

Development of the procedure for the stabilization of rainwater samples

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Abstract — This paper proposed a procedure of handling a remote rainwater sample to determine the pH values of the samples immediately after collecting. Then the initial chemical composition in the stored rainwater was estimated by a regression model.

Keywords: rainwater; regression model; acid rain.

1 Introduction

Investigation of acid rain on the island of Taiwan has been conducted by the Graduate Institute of Environmental Engineering at National Taiwan University since December 1984 (Jeng, 1987). Rainwater samples were collected at 52 sites in a precipitation sampling network which covered the whole island (Fig. 1). During this period, we found that chemical composition of a rainwater sample could be different before and after storage. The change of chemical composition was significant, especially for remote precipitation samples which could not be analyzed immediately in a central laboratory. The chemical composition of rainwater samples varied not only with storage time but also with storage conditions. Therefore, quality control on the chemical composition of remote precipitation samples would be crucial to obtain reliable experimental results.

It seems that the major problems in attempting to characterize the chemical composition are related to the collection and storage of samples, rather than analytical difficulties (Galloway, 1976). Previous research indicated that the pH value of rainwater samples might increase dramatically in storage, depending upon the conditions of storage (Guiang, 1984). Several mechanisms may be responsible for the rise in pH value: they are biological metabolization of organic acids (Verry, 1983; Keene, 1983), gas exchange with the open atmosphere (Guiang, 1984; Yuan, 1986), dissolution

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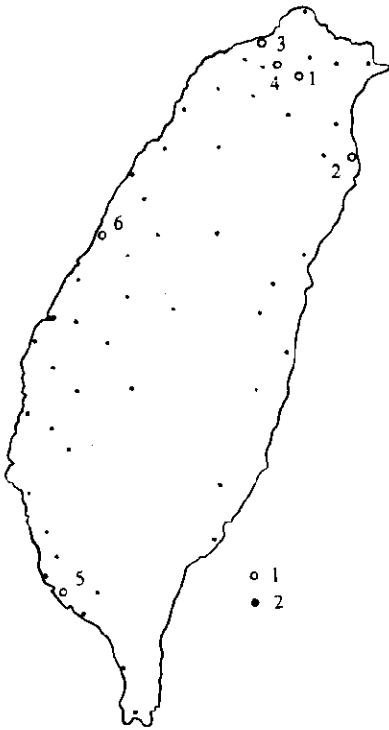


Fig.1 Samples were collected at six sites
 (1) in the precipitation sampling network
 (2) on the island of Taiwan

of mineral material (Verry, 1983), leaching or absorption of substances from or to the surface of the container (Galloway, 1976; Heydorn, 1982), and errors from analytical methods. However, it is still unclear how these mechanisms influence the pH value and which mechanism (s) will be the dominant factor (s) in controlling the change of pH value in stored rainwater samples. Some prior research suggested that the use of biocide could inhibit biological activity and eliminate the variation of the pH value in stored rainwater samples (Guiang, 1984; Keene, 1983; Galloway, 1984).

Actually, not only the pH value but other chemical composition in the rainwater samples might change with time. Previous research revealed that the concentrations of HCOO^- , CH_3COO^- , SO_4^{2-} , NO_3^- , Cl^- and NH_4^+ in a stored rainwater sample tended to increase after storage (Keene, 1983; 1984; Martin, 1978). The bacteria, in aerobic environments, can utilize HCOO^- and CH_3COO^- as sources of carbon and/or energy (Hamilton, 1979), while NH_4^+ and NO_3^- are suspected as sources of nitrogen for the organisms which consume formic and acetic acids (Keene, 1983). However, there is no information about the variation of cations and fluoride ion in stored rainwater samples. In this study, major cations (H^+ , NH_4^+ , K^+ , Na^+ , Ca^{2+} and Mg^{2+}), anions (F^- , Cl^- , NO_3^- , SO_4^{2-} , HCOO^- , CH_3COO^- , $\text{C}_2\text{H}_3\text{COO}^-$) and conductivity were measured periodically within a time span of nine weeks to follow the trends in the variation of chemical composition in the stored rainwater samples.

