



Effects of agricultural alkaline substances on reducing the rainwater acidification: Insight from chemical compositions and calcium isotopes in a karst forests area

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ABSTRACT

Two-year chemical and stable Ca isotopic compositions ($\delta^{44/40}\text{Ca}$) of rainwater were detected in a typical karst virgin forest site (Maolan National Nature Reserved Park, Southwest China, MNNRP). The results show that the pH values and the ionic concentrations of rainwater samples vary considerably, and about half of them are defined as acidic rain (pH < 5.0). NH_4^+ is the predominant cation in rainwater with a volume weighted mean (VWM) value of $110 \mu\text{mol L}^{-1}$ ($1.3\text{--}377 \mu\text{mol L}^{-1}$), and the second is Ca^{2+} with VWM value of $11.7 \mu\text{mol L}^{-1}$ ($0.9\text{--}67.7 \mu\text{mol L}^{-1}$). SO_4^{2-} and NO_3^- are the principal anions with VWM values of $51.8 \mu\text{mol L}^{-1}$ ($9.8\text{--}203 \mu\text{mol L}^{-1}$) and $24.7 \mu\text{mol L}^{-1}$ ($2.7\text{--}151 \mu\text{mol L}^{-1}$), respectively. Source identification shows that the NO_3^- and SO_4^{2-} of rainwater are controlled by anthropogenic sources, and the agricultural activities and natural processes are the main sources of NH_4^+ , while the part of Ca^{2+} , K^+ and Mg^{2+} originate from crustal inputs. The higher concentration of alkaline ions is a significant contributor to reduce rainwater acidification. Based on the reported data of previous literature, the stable Ca isotopes ($\delta^{44/40}\text{Ca}$) are applied to decipher the different sources. The three sources include as the carbonate weathering (low $\delta^{44/40}\text{Ca} \sim 0.6\text{‰}$, low $\text{NH}_4^+/\text{Ca}^{2+}$ and $\text{NO}_3^-/\text{Ca}^{2+}$ ratios), the silicate weathering which refers to the dissolvable soil dirt minerals from both local and the surrounding place (high $\delta^{44/40}\text{Ca} \sim 0.9\text{‰}$, low $\text{NH}_4^+/\text{Ca}^{2+}$ and $\text{NO}_3^-/\text{Ca}^{2+}$ ratios), and the anthropogenic source (mainly from fertilizers, moderate $\delta^{44/40}\text{Ca} \sim 0.8\text{‰}$, high $\text{NH}_4^+/\text{Ca}^{2+}$ and $\text{NO}_3^-/\text{Ca}^{2+}$ ratios). This study highlights the broader applicability of the chemical and Ca isotopic method in tracing the sources (particularly agricultural sources) of rainwater solute and atmospheric mixing/trapping processes, and can also provide additional insight regarding the elemental biogeochemical cycle in karst areas.

1. Introduction

The chemical characteristics of atmospheric wet deposition can provide significant information to assess the atmosphere quality (Özsoy et al., 2008), which is influenced by the natural materials and human emission (e.g. sulfur oxides, nitrogen oxides, and fine particulate matter) that have a serious threat to human and organisms (Han et al., 2019; Wei et al., 2019). Previous studies show that rainwater could serve as an effective tracer to assess the atmospheric quality because of the emission of contaminants which have influences on the rainwater chemistry (Cao et al., 2009; Vlastos et al., 2019). Besides the local and regional pollutant dispersion (Santos et al., 2011), the rainwater chemistry can also be influenced by several environmental factors, incorporating meteorology, orographic barriers, geographical position,

and human factors (Szépe et al., 2018, 2019). Thus, there are various chemical compositions of rainwater in various regions. Some obvious examples are the Na^+ and Cl^- in rainwater, which are enriched in the wet precipitation along coastal areas (Park et al., 2015); Ca^{2+} is rich in carbonate regions (Han et al., 2011); Ca^{2+} and Mg^{2+} are rich in China desert (Rao et al., 2017); SO_4^{2-} and NO_3^- are rich in megacity (Xu and Han, 2009; Yang et al., 2012). Since the late twentieth century, China was one of the global top three acid rain regions which was followed by Northeast America (Ito et al., 2002; Wang and Xu, 2009) and Central Europe (Topcu et al., 2002), due to the rapid increase of energy requirements, coal combustion and the emission of atmospheric pollution. Earlier researches show that acid rainwater is neutralized by alkaline components, mainly including ammonia and calcium carbonate (Xu et al., 2015). Therefore, it is vitally significant to distinguish the

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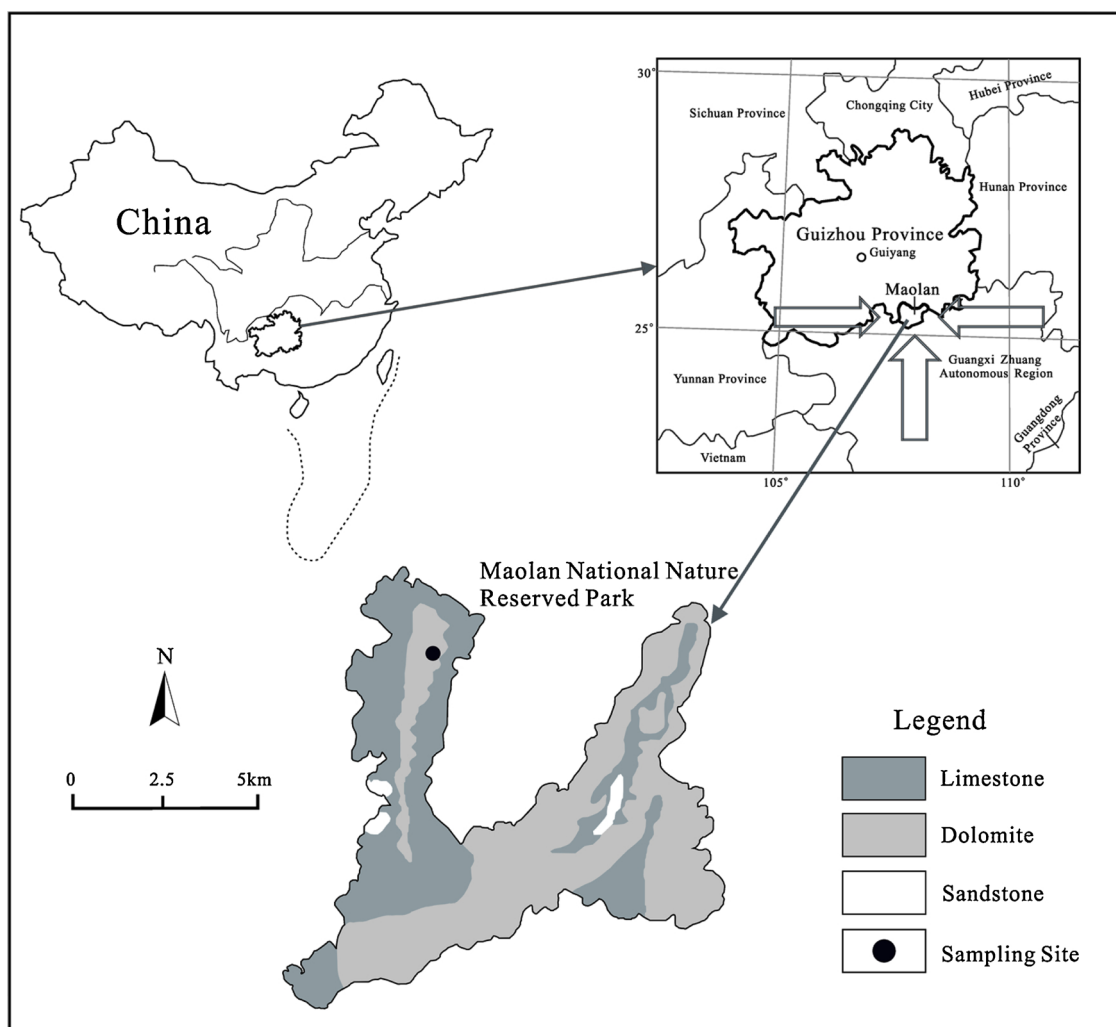


