Effects of Trajectory Wind Direction on Ion Concentration of PM₁₀¹

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Objective To study the characterization apportionment of main ion concentrations of PM_{10} under the influence of trajectory wind direction in London. **Methods** PM_{10} samples from 1 May 1995 to 30 October 1995 of Oxford Street of Central London were collected, the metals and anions of which were measured using atomic absorption spectrometry (AAS) and ion chromatography (IC). Composite trajectories representative of the air mass arriving in London at the same period were calculated based on basic routine back trajectories from the British Atmospheric Data Centre (BADC). **Results** Concentration apportionments of main ions were similar when the trajectory was plotted back at 6 h, 12 h, and 24 h, some were obviously different. Mg, Ba, Pb, and Cu had similar peak apportionments at the area of 220° , 300° , which showed that Cl⁻ mainly came from the North Sea. **Conclusion** Trajectory wind direction has important effect on ion concentration apportionment of PM_{10} in London. The ions have similar concentration peak apportionments or their correlation coefficients are statistically significant.

Key words: Ion concentration; PM₁₀; Trajectory wind direction

INTRODUCTION

PM₁₀ describes the mass of particles in the atmosphere with a size of less than 10 micrometers in diameter or has an aerodynamic diameter of 10 µm, and it is the commonly used international convention for measuring particles in ambient air^[1-7]. More recent researches showed that particle matter (PM_{10}) is harmful and increases the morbidity and mortality, especially in respiratory diseases, such as aggravated asthma, chronic bronchitis, chronic cough, and respiratory tract infections^[2,6,8-9]. The adverse effects from PM₁₀ on human being include local effects seen in the lung and system effects impacted on the cardiovascular system, such as increasing in heart rate and changing in heart rate variability hear^[2,10-13]. And fine particle matter from different sources was associated with daily mortality in six eastern U.S. cities $^{\left[14-15\right] }.$ The biological effect study of PM_{10} from different models indicates that it is driven by their transition metal content^[2]. Iron and other transition metals (eg. Cu) have ability to generate free radicals via fenton chemistry and lead to oxidative damages in DNA, inducing lung injury. Transition metals, particularly iron can be present at high levels in ambient PM samples^[2,8-9,16]. Furthermore, ionic species (such as anions: Cl⁻, NO₃⁻, and SO₄^{2^{-}}; cations: Na⁺, Fe²⁺, Mn²⁺, Ca²⁺, and Mg²⁺) of PM_{10} have been analysed and reported^[5,8-9,17-18]. Traffic, energy and industry have important effects on the ion kinds and concentrations of PM10. Relative compositions of particle morphology in central London appear to be linked to four major sources and activities in and around London: traffic (soot particles and rubber), combustion by-products (carbonaceous particles and inorganic fly-ashes), wind erosion of surface particles (e.g. soil dust), and biological particles (e.g. spores)^[19]. In the study of PM_{10} concentration influencing and factors. meteorological conditions and geography play important roles as the emission levels^[3-4,7,18-22]. Previously we have reported that geometric mean PM₁₀ in London against groupings of trajectory wind direction (TWD) shows a south-easterly peak in $PM_{10}^{[3]}$. The present study focused on the characterization apportionment of main ion concentrations of PM₁₀ under the influence of TWD and discussed related effect factors.

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MATERIAL AND METHODS

Oxford Street of Central London was selected to collect air samples from 1 May 1995 to 30 October 1995. The latitude and longitude (lat/long) of Central London are very close to 51.5°N, 00. The Oxford Street is a crowded commercial centre with many shops, restaurants and office buildings in the street. The most specific feature of the site is that only diesel-powered buses and taxis are allowed to pass through it. The Oxford Street is a road built on the pavement of the street. The sampling head is only 1 meter from the main road and about 2 m above the ground.

 PM_{10} samples were taken daily using Partisol 2000 sampler at a constant flow rate of 16.67 L/min and Whatman PTFE filters (47 mm o.d. and 2 μ m pore size) because of their superior qualities in filter weighting and low chemical backgrounds. The total volume was only 24 m³. The sampling usually started at around 12:00 pm and ended at the same time the next day. All the filters were examined to measure metals and anions using atomic absorption spectrometry (AAS) and ion chromatography (IC).

The basic routine back trajectories of air masses arriving over London at the same period (1 May 1995 --30 October 1995) were obtained from the British Atmospheric Data Centre (BADC). The trajectories were located at 1300 m above sea level^[3]. Four different time (midnight, 06:00, 12:00, and 18:00 each day) trajectories were observed and plotted back over 5 days to calculate a composite trajectory representative of the air mass arriving in London for one whole day.

