Hydrofluoric Acid in the Southern California Atmosphere

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Atmospheric hydrofluoric acid concentrations were measured at nine sites in Southern California during an 8-month period. Long-term average HF concentrations measured by the tandem filter method ranged from 0.13 μg m^{-3} (0.15 ppb) at San Nicolas Island to 0.22 μg m^{-3} (0.25 ppb) onshore at Rubidoux, CA. The ambient concentration of HF shows little change throughout the year, with the notable exception of an occasional spike which approaches or exceeds 1 μg m^{-3} (1.12 ppb) over a 24-h averaging time. Due to the wide-ranging uses of HF in industry, and lacking natural sources to account for such spikes, it is possible that these spikes are due to accidental emissions from industrial sources, although no direct evidence of accidents on the dates involved was found.

Introduction

Anhydrous hydrogen fluoride is a colorless, corrosive liquid or gas at room temperature. Hydrogen fluoride is readily soluble in a number of solvents; aqueous HF is typically referred to as hydrofluoric acid. Anhydrous hydrogen fluoride is one of the most acidic substances known and will readily attack such materials as concrete, glass, natural rubber, and metal (especially alloys containing silica).

On the basis of quantity of production, HF is the most important manufactured compound of fluorine (1). HF is the source of fluorine for most fluorine-containing chemicals, being used either to directly manufacture these chemicals or in the production of intermediate chemicals. HF is used in the production of refrigerants, high-octane gasoline, aluminum, plastics, electrical components, and fluorescent light bulbs. HF acts as a fluorinating source for herbicides, pharmaceutical intermediates, etchants, and stannous fluoride (used in toothpastes). While these uses rely primarily on the anhydrous form of HF, aqueous solutions of hydrofluoric acid are also used in the following capacities: stainless steel pickling, glass etching, metal coatings, exotic metals extraction, and quartz purification (2).

HF is an extremely toxic substance. HF gas can cause serious respiratory damage or skin burns on contact. Hydrogen fluoride is a direct cellular poison, resulting in the formation of deep, slow-healing ulcers in the respiratory tract and mucous membranes. Exposure to concentrations of 50 ppm over a period of 30–60 min is considered to be lethal (3). Because of the extreme toxicity of this compound, HF is subject to a number of federal and state regulations. A partial list of legislation that affects users of HF includes the Clean Air Act (toxic contaminants provisions); Comprehensive Emergency Response, Compensation, and Liability Act (CER-CLA); Superfund Amendments and Reauthorization Act (SARA Title III)/Emergency Planning and Community Right To Know Act (EPCRA); Resource Compensation and Recovery Act (RCRA); Hazardous Materials Transportation Act (HMTA); and the Occupational Safety and Health Act (4).

Volcanic activity is the only known natural source of hydrogen fluoride (5). In most cases HF is not the most abundant component of volcanic emissions but is the product of hydrolysis by moisture of fluorine-containing compounds such as boron trifluoride, carbonyl fluoride, phosphorus pentafluoride, silicon tetrafluoride, sulfur tetrafluoride, and phosphorus trifluoride. It is estimated that between 1 and 7.3 million metric tons of fluoride-containing compounds are lofted into the air by volcanic activity annually (6, 7). Other natural sources of airborne fluoride compounds include ocean spray and dust from the weathering of fluoride-containing rocks and soils. According to Barnard and Nordstrom, sea salt may contribute a varying amount of dissolved fluoride to the atmosphere, but this in comparison to other sources of airborne fluorides is still a negligible effect (8).

Many of the sources of airborne HF are anthropogenic in nature. HF is produced commercially through the reaction of sulfuric acid and fluorspar (calcium fluoride). Total HF production in the United States in 1984 was estimated to be ~193 000 metric tons (2). Emissions from the production of hydrogen fluoride (2400 metric tons yr^{-1}) are minor in comparison with emissions from coal combustion or from the aluminum, phosphate, and steel industries, which in the aggregate are estimated to release 150 000 metric tons of fluoride to the atmosphere annually. As much as 40% of industrial fluoride emissions to the atmosphere are estimated to be gaseous in form, with the remaining 60% emitted as particulate matter (8). Gaseous HF is hydrolyzed and dispersed in the atmosphere, and the major route of removal of airborne HF on a global scale is in precipitation.