Fig. 1. The location of sampling site in Maolan National Natural Reserved Park (MNNRP).

origins of the alkaline materials of rainwater, particularly in the karst forest region, where have a large potential in the emission of NH_3 and CaCO_3 .

Several researches on acid wet deposition in China indicate that SO_4^{2-} is the dominant anion, while Ca^{2+} is the predominant cation (Larsen and Carmichael, 2000; Larsen et al., 2006; Aas et al., 2007; Zhang et al., 2007). However, just as the previous study reported, the origins of alkaline cations remain large uncertainty and the deposition data are also relative lacked (Larsen and Carmichael, 2000). Rainwater chemical composition is an effective indicator for distinguishing the major source types and identifying the dispersion of elements (Negrel et al., 2007). However, there are many uncertainties in quantifying the detailed sources of ions, and its behavior in atmospheric wet deposition via the traditional analysis method of chemical compositions, which can be further explored by stable isotopic analysis (Andersson et al., 1990). In previous studies, $^{87}\text{Sr}/^{86}\text{Sr}$ and Ca/Sr ratios are applied to trace the calcium and strontium cycling of atmosphere and terrestrial surface (Pett-Ridge et al., 2009), while the stable Ca isotopes are rarely applied as a tracer to decipher Ca sources and their contributions in the atmospheric environment. Although the stable Ca isotope composition can reflect significant information on atmospheric environment (Schmitt and Stille, 2005), the currently available data of Ca isotopic compositions of rainwater are pretty limited, e.g. the global rainwater present a $\delta^{44/40}\text{Ca}$ value of -1.31 to 1.01‰ (Han et al., 2019), while most of the rainwater samples in Europe show a $\delta^{44/40}\text{Ca}$ value of dissolved Ca characteristics of carbonated-derived source ($\sim 0.6\text{‰}$)

(Schmitt and Stille, 2005). The previous study also suggests that the calcite dust originated from semi-arid systems in the global biogeochemical cycle is a predominant controlling factor of rainwater $\delta^{44/40}\text{Ca}$ values (Fantle and Tipper, 2014). Catchment-scale Ca isotopes data of rainwater are also available in the northeast of France (Cenki-Tok et al., 2009). The role of Ca isotopes in the identification of aerosol sources in a proglacial environment has also been highlighted (Hindshaw et al., 2011).

Karst geomorphology in Southwest (SW) China is one of the most typical geomorphology developed on carbonate rock and is also the global largest karst region (Liu et al., 2016). Since the intense karstification (rocky desertification), the underground and surface rivers are connected through near-surface fissures or ponors, and the precipitation could accelerate the migration of materials (within the thin and barren soil) between subterranean and aboveground via runoff and cause severe soil erosion (Yang et al., 2018; Liu et al., 2019; Zeng et al., 2019a). Moreover, rainfall can also contribute nutrients to the barren karst terrestrial ecosystem accompanied by the rainfall process (Zeng et al., 2019b). Thus, the rainwater is vitally important to the ecosystem balance of karst area and is also an essential participant in weathering process, which immediately impacts the function and structure of the ecosystem and the hydro-chemistry in karst regions (Lee et al., 2012; Zeng et al., 2019b).

In this study, the rainwater sampling was carried out almost two years in the Maolan National Nature Reserved Park (MNNRP) within the karst primeval forest region, southwest China, and the main ions

and Ca isotope compositions of all the samples were analyzed. As a typical karst ecosystem, the MNNRP is excellent in geographical position and extensive in karst development. To gain additional insight into rainwater chemistry and the potential impact of agriculture in the typical karst primitive forest area, the time series wet deposition samples were systematically collected, and the rainwater chemical compositions as well as $\delta^{44/40}\text{Ca}$, pH and EC were measured. The main purposes of this study are to explore the water-soluble ionic chemistry of wet deposition, to distinguish the potential sources of major ions (particularly Ca^{2+}) using the chemical composition and calcium isotope, and to provide some basic data in a karst forest area.

2. Methodology

2.1. Study area

The study site was located at Maolan National Nature Reserved Park (MNNRP, 107°52'10" to 108°05'40"E, 25°09'20" to 25°20'50"N; Fig. 1), Guizhou Province, Southwest China. The land cover of this area is significantly controlled by the primitive subtropical evergreen forest. The study area is characterized by a subtropical, monsoonal climate, and the mean annual air temperature is 15.3°C. The mean annual precipitation is 1750 mm, with the majority of annual rainfall (~ 80 %) occurring during the monsoon rainy season (April to September). MNNRP is a typical area representative of the cone and cockpit karst geomorphology with the synergy of the strong and the intermittent Cenozoic uplifts of Himalayan Orogeny and the heat-moisture matched Asian Monsoon in the world. The lithology exposes in MNNRP is mainly composed of shallow marine carbonate in middle and low Carboniferous of the last glaciation in Quaternary (Han et al., 2010a).