2 Experimental methods

2.1 Sample collection

Six sampling stations in the precipitation sampling network were selected to collect wet deposition samples (Fig.1). These samples were then analyzed immediately in the Air Pollution Laboratory at National Taiwan University. The rainwater sampling facility is a 5-liter polyethylene container with a funnel of 18.6 cm (7.3 inches) inside diameter (Fig.2). To avoid contamination of the rainwater samples, the facility was located on a flat surface, such as the flat roof of a building, where there were not any obstacles within an angle of 45 degrees. Fourteen event samples at six sites were collected between January 1986 and April 1986.

The fresh rainwater samples were carefully stored in an environment of 4°C and then sent back to the Air Pollution Laboratory for the analysis of chemical composition. This procedure was implemented as soon as possible after the samples were collected.

2.2 Sample storage

To eliminate the variation of chemical composition in the stored rainwater samples, the samples were stored in four different conditions to evaluate their ability to stabilize the samples' quality: (1) sample in a full, sealed aliquot at 25°C (at room temperature); (2) sample in a half-filled, unsealed aliquot at 25°C; (3) sample in a full, sealed aliquot at 4°C (under refrigeration); (4) sample in a half-filled, unsealed aliquot at 4°C.

The aliquot used to store rainwater samples in this research were 125 ml well-cleaned polyethylene bottles. To analyze the sample effectively, a rainwater sample of 3.6 liters was required for seven discrete analyses within a time span of nine weeks. In other words, a sufficient rainwater sample could be collected only in the event that rainfall was greater than 10.1 mm (0.4 inches). If the rainfall were lower than 10.1 mm, the rainwater samples would be discarded without analysis.

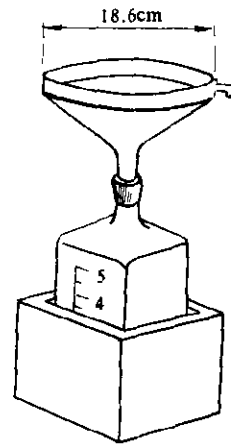


Fig.2 The rainwater sampling facility used to collect rainwater samples.

2.3 Sample analysis

In this study, fresh rainwater samples were filtered initially by a Whatman 4.7 cm GF/F, 0.45 μ m glass-fiber filter for the measurement of suspended solids, and were then stored in the aliquots under different storage conditions. The pH value was measured by a SP-5A Suntex pH meter. The conductivity was measured by a SC-17 Suntex conductivity meter. The measurement of suspended solids was conducted by the standard methods number 208-D. Besides, a Dionex-10 model ion chromatography (I.C.) based on the principle of ionic exchange was used to analyze the concentration of anions (F^- , Cl^- , NO_3^- , SO_4^{2-}), organic acids ($HCOO^-$, CH_3COO^- , $C_6H_5COO^-$) and ammonium ion (NH_4^+). A PERKIN-ELMER 4000 model Atomic Absorption Spectrophotometer (A. A. S.) was used to detect the concentration of cations (K^+ , Na^+ , Ca^{2+} , Mg^{2+}).

2.4 Analytical schedule

During the storage period, samples stored in different conditions were withdrawn and analyzed periodically to follow the trends of chemical composition variation in the stored rainwater samples. The time series of the sample analysis is shown in Table 1. The interval between two adjacent analyses was set at 1, 2, 4, 8, 16 and 32 days, respectively.

Table 1 Analytical schedule of stored rainwater samples

Times of sample analysis	Analytical schedule, days after collection	Interval between sample analyses, day
1	0	
2	1	1
3	3	2
4	7	4
5	15	8
6	31	16
7	63	32

3 Results and discussion

3.1 Equilibrium between the total anions and cations in rainwater samples

The ratio of the equivalent concentration between the measured anions and cations in a rainwater sample can be used as a criterion to evaluate the accuracy of chemical analysis. The ratio is also known as ion balance (I. B.) which can be expressed as (Guiang, 1984):

$$\text{Ion balance (I. B.)} = \frac{\text{Total equivalent anions (TEA)}}{\text{Total equivalent cations (TEC)}} \quad (1)$$

where the total equivalent anions and cations can be calculated as:

$$\text{TEA} = [\text{F}^-] + [\text{Cl}^-] + [\text{NO}_3^-] + 2[\text{SO}_4^{2-}] + [\text{HCOO}^-] + [\text{CH}_3\text{COO}^-] + [\text{C}_2\text{H}_5\text{COO}^-] \quad (2)$$

$$\text{TEC} = [\text{H}^+] + [\text{K}^+] + [\text{Na}^+] + 2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] + [\text{NH}_4^+] \quad (3)$$

