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# Application of ion chromatography to the Hong Kong rainfall monitoring program

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## Abstract

Results from a rainwater monitoring program in Hong Kong from May 1994 to April 1995, with 60 sample collection days, are presented for  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  concentrations from suppressed and non-suppressed column ion chromatography. Replicate sampling was employed on a daily basis using both bulk (B) and wet only (W) samplers, and there was no statistically significant difference between the B–W datasets for  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  concentrations in rainwater. From the more complete bulk sample collection dataset ( $n=60$ ), large changes in analyte concentrations were observed for samples collected on different days, with the ranges (in  $\mu\text{equiv. l}^{-1}$ ) 3–348 for  $\text{Cl}^-$ , 3–132 for  $\text{NO}_3^-$  and 12–303 for  $\text{SO}_4^{2-}$ . Neglecting the February 1995 dataset for which  $n=1$ , the volume-weighted monthly mean concentrations displayed narrower ranges, being 16–61, 7–42 and 27–87 respectively. The nature of the source of the analyte and its flux, type of weather system, season and atmospheric conditions, together with the rainfall amount and intensity are some of the factors which produce the changes in analyte concentrations. Below-cloud washout processes cause large changes in analyte concentration at the start of a single rain event, and contribute to the horizontal local variation in analyte concentrations. The ratio of  $\text{SO}_4^{2-}$ – $\text{NO}_3^-$  in Hong Kong rainwater has decreased since 1992 and the reasons for this are discussed.

*Keywords:* Water analysis; Environmental analysis; Inorganic anions

## 1. Introduction

A rainfall monitoring programme has been carried out for one-year at City University (CityU) in which the concentrations of the major anions and cations in rain, as well as relevant physical parameters, were routinely determined. This study documents results from ion chromatography (IC) for spatial and temporal studies of the concentrations of the anions chloride, nitrate and sulphate in Hong Kong rainwater. The project differed from the *weekly* monitoring programme of the Hong Kong Environmental Protection Department (EPD) [1,2] in that the sampling was carried out on a daily basis, replicate

samples were collected, and quality control procedures were employed. A study of the composition of Hong Kong rain during the hot, dry summer of 1992 has been published [3], but the results herein comprise the first comprehensive temporal study other than the publications from the EPD [1,2]. We have employed daily sample collection intervals, due to concerns of sample evaporation and analyte reaction under the sub-tropical climate. We have also investigated the differences in analyte concentrations obtained from bulk versus wet-only sampling of rainwater. The major aims of the monitoring program were to determine the ionic composition of rainfall, assess the prevalence of acid rain [4] and to investigate the seasonal changes in rain composition. Pollutant gas emissions of  $\text{SO}_2$  and  $\text{NO}_x$  have been

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documented regionally [5] and locally [6] up to the mid-1980s and early 1990s, respectively.

The routine use of non-suppressed IC in acid rain analysis has been described by Cape [7]. The advantage of IC is that it can simultaneously analyse the major anions in rainfall at satisfactory speed and sensitivity.

## 2. Experimental

Rainwater samples were collected at the locations shown in Fig. 1, using polythene bottles with wide polythene funnels. Two automatic wet and dry

deposition samplers (MIC Precipitation Collector, Type AU-241) were also situated at CityU for separate collection of the two types of deposition. The rainfall logged at CityU from May '94 to March '95 during this study was 2606 mm, whereas that recorded at the Royal Observatory (Fig. 1A) was 2735 mm [8]. In January, 21 mm of rain fell but we did not collect samples due to technical problems. The frequency of our daily sampling program was largely determined by the rainfall abundance. From October through November only 2 mm of precipitation occurred, so we were unable to collect samples during this period. Sampling vessels were washed with detergent, acid-soaked, and then rinsed thor-

