6
	Dec 18, 1981, 2315–0045	3	0.14	2.66	2190	131	30	1280	127	48	150[d]	2780	1280	3	1330	51	NA	NA	NA	13
	Jan 6, 1983, 0000–0430	5	0.17	3.63	237	41	8	464	39	18	68[d]	365	126	5	315	127	447	NA	25	5
San Nicholas Island	Aug 26, 1982, 2115–0755	7	0.052	3.86	138	6060	148	452	450	1500	5490	1580	2080	5	431	93	49	49	99	9
San Marcos Pass[f]	Aug 20, 1983, 2340–1200	14	0.43	4.49	32.1	10	3	97	3	4	19	74	55	9	22	3	23	12	6	NA
Morro Bay	July 14, 1982, 0500–0900	2	0.14	6.17	0.67	746	64	107	120	221	1200	114	214	1	192	21	11	57	21	3
Mt. Sutro	Aug 13, 1982, 2125–2225	1	0.056	3.99	102	648	52	183	93	170	851	87	319	1	160	10	24	50	28	NA
Pt. Reyes	Aug 9, 1982, 2200–0000	1	0.054	3.60	251	3520	91	327	242	890	3040	526	1280	1	484	67	67	87	209	NA
	Aug 10, 1982, 0230–1115	3	0.081	4.48	33.4	3150	72	95	153	782	4580	38	463	3	276	12	21	36	66	NA
	Aug 11, 1982, 0200–1155	7	0.13	3.88	132	498	12	59	27	118	645	36	208	4	301	10	38	151	59	NA
	Aug 12, 1982, 0340–0815	6	0.19	4.69	20	42	2	43	3	10	57	6	54	5	265	7	26	48	17	NA

[a] Date is that of the a.m. samples or that of the morning following the fog. Time is local time. [b] Average liquid water content (g m^{-3}), calculated from the total volume collected. [c] Number of samples analyzed for metals. [d] Cl^- may be overestimated due to interference from organic acids during analysis. At Del Mar, this uncertainty is significant only for the last three samples (see text). [e] 1981 events at Lennox have been previously reported (*1*). [f] Stratus cloud. [g] NA, not analyzed.

Table IV. Source Contributions to Fogwater Loading

site	mass loading,[a] $\mu g\ m^{-3}$ sea salt	secondary NO_3^-	secondary SO_4^{2-}	soil dust	cement dust	fuel oil fly ash	automobile exhaust
Del Mar	9.0	28	4.5	2.9	0.22	0.023	0.21
Corona del Mar	6.1	54	6.4	–[b]	0.80	–	–
Long Beach Harbor	1.1	3.9	5.8	0.58	0.44	0.0036	0.095
Lennox							
Dec 7, 1981	0.64	30	10	8.7	0.94	0.019	0.62
Dec 18, 1981	1.0	25	8.9	5.7	0.64	0.027	–
Jan 6, 1983	0.50	3.9	1.0	1.8	0.25	0.012	0.20
San Nicholas Island	23	5.2	3.4	0.55	0.41	0.0074	0.0064
San Marcos Pass	0.33	1.9	1.1	0.27	0.043	–	0.023
Morro Bay	7.5	1.1	0.9	0.97	0.55	0.0086	0.0055
Mt. Sutro	2.7	0.30	0.64	0.22	0.16	–	0.0033
Pt. Reyes							
Aug 9, 1982	14	1.8	2.2	0.74	0.21	–	0.0090
Aug 10, 1982	17	0.16	0.29	0.79	0.038	–	0.0034
Aug 11, 1982	5.2	0.28	0.9	1.6	0.017	–	0.014
Aug 12, 1982	0.48	0.074	0.45	1.6	0.0051	–	0.013

[a] Mass loadings defined as the mass of matrial in fogwater per cubic meter of air. Numbers given are averages for each event. [b] Missing data. Contributions from soil dust, fly ash, or exhaust were not determined when the concentrations of their respective tracers (Fe, V, and Pb) were missing.