In a natural environment, the equivalent concentration of total anions should be equal to the equivalent concentration of total cations. Therefore, the closer the ion balance is to 100%, the better the sample analysis can be achieved. Barrie (Barrie, 1984) reported that ion balance ranged from 77.0% to 127% in the analysis of snowpack in the eastern Canadian shield (Barrie, 1984), while Guiang (Guiang, 1984) revealed that ion balance was between 18.4% and 110.3% in Minnesota rainwater samples.

In this study, a very satisfactory ion balance, from 90.46% to 99.89%, was observed for all the samples except samples No.5 and No.6 (Table 2). This result indicated that almost all the dominant chemical composition was under measurement. Therefore, the analytical results should be highly reliable. The ion balance of samples No.5 and No. 6 were 89.27% and 64.7%, respectively. These two samples were collected at sampling station No.2 which were located in a limestone-rich region. It was possible for the alkali particles suspended in the atmosphere to be washed out by rain droplets and dissolved into rainwater. The dissociation of these alkali particles then raised the pH value of the rainwater. This could explain why samples No.5 and No. 6 had higher pH values and lower ion balance.

The ion balance of the rainwater samples stored at 4°C for nine weeks ranged from 63.05% to 117.22%. It was a little bit broader than that in the fresh rainwater samples (Table 2). The results indicated that rainwater became unstable after storage even though it was stored under refrigeration.

3.2 Influence of storage conditions and time on chemical composition of rainwater samples

The variation of chemical composition in the stored rainwater samples is shown in Fig.3 through 5. Experimental results indicated that at the beginning of the storage the chemical composition of the rainwater samples changed significantly, then the change slowed down, and finally became stable about four weeks after collection. Within the chemical composition measured in this study, the pH value and the concentration of $\text{C}_2\text{H}_5\text{COO}^-$ tended to rise while other chemical species fell. Furthermore, the concentration of F^- , HCOO^- , and CH_3COO^- decreased much faster than that of the other chemical composition. They tended to disappear within the first week. This phenomenon could explain why HCOO^- and CH_3COO^- were

not observed in the stored rainwater in some previous analyses (Keene, 1983; 1984). In addition, a rapid change of the pH value was observed if the initial pH value was greater than 4.5 (Fig.6). This is probably because the pH value is defined as the logarithm of hydrogen ion concentration.

Table 2 Ion balance of rainwater samples before and after storage

Sample number	Sampling station number	Sample analyzed immediately after collection			Sample analyzed 63 days after collection		
		TEA, 10^{-4}	TEC, 10^{-4}	I.B., %	TEA, 10^{-4}	TEC, 10^{-4}	I.B. %
1	1	1.52	1.63	93.23	1.32	1.18	111.86
2	1	3.12	3.15	99.17	2.74	2.56	107.03
3	1	2.50	2.76	90.58	1.94	1.93	100.52
4	1	2.24	2.25	99.66	1.53	1.53	98.04
5	2	4.91	5.50	89.27	3.89	4.56	85.31
6	2	3.08	4.75	64.74	2.44	3.87	63.05
7	3	2.96	3.08	96.30	2.06	2.65	77.74
8	3	6.07	6.25	97.09	4.34	4.88	88.93
9	4	2.40	2.65	90.46	1.94	1.74	111.49
10	4	3.49	3.49	99.89	2.32	2.58	89.92
11	4	1.97	2.07	95.06	1.38	1.35	102.22
12	5	2.42	2.46	98.28	2.11	1.80	117.22
13	6	1.93	1.97	98.18	1.29	1.55	83.28
14	6	3.38	3.50	96.35	2.25	2.64	85.23

TEA: total equivalent anions (eq/L); TEC: total equivalent cations (eq/L); I.B.: ion balance of rainwater sample (%)

