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HYDROCHLORIC ACID: A REGIONAL PERSPECTIVE ON CONCENTRATIONS AND FORMATION IN THE ATMOSPHERE OF SOUTHERN CALIFORNIA

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Abstract—Atmospheric gaseous hydrochloric acid (HCl) concentrations and water-soluble species in the aerosol phase were measured at nine sites in Southern California throughout the year 1986. Annual average HCl concentrations measured by the denuder difference method ranged from 0.39 ppb at an offshore island to 1.25 ppb onshore at Hawthorne, California. An ion balance on the aerosol shows that coarse particle chloride begins as sea salt over the ocean and is depleted relative to aerosol sodium with transport inland. Total chloride and sodium balances show that chloride depletion from the aerosol is matched by a comparable increase in gaseous HCl concentrations, consistent with the proposition that acid gas reactions with sea salt are the principal source of gaseous HCl in the Southern California atmosphere. Fine aerosol chloride exceeds fine particle sodium on a number of occasions, particularly at one inland site known for extraordinarily high NH_3 levels. There is evidence that coarse aerosol chloride from sea salt is being processed by atmospheric reactions through HCl to form fine aerosol, possibly NH_4Cl.

Key word index: Hydrochloric acid, aerosol chloride, nitric acid, aerosol nitrate, sodium, marine aerosol.

INTRODUCTION

Considerable attention has been focused historically on measurement and control of atmospheric weak acid gases such as SO_2 and NO_2. More recently, it has been learned that the strong acid HNO_3 is present at significant concentrations in the Southern California atmosphere (Miller and Spicer, 1975; Spicer, 1979; Appel *et al.*, 1980, 1986, 1987; Spicer *et al.*, 1982; Grosjean, 1983; Russell and Cass, 1984; Hering *et al.*, 1988; Solomon *et al.*, 1988a, b). Measurements also have been made of atmospheric nitric acid in the eastern U.S. (Cadle *et al.*, 1980; Shaw *et al.*, 1982), Ontario, Canada (Anlauf *et al.*, 1985), England (Dollard *et al.*, 1987), Italy (Allegrini *et al.*, 1987), Germany (Matusca *et al.*, 1984) and Hawaii (Galasyn *et al.*, 1987). Other strong acid gases likewise may be present in significant concentrations, including gaseous HCl, but little is known of the abundance, sources, and fate of HCl in most urban atmospheres.

It has been observed that Na^+ is often present in excess of Cl^- in atmospheric aerosol samples, suggesting that sea salt reacts with NO_2 or HNO_3, displacing the chloride, possibly as gaseous HCl (Robbins *et al.*, 1959; Green, 1972; Martens *et al.*, 1973; Wall *et al.*, 1988; John *et al.*, 1988; Grosjean, 1990). The presence and source of gaseous HCl in the atmosphere has been discussed by a number of investigators. Junge (1956, 1957) made measurements of gaseous chloride but did not attempt to attribute it to a source. Gorham (1958) reported the presence of HCl in air pollution reaching the Lake District of England. Cauer (1951) suggested that the reaction of ozone and aerosol chloride produced gaseous chloride (HClO or HCl and $HClO_3$). Early work by Erikkson (1960) found that the ozone mechanism was too slow to account for chlorine loss from the aerosol and proposed the generation of hydrogen chloride by the reaction of sea salt particles with SO_3. Robbins (1959) explored the reactions of sodium chloride and nitrogen dioxide. He found that HNO_3 is formed and hypothesized the subsequent reaction of nitric acid and sodium chloride to form hydrochloric acid and sodium nitrate. Valach (1967) reanalyzed Junge's data and cast doubts on the hypothesis that reactions involving sea salt are the source of atmospheric gaseous chlorine. He instead proposed that chlorine derived from volcanic activity is the major source. Duce (1969) argued that earlier studies were not influenced by volcanic activity, and that release from sea salt may be the major source of gaseous chlorine. In a study of the interactions between marine aerosols and polluted continental air, Green (1972) found evidence of reactions of sea salt and the gaseous pollutant NO_2 leading to the formation of HNO_3, HCl, and possibly Cl_2. Martens *et al.* (1973) reported a size-dependent loss of Cl^- from the aerosol as well as a linear relationship between gaseous NO_2 concentration and total chloride loss. Okita

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(1974) examined gaseous chloride levels in the marine environment, the urban environment, and near volcanoes, and could not distinguish between sea salt, volcanoes and human activities as sources of gaseous chloride. The source is still being debated with Hitchcock (1980) claiming to find evidence supporting Erikkson's explanation that aerosol chloride displacement from sea salt occurs by reaction with H_2SO_4. Lightowlers and Cape (1988) reported that man-made emissions (e.g. coal combustion, waste incineration) dominate as the source of HCl in Western Europe. Wall *et al.* (1988) completed an extensive study of the size distribution of ionic species in the aerosol and conclude that nitric acid reacts with sea salt to produce hydrochloric acid and coarse aerosol nitrate.

Finlayson-Pitts (1983) has established, using mass spectrometry, that NOCl can be produced by reactions of NaCl and NO_2, but has not reached a conclusion on the question of whether or nor the reaction is sufficiently fast to compete with the reactions of HNO_3 and H_2SO_4 with NaCl. These studies are based on measurements made with NO_2 concentrations greater than 5 ppm, much higher than atmospheric conditions. Singh and Kasting (1988) argue that NOCl cannot be an important intermediate in HCl formation in the unpolluted marine troposphere.

In the present paper, the long-term average HCl concentrations in the Southern California atmosphere will be determined. Experimental data collected at nine monitoring sites throughout the Los Angeles area in 1986 will be analyzed to obtain a gaseous HCl plus aerosol chloride balance for the Southern California atmosphere. Evidence for the transformation of aerosol chloride species to yield atmospheric HCl concentration will be sought, along with evidence for the transformation of gaseous HCl to form fine aerosol.

EXPERIMENTAL

During the calender year 1986, gas phase acids and atmospheric particulate matter concentrations were measured over 24 h averaging periods every sixth day at the nine locations in Fig. 1. Ambient HNO_3, HCl, fine particle Cl^-, and fine particle NO_3^- concentrations were measured by the denuder difference method (Appel *et al.*, 1980; Spicer *et al.*, 1982; Forrest *et al.*, 1982; Shaw *et al.*, 1982; Hering *et al.*, 1988; Solomon *et al.*, 1988a, b). Determination of HCl concentrations by the denuder difference method using nylon filters is discussed by Appel *et al.* (1986, 1987). Collection efficiency and breakthrough studies of HCl collection on nylon filters are reported by Sturges and Harrison (1989).