The relationship between ion concentration of PM_{10} and the composite trajectory was studied when it was plotted back at 6 h, 12 h, 24 h, and 48 h using Excel software. Related factors were investigated.

RESULTS

Distribution of Ion Concentrations of PM_{10} When Trajectory Was Plotted Back at 24 h

Figures 1, 2, 3, and 4 show that there were similar peak apportionments among Mg, Ba, Pb, and Cu, which exhibited a peak at the area $180^{\circ}-320^{\circ}$. The peak concentrations of Mg, Ba, Pb, and Cu were about 300-500, 80-100, 100-150, and 30-50 ng/m³ respectively. In contrast to the above metals, Zn and Ni had similar peak concentration apportionment areas of $90^{\circ}-270^{\circ}$ (Figs. 5 and 6). The peak concentrations of Zn and Ni were about 100-200, and 6-17 ng/m³ respectively.





FIG. 6. Relationship between Ni concentration and 24 h TWD.

Fe concentration did not show a peak distribution, however there was a higher concentration (1.0-2.5 μ g/m³) at the area of 70°-340° (Fig. 7). It was apparent that Mn distribution varied significantly from others, showing 2 peaks at the areas 60°-120° and 270°-330° (Fig. 8). In the concentration distribution based on collecting time (Fig. 9), there were 2 peaks, the smaller one on 20 May-31 May, and the bigger one on 30 July-24 August. The peak concentration of the bigger one was about 40-115 ng/m^3 .



FIG. 7. Relationship between Fe concentration and 24 h TWD.



FIG. 9. Relationship between Mn concentration and collecting time.

There was a narrow higher peak at the area $220^{\circ}-300^{\circ}$ of Cl⁻ concentration apportionment (Fig. 10) compared with other metals, and a smaller peak at $10-80^{\circ}$. The higher peak concentration was $1.5-6.0 \ \mu g/m^3$. Figs. 11 and 12 show the relationship between ion concentration and collecting time of both Mg and Cl⁻.

By comparison, NO₃⁻ and SO₄²⁻ had a similar peak apportionment area of 100°-220° (Figs. 13 and 14), and their peak concentrations were 6-25, and 10-20 μ g/m³, respectively.





FIG. 11. Relationship between Cl⁻ concentration and collecting time.



FIG. 12. Relationship between Mg concentration and collecting time.



FIG. 13. Relationship between NO₃⁻ concentration and 24 h TWD.



Correlation Coefficients

The correlation coefficients between metals and anions are listed in Table 1. According to Student's *t*-test, any correlation coefficient greater than 0.363 was considered statistically significant (P < 0.001).

Comparison With Different Times When Trajectory Was Plotted Back

The concentration distributions of Cu were similar at 6 h, 12 h, and 24 h, but different from that at 48 h (Fig. 15). Peak area of Zn at 24 h was similar to those at 12 h and 6 h at the area of 90° - 270° , however obviously different from that at 48 h (Fig. 16). The concentration distributions of Pb, Ba, Mg, Mn, Ni, and Fe were not obviously different at 6 h, 12 h, and 48 h, compared with those at 24 h.



FIG. 16. Relationship between Zn concentration and 48 h TWD.

No obvious change was found in Cl⁻ concentration distributions at 24 h, 6 h, 12 h, and 48 h. NO₃⁻ concentration distributions at 24 h, 6 h, and 12 h were similar, the peaks being at the area of 100°-220°. Although NO₃⁻ concentration distribution at 48 h had the similar peak (Fig. 17), the peak was wider (80°-240°) compared with that at 24 h. SO_4^{2-} concentration distribution was similar at 24 h, 6 h, and 12 h, the peak areas being at 100°-200°. Though the peak distribution was similar at 48 h, the peak area was at 50°-220°. In other words, the peak area at 48 h moved about 20°-50° (Fig. 18).

Correlation Coefficients Between Metals and Anion Concentrations										
	Ba	C u	Fe	Mg	Mn	Ni	Pb	Zn	Cl	NO ₃ ⁻
Cu	0.899									
Fe	0.707	0.719								
Mg	0.539	0.512	0.208							
Mn	0.016	0.017	0.422	-0.08						
Ni	0.482	0.554	0.741	0.135	0.442					
Pb	0.750	0.875	0.767	0.295	0.155	0.715				
Zn	0.812	0.849	0.733	0.429	0.042	0.796	0.857			
Cl	-0.10	-0.03	-0.24	0.629	-0.18	-0.15	-0.18	-0.14		
NO ₃ ⁻	0.284	0.360	0.474	0.092	0.155	0.761	0.547	0.647	-0.15	
SO_4^{2-}	0.306	0.321	0.499	0.018	0.314	0.574	0.511	0.583	-0.32	0.715

TABLE 1

30 24 18 29 12 6 0 30 60 90 120 150 180 210 240 270 300 330 360 48 h TWD Degree

FIG. 17. Relationship between NO₃⁻ concentration and 48 h TWD.



