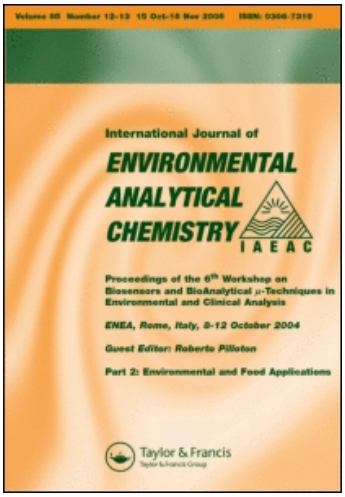

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ATMOSPHERIC GASES, PARTICULATES AND RAINFALL CONCENTRATIONS DURING SUMMER RAIN EVENTS

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Concentrations of the predominant ions and of hydrogen peroxide in rainwater were measured during two rain events in Hong Kong in August 1995. The ambient nitrogen oxides, sulphur dioxide and ozone concentrations, as well as respirable suspended particulates, were monitored throughout the month, and the concentration and composition of total suspended particulates were also measured before and after the events. Event 1 heralded the commencement of a typhoon. The concentrations of all analytes, with the exception of hydrogen ion, decreased during event 1, due to exhaustive washout of alkaline particulate matter. The pH reached 3.8 at the end of the event, compared with 5.1 at the start. The shorter, more intense event 2 followed a sharp build-up of atmospheric pollutants and rainwater pH varied in a narrower range, between 3.4–3.7. The concentrations of H^+, SO_4^{2-} and NO_3^- in rainwater were much higher than in event 1, and all analyte concentrations exhibited minima at maximum rainfall intensity. Contributions from in-cloud scavenging and below-cloud gas scavenging to rainwater acidity were both identified, and neutralization by suspended particulate matter also played an important role. The rainwater acidity is attributed to mainly local sources in both events. Both events were characterized by tropical cyclones in the China Seas, which when approaching Hong Kong, lead to a stagnation of local air pollutants. Strengthening winds at the time of event 1 provided more ventilation. Hydrogen peroxide concentrations in rainwater decreased rapidly during both events, and were higher in event 1 than in event 2 because SO_2, and NO_x levels were lower. Elevated concentrations of nitrogen (II) oxide were found to occur during periods of thunderstorm activity, in conjunction with low levels of ozone.

Keywords: Rain event; particulates; washout; lightning; nitrogen(II) oxide; hydrogen peroxide; sulphate

INTRODUCTION

Rainout refers to in-cloud scavenging and involves nucleation scavenging and the scavenging of gases and particles and subsequent reactions during the growth

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of raindrops. The concentrations of analytes in rainwater may also be controlled by below-cloud processes which include coalescence, breakup and evaporation as well as *washout*, the scavenging of gases and particles followed by chemical reactions. We anticipated the washout process to be important in Hong Kong summer rain events because the incoming air mass is usually from a south-east or south-west direction, and has traversed the sea before encountering the high total suspended particulate (TSP) and pollutant gas levels on land. The main aim of this study was to monitor rainfall composition during a single rain event, and to interpret the changes in concentration of analytes during the event. To facilitate the study of the importance of the washout process, additional information was also collected concerning the weather system and physical conditions, together with the aerosol and ambient gas concentrations. The previous reports of Hong Kong rainfall have utilized daily or weekly sampling programs[1–5] and have mainly been concerned with the changes in analyte concentration with season and location.

It is well-known that the duration of the sampling period has a profound influence upon analyte concentrations in rainwater, lower concentrations having been found from weekly sampling compared with event sampling in one study[6]. Sisterson *et al.*[7] found differences in the concentrations of Ca^{2+}, Mg^{2+}, H^+, NH_4^+ and SO_4^{2-} in samples collected on a daily event basis, compared with those collected on a weekly basis, due to chemical degradation of the latter samples. More information, especially concerning the washout processes, can be obtained from the study of shorter-term rain events. Many previous studies of single events have been carried out at other geographic locations. Ames *et al.*[8] have given detailed experimental results from an automatic rain gauge for analyte concentrations in rainfall during several events at Leatherhead, U.K., but without significant interpretation of the data. Seymour and Stout[9] found a rapid decrease of the concentrations of all analytes studied, during the initial part of an event in Michigan USA, with the exception of H^+. The behaviour was attributed to the rapid washout of basic atmospheric particulates. From the concentration (C)-rain intensity (I) variations found by De Pena *et al.*[6] at the Penn State MAP3S Site, USA, correlations of the type:

$$C = aI^{-b} \tag{1}$$

where a and b are constants for a particular event, were found. Applin and Jersak[10] also observed an increase in hydrogen ion concentration in extended rainfall events in Central Missouri, and assumed that neutralization by calcite dust occurred more rapidly and extensively during the initial stages. Durana *et al.*[11] studied 103 rain events at Vitoria, Spain, and observed similar behaviour as above. They concluded that precipitation scavenging is mainly controlled by the

