Analysis of Urban-Rural Differences in Atmospheric Pollution in the Weinan Region Based on Precipitation Chemistry (Postprint)

Authors: Lu Aigang, Liu Hui, Lu Aigang

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Abstract

Based on measurement results of major ion concentrations in precipitation samples collected from urban and rural areas of Weinan from June 2013 to September 2014, trend analysis was employed to characterize the chemical features of major inorganic ions in precipitation at both sites, and the enrichment factor method combined with end-member contribution method was utilized to investigate their sources. The results demonstrate that, influenced by anthropogenic activities, the average total concentration of precipitation ions in the urban area (775.59 eq·L-1) was substantially higher than that in the rural area (383.60 eq·L-1). The predominant cations at both locations were Ca2+ and NH4+, accounting for 80.05% and 89.82% of total cations, respectively; the predominant anions were SO42- and NO3-, accounting for 93.54% and 92.51% of total anions, respectively. The ionic concentration sequence in urban precipitation was: Ca2+>NH4+>SO42->NO3->Na+>K+>Mg2+>Cl->F->NO-2, while that in rural precipitation was: NH4+> SO42->Ca2+> NO3->Mg2+>Cl->Na+>K+>F->NO2-. Affected by emission sources, precipitation amount, and meteorological factors, the total ion concentration in precipitation within the study area exhibited pronounced seasonal variation, following the order: winter > autumn > spring > summer. Through quantitative source apportionment analysis, the total ion concentration in precipitation at both urban and rural sites was impacted by anthropogenic sources. Specifically, NH4+ and F- in precipitation at both locations were entirely derived from anthropogenic sources, over 95% of SO42- and NO3- were contributed by anthropogenic sources, and Mg2+ and K+ were predominantly from non-sea-salt sources, with the urban non-sea-salt source contribution being slightly greater than that in the rural area. Na+ in the urban area was mainly contributed by non-sea-salt sources, whereas Na+ in the rural area was primarily derived from sea-salt sources.

Full Text

Preamble

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Authors: LU Aigang[1], LIU Hui[2]
Affiliations: [1]Shaanxi Province Key Laboratory for Ecology and Environment of River Wetlands/College of Agriculture Business, Weinan Normal University, Weinan 714000, Shaanxi, China; [2]School of Geography and Ocean Science, Nanjing University, Nanjing 210023, Jiangsu, China

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Corresponding Author: LU Aigang (1968-), male, professor, doctoral supervisor, mainly engaged in global change research. Email: lagx1088@163.com

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1. Introduction

This study investigates the chemical composition of precipitation in Weinan City, Shaanxi Province, with simultaneous sampling in urban and rural areas to characterize spatial differences and seasonal variations in ion concentrations. The research aims to identify major ion sources and assess anthropogenic influences on regional atmospheric chemistry.

2. Materials and Methods

2.1 Sampling Sites and Period

Rainwater samples were collected from June 2013 to September 2014 at two monitoring stations: an urban site and a rural site in Weinan City. The urban sampling point was located at coordinates 109°29 E, 34°29 N at an elevation of 413 m. The rural site was situated at 110°30 E, 35°31 N at 387 m elevation [Figure 1: see original paper].

2.2 Sample Collection and Analysis

A total of 77 precipitation events were monitored, with 52 samples collected in the urban area and 25 in the rural area. Sampling procedures followed the national standard GB13580.2-1992 "Collection of Precipitation Samples." Samples were collected using automated rainwater samplers equipped with 10 L polyethylene buckets. To prevent contamination, sampling buckets were thoroughly cleaned 24 hours before each precipitation event and replaced immediately after rainfall ceased. All samples were filtered through 0.45 m membrane filters within 24 hours of collection and stored at 4°C until analysis.

Ion chromatography was performed using a DX-600 system for cation analysis (Na , NH , K , Mg^{2} , Ca^{2}) and an ICS-2500 system for anion analysis (Cl , F , NO , NO , SO ^{2}). All reagents were prepared with ultrapure water (18.2 MΩ · cm). Quality control measures included parallel sample analysis and calibration with certified reference materials.

