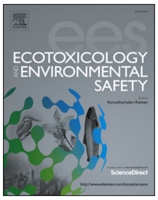
Ecotoxicology and Environmental Safety 163 (2018) 558–566

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv



On the chemical nature of precipitation in a populated Middle Eastern Region (Ahvaz, Iran) with diverse sources

Abolfazl Naimabadi[a,b], Mohammad Shirmardi[c,d], Heidar Maleki[e], Pari Teymouri[f,g], Gholamreza Goudarzi[b,h,*], Abbas Shahsavani[i,j], Armin Sorooshian[k,l], Ali Akbar Babaei[b,h], Nasim Mehrabi[m], Mohammad Mehdi Baneshi[n], Mohammad Reza Zarei[n], Abdolmajid Lababpour[o], Mohammad Ghanbari Ghozikali[f]

[a] Department of Environmental Health Engineering, Neyshabur University of Medical Sciences, Neyshabur, Iran
[b] Environmental Technologies Research Center (ETRC), Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran
[c] Environmental Health Research Center, Health Research Institute, Babol University of Medical Sciences, Babol, Iran
[d] Department of Environmental Health Engineering, Faculty of Paramedical Sciences, Babol University of Medical Sciences, Babol, Iran
[e] MS of Environmental Engineering, Faculty of Water Sciences Engineering, Shahid Chamran University of Ahvaz, Ahvaz, Iran
[f] Health and Environment Research Center, Tabriz University of Medical Sciences, Tabriz, Iran
[g] Department of Environmental Health Engineering, School of Health, Tabriz University of Medical Sciences, Tabriz, Iran
[h] Air Pollution and Respiratory Diseases Research Center, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran
[i] Environmental and Occupational Hazards Control Research Center, Shahid Beheshti University of Medical Sciences, Tehran, Iran
[j] Department of Environmental Health Engineering, School of Public Health, Shahid Beheshti University of Medical Sciences, Tehran, Iran
[k] Department of Chemical and Environmental Engineering, University of Arizona, Tucson, AZ, USA
[l] Department of Hydrology and Atmospheric Sciences, University of Arizona, Tucson, AZ, USA
[m] Ahvaz Jundishapur University of Medical Sciences and Baghmalek Health Center, Water Laboratory, Baghmalek, Iran
[n] Social Determination of Health Research Centre, Yasuj University of Medical Sciences, Yasuj, Iran
[o] Shohadaye Hoveizeh University of Technology, Faculty of Engineering, Susangerd, Iran

ARTICLE INFO

Keywords:
Rainwater chemistry
Chemical elements
Factor analysis
Trace elements
Ahvaz

ABSTRACT

This study reports on the chemical composition of rainwater collected at three ground sites with varying degrees of pollution in Ahvaz, Iran, between January 2014 and February 2015. A total of 24 rainwater samples were analyzed for pH and concentrations of trace elements (Fe, Al, Pb, and Cd) and major ions (Na^+, NH_4^+, Ca^{2+}, Mg^{2+}, HCO_3^-, NO_3^-, Cl^- and SO_4^{2-}). Principle Component Analysis (PCA) was used to identify sources of the measured species. The equivalent concentration of the components followed the order of $Ca^{2+} > SO_4^{2-} > HCO_3^- > NH_4^+ > Cl^- > Na^+ > NO_3^- > Mg^{2+}$. The average pH of the rainwater samples was 6, and only three events exhibited acidic conditions below a pH of 5.6. The lowest and the highest average pH values were observed in the high traffic area (5.96) and industrial area (6.54), respectively. The highest and lowest Ca^{2+} levels were observed in the industrial and high traffic areas, respectively. Na^+, Mg^{2+}, and SO_4^{2-} exhibited their highest and lowest concentrations in the industrial and high traffic areas, respectively. 70.36% of the total variance was due to anthropogenic species (Ca^{2+}, SO_4^{2-}, Mg^{2+}, NO_3^-, Cl^-), soil particles (Cl^-, Na^+, and HCO_3^-), and biomass burning (NH_4^+, pH). The results of this study show that local anthropogenic sources and Middle Eastern Dust (MED) storms affect the rainwater chemistry strongly, which the latter stems from the Arabian Peninsula, Kuwait, Iraq, and some parts of Iran.