In the present experiments, ambinet air at a flow rate of 24.8 $\ell\ min^{-1}$ was drawn through an acid-washed Pyrex glass inlet and a Teflon-coated cyclone separator for removal of coarse particles. At a flow rate of 6.0 $\ell\ min^{-1}$, a portion of this flow was ducted through a MgO-coated diffusion denuder for removal of HCl and HNO_3, followed by collection of fine aerosol nitrate and chloride on two parallel filter holders, one containing a nylon filter (1 μm pore size Nylasorb, Gelman Science, B1 in Fig. 2) and the other containing a KOH impregnated quartz fiber filter (Pallflex 2500 QAO spiked with 1 ml of 0.1M KOH, B2 in Fig. 2). Total inorganic nitrate and chloride (gas phase HNO_3 plus fine aerosol nitrate; gas phase HCl plus fine aerosol chloride) were collected on parallel nylon and KOH impregnated filters. HNO_3 and HCl concentrations were measured by difference between the acid denuded .and undenuded branches. The HNO_3 and fine NO_3^- concentrations were determined entirely from the difference between collection on the nylon filter pairs. The HNO_3 concentration data are discussed elsewhere (Solomon *et al.*, 1988a, 1991) while the fine particle NO_3^- concentration data are used in the present discussion. HCl and fine particle Cl^- concentrations were measured from the collected nylon filter pairs over the period 2 January–14 April. Thereafter, collection of Cl^- on the paired KOH substrates was employed for HCl and fine Cl^- measurements due to the receipt of a batch of nylon filters from the manufacturer that had a higher than desired chloride blank.

A second method for measurement of HCl and HNO_3 was employed as a precaution should the denuder difference

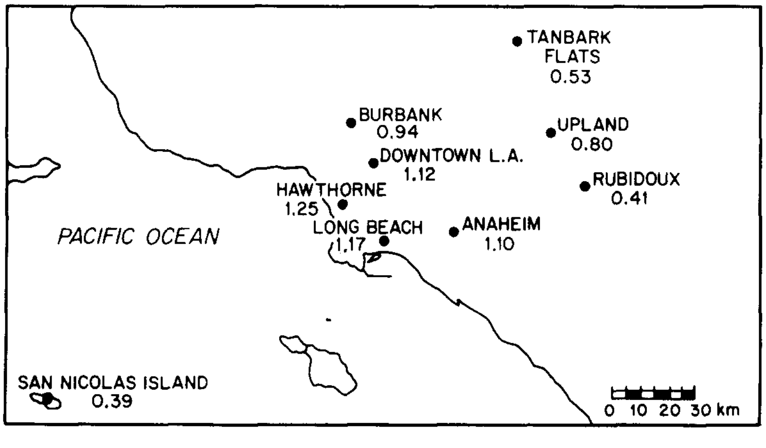

Fig. 1. Los Angeles area monitoring network. All sites are at an elevation within 400 m of sea level except Tanbark Flats which is at an elevation of 870 m in the San Gabriel Mountains. Annual average HCl concentrations are given in ppb.

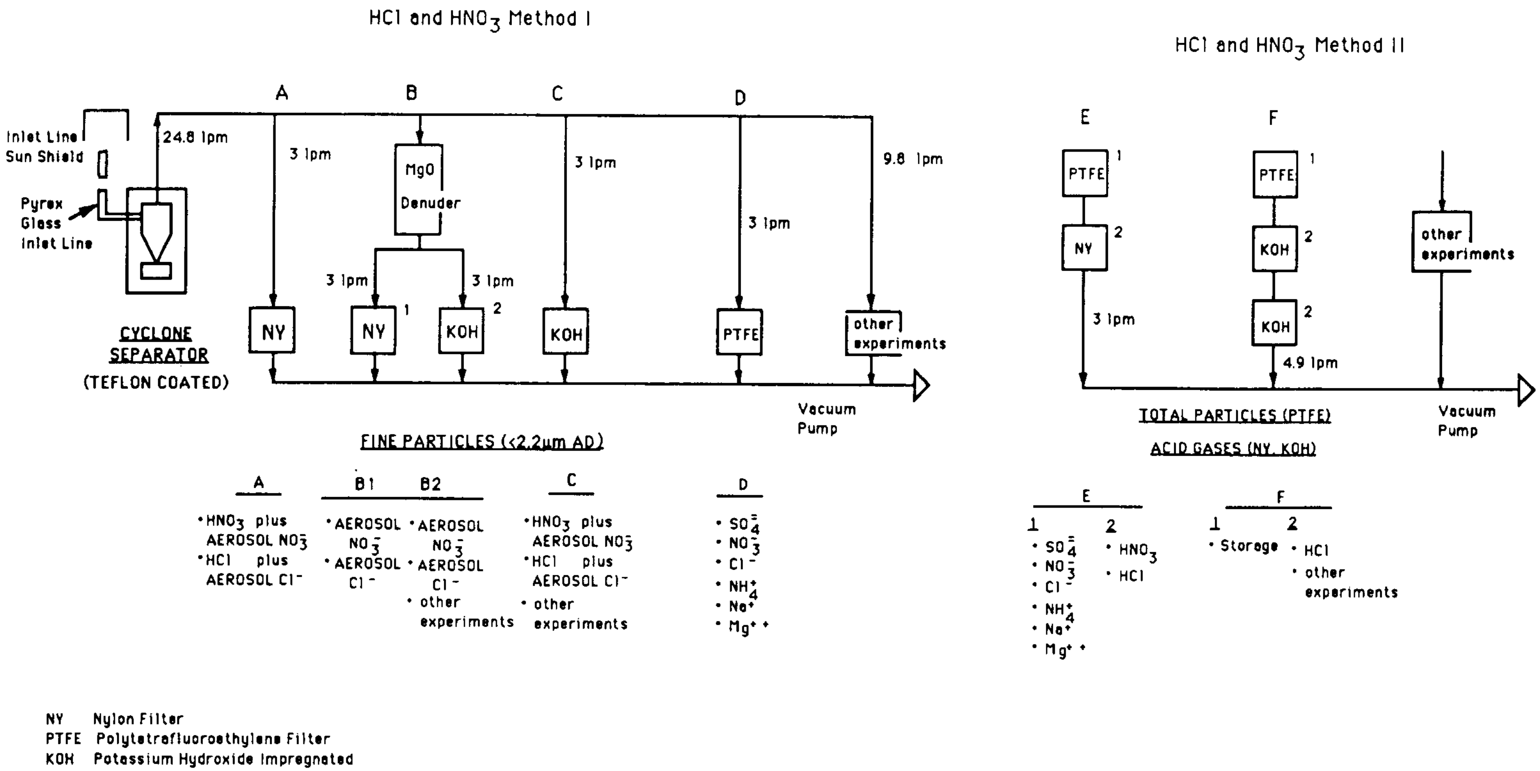

Fig. 2. Sampler configuration.

