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Research Article

The Annual Characteristics of Rainwater HCHO in Guiyang City, Southwest of China

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HCHO is ubiquitous and important chemical constituents in the troposphere. The concentrations of the HCHO (aq) in the rainwater were measured in the Guiyang city, southeastern of China from May 2006 to April 2007 and 153 discrete samples were collected. Rainwater ($N = 151$) HCHO (aq) concentrations ranged from lower than method detection limit (MDL) to $40.2 \mu\text{mol/L}$ with a volume weighted mean value of $7.4 \pm 8.8 \mu\text{mol/L}$. The strong correlations between HCHO (aq) and HCOO^- ($r = 0.69$, $n = 137$), HCHO (aq) and nss-SO_4^{2-} ($r = 0.74$, $n = 137$), HCHO (aq) and NO_3^- ($r = 0.67$, $n = 137$), HCHO (aq) and NH_4^+ ($r = 0.74$, $n = 133$) suggest the significant influence of the anthropogenic input for the HCHO (aq) levels. The concentration levels of rainwater HCHO (aq) was inversely proportional to the amount of rainfall, indicating the below-cloud process is the most important mechanism for rainwater HCHO (aq) scavenging processes. More than 70% of the HCHO (aq) wet deposition took place during the early stage of the rainfall. According to the air mass back-trajectory analysis, the rainwater with industrial back-trajectories coming from the north had the highest levels of HCHO (aq) while the rainwater with the green-covered or marine back-trajectories from the southeast had the lowest concentrations, and this indicate the HCHO (aq) originated from urban or industrial regions served as an important source of the rainwater. The annual HCHO (aq) wet deposition flux was calculated as 6.96 mmol/m^2 per year and the total deposition flux was estimated as 24.35 mmol/m^2 per year, 71.4% of which was dominated by dry deposition.

Keywords: Air mass back-trajectory; HCHO; Dry deposition; Wet deposition

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1 Introduction

Carbonyl compounds are the toxic chemical compounds ubiquitously found in the troposphere [1]. The gaseous HCHO (g) is the most abundant carbonyl compounds and accounts for about 70–80% of the carbonyl compounds in atmosphere [2]. It is an important compound that involves in several atmospheric processes occurring in the troposphere. HCHO (g) can affect the acid rain formation in the atmosphere because it can act as a somewhat stable reservoir of S(IV) through the reaction with SO_2 [3] and it is also a precursor to formic acid in aqueous phase [4]. In addition, atmospheric deposition of HCHO (g) is a significant source to the aquatic system since the rainwater HCHO (aq) concentration has been estimated to be up to three orders of magnitude higher than in the surface waters [5].

HCHO (g) can be directly emitted into atmosphere by anthropogenic and natural sources. Natural sources include direct emissions

from the growing vegetation, the biomass burning, and the living organisms [6]. Anthropogenic sources of HCHO (g) include direct sources such as fuel combustion, industrial on-site uses, and off-gassing from building materials and consumer products [7]. Photochemical degradation of volatile organic compounds is identified as important sources of HCHO (g) especially in remote regions. In urban continental regions, the anthropogenic sources contribute significantly to the formation of HCHO (g) [8]. The major sinks consist largely of photolysis and radical reactions [6].

Numerous studies of HCHO (g) in the gas phase have conducted presumably because of the important role of HCHO (g) in the photochemical smog formation [7, 9]. However, to the best of our knowledge, few studies have addressed on its presence and variability in rainwater. There has been no previous study on HCHO (aq) in rainwater in Guiyang city, southwest of China. Research on annual characteristics of rainwater HCHO could help us understanding the geochemical cycle of HCHO in atmosphere. So the objective of this study include: (i) to measure directly the rainwater HCHO (aq) concentration level and to investigate the variations and characteristics as a function of rain amount or rain fraction; (ii) to investigate the possible correlations with other species and the possible sources of HCHO (aq) as a function of air-mass back trajectory; (iii) to calculate the wet deposition of HCHO (aq) and determine its relative significance in total deposition.

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Abbreviations: HYSPLIT, Hybrid Single Particle Lagrangian Integrated Trajectory; VWM, volume weighted mean.