3.3 Estimation of initial chemical composition of stored rainwater samples

Experimental results strongly suggested that chemical composition of stored rainwater samples varied with both storage time and storage conditions. Therefore, the analytical results might be quite different for a sample analyzed before and after storage. However, the variation of chemical composition has not been seriously considered in the past. The variation of chemical composition should be taken into consideration for rainwater samples, especially for the remote samples which had to be stored for a longer time before they were analyzed in a central laboratory. In this study, we observed that the concentration of SO_4^{2-} was 2.952 mg/L when the sample was collected and dropped to 2.415 mg/L after the sample was stored at 4°C for 63 days (Fig. 5). The concentration of SO_4^{2-} decreased by 0.537 mg/L or 18% from its initial concentration. Some chemical species changed

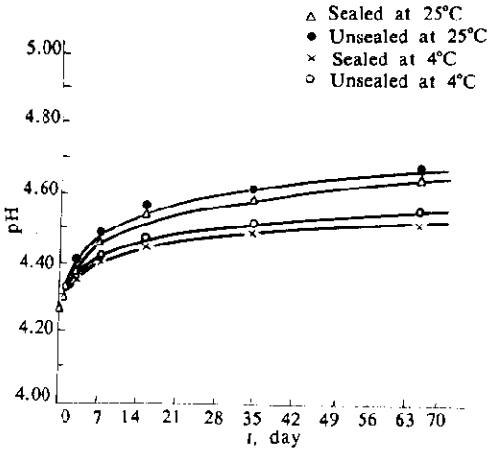


Fig.3 The pH value of stored rainwater as a function of storage time

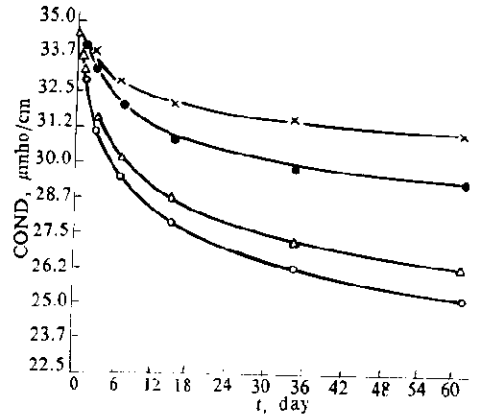


Fig. 4 The conductivity of stored rainwater as a function of storage time

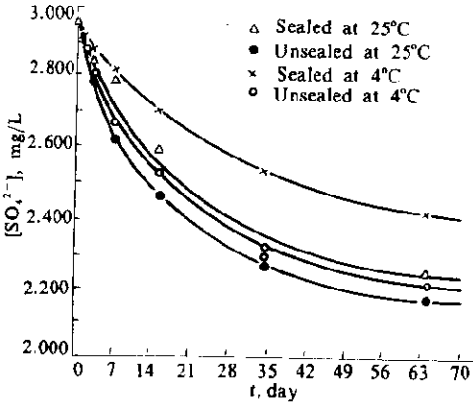


Fig. 5 The concentration of potassium ion in store rainwater as a function of storage time

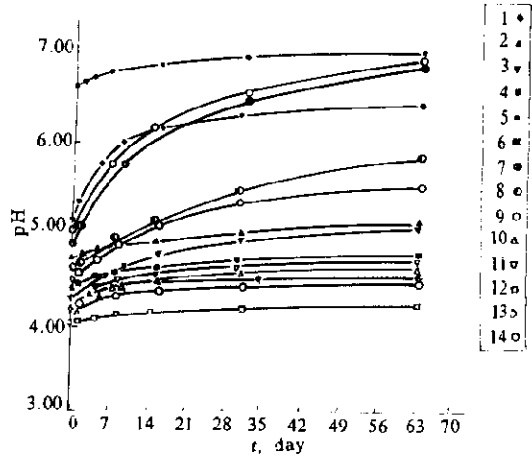


Fig. 6 The pH value as a function of storage time for fourteen rainwater samples stored under refrigeration

even more than SO_4^{2-} . For instance, CH_3COO^- disappeared within the first week while the concentration of HCOO^- dropped to zero after two weeks. Therefore, it would be important to establish a standard for expressing the analytical results in a reasonable way. Moreover, the establishment of such a standard will make it possible for comparison of the analytical data obtained from different research studies.