2.2. Sampling and chemical analysis

Three 20 L polypropylene (PE) samplers were placed on the rooftop of a construction about 12 m above the ground to collect the rainwater samples, and there is no potential cover around the sampler such as tree canopy. The rainwater was collected manually until the ending of the rainfall event. The polypropylene samplers were pre-cleaned successively with 2–3 N HCl and deionized-water, and air-dried before sampling. A polyethylene lid was used to bypass dry particle fallout in the absence of rain for wet deposition. When it begins to rain, the lid was opened as quickly as possible. A total of 52 rainwater samples were sampled from Feb. 2009 to Oct. 2010. Most of the samples were collected in the wet season from May to October. Only one rainwater sample was selected in each month to determine isotopic composition due to the difficulties inherent to measurements of Ca isotope composition. A total of 25 Ca isotope ratios of different rainwater samples were determined.

The pH values of rainwater samples were determined immediately using a portable multiple parameter meters after collection. The samples were then filtered through 0.22 μm acetate membrane filters (Millipore). The filtrate of each sample was divided into two parts. One part was stored directly in a pre-cleaned polyethylene bottle for measurements of anions, another part was acidified with ultra-purified HNO_3 (pH < 2) for analyses of cations. All the rainwater samples were

kept refrigerated at 4°C until determination. The main cations (K^+ , Na^+ , Ca^{2+} and Mg^{2+}) concentrations in rainwater were detected by using ICP-OES (Varian Vista MPX) with an analytical precision $\sim \pm 5\%$. The rainwater NH_4^+ concentration was measured by using a spectrophotometer with the Nessler method. The major anions (Cl^- , SO_4^{2-} and NO_3^-) were determined by using ion chromatography (Dionex DX-120) with an analytical precision of $\sim \pm 5\%$. All the samples and standards were analyzed in batches with the reagent and procedural blanks using identical procedures.

2.3. Calcium isotope analytical techniques

For the chemical purification, a ^{43}Ca - ^{48}Ca double spike was appended to the rainwater samples in advance. All the samples containing Ca were subsequently separated and purified using a cation exchange resin (Heuser et al., 2002; Han et al., 2019). Then, the Ca isotopic compositions were measured using a thermal ionization mass-spectrometer (TIMS, Triton T1, ThermoFisher, Bremen, Germany) at GEOMAR (Helmholtz Centre for Ocean Research, Germany) according to the technique characterized previously (Heuser et al., 2002; Han et al., 2019). The Ca isotopic compositions are expressed in the delta notation ($\delta^{44/40}\text{Ca} = [({}^{44}\text{Ca}/{}^{40}\text{Ca})_{\text{sample}}/({}^{44}\text{Ca}/{}^{40}\text{Ca})_{\text{standard}} - 1] \times 1000$). The external analytical precision is given as 2 standard deviations (2SD) of the mean, determined by sample repeated measurements. The $\delta^{44/40}\text{Ca}$ values for each session were calculated with the session mean NIST SRM 915a value. The average precision for NIST SRM 915a during a session was $\pm 0.09\%$ (2SD, $n = 4$). During the course of the project mean ${}^{44}\text{Ca}/{}^{40}\text{Ca}$ value of NIST SRM915a was determined to 0.021182 ± 0.000006 (2σ , $n = 36$). Total Ca blank were determined as less than 2 ng corresponding to $\sim 0.7\%$. The standard reference material (CaF_2) was applied across the determining process to monitor the stability of TIMS and the $\delta^{44/40}\text{Ca}$ value of CaF_2 was $1.41 \pm 0.01\%$ (2SD, $n = 9$), which is similar to the previous study ($1.41 \pm 0.01\%$) (Han et al., 2019).

2.4. Backward trajectories

The trajectories are effective tools in the atmospheric research, which are frequently applied to investigate the horizontal migration of atmospheric contaminants and the coherency of air mass sources (Avery et al., 2006). The contaminants may be trapped by air masses trace their motion path. The polluted levels of atmospheric clouds are thereby affected by their geographic sources and their migrating routes. The rainfall events were classified based on the HYSPLIT (Hybrid Single-Particle Lagrangian Intefrated Trajectory) model access via NOAA ARL READY Website (<http://www.arl.noaa.gov>) (Wu and Han, 2015). For each rainfall event, 48 h backward trajectories were started at the recorded onset of rainfall, from 1500 m above ground level over the sampling site.

3. Results

The concentrations of major ions and calcium isotopic compositions in rainwater are given in Table S1. The statistic results of pH, major ionic concentrations and Ca isotope compositions in rainwater are

Table 1
Statistical result of rainwater pH, ionic concentration ($\mu\text{mol L}^{-1}$), and $\delta^{44/40}\text{Ca}$ (‰) in MNNRP.

	pH	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	Mg^{2+}	K^+	Ca^{2+}	NH_4^+	$\delta^{44/40}\text{Ca}$
Min	3.8	0.0	0.4	0.0	9.8	0.8	0.2	1.0	0.9	1.3	0.370
Max	6.3	7.1	27.9	150.7	202.7	33.5	17.7	15.3	67.7	376.8	1.090
Median	5.1	1.1	4.2	16.1	45.2	4.9	3.5	3.9	9.7	83.3	0.810
S.D.	0.6	1.8	5.8	37.1	38.6	7.5	3.5	3.3	15.6	85.5	0.176
Mean	5.04	1.8	5.9	28.1	54.4	7.9	4.0	5.0	14.9	108.2	0.753
VWM	5.2	2.0	5.2	24.7	51.8	7.0	3.0	4.4	11.7	110.4	0.322

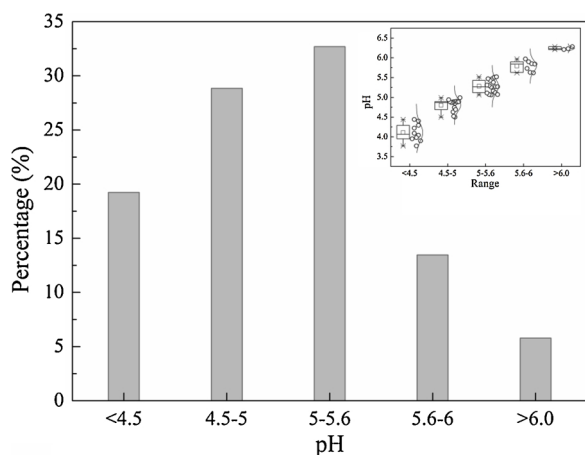


Fig. 2. The pH distribution (in %) of rainwater from MNNRP.

shown in Table 1.