2 Materials and Methods

2.1 Experimental Site Description

Guiyang city (106°07' -107°17' E, and 26°11' -27°22' N), the capital of Guizhou province, is one of the most polluted city in the southwest of China. The city lies in a wide Karst valley basin with mountains around it, which is hard for the pollutions to diffuse in the atmosphere. The sampling site locates in the central of the Guiyang city (Fig. 1), with no specific pollution sources or point sources around and can represent the normal background of the city. Rainwater samples were collected on the roof of the doctoral dormitory in the Chinese Academy of Sciences (CAS) Institute of Geochemistry which is about 20 m higher than the ground and higher than the surrounding buildings.

2.2 Methods

Rainwater was collected on an event basis from May 2006 to April 2007 and 153 discrete samples were collected. The rainwater samples were collected with 1.5 m \times 2 m disposable polyethylene bags, which were cleaned with acid (2–3 N HCl) and thoroughly rinsed with Milli-Q water (18.2 M Ω). In order to minimize the contamination from dry deposition, special attention was paid to open the sampler as soon as possible after the onset of rainfall. The collector was mounted at 1.5 m on an iron stand on roof of the sample building. Immediately after collection, the samples were treated with chloroform and stored in the dark at 4°C to minimize biological degradation of HCHO (aq) in rainwater. The preservation test of adding standard to the sample collection bottle showed no significant change (<5%) in HCHO (aq) levels within 6–7 days of the storage.

HCHO (aq) in rainwater was analyzed by Nash method [10]. This technique has been used successfully in the past [9, 11, 12]. Analyses were done with a 1:10 mixture of Nash reagent (acetylacetone, acetic acid, ammonium acetate) and sample. This reaction is complete after 2 h at 50°C and the product is determined by spectrophotometry at its maximum absorption at 412 nm. The detection limit was 1.67 μ mol/L and the reproducibility defined as SD of six consecutive measurements of the same sample was better than 5%. Carboxylic acids and major anions were determined using Dionex ICS-90 ion chromatography [13] and the major cations were measured with Flame atomic absorption spectrophotometric method spectroscopy.

3 Results

3.1 The Concentration Level of HCHO in the Rainwater

HCHO (aq) concentrations in the rainwater ($N = 151$) ranged from lower than method detection limit (MDL) to 40.2 μ mol/L with a volume weighted mean (VWM) value 7.4 ± 8.8 μ mol/L. Two fresh snow samples were collected during 2007-1-16 and 2007-1-18 with the concentration level of 7.2 and 11.7 μ mol/L. The monthly VWM concentration of HCHO (aq) is shown in Fig. 2. It can be seen that rainwater HCHO (aq) followed an obvious seasonal trend with higher values during the non-growing season and lower values during growing season, which was not in agreement with the observations made by previous studies [7, 9]. The seasonal variation may result not only from a variation in the nature and strength of sources but also from the relatively weak scavenging effect of precipitation during the non-growing season [14, 15]. In Guiyang city, the precipitation increases significantly after May every year, and the leaching of the trace species in the atmosphere may be enhanced by the larger rainfall, so the concentrations of the HCHO (aq) in the rainwater may be reduced by the purification of the air pollutants. However, during the dry season after November, the frequency of the rainfall reduced, most of the rainfall was less than 1 mm and continued for a longer time. As a consequence, the pollutants in the atmosphere could not be timely and effectively removed. In addition, the organic pollutants were prone to accumulate in atmosphere, as a result the concentrations of the HCHO (aq) in the rainwater increased in non-growing season [15].

The HCHO (aq) concentration in rainwater from other sites over the world was compiled from literature shown in Table 1. The HCHO (aq) levels did not vary to a great extent with respect to the study sites (urban, marine or rural) and the values ranged in 0.1–10 μ mol/L. Our data fall within the range observed at rural sites and are twofold and threefold higher than the values for Camarillo, California [16] and Wilmington in North Carolina [7], respectively.

