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GAS PHASE ACIDS IN THE SOUTH COAST AIR BASIN

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Given the infrequent occurrence of rainfall in Southern California, deposition of acidic air pollutants at the earth's surface in the Los Angeles area is thought to be dominated by dry deposition processes. Liljestrand (1) and McRae and Russell (2) have estimated that the total dry flux of the major acidic species in the Los Angeles area is about an order of magnitude greater than the wet flux of these species to the earth's surface. Liljestrand (1) estimated the average annual dry acid flux of SO_2 , NO_2 , NO , NH_3 , aerosol NO_3^- and SO_4^{2-} in downtown Los Angeles to be 3840, 5630, 1370, -1060, 8.8 ($\text{NO}_3^- + \text{SO}_4^{2-}$) equivalents/ha-yr, respectively.

The dry flux of acid gases and aerosols to the earth's surface can be estimated if the atmospheric concentration of the pollutants of interest is known in conjunction with meteorological conditions and ground surface characteristics. Unfortunately, many key atmospheric acid gases (e.g., HNO_3 , HCl) have not been measured by routine air monitoring networks in the past. As a result, the long-term pattern of atmospheric concentration data required for even rough estimates of long-term average acid flux to the earth's surface is unavailable.

The primary objective of this study was to measure the spatial and temporal concentration distributions of several gas phase acids in the Los Angeles area atmosphere. Gas phase species were collected by the denuder difference method and by the tandem filter method using treated or reactive backup filters (3-11). Samples were collected over a one-year period at the nine locations shown in Figure 1. These samples were analyzed to determine the atmospheric concentrations of the following gaseous acidic species: HNO_3 , HCl , HBr , HF , and HCOOH .

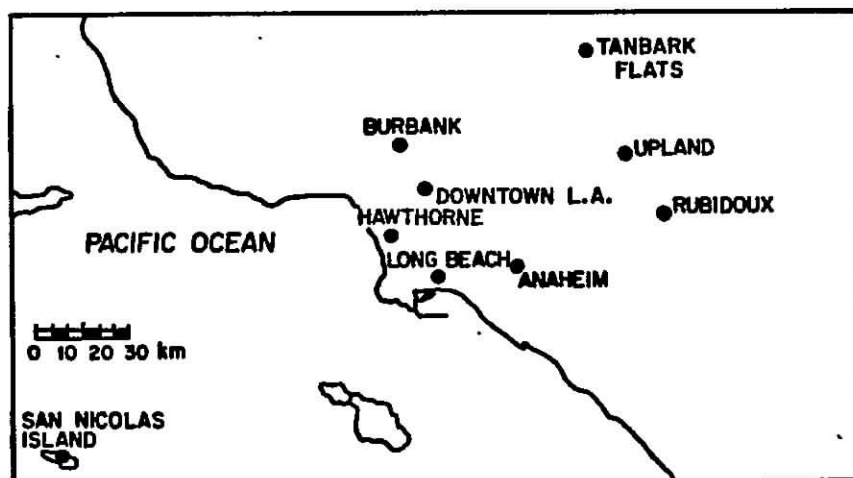


Figure 1. Los Angeles area monitoring network. All sites are at an elevation within 400m of sea level except Tanbark Flats which is at an elevation of 870m in the San Gabriel Mountains.

The denuder difference method employing nylon filters was used to measure atmospheric HNO_3 concentrations. One nylon filter located downstream of an AIHL-design cyclone separator (12) collected fine particle nitrate plus HNO_3 , while the other nylon filter, located behind an AIHL-design cyclone and a MgO -coated diffusion denuder (designed to quantitatively remove HNO_3) collected only fine particle nitrate. Nitric acid concentration data were obtained from the difference between nitrate ion measured on these two nylon filters.

In the tandem filter method, gas phase acids were collected on reactive or treated backup filters after particles were removed by the use of open face, inert polytetrafluoroethylene (PTFE) prefilters. Nitric acid and HCl were collected on a nylon backup filter. HCl , HF , HBr , and HCOOH were collected on two KOH impregnated filters in series. For the collection of nitric acid, the tandem filter method has been shown to suffer from a positive artifact due to the loss of NO_3^- , as HNO_3 , from the PTFE prefilter, with the subsequent collection of that HNO_3 on the nylon backup filter. Therefore the HNO_3 data presented here are from the denuder difference method samples.

