

Characteristics of water-soluble organic nitrogen in fine particulate matter in the continental area of China



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H I G H L I G H T S

- High concentrations of WSON and organic nitrogen species in PM_{2.5} are determined in Xi'an.
- High concentration of some organic nitrogen species in spring is due to the enhanced release of pollen and spores.
- Secondary sources and biomass burning are the major factors influencing the levels of WSON.

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In recent years growing evidence has shown that organic nitrogen (ON) constitutes a significant fraction of the nitrogen budget in particulate matter (PM). However, the composition and sources of ON in Chinese PM are not clear to date due to the lack of field measurements and receptor modeling interpretations. In this study, water-soluble ON (WSON), free amino acids (FAAs) and primary amines, together with water-soluble ionic species and carbonaceous components, were quantified in PM_{2.5} collected in Xi'an, China from 2008 to 2009. The yearly average WSON concentration (300 nmol N m⁻³, ranging from 29 to 1250 nmol N m⁻³) was one order of magnitude higher than that reported in other urban and rural regions in U.S. A total of 24 organic nitrogen species were determined, with an average total concentration of 2180 pmol m⁻³, which account for 1.2% of the WSON in PM_{2.5}. Glycine, β-alanine and methylamine were the most abundant protein type amino acid, non-protein type amino acid and primary amine, respectively, contributing to 21.1%, 5.2% and 20.6% of the total quantified organic nitrogen species (TONS). Strong linear correlations (Pearson's correlation) ($r = .72, p < 0.001$) between WSON and one of biomass burning tracer (K^+) potentially indicate the contribution from biomass burning (especially in spring and fall) and the correlation ($r = .76-.87, p < 0.001$) between WSON and secondary species (NH_4^+ , NO_3^- , and SO_4^{2-}) also suggests the important contribution to WSON from secondary formation processes. Moreover, both protein type amino acids and primary amines revealed good correlations with water-soluble ions in spring, which indicates that seasonal variability occurred in primary sources and secondary formation pathway of the organic nitrogen species were found in Xi'an.

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1. Introduction

Particulate nitrogen is ubiquitous in the atmosphere and affects air quality, human health and nitrogen geochemistry (Herrera,

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2007; Jickells et al., 2013; Samy and Hays, 2013; Sugimura et al., 2004; Wedyan and Preston, 2008; Zhang and Anastasio, 2003). The base-stabilization property of certain nitrogen-containing functional groups (e.g. amines) also influences the acid neutralizing capacity of aerosols (Huang et al., 2014; Zhang et al., 2002). Many previous studies have focused on the identification of sources and concentrations of inorganic nitrogen (ammonium, nitrate and nitrite). However, concentrations of individual species and sources of organic nitrogen (ON) in particulate matter (PM) are still uncertain (Cape et al., 2011; Kanakidou et al., 2012; Violaki and Mihalopoulos, 2010).

ON includes a wide variety of nitrogen-containing organic species of anthropogenic or natural origin (Cornell et al., 2003; Neff et al., 2002). Possible anthropogenic sources include fertilizers and fossil fuel combustion, while natural sources include soil dust and marine emissions (Jickells et al., 2013; Lesworth et al., 2010; Mace et al., 2003b, 2003c; Neff et al., 2002). Beside primary emissions, ON can also be produced from secondary processes, e.g. the atmospheric reactions of volatile organic compounds (VOCs) with nitrogen oxides (NO_x) (Atkinson, 2000; Lim and Ziemann, 2005; Ng et al., 2008). Recently, Rollins et al. (2012) found the nighttime formation of ON at increased NO_x level in California. In previous studies, a wide variety of ON compounds have been measured, including amino acids (Barbaro et al., 2011; Matsumoto and Uematsu, 2005), organic nitrates (Rollins et al., 2010a, 2010b), nitrogen heterocycles (Ma and Hays, 2008; Rogge et al., 1993; Samy and Hays, 2013), nitro-aromatics (Dimashki et al., 2000) and urea (Fu et al., 2014; Mace et al., 2003b; Simoneit et al., 2004).

Most of the ON compounds are water soluble, namely water-soluble ON (WSON), which is considered an important species in the nitrogen cycle (Cornell et al., 2003; Duce et al., 2008). However, the sources and atmospheric chemistry of these compounds have not been thoroughly investigated. WSON in aerosols contributes a large fraction of the total particulate nitrogen. For example, WSON accounted for ~30% of the total nitrogen in $\text{PM}_{2.5}$ in Beijing (Duan et al., 2009) and Chapel Hill (Lin et al., 2010), although the contribution dropped to ~20% in Davis (Zhang et al., 2002) and ~10% at Atlanta (Rastogi et al., 2011). Given that ON is composed of a large number of different species at trace level, quantification of individual ON species is a challenging analytical task. In previous studies, more attention has been paid to free amino acids (FAAs) and amines (Ge et al., 2011; Huang et al., 2014; Zhang and Anastasio, 2003) because they have significant effects on the atmospheric chemistry (McGregor and Anastasio, 2001; Milne and Zika, 1993), particle hygroscopicity (Saxena and Hildemann, 1996), and ultimately, cloud formation processes (Facchini et al., 1999; McGregor and Anastasio, 2001; Zhang and Anastasio, 2003). FAAs can be jetted in the marine atmosphere via the bubble bursting mechanism at the air–sea interface. Agricultural activities, such as biomass burning and livestock farming, could also be major sources of proteinaceous matters and particulate FAAs and amines (Milne and Zika, 1993; Zhang and Anastasio, 2003). Primary amines, e.g. alkyamines, are abundant atmospheric ON species which can be from animal husbandry (Sorooshian et al., 2008). The gas-phase aliphatic amines are strong bases which can react with nitric acid and sulfuric acid to form aminium salts of nitrate and sulfate (secondary aerosol formation). Industrial emissions of alkylamines have been proposed as another source of ON species (Tarr et al., 2001).

Measurements of FAAs and primary amines in atmospheric aerosols, especially in continental areas, are still very scarce. Samy, Hays, and their co-researchers have done a comprehensive study on heterocyclic nitrogen in U.S. (i.e., Ma and Hays, 2008; Samy et al., 2013; Samy and Hays, 2013). The aim of this work was to quantify the concentrations of WSON and organic nitrogen species in $\text{PM}_{2.5}$

collected in Xi'an, China. The associated seasonal variations, the mass contribution of WSON to $\text{PM}_{2.5}$ and the contribution of FAAs and primary amines to WSON were determined to better understand their chemistry.