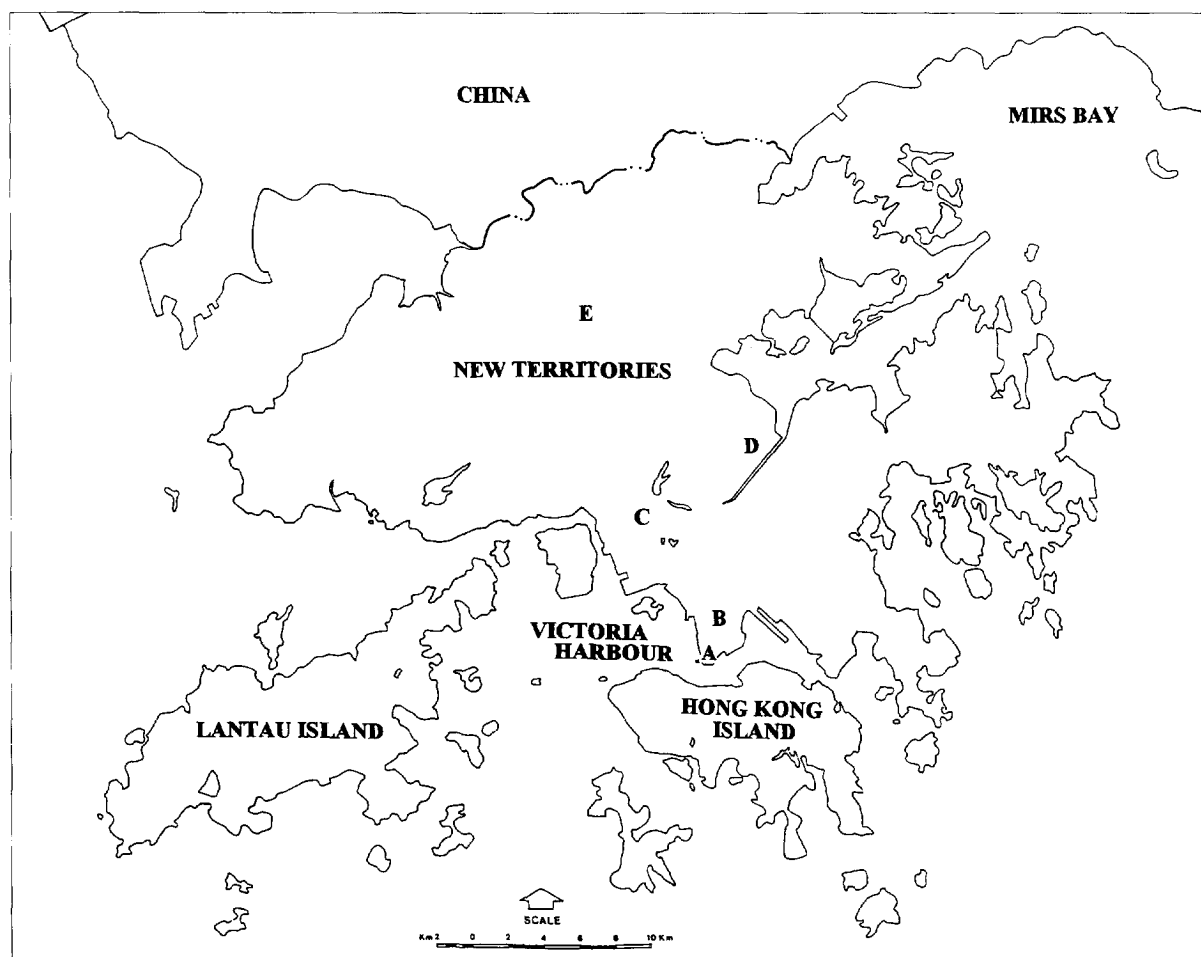


Fig. 1. Location of the rainwater sampling sites in Hong Kong. A. Royal Observatory; B. CityU site, at rooftop level (51 m P.D.) in an urban-residential area; C. Kwai Chung site, (15th Floor, Wing Hang Building), Kwai Chung: industrial area; D. Shatin site, (6th Floor, Fung Wong Fung Ting College): new town development; E. Fanling site, (So Kee Farm): rural.

oughly with double-distilled deionized (3D) water. After collection, samples were filtered through a 0.2- $\mu\text{m}$  nylon-66 membrane prior to IC injection.

A robust and inexpensive IC module, the Wescan 300, was employed with an analysis time of between 20–40 min per sample. Initially, a non-suppressed system with a single column and guard column was used, but nitrate concentrations were frequently below the limit of detection (LOD, as defined in [9], see Table 1) so that a solid-phase chemical suppressor (SPCC) was incorporated. Three anions were resolved and routinely analysed in the chromatograms. Chloride eluted first and then nitrate, each with a standard deviation (SD) in retention time ( $t_R$ ) of approximately 1%. Sulphate gave a peak near 20 min with a SD of 3%. Baseline drift of the chromatogram was minimized by thermostating the column. External linear calibration of peak area by four mixed standards was routinely employed, together with the use of a bromide internal standard. Fig. 2 shows some representative chromatograms using the latter method. Replicate samples were collected throughout, and replicate injections were made for each sample analysed by IC. The use of blanks and control samples was routinely employed [10]. For bulk-collected rainwater samples, the average relative deviation from the mean for the two replicates was 4.2, 9.2 and 5.9% for  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , respectively. Maximum concentrations of phosphate in Hong Kong rainwater (determined by Lachat QuickChem FIA) were near 1 equiv.  $\text{l}^{-1}$ .