A model based on statistical regression was developed for estimating the initial chemical composition in the stored rainwater samples. The pH value versus storage time for different samples stored at 4°C is shown in Fig.6. To describe the variation of the pH value, a new variable defined as the change of the pH value from its initial value is expressed as:

$$\text{pH} - \text{pH}_0 = \text{pH}_t, \quad (4)$$

where pH_0 is the initial pH value of the sample and pH_t is the pH value of the sample stored after t days. The best regression fit for the change of pH value versus storage time is shown in Equation 5.

$$\text{pH} = \frac{t}{a + b \cdot t}, \quad (5)$$

where t is the number of storage days; and a and b are regression constants. The initial pH value of the sample can then be estimated by Equation 6.

$$\text{pH}_0 = \text{pH}_t + \frac{t}{a + b \cdot t}. \quad (6)$$

Since the change of other chemical composition in the stored rainwater samples was similar to that of the pH value, the initial value of this composition might also be estimated by the following regression model:

$$Y_0 = Y_t + \frac{t}{a + b \cdot t}. \quad (7)$$

where Y_0 is the initial chemical composition; Y_t is the chemical composition after t days.

3.4 Influence of organic acids on change of pH value

The loss of organic acids was suspected as the main reason of raising the pH value in stored rainwater samples (Verry, 1983; Keene, 1983). Thus, it is important to ascertain how and why the existence of organic acids influences the change of the pH value. In this study, the concentration of HCOO^- , CH_3COO^- , $\text{C}_2\text{H}_3\text{COO}^-$ and the pH value were measured during the time period of nine weeks. The results indicated that organic acids were absent seven weeks after collection. HCOO^- and CH_3COO^-

disappeared within the first week while the concentration of $C_2H_5COO^-$ tended to rise. Organic acids with one or two carbons can be easily assimilated by microbes, but organic acids with three or more than three carbons are difficult and will take longer time to be digested by microbes. In a natural environment, organic compounds with high molecular weight tended to decompose to lower molecular weight compounds. Therefore, we observed that $C_2H_5COO^-$ was accumulated at the beginning of storage. These organic compounds could be decomposed to $HCOO^-$ and/or CH_3COO^- and consumed by microbes eventually.

To ascertain the influence of organic acids on the change of pH value, the dissociated fraction of $HCOO^-$ and CH_3COO^- was regressed with the change of the pH value (Fig.7 and Table 3). The dissociated fraction of organic acids, $[RCOO^-]^*$, in the rainwater samples can be estimated by the following equation (Keen, 1984):

$$[RCOO^-]^* = \left(\frac{10^{-pK_a}}{10^{-pH}} [RCOO^-] \right) / \left(1 + \frac{10^{-pK_a}}{10^{-pH}} \right), \quad (8)$$

where $[RCOO^-]^*$ is the concentration of dissociated organic acid; $[RCOO^-]$ is the concentration of the total organic acid; and K_a is the equilibrium constant of organic acid. The results indicated that the concentration of the dissociated organic acids in the fresh rainwater sample was proportional to the change of the pH value. It suggested that the higher the concentration of dissociated $HCOO^-$ and CH_3COO^- in the sample, the greater the change of the pH value will be achieved.

3.5 Stabilization of rainwater quality by biocide

Experimental results revealed that the loss of $HCOO^-$ and CH_3COO^- in the rainwater samples was proportional to the change of the pH value (Fig. 7). If the assimilation of $HCOO^-$ and CH_3COO^- by microbes is the dominant factor which controls the change of the pH value in the rainwater samples, the elimination of biological activity in the samples should be able to minimize the loss of organic acids and to decrease the change of the pH value. To prove this, chloroform ($CHCl_3$) was used as a biocide