2. Methodology

2.1. Sampling locations

Xi'an is the capital of Shaanxi Province, which is situated in the Guanzhong Plain and close to the south edge of the Chinese Loess Plateau. Sampling was performed on the rooftop of a two story building (10 m above the ground) at the Institute of Earth Environment, Chinese Academy of Sciences, which is surrounded by a commercial and residential area and is ~15 km south of downtown Xi'an.

2.2. Sampling method

Twenty-four hour integrated filter samples were collected every six days on pre-baked (780 °C, 3 h) quartz fiber filters (203 mm × 254 mm, QMA, Whatman, Clifton, NJ, USA) using TE-6070MFC Hi-Vol $\text{PM}_{2.5}$ air samplers (Tisch, Cleves, USA) at a flow rate of 1.13 $\text{m}^3 \text{min}^{-1}$ from 5 July, 2008 to 8 August, 2009. The samples were stored in a freezer (<−10 °C) until the analysis. Meteorological data (e.g., wind speed, temperature, and relative humidity) were collected during the sampling period. Three field blanks were collected, analyzed and used to perform background corrections for the target species.

2.3. Chemical analysis

To determine the water soluble organic carbon (WSOC) and water-soluble nitrogen (WSN; representing WSON and water-soluble inorganic nitrogen (WSIN)), a total area of 4.3 cm^2 of the sample filter was cut from each sample and placed into a 30 mL screw-cap vial. Two portions of 10 mL (a total of 20 mL) of organic-free Milli-Q water (18 M Ω) were added to the vial. Samples were extracted in an ultrasonic water bath for 1 h for each extraction. A syringe filter with a .45 μm PTFE membrane, was used to filter insoluble particles and filter debris from the water extracts and each filtrate was then transferred into an autosampler fitted vial. The total organic carbon (TOC) and nitrogen (TN) contents in the filtrates were determined by a TOC/TN analyzer (TOC-L, Shimadzu, Kyoto, Japan) using a thermo-catalytic oxidation approach. The carbon content was determined by a non-dispersive infrared (NDIR) detector after the extract was oxidized by a catalyst (fiber platinum on quartz), whereas the nitrogen content was analyzed by determining the oxides of nitrogen with a chemiluminescence detector. The detection limits were 4 $\mu\text{g L}^{-1}$ and 5 $\mu\text{g L}^{-1}$ with a precision of $\pm 3.1\%$ and $\pm 8.8\%$ for TOC and TN, respectively. The measurement uncertainties ranged from ± 2.4 to $\pm 5.5\%$ and ± 4.4 to $\pm 9.7\%$ for TOC and TN, respectively. The results reported in this study were all corrected by the field blanks (TOC: 120 $\mu\text{g L}^{-1}$; TN: 60 $\mu\text{g L}^{-1}$).

The concentrations of five cations (sodium [Na^+], ammonium [NH_4^+], potassium [K^+], magnesium [Mg^{2+}] and calcium [Ca^{2+}]) and three anions (chloride [Cl^-], nitrate [NO_3^-] and sulfate [SO_4^{2-}]) were reported in this study. To determine the water-soluble ions, a 2 cm^2 area of each sample was placed into a 15 mL vial containing 10 mL of Milli-Q water (18 M Ω cm). The vials were placed into an ultrasonic water bath for 1 h. A syringe filter (.45 μm pore size membranes) was used to filter the water extracts, and the filtrates were stored in a fridge (4 °C) until the analysis. The cations and anions were determined by a Dionex-600 Ion Chromatograph (Dionex Inc.,

Sunnyvale, CA, USA). For the anions analyses, an IonPac AS14A column (8 mM Na₂CO₃/1 mM NaHCO₃ was the eluent) was used. For the cation analyses, an IonPac CS12A column was used for separation (20 mM methanesulfonic acid was the eluent). The detection limits were .5 µg L⁻¹ for Na⁺, 1.0 µg L⁻¹ for NH₄⁺, 1.1 µg L⁻¹ for K⁺, 8.7 µg L⁻¹ for Cl⁻, 25 µg L⁻¹ for NO₃⁻, 5.0 µg L⁻¹ for NO₂⁻ and 27 µg L⁻¹ for SO₄²⁻. Analysis reference materials (National Research Center for Certified Reference Materials, China) of the five cations and three anions agreed well with the certified values within ±4%. The measurement uncertainties ranged from ±2.2 to ±5.1% for the targeted ions. One in 10 extracts was reanalyzed, and none of the differences between these replicates exceeded the precision intervals. The blank concentrations were corrected from the sample values.

NH₄⁺, NO₂⁻ and NO₃⁻ were the major water-soluble inorganic nitrogen (WSIN) species in the aerosols, and WSON was defined as the difference between WSN and WSIN. The concentrations of NO₂⁻ in all samples were below the detection limit and thus is negligible. The calculation of WSIN and WSON (nmol N m⁻³) is shown in Eqs. (1) and (2):

$$[\text{WSIN}] = [\text{NH}_4^+ - \text{N}] + [\text{NO}_2^- - \text{N}] + [\text{NO}_3^- - \text{N}] \quad (1)$$

$$[\text{WSON}] = [\text{WSN}] - [\text{WSIN}] \quad (2)$$

Twenty-four organic nitrogen species (protein type AC: alanine [Ala], arginine [Arg], aspartic acid [Asp], cysteine [Cys], glutamic acid [Glu], glycine [Gly], histidine [His], isoleucine [Ile], leucine [Leu], lysine [Lys], methionine [Met], phenylalanine [Phe], proline [Pro], threonine [Thr], tyrosine [Tyr], serine [Ser], valine [Val]; non-protein AC: β-alanine [β-Ala], γ-aminobutyric acid [γ-Aba], ornithine [Orn]; primary amines: ethanolamine [ECA], ethylamine [EA], galactosamine [Gal], methylamine [MA]) in the water extracts were determined by high performance liquid chromatography (HPLC) equipped with a fluorescence detector following a derivatization step using 6-aminoquinolyl-*N*-hydroxysuccinimidyl carbamate (AccQ-Fluor reagent [AQC]). The AccQ-Fluor reagent kit (WAT052880), consisting of AQC, AccQ.Tag borate buffer and AccQ.Tag Eluent A, was purchased from Waters Corporation (Milford, MA) and was reconstituted and stored in a desiccator at room temperature before use.

