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Chemical compositions of precipitation at three non-urban sites of Hebei Province, North China: Influence of terrestrial sources on ionic composition

Yao Wu, Zhifang Xu *, Wenjing Liu, Tong Zhao, Xuan Zhang, Hao Jiang, Chong Yu, Li Zhou, Xiaode Zhou

Key Laboratory of Shale Gas and Geoengineering, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China
College of Earth Science, University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

Studies on precipitation chemistry were carried out from April to October in 2008 at three non-urban sites in North China. A total of 122 rainwater samples were collected, and all the samples were analyzed for pH, EC and major ions (F^-, Cl^-, NO_3^-, SO_4^{2-}, K^+, Na^+, Ca^{2+}, Mg^{2+}, and NH_4^+). The predominant ions in the precipitation were SO_4^{2-}, NO_3^- and Ca^{2+} at all sampling sites. The low VWM pH value (5.29) reflected the increasing air pollution in this region. But there was still more than 60% of the total precipitation had a pH value higher than 6.0, indicating the considerable neutralizing effects of alkaline aerosols in northern China. The volume-weighted mean (VWM) concentrations of major ions and pH values showed obvious seasonal differences, the precipitation had higher pH values and VWM concentrations of major ions in dry season. This is mainly attributed to the different sources of air masses in different seasons and the dilution effect on suspended particles. According to the equivalent ratio of $[nssCa^{2+} + NH_4^+] / [nssSO_4^{2-} + NO_3^-]$ and the results of neutralization factors, the strong acid neutralization was mainly brought about by Ca^{2+} followed by NH_4^+ and Mg^{2+}. Using Na as an indicator of marine origin, the proportions of sea salt and non-sea-salt were estimated from elemental ratios. Combining with the results of correlation analysis, the main acidic ions (SO_4^{2-} and NO_3^-) and NH_4^+ were mainly derived from anthropogenic activities, and Ca^{2+} and Mg^{2+} mostly originated from terrestrial sources. In general, the results reflect that terrestrial source was an important source of major cations in rainwater and strongly influenced the precipitation chemistry, especially in dry season.

1. Introduction

Rapid economic development and increased energy demand have resulted in severe air pollution problems throughout China, and the increasing emissions of man-made acidic oxides of sulfur and nitrogen have led to significant deposition of acid rain in China (Larssen and Seip, 1999; Larssen et al., 2006; Huang et al., 2008b; Li et al., 2010). The Administration of Environmental Protection of the People's Republic of China (2009) estimated that about half of China's cities were affected by acid rain in 2008. Despite high SO_2 concentrations were observed in both southern and northern China, acid rain was mainly observed in the south area in history (Zhao et al., 1988; Wang and Wang, 1995; Larssen and Seip, 1999; Fujita et al., 2000; Larssen and Carmichael, 2000). So the rainwater in North China must be influenced by neutralizing compounds like calcium carbonate and ammonia (Norman et al., 2001; Tang et al., 2005). As there are several deserts and semi-arid areas distributed in North China (Fig. 1), atmosphere in this region is always laden with soil dust containing high content of alkaline salts during springs (Zhao et al., 1988; Wang and Wang, 1995; Xu and Han, 2009; Xu et al., 2015). In addition, rainwater is an effective way to remove and absorb aerosol particles in atmosphere due to the "in-cloud" and "below-cloud" scavenging processes (Tang et al., 2005; Xu et al., 2015). Thus, the regional characteristics of soils have significant impacts on pH and chemical compositions of rainwater (Gillette and Sinclair, 1990; Rastogi and Sarin, 2005; Niu et al., 2014a).

Most studies on acid deposition in China have focused on the distribution of precipitation pH and sulfur deposition in South China (Zhao et al., 1988; Wang and Wang, 1995; Yu et al., 1998; Feng et al., 2001; Larssen et al., 2006; Aas et al., 2007; Huang et al., 2008a). Until now, there have been fewer studies focused on the precipitation in North China. However, an increasing trend of the precipitation acidity was

* Corresponding author at: Key Laboratory of Shale Gas and Geoengineering, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China.
E-mail address: zfxu@mail.iggcas.ac.cn (Z. Xu).

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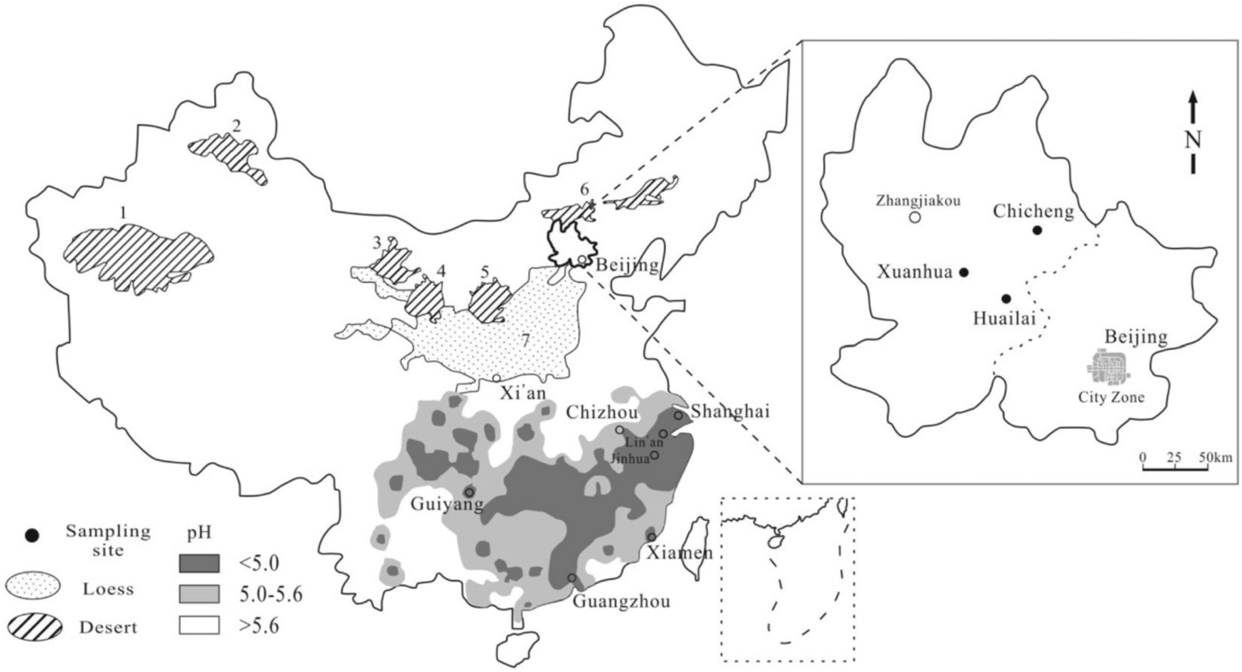