Table V. Ratios of Equivalent Fogwater Concentrations

site	Mg^{2+}/Na^+	Cl^-/Na^+	Ca^{2+}/Na^+	SO_4^{2-}/Na^+	K^+/Na^+
Del Mar	0.25	1.20	0.096	0.92	0.018
Corona del Mar	0.26	1.45	0.27	1.8	0.098
Long Beach Harbor	0.42	3.6	0.73	7.9	0.20
Lennox					
Dec 7, 1981	0.65	2.7	1.7	14	0.19
Dec 18, 1981	0.36	1.15	0.96	9.7	0.23
Jan 6, 1983	0.43	1.66	0.95	3.0	0.21
San Nicholas Island	0.25	0.91	0.074	0.34	0.024
San Marcos Pass	0.40	1.96	0.33	5.6	0.27
Morro Bay	0.30	1.61	0.16	0.29	0.086
Mt. Sutro	0.26	1.31	0.14	0.49	0.080
Pt. Reyes					
Aug 9, 1982	0.25	0.86	0.069	0.36	0.026
Aug 10, 1982	0.25	1.45	0.049	0.15	0.023
Aug 11, 1982	0.24	1.30	0.054	0.42	0.025
Aug 12, 1982	0.24	1.37	0.063	1.29	0.039
sea salt	**0.23**	**1.17**	**0.043**	**0.12**	**0.021**

trations of metals and non-sea salt (NSS) Ca at all sites show that the air sampled was of partly continental origin even under onshore wind conditions. Fogwater collected at Pt. Reyes under offshore wind conditions (Aug 12, 1983) contained less sea salt, more soil dust, and more automobile exhaust than fogwater collected on other nights under the more usual onshore N–NW wind conditions.

Nitrate and secondary sulfate loadings at San Nicholas Island were higher than those at other nonurban sites, even though impact of Los Angeles pollutants is very unlikely under the type of wind conditions observed on that night. High concentrations of metals and NSS Ca indicated that the air over the island was of mixed marine/continental origin. The high ratio of fly ash to automobile exhaust at that site (as opposed to the Los Angeles samples) suggests that the acid input could have been mostly due to a plume from either oil drilling operations off Pt. Conception or the Morro Bay power plant, advected over the site by NNW winds; dilution of the plume would have been limited by the low mixing height observed on that night and the slow horizontal dispersion over the ocean (*15*). Transport from the Pt. Conception area over San Nicholas Island has been previously documented (*30*).

Acidity of Coastal Fogs in California. Ubiquitous acidic conditions were observed along most of the California coastline. However, the precise origin of the acidity observed at remote sites is difficult to ascertain from the data available. Acidic species can be transported over long distances with slow dispersion along the coast, because of the sea breeze/land breeze circulation system and the persistent temperature inversions which limit vertical mixing (*12*, *15*). In the case of Mt. Sutro and Pt. Reyes the low NO_3^-/SO_4^{2-} ratios observed suggest a source of acidity especially rich in H_2SO_4. Two possible sources are sulfate emitted from residual oil combustion by ships, or oxidation of dimethyl sulfide and other reduced sulfur species volatilized from the ocean surface (*31*, *32*).

Fogwater at remote coastal sites was acidic even though the acid input was small. Obviously, there was little alkalinity available in the coastal air to neutralize acid inputs. The nonneutralized fraction of the acidity, $[H^+]/([NO_3^-] + 2[(NSS)SO_4^{2-}])$, was on the average 25% at San Marcos Pass, 31% at Mt. Sutro, and 48% at Pt. Reyes. Ammonia emitted by agricultural sources was found to be the main acid-neutralizing component at inland sites in California (*33*). An excess of NH_3 (H = 140 M atm^{-1}; K_a = 1.6×10^{-5} M at 10 °C) maintains fogwater pH above 5. Fogwater below pH 5, as found along the coast, supports only a very low NH_3 vapor pressure at equilibrium; under those conditions, NH_3 is expected to be nearly 100% scavenged by the fog droplets. The relatively low NH_3 fogwater concentrations observed at coastal sites (as com-

Table VI. Chemical Equilibria Involving Cl^- Loss in the $NaCl-H_2SO_4-HNO_3-H_2O$ System

no.	reaction	equilibrium constant[a]
1	$HNO_3(g) + NaCl(s) = HCl(g) + NaNO_3(s)$	3.5
2	$2NO_2(g) + NaCl(s) = NOCl(g) + NaNO_3(s)$	2.2×10^3
3	$H^+(aq) + Cl^-(aq) = HCl(g)$	5.6×10^{-7}
4	$H^+(aq) + NO_3^-(aq) = HNO_3(g)$	3.1×10^{-7}
5	$H^+(aq) + SO_4^{2-}(aq) = HSO_4^-(aq)$	7.8×10^1

[a] Equilibrium constants calculated at 298 K from free enthalpies of formation (*39*).

pared to NO_3^- and SO_4^{2-} concentrations) show that alkalinity from NH_3 was lacking in coastal air. Soil dust is an alternate source of alkalinity, but the extent of H^+-neutralizing ion-exchange surface reactions is limited by the small amount of soil dust present in the fogwater (Table IV). These reactions would mostly involve the cations Ca^{2+} and Mg^{2+}, but as mentioned previously we found these ions to be almost totally dissolved. Alkalinity from scavenged soil dust was therefore exhausted.