1. Introduction

The study of precipitation chemistry is important with regard to both determining the impacts of the wet deposition on surface ecosystems and understanding pollutant interactions with clouds. Although rainwater chemistry has been characterized in a number of urban and rural areas (Al-Khashman, 2005; Cong et al., 2010; Facchini Cerqueira et al., 2014; Sorooshian et al., 2013; Tiwari et al., 2012), to the best of our knowledge, to date, no study has been conducted to examine this issue in Ahvaz, a sensitive area in Iran, which is known to be one of the most polluted cities in the world owing to dust storms (Dianat et al., 2016; Marzouni et al., 2017). Ahvaz is the capital city of Khuzestan

---

* Corresponding author at: Environmental Technologies Research Center (ETRC), Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran.
E-mail address: ghgoodarzi@ajums.ac.ir (G. Goudarzi).

https://doi.org/10.1016/j.ecoenv.2018.07.103
Received 6 February 2018; Received in revised form 23 July 2018; Accepted 24 July 2018

province and located in southwestern Iran near major sources of dust in the Middle East, including Iraq, Saudi Arabia, and Kuwait. Ahvaz also has low vegetation cover, strong surface winds, and high temperatures and humidity, all of which can promote dust storms (Farsani et al., 2018; Goudarzi et al., 2014). Ahvaz is one of the most important industrial centers of Iran due to the presence of large industrial plants, including oil and drilling facilities (Goudarzi et al., 2014). During rain events in autumn 2013, there was an outbreak of airway hyper-responsiveness, for which about 20,000 patients were admitted to the emergency rooms. Similar severe symptoms were observed among the regional population in autumn 2014 and 2015 (Idani et al., 2016). Potential causes for these outbreaks were assumed to be some combination of acid rain, bio-allergens (pollen or spores of fungi), ozone pollution, and dust storms. Although several studies on dust storms and ozone have been conducted and were ruled out as the culprit (Goudarzi et al., 2015; Naimabadi et al., 2016; Soleimani et al., 2016, 2015), no research has been carried out to investigate whether acidic or contaminated wet deposition promoted these health issues in Ahvaz. Wet deposition by rain is due to two main processes: rainout and washout (Steinfeld, 1998). Acidic precipitation is mainly due to the incorporation of SO_x, NO_x, and other acidic precursors with anthropogenic sources (Das et al., 2005; Migliavacca et al., 2005). Neutralization of acidity in rainwater might occur either by airborne $CaCO_3$ and atmospheric ammonia and amines, released from both anthropogenic and natural sources (Schuurkes et al., 1988). Accumulated Pb, Cd, and Hg in the biosphere are toxic to living organisms (Barrie et al., 1987; Galloway et al., 1982). Anthropogenic emissions, from mobile and stationary sources, are the main reason for the elevated trace metal levels in atmospheric deposition (Dobaradaran et al., 2016). Acid precipitation facilitates the dissolution of trace metals and enhances their bioavailability, consequently leading to deleterious health effects for human, and aquatic and forest ecosystems (Báez et al., 2007). Rainwater can dissolve more than 80% of wet deposited trace metals, introducing them to vegetation canopy for subsequent uptake (Valenta et al., 1986). Therefore, it would be said that atmospheric transport and deposition processes are necessary for the global recycling of trace metals.

The goal of this study was to investigate the chemical composition (i.e., pH, major water-soluble anions and cations, and trace metals) of rainwater in the populated city of Ahvaz. Samples were collected in three areas with varying types of pollution influence, including areas with high traffic, industrial emissions, and a residential area. Statistical analysis is presented to identify possible sources of a variety of species.

2. Experimental methods

2.1. Sampling sites and events

The three sampling sites in Ahvaz are shown in Fig. 1, including a high traffic area (Shohada), an industrial area 1 km away from a steel plant (Kooye-Mahdis), and a residential area (Golestan). According to the Iranian Meteorological Organization, for Ahvaz city, the number of days per year with rainfall accumulation exceeding 10 mm and 5 mm, based on a 10-year average, was 6.9 and 12, respectively. These events, although uncommon, afford the opportunity to collect sufficient sample volume (200 mL) for analyzing the samples with atomic absorption and ion chromatography techniques. Between January 2014 and February 2015, eight rainfall events were examined, yielding a total of 24 rainwater samples (i.e., eight per site) that were analyzed for trace elements, water-soluble ions, and pH.