Despite the well-documented toxic effects of HF and the assortment of regulations by which HF producers and consumers must abide, there is relatively little known about the concentrations and characteristics of HF in ambient air either in industrial or in nonindustrial communities. A recent review article that summarizes the state of knowledge of the 189 toxic air contaminants regulated by the 1990 Amendments to the Clean Air Act notes that ambient concentration measurements of HF are available for only one location, with only 20 samples taken at this location (9). There has, however, been considerable attention devoted to reporting the atmospheric concentrations of total inorganic fluorides (which includes fluoride from HF as well as other fluoride-containing compounds). In rural areas, far away from industrial sources of fluoride, only trace amounts of fluoride are typically found in ambient air ($\ll$1 μg m^{-3}). In urban areas, the atmospheric fluoride concentration is much higher due to industrial pollution and the burning of coal (and other fluoride-containing fuels), but concentrations rarely exceed 2 μg m^{-3} (10). Additionally, there is a seasonal variation in fluoride concentration due to increased burning of coal and other fuels during winter months (10).

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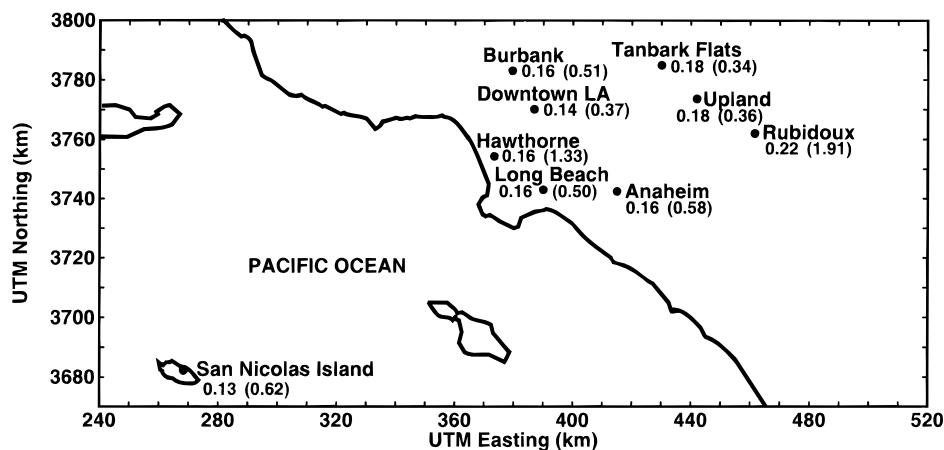
FIGURE 1. Map of Southern California showing the long-term average HF concentrations (μg m^{-3}) immediately adjacent to dots that represent the air monitoring sites used in this study over the period May–December 1986. The maximum 24-h average HF concentrations at each site over that period are shown in parentheses.

The concentration of fluoride in the air can be much greater than 1 or 2 μg m^{-3} in the vicinity of a point source of emissions, such as a factory or power plant. Air quality near major fluoride point sources has been studied in eastern European countries. Near certain European aluminum plants airborne fluoride concentrations of 140–220 μg m^{-3} have been measured (11). In 1979, Smith and Hodge studied the fluoride concentrations in air near several different types of industries throughout the United States. Their results demonstrated that mean concentrations were almost always less than 8.2 μg m^{-3} (12). Due to improving technology and emission control practices, it is thought that fluoride concentrations near industrial sources are decreasing.

The purpose of the present paper is to report the HF concentrations in the Southern California atmosphere. An 8-month-long air monitoring experiment will be described in which HF concentrations were measured at nine sites distributed throughout Southern California. The measurements from this study will be explored in relation to the character and locations of known potential sources of HF emissions in order to draw inferences regarding processes affecting HF concentrations in the atmosphere.

Experimental Section

Air Monitoring Network. In order to measure the concentration of gas phase acids, ammonia, and atmospheric particulate matter, a monitoring network was operated at nine sampling sites located throughout the Los Angeles area during calendar year 1986. The stations are illustrated in Figure 1. With the exception of Tanbark Flats and San Nicolas Island, all sites were colocated with present South Coast Air Quality Management District (SCAQMD) continuous air monitoring stations. The U.S. Environmental Protection Agency provides a description of the SCAQMD sites (13, 14).