3.2 Calculation of the Deposition Flux of the HCHO(aq)

HCHO (g) in the ambient atmosphere are removed by the wet and dry deposition, and also by gas phase reaction because they were

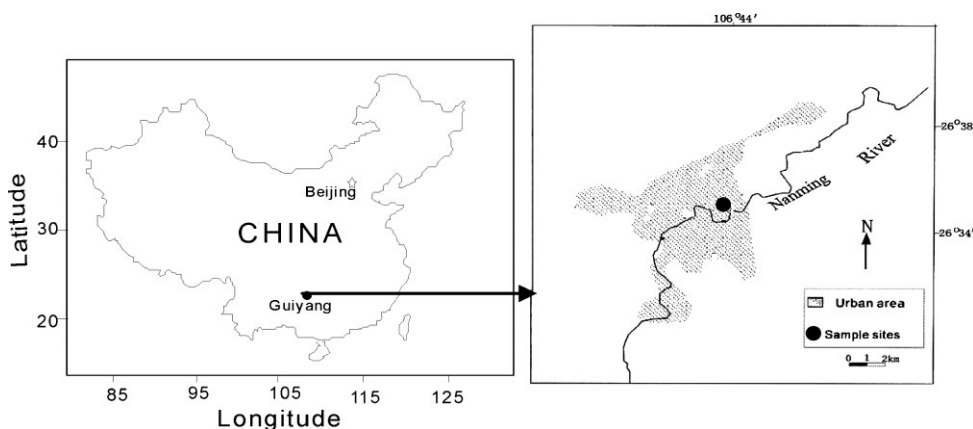


Figure 1. Map of the Guiyang city, showing the location of the sample site.

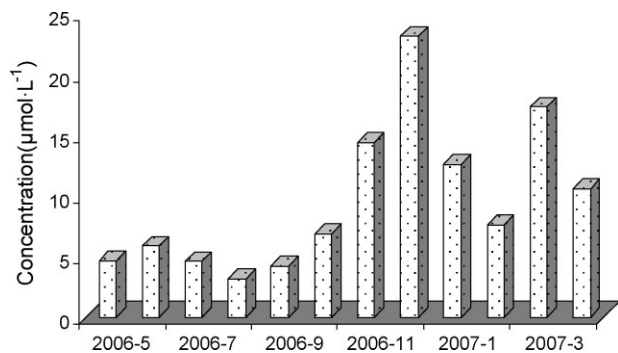


Figure 2. The monthly volume-weighted mean (VMW) concentrations of the rainwater HCHO (aq) during the study period in Guiyang city.

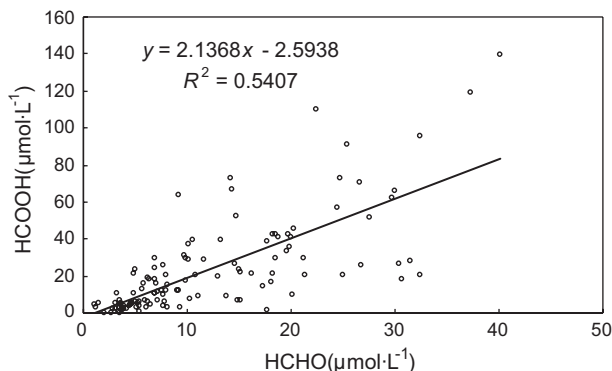


Figure 3. Relationship between HCHO (aq) and HCOOH (aq) in rainwater in Guiyang city.

decomposed by rapid photolysis. Furthermore, the laboratory experiment suggested that the air-water exchange may be an important removal mechanism for atmospheric HCHO (g) [12].

Using the volume weighted average concentration of $7.35 \mu\text{mol/L}$ and rainfall amount of 0.947 mm during the study period, an annual HCHO (aq) wet deposition flux of 6.96 mmol/m^2 per year can be calculated for the Guiyang city. The annual wet deposition flux is significantly higher than the 1.05 mmol/m^2 per year and 1.5 mmol/m^2 per year reported by Seyfioglu [12] and Economou [9] for Izmir, Turkey and Heraklion, Greece, respectively. It was also higher than 4.6 mmol/m^2 per year at Wilmington which was estimated by Kieber [7]. Based on the mean concentration of HCHO (aq) in the rainwater and the Henry's Law constant [17], the equilibrium gas-phase HCHO (g) concentration of 2.47 ppb was calculated. The annual dry deposition flux of HCHO (g) was calculated by multiplying the gas-phase concentration by the dry deposition velocity of 0.5 cm/s recommended by Sakugawa [18]. As a result, the annual dry deposition flux of HCHO (g) was determined as 17.39 mmol/m^2 per year and the total deposition flux was determined as 24.35 mmol/m^2 per year, 71.4% of which was dominated by dry deposition. Sakugawa [18] also suggested that about 97% of atmospheric HCHO (g) lost by dry deposition in the Los Angeles Air Basin.