The calibration standards of the organic nitrogen mixtures (from Agilent Technology, Santa Clara, CA) were diluted into concentration ranges of .1–120 nmol mL⁻¹. An internal standard (IS) of glucosamine (Sigma, St. Louis, MO) was prepared at a concentration of 20 nmol mL⁻¹. The calibration standard mixture and IS solution were pipetted into a sample tube. The AccQ.Tag borate buffer was added into the sample tube and vortexed for 10 s before AQC was added. The mixture was vortexed immediately for another 10 s. After 1 min, the solution in the sample tube was transferred to a low volume insert placed in an autosampler vial and capped tightly. The bubbles in the low volume insert were removed and the sample vial was heated at 55 °C for 10 min in an oven. The linearity of the calibrations was revealed by the correlation coefficient (*r*²) >.999.

Each filter sample (14.7 cm²) was extracted with two portions of 5 mL of Milli-Q water (18 MΩ cm) in an ultrasonic water bath (15 min for each extraction) for further organic speciation. The water extracts were then filtered and concentrated to a volume of .5 mL by rotary evaporator before analysis (Yang et al., 2005). They were then transferred to a clean tube and evaporated to dryness with a gentle stream of ultra-high purity (UHP) grade nitrogen gas at 40 °C. This process took ca. 1.5–2 h. The AccQ.Tag borate buffer and IS solution were added to the sample tube which was vortexed briefly. The mixture was gently purged with UHP grade

nitrogen for 50 min. The flow rate of gas must be regulated so that the volume loss of the sample solution does not exceed 30%. The purpose of this step was to remove abundant ammonia that potentially changes the quantification of the adjacent amino compounds in the chromatogram. The derivatization step was identical to that for the calibration standards. The extraction recovery for the target organic nitrogen species ranged from 79.6 to 96.8 %.

A 20 µL aliquot of the derivatized sample extracts or standards was injected into an HPLC (Agilent 1200 Series) equipped with a fluorescence detector. The column for separation was a 3.9 × 150 mm AccQ.Tag Amino Acid Analysis Silica base bonded 4 µm C-18 reversed-phase column (Waters Corporation, Milford, MA) operated at 37 °C. The mobile phase consisted of three solvent mixtures: (A) AccQ.Tag Eluent A, (B) acetonitrile, and (C) water. The gradient program was 100% A for 1 min, followed by linear gradients to 90% A/5.9% B/4.1% C for 17 min, 80% A/17% B/3% C for 8 min, 68% A/20% B/12% C for 11 min, and, finally, 60% B/40% C for 5 min. The flow rate was 1.0 mL min⁻¹. The excitation at 250 nm and the emission at 395 nm were used to identify fluorescence organic nitrogen derivatives. The minimum detection limit (MDL) was obtained by analyzing ten replicates of a standard solution and was calculated using Eq. (3):

$$\text{MDL} = t_{(n-1, 1-\alpha=99\%)} \times S \quad (3)$$

Table 1

A statistical summary of chemical species measured in this study.

Compounds	Mean	Standard deviation	Range
OC (µg C m ⁻³)	20	16	3.2–64
EC (µg C m ⁻³)	7.2	3.1	2.1–17
WSOC (µg C m ⁻³)	8.6	6.6	2.1–36
Ammonium (µg m ⁻³)	3.4	3.1	2–15
Nitrate (µg m ⁻³)	2.0	1.8	.2–9.5
Sulfate (µg m ⁻³)	16	10	3.4–48
K ⁺ (µg m ⁻³)	1.3	1.0	.1–3.9
WSN (nmol N m ⁻³)	677	594	64–2990
WSIN (nmol N m ⁻³)	377	349	35–1740
WSON (nmol N m ⁻³)	300	263	29–1250
<i>Protein type amino acid (pmol m⁻³)</i>			
Alanine (Ala)	149	111	20–553
Arginine (Arg)	nd	nd	nd
Aspartic acid (Asp)	21	20	4.0–145
Cysteine (Cys)	234	163	59–963
Glutamic acid (Glu)	13	8.8	2.5–42
Glycine (Gly)	459	350	71–1550
Histidine (His)	14	8.8	2.6–40
Isoleucine (Ile)	31	18	6.2–85
Leucine (Leu)	34	22	4.3–100
Lysine (Lys)	60	32	20–164
Methionine (Met)	12	10	1.6–56
Phenylalanine (Phe)	40	25	10–110
Proline (Pro)	49	31	9.3–140
Serine (Ser)	31	22	4.2–97
Threonine (Thr)	4.3	3.3	.4–14
Tyrosine (Tyr)	32	19	5.6–105
Valine (Val)	137	82	34–388
Total protein type AA	1320	852	322–4320
<i>Non-protein type amino acids (pmol m⁻³)</i>			
β-alanine (β-Ala)	113	69	22–297
γ-aminobutyric acid (γ-Aba)	15	9.8	3.0–53
Ornithine (Orn)	15	10	3.6–71
Total non-protein type AA	143	85	29–416
<i>Primary amine (pmol m⁻³)</i>			
Ethanolamine (ECA)	173	100	33–491
Ethylamine (EA)	72	52	10–235
Galactosamine (Gal)	22	16	2.5–64
Methylamine (MA)	450	301	72–1640
Total primary amines	717	452	159–2430
TONS (pmol m ⁻³)	2180	1370	519–7160

where $t_{(n-1, 1-\alpha=99\%)}$ is the value of the t-distribution at $n - 1$ degrees of freedom and S is the standard deviation of the replicates. The MDLs of the measured organic nitrogen species ranged from .036 to .086 nmol mL⁻¹ (.262–.626 $\mu\text{mol m}^{-3}$). The measurement precision had a range of 3.6–8.5%. The measurement uncertainties ranged from ± 3.2 to $\pm 9.1\%$ for the targeted amino acids.