Volatilization of HCl from Sea Salt Nuclei. Marine aerosols have been observed previously to exhibit Cl^- loss relative to its calculated sea salt contribution. Chloride losses ranging from 0% (no loss) up to 100% (no Cl^- aerosol) have been reported (*34*, *35*). Chloride loss proceeds by incorporation of a strong acid in a sea salt containing aerosol, resulting in pH lowering and volatilization of HCl. The strong acid can be HNO_3 (*34*) or H_2SO_4 (*35*, *36*). Displacement of Cl^- by $NO_2(g)$ on NaCl(s) has also been found to occur (*37*, *38*).

Table VI is a summary of chemical equilibria involving Cl^- loss. Above the deliquescence point, volatilization of HCl is given by the position of equilibrium 3. Both H_2SO_4 and HNO_3 added to a NaCl(aq) aerosol will displace Cl^-, but HNO_3 is less efficient than H_2SO_4 because it is only slightly less volatile than HCl. Hitchcock et al. (*35*) inferred from field data that HSO_4^- does not displace Cl^-; however, equilibria 3 and 5 indicate that HSO_4^- could displace a substantial fraction of Cl^- at the liquid water contents typical of haze ($<10^{-3}$ g m^{-3}).

Although volatilization of HCl proceeds effectively in acidic haze, consideration of equilibrium 3 indicates that HCl is not volatilized in neutral or acidic fog. This is due to the high liquid water content of fogs and to the lower acidities of fog droplets as compared to the smaller haze droplets. If Cl^- were lost in the precursor aerosol, it should still be recovered in the fog by scavenging of HCl(g). Chloride deficiency with respect to its sea salt contribution in the fog therefore implies either that diffusion-limited scavenging of HCl(g) by the fog droplets did not proceed to completion or that the HCl(g) volatilized from the precursor aerosol was removed from the air parcel during transport before droplet activation.

The fogs sampled in our study were acidic, and Cl^- loss from the precursor aerosol would be expected. However, measured Cl^- concentrations were in excess of the sea salt contribution at most of our sites; this would be due to either anthropogenic sources of Cl^- or interference of organic acids with Cl^- in analysis. Significant Cl^- loss (>10%) was observed in one sample from Del Mar (18%), all samples from San Nicholas Island (12–35%), and four samples from Pt. Reyes (10–28%). Therefore, Cl^- loss was observed in the fogwater only at those sites where a long residence time over the ocean was involved. Transport may have led to separation of HCl(g) from the nuclei; one way this could occur is if HCl(g) was removed to the ocean surface faster than aerosol Cl^-. Kritz and Rancher (*40*) have reported deposition velocities over the ocean surface of 0.4 cm s^{-1} for aerosol Na and 0.8 cm s^{-1} for gaseous inorganic Cl.

Conclusion

Fogwater samples collected at both urban and nonurban sites along the coast of California were consistently acidic. Substantial continental and anthropogenic influences were determined at remote coastal sites. Acid-neutralizing capacities in coastal air were found to be very low and insufficient to neutralize even low acid inputs. Chloride loss in fogwater relative to its sea salt contribution was observed at sites furthest from anthropogenic sources.

Extremely high fogwater acidities were observed in the Los Angeles basin and downwind. Fogwater pH dropped down to 1.69 at a site downwind of the basin during a high sulfate pollution episode. Millimolar NO_3^- concentrations, and pH values below 3, were associated with the advection of the Los Angeles plume over a site near San Diego.

Acknowledgments

We thank the organizations who provided us with sampling sites: the U.S. Navy, the National Park Service, the South Coast Air Quality Management District, the San Luis Obispo Air Pollution Control District, and the San Diego Air Pollution Control District.

Registry No. H^+, 12408-02-5; K, 7440-09-7; Na, 7440-23-5; Mg, 7439-95-4; Ca, 7440-70-2; NH_4^+, 14798-03-9.

