

Chemical characterization of water-soluble ionic component of atmospheric PM₁₀ and PM_{2,5} in winter in Urumqi

Қыс мезгіліндегі Үрімшедегі суда ерігіш PM₁₀ и PM_{2,5} иондық компоненттердің химиялық сипаттамасы

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PM₁₀ мен PM_{2,5} аэрозольді сынамалар Үрімшедегі алты түрлі аймақтан 2007 жылдың желтоқсаны 2008 жылдың қаңтар айлары аралығында NL-20 каскадты импульспен жиналды. Суда ерігіш компонент зерттелді. Нәтижелер көрсеткендей, басты ионды компонент SO₄²⁻ екені анықталды, оның PM₁₀ мен PM_{2,5}-дегі мөлшері сәйкесінше 23,9 %-дан 21,5 %-ға дейін. PM₁₀ мен PM_{2,5}-те [NO₃⁻]/[SO₄²⁻]-нің төмен масса қатынасы табылды, бұны сульфқұрамды көмірдің кең қолданылуымен түсіндіруге болады.

Аэрозольные пробы PM₁₀ и PM_{2,5} собраны с каскадным импульсом NL-20 из шести разных участков Урумчи в период с декабря 2007 по январь 2008 г. Анализирован водорастворимый ионный компонент. Результаты показывают, что главный ионный компонент — SO₄²⁻ и его содержание в PM₁₀ и PM_{2,5} — от 23,9 до 21,5 % соответственно. В PM₁₀ и PM_{2,5} найдено низкое соотношение масс [NO₃⁻]/[SO₄²⁻] (главное значение от 0,32 к 0,27), что объясняется широким использованием сульфосодержащего угля.

1. Introduction

Aerosol is a main atmospheric pollutant. Different forms of particle's size, shape, composition and movement determine the characteristics of aerosol pollution on the environment and human health [1]. In them water-soluble inorganic ions of aerosol are the important characteristic [2]. The water-soluble inorganic ions are closely related to gaseous pollutants in the atmosphere, and reflect the quality of atmospheric environment to some extent. Therefore analysis of water-soluble ions (such as Cl⁻, NO₃³⁻, SO₄²⁻, NH₄⁴⁺, etc.) helps to study their impact on wet droplets and surface water as well as helps to understand atmospheric pollution levels [3]. In addition, water-soluble ions directly affect the acidity of atmospheric [4], because of the water-soluble inorganic ions have the ability of absorption moisture in atmospheric, therefore they will affects atmospheric visibility and bring about a series of ecological and environmental effects.

Urumqi (E86°38'~88°58', N42°45'~44°08'), the capital of Xinjiang Uygur Autonomous Region of China, is in the middle zone of Xinjiang, which is on the north foot of Tianshan Mountain and the south edge of Jungger Basin. It is almost in the center of Asia, and located in the north of Taklamagan desert and in the south of Guerbantonggute desert. The urban area of Urumqi is surrounded by Tianshan Mountain from three directions with peaks up to 5000 m and there is only a mouth facing north, where the wind could carry the soil dust to the urban area of the city. For the past two decades, Urumqi has been heavily air-polluted and it was evaluated as 1 of the 10 heaviest air-polluted cities over World in 1998 [5].

2 Experimental

2.1 Sampling sites

Urumqi city divided into six functional areas, namely Tianshan District, Saybag district, Xinshi district, Shuimogou district, Midong district, Toutunhe district (A to B). Urumqi city is under continental arid climate; all of these cities were heats in cold season for six months for and coal is the main fuel for heating. In this study, five of those areas were chosen to sampling from December 2007 to January 2008 for 24-hour continuous sampling, the effective, sampling location information are as shown in (Fig. 1).

2.2 Sampling methods

Sampling was conducted over a 24-h period, during the winter period from December 2007 to January 2008. NILU filter holders (Tokyo Dylec, Co., modelNL20) with cascaded impactors were used to classify aerosols depending on their sizes of PM₁₀ and PM_{2,5} at a pumping rate of 20l_m⁻¹. Silica fiber filters were equipped in the filter holders (for PM₁₀, Tokyo Dylec, Co., 2500QAT-UP, 47 mm outside diameter with a pore

of 20 mm diameter; for PM_{2,5}, Advantec, Co., QR-100, 47 mm diameter). In all the sampling periods, the sampling filters were exchanged with new ones every other day at six sites and every 7 days. Before and after sampling, all the filters were conditioned for 48 h in a chamber at room temperature at a relative humidity of 50 % for over 24 h and then weighed with an electronic balance (detection limit, 10 mg). Table 1 show the meteorological data, including temperature (Temp.), relative humidity (RH), wind speed, wind direction, etc.