3.1. pH

The pH value distribution (in percentage) of all rainwater samples from MNNRP is presented in Fig. 2. Rainwater pH values range between 3.8 and 6.3, and most of these rainwaters are within the range of 4.0–5.6, with a volume weight mean (VWM) value of 5.2. However, approximately 48 % of the rainwater samples are defined as acidic rain (pH < 5.0) (Fig. 2). The lowest pH (3.8) was observed on May 21st, 2010, while the highest pH (6.3) was observed on August 30th, 2009. The VWM of pH is higher than arithmetic mean values of pH, implying that the higher concentrations often accompanied by a higher rainfall amount. Generally, since the airy carbon dioxide, nitrogen oxides and sulfur oxides could be trapped and dissolved by raindrops and clouds, the pH of natural rainwater should be ranged from 5.0–5.6 (Galloway et al., 1993; Wu et al., 2012). Rainwater samples with pH < 5.0 indicate the input of weak organic acids from nature release, or sulfuric and/or nitric acid from anthropogenic sources, while the rainwater with pH > 6.0 may reveal the certain alkaline substances exist in the wet deposition. If the pH > 5.5, HCO_3^- abundantly exists in the rainwater, but can be negligible when pH < 5.5 (Noguchi et al., 1995).

The high-pH rainwater observed in MNNRP is most likely controlled by the solvation of windblown dust originated from the atmospheric dry deposition (high content of CaCO_3 and MgCO_3) in the study area. Therefore, the high pH value does not support the high HCO_3^- concentration (Wu et al., 2012). Even at a pH higher than 5.5, the HCO_3^- concentrations in this study were below the detection limit.

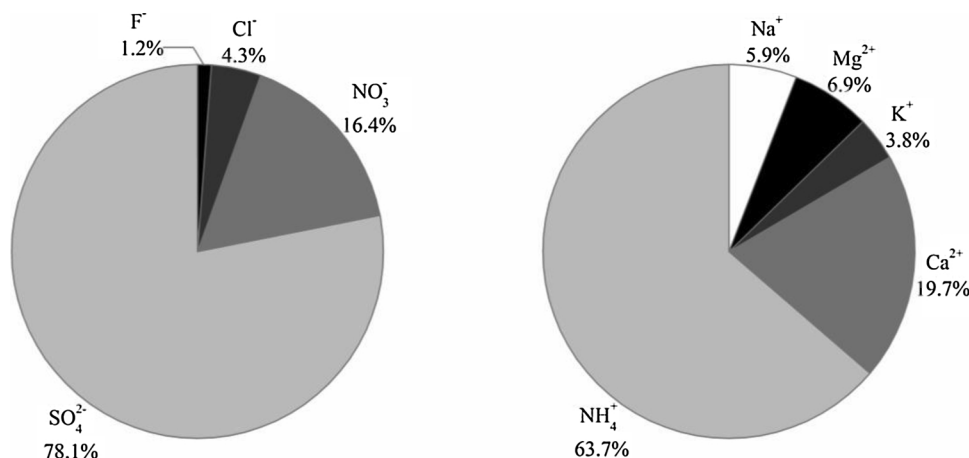


Fig. 3. Chemical composition percentages of rainwater in MNNRP.

3.2. Major ions composition

The equivalence ratio of the total cations to the total anions (TZ^-/TZ^+ , $\text{TZ}^- = \text{SO}_4^{2-} + \text{NO}_3^- + \text{Cl}^- + \text{F}^-$, $\text{TZ}^+ = \text{K}^+ + \text{Na}^+ + \text{Ca}^{2+} + \text{Mg}^{2+} + \text{NH}_4^+$) is generally applied to assess the completeness of the detected major components (Al-Khashman, 2005). The ratios of TZ^-/TZ^+ were 0.88, implying that approximately all major ions were measured and the anions absence might be associated with the slight undetermined organic anions in rainwater. Meanwhile, since the organic anionic species are mainly released by plants (Zeng et al., 2019c; Zhang et al., 2011), and the ratio of TZ^-/TZ^+ is close to 1, indicating that the contribution of plant sources to the rainwater ion composition is negligible.

The VWM concentrations (in $\mu\text{mol L}^{-1}$) of cations and anions were decreased in the following sequence: $\text{NH}_4^+ > \text{Ca}^{2+} > \text{Na}^+ > \text{K}^+ > \text{Mg}^{2+}$ and $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^- > \text{F}^-$ (Table 1). All the ion concentrations present high dispersion nearby their arithmetic mean values with the large standard deviations (SD), which indicates great variation in the rainwater ionic composition levels. Fig. 3 shows that the predominant ions in the rainwater samples were NH_4^+ , SO_4^{2-} , Ca^{2+} , and NO_3^- (equivalence percentage). Similar results were also reported by previous study (Han et al., 2010a). The SO_4^{2-} was the most plentiful anion and accounted for 78.1 % of the total measured anions. NO_3^- was the second rich anion and contributed 16.4 % of the total measured anions. SO_4^{2-} and NO_3^- occupied 94.5 % of the total anionic masses.

As shown in Fig. 3, NH_4^+ was the richest ion of the cations, accounted for 63.7 %. Ca^{2+} was the second plentiful cation and contributed 19.7 % of the total determined cations. NH_4^+ together with Ca^{2+} whose concentration totally reached to took up 83.4 % of the total cationic masses. After calculation, the VWM concentration of anion and cation were $83.7 \mu\text{mol L}^{-1}$ and $136.6 \mu\text{mol L}^{-1}$, respectively, which implies that the atmosphere quality is pretty good in the study area. But the sum of SO_4^{2-} , NO_3^- and NH_4^+ which were main anthropogenic ions, took up 79.1 % of the total ionic masses, implying the significant contribution of anthropogenic sources to the rainwater chemistry.