4 Discussion

4.1 Relationship Between the HCHO (aq) and Other Species

As is shown in Fig. 3, there is a statistically significant correlation between HCHO (aq) and HCOOH in the rainwater of Guiyang city. Chameides [19] suggested the aqueous phase oxidation of HCHO (aq) produce $1\text{--}10 \mu\text{mol/L}$ of HCOO^- with mean of $2.7 \mu\text{mol/L}$ which indicate an important correlation between HCHO (aq) and HCOO^- [19, 20]. However, no evidence was found for significant production of HCOOH from aqueous-phase oxidation of HCHO (aq) [21]. Our work present a good example for studying the correlation between HCHO (aq) and HCOOH since the rainwater acidity ranged from 3.0 to 6.0. According to the calculation in theory, the ratio of HCOOH/HCHO is close to 1 when the pH of rainwater higher than 5, and increases dramatically to 8 when the pH of rainwater decreases to 2. However, no variation was observed between the ratio of HCOOH/HCHO and the measured rainwater acidity [22]. As a consequence, the correlation between HCHO (aq) and HCOOH may indicate the common sources or different sources which have fairly constant strengths or products of the same reaction for the two species [9, 23].

In addition, several source indicators were selected to elucidate the origin of the rainwater HCHO (aq), which include Mg^{2+} and Ca^{2+}

Table 1. Comparison of concentration levels of HCHO (aq) in rainwater reported in literatures.

Sites	Period	VWM or mean ($\mu\text{mol/L}$)	N	References
Rural				
Mainz, Germany	1975–1978	5.8 ± 2.8 (mean)	38	(Klippel et al. 1978)
IVCC, Venezuela	1990	5.7	7	(Sanhueza et al. 1991)
Chaguaramas, Venezuela	1990	9.8	10	(Sanhueza et al. 1991)
Agra, India	1995–1996	4.4	17	(Khare et al. 1997)
Heraklion, Greece	1999–2000	3.05	66	(Economou et al. 2002)
Galicia, Spain	1996–1997	0.42	272	(Peña et al. 2002)
Semiurban				
Florance, Italy	1996(spring)	1.6	–	(Largiuni et al. 2002)
Florance, Italy	1996(winter)	3.9	–	(Largiuni et al. 2002)
Izmir, Turkey	2003–10–2004–4	3.1 ± 2.0 (mean)	27	(Seyfioglu et al. 2006)
Urban				
Camarillo, California	1982	2 (mean)	2	(Grosjean et al. 1983)
Wilmington, NC	1996–1998	2.7 ± 0.2	116	(Kieber et al. 1999)
Westwood, Los Angeles	1985.9–1991.8	3.3	82	(Sakugawa et al. 1993)
Guiyang, China	2006-5–2007-4	7.4 ± 8.8	151	Present study

Table 2. Correlation analysis of rainwater HCHO with other species.

	HCOO ⁻	CH ₃ COO ⁻	C ₂ O ₄ ²⁻	NO ₂ ⁻	Cl ⁻	NO ₃ ⁻	Nss-SO ₄ ²⁻	Na ⁺	K ⁺	NH ₄ ⁺	Mg ²⁺	Ca ²⁺
HCHO	0.69*	0.59	0.63*	0.65*	0.59	0.67*	0.74*	0.39	0.70*	0.74*	0.50	0.58

* $P < 0.001$

for crust, K⁺ and NH₄⁺ for biomass burning, NO₂⁻ for traffic emissions, Cl⁻ for waste or coal burning, Nss-SO₄²⁻ for secondary formation of different mechanism, Na⁺ for marine source [24]. Positively correlations were also observed between HCHO (aq) and NO₂⁻, NO₃⁻, Nss-SO₄²⁻, NH₄⁺, K⁺ (Table 2), which indicate that HCHO might be from the direction emissions of fuel/coal/biomass/waste burning, or from the secondary formations of previous gases.