Average analyte concentrations reported in this study are (i) arithmetic mean values and (ii) volume-weighted (vw) mean values. In order to make clear

comparisons of ionic balance, units of  $\mu\text{equiv. l}^{-1}$  were employed. Statistical tests were carried out (at  $\alpha=0.05$ ) using Sigmastat software, according to the methods of Zar [11].

### 3. Results and discussion

#### 3.1. Long-term monitoring program

The weather in Hong Kong is generally cool and dry during the November–March winter months, and hot and wet during the summer, with the occurrence of several tropical cyclones. The results for the concentrations of the anions  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in bulk (B) and wet-only (W) samples collected between May 1994 to April 1995 are listed in Table 2.

Concentrations of  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in rainwater samples collected by bulk samplers were compared with those from wet deposition samplers on about 25 occasions during the sampling period. The analyte concentrations are generally similar for corresponding B and W samples, with no systematically greater magnitudes for the B samples. The overlapping B and W datasets were tested by the Kolmogorov–Smirnov test and were all found to be not normally distributed. Overlapping B and W subsets for  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  were then tested by the Mann–Whitney Rank Sum test and in each case the difference in median values between the groups was not great enough to exclude the possibility that it was due to random sampling variability.

Other studies have found significant differences

Table 1  
Conditions and parameters for non-suppressed (NS) and suppressed (S) IC

| Conditions/parameters                          | NSIC  | SIC  |
|--|---|--|
| Flow-rate ( $\text{cm}^3 \text{min}^{-1}$ )    | 1   | 1  |
| Column   | Resin-based<br>anion exchanger<br>150 $\times$ 4.6 mm | Universal anion<br>column<br>150 $\times$ 4.6 mm               |
| Buffer   | 5 mM <i>p</i> -HBA with<br>LiOH (pH 8.5)              | 1.7 mM $\text{NaHCO}_3$ and<br>1.2 mM $\text{Na}_2\text{CO}_3$ |
| Injection volume (ml)                          | 500   | 500  |
| LOD for chloride ( $\mu\text{equiv. l}^{-1}$ ) | 6   | 3  |
| LOD for nitrate ( $\mu\text{equiv. l}^{-1}$ )  | 16  | 3  |
| LOD for sulphate ( $\mu\text{equiv. l}^{-1}$ ) | 24  | 12   |

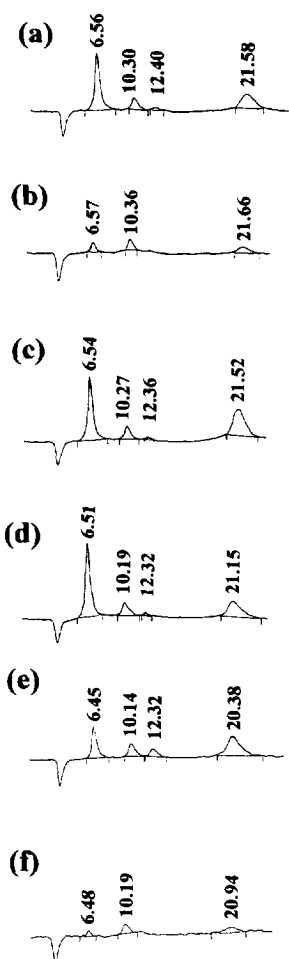


Fig. 2. Chromatograms of rainwater samples from different locations in Hong Kong (a–d), and from different times of a single event, (e) and (f). Retention times are labelled in min and represent chloride, 4 ppm bromide internal standard, nitrate and sulphate. Instrumental conditions are as in Table 1, SIC. Samples (a–d) were collected during the South-Westerly monsoon on 16 August 1994 from (a) Shatin site; (b) Fanling site; (c) Lau Yi Guk Building, Street Level, Mongkok; (d); and represent (a) urban new-town, (b) rural, (c) urban and (d) industrial areas. The samples for chromatograms (a) and (d) were diluted 3.125 and 3.5 times respectively with doubly-distilled deionized water. Samples (e) and (f) were collected at the CityU site during (e) the first 0–15 min and (f) from 16–30 min of the rain event on 16 August 1994.