Sampling was conducted with the sampling collectors installed 1.5 m above the rooftop of a structure 3 m high from ground level, away from any possible pollution sources and surface soil. Samples representing single rainfall events included one hour to several days of collection. Samples were collected in glass containers (1 l) fitted with a funnel (24 cm in diameter) with the same material. Before sampling, the collectors (glass bottle and funnel) were carefully acid washed, and then were rinsed with deionized water several times and dried. Each collecting sampler was covered with a plastic lid to prevent contamination from dry deposition, especially in conditions of dusty air (Fig. 2). This cover was removed just before the onset of rainfall events. Samples were collected immediately after the glass bottles were filled up or after the rainfall stopped (Niu et al., 2014; Xu et al., 2015). After rainwater collection, samples were filtered through a 0.45 µm filter to remove insoluble particles, and then each sample was divided into two pre-cleaned bottles. One bottle whose contents were analyzed for pH, $NH_4{}^+$, Cl^-, $NO_3{}^-$, and $SO_4{}^{2-}$ was rinsed several times by deionized water and dried before use. The other bottle was soaked in 20% HNO_3 for 24 h, rinsed several times with deionized water and dried before use. After that, 1 mL of 5% reagent grade HNO_3 was used to acidify the samples collected in pre-acid-washed bottles to prevent the adsorption of the metals on the surface of the polyethylene bottles (Al-Khashman, 2005; Al-Momani, 2003; Báez et al., 2007; Facchini Cerqueira et al., 2014). These bottles were kept in a refrigerator (at 4 °C) until further examination for the ions (Ca^{2+}, $HCO_3{}^-$, Na^+, Mg^{2+}) and the metals (Fe, Al, Pb, Cd) within two days after collection.

2.2. Analytical methods

Collected samples were examined for pH using a 550 Jenway pH meter, which was calibrated using buffer solutions with pH values of 4 and 7. Ammonium concentrations were quantified using a spectrophotometer and the Nessler method (Kulshrestha et al., 2003; Mimura et al., 2016; Xu et al., 2015). Concentrations of other ionic cations were obtained with ion chromatography (Metrohm 850 Professional IC), specifically with a CS12 analytical column and CG 12 guard column. Anions (i.e., Cl^-, $NO_3{}^-$, $SO_4{}^{2-}$) were speciated and quantified with a 100 Dionex IC system equipped with an AG4A-SC guard column and AS4ASC separating column. Trace metals (i.e., Fe, Al, Cd, Pb) were speciated and quantified with a Graphite Furnace Atomic Absorption Spectrophotometer (GF-AAS; Varian model GTA 100) (Baez and Belmont, 1987; Mimura et al., 2016; Xu et al., 2015).

3. Results and discussion

Dissolved CO_2 in rain droplets gives rainwater a pH around 5.6 in a clean atmosphere (Bayraktar and Turalioglu, 2005; Boubel et al., 2008). In this study, the pH of the rainwater samples ranged from 4 to 7.59 with an average value of about 6. Therefore, the rainwater of Ahvaz City can be put into neutral rainfall category (Niu et al., 2014). Abundant calcium carbonate and bicarbonate particulates in the atmosphere during dust storms buffer the acidity of rainwater, decreasing its acidity. Of the 24 samples, only three were observed to be in acidic range ($pH < 5.6$), but they were not coincident with the thunderstorm asthma syndrome outbreak, which was the primary motivation for conducting this study. Weighted means of pH were 6.54, 5.93, and 6.45 for industrial, high traffic, and residential areas, respectively. The highest pH of the samples (7.59) was observed in the high traffic area, where sulfate and nitrate concentrations were 0.73 meq/L and 0.24 meq/L, respectively. The lowest pH value (4) was associated with the high traffic area, coincident with higher concentrations of sulfate (1.32 meq/L) and an average nitrate concentration of 0.21 meq/L. The ratio of the sum of the cations to the sum of the anions (Σcations/Σanions) is an indicator to decide the completeness of measured ions. The acceptable range for this ratio for rain samples is 0.67–1.5 (Park et al., 2015). In this study, this ratio was 0.88 ± 0.38. Linear regression of the relationship between Σcations versus Σanions exhibits $R^2 = 0.90$, which is significant at 95% confidence using a two-tailed Student's *t*-test (Fig. 3a). The average volume-weighted concentrations of the ions in the investigated areas are shown in Table 1 to compare our findings with those found by others researchers in various areas around the world.