The Tanbark Flats site was located at an elevation of ~870 m in the mountains north of San Dimas, in the Angeles National Forest. The location of the Tanbark Flats site was chosen to determine the concentration of acidic pollutants present in the national forests surrounding Los Angeles. The ninth site was located ~140 km southwest of the Los Angeles coastline at the meteorological station on San Nicolas Island (SNI). The purpose of this remote, off-shore location was to determine background pollutant levels entering Los Angeles from the upwind marine environment. The sampling systems at four of the sites (Burbank, downtown Los Angeles, Long Beach, Upland) were placed on the roofs of one- or two-story buildings. At the other monitoring stations, the systems were placed with the inlets located 2–3 m above ground level. All sites except Tanbark Flats were below an elevation of 390 m above sea level.

Sampler Design and Sampling Protocol. Gas phase acids and bases and atmospheric particulate matter samples in three size ranges (i.e., fine, PM$_{10}$, and total particles) were measured during this air monitoring campaign using the sampling systems that are illustrated schematically by Solomon et al. (15) and by Eldering et al. (16). The sampling protocol was designed to permit duplicate measurements, by different methods, of several of the gas phase pollutants of interest and to obtain a nearly complete material balance on the chemical composition of fine (diameter, d_p < 2.2 μm), PM$_{10}$ (d_p < 10 μm), and total (no size discrimination) aerosols.

Using the tandem filter method, certain gas phase acids and bases were collected on reactive or treated backup filters after particles first were removed by the use of an inert polytetrafluoroethylene (PTFE) prefilter located in an open face filter holder. HF, HCl, HBr, CH$_3$COOH, and HCOOH were collected at a flow rate of 4.9 L min^{-1} on two KOH-impregnated quartz fiber filters in series (47 mm diameter, Pallflex 2500 QAO) located downstream of a PTFE particle prefilter (47 mm diameter, 2 μm pore size, Teflo, Gelman Sciences). The open face filter holders were protected from the sun and from wet or dry fallout. In the absence of a large data base on organic acid concentrations in the Los Angeles atmosphere, the quantity of KOH used to prepare the alkaline-impregnated filters had to be estimated initially. Analysis of the earliest samples taken showed excessive breakthrough of organic acids from the first KOH-impregnated filter to the second KOH-impregnated filter. The quantity of KOH spiked onto each filter was increased to 1 mL of 0.1 M KOH in distilled, deionized water, and for the final 8 months of 1986, the collection of organic acid data proceeded without incident. HCl and HNO$_3$ were measured by the denuder difference method and also by a second tandem filter system employing nylon filters. These results are reported elsewhere (15, 16).

Samples were collected every sixth day for 24-h sampling periods during the last eight months of 1986. The first HF sample was collected on May 8, in coordination with the National Air Surveillance Network high-volume sampling schedule. Filters were installed the day prior to sample collection and removed the day after. KOH-impregnated filters were leached by lightly shaking each of them in 20 mL of distilled, deionized water for 3 h or more at 10 °C. After extraction, the concentrations of HF, measured as F$^-$ on the KOH-impregnated quartz filters were determined using ion chromatography (Models 2020i and 10, Dionex Corp.).