3.3. Ca and Ca isotopic composition

According to Table S1, Ca^{2+} was the second abundant cation with a high VWM concentration ($11.7 \mu\text{mol L}^{-1}$) and varied from $0.9\text{--}67.7 \mu\text{mol L}^{-1}$. The $\delta^{44/40}\text{Ca}$ values of rainwater samples ranged from 0.37‰ to 1.09‰ with a mean value of 0.75‰. Most of the samples lie around 0.80‰. The highest $\delta^{44/40}\text{Ca}$ value occurred on 6th May 2010 and the lowest value occurred on 9th June 2009. The light ^{40}Ca are enriched in all the rainwater samples relative to seawater (1.88‰) (De La Rocha and DePaolo, 2000), which is similar to the data

Table 2
Correlation coefficients (R) between major ions and pH in rainwater at MNNRP.

Ion	pH	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	Mg ²⁺	K ⁺	Ca ²⁺	NH ₄ ⁺
pH	1									
F ⁻	-0.13	1								
Cl ⁻	-0.35	0.57*	1							
NO ₃ ⁻	-0.43*	0.70*	0.70*	1						
SO ₄ ²⁻	-0.38*	0.72*	0.75*	0.65*	1					
Na ⁺	-0.51*	0.59*	0.76*	0.83*	0.52*	1				
Mg ²⁺	-0.45*	0.42*	0.53*	0.79*	0.38*	0.71*	1			
K ⁺	-0.46*	0.27	0.59*	0.61*	0.57*	0.54*	0.58*	1		
Ca ²⁺	-0.35	0.57*	0.68*	0.84*	0.62*	0.66*	0.84*	0.70*	1	
NH ₄ ⁺	-0.28	0.74*	0.72*	0.61*	0.96*	0.48*	0.25	0.44*	0.47*	1

* Correlation is significant at the 0.01 level (2-tailed).

of rainwater samples in other areas (Fantle and Tipper, 2014; Han et al., 2019).

4. Discussions

4.1. Sources of major ions

4.1.1. Correlation factors and ion mole ratio

The correlation coefficients between ions in rainwater samples of MNNRP were performed to explore the association among ionic constituents and to identify the possible common sources of major ions. As shown in Table 2, there is a weak negative correlation between pH and SO₄²⁻ and NO₃⁻. Moreover, there is a moderate association between SO₄²⁻ and NO₃⁻ (R = 0.65) in rainwater samples. This indicates that SO₄²⁻ and NO₃⁻ in rainwater derive from the sulfate and nitrate salts ionization (e.g. CaSO₄ and NH₄NO₃), which is related to the neutralizing processes (Zeng et al., 2019c), while the H₂SO₄ and HNO₃ are unlikely to be the principal sources. Significant positive correlations are observed between NH₄⁺ and SO₄²⁻ and NO₃⁻ (R = 0.96 and 0.61, respectively). This suggests NH₃ reacts preferentially with sulfuric acid and the residual NH₃ will be neutralized by nitric acid (Seinfeld, 1986). Positive correlations between Ca²⁺ and SO₄²⁻ and NO₃⁻ (R = 0.62 and 0.84, respectively) indicate that acidic anions could also be neutralized by base cations (Nakano and Tanaka, 1997; Larssen and Carmichael, 2000).

Na⁺ and Cl⁻ also show the correlation coefficient of 0.76, indicating they may be from comparable sources. As shown in Fig. 4, the high Cl⁻/Na⁺ mole ratio in some rainwater samples compared to that in seawater is primarily caused by anthropogenic inputs, while the rest of rainwater samples with low Cl⁻/Na⁺ is related to the additional Na⁺ from weathering process inputs (e.g. silicate weathering) (Rao et al., 2017). The positive correlation of Cl⁻ with NO₃⁻ and SO₄²⁻ (Fig. 4a, b) implies that the ions maybe come from coal-fired or biomass burning, while the vehicle exhaust and emission of the chemical industry are relatively scarce at MNNRP. NH₄⁺, Ca²⁺, Mg²⁺, and Na⁺ have a good correlation suggesting a common source (Fig. 4c, d). However, the NH₄⁺ is usually high in the rainwater and has different sources (Lee et al., 2012; Zeng et al., 2019b). In general, the high NH₄⁺ content in rainwater is controlled by several factors, including biomass burning, fertilizers and livestock wastes, industrial emission, and wastewater treatments (Dentener and Crutzen, 1994; Migliavacca et al., 2005). There are few impacts from industry in this natural forest park of MNNRP. Additionally, the ammonia volatilization enhances with an increase of soil pH (Lau and Charlson, 1977; Zhao et al., 1988), and the pH values of soil in the study area are around 7–8 (Han et al., 2017). The atmospheric diffusion distance of gaseous ammonia is relatively short (Asman and van Jaarsveld, 1992), and the rainwater can wash out gaseous ammonia effectively in a shorter time (atmospheric retention time < 2d) (Xiao and Liu, 2002; Xiao et al., 2012). Therefore, long-range transported NH₄⁺ from the industrial emission is very low in this

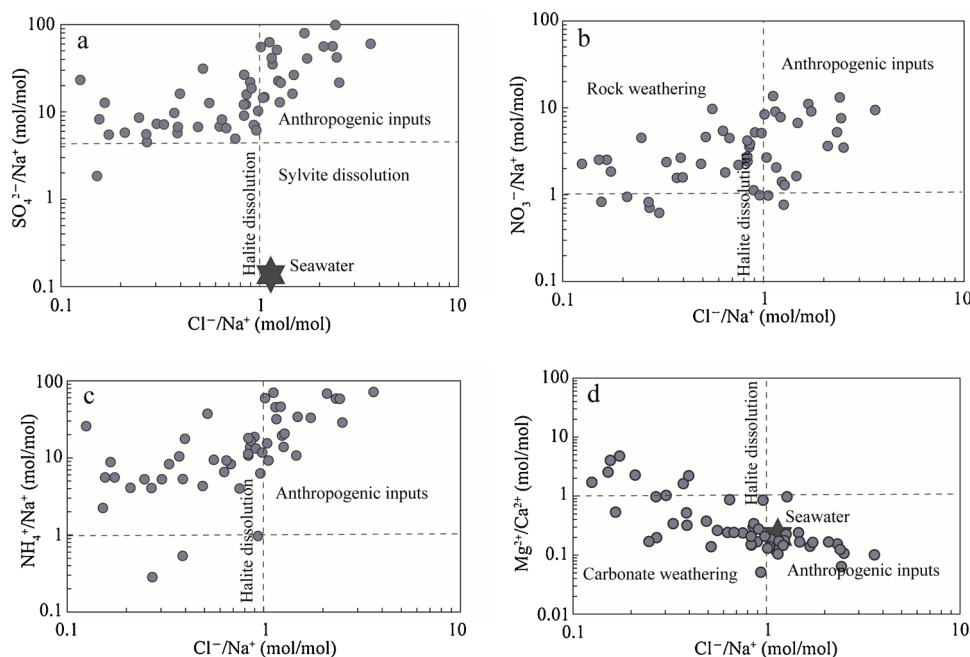


Fig. 4. Variation of SO₄²⁻/Na⁺, NO₃⁻/Na⁺, NH₄⁺/Na⁺, Mg²⁺/Ca²⁺ versus Cl⁻/Na⁺ molar ratios in the rainwater samples.