2.3 Source Apportionment Methods

Enrichment factors (EF) were calculated relative to seawater composition using the formula:

$$EF_{sea} = \frac{[X/Cl^-]_{rain}}{[X/Cl^-]_{sea}}$$

where $[X/Cl^-]_{rain}$ represents the concentration ratio of ion X to chloride in rainwater, and $[X/Cl^-]_{sea}$ is the corresponding ratio in seawater. Source contributions were quantified using established criteria from Keene et al. [12] and Xiao et al. [13]:

1. If $[Cl^-/Na^+]_{rain} \geq 1.165[Cl^-/Na^+]_{sea}$ and $[Mg^{2+}/Na^+]_{rain} \geq 0.227[Mg^{2+}/Na^+]_{sea}$, then Na is considered to originate primarily from non-marine sources.
2. If $[Na^+/Cl^-]_{rain} \geq 0.859[Na^+/Cl^-]_{sea}$ and $[Mg^{2+}/Cl^-]_{rain} \geq 0.195[Mg^{2+}/Cl^-]_{sea}$, then Cl is considered to originate primarily from non-marine sources.
3. If $[Na^+/Mg^{2+}]_{rain} \geq 4.403[Na^+/Mg^{2+}]_{sea}$ and $[Cl^-/Mg^{2+}]_{rain} \geq 5.126[Cl^-/Mg^{2+}]_{sea}$, then Mg^{2} is considered to originate primarily from non-marine sources.

3. Results

3.1 Ion Concentrations

The total ionic concentration in urban precipitation (775.59 eq · L ^{1}) was significantly higher than in rural precipitation (383.60 eq · L ^{1}), reflecting stronger anthropogenic influences in the urban environment . The coefficient of variation for major ions ranged from 59.61% to 80%, indicating substantial temporal variability. Minimum detectable concentrations were as low as 0.62 eq · L ^{1} for certain ions.

The dominant cations in both areas were Ca^{2} and NH , which together accounted for 80.05% of total cation concentration in the urban area and 89.82% in the rural area. The predominant anions were SO ^{2} and NO , contributing

93.54% and 92.51% of total anion concentration in urban and rural precipitation, respectively.

3.2 Seasonal Variations

Ionic concentrations exhibited pronounced seasonal patterns, following the order: winter > autumn > spring > summer in both locations. This seasonal trend reflects combined effects of emission source strength, rainfall amount, and meteorological conditions. The total ionic concentration in winter was approximately 3.3 times higher than in summer, consistent with reduced wet deposition and enhanced pollutant accumulation during the dry heating season.

3.3 Ion Enrichment

Enrichment factor analysis revealed significant deviations from seawater composition . For urban precipitation, EFsea values ranged from 0.104 for Cl /Cl to 13,901 for certain ion ratios, indicating strong enrichment of crustal and anthropogenic components. Rural precipitation showed similar but less pronounced enrichment patterns.

4. Discussion

4.1 Source Identification

Quantitative source apportionment demonstrated that all measured ions were predominantly influenced by anthropogenic sources in both urban and rural areas. Specifically:

- **NH and NO** : More than 95% originated from anthropogenic sources (vehicular emissions, agricultural activities, and industrial processes) in both areas.
- **SO^{2}** : Over 95% was derived from anthropogenic sources, primarily coal combustion and industrial emissions, with slightly higher contributions in the urban area.
- **Ca^{2}** : Predominantly from crustal sources (soil dust, construction activities), with enrichment factors indicating significant non-marine origin.
- **Mg^{2} and K** : Mainly from non-marine sources, with proportions slightly higher in urban precipitation due to local industrial and biomass burning activities.
- **Na** : In the urban area, 79.11% of Na was from non-marine sources, whereas in the rural area, 94.71% originated from sea-salt sources, reflecting the rural site' s greater exposure to long-range marine aerosol transport.

4.2 Urban-Rural Contrasts

The twofold higher ionic concentration in urban precipitation underscores the impact of localized anthropogenic emissions. The urban environment showed elevated levels of Ca^{2} , NH , and SO ^{2} , consistent with construction dust, vehicular emissions, and industrial coal combustion. In contrast, the rural site exhibited stronger marine influences and lower overall pollution levels.

5. Conclusions

(1) The total ionic concentration in urban precipitation (775.59 eq · L ^{1}) was significantly higher than in rural precipitation (383.60 eq · L ^{1}). The major ions were Ca^{2} , NH , SO ^{2} , and NO , accounting for over 80% of total ionic content in both areas.

(2) Seasonal variations were significant, with winter concentrations exceeding summer values by more than threefold, attributable to increased emissions and reduced precipitation during the heating season.

(3) Source apportionment revealed that anthropogenic sources dominated the ionic composition in both urban and rural precipitation. While Mg^{2} and K were primarily from non-marine sources, Na showed contrasting origins: predominantly non-marine in urban areas but mainly sea-salt derived in rural areas.

(4) The results demonstrate clear urban-rural differences in precipitation chemistry, reflecting the strong influence of local emission sources and atmospheric transport processes on regional air quality.

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Note: Figure translations are in progress. See original paper for figures.