Quality Assurance/Quality Control. Reactive and treated filters were stored before use and during transport at reduced temperatures (-4 °C). After sample collection, all KOH filters
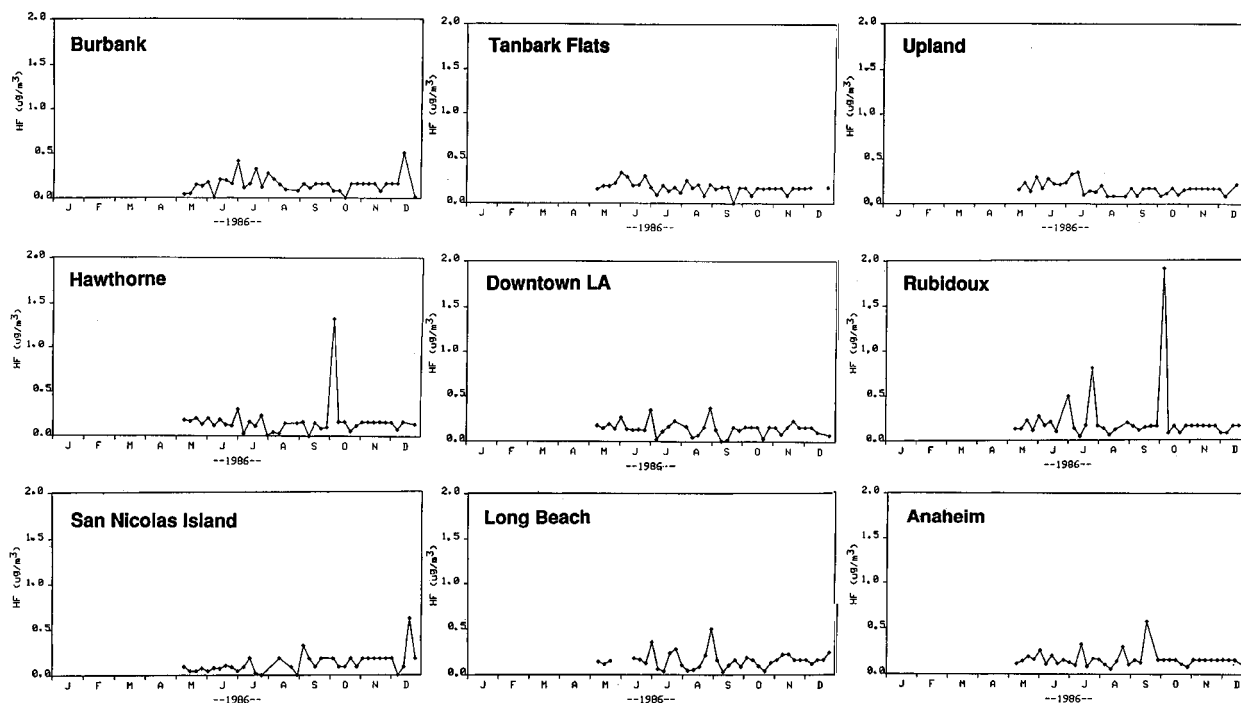
FIGURE 2. Time series of 24-h average HF concentrations at Southern California air monitoring sites.

were placed back into their original prelabeled petri dish, sealed with Teflon tape, and stored in a freezer at −30 °C. Samples remained at reduced temperatures until they were analyzed for the species of interest. The concentrations of all chemical species were determined relative to primary or secondary laboratory standards of known concentration. Aqueous standards were diluted daily from more concentrated solutions prepared monthly from ACS grade analytical reagents. The matrix of the daily standards matched that of the leaching solution. For strong acid analysis, an independent QC standard was obtained from Dionex and routinely analyzed during the last half of the year. Accuracy, relative to this standard was typically better than 5%.

Field blanks equal in number to 10% of the actual ambient samples were taken at periodic intervals throughout the sampling program. The average filter blank value for fluoride on the KOH-impregnated filters was 0.3 ± 0.2 μg/filter and the instrument detection limit (IDL) for F^- was 0.3 μg/filter. The analytical precision was defined as the average coefficient of variation obtained from many pairs (typically $n > 50$) of duplicate (split filters analyzed separately) or replicate (repeat analysis of a filter extract) measurements and was found to average 23.6% for gaseous HF; this value is higher than for the other strong acids because the HF concentrations are quite low at most times. Final error bound estimates were obtained by the statistical propagation of the sample, filter blank, and sampling volume precisions.

Results

Average HF concentrations measured by the tandem filter method during the last eight months of 1986 ranged between 0.13 (0.15 ppb) and 0.22 μg m^{-3} (0.25 ppb) over the nine sampling stations shown in Figure 1. The minimum long-term average value occurred offshore at San Nicolas Island, and the maximum long-term average value occurred inland at the Rubidoux site.

The time series of 24-h average ambient HF concentrations at all nine sites is presented in Figure 2. HF concentrations do not seem to exhibit a strong seasonal variation in the Southern California atmosphere but, instead, experience small fluctuations about the long-term average concentration accompanied by occasional isolated peaks in the HF con-

centration at certain sites. Maximum single-day concentrations at the on-land sites varied between a low value of 0.34 μg m^{-3} (0.38 ppb) to a high value of 1.91 μg m^{-3} (2.14 ppb), corresponding to the sampling stations at Tanbark Flats and Rubidoux, respectively. The spatial distribution of maximum single-day HF concentrations is shown by the values in parentheses in Figure 1.