between B and W sampling data [12]. The correlations of the B data (in  $\mu\text{equiv. l}^{-1}$ ) with the W are:

$$B(\text{Cl}^-) = 5.04 + 0.913 W(\text{Cl}^-) \quad (1)$$

$$(R^2 = 0.984, n = 27)$$

$$B(\text{NO}_3^-) = 1.81 + 0.912 W(\text{NO}_3^-) \quad (2)$$

$$(R^2 = 0.954, n = 27)$$

$$B(\text{SO}_4^{2-}) = 1.05 + 0.990 W(\text{SO}_4^{2-}) \quad (3)$$

$$(R^2 = 0.974, n = 24)$$

In view of the above dataset similarities, the following discussion is limited to the more complete B datasets. These were split up into monthly records, and then tested by Kruskal–Wallis One-Way Analysis of Variance on Ranks. The differences in the median values for the monthly data were found to be significant for  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , but not for  $\text{Cl}^-$ . However, the May–August data subsets for each of the former two anions did not have significant differences.

The observations can be rationalized from the combination of several factors. First,  $\text{Cl}^-$  originates mostly from sea-spray, whereas  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  originate mostly from stationary and mobile anthropogenic sources, respectively. Second, the type of weather system may affect the analyte concentrations in rainwater. The build-up of pollutant aerosols and gases can occur in temperature inversions, which are less frequent from May to August. Other factors are the prevailing wind direction and speed, which vary from moist Easterly/South-Westerly airstreams to the dry winter North-Easterly monsoon. Changes in the rain intensity also give rise to changes in analyte concentration. Nieto et al. [13] have calculated that a given volume of persistent drizzle scavenges as efficiently as four times that volume of heavy rain. High-intensity rain occurred in some summer rain events, particularly in July, and was exemplified by lower analyte concentrations. Prolonged rainfall events may also be associated with lower analyte concentrations, if substantial washout of gases and particulates occurs early in the event and if this material is not replaced by advection. Considering the entire B datasets, the concentrations of all three anions were found to exhibit weak negative correlations with rainfall amount (with all Pearson Product Moment Correlation Coefficients near  $-0.35$ ,  $n > 57$ ). The importance of rain intensity and rainfall amount may also be seen from the comparison of the monthly means and monthly vw-means in Table 2;

Table 2  
Rainfall and anion concentrations in rainwater at CityU from May 1994 to April 1995<sup>a</sup>