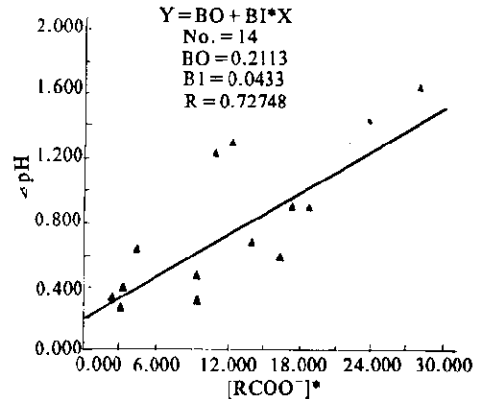


Fig.7 The influence of dissociated fraction $HCOO^-$ and CH_3COO^- on the change of pH value

Table 3 pH value and dissociation fraction of HCOO^- and CH_3COO^- on the change of pH value

Sample number	Initial pH	Final pH	Change of pH	Total Acidity ^a		Dissociated acidity ^a		Total dissociated acidity ^a
				HCOO^-	CH_3COO^-	HCOO^-	CH_3COO^-	
	(1)	(2)	(2)-(1)	(3)	(4)	(5)	(6)	(5)+(6)
1	4.27	4.54	0.27	10.97	4.12	8.64	1.12	9.76
2	4.70	5.08	0.38	7.20	3.10	2.82	1.55	4.37
3	4.27	4.94	0.67	14.64	8.62	11.54	2.34	13.88
4	4.31	4.64	0.33	16.39	5.06	0.80	1.47	2.27
5	5.05	6.29	1.24	7.26	5.69	6.95	3.93	10.88
6	6.61	6.91	0.30	0.00	9.53	0.00	9.41	9.41
7	4.78	6.41	1.63	22.43	13.59	20.71	7.37	28.08
8	4.63	5.76	1.13	16.99	4.50	15.20	2.07	17.27
9	4.17	4.43	0.26	3.11	3.25	2.32	0.74	3.06
10	4.03	4.61	0.58	21.06	8.76	14.76	1.54	16.30
11	4.25	4.72	0.47	9.73	6.91	7.59	1.81	9.40
12	4.02	4.16	0.14	3.84	2.05	2.60	0.35	2.95
13	4.94	6.82	1.88	9.60	5.05	9.04	3.21	12.25
14	4.47	5.44	0.97	17.15	10.75	14.66	3.98	18.64

a: unit is 10^{-6} eq/L

to eliminate biological activity and to stabilize the chemical composition in the stored rainwater samples. Since HCOO^- and CH_3COO^- disappeared very quickly in stored rainwater samples, the schedule of chemical analysis was set at 0, 1/4, 1/2, 1, 2, 3, 4, 9 and 14 days after collection. Four storage conditions used to evaluate their capability of stabilizing chemical composition in the rainwater samples are described as follows: (1) sample with CHCl_3 in a full, sealed aliquot at 25°C ; (2) sample without CHCl_3 in a full, sealed aliquot at 25°C ; (3) sample with CHCl_3 in a full, sealed aliquot at 4°C ; (4) sample without CHCl_3 in a full, sealed aliquot at 4°C .

The changes of $[\text{HCOO}^-]$, $[\text{CH}_3\text{COO}^-]$ and $[\text{C}_2\text{H}_3\text{COO}^-]$ and pH value in the rainwater samples with/without the use of CHCl_3 are shown in Fig.8 through Fig.11. Experimental results indicated that CHCl_3 could eliminate the change of not only pH value but also the concentrations of HCOO^- , CH_3COO^- and $\text{C}_2\text{H}_3\text{COO}^-$ in the stored rainwater samples. The quality of the rainwater samples with the use of CHCl_3 was more stable than those without CHCl_3 . The changes of chemical composition in the rainwater samples stored under refrigeration were less than those stored at room temperature.

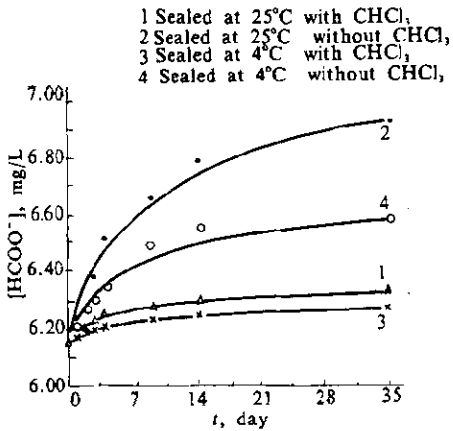


Fig. 8 The variation of pH value with storage time for the rainwater stored under different storage conditions. CHCl_3 was used as a biocide to stabilize the quality of rainwater