Samples were collected every six days for 24-h sampling periods during the calendar year 1986. Filters were installed the day prior to, and removed the day after, sample collection. Flow rates were monitored before and after sampling with a rotameter which had been factory calibrated with an accuracy of 1 percent full scale. The filters were stored in self-sealing, plastic petri dishes, sealed with Teflon tape, and refrigerated until sample analysis.

Sample Analysis

Nylon filters were leached by lightly shaking each of them in 20ml of a $\text{CO}_3^{2-}/\text{HCO}_3^-$ buffer (eluent for the ion chromatograph) for 3 hours or more at 10°C . Reduced temperatures were used for the extraction to avoid loss of volatile species. KOH impregnated filters also were leached with distilled, deionized water in the same manner as the nylon filters. After extraction, the concentrations of HNO_3 and HCl measured as NO_3^- and Cl^- on nylon filters and the concentrations of HCl , HBr , HF , and HCOOH , measured as Cl^- , Br^- , F^- , and HCOO^- , on KOH impregnated quartz filters were determined using ion chromatography (Models 2020i and 10, Dionex Corp.) (13,14).

RESULTS

Long term average gas phase acids concentrations are shown in Table I. Upwind of the air basin at San Nicolas Island, gas phase acids concentrations are very low: averaging $0.3\mu\text{g m}^{-3}$ (0.1 ppb) for HNO_3 , $0.8\mu\text{g m}^{-3}$ for HCl , $0.13\mu\text{g m}^{-3}$ for HF , and $2.6\mu\text{g m}^{-3}$ for formic acid. Annual average HNO_3 concentrations ranged from $3.1\mu\text{g m}^{-3}$ (1.2 ppb) near the Southern California coast to $6.9\mu\text{g m}^{-3}$ (2.7 ppb) at an inland site in the San Gabriel Mountains. HCl concentrations within the South Coast Air Basin averaged from $0.8\mu\text{g m}^{-3}$ to $1.8\mu\text{g m}^{-3}$ during the year 1986. Long-term average HF concentrations within the air basin are very low, in the range from 0.14 to $0.22\mu\text{g m}^{-3}$ between monitoring sites and HBr concentrations are even lower. Long-term average formic acid concentrations are lowest near the coastline ($5.0\mu\text{g m}^{-3}$ at Hawthorne), with the highest average concentrations ($10.7\mu\text{g m}^{-3}$) observed inland at Upland.

Peak 24-h average gas phase acids concentrations have approximately the same spatial distribution as just described for the long-term mean values. The 24-h average maximum values are typically three to four times higher than is observed for the annual means, with peak 24-h average concentrations of $21\mu\text{g m}^{-3}$ for HNO_3 , $6.3\mu\text{g m}^{-3}$ for HCl , $1.91\mu\text{g m}^{-3}$ for HF and $25.1\mu\text{g m}^{-3}$ for HCOOH , as seen in Table I.

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Table I. Gas phase acids concentrations observed in the Los Angeles area, 1986
(concentrations in $\mu\text{g m}^{-3}$)

Site	$\text{HNO}_3(\text{DD})^a$		HCl^b		HF^c	HCOOH^c		
	Annual Average	Max 24-h Average	Annual Average	Max. 24-h Average		8-Month Average	Max. 24-h Average	8-Month Average
Burbank	6.7	17.4	1.4	4.2	0.16	0.51	10.0	17.4
Downtown LA	6.0	16.6	1.8	5.2	0.14	0.37	9.2	16.0
Hawthorne	3.1	13.0	1.7	5.5	0.16	1.33	5.0	9.5
Long Beach	3.4	15.7	1.8	6.3	0.16	0.50	6.1	10.4
Anaheim	3.2	13.5	1.5	5.3	0.16	0.58	7.0	11.3
Rubidoux	1.7	6.7	0.8	4.6	0.22	1.91	6.8	17.4
Upland	6.0	18.8	1.4	4.3	0.18	0.36	10.7	25.1
Tanbark Flats	6.9	21.0	0.9	3.3	0.18	0.34	9.8	23.4
San Nicolas Island	0.3	4.7	0.8	2.4	0.13	0.62	2.6	7.4

- a. By denuder difference method employing nylon filters.
- b. By tandem filter method employing nylon or KOH impregnated backup filters.
- c. By tandem filter method employing KOH impregnated backup filters.
- d. May-December, 1986.