method sampler fail on any given day. In the tandem filter method, shown as Method II in Fig. 2, gas phase acids were collected on reactive or treated backup filters after particles were removed with open face polytetrafluoroethylene (PTFE) prefilters (2.0 μm pore size, Teflo, Gelman Science, Fig. 2, lines E and F). Nitric acid and HCl were collected on a nylon backup filter (Nylasorb, Membrana Corp., 2.0 μm pore size, filter E2 in Fig. 2). Following 2 May, HCl was measured on the KOH impregnated quartz fiber backup filters (Pallflex 2500 QAO spiked with 1 ml of 0.1M KOH) shown in line F of Fig. 2, to avoid the high chloride blank present in a particular lot of nylon filters.

Airborne particulate matter samples were collected in two size ranges: fine ($d_p < 2.2$ μm) and total particulate matter (no size discrimination). The fine particle samples for SO_4^{2-}, NH_4^+, Na^+, and water-soluble Mg^{2+} were collected on a Teflon membrane filter (Teflo, Gelman Science, 0.5 μm pore size, filter holder D in Fig. 2), located downstream of a cyclone separator that removed the coarse particles with nominal aerodynamic diameters greater than 2.2 μm. Water-soluble Br^- also was measured, but was found to be below the detection limit in greater than 95% of the samples, and will not be discussed further here. Fine particle NO_3^- and Cl^- data were obtained from the denuder difference sampler as discussed previously. Data on total particulate matter ionic composition were obtained from the open face prefilters of the tandem filter units used for collecting gas phase species (lines E and F, Fig. 2).

All nylon filters and KOH filters from lines B and C were leached by lightly shaking each of them in 20 ml of CO_3^{2-}/HCO_3^- buffer solution, the eluent for the ion chromatograph, for 3 h or more at 10°C. Polytetrafluoroethylene filters were wetted with 0.2–0.25 ml of ethanol to reduce the hydrophobic nature of the material (Derrick and Moyers, 1981), and they were then leached with distilled, deionized water in the same manner as the nylon filters. KOH impregnated filters from line F were leached with distilled, deionized water in the same manner as the Teflon filters.

The concentrations of HNO_3 and HCl measured as NO_3^-, and Cl^- on nylon filters and HCl measured as Cl^- on the KOH impregnated filters were determined by ion chromatography (Models 2020i and 10, Dionex Corp.). The concentrations of particulate SO_4^{2-}, NO_3^-, and Cl^- also were determined from the extracts of the PTFE filters using ion chromatography (Mulik *et al.*, 1976). The same PTFE filter extracts were analyzed for particulate ammonium ion by an indophenol colorimetric procedure (Bolleter *et al.*, 1961) and for water soluble Na^+ and Mg^{2+} by flame atomic absorption (Model AA-6, Varian Techtron). Instrument detection limits for NO_3^-, Cl^-, SO_4^{2-}, NH_4^+, Na^+, and Mg^{2+} were 0.6, 0.1, 0.6, 0.8, 0.2 and 0.2 μg/filter, respectively. Single sample analytical precisions for HCl, HNO_3, SO_4^{2-}, NO_3^-, and NH_4^+ were all in the range $\pm$4–6%; the precision for total aerosol Cl^- was $\pm$9% and $\pm$7% for the fine Cl^-. Precisions for single samples of species present at low concentration that were analyzed by flame atomic absorption were wider: Na^+ ($\pm$14–18%), Mg^{2+} ($\pm$28–34%). Monthly average values of n samples (generally 5 or 6) are more precise by a factor inversely proportional to the square root of n-1 (e.g. by a factor of 2.0 or 2.2).

Nitric acid concentrations measured by the tandem filter method on nylon filters located downstream of a Teflon prefilter often are biased high due to decompositon of ammonium nitrate collected on the prefilter (Appel *et al.*, 1980; Solomon *et al.*, 1988b). Likewise, aerosol nitrate levels collected on Teflon filters often are biased low, as confirmed in this experiment by comparison of the fine particle nitrate collected downstream of the denuder system (filter B1) vs that collected on the Teflon filter D in Fig. 2. On average, the NO_3^- concentrations collected on Teflon filter D were 45% lower than those collected on nylon filter B1. To obtain the best estimates of the true ionic composition of the aerosol for use in subsequent calculations, the amount of NH_4NO_3 volatilized from Teflon filter E1 was computed and then added to the NH_4^+ and NO_3^- content of the total aerosol samples collected on filter E1. This artifact adjustment proceeded as follows. The HNO_3 data computed from the denuder difference filter set A and B in Fig. 2 is known to be virtually free of filter artifacts (Hering *et al.*, 1988), while the decomposition of $NH_4NO_3^-$ aerosol collected on Teflon filter E1 is known to be reflected in an increase in apparent HNO_3 collected on downstream nylon filter E2 (Solomon *et al.*, 1988b). The excess HNO_3 collected on filter E2 due to decomposition of NH_4NO_3 from filter E1 was determined by difference between the HNO_3 collected on filter E2 vs that determined from the denuder difference filter set A and B. Then the excess HNO_3 on filter E2 was equated to the amount of aerosol NO_3^- lost from Teflon filter E1, and an equivalent amount of NH_4NO_3 was added to the total aerosol NO_3^- and NH_4^+ measured on filter E1 in order to correct for the aerosol nitrate sampling artifact. Some NH_4NO_3 likewise will be lost during sampling from the Teflon fine particle filter D. Since NH_4NO_3 in the Los Angeles atmosphere is found predominantly in the fine particles (Wall *et al.*, 1988), the total aerosol NH_4NO_3 loss just determined also provides a reasonable estimate of the amount of NH_4^+ lost from the fine particle samples, and that increment therefore was added to the composition of the fine aerosol samples; fine aerosol Cl^- and NO_3^- data are taken from the denuder difference system rather than from filter D.