| Date        | Rainfall<br>(mm) | Bulk chloride<br>( $\mu\text{equiv. l}^{-1}$ ) | Wet chloride<br>( $\mu\text{equiv. l}^{-1}$ ) | Bulk nitrate<br>( $\mu\text{equiv. l}^{-1}$ ) | Wet nitrate<br>( $\mu\text{equiv. l}^{-1}$ ) | Bulk sulphate<br>( $\mu\text{equiv. l}^{-1}$ ) | Wet sulphate<br>( $\mu\text{equiv. l}^{-1}$ ) |
|-------------|------------------|--|---|---|--|--|---|
| 2-5-94      | 45.4             | 2-33.2-0.9                                     | m   | 2-15.2-0.7                                    | m  | 2-47.9-4.9                                     | m   |
| 3-5-94      | 21.2             | 2-34.4-1.9                                     | m   | 2-26.4-3.4                                    | m  | 2-213.4-0.1                                    | m   |
| 30-5-94     | 33.1             | 2-46.3-0.7                                     | 2-45.2-0.7                                    | 2-27.1-1.9                                    | 2-25.1-1.2                                   | 2-58.1-0.2                                     | 2-57.2-5.1                                    |
| Mean (SD,n) | -                | 38.0(7.2,3)                                    | -   | 22.9(6.7,3)                                   | -  | 106.5-92.7-3                                   | -   |
| vw-Mean (n) | -                | 37.8(3)  | -   | 21.5(3)                                       | -  | 86.4(3)  | -   |
| 3-6-94      | 8.8              | 2-347.9-2.1                                    | 2-392.6-1.9                                   | 2-107.2-28.3                                  | 2-152.6-0.9                                  | 2-302.9-2.0                                    | 2-326.2-12.5                                  |
| 6-6-94      | 14.8             | 2-113.2-61                                     | 2-98.1-4.4                                    | 1-16.4  | 1-24.3                                       | 2-39.8-1.1                                     | 2-43.3-0.9                                    |
| 7-6-94      | 13.1             | 2-168.5-4.1                                    | 1-153.3                                       | 2-12.9-1.1                                    | 1-11.7                                       | 1-25.4   | 1-30.5  |
| 8-6-94      | 11.9             | 2-50.3-3.5                                     | 1-51.5  | 1-10.7  | 1-11.0                                       | 1-6.1R   | 1-22.6R                                       |
| 9-6-94      | 13.7             | 2-77.2-1.3                                     | 1-60.3  | 2-7.6-4.5                                     | 1-10.9                                       | 2-67.7-2.8                                     | 1-77.2  |
| 10-6-94     | 59.6             | 2-22.7-2.0                                     | 1-22.4  | 1-9.4   | 1-ND   | 2-26.4R-16.2                                   | 1-75.9R                                       |
| 17-6-94     | 66.8             | 2-18.7-1.3                                     | m   | 1-3.8   | m  | 2-64.1-13.1                                    | m   |
| 18-6-94     | 51.5             | 2-12.7-1.1                                     | m   | 1-3.6   | m  | 1-33.6   | m   |
| 19-6-94     | 88.4             | 2-11.1-0.3                                     | m   | 1-7.3   | m  | 1-10.9   | m   |
| 20-6-94     | 11.5             | 2-17.4-1.4                                     | m   | 2-12.8-0.8                                    | m  | 2-35.4-3.0                                     | m   |
| 24-6-94     | 20.4             | 2-147.3-7.0                                    | m   | 2-17.0-2.8                                    | m  | 2-47.2-1.5                                     | m   |
| Mean (SD,n) | -                | 89.7(102.6,11)                                 | -   | 19.0(29.6,11)                                 | -  | 69.7(89.3,9)                                   | -   |
| vw-Mean (n) | -                | 44.4(11)                                       | -   | 10.3(11)                                      | -  | 37.9(9)  | -   |
| 3-7-94      | 19.5             | 2-111.2-3.6                                    | m   | 2-19.1-0.2                                    | m  | 2-33.8-3.2                                     | m   |
| 4-7-94      | 44.9             | 2-23.0-2.4                                     | m   | 2-ND  | m  | 2-26.9-0.2                                     | m   |
| 5-7-94      | 41.8             | 2-52.9-0.5                                     | m   | 2-19.0-0.1                                    | m  | 2-50.0-0.6                                     | m   |