total amount of rainfall, but that intensity modifies the deposition rate also. Convective rain events were investigated by Gatz and Dingle[12], who found that analyte concentrations were negatively correlated with rainfall amount because of scavenging and all drop-growth processes. However, short periods of positive correlation sometimes appeared due to advection. In addition to the above processes, Lim *et al.*[13] cited other mechanisms for the changes in concentration of constituents during rainfall. These were dilution with cloud droplet growth, prompt (initial) removal of the largest particle or droplet, evaporation, and evaporation followed by scavenging of accumulated aerosol particles. The analyte concentrations observed during a rainfall event at a remote coastal site in Ireland were high, and the trends were irregular during the event, but overall a decrease in concentration with time was apparent[13]. These authors noted that sodium chloride particles of marine origin had mass median diameters of 4 to 8 μm and were more abundant near sea-level, so that they were rapidly scavenged. Within-cloud scavenging was thought to be the mechanism for incorporation of the large number of accumulation mode particles into the rainwater. It was interesting that elements of marine origin were found to correlate with one another, but not with rainfall intensity. Event studies at Florida, USA[14] showed considerable depletion of >1 μm atmospheric particles (containing Al, Si, Ca, Fe, Mn and Cl) by rainfall, but rather less for smaller ones (containing K, Zn, Br, Pb and S). The recovery of soil-derived particles was delayed after a rainfall event, but anthropogenically-produced particles (containing S, Zn, Pb and Br) recovered more rapidly. Hogan[15] monitored the meteorological conditions during two rain events and found from samples collected that chloride to sodium ion molar ratios were near unity for moist maritime air, but rather greater in magnitude when convection introduced continental air. Relatively fewer studies have simultaneously monitored ambient gas concentrations along with rainwater composition during single events. Davies[16] found considerable variation of SO_2 concentrations, and also of pH, during individual events at East Anglia, U.K.

Hong Kong provides a unique and challenging environment for air pollution studies which differs markedly from those in Europe and USA. The high population density and associated tall buildings and busy highways in Kowloon are set in a coastal environment in proximity to hills with elevation up to 1000 m. Factories are small, in high rise buildings, and are close to residential areas. The land area of only 1000 km^2 produced 11267 tonnes of particulates, 148759 tonnes of SO_2, and 151811 tonnes of NO_x in 1994[17]. The latter two gaseous pollutants undergo oxidation to acids by gas phase, aqueous phase or aerosol conversions and the humid, sub-tropical climate is expected to accelerate these processes. Elevated concentrations occur for total suspended particulates (TSP) and the annual Hong Kong Air Quality Objective of 80 μg m^{-3} was exceeded at 6 of the

7 Environmental Protection Department (EPD) rooftop monitoring stations in 1995[18]. The typical composition of the TSP is about 50% carbon and 18% SO_4^{2-} by mass with many other minor constituents such as NaCl (roughly 5%), NH_4^+ (ca. 4%) and Ca^{2+} (ca. 2%)[19]. On 3 different sampling occasions in July and August 1995, in periods of dry weather, the mean % by mass of water-soluble SO_4^{2-} and NO_3^- in TSP measured at CityU were 17.1 (s.d. 1.6) and 11.3 (s.d. 0.5) respectively. The particle size distribution for some elements of crustal/marine and anthropogenic origins have been investigated by Fung and Wong[20]. Na and Ca were found to predominate in particles larger than 1 μm, whereas Zn, Cd, Pb and As were distributed in particles of this size or smaller.

In order to more fully understand the variations of analyte concentrations in rainwater during the two rain events studied, measurements of pollutant gas concentrations and of suspended particulates were carried out, and these are described together with the physical conditions, before the discussion of the rain events. This additional information has helped in the understanding of the relative contributions of several different processes to the acidity of the rain in Hong Kong.

EXPERIMENTAL

Instruments

Sulphur dioxide, ozone, nitrogen(II) oxide and nitrogen(IV) dioxide were monitored at 5-minute intervals using Thermo Environmental Instruments gas analyzers: Pulsed Fluorescence SO_2 Analyzer, Model 43A; U.V. Photometric O_3 Analyzer, Model 49; and Chemiluminescence NO-NO_2-NO_x Analyzer, Model 42. A Hewlett-Packard HP 8452A Diode Array spectrophotometer was used to determine hydrogen peroxide. Wind speed and direction were monitored by a Rain Wise Inc. Weatherlog Weather Monitoring System. TSP was collected by a high-volume air-sampler, model GMWL–2000. PM_{10} (particulate matter with nominal diameter <10 μm) was monitored at 5-minute intervals during August 1995 by a TEOM instrument (Rupperecht and Patashnick). A malfunction occurred at the time of event 2, from 09.00 to 14.00 on 24 August. Anions were determined by a Wescan ICM–300 Ion Chromatography Module, with an Alltech 335 Suppressor Module, a Wescan 315 Conductivity Detector, and a Rheodyne 9125 metal-free injection valve. A 150 × 4.6 mm Universal Anion Column was employed, with 1.7mM $NaHCO_3$ and 1.2mM Na_2CO_3 buffer. The injection volume was 0.2 cm^3 and a flow rate of 1.0 cm^3 min^{-1} was used. Hydrogen ion concentrations were determined by a Hanna HI8314 Membrane pH meter. Other

cations were determined by a Shimadzu AA–6501-S Atomic Absorption Spectrometer (Ca at 422.7 nm, Mg at 285.2 nm), a Jenway PFP 7 Flame Photometer (Na at 589.0 nm, K at 766.5 nm) and a Perkin-Elmer Plasma 1000 ICP-AES (Ca at 393.366 nm, Mg at 279.553 nm, K at 766.369 nm and Na at 589.592 nm) with an AS–90 autosampler. The ICP-AES conditions were: nebulizer flow 1.0 dm^3 min^{-1}, auxiliary flow 1.0 dm^3 min^{-1}, plasma flow 15 dm^3 min^{-1}, sample pump rate 1.0 dm^3 min^{-1}.