3. Results and discussion

3.1. Concentrations of WSN, WSIN, WSON and organic nitrogen species in PM_{2.5}

A total of 65 PM_{2.5} samples collected at Xi'an have been analyzed. A statistical summary (mean, range, and standard deviation) of all of the compounds measured in this study is provided in Table 1. The concentrations of WSN ranged from 64 to 2990 nmol N m⁻³ (average of 677 nmol N m⁻³), whereas the concentrations of WSIN and WSON ranged from 35 to 1740 nmol N m⁻³ (average of 377 nmol N m⁻³) and from 29 to 1250 nmol N m⁻³ (average of 300 nmol N m⁻³), respectively. As shown in Fig. 1, the concentrations of WSON were one order of magnitude higher than those measured from other continental, coastal and oceanic sites, such as Atlanta (USA), Chapel Hill (USA), Tasmania (Australia), and Keelung (Taiwan). Although studies on WSON over China are limited, our data are of a similar magnitude to the ON concentration in the total suspended particulates (TSP) collected in Beijing (257 nmol N m⁻³) (Duan et al., 2009) and in the PM₁₀ collected in Xi'an (400 nmol N m⁻³ in the daytime and 464 nmol N m⁻³ in the nighttime during spring) (Wang et al., 2013). However, the value is 40% higher than that reported in coastal Qingdao, China (180 nmol N m⁻³) (Shi et al., 2010). WSON accounted for 45% (range: 22–68%) of the WSN during the entire sampling period, which is a factor of 2 higher than that reported from other studies at continental sites (~20–30%) (Duan et al., 2009; Lin et al., 2010; Zhang et al., 2002). Our results are similar to those measured in the Amazon Basin (up to 43%) (Mace et al., 2003a), where significant influence from biomass burning was identified. In addition to WSON, WSIN accounted for 55% (34–78%) of the WSN; the highest contributions were from NH₄⁺-N (~34%) and NO₃⁻-N (~21%).

A total of 24 organic nitrogen species (i.e. FAA and amines) were analyzed by HPLC following a precolumn derivatization. The concentration of total quantified organic nitrogen species (TONS) found in PM_{2.5} ranged from 519 to 7160 pmol m⁻³, with an average concentration of 2180 pmol m⁻³ (Table 1), which is much higher than those measured at the California coast (427 pmol m⁻³ for 22 organic nitrogen species, (Zhang and Anastasio, 2003)) and Venice (334 pmol m⁻³ for 18 FAAs, (Barbaro et al., 2011)). According to the 72 h air mass back trajectory analysis (HYSPLIT, NOAA Hybrid Single-Particle Lagrangian Integrated Trajectory model was applied) (shown in Fig. 2), the air mass were mainly from northwest of the sampling site during fall and winter. This indicates the influence of terrestrial sources on organic nitrogen species in this region as Xi'an is located at the south edge of the Loess Plateau.

These 24 species are grouped into protein-type amino acid, non-protein-type amino acid and amine. The total concentration of protein-type amino acids were on average ~9 times that of the total non-protein type compounds (Table 1). Regarding the concentration of individual FAAs, glycine (Gly) was the most abundant protein type amino acid, with a mean concentration of 459 pmol m⁻³, followed by cysteine (Cys, 234 pmol m⁻³) and alanine (Ala, 149 pmol m⁻³). On average, Gly, Cys and Ala accounted for 21%, 11%, and 7% of the TONS in PM_{2.5}, respectively. The results are similar to previous measurements of organic nitrogen species in continental aerosols, where Gly and Ala were observed to be the dominant FAAs (Barbaro et al., 2011; Violaki and Mihalopoulos, 2010). For non-protein type amino acid and primary amines, β -alanine (β -Ala) and methylamine (MA) were the most abundant species, with a mean concentration of 113 and 450 pmol m⁻³, respectively (Table 1). MA and β -Ala also have high contribution to organic nitrogen species measured, accounting for on average 21% and 5.2% of total organic nitrogen species measured, respectively. In contrast, Arginine (Arg) and Threonine (Thr) were always below the detection limits in this study. China is one of the fastest growing production regions for Gly and MA, and they ubiquitously present in foods and are used as intermediates in several products. Their regional/local sources in China need to be further characterized or apportioned.

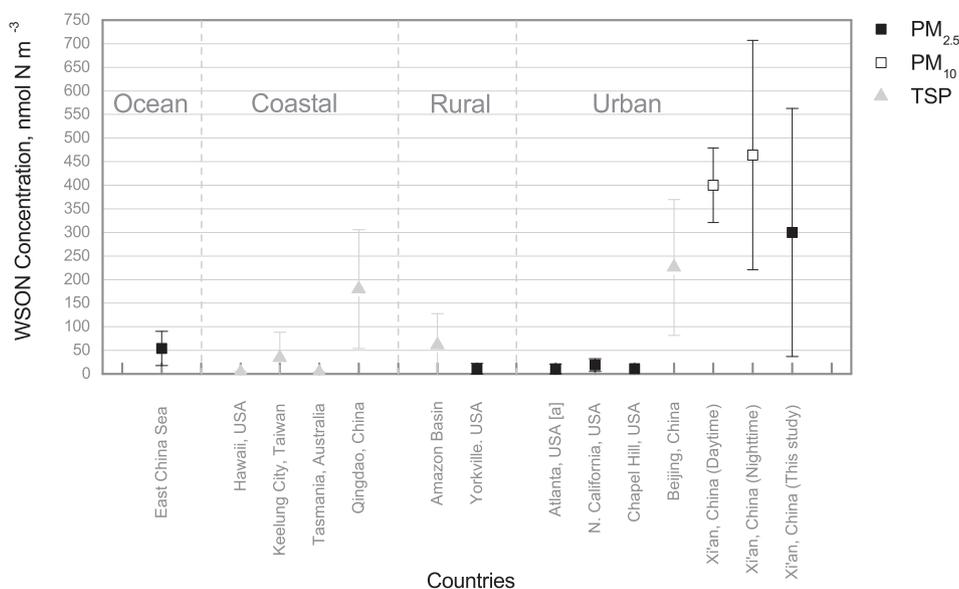


Fig. 1. Comparison of WSON levels with those reported in the literature [East China Sea (Nakamura et al., 2006); Hawaii, USA (Cornell et al., 2001); Keelung City, Taiwan (Chen and Chen, 2010); Tasmania, Australia (Mace et al., 2003b); Qingdao, China (Shi et al., 2010); Amazon Basin (Mace et al., 2003c); Yorkville, USA (Rastogi et al., 2011); Atlanta, USA (Rastogi et al., 2011); N. California, USA (Zhang et al., 2002); Chapel Hill, USA (Lin et al., 2010); Beijing, China (Duan et al., 2009); Xi'an, China (Wang et al., 2013); Xi'an, China (This study)].