The tandem filter measurements may be biased if NaCl particles collected on the prefilter reacted with strong acid gases passing through that filter. In the discussion that follows, the denuder difference data are used with the substitution of tandem filter HCl data on the 3 sampling days that occurred during transition from the nylon to the KOH impregnated filters, and on the 6% of occasions when the denuder difference value was unavailable. Regression of monthly average HCl concentrations measured by the tandem filter method on monthly average HCl concentrations measured by the denuder difference method yields a slope of 0.92 ($\pm$0.047) with an intercept of 0.22 ($\pm$0.069) $\mu g\,m^{-3}$ with a correlation coefficient (r) of 0.89. The mean of the 108 monthly HCl values from tandem filter measurements is 1.35 $\mu g\,m^{-3}$ with a standard deviation of the mean 0.082 $\mu g\,m^{-3}$, while for the denuder difference data, the mean is 1.23 $\mu g\,m^{-3}$ with a standard deviation of the mean of 0.079 $\mu g\,m^{-3}$.

RESULTS

Annual average HCl concentrations measured by the denuder difference method during the year 1986 ranged between 0.39 and 1.25 ppb (0.57 and 1.84 $\mu g\,m^{-3}$) over the nine stations shown in Fig. 1. The annual average HCl values measured by the tandem filter method ranged from 0.54 to 1.2 ppb (0.8 to 1.8 $\mu g\,m^{-3}$). These concentrations are comparable to annual average HNO_3 measurements made over the same time period, 0.12–2.6 ppb using the denuder difference method (Solomon *et al.*, 1988a, 1991).

The daily time series of ambient HCl concentrations is shown in Fig. 3. HCl concentrations peak in the summer months, with peak single day concentrations of 4.02 ppb (Hawthorne) and 3.20 ppb (downtown Los Angeles). Offshore, at San Nicolas Island, HCl concentrations are usually very low, with little seasonal variation.

Before comparing gas phase HCl to aerosol phase Cl^-, it is useful to examine an ion balance on the water

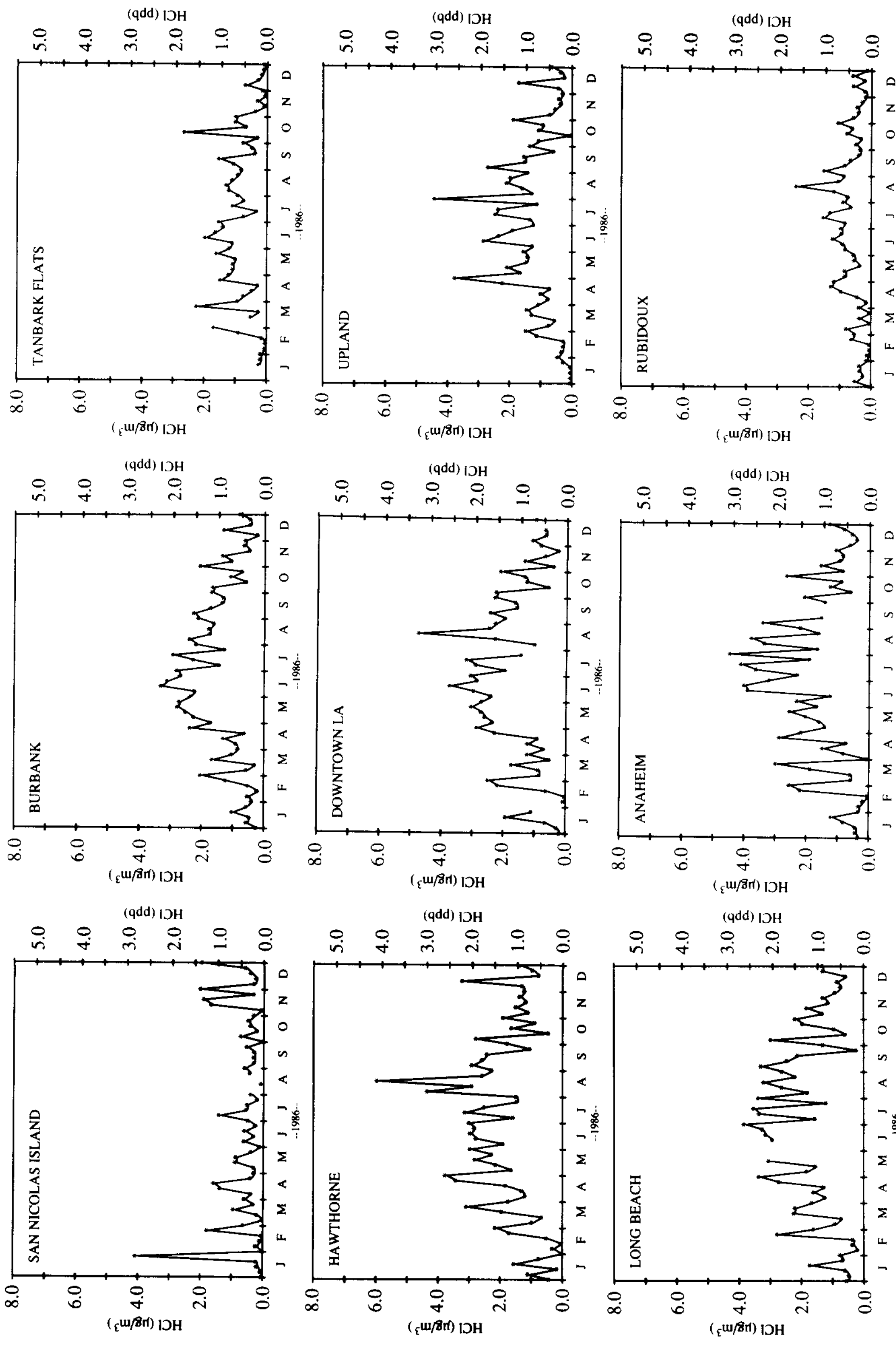

Fig. 3. Daily hydrochloric acid concentrations as measured by the denuder difference method.

soluble portion of the aerosol, as shown in Figs 4 and 5. The data of Wall *et al.* (1988) show that hydrogen ion concentrations in the Los Angeles aerosol are a very minor contributor, and therefore an ion balance should close without considering H^+ data. Indeed, the ion balances of Figs 4 and 5 show good agreement. There is no detectable trend in anion or cation deficit, except in the total aerosol measured at Rubidoux. The Rubidoux site experiences very high ammonium nitrate concentrations (Hildemann *et al.*, 1984; Solomon *et al.*, 1988b, 1989), and the small ionic imbalance at Rubidoux may be related to filter artifacts resulting from total aerosol collection on Teflon filters.