| 6-7-94      | 46.9             | 2-18.7-0.9                                     | m   | 2-14.8-0.4                                    | m  | 1-24.2   | m   |
| 7-7-94      | 44.7             | 2-43.0-1.8                                     | m   | 2-ND  | m  | 1-25.2   | m   |
| 11-7-94     | 79.9             | 2-12.2-2.3                                     | m   | 2-16.6-0.5                                    | m  | 2-44.7-1.0                                     | m   |
| 13-7-94     | 67.9             | 2-12.0-0.8                                     | m   | 1-11.0  | m  | 1-36.6   | m   |
| 14-7-94     | 49.3             | 2-22.8-1.9                                     | m   | 1-9.0   | m  | 2-33.4-1.0                                     | m   |
| 20-7-94     | 25.5             | 2-20.3-0.3                                     | m   | 2-9.4-2.2                                     | m  | 2-42.7-6.2                                     | m   |
| 21-7-94     | 164.8            | 2-9.5-0.4                                      | m   | 2-ND  | m  | 2-20.4-1.5                                     | m   |
| 22-7-94     | 155.8            | 2-7.5-0.2                                      | m   | 2-ND  | m  | 2-15.1-2.0                                     | m   |
| 23-7-94     | 167.4            | 2-ND   | m   | 2-ND  | m  | 1-18.7   | m   |
| 24-7-94     | 71.1             | 2-5.8-0.1                                      | m   | 1-7.6   | m  | 2-34.4-4.2                                     | m   |
| 27-7-94     | 28.7             | 2-32.7-2.5                                     | m   | 2-7.3-1.6                                     | m  | 2-31.1-0.5                                     | m   |
| Mean (SD,n) | -                | 26.8(28.2,14)                                  | -   | 9.2(6.1,14)                                   | -  | 31.2(10.2,14)                                  | -   |
| vw-Mean (n) | -                | 16.1(14)                                       | -   | 7.0(14)                                       | -  | 27.0(14)                                       | -   |
| 4-8-94      | 56.4             | 2-15.1-0.7                                     | m   | 1-8.3   | m  | 2-31.7-1.8                                     | m   |
| 5-8-94      | 60.0             | 2-38.0-1.3                                     | m   | 2-ND  | m  | 2-17.6-0.2                                     | m   |
| 6-8-94      | 30.5             | 2-39.5-3.1                                     | m   | 2-11.3-1.5                                    | m  | 2-33.5-2.9                                     | m   |
| 8-8-94      | 20.5             | 2-36.3-0.5                                     | m   | 2-11.1-0.9                                    | m  | 2-53.8-2.1                                     | m   |
| 9-8-94      | 87.6             | 2-38.8-2.2                                     | m   | 2-ND  | m  | 2-21.6-2.5                                     | m   |
| 14-8-94     | 45.0             | 2-9.0-0.4                                      | m   | 1-7.8   | m  | 2-40.5-4.4                                     | m   |
| 15-8-94     | 196.1            | 2-6.3-0.1                                      | m   | 2-6.8-0.9                                     | m  | 2-21.3-2.0                                     | m   |
| 16-8-94     | 32.4             | 2-38.7-1.6                                     | 1-41.0  | 2-14.3-0.4                                    | 1-14.4                                       | 2-63.2-5.4                                     | 1-69.9  |
| 19-8-94     | 27.5             | 2-12.3-0.2                                     | 1-12.0  | 2-43.6-1.3                                    | 1-42.6                                       | 2-93.9-2.5                                     | 1-92.6  |
| 25-8-94     | 25.6             | 2-10.9-0.5                                     | 1-11.6  | 1-9.9   | 1-9.2  | 2-25.4-2.4                                     | 1-21.1  |
| 26-8-94     | 69.4             | 2-64.3-1.2                                     | m   | 2-ND  | m  | 1-31.0   | m   |
| 27-8-94     | 16.7             | 2-54.8-0.3                                     | m   | 1-9.1   | m  | 2-20.9-0.1                                     | m   |
| Mean (SD,n) | -                | 30.3(19.2,12)                                  | -   | 10.9(10.9,12)                                 | -  | 37.9(22.4,12)                                  | -   |
| vw-Mean (n) | -                | 26.0(12)                                       | -   | 8.2(12)                                       | -  | 30.9(12)                                       | -   |