Table 3

Varimax rotated component matrix for eleven physico-chemical variables of rainwater samples.

	PC1	PC2	PC3
pH	-0.61	0.38	0.45
F ⁻	0.71	0.49	0.18
Cl ⁻	0.83	0.21	-0.19
NO ₃ ⁻	0.92	-0.08	0.30
SO ₄ ²⁻	0.85	0.44	-0.12
Na ⁺	0.91	-0.05	-0.01
Mg ²⁺	0.83	-0.42	0.26
K ⁺	0.70	-0.33	0.05
Ca ²⁺	0.89	-0.22	0.35
NH ₄ ⁺	0.75	0.58	-0.21
δ ^{44/40} Ca	0.56	-0.38	-0.47
Eigenvalue	6.81	1.45	0.84
Variance (%)	61.91	13.16	7.65
Cumulative (%)	61.91	75.07	82.71

virgin forest area, while the natural process and surrounding agricultural activities are the principal origins of NH₄⁺ in rainwater.

4.1.2. Principal components analysis

In this study, principal component analysis (PCA) with the varimax rotation method was performed by using SPSS 23.0 to reveal the relationships between major ions and to further explore the origins of rainwater chemical species. Three principal components (PCs) with high eigenvalues (> 1) are extracted and summarized in Table 3. In total, these three PCs account for 82.7 % of the total variance.

The PC1 accounts for 61.9 % of the total variance. From Table 3, it can be seen that PC1 enhances with an increase of Na⁺, K⁺, Ca²⁺, SO₄²⁻, Cl⁻, NH₄⁺, and Mg²⁺ concentrations and δ^{44/40}Ca values. The significant negative covariation of pH and δ^{44/40}Ca (PC1 = 0.56) can also be explicated by the variations of rock weathering contributions. This PC represents an integrated source affected by marine, terrestrial, and anthropogenic origins. The PC2 with 13.2 % of the total variance obviously shows that the decreasing of NH₄⁺, SO₄²⁻ and F⁻ is along with the increasing of δ^{44/40}Ca, indicating that the PC2 (NH₄⁺, SO₄²⁻ and F⁻) are likely to originate from the anthropogenic sources (integrated source of agriculture and other human activities). The PC3 explains 7.7 % of the total variance which features high Ca²⁺, Mg²⁺ and NO₃⁻, implying that they come from the fertilizer.

4.1.3. Source contributions

Identifying the relative source contribution of the major ions of rainwater is vitally important to study the atmospheric environment. To evaluate the source contribution of sea salt, crustal and anthropogenic inputs to the rainwater chemistry, all the Cl⁻ is considered to derive from non-terrestrial sources, while F⁻, NO₃⁻ and NH₄⁺ are presumed to have an anthropogenic source (Huang et al., 2008; Rao et al., 2017). Cl⁻ is applied to calculate the marine inputs based on the average value of rainwater Cl⁻/Na⁺ ratio (lower than 1.17 over the sampling period of MNNRP). The contribution of marine components for a given element X (X = NO₃⁻, SO₄²⁻, K⁺, Na⁺, Ca²⁺, Mg²⁺, and NH₄⁺) is as follows (Wang and Han, 2011):

$$[X]_{\text{marine}} = [\text{Cl}^-]_{\text{rainwater}} \times (X/\text{Cl}^-)_{\text{seawater}} \quad (1)$$

The elemental ratios (X/Cl⁻)_{seawater} come from the compositions of seawater (Berner and Berner, 1987). According to the previous study, the Ca²⁺ and K⁺ derived from crustal source can be calculated by the equivalent (Ca/Mg)_{crustal} = 1.87 and (K/Mg)_{crustal} = 0.48 (Huang et al., 2008), if Mg²⁺ is presumed only to be originated from oceanic and crustal sources. Moreover, [SO₄²⁻]_{crustal} = 0.47 [Ca²⁺]_{crustal}, so the anthropogenic sulfate could be estimated using the equations: [SO₄²⁻]_{Anthropogenic} = [SO₄²⁻]_{rainwater} - [SO₄²⁻]_{marine} - [SO₄²⁻]_{crustal} (Huang et al., 2008; Wang and Han, 2011). The calculated results of relative source

Table 4

The relative contributions of different sources to rainwater chemical compositions at the MNNRP.

	Sea salt fraction (%)	Crustal fraction (%)	Anthropogenic fraction (%)
NO ₃ ⁻	0	0	100
SO ₄ ²⁻	1	3.3	95.7
Mg ²⁺	34.8	65.2	0
K ⁺	2.2	21.2	76.6
Ca ²⁺	1.7	31.2	67.1
NH ₄ ⁺	0	0	100

contribution (%) are summarized in Table 4. The proportion of Ca²⁺ mainly came from anthropogenic sources is 67.1 %. The K⁺ came from anthropogenic sources is approximately 77 %. The proportion of SO₄²⁻ is almost dominated by anthropogenic sources with 96 % relative source contribution.

4.2. Acid neutralization

Generally, the rainwater acidification is controlled by the existence of sulfuric, nitric, and organic acids (Kaya and Tuncel, 1997; Xu et al., 2015). However, these acid species can be neutralized by the inputs of alkaline substances, including NH₃ and CaCO₃ (Charlson and Rodhe, 1982). Referring to the previous studies (Wu et al., 2012), the neutralization factor (NF) is applied to assess the rainwater neutralization by each cation and estimated as an equation of $NF_{X_i} = [X_i]/([SO_4^{2-}] + [NO_3^-])$. X_i points interesting chemical components, and all concentrations of ions are expressed in μeq L⁻¹ (Mouli et al., 2005; Wu et al., 2012). NF of NH₄⁺ (0.76) is higher than both NF of Ca²⁺ (0.12) and Mg²⁺ (0.04), indicating that NH₄⁺ is the main contributor during the neutralization of acidity.