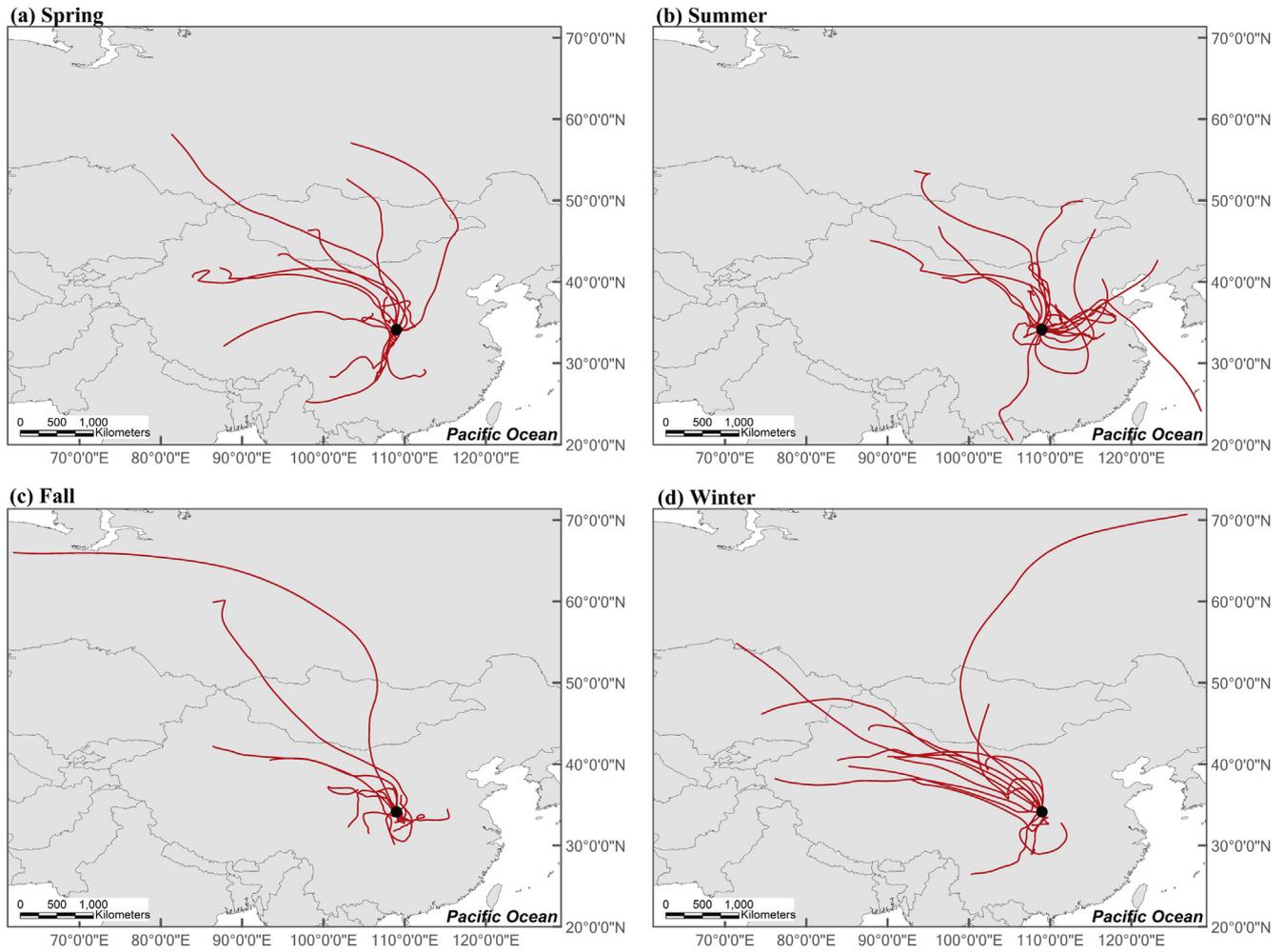


Fig. 2. 3-day air mass back trajectories at Xi'an in four seasons (back trajectory analyses were conducted using the NOAA HYSPLIT model [Hybrid Single-Particle Lagrangian Integrated Trajectory, NOAA/ARL]).

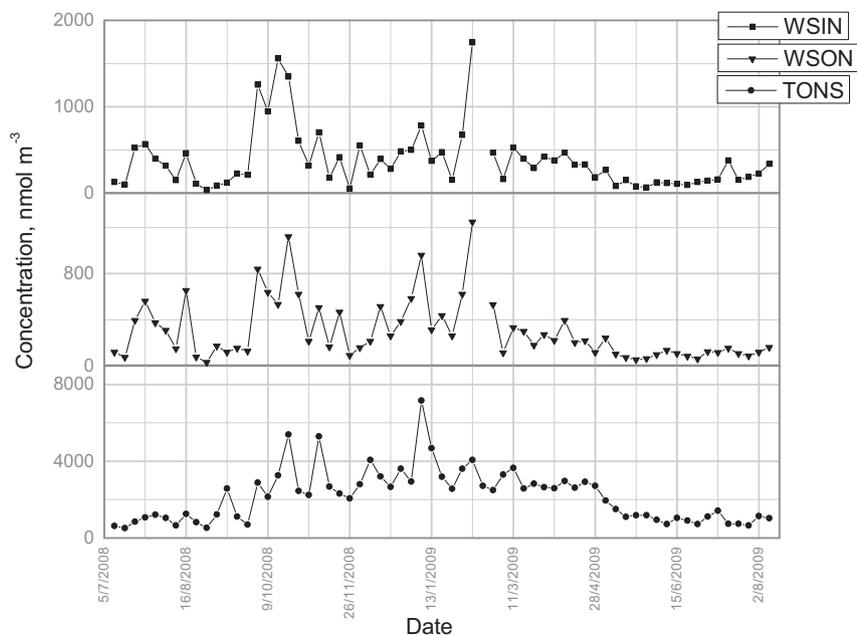


Fig. 3. Time series of the WSIN, WSON and TAC concentration in Xi'an.

3.2. Seasonal trends in WSIN, WSON and organic nitrogen species

The time series of WSIN, WSON and total organic nitrogen species measured are shown in Fig. 3 and are classified into spring (March–May), summer (June–August), fall (September–November) and winter (December–February) to explore the seasonal variations.

The concentrations of WSIN and WSON peaked in fall (October) and winter (January–February) (Fig. 3), and reached the minimum in summer (~40 times lower, see Table 2). The seasonal trends of particulate nitrogen could be the consequence of variations in the mixing layer height, emission strength, temperature, relative humidity, and atmospheric chemistry (Zhang et al., 2002). There are several factors determining the WSON variability. The higher values of particulate WSON determined in fall and winter are consistent with the observations of high concentrations of organic carbon (OC) and elemental carbon (EC) during winter in Xi'an (Cao et al., 2005; Dai et al., 2012).