The composition of the ion balance at San Nicolas Island reflects the marine nature of the aerosol. The sodium to chloride molar ratio is more similar to that of seawater than is observed for the near coastal urban aerosol. The Na^+/Cl^- molar ratio of annual average concentrations is 1.04 at San Nicolas Island, compared to 1.96 at Hawthorne and 0.858 for seawater (Stumm and Morgan, 1981). For both Na^+ and Cl^-, only 12.0% and 11.3% of their respective mass concentrations are found in the fine particle fraction at San Nicolas Island, confirming that sea salt is largely a coarse aerosol component. The average composition of the ionic material in the coarse aerosol fraction at San Nicolas Island (total aerosol less fine aerosol) in per cent of total equivalents is 40.6% Na^+, 39.1% Cl^-, 0.7% NH_4^+, 4.8% NO_3^-, 9.9% Mg^{2+}, and 4.8% SO_4^{2-}. In contrast, the fine aerosol at San Nicolas Island is largely ammonium sulfate plus ammonium nitrate mixed with a lesser amount of fine sea salt aerosol with an average composition in per cent of total equivalents of 19.0% Na^+, 18.4% Cl^-, 28.0% NH_4^+, 10.1% NO_3^-, 4.1% Mg^{2+}, and 20.3% SO_4^{2-}.

Near the coast at Long Beach a different average composition is seen, with more aerosol nitrate present. The coarse particles at Long Beach average 24.1% Na^+, 10.1% Cl^-, 16.1% NH_4^+, 30.7% NO_3^-, 9.3% Mg^{2+}, and 9.6% SO_4^{2-}. The fine aerosol at Long Beach is mostly ammonium nitrate and ammonium sulfate with 4.6% Na^+, 3.6% Cl^-, 42.6% NH_4^+, 25.4% NO_3^-, 1.1% Mg^{2+}, and 22.6% SO_4^{2-}.

At the onshore sites, total aerosol sodium and chloride concentrations are lower than at San Nicolas Island. Annual average total aerosol sodium concentrations decline from 6.33 $\mu g\,m^{-3}$ at San Nicolas Island to 2.32 and 2.67 $\mu g\,m^{-3}$ near the coast at Long Beach and Hawthorne to 1.12, 1.07, and 0.49 $\mu g\,m^{-3}$ at the farthest inland sites at Rubidoux, Upland and Tanbark Flats. Depletion of Cl^- relative to Na^+ is noted. The coarse particle Na^+/Cl^- molar ratio (of annual average concentrations) increases from 1.04 at San Nicolas Island to 1.96 at Hawthorne and 2.31 at Long Beach. The molar ratio is 3.92 and 3.44 at Rubidoux and Upland. Depletion of Cl^- from the fine aerosol also is evident with an annual average Na^+/Cl^- molar ratio of 0.97 at San Nicolas Island increasing to 1.22 and 1.29 at Long Beach and Hawthorne. At the inland sites of Upland and Tanbark Flats the fine particle Na^+/Cl^- molar ratios are 1.27 and 3.0, respectively.

The situation at the Rubidoux monitoring site is a very interesting one. The chloride depletion from the aerosol phase is almost complete. The coarse particle ion balance at Rubidoux on average contains only 4.3% Cl^-, vs 14.7% Na^+ (percentage of total equivalents) with the remainder of the ionic material consisting of 8.8% NH_4^+, 35.6% NO_3^-, 20.6% Mg^{2+}, and 16.0% SO_4^{2-}. In contrast, the fine aerosol is mostly ammonium nitrate with 1.8% Na^+, 2.5% Cl^-, 44.8% NH_4^+, 38.0% NO_3^-, 0.6% Mg^{2+}, and 12.3% SO_4^{2-}. Note that fine particle Cl^- exceeds Na^+, and this is the only site monitored in the basin where that phenomenon occurs as an annual average.

Rubidoux is well known for its very high aerosol nitrate concentrations that are due in part to reactions of gas phase HNO_3 with NH_3 to produce aerosol NH_4NO_3 (Hildemann *et al.*, 1984; Russell *et al.*, 1986, 1988; Solomon *et al.*, 1989). In a similar fashion, fine aerosol Cl^- in excess of Na^+ could be produced if gas phase HCl evolved from the coarse sea salt aerosol and then reacted with the high local NH_3 concentrations to produce a small amount of NH_4Cl. If the concentration product $[HCl][NH_3]$ can be calculated over short averaging times, then it is possible to determine whether the gases could be in equilibrium with aerosol NH_4Cl. Short term average data (e.g. hourly) are needed to accurately compare HCl and NH_3 concentrations against this equilibrium hypothesis, and the present experiments are not designed expressly for that purpose. However, from the present data, typical conditions at Rubidoux and at Riverside (near Rubidoux) can be used to show that conditions are present that are close to those required for NH_4Cl formation from gas phase precursors (Pio and Harrison, 1987; Harrison *et al.*, 1989; Allen *et al.*, 1989).

At Riverside, the summertime (1 June–29 September 1986) average daytime maximum temperature is 32°C with an average daily minimum relative humidity of 25%, while the night-time minimum temperatures average 15°C with an average daily maximum relative humidity of 78%. The wintertime (January, February, December, 1986) average maximum daytime temperature is 22°C with an average daily minimum relative humidity of 19%, and the average night-time minimum temperature is 8.6°C with an average daily maximum relative humidity of 58% (Hawkins, 1989). At these conditions the concentration product $[HCl][NH_3]$ predicted at equilibrium with solid phase NH_4Cl is approximately (to one significant figure): 400 ppb^2 (32°C, 25% r.h.); 6 ppb^2 (15°C, 78% r.h.); 40 ppb^2 (22°C, 19% r.h.); and 1 ppb^2 (8.6°C, 58% r.h.) (Pio and Harrison, 1987). Referring to 24-h average NH_3 concentration data collected concurrently with the present samples by Solomon *et al.* (1988a) at Rubidoux, 24-h average NH_3 concentrations are seen to undergo wide variation, ranging from 7.2 to 86 ppb (5–60 $\mu g\,m^{-3}$), with an annual average of 43 ppb (30 $\mu g\,m^{-3}$). Considering that HCl concentra-