(Continued on p. 254)

Table 2 (continued)

| Date                 | Rainfall (mm) | Bulk chloride ( $\mu\text{equiv. l}^{-1}$ ) | Wet chloride ( $\mu\text{equiv. l}^{-1}$ ) | Bulk nitrate ( $\mu\text{equiv. l}^{-1}$ ) | Wet nitrate ( $\mu\text{equiv. l}^{-1}$ ) | Bulk sulphate ( $\mu\text{equiv. l}^{-1}$ ) | Wet sulphate ( $\mu\text{equiv. l}^{-1}$ ) |
|----------------------|---------------|---|--|--|---|---|--|
| 4-9-94               | 11.7          | 2-41.8-1.2                                  | 1-37.6                                     | 2-6.8-0.2                                  | 1-7.4                                     | 2-38.8-0.5                                  | 1-35.9                                     |
| 5-9-94               | 12.1          | 2-43.1-1.7                                  | 1-43.0                                     | 1-12.7                                     | 1-12.6                                    | 2-30.0-0.6                                  | 1-33.6                                     |
| 6-9-94               | 29.9          | 2-84.4-2.3                                  | 1-81.3                                     | 2-10.5-2.1                                 | 1-13.7                                    | 2-40.7-4.4                                  | 1-38.7                                     |
| 9-9-94               | 9.2           | 2-29.9-0.4                                  | 1-24.4                                     | 2-126.5-3.2                                | 1-126.3                                   | 2-181.6-18.6                                | 1-176.5                                    |
| 10-9-94              | 25.4          | 2-21.5-0.2                                  | 1-20.0                                     | 2-89.7-3.0                                 | 1-82.2                                    | 2-167.4-1.2                                 | 1-166.7                                    |
| 11-9-94              | 22.5          | 2-36.9-1.4                                  | 1-39.0                                     | 2-10.2-0.2                                 | 1-10.0                                    | 2-42.2-4.6                                  | 1-45.9                                     |
| 12-9-94              | 12.4          | 2-70.2-3.6                                  | 1-71.0                                     | 2-15.0-0.3                                 | 1-18.9                                    | 2-49.1-3.6                                  | 1-38.3                                     |
| 17-9-94              | 14.5          | 2-23.3-0.1                                  | 1-20.9                                     | 2-132.2-3.4                                | 1-125.1                                   | 2-167.2-1.1                                 | 1-160.4                                    |
| 20-9-94              | 34.7          | 2-17.0-0.7                                  | 1-17.3                                     | 2-20.6-2.5                                 | 1-21.1                                    | 2-74.3-0.9                                  | 1-77.0                                     |
| 22-9-94              | 36.6          | 2-3.7-0.1                                   | 1-3.7                                      | 2-34.1-0.7                                 | 1-37.6                                    | 2-70.8-3.0                                  | 1-70.6                                     |
| 23-9-94              | 35.3          | 2-26.7-0.8                                  | 1-30.9                                     | 2-18.9-1.6                                 | 1-22.5                                    | 2-61.0-3.9                                  | 1-66.0                                     |
| 27-9-94              | 16.7          | 2-52.7-0.2                                  | 1-62.9                                     | 2-118.2-0.8                                | 1-127.1                                   | 2-207.9-0.7                                 | 1-232.4                                    |
| Mean (SD, <i>n</i> ) | -             | 37.6(22.8,12)                               | -  | 49.6(51.0,12)                              | -   | 94.2(66.1,12)                               | -  |
| vw-Mean ( <i>n</i> ) | -             | 34.2(12)                                    | -  | 41.8(12)                                   | -   | 87.1(12)                                    | -  |
| 7-12-94              | 74.6          | 2-98.5-0.8                                  | 1-97.4                                     | 2-12.1-1.1                                 | 1-13.4                                    | 2-66.6-4.1                                  | 1-58.9                                     |
| 8-12-94              | 12.6          | 2-8.5-0.2                                   | 1-15.9                                     | 2-10.0-0.6                                 | 1-11.1                                    | 2-38.0R-1.1                                 | 1-59.4                                     |
| 12-12-94             | 10.8          | 2-30.7-1.4                                  | m  | 2-22.3-1.6                                 | m   | 2-113.8-4.9                                 | m  |
| 23-12-94             | 9.7           | 2-57.1-3.1                                  | m  | 2-42.2-2.2                                 | m   | 2-107.7-1.7                                 | m  |
| 24-12-94             | 31.8          | 2-ND  | m  | 1-10.9                                     | m   | 1-18.8                                      | m  |
| Mean (SD, <i>n</i> ) | -             | 39.6(39.2,5)                                | -  | 19.5(13.6,5)                               | -   | 76.7(43.9,4)                                | -  |
| vw-Mean ( <i>n</i> ) | -             | 60.5(5)                                     | -  | 14.5(5)                                    | -   | 61.8(4)                                     | -  |
| 13-2-95              | 18.9          | 2-18.4-1.7                                  | 1-19.6                                     | 2-88.5-1.0                                 | 1-80.7                                    | 2-286.7-41.9                                | 1-240.9                                    |
| Mean (SD, <i>n</i> ) | -             | 18.4(-,1)                                   | -  | 88.5(-,1)                                  | -   | 286.7(-,1)                                  | 240.9(-,1)                                 |
| Mean (vw, <i>n</i> ) | -             | 18.4(1)                                     | -  | 88.5(-,1)                                  | -   | 286.7(1)                                    | 240.9(1)                                   |
| 1-3-95               | 15.2          | 2-53.8-2.5                                  | 1-43.0                                     | 2-32.8-5.3                                 | 1-29.7                                    | 2-80.2-3.8                                  | 1-83.7                                     |
| 31-3-95              | 35.7          | 2-12.7-0.3                                  | 1-12.7                                     | 2-25.0-0.5                                 | 1-23.6                                    | 2-61.0-5.3                                  | 1-55.8                                     |
| Mean (SD, <i>n</i> ) | -             | 33.2(29.1,2)                                | -  | 28.9(5.5,2)                                | -   | 70.6(13.6,2)                                | -  |
| vw-Mean ( <i>n</i> ) | -             | 24.9(2)                                     | -  | 27.4(2)                                    | -   | 66.8(2)                                     | -  |

\*Sampling commenced at 15.00 on the dates shown, for a period of one day. The rainfall amounts are logged correspondingly and may differ from those reported by the Royal Observatory [8] from 0.00 on one day to 0.00 on the next. Data are tabulated as X-Y-Z, where X is the number of distinct samples analyzed; Y is the arithmetic mean concentration; Z is the deviation of each sample from the mean. m,R indicate missing and rejected data respectively. SD, standard deviation; *n*, number of days; ND, not detected.

the latter being smaller because more emphasis is placed upon the more intense (copious) rain events.