TONS and most FAAs (Ala, Glu, Gly, Ile, Phe, Pro, Thr and Ser, see Table 1 for the abbreviation of the measured organic nitrogen species) showed a seasonal pattern similar to that of WSON: higher concentrations occurred in fall and winter (a factor of ~10 between the minimum and maximum values, see Table 2). In contrast, the concentrations of Orn and Lys were more consistent throughout the year and varied by a factor of 2 between winter and summer. For total protein-type and total non-protein-type amino acids, high concentrations were observed in winter followed by fall. For primary amines, high concentrations were observed in winter, followed by spring. Gly was the most abundant of total organic nitrogen species measured in fall and winter, whereas MA was the

Table 2
Seasonal variations of WSIN, WSOC, FAA and amines measured in this study.

Compounds	Spring	Summer	Fall	Winter
WSN (nmol N m ⁻³)	466 ± 251	409 ± 311	985 ± 800	1044 ± 688
WSIN (nmol N m ⁻³)	275 ± 149	223 ± 154	573 ± 511	544 ± 399
WSON (nmol N m ⁻³)	192 ± 105	186 ± 167	412 ± 317	499 ± 311
<i>Protein type amino acids (pmol m⁻³)</i>				
Alanine (Ala)	134 ± 60	60 ± 27	192 ± 113	261 ± 115
Arginine (Arg)	nd	nd	nd	nd
Aspartic acid (Asp)	24 ± 16	8.3 ± 3.8	26 ± 15	34 ± 33
Cysteine (Cys)	301 ± 93	94 ± 24	225 ± 126	390 ± 200
Glutamic acid (Glu)	14 ± 5.3	5.1 ± 2.0	17 ± 11	20 ± 7.6
Glycine (Gly)	388 ± 169	138 ± 50	662 ± 356	836 ± 252
Histidine (His)	14.9 ± 6.6	6.1 ± 2.2	20 ± 10	21 ± 5.9
Isoleucine (Ile)	32 ± 7.0	14 ± 4.9	39 ± 23	47 ± 14
Leucine (Leu)	39 ± 14	15 ± 7.0	45 ± 28	45 ± 19
Lysine (Lys)	59 ± 21	37 ± 10	67 ± 35	91 ± 35
Methionine (Met)	19 ± 7.3	4 ± 1.8	10 ± 6.7	21 ± 13
Phenylalanine (Phe)	39 ± 10	20 ± 5.8	55 ± 32	59 ± 23
Proline (Pro)	47 ± 20	24 ± 10	69 ± 37	70 ± 30
Threonine (Thr)	2.0 ± .8	.9 ± .8	6.2 ± 4.1	5.9 ± 2.2
Tyrosine (Tyr)	41 ± 16	15 ± 6.4	31 ± 15	49 ± 20
Serine (Ser)	26 ± 12	12 ± 4.8	47 ± 27	52 ± 13
Valine (Val)	163 ± 59	60 ± 22	152 ± 83	214 ± 69
Total protein type AA	1340 ± 470	514 ± 143	1659 ± 836	2217 ± 720
<i>Non-protein type amino acids (pmol m⁻³)</i>				
β-alanine (β-Ala)	121 ± 43	51 ± 20	140 ± 82	175 ± 53
γ-aminobutyric acid (γ-Aba)	17 ± 5.7	7.7 ± 3.5	17 ± 12	24 ± 10
Ornithine (Orn)	19 ± 6.3	8.6 ± 4.2	17 ± 9.9	20 ± 15
Total non-protein type AA	157 ± 50	67 ± 22	174 ± 98	219 ± 73
<i>Primary amines (pmol m⁻³)</i>				
Ethanolamine (ECA)	99 ± 46	26 ± 11	75 ± 48	113 ± 47
Ethylamine (EA)	216 ± 86	84 ± 32	187 ± 94	254 ± 90
Galactosamine (Gal)	25 ± 12	7.1 ± 3.4	30 ± 18	35 ± 11
Methylamine (MA)	544 ± 178	201 ± 65	472 ± 317	717 ± 334
Total primary amines	885 ± 300	318 ± 93	763 ± 459	1119 ± 454
TONS (pmol m ⁻³)	2380 ± 805	900 ± 249	2600 ± 1360	3554 ± 1229

most abundant species in spring and summer. Moreover, certain organic nitrogen species (i.e., ECA, MA, Cys, Tyr, Val, Met, EA, Orn) exhibited higher concentrations in spring than in fall, most likely due to the increasing release of proteinaceous matter or primary biological products (e.g. soil, spore, pollen, and bacteria.) in spring (Barbaro et al., 2011; Miyazaki et al., 2014).

3.3. Mass of amino compounds in WSON and PM_{2.5}

On average, WSN, WSIN and WSON contributed to 7.2%, 3.9% and 3.3% of the PM_{2.5} mass, respectively. Therefore nitrogen is considered one of the abundant elements in PM_{2.5} (aside from carbon and sulfur). The mass concentrations of nitrogen in the TONS (TONS-N) in Xi'an PM_{2.5} ranged from 8.63 to 117 ng m⁻³ (average 35.2 ng m⁻³), which accounts for .2–3.4% of the WSON mass (average 1.2%). Mass balance of PM_{2.5} by season was shown in Fig. 4a. OC and sulfate were the major PM_{2.5} components during the four seasons, which account for 19%–38% of PM_{2.5}. The contributions of WSIN and WSON in PM_{2.5} were higher during fall and winter. The contribution of TONS-N (especially protein type AA) in WSON (Fig. 4b) was generally highest during spring (~1.5%), most likely due to the increased emissions of proteinaceous matter (e.g. spores and pollens) during this season and the increased formation of FAAs (due to hydrolysis of combined amino acids) and ammonium nitrate/sulfate salts in the presence of water (the ammonium salts dissolve into their ionic forms, shifting the equilibrium of the gas phase amines toward the particle phase) (Angelino et al., 2001; Barbaro et al., 2011; Gorzelska et al., 1992; Mopper and Zika, 1987). According to the approach applied by Zhang et al. (2002), the total mass of WSON was estimated by assuming WSON species had an average N-normalized molecular weight of 100 Da per N atom. On the basis of this assumption, the average WSON mass was 30 μg m⁻³, which represents 21% of the mass of PM_{2.5} (ranging from 6 to 53%). Our data are of a similar magnitude to the observations in California where the average percentage of ON in PM_{2.5} was 18% with the peak value (31%) occurring in winter (Zhang et al., 2002). Similar to previous studies, the highest WSON concentrations were found in winter (50 μg m⁻³).