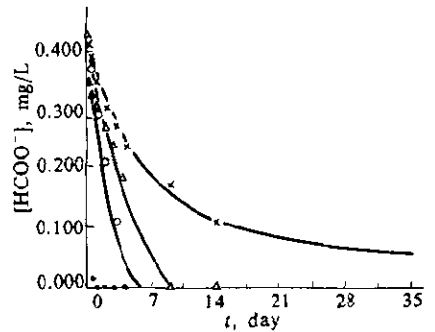


Fig. 9 The variation of $[\text{HCOO}^-]$ with storage time for the rainwater stored under different storage conditions. CHCl_3 was used as a biocide to stabilize the quality of rainwater

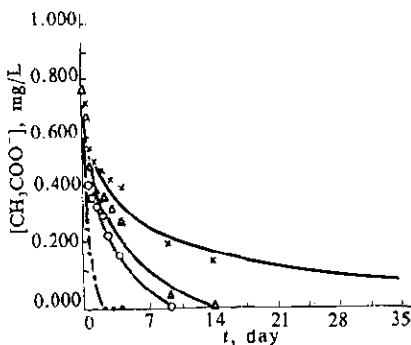


Fig. 10 The variation of $[\text{CH}_3\text{COO}^-]$ with storage time for the rainwater stored under different storage conditions. CHCl_3 was used as a biocide to stabilize the quality of rainwater

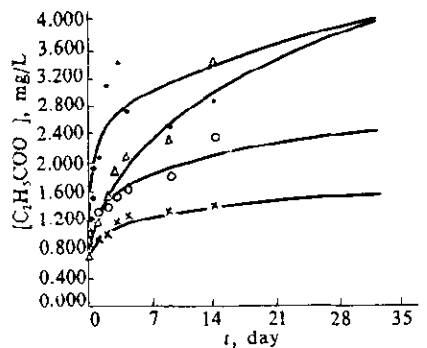


Fig. 11 The variation of $[\text{C}_2\text{H}_3\text{COO}^-]$ with storage time for the rainwater stored under different storage conditions. CHCl_3 was used as a biocide to stabilize the quality of rainwater

The quality of chemical composition in the rainwater samples was improved significantly by the addition of CHCl_3 . For instance, the pH value of the sample without CHCl_3 increased about 0.40-0.62, while the pH value of the sample with CHCl_3 increased only 0.10-0.15. The change of the pH value in the rainwater sample with CHCl_3 decreased about 75%. These results strongly suggested that CHCl_3 was effective in stabilizing the chemical composition in remote precipitation samples.

4 Conclusions

In this study, experimental results indicated that the chemical composition of rainwater samples varied under differing storage conditions and changed with time. In general, the chemical composition changed very quickly at the beginning of storage and became stable after about four weeks. Within the chemical composition measured in this study, the pH value and the concentration of $\text{C}_2\text{H}_3\text{COO}^-$ tended to rise while other chemical composition fell. Experimental results indicated that the loss of organic acids due to biological activity could be the dominant factor which controlled the pH value in stored rainwater samples. Chloroform used as a biocide was able to stabilize the rainwater quality and to minimize the change of pH value in the rainwater samples.

To determine the original rainwater quality, it is important to estimate the initial chemical composition of the stored rainwater samples. The best policy is to analyze the rainwater samples immediately after collection. However, it is difficult to immediately analyze the samples which were collected at remote areas; thus, the minimization of the change of the chemical composition becomes crucial in obtaining reliable results. The proposed procedure of handling a remote rainwater sample is to determine the pH value of the sample immediately after collection, add chloroform to the sample to stabilize the rainwater quality, seal the sample to prevent gas exchange from the atmosphere, and then store the sample under refrigeration. Finally the initial chemical composition in the stored rainwater sample can be estimated by a regression model expressed as follows:

$$Y_0 = Y_t + \frac{t}{a + b \cdot t}$$

where Y_0 is initial chemical composition; Y_t is chemical composition after storage; t is storage time in days; and a and b are regression constants.

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