Short Communication

Water-soluble ions in hailstones in northern and southwestern China

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Abstract

Natural hailstones were collected and analyzed in the laboratory not only for their physical properties (e.g., structure, density, shape, and air bubbles), but also for their chemical properties (e.g., organic particles, biological particles, and water-soluble ions), which can help clear understanding on microphysics and development of hailstorms [1–4]. Aerosol particles were carried up from the atmospheric boundary layer to the free atmosphere into the cloud base by updrafts, and could be scavenged into cloud water droplets and ice particles to act as cloud condensation nuclei (CCN) and ice nuclei (IN) [5], further affecting hailstones formation. Interactions between aerosols and hailstones have been studied usually by models [6], because it is difficult to study the processes involved in this interaction in deep convective storms using instruments in the laboratory [7]. Water-soluble particles, which can initiate the liquid phase much more effectively than insoluble particles can, have been less well studied in hailstones [4]. This is particularly true in comparison with the number of studies undertaken to determine the levels of surface pollution. Understanding the role of these water-soluble matters in hailstorm is of great significance but remains a lack of evidence that what kind of particles could be scavenged by hailstone, including nucleation scavenging and impaction scavenging [4,5,7].

Considering the increasing concentrations of anthropogenic pollutants in eastern China [8], cloud microphysical and radiative properties may have been changed and an enormous amount of aerosols are likely to have been input to the atmosphere. It is essential to determine the concentrations of pollutants in hailstones in China. However, there have been almost no measurement of water-soluble ion concentrations in hailstones in China, except for a study in the Tianshan Mountains by Wang et al. [9]. The study found that the inhomogeneous ionic concentration of rainwater was higher than in hailstones, because hail forms at a higher altitude and different chemical uptake processes could occur in the ice phase than in rainwater during precipitation. However, the levels of pollutants in hailstones remain largely unknown from the perspective of water-soluble ions.

In this study, hailstone samples were collected from 15 different hailstorm events across China (Figs. S1, S2 online), each of which occurred on a different date in 2016 (Table S1 online). The concentrations of 10 water-soluble ions, consisting of 4 inorganic cations (Na+, K+, Mg2+, and Ca2+), 4 inorganic anions (Cl−, SO4 2−, NO3 −, and NO2 −), and 2 organic anions (HCOO− and CH3COO−), were determined in 15 hailstone samples (Figs. S3, S4 online). Inorganic cation concentrations in the melted hailstone samples ranged from 0.0 to 14.9 mg/L. Inorganic anion concentrations in the melted hailstone samples ranged from 0.0 to 16.4 mg/L. Organic anion concentrations in the melted hailstone samples ranged from 0.3 to 29.7 mg/L. Hailstones collected in Yucheng City (YC) and Langfang City (LF) were always in the top five when the 15 events were ranked in order from the highest to the lowest ion concentrations, while Quanzhou County (QZ) and Harbin City (HB) were always present at the lowest concentrations.

There are many sources of water-soluble ions in atmospheric precipitation both from natural and anthropogenic sources (e.g., soil dust coated with soluble materials, sea salt and sea spray, aerosols from biomass and fossil fuel combustion, product of the conversion of gaseous precursors) [10]. YC and LF were always in the top five with respect to the ranked order from the highest to the lowest concentrations of AOD (aerosol optical depth), PM10 (particulate matter with an aerodynamic diameter ≤ 10 μm) and PM2.5 (particulate matter with an aerodynamic diameter ≤ 2.5 μm) (Fig. S5 online), which was very similar to the order observed for the ions. To determine the sources of the ions, we calculated the Pearson correlation coefficients between the concentrations of the 10 ions and 6 surface environmental pollutants, as well as

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Table 1 Pearson correlation coefficients (R) and the results of significance tests (P) between the concentrations of ten ions and six environmental pollutants, as well as the aerosol optical depth (AOD) retrieved from the Moderate Resolution Imaging Spectroradiometer (MODIS) for the 15 hailstorm events.