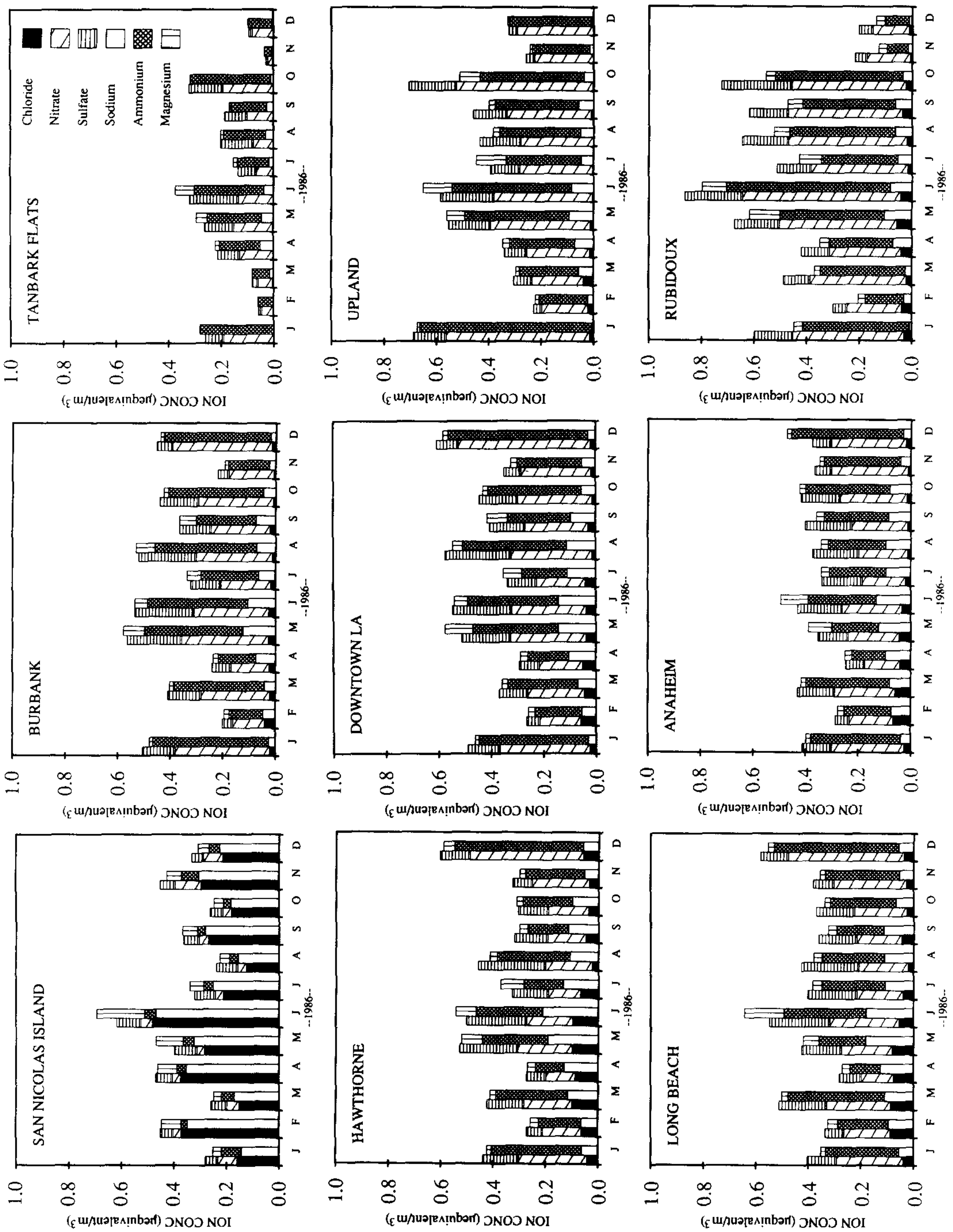

Fig. 4. Anion and cation balances on the total suspended particulate matter samples.