FIG. 18. Relationship between SO_4^{2-} concentration and 48 h TWD.

DISCUSSION

Distribution of Ion Concentration of PM_{10} When Trajectory Was Plotted Back at 24 h

Mg, Ba, Pb, and Cu had a similar peak concentration apportionment at the area of 180°-320°. Zn and Ni had a similar peak concentration apportionment at the area of 90°-270°. The correlation coefficient of Mg, Ba, Pb, Zn, and Ni (not including Mg-Pb, Mg-Ni) was 0.429-0.899, indicating a

statistical significance. All these show that it is possible for them to come from the same sources. Fe is a normal element, which has a higher concentration $(800-1500 \text{ ng/m}^3)$ than other metals in the air. The effect of trajectory wind direction on Fe is not obvious.

Mn had 2 peaks at its concentration distribution, and in the correlation coefficient analysis (Table 1), just Mn-Ni and Mn-Fe were statistically significant. Furthermore, in the Mn concentration and collecting time analysis, Mn showed 2 peaks, one on 20-31 May (30-60 ng/m³), and the other on 30 July-24 August (30-115 ng/m³). Based on these data, we believe that Mn comes from a different source. Local factor had an important effect, which is possibly attributed to increased concentrations of dissolved Mn(II) and its subsequent rapid oxidative precipitation to Mn (IV) at higher summer water temperatures^[21].

Cl⁻ had a narrow high peak of 1.5-6.0 μ g/m³ at the area of 220°-300°, suggesting that the North Sea has an important effect on Cl⁻. Cl⁻ mainly comes from the North Sea with sea-spray, driven by wind from the ocean surface^[22]. The graphs of concentration apportionment of Cl⁻ and Mg are very similar (Figs. 1 and 10). The relationships between concentration and collecting time of both Mg and Cl⁻ showed similar changes in their graphs (Figs. 11 and 12). Furthermore, just Cl⁻-Mg correlation coefficient had statistical significance (Table 1), suggesting that Cl⁻ and Mg come from the same source (the North Sea).

By comparison, NO₃⁻ and SO₄²⁻ had a similar peak apportionment at the area of 100°-220° and the correlation coefficient of them (0.715) was statistically significant, indicating that they come from the same source. The research of exposure efficiencies of urban air pollution sources of Beijing city has shown that SO₂ and PM₁₀, NO_x exposure efficiencies are 2×10^{-6} - 20×10^{-6} , and 2×10^{-6} - 50×10^{-6} , respectively. The exposure efficiencies of heating and transportation industries are much higher^[23].

Comparison With Different Times When Trajectory Was Plotted Back

Mg, Ba, Pb, and Cu had similar concentration peak apportionments at 24 h, 6 h, 12 h, and 48 h, except Cu concentration apportionment at 48 h (Fig. 15). Zn also had a very different concentration distribution at 48 h compared with those at 6 h, 12 h, and 24 h (Fig. 16).

 $SO_4^{2^2}$ concentration peak distribution at 48 h moved about 20°-50° compared with that at 24 h. The above data show that the time is an important effect factor, the longer the time, the bigger the change.

CONCLUSIONS

Trajectory wind direction has an important effect on ion concentration apportionment of PM_{10} in London. When the trajectory is plotted back at 6 h, 12 h, and 24 h, main ions concentration apportionments are similar, whereas Cu and Zn distributions at 48 h are different.

Mg, Ba, Pb, and Cu have similar peak apportionments at the area $180^{\circ}-320^{\circ}$, while Zn and Ni at the area of $90^{\circ}-270^{\circ}$, NO₃⁻ and SO₄²⁻ at the area of $100^{\circ}-220^{\circ}$. Fe concentration peak apportionment is not obvious because Fe is a normal metal in the air. Mn concentration distribution mainly influenced by local factor has 2 peaks at the areas of $60^{\circ}-120^{\circ}$ and $270^{\circ}-330^{\circ}$. Cl⁻ concentration peak apportionment is at the area of $220^{\circ}-300^{\circ}$, showing that Cl⁻ mainly comes from the North Sea.

The ions which have similar concentration peak apportionments or with their correlation coefficients being statistically significant come from the same sources.

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