| Ion   | SO₂ | NO₂ | CO  | O₃  | PM₉₀ | PM₂.₅ | AOD |
|-------|-----|-----|-----|-----|------|-------|-----|
| Na⁺   | 0.617 | 0.238 | 0.334 | 0.328 | 0.774 | 0.554 | 0.855 |
| K⁺    | 0.014 | 0.393 | 0.223 | 0.233 | 0.001⁺ | 0.032 | 0.000⁺ |
| Mg²⁺  | 0.620 | 0.220 | 0.340 | 0.311 | 0.756 | 0.533 | 0.850 |
| Ca²⁺  | 0.014 | 0.431 | 0.215 | 0.259 | 0.001⁺ | 0.041 | 0.000⁺ |
| Cl⁻   | 0.631 | 0.232 | 0.357 | 0.298 | 0.765 | 0.544 | 0.847 |
| NO₃⁻  | 0.012 | 0.404 | 0.191 | 0.281 | 0.001⁺ | 0.036 | 0.000⁺ |
| SO₄²⁻ | 0.629 | 0.179 | 0.330 | 0.265 | 0.760 | 0.545 | 0.826 |
| HCOO⁻ | 0.012 | 0.523 | 0.230 | 0.341 | 0.001⁺ | 0.036 | 0.000⁺ |
| CH₃COO⁻| 0.023 | 0.377 | 0.140 | 0.242 | 0.001⁺ | 0.032 | 0.000⁺ |
| Na⁺   | 0.510 | 0.114 | 0.052 | 0.424 | 0.156 | 0.407 | 0.795 |
| K⁺    | 0.406 | 0.483 | 0.631 | 0.222 | 0.690 | 0.503 | 0.507 |
| Mg²⁺  | 0.133 | 0.068 | 0.012 | 0.426 | 0.004⁺ | 0.056 | 0.054 |
| Ca²⁺  | 0.420 | 0.218 | 0.391 | 0.391 | 0.672 | 0.480 | 0.779 |
| Cl⁻   | 0.119 | 0.436 | 0.149 | 0.150 | 0.006⁺ | 0.070 | 0.001⁺ |
| NO₃⁻  | 0.568 | 0.145 | 0.208 | 0.331 | 0.841 | 0.782 | 0.600 |
| SO₄²⁻ | 0.027 | 0.607 | 0.456 | 0.228 | 0.000⁺ | 0.001⁺ | 0.018 |
| HCOO⁻ | 0.617 | 0.222 | 0.341 | 0.320 | 0.783 | 0.569 | 0.847 |
| CH₃COO⁻| 0.014 | 0.427 | 0.214 | 0.245 | 0.001⁺ | 0.027 | 0.000⁺ |

* P < 0.01.

the AOD by using these 15 hail events data (Table 1). According to the correlation analysis, AOD had a strong positive correlation with the concentration of seven ions (Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, NO₃⁻, and CH₃COO⁻), while PM₁₀ had strong positive correlations with all ions (except NO₃⁻), and these correlations were significant at the 0.01 level. The correlation between PM₂.₅ and HCOO⁻ was also significant at the same level, while the correlations with the concentrations of the other environmental pollutants, i.e., SO₂, NO₂, CO, and O₃, were not significant, although there were positive correlations with all ions. The Pearson correlation analysis and the combined significance test in our study revealed that PM₁₀ was the most likely source of the water-soluble ions in the hailstone samples. The strong correlation between PM₁₀ and the ion concentrations pointed to a predominantly terrestrial source of atmospheric particles. The majority of PM₁₀ particles are usually condensed below the cloud base and are likely to be lifted by atmospheric ascending motions to a higher atmospheric elevation and partitioned into clouds in a convective storm [2,3]. PM₁₀ contains not only general CCN but also giant CCN (dry particle diameter > 5 µm), which may inhibit the activation of the smaller particles and therefore play a larger role in nucleation scavenging of aerosols above cloud base [5,10]. In addition, it is easier for large particles in PM₁₀ to deviate from the streamlines of air flowing around a hailstone than small particles during the impaction scavenging either inside the cloud or below cloud base [5].

However, in contrast to the concentrations of the ions in different hailstorm events, the concentrations of the ions in one hailstorm (Beijing, June 10, 2016) varied little (Figs. S6, S7 and Table S2 online). Following a possible explanation, the wind shear has a gradient in the different parts of a convective storm, which may result in a gradient distribution of aerosol concentration in this storm [2]. Meanwhile, the collisions between aerosols particles and hailstones as well as it between other hydrometeors and hailstones would be affected not only by wind speed but also by the radius of hailstone [5].

In summary, 10 ions were detected, but at different concentrations in 15 hailstone samples in China. The presence of these ions suggests that hailstones are likely to scavenge ions along its growth route, based on the correlation of ion concentrations with AOD. PM₁₀ was found to have the most significant positive correlation with all ions in hailstones (except NO₃⁻), which suggests that most of these detected ions in hailstones are likely originated from PM₁₀. This was a preliminary study designed to provide evidence of the presence of water-soluble ions and the possible sources in natural hailstones.

Conflict of interest

The authors declare that they have no conflict of interest.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.scib.2018.07.021.

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