4.2 The Possible Sources of HCHO (aq) as a Function of Air-Mass Back Trajectory

By using the Hybrid Single Particle Langrangian Integrated Trajectory (HYSPLIT 4) model (www.arl.noaa.gov/ready/Hysplit4.html), 48 h air-mass back trajectories were calculated for each rainwater sample to investigate the role of air mass origin on the HCHO (aq) levels in rainwater. Trajectories were generated using a on-line version of the model, vertical wind fields at 6-h intervals based on the Global Data Assimilation System (GDAS) and the starting height at the 500 m level to represent the air mass near the well-mixed boundary layer likely to contribute more heavily to in-cloud processes and wet deposition [25]. The criteria to select these sectors in our study were based on the geographical direction of large urban and industrial areas around the sampling site and the direction of prevailing winds during the study period [26]. Therefore, the NW/N/NE sector represents large urban and industrial areas, and air-masses from E/SE sector correspond to the wind direction frequently observed at the rear sector of easterly waves. According to the air-mass back trajectory analysis, the rainwater samples were classified into three categories which referred to the wind sectors from NW/N/NE (-90–90°), E/SE(90–180°) and W/SW(180–270°).

As is illustrated in Fig. 4, the HCHO (aq) levels were highest in the rainwater of air-mass originated from NE/N/NW and lowest in the rainwater of air-mass originated from the E/SE. Because most of the industrial or urban regions locate in the north or northeast of Guiyang city, a lot of incomplete organic compounds released by the industrial manufactory and anthropogenic activities came from this side and may be the precursor of HCHO (aq) [27]. This result is in good agreement with correlation analysis which indicated an important anthropogenic input for rainwater HCHO (aq) levels in Guiyang city. However, the rainwater HCHO (aq) values were lowest when air-masses came from E/SE. The southeast of Guizhou province, 200 km away from Guiyang city, approximately of 60% of the sampling site was surrounded with trees, with no intense traffic of light and heavy vehicles. There were no big cities or factories within a radius of 50 km. This site may thus be said to be representative of rural conditions. It was estimated the major sources of rainwater HCHO (aq) were the direct emissions from growing vegetations or soils [28]. Although, there are some urban and industrial regions situated in this southwest of Guizhou province, the volume-weighted mean HCHO (aq) concentrations were lower compared to that from NW/N/NE sector. This observation may be a result of great dilution of rainwater from W/SW sector which can be summarized from the per-event deposition of HCHO (aq) for every air-mass sectors.

4.3 Scavenging of Atmospheric HCHO (aq) by Wet Deposition

In-cloud and below-cloud processes are the two major mechanisms that transfer the pollutants into the rainwater. In-cloud process refers to the process that takes place in the clouds (i.e., nucleation,