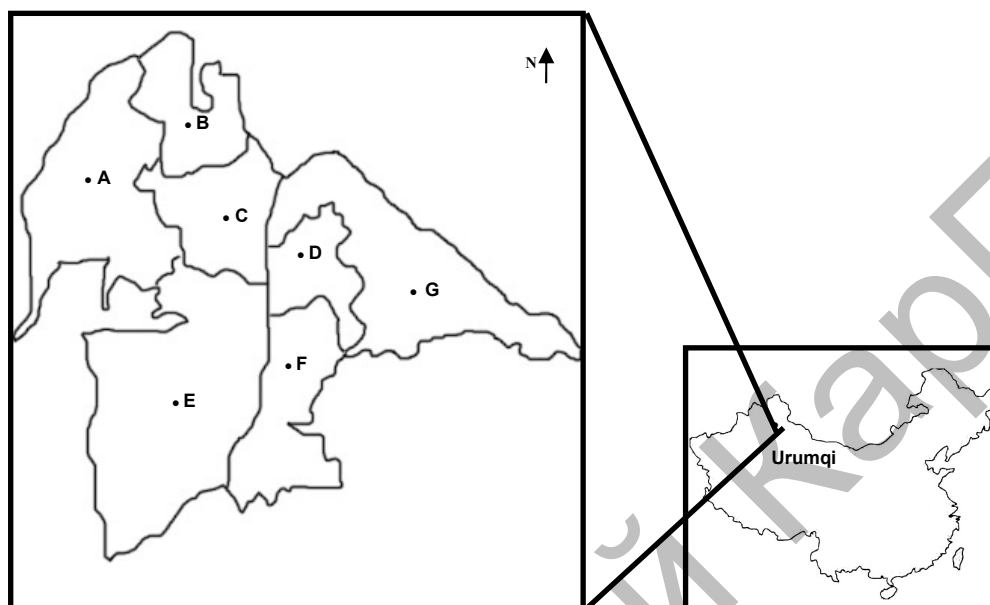


Fig. 1. Sampling sites of aerosol

2.3 Analytical methods

Water-soluble components were extracted from the filters into 50 ml ultra pure water in a Teflon beaker by irradiating with ultrasonic waves for 1 h. The water samples were filtered with a 0,45-mm pore-size membrane filter (Advantec, Co., A045A 025A). Ions (Cl^- , NO_3^- , and SO_4^{2-}) were measured using ion chromatographs (ICS-15 00), Na^+ , K^+ , Ca^{2+} were determined by AAS (PE300). Ammonium-ion was determined spectrophotometrically using a UV-VIS spectrometer. Samples were colored with Nessler method and absorbance of the colored solution was measured at 425 nm in a cell with 1,0 cm optical thickness.

3. Results and discussion

3.1 Mass concentrations

Table 1

Mass concentration and meteorological conditions of sampling date*

Sampling sites	Concentration $\mu\text{g}/\text{m}^3$		PM _{2,5} /PM ₁₀	Average temp. ($^{\circ}\text{C}$)	Wind	Wind direction	RH (%)
	PM ₁₀	PM _{2,5}					
Xin Jiang University	165	261	1,58	-19,2	2	SSW	73
North camp	212	282	1,33	-15,8	3	SSW	64
Liu dawan	267	318	1,19	-16,2	2	ENE	71
Ke xueyuan	145	371	2,56	-11,2	3	SW	68
Da wan	181	253	1,40	-12,8	3	SSW	72
Wu shihua	153	188	1,23	-12,6	2	ENE	81

*The meteorological data are average of 24-hour sampling

Table 1 visualized the larger differences of mass concentration of the PM₁₀ and PM_{2,5} from different sampling locations. PM₁₀ mass concentration range from 145 $\mu\text{g}/\text{m}^3$ to 267 $\mu\text{g}/\text{m}^3$, average 187 $\mu\text{g}/\text{m}^3$, was 1,25 times higher than national second-class air quality standard (150 $\mu\text{g}/\text{m}^3$) but did not exceed national third-class air quality standard (300 $\mu\text{g}/\text{m}^3$). Among the six district, the highest mass concentration of PM₁₀

was Liu dawan ($368,33 \mu\text{g}/\text{m}^3$) exceed 3,68 times the National third-class air quality standard, the lowest was Ke xueyuan was $145 \mu\text{g}/\text{m}^3$. For all the six sampling sites, the 24-h average concentrations of $\text{PM}_{2,5}$ varied from $188 \mu\text{g}/\text{m}^3$ to $371 \mu\text{g}/\text{m}^3$. The $\text{PM}_{2,5}$ concentration were above the 24-h $\text{PM}_{2,5}$ US National Ambient Air Quality Standard ($65 \mu\text{g}/\text{m}^3$) by 4,3 times, 1,7 times exceed the value of Xi'an in 2006 spring and summer witch is $163,11 \mu\text{g}/\text{m}^3$ [6]. The high concentration could be attributed to local anthropogenic emissions (industrial emissions and heavy vehicular traffic) of particulate matter.