Literature Cited

(1) Munger, J. W.; Jacob, D. J.; Waldman, J. M.; Hoffmann, M. R. *J. Geophys. Res.* **1983**, *88*, 5109–5123.
(2) Brewer, R. L.; Ellis, E. C.; Gordon, R. J.; Shepard, L. S. *Atmos. Environ.* **1983**, *17*, 2267–2271.
(3) Richards, L. W.; Anderson, J. A.; Blumenthal, D. L.; McDonald, J. A.; Kok, G. L.; Lazrus, A. L. *Atmos. Environ.* **1983**, *17*, 911–914.
(4) Waldman, J. M.; Munger, J. W.; Jacob, D. J.; Hoffmann, M. R. *Tellus*, in press.
(5) Scherbatskoy, T.; Klein, R. M. *J. Environ. Qual.* **1983**, *12*, 189–195.
(6) Granett, A. L.; Musselman, R. C. *Atmos. Environ.* **1984**, *18*, 887–891.
(7) Hoffmann, M. R. *Environ. Sci. Technol.* **1984**, *18*, 61–63.
(8) Martin, L. R. "Acid Precipitation: SO_2, NO, and NO_x Oxidation Mechanisms: Atmospheric Considerations"; J. G. Calvert, Ed.; Butterworth: Boston, MA, 1984; pp 63–100.
(9) Kaplan, D. J.; Himmelblau, D. M. *Atmos. Environ.* **1981**, *15*, 763–773.
(10) Cass, G. R. *Atmos. Environ.* **1981**, *15*, 1227–1249.
(11) Hegg, D. A.; Hobbs, P. V. *Atmos. Environ.* **1982**, *16*, 2663–2668.
(12) Cass, G. R.; Shair, F. H. *J. Geophys. Res.* **1984**, *89*, 1429–1438.
(13) Zeldin, M. D.; Davidson, A.; Brunelle, M. F.; Dickinson, J. E. Southern California Air Pollution Control District, El Monte, CA, 1976, Evaluation and Planning Report 76-1.
(14) deVolini, R. Pacific Missiles Range, Pt. Mugu, CA, 1974, Technical Publication TP/74/1.
(15) Reible, D. D. Ph.D. Dissertation, California Institute of Technology, Pasadena, CA, 1982.
(16) Azevedo, J.; Morgan, D. L. *Ecology* **1974**, *55*, 1135–1141.
(17) California Air Resources Board "Air Quality Aspects of the Development of Offshore Oil and Gas Resources"; California Air Resources Board: Sacramento, CA, 1982.
(18) Jacob, D. J.; Wang, R.-F. T.; Flagan, R. C. *Environ. Sci. Technol.* **1984**, *18*, 827–833.
(19) Hering, S. V.; Blumenthal, D. L. "Fog Sampler Intercomparison Study: Final Report". Coordinating Research Council, Atlanta, GA, 1985.

(20) Katz, U. "Communications a la 8eme Conference sur la Physique des Nuages"; Laboratoire Associe de Meteorologie Physique: 63170 Aubiere, France, 1980; pp 697–700.
(21) Nagamoto, C. T.; Parungo, F.; Reinking, R.; Pueschel, R.; Gerish, T. *Atmos. Environ.* **1983**, *17*, 1073–1082.
(22) Waldman, J. M. Ph.D. Dissertation, California Institute of Technology, Pasadena, CA, 1985.
(23) Friedlander, S. K. *Environ. Sci. Technol.* **1973**, *7*, 235–240.
(24) Cooper, J. A.; Watson, J. G., Jr. *J. Air Pollut. Control Assoc.* **1980**, *30*, 1116–1125.
(25) Weast, R. C., Ed. "Handbook of Chemistry and Physics", 56th ed.; CRC Press: Cleveland, OH, 1975; p F-199.
(26) Miller, M. S.; Friedlander, S. K.; Hidy, G. M. *J. Colloid Interface Sci.* **1972**, *39*, 165–176.
(27) Jacob, D. J. Ph.D. Dissertation, California Institute of Technology, Pasadena, CA, 1985.
(28) Unger, C. D. "An Analysis of Meteorological and Air Quality Data Associated with the Occurrence of Fogwater with High Acidity in the Los Angeles Basin"; California Air Resources Board, Sacramento, CA, July 18, 1984, memorandum.
(29) Brown, H. W. "An Analysis of Air flow over the Southern California Bight and Northern San Diego County on January 8, 1983". San Diego Air Pollution Control District, San Diego, CA, 1983.
(30) Rosenthal, J.; Battalino, T. E.; Hendon, H.; Noonkester, V. R. Pacific Missiles Test Center, Pt. Mugu, CA, 1979, Technical Publication TP/79/33.
(31) Atkinson, R.; Perry, R. A.; Pitts, J. N., Jr. *Chem. Phys. Lett.* **1978**, *54*, 14–18.
(32) Nguyen, B. C.; Bonsang, B.; Gaudry, A. *J. Geophys. Res.* **1983**, *88*, 10903–10914.
(33) Jacob, D. J.; Munger, J. W.; Waldman, J. M.; Hoffmann, M. R. Proceedings of the 77th Annual Meeting of the Air Pollution Control Association, San Francisco, CA, Air Pollution Control Association, Pittsburg, PA, 1984, paper 24–5.
(34) Martens, C. S.; Welosowski, J. J.; Harriss, R. C.; Kaifer, R. *J. Geophys. Res.* **1973**, *78*, 8778–8792.
(35) Hitchcock, D. R.; Spiller, L. L.; Wilson, W. E. *Atmos. Environ.* **1980**, *14*, 165–182.
(36) Eriksson, E. *Tellus* **1960**, *12*, 63–109.
(37) Robbins, R. C.; Cadle, R. D.; Eckhardt, D. L. *J. Met.* **1959**, *16*, 53–56.
(38) Finlayson-Pitts, B. J. *Nature (London)* **1983**, *306*, 676–677.
(39) Latimer, W. D. "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions", 2nd ed.; Prentice-Hall: New York, 1952.
(40) Kritz, M. A.; Rancher, J. *J. Geophys. Res.* **1980**, *85*, 1633–1639.