Discussion

As seen in Figure 1, the long-term average HF concentration varied between 0.13 and 0.22 μg m^{-3} (0.15 and 0.25 ppb) throughout the Los Angeles area during 1986. The time series data recorded at each site indicate that there is little seasonal variation in the typical concentrations; the 24-h average concentrations usually persist near the long-term average value. An exception to this generalization occurs on October 5 when the measured concentration "spikes" to levels far above the long-term average at Hawthorne and Rubidoux. The extensive use of HF as an industrial chemical and the isolated nature of these spikes suggests that these spikes might result from an accidental release from an industrial source. Three other dates are noted on which HF concentrations were higher than average but possibly within the range expected due to meteorological fluctuations acting on routine release rates. The first such high-concentration event occurs on July 1 and is detected at the Rubidoux, Long Beach, Hawthorne, downtown Los Angeles, and Burbank sites. A second high-concentration event occurs on July 25 and is detected at the Burbank, downtown Los Angeles, Hawthorne, Long Beach, and Rubidoux sites. A third high-concentration event detected at the downtown Los Angeles and Long Beach sites occurs on August 30.

In order to assess the frequency of industrial accidents involving HF that might account for an event like that seen on October 5, records related to the sources of HF emissions in the Los Angeles area were surveyed. Los Angeles and the surrounding areas are home to a large number of industrial facilities which, for hydrogen fluoride use, report to the Toxic Release Inventory (TRI) that is maintained by the U.S. Environmental Protection Agency (17). The five largest of these (in terms of quantity of HF reported) include four petroleum refineries, as well as a chemical processing facility

(*18*), each of which has permanent on-site storage of anhydrous HF. These major facilities are located near the coast in the area roughly between the Long Beach and Hawthorne air monitoring stations shown in Figure 1. The combined daily consumption of HF for these five facilities was ~19 000 L in 1993, which required an inventory of ~450 000 L to be maintained between these locations. Each of the refineries at that time used HF as an alkylation catalyst in the processing of high-octane gasoline, and as a result, much of the acid was recycled and reused at these facilities. The chemical processing facility consumed HF in the formation of hydrochlorofluorocarbons (HCFCs). As a result, this facility consumed 83% of the anhydrous HF used in the Los Angeles area during 1993. There are a host of other "minor" HF users in the Los Angeles basin, but these facilities utilize much smaller quantities than the five facilities mentioned above and use primarily the aqueous form of HF.

Given that potential sources of HF emissions are present in the Los Angeles basin, it was next necessary to determine the frequency (if any) at which accidents involving hydrogen fluoride have occurred. According to the Toxic Release Inventory, there have been 265 accidents involving hydrogen fluoride between 1987 and 1993 in California alone (*17*). This averages >30 accidents per year in the state of California. Due to the relatively low boiling point of HF (19.54 °C), which is routinely exceeded in the Los Angeles area, and its high vapor pressure, HF releases would be expected to produce airborne vapors. With these data in mind, it does not seem unreasonable that an occasional spike in the ambient HF concentration data for 1986 could be due to an accidental release.

Accidents reported to the SCAQMD by each of the five largest HF users in the Los Angeles area were examined in relation to the dates in 1986 on which HF spikes were observed. Two of the refineries and the facility that manufactured HCFCs had no reported accidents involving HF during the year 1986. A third refinery reported three accidents during 1986 (in January, March, and June), all of which involved acid burns to workers. The fourth refinery, however, reported three accidents which involved acid leaks: in April a ratio glass leak was reported; in September an acid unloading hose leak was reported; and in November a pinhole leak on an acid regenerator was reported.

It is impossible to correlate these reported accidents with the spikes registered in the 1986 ambient HF sampling data. The records demonstrate, however, that accidents involving HF do occur and in fact are fairly common among the largest HF users in the Los Angeles area. Alternative potential sources of an accidental release include a number of smaller HF users in the Los Angeles area as well as losses from vehicles that transport HF.

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