The concentrations of major ions and pH values of rainwater in this study, and the reported data across China are summarized in Table S2. The ionic concentrations of rainwater in MNNRP are not only significantly lower than those megacities such as Xi'an, Beijing, Shanghai, and Nanjing, but also lower than those in Lanzhou. The previous study suggested that rainwater acidification is greatly affected by the relative contribution of Ca²⁺, NH₄⁺, SO₄²⁻ and NO₃⁻ (Larsen and Carmichael, 2000). Compared to the previous study (Han et al., 2010a), it is also observed that the SO₄²⁻ and NO₃⁻ concentrations presented a distinct enhancement, the SO₄²⁻ concentration increased from 40.6 μeq L⁻¹ to 103.5 μeq L⁻¹, the concentration of NO₃⁻ increased from 3.1 μeq L⁻¹ to 24.7 μeq L⁻¹, this is the reason of the decrease in pH value. However, in fact, the pH value only decreased by 0.2. Meanwhile, it can be seen that there was no change of the Ca²⁺ concentration, while the NH₄⁺ exhibited a distinct increase (from 30.2 to 110.1 μeq L⁻¹). This is ascribed to the enhancement of base cations (mainly NH₄⁺), which neutralized the acidic ions. NH₄⁺ in rainwater from MNNRP is mainly attributed to the agricultural activity, while Ca²⁺ in rainwater integrates the anthropogenic and carbonate weathering sources, which can be supported by the surrounding agricultural production and the wide carbonate terrain located in MNNRP (Fig. 1).

4.3. Tracing alkaline ion origins with Ca isotope compositions in the rainwater

As previously mentioned, the pH values of approximately half of the rainwater sample in this study are greater than 5.0 (Fig. 2). This can be attributed to the alkalization of rain. Although NH₄⁺ is the most alkaline ions in this area, Ca²⁺ is also an important alkaline substance to neutralization acidic ions. Moreover, calcium can contribute to soil fertility and is an important nutrient for vegetation growth (Hedin and Likens, 1996). Thus, distinguishing the derivation of the Ca²⁺ in rainwater is significant. Previous studies suggested that Ca isotope can be treated as a tracer to determining the provenance of Ca in aerosols

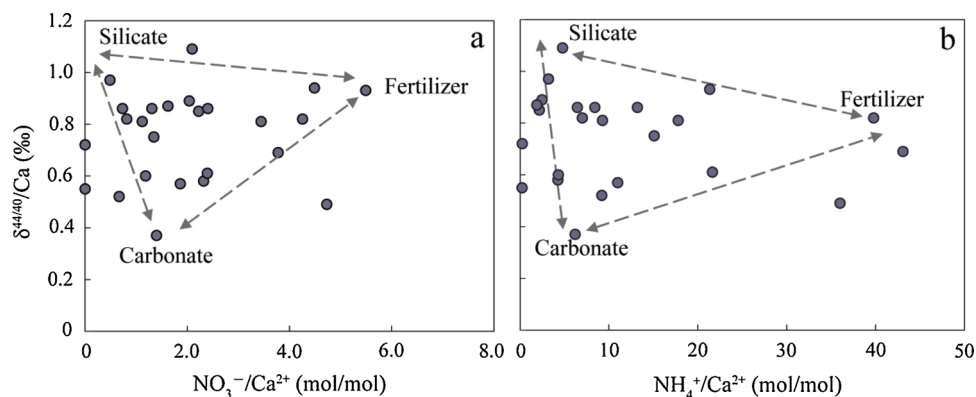


Fig. 5. Variation of $\delta^{44/40}\text{Ca}$ versus $\text{NO}_3^-/\text{Ca}^{2+}$, $\text{NH}_4^+/\text{Ca}^{2+}$ molar ratios in the rainwater samples.

(Schmitt et al., 2003; Schmitt and Stille, 2005; Hindshaw et al., 2011). However, the rainwater chemical and Ca isotopic characteristics were rarely reported in the literature (Han et al., 2019), particularly in the karst forest areas where have a large potential sources of calcium.

As shown in Table S1, the $\delta^{44/40}\text{Ca}$ values of all rainwater samples in MNNRP are lower than that of seawater (1.88‰) (De La Rocha and DePaolo, 2000), suggesting that the contribution of sea salts is rare. The most likely source may come from natural or/and anthropogenic origins. Soil dust is generally believed as the natural origin of rainwater Ca due to the broad existence of calcareous materials on the earth's surface. Moreover, the surface soil is easily blown up into the atmosphere continuously as particulate matter or atmospheric dust by wind (Xu et al., 2009; Zeng et al., 2019c). The anthropogenic sources commonly include engineering construction, agricultural activities, and industrial production (Rao et al., 2017).

The plots $\delta^{44/40}\text{Ca}$ vs. $\text{NO}_3^-/\text{Ca}^{2+}$, $\text{NH}_4^+/\text{Ca}^{2+}$ (Fig. 5) suggest that rainwater from MNNRP is from at least three-end-member integration are needed to decipher the data: carbonate weathering, soil dust from a distance (silicate weathering), and the third end-member. Based on the studies of $\delta^{44/40}\text{Ca}$ ratio in rocks and their weathering processes, we can infer the $\delta^{44/40}\text{Ca}$ ratios of soil dust. According to the previous study (Fantle and Tipper, 2014), the $\delta^{44/40}\text{Ca}$ ratio of carbonate is about 0.6‰, the $\delta^{44/40}\text{Ca}$ ratio of silicate is about 0.94‰. It is apparent that the first non-marine component (carbonate) has low $\delta^{44/40}\text{Ca}$ ratio, low $\text{NO}_3^-/\text{Ca}^{2+}$, $\text{NH}_4^+/\text{Ca}^{2+}$ ratios, and the second end-members (silicate) have high $\delta^{44/40}\text{Ca}$ ratio, low $\text{NO}_3^-/\text{Ca}^{2+}$, $\text{NH}_4^+/\text{Ca}^{2+}$ ratios. The third component is most likely of the anthropogenic inputs, which also have a relatively high $\delta^{44/40}\text{Ca}$ ratio (~1.2‰) (Han et al., 2019). Although the Ca isotopic compositions of representative anthropogenic inputs for the wet deposition in MNNRP have not been well characterized, the fertilizers usually possess high $\text{NO}_3^-/\text{Ca}^{2+}$, $\text{NH}_4^+/\text{Ca}^{2+}$ ratios, here we can reasonably infer that the agricultural production (fertilization) would be one of the non-marine Ca origin in the rainwater in MNNRP.