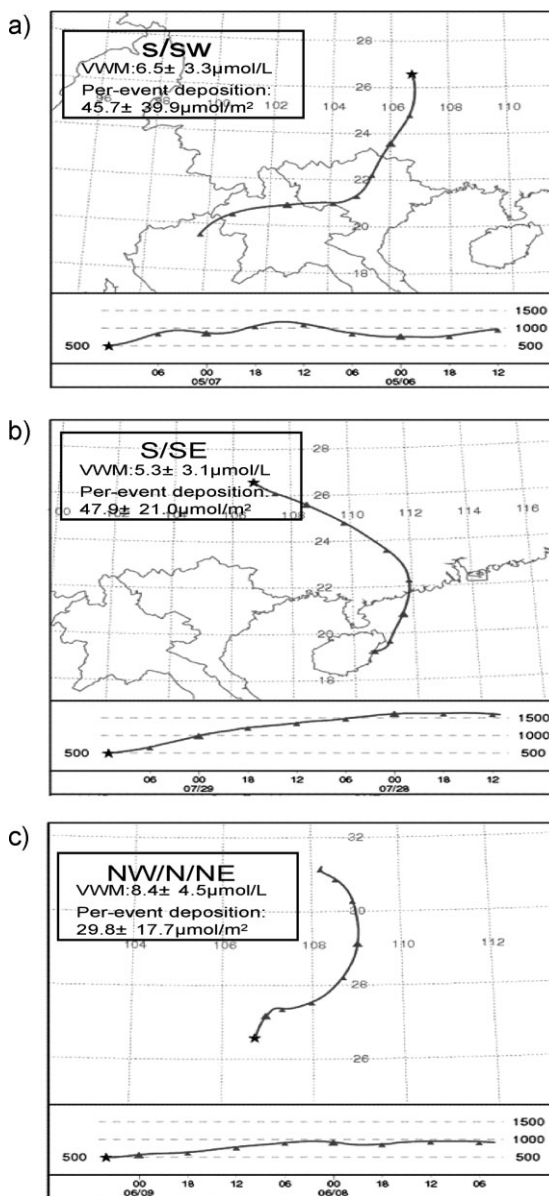


Figure 4. Representative 48 h back trajectories, indicating transport of air masses to Guiyang city, (★ indicate sample site, end of the trajectory: a-12 UTC 07 May 2006, b-11 UTC 29 Jul 2006, c-04 UTC 09 Jun 2006. The numbers in the pane indicate: the per sector VWM of HCHO; the mean per event deposition within each sector).

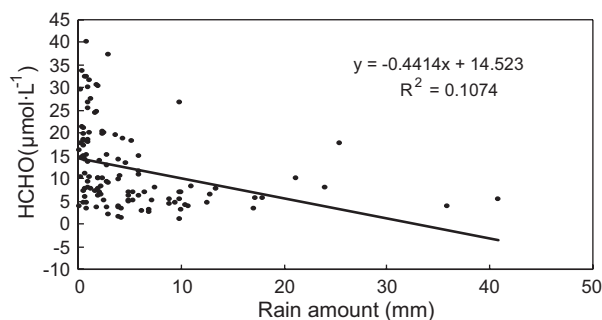


Figure 5. The rainwater formaldehyde variation as a function of rain amount.

condensation, gas dissolution). Below-cloud process refers to the process that scavenges air pollutants between the cloud and the earth surface. In some previous studies [9, 14, 29], no correlation was found between the rainfall amount and HCHO (aq) concentrations, suggesting continuous supply or in situ photochemical production in aqueous phase during rain events. Sakugawa [18] found that rainwater HCHO (aq) concentrations were strongly dependent on precipitation amount and the concentration decreased with increasing precipitation volume, suggesting that the rainwater concentrations were dominated by below-cloud process. However, a negative correlation between rainwater HCHO (aq) level and rainwater amount was observed as shown in Fig. 5 in our study. This seems to indicate that the atmospheric HCHO (g) was mainly incorporated into rainwater within the below-cloud process although this correlation is poor ($r^2 = 0.11$, $n = 137$). Kieber [7] has suggested that if the gas-phase HCHO concentrations are extremely high, below-cloud process may dominate rainwater concentrations relative to continuous supply during rain events and this may explain why a correlation between precipitation amount and HCHO (aq) concentrations is observed at some locations and not in others. To better understand the mechanism by which HCHO (aq) was incorporated into rainwater, concentrations of HCHO (aq) in rain fractions within entire rainfall events are proposed during the rainy season of 2006 in Guiyang city. During that season, five discrete events were collected (1, 2, 3, 4, 5).

In general, a decrease in HCHO (aq) concentration was observed during the early stage of the rainfall events although it increased a little during the latter portion of the rainfall event (Fig. 6). Concentrations of rainwater HCHO (aq) may be controlled by the captured particles and gases, their solubility and the rainwater amounts. Because HCHO (aq) is mostly present in gas phase and is water soluble, the gas phase HCHO may be supersaturated to the

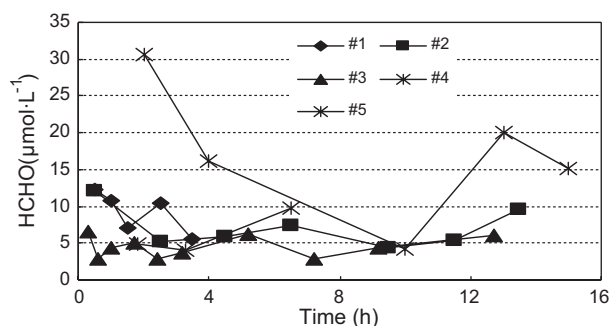


Figure 6. The rainwater HCHO levels in time sequence samples.