Sampling

Rainwater samples were collected in two rain events in replicates on the roof of Administration Building 3, CityU (45 m P.D.) in 125 cm^3 polythene bottles with 19 cm diameter polythene funnels. Approximately 20 cm^3 was collected in each bottle, and the amount was later determined by weighing. The site is located in residential Kowloon Tong, and is 3.5 km from Victoria Harbour, several km south of Lion Rock Peak, and some 30 km distant from the new airport construction site. Glassware and sampling equipment were washed with detergent, followed by tapwater, then soaked in a 10% nitric acid acid bath for 48 hours, washed with deionized water and finally with double-distilled-deionized water prior to air-drying before use. Each sampling bottle for hydrogen peroxide determination contained 10 cm^3 of vanadate(V) reagent, and rainwater was collected up to a total volume of 20 cm^3.

Methods

Rainwater samples were weighed to determine the sample volumes and separate aliquots were taken for pH measurement. The samples were then filtered through a 0.2-μm Nylon–66 membrane filter. Subsamples for IC were stored at 4°C, whilst those for FP, AAS and ICP-AES were acidified to pH = 2 by nitric acid prior to storage. All samples were analyzed within 48 hours, with the exception of the anions in event 2. The IC, FP, AAS, ICP-AES analyses all employed standard solutions with external calibration, and blanks and control samples were run routinely. Samples outside the calibration range were diluted.

pH was measured by placing three aliquots of the sample in separate test tubes, and dipping the pH meter electrode in each one sequentially after a steady reading was obtained. The meter was calibrated by pH = 4.01 and 7.00 buffers, and a 0.05 M potassium hydrogen phthalate solution was used as a control.

Hydrogen peroxide in rainwater was determined spectrophotometrically from the oxo-peroxo-pyridine–2,6-dicarboxylato-vanadate(V) complex using modifi-

cations of the impinger[21] and cold trap[22] methods. Samples were weighed after collection, and the absorbance at 432 nm was measured with respect to an appropriate reference beam blank. All rainwater samples were analyzed for H_2O_2 within 2 hours after collection. Total suspended particulates (TSP) were collected for 4-hour periods on previously conditioned and weighed glass fibre and cellulose filter paper in a high volume air sampler. After reconditioning and weighing, the filters were cut into small pieces, placed in sealed 250 cm^3 beakers with 75.00 cm^3 double distilled-deionized water, and the mixture was sonicated for 15 min. The mixture was filtered through Whatman filter paper with suction, and then the filtrate was passed through a 0.2-μm Nylon–66 membrane filter. The solution was placed in a 125 cm^3 plastic bottle for subsequent analysis of anions and cations.

During event 2, the rainwater intensity was also estimated by timing the fixed volumes collected.

The limits of detection (LOD, as defined in ref. 23, in units of μmol dm^{-3}) for the analytical methods using the stated instruments in parentheses were as follows: Na (FP), Mg (AAS), K (FP), Ca (AAS): 2.5, 0.08, 0.15, 1.9 respectively; F^-, Cl^-, NO_3^-, SO_4^{2-}(all IC): 2.3, 1.4–2.6, 2.5–3.9, 3.7–5.6 respectively; H_2O_2 (spectrophotometer) 0.6.

Data analysis was made using Sigmastat software at a = 0.05.

Chemicals

AAS and ICP-AES standards were obtained from BDH (for K, Na, Mg), Fluka (Cd) and Buck Scientific (Pb). 50 ppm stock solutions were stored at 4°C, and calibration working standards were prepared daily. IC standards were prepared from alkali metal salts, from Reidel-de-Haën (RDH), reagent grade (RG). Reagents for hydrogen peroxide determination were obtained from RDH, RG. The 35% aqueous hydrogen peroxide stock solution was standardized by potassium permanganate titration, and the permanganate was in turn standardized by sodium oxalate.

RESULTS AND DISCUSSION

Meteorological Conditions

The two events studied, labelled events 1 and 2 in the following, occurred on 11 August and 24 August 1995 respectively. Fine weather prevailed in Hong

Kong on August 9 and 10, when Tropical Storm Helen entered the South China Sea, being < 500 km distant from Hong Kong on 11 August. Rain commenced at CityU at 10.00 on August 11, and persisted through the cloudy afternoon. The Strong Wind Signal No. 3 was hoisted at the RO at 17.45. Gale force winds (Typhoon Signal No. 8) and 242 mm of torrential rain were recorded at the Royal Observatory (RO)[24], on the day following event 1, 12 August when Helen made landfall over Guangdong Province. Tropical Storm Janis was about 1300 km from Hong Kong on August 23 and made landfall over northeast China on August 25/26. Event 2 followed a fine spell of 8 days. Heavy showers and thunder-storms, which had developed over Guangdong in China, drifted south across Hong Kong near mid-day on 24 August and the rainfall was concentrated over a narrow belt including the centre of Kowloon. The rainfall recorded at the RO was about 6–7 mm h^{-1} between 11.00 to 13.00, and then 19.3 mm h^{-1} between 13.00 to 14.00. The rain stopped at CityU after 14.10. Periods of sunshine occurred towards the end of the event, and after sampling. Approaching cyclones, 500-1000 km distant from Hong Kong, produce fine, hot weather. The subsidence of warm, hot air enables local pollutants to accumulate. The diurnal wind speed increased from 3.2 ms^{-1} on August 8 to 13.9 ms^{-1} for the day of event 1, dispersing local air pollution. However the windspeed remained low throughout the day of event 2, and an inflow of continental air from the north occured. A summary of the sampling times and meteorological conditions for events 1 and 2 is given in Table I.