4.4. Source identification by backward trajectories

In order to obtain more clear information about the wind pattern over the sampling period, all samples are assessed by using backward trajectories. According to the 1500 m AGL and 48 h backward trajectories, the air mass motion route in the rainy days at MNNRP can be classified as 3 clusters (Fig. 6).

The lowest Ca isotopic ratio was observed in cluster 1 (e.g. on June 9, 2009; $\delta^{44/40}\text{Ca}$ = 0.37‰; the wind started from west of MNNRP; Fig. 6a), corresponding to the upper and lower reaches of Wujiang River located in this wind direction, the carbonate rocks are widely distributed in this area (Han et al., 2010b).

Cluster 2 (e.g. April 19, 2009; $\delta^{44/40}\text{Ca}$ = 0.52‰; the wind started from the east of MNNRP, Fig. 6b) includes potential sources from

fertilizer and carbonate rocks weathering which had a moderate Ca isotope ratios. The wind traversed through the north of Guangxi province which is a typical karst area and there is a lot of farmland.

The relative high Ca isotope ratios was associated with trajectories from Cluster 3 (e.g. May 14, 2010; $\delta^{44/40}\text{Ca}$ = 0.87‰; the wind started from south of MNNRP), wind backward trajectory went across a route through the silicate terrains of south China before it comes to MNNRP (Fig. 6c). The previous discussion reveals the sensitivity of the Ca isotope composition in tracing the wind sources from various lithological areas.

5. Conclusions

This study reports the two-year records of the chemical and Ca isotopic compositions of wet deposition in a karst primeval forest (MNNRP). Our results show the relatively high frequency of acid rain with a VWM pH of 5.2. The stable Ca isotope ratios ($\delta^{44/40}\text{Ca}$) of rainwater from the MNNRP show significant variations. These variations, together with $\text{NO}_3^-/\text{Ca}^{2+}$ and $\text{NH}_4^+/\text{Ca}^{2+}$ ratios, reflecting the relative contribution of fertilizer, silicate weathering, and carbonate weathering to the rainwater Ca. These correlations help to decipher at least three potential end-members contributing to the rainwater chemistry from MNNRP: 1) the carbonate origin with the characteristics of relative low $\delta^{44/40}\text{Ca}$ values, low $\text{NH}_4^+/\text{Ca}^{2+}$ and $\text{NO}_3^-/\text{Ca}^{2+}$ ratios; 2) the silicate weathering origin with the relative high $\delta^{44/40}\text{Ca}$ values, low $\text{NH}_4^+/\text{Ca}^{2+}$ and $\text{NO}_3^-/\text{Ca}^{2+}$ ratios; and 3) an anthropogenic component containing moderate $\delta^{44/40}\text{Ca}$ values, relative high $\text{NH}_4^+/\text{Ca}^{2+}$ and $\text{NO}_3^-/\text{Ca}^{2+}$ ratios. The majority of our samples can be deciphered by the integration of the carbonate source, silicate source, and anthropogenic input, indicating Ca sources in rainwater are dominated by atmospherically-derived carbonate minerals, as well as a significant influence of the anthropogenic inputs in different seasons of MNNRP. The origins of dissolved substances in rainwater inferred from $\delta^{44/40}\text{Ca}$ values are also greatly supported by the wind back trajectory results received from the NOAA HYSPLIT model. In conclusion, this study provides a new insight of the chemical compositions and stable Ca isotopic compositions of rainwater, which is valuable to trace sources of rainwater solute and their mixing/trapping processes in the atmosphere, and also provides wet deposition data support for the elemental biogeochemical cycle in a karst area.

Declaration of Competing Interest

The authors declare no conflict of interest.

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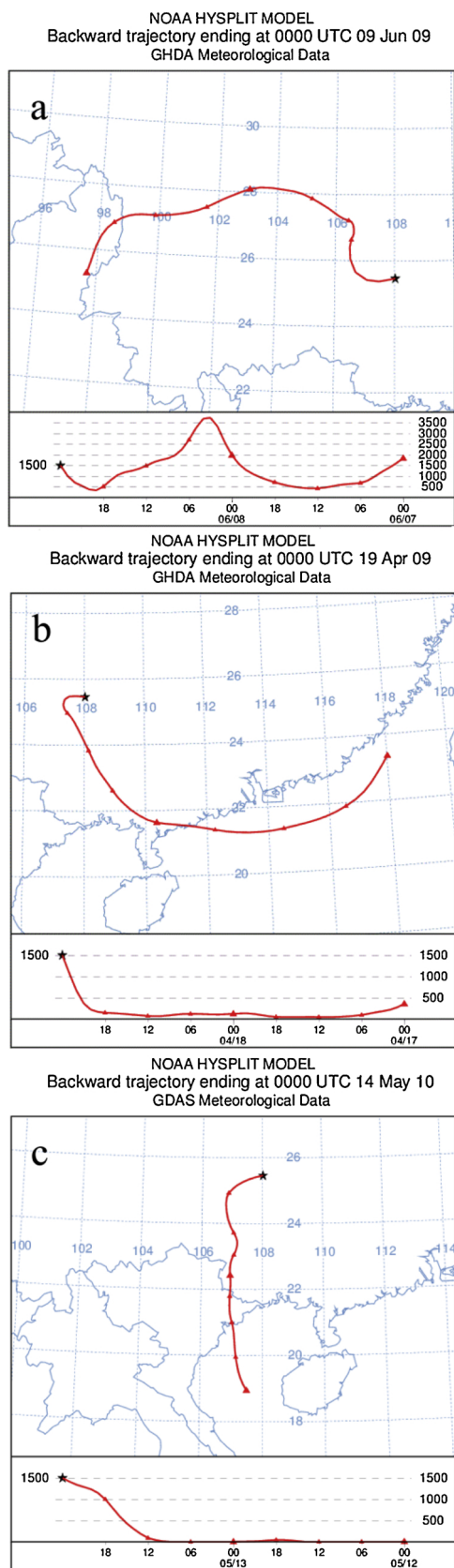


Fig. 6. Representative trajectories of air masses of rainfall events from the three classified clusters; a. West of MNNRP; b. East of MNNRP; c. South of MNNRP.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.agee.2019.106782>.

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