The results show that the ratio of $\text{PM}_{2,5}$ to PM_{10} higher than 1 and the main Atmospheric particulate matter of Urumqi was $\text{PM}_{2,5}$. In short, winter particle pollution of Urumqi City was relatively serious, reason has the following aspects: (1) winter temperatures lower heating substantial combustion of fossil fuels, especially coalfi red substantial particulate matter emissions, while coal-fired also because of sec on dary particulate matter emissions precursors (NO_x , SO_2 , etc.). (2) Winter solar radiation is weak, easy to form neutral and stable atmospheric conditions, not conducive to the spread of particulate matter [7]. (3) Winter plants withered, the absorptive capacity of the particles decreased, and bare ground and conducive to the occurrence of dust and cold air to control the relative dry atmosphere is also conducive to lead dust.

3.2 Water-soluble ion species

Fine particles are formed primarily by combustion or secondary chemical reactions in the atmosphere [8]. Higher SO_4^{2-} and NO_3^- concentrations suggest that the photochemical oxidation would have occurred and more secondary aerosols can exist in the atmosphere [9]. The fraction of sulfate sulfur (or nitrate nitrogen) to total sulfur (or total nitrogen) (in sulfate plus sulfur dioxide or nitrate plus nitrogen dioxide) could be used to evaluate the degree of atmospheric conversion from SO_2 to SO_4^{2-} and from NO_2 to NO_3^- [9–10].

From the correlation analysis we can conclude that, in PM_{10} SO_4^{2-} and Cl^- , NH_4^+ were positively correlated, while SO_4^{2-} and Cl^- also showed positive correlation. Research has shown that NH_4^+ is the major ion, it can combined with SO_4^{2-} make the form of $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 , Cl^- may come from the NH_4Cl . Ca^{2+} and NO_3^- also showed positive correlation, so the $\text{Ca}(\text{NO}_3)_2$ is the main form in PM_{10} particles.

In $\text{PM}_{2,5}$ the NO_3^- and H^+ showed positive correlation, studies have shown that the amount of the NO_3^- concentration can reflect the acidity of atmospheric deposition. SO_4^{2-} and Zn^{2+} and Ca^{2+} was positively correlated, calcium particles generally come from the earth's crust, particles in atmosphere is probably make reaction with anthropogenic emissions of SO_2 .

Table 2

The average mass concentration of water-soluble inorganic ions in PM_{10} and $\text{PM}_{2,5}$

Ions	PM_{10}		$\text{PM}_{2,5}$		$\text{PM}_{2,5}/\text{PM}_{10}$
	Concentration range	Average	Concentration range	Average	
Na^+	3,19–5,07	4,11	5,39–11,1	7,02	1,70
K^+	0–0,83	0,45	0–1,91	1,00	2,22
Zn^{2+}	24,3–39,1	31,1	23,2–35,0	31,5	1,01
Ca^{2+}	2,49–9,40	5,61	2,23–11,1	5,03	0,90
NH_4^+	0,687–21,3	6,45	6,18–20,3	11,2	1,74
Cl^-	11,7–34,9	20,1	14,0–31,1	22,6	1,12
SO_4^{2-}	33,7–69,0	44,7	47,8–86,4	59,9	1,34
NO_3^-	8,45–16,3	12,1	10,3–20,7	14,4	1,19
Σ		124		152	
Σ particulate concentration		0,67		0,58	

Generally the ratio of $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ represent the relative importance of stationary sources and mobile sources of atmospheric particulate matter [11]. If $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ ratio was higher the mobile sources of pollution (such as motor vehicle exhaust gas) accounted for the major contribution. If $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ ratio was lower fixed sources of pollution (sulfur content of coal combustion) accounted for the major contribution [12]. As can be seen from Table 3, the $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ ratio in two atmospheric particulate matters was lower so the main pollutants in Urumqi was from stationary source emissions.

Table 3

Mass ratio of $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$

	NO_3^-	SO_4^{2-}	$\text{NO}_3^-/\text{SO}_4^{2-}$
PM_{10}	12,11	44,74	0,271
$\text{PM}_{2,5}$	15,50	47,75	0,325

4. Conclusion

1. The average mass concentration of PM_{10} in Urumqi exceed the national second-class air quality standard by 1,25 times, $\text{PM}_{2,5}$ pollution is more serious and above the 24-h $\text{PM}_{2,5}$ US National Ambient Air Quality Standard ($65 \mu\text{g}/\text{m}^3$) by 4,3 times.

2. Sulfate is the most abundant inorganic species measured in $\text{PM}_{2,5}$ and PM_{10} , the average concentration of SO_4^{2-} in PM_{10} and $\text{PM}_{2,5}$ was $44,7 \mu\text{g}/\text{m}^3$, $59,9 \mu\text{g}/\text{m}^3$ respectively. The main source of Sulfate was the SO_2 emission from coal combustion.

3. In the PM_{10} (NH_4) $_2\text{SO}_4$, NH_4HSO_4 , NH_4Cl , $\text{Ca}(\text{NO}_3)_2$, and in $\text{PM}_{2,5}$ majority form of particles was ZnSO_4 , CaSO_4 particles.

4. The $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ ratio in two atmospheric particulate matter was lower so the main pollutants in Urumqi was from stationary source emissions.

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