Concentrations of Ambient Gases

Ambient gas levels fluctuated over the short sampling periods of the two rain events and it is more instructive to consider the longer-term variation of the concentrations. Figure 1A shows the daily mean values of NO, NO_2, O_3 and SO_2 concentrations measured at CityU in August 1995. With respect to event 1, the pollutant gas concentrations on August 11 were near the mean values for the month, but SO_2, NO and NO_2 all dropped during the prolongued rainfall from 11 to 12 August, when minima occurred. This was due to dispersion by the strengthening winds, as wel as incorporation of these pollutants into rainwater following oxidation in the gaseous phase or at the surface of aerosol particles, and the solubilization reactions[25] (1a)-(1g):

$$NO(g) \leftrightarrow NO(aq),\ H(NO) = 1.93 \times 10^{-3} mol\ dm^{-3}\ atm^{-1} \quad (1a)$$

$$NO_2(g) \leftrightarrow NO_2(aq),\ H(NO_2) = 1.0 \times 10^{-2} mol\ dm^{-3}\ atm^{-1} \quad (1b)$$

$$2NO_2(g) + H_2O \leftrightarrow 2H^+ + NO_2^- + NO_3^-,\ K_1 = 2.44 \times 10^2 mol^4\ dm^{-12}\ atm^{-2} \quad (1c)$$

TABLE I Meteorological conditions of rain events 1 and 2

		Event 1	*Event 2*
Date		11/8/95	24/8/95
Sampling time duration		10:30-1:25	11:40-13:15
*Temperature (°C)		27.0	28.3
*R elative Humidity (%)		85	84
*Daily Rainfall (mm)		28.1	32.7
*Typhoon signal		No. 3	Not raised
*Storming		Not Recorded	Recorded
*Prevailing wind direction (°)		60	260
During sampling: direction (°)/speed (ms^{-1})		134.7/2.7	260/1.17
Average direction 1 hr before sampling (°)		95.7 (77.7)	218.4 (90.4)
Average direction 3 hr before sampling (°)		85.0 (87.2)	203.3 (99.8)
Average speed 1 hr before sampling (ms^{-1})		2.0 (0.9)	0.7 (0.4)
Average speed 3 hr before sampling (ms^{-1})		2.5 (1.1)	1.0 (0.9)
High level air mass wind direction (°)	1000m	82[a]	359[b]
	2000m	91[a]	30[b]
wind speed (ms^{-1})	1000m	11.8[a]	2.8[b]
	2000m	12.0[a]	5.3[b]
Low level air mass (< 66 m) wind direction (°)		80[a]	270[b]
wind speed (ms^{-1})		2.0[a]	0.5[b]
Climatic condition before sampling		5 dry days preceded rain event	8 dry days preceded rain event
Climatic condition after sampling		continuous raining: > 200 mm rainfall recorded on next day	drizzle and sunshine

Data available [a]2 hours and [b]3 hours before rain event.
Starred data are taken from ref. 24 and are daily averages. Numbers in parentheses are standard deviations of the preceding quantities.

$$NO(g) + NO_2(g) + H_2O \leftrightarrow 2H^+ + 2NO_2^-,\ K_2 = 3.28 \times 10^{-5}\ mol^4\ dm^{-12}\ atm^{-2} \quad (1d)$$

$$SO_2(g) \leftrightarrow SO_2(aq),\ H(SO_2) = 1.24\ mol\ dm^{-3}\ atm^{-1} \quad (1e)$$

$$SO_2 \cdot H_2O \leftrightarrow H^+ + SO_3^-,\ K_1 = 1.29 \times 10^{-2}\ mol\ dm^{-3} \quad (1f)$$

$$HSO_3^- \leftrightarrow H^+ + SO_3^{2-},\ K_2 = 6.01 \times 10^{-8}\ mol\ dm^{-3} \quad (1g)$$

The reactions (la)-(lg) may be followed by subsequent aqueous phase oxidation reactions. These have been discussed elsewhere in detail for SO_2(aq) and involve species such as H_2O_2, O_3, O_2 plus a catalyst, etc.[26].

Event 2 was characterized by much higher pollutant gas concentrations than event 1: the 10-h average concentrations of NO and NO_2 before this event being more than twice as large compared with those prior to event 1. Event 2 followed

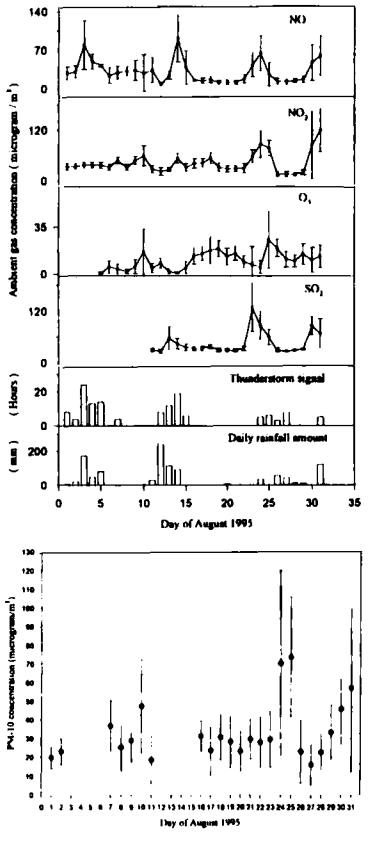

FIGURE 1 Variation A) of ambient gas concentrations, and B) of respirable particulate matter (PM_{10}) concentrations, with meteorological conditions during August 1995 in Hong Kong. The error bars represent the standard deviations of the daily averages of 5-minute readings in each case. Thunderstorm and rainfall data are from ref. 24