Data available from the EPD for the period 1985–1989 [14] indicate  $\text{SO}_4^{2-}$ – $\text{NO}_3^-$  ratios in rainwater between 2.1:1 to 12.5:1, depending upon the location and time of year. From the monthly vw-means of May 1994 through March 1995 from the present study, the ratio of  $\text{B}(\text{SO}_4^{2-})$ – $\text{B}(\text{NO}_3^-)$  is between 2.1:1 to 4.3:1. In our earlier studies during August and September 1992, sulphate was by far the most abundant anion in Hong Kong rainfall, with  $\text{SO}_4^{2-}$ – $\text{NO}_3^-$  ratios of  $11.0 \pm 0.7:1$  in August and September. The ratios of the vw-concentrations for the same months in 1994 are  $2.9 \pm 0.9:1$ . The rainfall amount in 1994 was nearly seven times more plentiful than

during these months in 1992, but the effects of this upon the  $\text{SO}_4^{2-}$ – $\text{NO}_3^-$  ratios are complex [15] and not readily evaluated. Other factors may have played an important role in changing the ratio. First, following the impact of legislation concerning the sulphur content of fuel oil, there has been a reduction in local  $\text{SO}_4^{2-}$  emissions since 1992. Second, the number of registered vehicles in Hong Kong increased by 11.2% from 1992 to 1994 [16], so that an increase in  $\text{NO}_x$  emissions has occurred. The role of long-range transport of  $\text{SO}_2$ ,  $\text{NO}_x$  and their reaction products to this region is at present unknown. The  $\text{SO}_4^{2-}$ – $\text{NO}_3^-$  ratio in rainwater in South-Western China (in Guiyang), was between 10–20:1 in 1982–1984 [17], but may have changed considerably since that time.

$\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  are strongly correlated (but not with  $\text{Cl}^-$ ), with the equation:

$$\begin{aligned} B(\text{SO}_4^{2-}) &= 24.5 + 1.72 B(\text{NO}_3^-) \\ (R^2 &= 0.722, n = 57) \end{aligned} \quad (4)$$

### 3.2. Horizontal spatial studies of Hong Kong rainfall

Rainfall was collected simultaneously at four locations within a 0.5-km radius of CityU in July 1994; on the roof, on grassy ground, at the perimeter of a neighbouring construction site and at a fairly quiet road. The concentrations of the three analytes in this study were very similar, demonstrating that the CityU rooftop sampling site was representative of the local residential environment. In order to investigate the effects of local emission sources and topography upon rainfall composition, sampling was undertaken at industrial, rural and new town development sites during August 1994 (Fig. 2a–d). The concentrations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in rain were found to be up to nine times smaller at the rural site at Fanling than at industrial Kwai Chung. Intermediate concentrations were measured at Shatin New Town in the New Territories. For rural *versus* coastal locations,  $\text{Cl}^-$  differed by a factor of five. These results indicate that local sources and topography make significant contributions to the composition of Hong Kong precipitation.

### 3.3. Rainfall event sampling

The chemical composition of falling rain can change significantly during the sampling period. Seymour and Stout [18] found a rapid decrease, in the concentration of anions during the initial part of a rain event in Michigan, USA, with half of the total  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  deposition occurring in the first 15–20% of the total rainfall. Indeed, from one individual raindrop to another, very large changes in concentration have been detected by micro-HPLC [19]. Samples were collected at CityU during the first 5 h of the single rain event of 16 August 1994. This episode followed a rainy period of several days. A significant drop in *all* analyte concentrations was observed for samples collected from 16–30 min from the start of the event, compared with those collected

from 0–15 min (Fig. 2e,f). The total rainfall during these periods was 0.5 mm and 3.6 mm, respectively. Although the higher evaporation rates of raindrops in the drier air at the start of a rain event would produce higher initial analyte concentrations, we consider that below-cloud washout of aerosols and gases is however the dominant factor. The behaviour of analyte concentrations during the later part of the event was more complex and is not discussed here.

## 4. Conclusions

The results from this study indicate that the bulk and wet-only sampling techniques did not give statistically different results for each of the three analytes in the rainwater samples. The *daily* dry deposition flux was thus insignificant compared to the changes in wet deposition flux from one day to another. Many factors need to be taken into account in order to understand the large variations in analyte concentrations in rainwater within each month, and several of these have been identified. Both the studies of the horizontal variation of rainwater composition at different areas of Hong Kong, and of the single rainfall event have indicated that below-cloud washout by gases and aerosols originating from local sources may contribute appreciably to the analyte concentrations in rainwater. We will study further the changes in rainfall composition during single events in more detail, by simultaneously monitoring gas concentrations together with cloudwater, aerosol and rainwater compositions, in order to ascertain the relative importance of rainout and washout processes, and to simulate the rainwater concentrations.

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