Fig. 1. The location of the sampling sites and the distribution of desert and loess areas and precipitation acidity during 2008 in China. 1. Taklimakan Desert; 2. Gurbantonggut Desert; 3. Badain Jaran Desert; 4. Tungeli Desert; 5. Muus Desert; 6. Hunshandake Desert; 7. Loess Region. This map is modified after Xu and Han (2009).

observed at many sites in North and Central China after 2000 (Huang et al., 2008a; Xu and Han, 2009; Li et al., 2010; Tang et al., 2010). This is mainly due to the rapidly increasing emissions of SO_2 and NO_x, which are the result of the economic booming since 2000 and the increasing number of vehicles in recent decades in urban areas (Van-Aardenne et al., 1999; Tu et al., 2005; Li et al., 2010). In recent years, studies in the Beijing-Tianjin region, Bohai Sea surrounding area and the eastern part of the Loess Plateau reported a decrease in the concentration of alkaline matters in precipitation, which may be another reason for rainwater acidification (Jin et al., 2006; Tang et al., 2007; Xu and Han, 2009; Tang et al., 2010).

In this paper we will present, for the first time, the chemical compositions of rainwater collected at three rural sites in Hebei province, North China. The aim of this paper is to gain an initial understanding of the rainwater chemistry, to identify possible sources that contribute to its chemical composition and finally to explore the influence of terrestrial sources on ionic composition at non-urban region of North China, where the proper data are not available.

2. Methods

2.1. Sampling site description

The sampling sites are located to the northwest of Beijing city (Fig. 1). The area is situated between southern end of the Inner Mongolia Plateau and northern tip of the North China Plain, with elevation increasing from southeast to northwest. It has a continental monsoon climate with hot and humid summers due to the East Asian monsoon, and cold and dry winters due to the influence of the Siberian anticyclone. Prevailing wind is northwest wind in winter and southeast wind in summer. Dust from the erosion of deserts and loess soils in northern and northwestern China results in seasonal dust storms.

Chicheng (CC), Huailai (HL) and Xuanhua (XH) are three counties under the administration of Zhangjiakou city, Hebei province. CC locates about 180 km northwest to Beijing, it has an area of 5287 km^2 and a population of 280,000 people. The annual average temperature and precipitation are 5.7 °C and 424 mm, respectively. HL locates about 87 km southeast to Zhangjiakou and 120 km northwest to Beijing, it has an area of 1801 km^2 and a population of 338,000 people. Average annual mean temperature and precipitation are 9.6 °C and 370 mm, respectively. XH is located 170 km northwest to Beijing, it has an area of 2146 km^2 and a population of 288,000 people. The annual average temperature and precipitation are 7.7 °C and 381 mm, respectively.

As the weather is suitable for a variety of crop growth, such as corn, potato and grape, agriculture is an important economic activity in this region. Cultivated area accounts about 50% percent of the total area. Meanwhile, industrial activities are developing quickly due to the excellent location close to Beijing; many factories have been constructed in recent years. Coal is the dominant source of energy in Hebei Province, accounts for about 90% of the total energy consumption, and it is used extensively in winter and spring for heating (Cao et al., 2014). In addition, domestic pollution also influences the environment significantly because of the increasing population density in this region (Niu, 2014b).

2.2. Sampling and analytical procedure

All the sampling sites are far from the city area. The rainwater samples were collected manually from the beginning of each rain event using a polyethylene bucket (inner diameter, 40 cm) with a polyethylene lid. It was located about 120 cm above the roof of a building. Prior to use, the collector and container were pre-cleaned with hydrochloric acid (2 M) and rinsed thoroughly with Milli-Q water (18.2 MΩ cm). To prevent contamination by dry deposition, the collector was covered by the lid, which was removed just before the onset of each rain event. A total of 122 rainwater samples (36 samples at CC, 47 at HL and 39 at XH) were collected from April to October in 2008. According to the records on China Meteorological Data Sharing Service System (cdc.cma.gov.cn), there was totally 442 mm rainfall in HL meteorology station during the sampling period, and the precipitation occurred mainly in summer in this area. Only the major rainfall events were collected in this study, and the rainwater samples accounted for more than 55% of the total rainfall of all the sampling sites.

Electrical conductivity (EC) and pH values were measured immediately after sample collection with a portable pH and conductivity meter (HANNA HI98129). It was calibrated before the measurement by using standard buffer solutions of pH 4.01 and 6.86 and KCl standard