more than a week without rainfall, with prevailing mild easterly winds, but the sharp rise in SO_2 concentration occurred only on August 23, when windspeed was lowest. The rise is attributed to the buildup of local emissions and the inflow of a northerly airmass. The effects of the power stations to the west of Hong Kong are evident from the contributions to the total emissions in Hong Kong in 1991[27]: 86% of total SO_2, 72% of NO_x and 42% of particulates. Dispersion was slow under the very low wind-speed (Table I). A decrease in SO_2 concentration, predominantly by reactions (1e)-(1g) and subsequent oxidation, then ensued during the rain event 2, on 24 August. By contrast, the concentration of the less-soluble NO(g) continued to rise throughout the rain event, and reached a maximum

concentration on 24 August (Figure 1A). The initial rise of NO(g) concentration on 23 August was due to the build-up of power station and local mobile source emissions. The continuing build-up during the rain event on 24 August is in addition attributed to the natural process[28]:

$$N_2(g) + O_2(g) \leftrightarrow 2NO(g),\ \Delta H^\circ = +180 kJ\ mol^{-1} \quad (2)$$

occurring during the thunderstorm. The periods during which thunderstorm warnings were in effect in August are also shown in Figure 1A, and the high NO levels on 3, 14 and 31 August may also be associated with thunderstorm activity, showing that the natural source inputs may exceed anthropogenic inputs of NO at these times[29]. Ambient NO_2 concentrations were generally low on these other occasions because ozone concentrations were low:

$$NO(g) + O_3(g) \leftrightarrow NO_2(g) + O_2(g). \quad (3)$$

Under the stagnation of pollutants on 24 August ozone levels were also low when NO peaked. NO_2 levels peaked on the day *following* the maximum SO_2 level, Figure 1A, partly because of the thunderstorm production of NO and the limitation of oxidant, but also because of the gas phase removal of NO_2:

$$NO_2(g) + SO_2(g) \leftrightarrow NO(g) + SO_3(g) \quad (4)$$

Regression of O_3 concentration against the ratio of $NO_2$and NO concentrations for data from the entire month gave a significant correlation ($R = 0.81$)[28], as expected from (3). Local wind speed and direction measured at 51 m P.D. at CityU fluctuated rapidly and so that no significant correlations were observed between these parameters and ambient gas concentrations. The microscopic surface windfield at CityU is variable due to the complex topography and proximity to the sea[30].

Particulate Matter Measurements

The ambient TSP concentrations measured before and after each event are summarized in Table II. The concentration and composition of the TSP were fairly similar for measurements prior to each event, but the percentage changes (by mass) in experiments performed before and after the events were –36% for event 1, and +104% for event 2. The respirable suspended particulate matter (PM_{10}) concentration monitored throughout August at CityU is shown in Figure 1B, and it exhibits the same trend as TSP over the timescales of events 1 and 2. The particularly large standard deviation of the daily PM_{10} value on the day of event 2, August 24, is readily interpreted. In the early hours of this day PM_{10} levels were near 10 $\mu g\ m^{-3}$. Then followed the morning build-up of pollutants under the lowest wind speed in August, so that at around 09.00 the PM_{10}level was near 50 μg

m^{-3}. The rain event washed out PM_{10}down to 20 μg m^{-3} at 14.00, but the build up continued so that at 20.00 the concentration was near 150 μg m^{-3}. A wide spectrum of PM_{10}levels therefore occurred during the day of event 2.

Although the sampling times of TSP were not exactly synchronized with the rain events, the removal of particulate matter by washout during event 1, and the buildup of atmospheric pollutants after event 2 are both evident. With respect to the composition of the TSP, the ambient concentrations of Na^+ and Cl^- were similar before and after event 1. This is expected for an incoming mainly maritime air mass at both low and high levels (Table I) since the location of CityU is only several km from the sea. Most notably, a large decrease in the ambient basic crustal cation concentrations (Mg, Ca and K) occurred in the sample taken after event 1, compared with that taken prior to it (Table II). We subsequently show that this is consistent with neutralization of particulate matter by hydrogen ions in the washout process of event 1. By contrast, the relative proportions of analytes in TSP did not greatly change between the sampling on August 23 and that on August 24. However, all of the ambient concentrations roughly doubled from the first sampling to the second. The windspeed remained low until after August 25, although surface wind direction changed markedly between August 23 to 25.

TABLE II Total suspended particulates (TSP) measurements before and after rain events 1 and 2

sampling time[a]	*TSP*[b] (μg m^{-3})	*analyte concentration in water-soluble TSP* (μeq m^{-3}) × 10^3							
		F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	Mg^{2+}	K^+	Ca^{2+}
10/8:11.00	59.0	2.9	97.5	103.7	213.9	126.9	15.5	24.3	66.7
11/8:12.00	37.8	<0.5	103.8	3.0	48.0	95.8	8.6	4.4	18.0
23/8:13.00	56.5	0.6	37.5	103.0	210.2	125.8	10.9	14.2	55.0
24/8:15.20	114.9	0.6	75.7	183.7	566.0	181.7	20.0	42.8	79.3

[a]Sampling commenced at the time indicated for four hours in each case. The times are not exactly synchronized with the events 1 and 2, see Table I. [b]The concentrations are converted to μg (standard m)$^{-3}$ abbreviated to μg m^{-3} throughout the text.