Received for review September 17, 1984. Accepted February 12, 1985. This research was funded by the California Air Resources Board (Contract A2-048-32).

Identification of New, Fluorinated Biphenyls in the Niagara River–Lake Ontario Area

Rudolf Jaffe and Ronald A. Hites*

School of Public and Environmental Affairs and Department of Chemistry, Indiana University, Bloomington, Indiana 47405

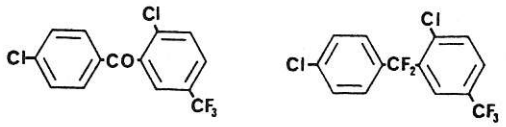
■ Sediment and fish samples from the Niagara River and Lake Ontario were analyzed by capillary gas chromatographic mass spectrometry using negative ion methane chemical ionization. A series of bis(trifluoromethyl)-substituted polychlorinated biphenyls was discovered. These compounds were present in fish as well as in sediments, and their major source seems to be the Hyde Park dump in the city of Niagara Falls, NY.

Introduction

Several hazardous waste disposal sites are located along the shores of the Niagara River. Most of these sites are located in the city of Niagara Falls and are known to pollute the Niagara River (*1*). This is unfortunate because the Niagara River is the major water source for Lake Ontario; 83% of Lake Ontario's total water input and 50% of the lake's annual suspended solid load enter through the Niagara River each year (*2*). As a result, anthropogenic pollutants have been found to be transported by the Niagara River to Lake Ontario and to accumulate in the sediment (*3–8*) and in fish and other aquatic organisms (*9–14*).

A large percentage of the toxic wastes placed into the dumps in the city of Niagara Falls consisted of halogenated organic compounds (*15*), a significant (but unknown) fraction of which were fluorinated chemicals. Some of these fluorinated organic compounds have previously been identified in sediment from the Bloody Run Creek (*1*) and in fish from the Niagara River (*9*).

Bloody Run is a small creek that drains the Hyde Park dump in Niagara Falls. This hazardous waste disposal site was operated by the Hooker Chemical Co. from about 1953 to 1975. Approximately 55 000 tons of halogenated waste was buried at the site, and of this, about 10% was liquid and solid waste from Hooker's production of 4-chloro-(trifluoromethyl)benzene (*15*). Therefore, it is not surprising that a variety of fluorinated organic compounds were detected in sediments of Bloody Run Creek (*1*). The two most abundant were compounds 1 and 2; they were



1 2

shown to be byproducts from the synthesis of 4-chloro-(trifluoromethyl)benzene and seem to come from the Hyde Park dump (*1*). These two compounds were also detected in sediments from the western and central sedimentation basins of Lake Ontario itself (*8*). This paper reports on some related, potentially persistent, fluorinated organic compounds that were discovered through analyses of Niagara River and Lake Ontario sediment and fish.

Experimental Section

Sediments. Lake Ontario sediment cores were taken from the major sedimentation basins: the Niagara, Mississagua, Rochester, and Kingston Basins. Sampling was done in Aug 1982 by researchers at the National Water Research Institute of the Canada Centre for Inland Waters at Burlington, Ontario; sampling was carried out from the CSS Limmos. The sediment grab sample from Bloody Run Creek was obtained with the cooperation of the New York State Department of Environmental Conservation

0013-936X/85/0919-0736$01.50/0