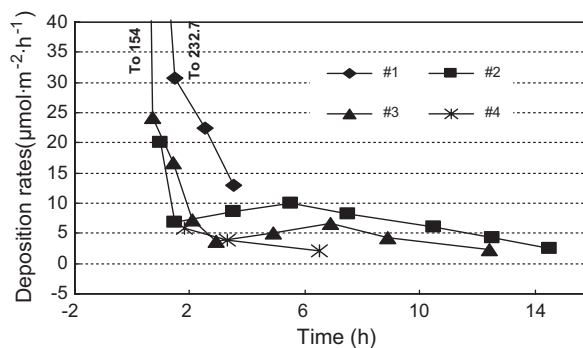


Figure 7. The deposition rates of rainwater HCHO in the time sequence samples (Deposition rates were calculated by multiplying rainwater HCHO concentration by rainfall intensity).

rainwater during the early stage of the rainfall event. So the rainwater HCHO (aq) was sharply decreased because the gas phase HCHO(g) was significantly washed out by the high precipitation. That was, however, not the case to the latter part of the event, and there may be other important input of HCHO (g) to the atmosphere with the slow precipitation at the same time. Figure 7 presents the deposition rates of HCHO (aq) for the four rain event as a function of time series. The deposition rates enhanced greatly during the first 2–3 h of the rain events and then decreased sharply until to the end of the rainfall which was more obvious than the changes of rainwater HCHO (aq) levels during the rain fractions. It was estimated more than 70% of the HCHO (aq) wet deposition taken place during the first 2–3 h of the rainfall so the gas phase HCHO (g) was mainly incorporated into the rainwater during the early stage of the rain event.

Similar variations of chemical constituents during rain fraction have also been reported by other author [30]. The results suggest that HCHO gases and particles in the atmosphere were scavenged by rain droplets during the early stages of precipitation events and then diluted by the subsequent rainfall. What's more, the rapid decrease of HCHO (aq) during the early stage of the rainfall is consistent with the fact that concentrations of HCHO (aq) are higher at lower precipitation levels as shown in Fig. 4.

5 Concluding Remarks

HCHO (g) is a labile compound that is involved in several important processes in the troposphere. 153 discrete precipitation samples were collected from May 2006 to April 2007 in Guiyang city to evaluate the occurrence, sources and deposition of HCHO (aq). Rainwater ($N = 151$) HCHO (aq) concentrations ranged between 1.1 and 40.2 $\mu\text{mol/L}$ with a volume weighted mean value $7.4 \pm 8.8 \mu\text{mol/L}$. The rainwater HCHO (aq) concentration levels seemed to depend on air mass origin, the rainwater with industrial back-trajectories coming from the north had the highest levels of HCHO (aq) while the green-covered or marine back-trajectories from southeast or southwest had the lower concentrations. The significant correlations observed between HCHO (aq) and HCOO^- ($r = 0.69$, $n = 137$), HCHO (aq) and nss-SO_4^{2-} ($r = 0.74$, $n = 137$), HCHO (aq) and NO_3^- ($r = 0.67$, $n = 137$), HCHO (aq) and NH_4^+ ($r = 0.74$, $n = 133$) suggested an important anthropogenic input for HCHO (aq) levels. The concentration levels of rainwater HCHO (aq) was inversely proportional to the amount of rainfall and it was also estimated more than 70% of the HCHO (aq) wet deposition taken place during the

starting 2–3 h of the rainfall. All of these seem to indicate that the below-cloud process is the most important mechanism for rainwater HCHO (aq). The annual HCHO (aq) wet deposition was calculated as 6.96 mmol/m² per year using the volume weighted average concentration of 7.35 μmol/L and 0.947 m of rainfall amount. The dry deposition was estimated as 17.39 mmol/m² per year in the case of calculated gas-phase HCHO (g) levels (2.47 ppb) and the recommended dry deposition velocity (0.5 cm/s). 71.4% of the annual HCHO (g) total deposition was dominated by dry deposition.

Acknowledgments

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