Analyte Concentrations in Rain During Event 1

Figure 2 shows the concentration of (A) the anions Cl^-, NO_3^-, SO_4^{2-} and (B) the cations H^+, Na^+, K^+, Ca^{2+}, Mg^{2+} in replicate rainwater samples taken during the rain event on 11 August. The mean Cl^-/Na^+molar ratio in rainwater from event 1 was 1.2 (s.d. 0.3, N = 6), typical of a maritime air mass, being fairly constant throughout the event. The prevailing low and high level meterological conditions indicate (Table I) that advection was not important during event 1. With the

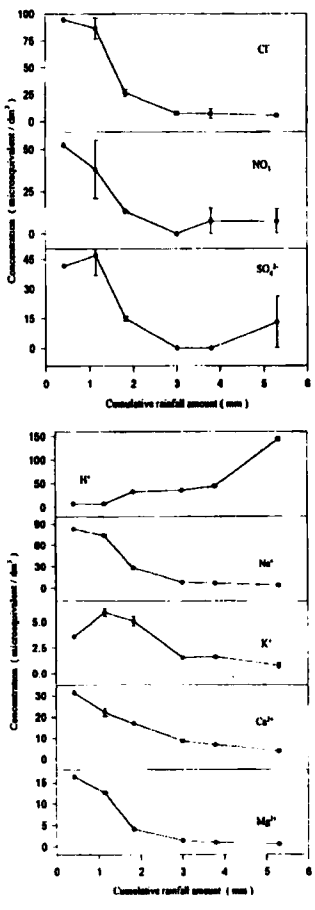

FIGURE 2 Selected A) anion and B) cation concentrations in rain as a function of cumulative rainfall amount for the event 1 on 11 August 1995.

exception of H^+, the highest concentrations occurred at the start of the rain event. Raindrop evaporation would be more likely at this time but was not important due to the high relative humidity (Table I). The major factor which produced the changes in concentration (Figure 2) is considered to be the almost complete below-cloud washout of soluble particulate matter. The particulate matter provided a substantial contribution of aerosol nitrate and sulphate (in the form of ammonium and calcium salts) to the hydrometeors. Most notably, however, the aerosol was exhaustively scavenged of the basic cations Mg^{2+}, Ca^{2+} and K^+. The increase in H^+ concentration up to 3.8 mm of rainfall, from a low initial value, (producing a drop in pH from 5.1 to 4.4), thus resulted from the almost complete

removal of alkaline atmospheric particulates. The final H^+ concentration is however unexpectedly high (pH = 3.8) if it approximates the rainout and below-cloud gas scavenging contributions. This type of behaviour has previously been documented by Seymour and Stout[9]. Table IIIA lists the correlation coefficients between analytes for samples taken during event 1 and all those involving H^+ are negative, since particulate matter removes H^+ from the hydrometeors but contributes the other analytes to the rain water.

TABLE III Correlation coefficients between analyte concentrations in rainwater for events 1 and 2

A. Event 1

	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}
H^+	−0.663	−0.681	−0.728	−0.641	−0.638	−0.548	−0.437
Na^+		0.735	0.959	0.994	0.998	0.973	0.950
K^+			0.722	0.660	0.711	0.608	0.717
Mg^{2+}				0.962	0.942	0.934	0.846
Ca^{2+}					0.993	0.985	0.931
Cl^-						0.977	0.958
NO_3^-							0.932
SO_4^{2-}							

B. Event 2

	Na^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}
H^+	0.656	0.908	0.424	0.476	0.533	0.771	0.747	0.750
Na^+		0.811	0.910	0.942	0.855	0.957	0.678	0.475
K^+			0.592	0.986	0.894	0.830	0.687	0.423
Mg^{2+}				0.667	0.720	0.895	0.763	0.722
Ca^{2+}					0.921	0.891	0.726	0.492
F^-						0.854	0.851	0.681
Cl^-							0.789	0.653
NO_3^-								0.941
SO_4^{2-}								

Analyte Concentrations in Rain During Event 2

For event 2, the faster upper level air mass moved from a north/north-easterly direction, whilst the slower lower level prevailing airmass moved from a south/south-westerly direction (Table I). Figure 3 shows the concentrations in rainwater of the selected anions and cations during this event, together with the variation in rainfall intensity during the sampling period. The concentration-rainfall amount profiles differ considerably from those in event 1. Although storming developed over Hong Kong during the event so that convective motion was probable, and raindrop evaporation may have occurred in the sunshine periods, these two factors are not considered to be the most important ones determining the

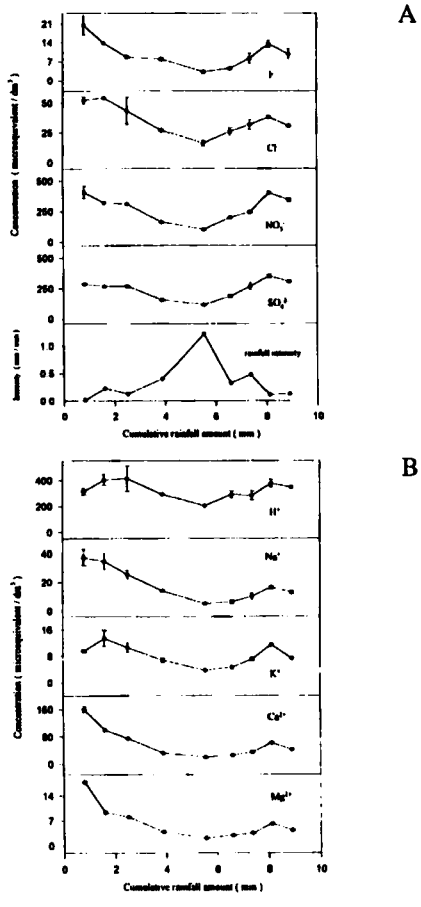

FIGURE 3 Selected A) anion and B) cation concentrations in rain as a function of cumulative rainfall amount for the event 2 on 24 August 1995