The TONS in Xi'an was 211 ng m⁻³ which is generally negligible (.15%) for the PM_{2.5} mass, indicating the presence of other ON species in large quantities (>99%). The average carbon concentration in organic nitrogen species in PM_{2.5} ranged from 19.1 to 238 ng C m⁻³ (average of 76.1 ng C m⁻³), which constituted .3–2.9% of the WSOC that ranged from 2.06 to 36.3 μg C m⁻³ (average of 8.62 μg C m⁻³). Similar to the results of WSON, higher concentrations of WSOC and amino carbon content were found in winter, while lower concentrations were found in summer. The contribution of amino carbon to WSOC was generally the highest in spring (~1.5%), which further confirmed the presence of additional sources (e.g. pollen) of organic nitrogen species in Xi'an during spring.

3.4. Water-soluble organic C:N ratio and relationship between WSON and other species

The mass ratios of WSOC/WSON (i.e., water-soluble organic C:N mass ratio) in Xi'an were determined, which can provide an insight into the origin and chemical properties of WSON. The temporal variability of the C:N ratios is shown in Fig. 5. The ratio ranged from .53 to 9.99 (average 2.85 ± 2.01). It is interesting to observe that the average C:N ratio found in this study is similar to that of organic nitrates (e.g., hydroxy nitric acid esters and nitric acid esters) that have C:N ratios of 2–12, but is lower than most of the values reported in other studies (e.g., Aiken et al., 2009; Fry et al., 2009; Lin et al., 2010; Rastogi et al., 2011; Rollins et al., 2010a, 2010b). However, considering the multiple sources of WSON at continental sites,

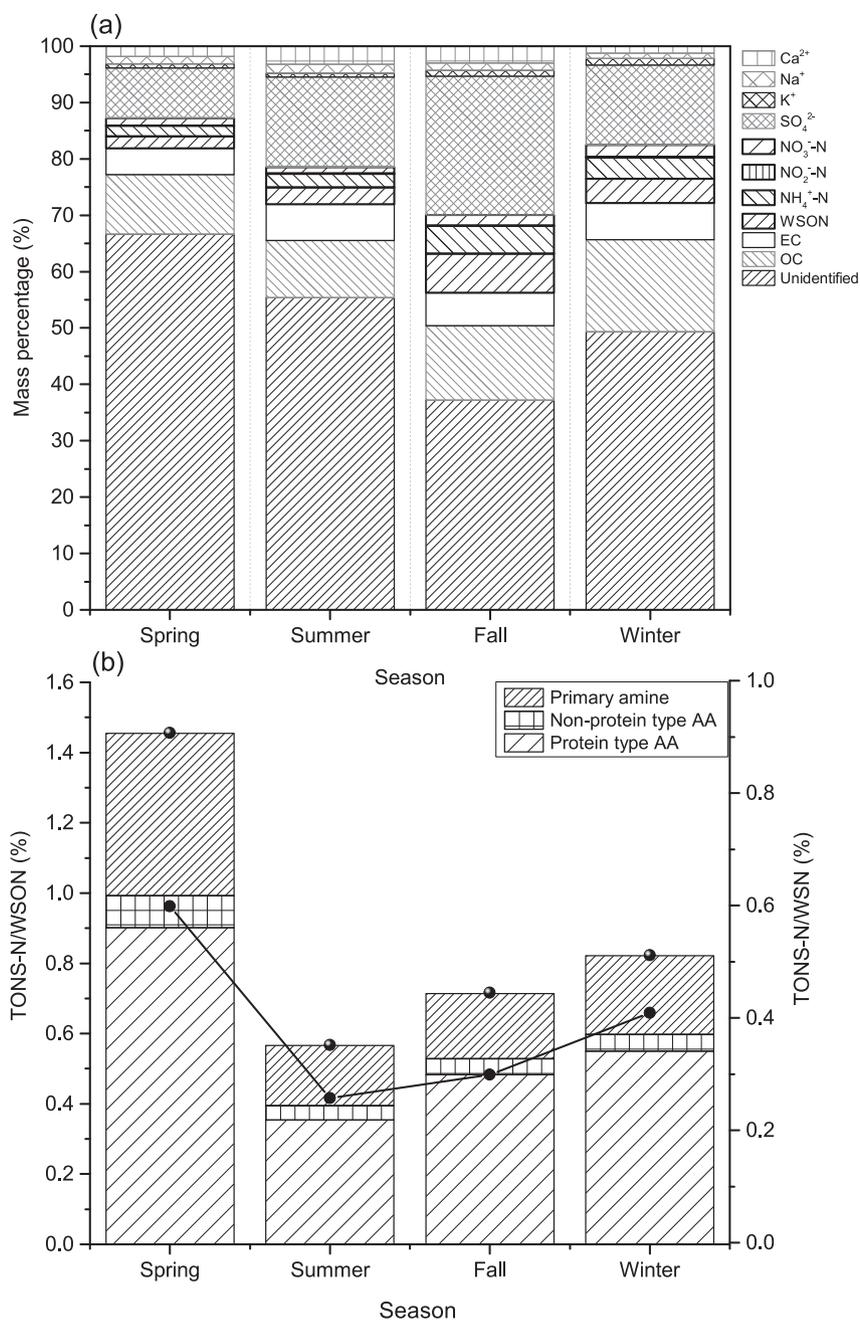


Fig. 4. Mass balance calculation by season: (a) The percentage of major components in PM_{2.5}; (b) The percentage of TONS-N in WSON.

care should be taken to determine the major species contributing to WSON based on C:N ratios alone (Rastogi et al., 2011).

The correlations of WSON and TONS with major anions, cations, OC, EC and organic tracers were investigated to further study their sources by Pearson's correlation. Previous studies have showed that certain water-soluble ions can be used to investigate the potential PM sources (including sea salt and biomass burning) as well as the formation of secondary aerosol (e.g., SO₄²⁻, NO₃⁻ and NH₄⁺). A high correlation coefficient between two species in PM_{2.5} may indicate their similar source/sink or similar formation mechanisms (Kocak et al., 2004). As shown in Table 3, significant correlations ($r = .72-.86$, $p < 0.001$) between WSON and water-soluble ions (NH₄⁺, NO₃⁻, SO₄²⁻ and K⁺) were observed at Xi'an for the entire campaign period, suggesting that secondary formation and biomass burning may be the significant contributors to WSON at

this urban site. In other studies, biomass burning has been found to be a major source of WSON (Laskin et al., 2009; Mace et al., 2003a), which is similar to our finding in this study. The TONS in PM_{2.5} exhibited fair relationships ($r = .49-.67$, $p < 0.001$) with most of the species determined (e.g., $r = .58$ with OC and $r = .67$ with K⁺) in this study except SO₄²⁻, which was an indication of multiple sources for the TONS (Table 3). Similar to TONS, the total protein-type and total non-protein-type amino acids also have similar correlations with most of the ions measured here. Non-protein type amino acids and primary amines showed a strong correlation with NO₃⁻ ($r = .60$, $p < 0.001$) (Table 3), which can be explained by the acid–base reaction of amines (e.g., MA and EA) and nitric acid in the atmosphere. In contrast, protein type amino acid exhibited a strong correlation with carbonaceous compounds (OC, EC, and WSOC) and biomass markers (K⁺), suggesting the link with biomass burning.