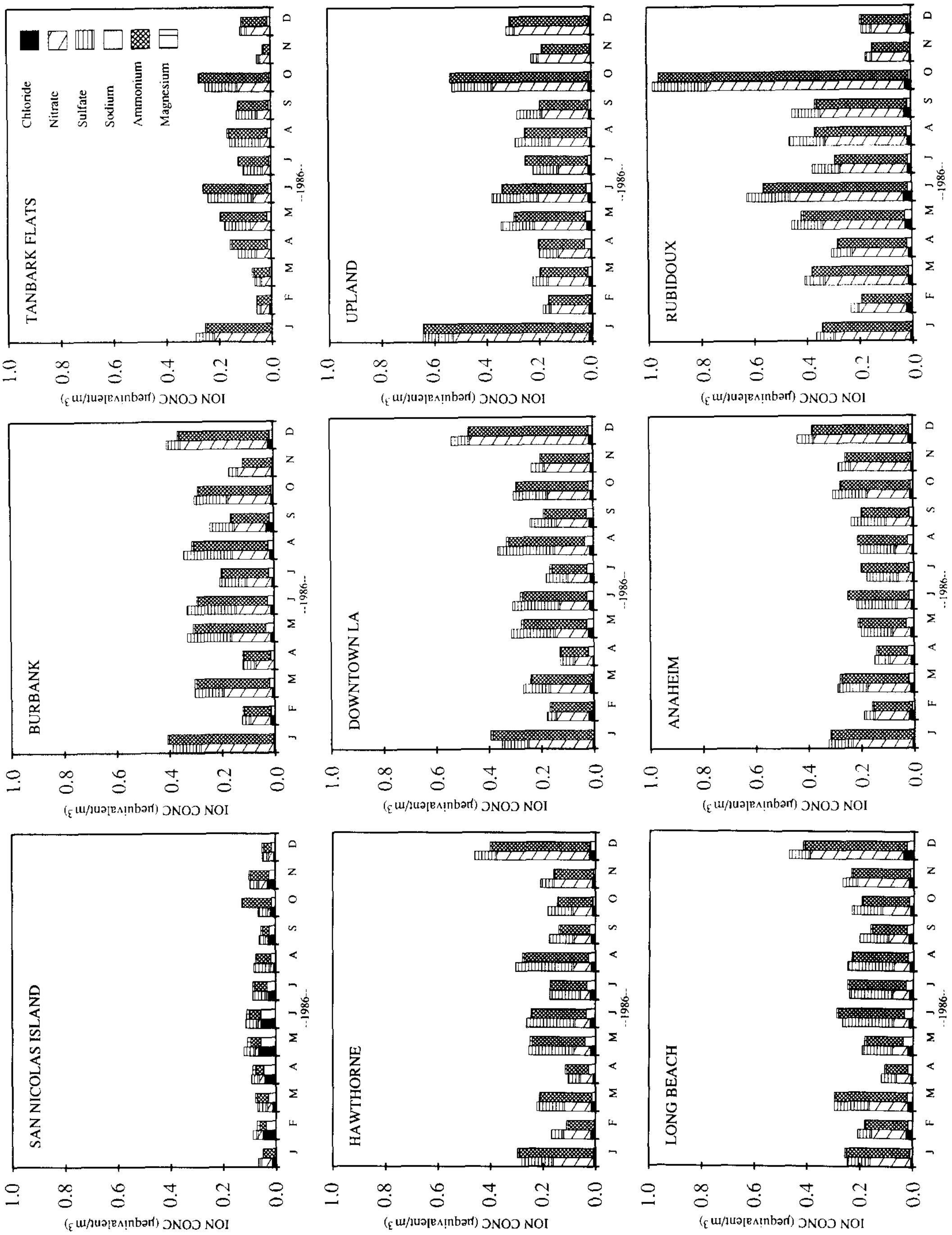

Fig. 5. Anion and cation balances on the fine suspended particulate matter samples.

tions found upwind at Anaheim and Los Angeles average about 1.1 ppb, it is likely that the concentration product $[HCl][NH_3]$ approaches 50 ppb^2 on many days as air masses approach Rubidoux from upwind, high enough to produce NH_4Cl formation in winter months and under the lower temperature conditions observed in summer months. If NH_4Cl formation takes place, then HCl concentrations will decline at Rubidoux relative to upwind sites, as is indeed suggested by Fig. 1. The annual average of the product of the 24 h average concentrations of HCl times NH_3 at Rubidoux is 19 ppb^2, which is below the potential 50 ppb^2 if all of the upwind NH_3 and HCl were still in the gas phase. This is still almost four times the average concentration product observed at other stations. For example, the annual average products of concentrations are 4.1 ppb^2 at Upland and 4.6 ppb^2 at Anaheim. The concentration product is generally higher at Rubidoux than at the other stations due to the high ammonia concentrations at Rubidoux (Russell and Cass, 1984; Solomon *et al.*, 1988a,b). At all monitoring stations other than Rubidoux, ammonia concentrations show little seasonal variation and are generally lower than 5.7 ppb (4 $\mu g\,m^{-3}$).

Fine particle Cl^- in excess of fine particle Na^+ occurs in some months at stations other than Rubidoux. Wall *et al.* (1984) present evidence that fine Cl^- in excess of Na^+ at Claremont (near our Upland site) may be derived from HCl reactions with fine soil dust, not NH_3. This is quite likely, since ammonia concentrations at Upland/Claremont on average are much lower than at Rubidoux. However, it is possible that NH_4Cl formation does occur at times elsewhere in the air basin, particularly under colder conditions within the observed temperature range. Due to the strong dependence of the NH_4Cl equilibrium dissociation constant, K_p, on temperature and relative humidity, the existence of equilibrium with the aerosol phase can only be suggested by the data presented here, but the evidence is strong enough to warrant further investigation.

If ambient HCl concentrations are derived from the attack of acid gases on sea salt particles, then there may be a systematic relationship between the chloride depletion of the aerosol (relative to sodium) and the increase in ambient HCl levels. Monthly average values for all sodium and chloride species are compared in Fig. 6. The values reported for the coarse aerosol mode are determined by the difference between total aerosol and fine aerosol values. Total chloride and sodium species show a seasonal cycle in 1986 at all nine stations studied. Concentrations peak in the summer and are lowest in the winter. Sodium is a larger fraction of the total aerosol in summer than in winter, probably due to the general pattern of offshore winds in the winter and onshore winds in the summer (DeMarrais *et al.*, 1965). Surprisingly good agreement is seen between aerosol sodium and the summation of HCl plus aerosol Cl^-, with a pattern to the degree of disagreement. Chloride species in the aerosol are deficient relative to Na^+ in the summer, most notably in June and July. HCl accounts for 5.5% of the total chloride species at San Nicolas Island, rising to 44 and 48% at Long Beach and Hawthorne near the coast, increasing to 74 and 95% inland at Upland and Tanbark Flats. Rubidoux is an exception, where most of the Cl^- is in the aerosol phase (only 36% is present as HCl).

Figure 6 shows that chloride and sodium species are either conserved or undergo dry deposition at nearly the same rate. Using the size distribution of sodium in an aerosol with a strong maritime influence as reported by Wall *et al.* (1988), and the aerosol deposition velocities as discussed by Sehmel (1980), it is estimated that the deposition velocity for coarse sea salt particles is in the range 1.5–4.2 $cm\,s^{-1}$. Harrison *et al.* (1989) report deposition velocities for HCl in the range of 0.3–6.9 $cm\,s^{-1}$, averaging 1.9 $cm\,s^{-1}$. These values suggest that the deposition rates of coarse sea salt particles and gaseous HCl have roughly the same magnitude. The tendency toward a small deficit in chloride relative to sodium could be explained by a faster deposition or removal of HCl than aerosol sodium and aerosol chloride. The near equality of sodium and total gaseous plus aerosol chloride as concentrations change from month to month supports the hypothesis that sea salt is the principal source of chloride in the Los Angeles atmosphere. The loss of aerosol Cl^-, the gain in aerosol NO_3^- and SO_4^{2-}, and the gain in gaseous HCl relative to Na^+ as the air masses encounter the polluted urban area supports the hypothesis that reaction of acid gases with sea salt is the source of the HCl.

There is a sharp rise in HCl concentrations at the urban coastal stations when compared to San Nicolas Island, and then HCl concentrations decrease with further distance inland. Concentrations are lowest in the winter months (November–February) and at the inland station at Rubidoux. In summer months, coastal concentrations of HCl are 7–10 times higher than those at San Nicolas Island, and do not decrease as rapidly with distance inland as they do in the winter months. Total particulate chloride is about one fifth as high at Long Beach and Hawthorne than it is at San Nicolas Island. It decreases with further distance inland to about one tenth of the concentrations found at San Nicolas Island. Loss from the fine mode is not as rapid as loss from the total aerosol, indicating that chloride is preferably lost from the coarse mode. Sodium does not drop as sharply as chloride. At near coastal stations sodium is present at approximately half the concentration observed at San Nicolas Island. Sodium concentrations at inland sites decrease to 20 to 30% of the values observed at San Nicolas Island. The decrease is not as pronounced in November, December or January. The sodium loss from the fine mode is not as large as from the total aerosol, indicat-