analyte concentrations, except perhaps towards the end of the event. Comparing the $Ca^{2+}$and H^+ concentration changes in particular, only during the start of the event when rainfall intensity was lowest was the neutralization replacement the determining factor for the curve profile: in the first 1.6 mm of rain, the decrease in Ca^{2+} concentration was associated with an increase in H^+ concentration. Thereafter, the concentration-rainfall amount profiles of both Ca^{2+} and H^+ exhibited a similar variation pattern. The correlation coefficients between these two analytes, and in fact between H^+ and *all other* analytes, in event 2 turned out to be positive (Table IIIB). This type of behaviour has been documented, but not explained, previously (Case III in ref. 6). In the present case, the initial concen-

tration of H^+ was much higher than in event 1. This was because the high ambient gas concentrations led to the formation of HNO_3 and H_2SO_4 by in-cloud scavenging and oxidation processes, as exemplified by the high NO_3^- and SO_4^{2-} anion concentrations.

The rainfall amount in event 2 was nearly double that in event 1, but the duration was only half as long. The rainfall intensity was thus much greater, and it is well-known that below-cloud soluble gas scavenging is less effective for high intensity raindrops[25]. We assume that the concentration of hydrogen ion is essentially independent of raindrop radius just below the cloud base[31]. Below-cloud gas scavenging could then account for the slight minimum in the H^+ concentration at the time of maximum rain intensity. This process has been discounted as negligible in USA[25], but our model calculations of rainfall composition in China reveal its importance at high ambient pollutant gas levels. The scavenging of particulate matter by the hydrometeors was not as exhaustive as in event 1. Although the scavenging by medium-intensity urban rain droplets is more effective for coarse mode particles (by impaction) than accumulation/ Aitken nuclei modes (by diffusion), both rates increase with the intensity of the rain[32]. The fact that neutralization processes did occur in event 2, just as in event 1, was shown by the increasing molar proportion of hydrogen ion in rainwater, with respect to basic cations, as the event progressed. To summarize, the hydrogen ion concentration in event 2 was thus largely determined by (i) in-cloud scavenging and oxidation of pollutant gases, (ii) below-cloud gas scavenging and oxidation, and (iii) neutralization of hydrometeors by basic particulates. Process (i) occurred to a much larger extent than in event 1 because of the slow approach of the scavenging clouds.

The measured molar ratio Cl^-/Na^+ was anomalous in event 2, being < 1 in TSP, and >1 in rainwater. Rossby and Egner[33] have previously attributed the reason for the production of an increase in the ionic ratio of chloride to sodium in rainwater as the participation of a continental air mass. Replacement of Cl^- by NO_3^- in sea-salt particles is possible by reaction with $HNO_3(g)$, but other more complex factors are involved[34]. The volume-weighted means of the ratio $R = [SO_4 2^-]/[NO_3^-]$ in rainwater were near unity (1.0 ± 0.1) for both events 1 and 2 which indicates the importance of local *versus* long range pollution sources. The seasalt contribution to SO_4^{2-} was relatively greater in event 1 than event 2. This index R has decreased considerably during the past ten years, reflecting both the impact of Hong Kong fuel oil legislation upon local SO_2 emissions, and of the proliferation of mobile emission sources during this period[5].

The H_2O_2 concentration in rainwater at the start of event 1 (Figure 4A) was higher than at the start of event 2 (Figure 4B), as expected from the lower ambient levels of SO_2 and NO_x. The very soluble H_2O_2 gas was rapidly washed out of

the atmosphere during each event. Application of Henry's law gives gaseous H_2O_2 concentrations between 4.8 to <0.25 nmol m^{-3} in event 1, and 1.5 to <0.25 nmol m^{-3} in event 2.

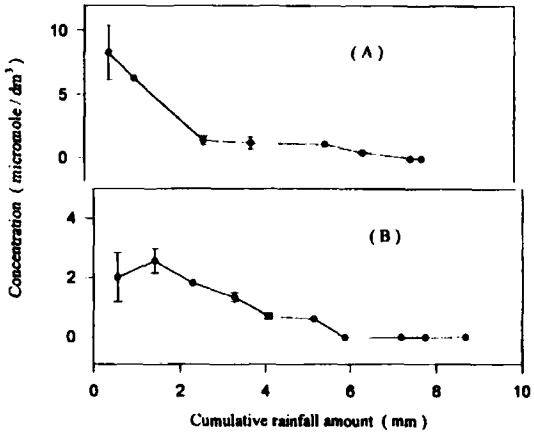

FIGURE 4 Variation of hydrogen peroxide concentrations in rain for A) event 1 on 11 August, and B) event 2 on 24 August 1995

SUMMARY AND CONCLUSIONS

The two rain events have indicated the substantial contribution of in-cloud scavenging, as well as washout of suspended particulate matter and gases to the ionic concentrations in rainwater. In both cases the mole ratio of hydrogen ion increased during the event, with respect to the basic cations. This is interpreted as an indication of the lower aerosol washout contribution as the event proceeded. In event 1, exhaustive scavenging of atmospheric particulates occurred. This was not so for the shorter event 2, and the very low wind speed enabled ambient particulate levels to recover quickly after the event. Without the occurrence of neutralization by suspended particulate matter, Hong Kong rainfall may attain pH values near 3.4–3.7. The acidity of the rain has been attributed to local stationary and mobile land/sea sources but the contribution from regional/continental sources is not well-defined without backward trajectory analyses. Although long-range transport may be responsible for rainfall acidity in other areas, such as Europe and USA[35], local sources appear to mainly account for acid rain in Hong Kong.

For both events studied, the ionic balance between cations and anions in the rainwater was generally poor, due to the omission of certain ions from our stud-

ies, most notably NH_4^+. NH_3 gas scavenging has been shown to strongly influence the composition of precipitation in some other cases[36]. More comprehensive measurements, as well as modeling of the gas and aqueous phase acidification processes, will receive attention in our further studies.

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References

[1] Lee, F. Y. P., in Polmet '91: Proceedings, vol. 2 (ed. J. Boxall, HKIE, Hong Kong, 1991) p. 501–515.
[2] Sequeira, R. and Peart, M. R. (1995). Sci. Total Environ., **159,** 177–183.
[3] Sequeira, R. and Lung, F. (1995). Atmos. Environ., **29,** 2439–2447.
[4] Tanner, P. A., Cheung, S. C., Cheung, K. Y., Ho, L. M., Kan, F. P., Lam, H. P., Lam, Y. S. and Lee, W. Y. (1986). Atmos. Environ., **30,** 2453–2454.
[5] Tanner, P. A. and Chan, S. M. (1996). J. Chromatogr., 739A, 249-256.
[6] DePena, R. G., Walker, K. C., Lebowitz, L. and Micka, J. G. (1985). Atmos. Environ., **19,** 151–156.
[7] Sisterson, D. L., Wurfel, B. E. and Lesht, B. M. (1985). Atmos. Environ., **19,** 1453–1469.
[8] Ames, D. L., Roberts, L. E. and Webb, A. H. (1987). Atmos. Environ., **21,** 1947–1955.
[9] Seymour, M. D. and Stout, T. (1983). Atmos. Environ., **17,** 1483–1487.
[10] Applin, K. R. and Jersak, J. M. (1986). Atmos. Environ., **20,** 965–969.
[11] Durana, N., Casado, H., Ezcurra, A., Garcia, C., Lacaux, J. P. and Dinh, P. V. (1992). Atmos. Environ., **26A,** 2437–2443.
[12] Gatz, D. F. and Dingle, A. N. (1971). Tellus, **23,** 14–27.
[13] Lim, B., Jickells, T. D. and Davies, T. D. (1991). Atmos. Environ., **25A,** 745–762.
[14] Tanaka, S., Darzi, M. and Winchester, J. W. (1980). Atmos. Environ., **14,** 1421–1426.
[15] Hogan, A. W. (1983). Tellus, **35B,** 121–130.
[16] Davies, T. D. (1984). Atmos. Environ., **18,** 2499–2502.
[17] Cheng, C. T., Hong Kong Environmental Protection Department, private communication, 4 May 1996.
[18] Environment Hong Kong 1995, Government Printer, Hong Kong, 1996.
[19] Air Quality in Hong Kong 1994, Report #EPD/TR 2/1996, Air Services Group, Hong Kong Environmental Protection Department, Hong Kong, 1996.
[20] Fung, Y. S. and Wong, L. W. Y. (1995). Atmos. Environ., **29,** 2041–2048.
[21] Sakugawa, H. and Kaplan, L. R. (1987). Atmos. Environ., **21,** 1791–1798.
[22] Hartkamp, H. and Bachhausen, P. (1987). Atmos. Environ., **21,** 2207–2213.
[23] Winefordner, J. D. and Long, G. D). (1983). Anal. Chem., **55,** 712A–724A.
[24] Royal Observatory, Monthly Weather Summary: July 1995 and August 1995 (R. O., Hong Kong, 1995).
[25] Seinfeld, J. H. Air Pollution (Wiley Intersci., New York, 1986) pp. 195–246, 617–657, 695–723.
[26] Brandt, C. and van Eldick, R. (1995). Chem. Rev., **95,** 119–190.
[27] Chung, F. (1993). Green Productivity, **2,** 8–19.
[28] Bunce, N., Environmental Chemistry (Wuertz Publishing Co., Winnipeg, Canada. 2nd ed. 1994) pp. 57, 78–80.
[29] Biazar, A. P. and McNider, R. T. (1995). J. Geophys. Res., **100,** 22861–22874.

[30] Yeung, K. K., Chang, W. L., Wan, B., Kimura, F. and Yoshikawa, T. (1991). Atmos. Environ., **25A,** 2161–2172.
[31] Baechmann, K., Ebert, P., Haag, I. and Prokop, T. (1996). Atmos. Environ., **30,** 1019–1025.
[32] Nieto, P. J. G., Garcia, B. A., Diaz, J. M. F. and Brana, M. A. R. (1994). Atmos. Environ., **28,** 2335–2342.
[33] Rossby, C. G. and Egner, H. (1955). Tellus, **7,** 118–133.
[34] Wurzler, S., Flossmann, A. I., Pruppacher, H. R. and Schwartz, S. E. (1995). J. Atmos. Chem., **20,** 259–280.
[35] Wayne, R. P., Chemistry of Atmospheres (Clarendon Press, Oxford, UK, 1985) pp. 200–216.
[36] Oberholzer, B., Volken, M., Collett, J. L., Staehelin, J. and Waldvogel, A. (1993). Water, Air and Soil Pollution, **68,** 59–73.