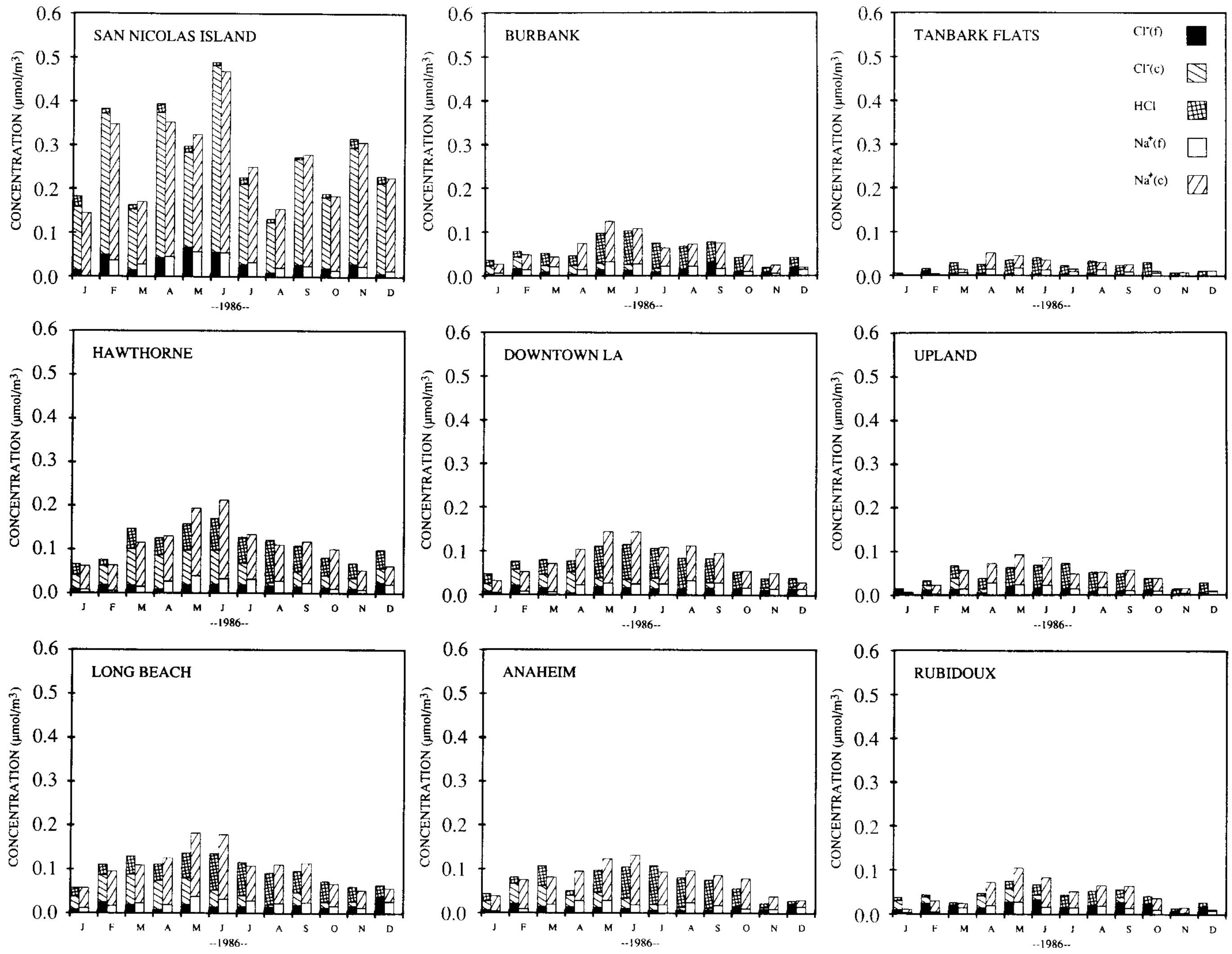

Fig. 6. Aerosol sodium and total chloride balances. Fine suspended particulate matter is denoted by (f) and coarse by (c).

ing preferential loss from the coarse mode as expected given the higher dry deposition rates for coarse mode aerosol.

Wall *et al.* (1988) present three points as evidence for the occurrence of Reaction (1),

$$HNO_3 + NaCl \rightarrow NaNO_3 + HCl \quad (1)$$

all of which are supported by the data presented in this paper. Noted are high concentrations of coarse particle nitrate, sodium, and chloride during periods of westerly winds (from the ocean towards land), a higher concentration of coarse particle nitrate than coarse particle ammonium, indicating that some coarse particle NO_3^- must be associated with other cations (e.g. Na^+), and coarse chloride depletion relative to coarse sodium. To these experiments, we add the year long data set on HCl, Cl^-, and Na^+ balances of Fig. 6 which show that the HCl reaction product is present in the atmosphere in the proper amounts. The annual time series of HNO_3 concentrations measured concurrently with the present experiments at these monitoring sites during 1986 by Solomon *et al.* (1988a,1991) show that ambient HNO_3 concentrations peak in summer months at these sites. When coupled with summer peaks in total chloride and sodium concentrations, these higher summer HNO_3 levels are consistent with production of the summer seasonal increase in HCl concentrations (see Fig. 3) via Reaction (1).

CONCLUSIONS

The concentrations of gas phase acids and particulate matter in the fine mode and in the total aerosol were measured at nine sites throughout Southern California during the year 1986. Ammonium, nitrate, sulfate, sodium, and chloride were the major ionic materials studied. Annual average HCl concentrations as high as 1.25 ppb were measured, which is close to the annual average HNO_3 concentrations measured in the Southern California atmosphere during the course of this study.

Evidence of the production of HCl from sodium chloride aerosol in photochemical smog was found in the nature of the coarse particle ionic composition and the balance between aerosol sodium, aerosol chloride, and gaseous HCl. The coarse aerosol fraction changes from one dominated by chloride and sodium at San Nicolas Island to high percentages of nitrate, ammonium, sodium, and sulfate at the inland stations. Chloride depletion with respect to sodium in the aerosol along with the near equality of monthly average aerosol sodium and total gaseous plus aerosol chloride concentrations point to the transformation of coarse particle sea salt derived chloride to form gaseous HCl by acid gas reaction. The likelihood that fine particle NH_4Cl then is formed from gaseous HCl at Rubidoux where high ammonia concentrations are present was noted. In this sequence of events, an atmospheric process occurs in which coarse sea salt aerosol can in part be converted to fine particle chloride, in contrast to processes such as condensation and coagulation which generally lead to aerosol growth over time from smaller particles into larger particle sizes.

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