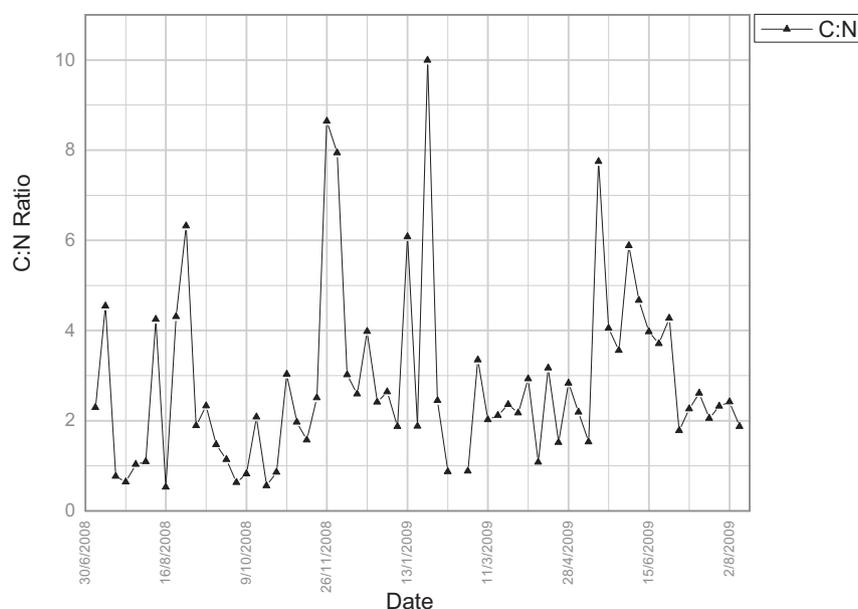


Fig. 5. The temporal variations of WSOC to WSON mass ratios in Xi'an.

We have examined the potential correlations of WSON and TONS with meteorological data, such as wind speed, relative humidity and temperature. TONS, total protein type and total non-protein type amino acids as well as primary amines negatively correlated with temperature ($r = -.69$ to $.76$, $p < 0.001$) but only weakly correlated with wind speed ($r = -.25$ to $-.30$, $p < 0.05$). The correlations with the other parameters were even weaker. The negative correlation between temperature and TONS might be an indication that there was a more direct emission during the cold season and larger amounts of partitioning of gas phase species into the particulate phase under low temperatures.

In each season, significant correlations ($r = .76$ – $.86$, $p < 0.001$) between WSON and water-soluble ionic species (NH_4^+ , NO_3^- , SO_4^{2-}) were observed, which further confirm that a large fraction of WSON is mainly from the secondary formation process, e.g. over 150 gaseous amines have been identified in the atmosphere from both natural and anthropogenic sources. They can undergo acid–base reactions with nitric and sulfuric acid to form low-volatility aminium salts which can undergo photooxidation and oxidation reactions with oxidants such as OH, NO_3 and O_3 , producing non-volatile ON (Huang et al., 2012). However, in spring and fall, WSON correlated significantly with EC and K^+ , which indicates the significant contribution from biomass burning. Both protein-like amino acids and primary amines showed good correlations with water-soluble ions (NH_4^+ , NO_3^- , SO_4^{2-} and K^+) in spring, but they exhibited weak correlations in winter and summer, which further indicates seasonal variability in primary sources and secondary production processes for the organic nitrogen species in Xi'an. It is remarkable that the large fraction of unidentified organic N could appoint to other potential sources (e.g., fossil fuel combustion). Further work should be done for their source apportionment.

4. Summary and conclusions

During the one-year measurement campaign of 2008–2009 in Xi'an, the concentrations of WSON, carbonaceous compounds, major water-soluble ionic species and water soluble organic nitrogen species in $\text{PM}_{2.5}$ were determined. The average concentrations of WSIN and WSON were $377 \text{ nmol N m}^{-3}$ and

$300 \text{ nmol N m}^{-3}$, respectively. WSON accounted for 45% of the WSN, which was higher than measurements at other continental sites in China. For the rest of the WSN fraction, the largest contributors are $\text{NH}_4^+\text{-N}$ ($\sim 34\%$) and $\text{NO}_3^-\text{-N}$ ($\sim 21\%$). A total of 24 organic nitrogen species were quantified, and the concentration of TONS ranged from 519 to 7160 pmol m^{-3} (an average of 2180 pmol m^{-3}). MA was the most abundant primary amines with a mean concentration of 450 pmol m^{-3} ; while $\beta\text{-Ala}$ was the most abundant non-protein type amino acid with a mean concentration of 113 pmol m^{-3} . The concentrations of WSIN and WSON peaked in fall and winter but dropped to a minimum in summer. Such a seasonal trend can be attributed to variations in meteorological factors, primary emissions, and secondary formation chemistry.

Most of the individual organic nitrogen species (except Thr) showed a very consistent seasonal variability with a lower variability in summer but a high variability in winter. Certain organic nitrogen species (i.e., ECA, MA, Cys, Tyr, Val, Met, EA and Orn) reached their highest concentrations in spring, which is likely due to the enhanced emission of proteinaceous matter (spores and pollen) and the increased formation of FAAs (due to hydrolysis of combined amino acids) and aminium salts of nitrate and sulfate. Similar to the results of WSON, high concentrations of WSOC and amino carbon content were found in winter, while low concentrations were found in summer. The contribution of amino carbon to WSOC was generally the highest in spring ($\sim 1.5\%$), which further indicates the presence of potential sources of TONS in Xi'an during that season. However, the measured organic nitrogen species account for only 1.2% of the WSON mass fraction. Thus further studies concerning the quantification of unidentified organic nitrogen species are clearly needed to determine their role in atmospheric chemistry.

Significant correlations ($r = .72$ – $.87$, $p < 0.001$) between WSON and water-soluble ions (NH_4^+ , NO_3^- , SO_4^{2-} and K^+) were observed at Xi'an, suggesting that secondary formation and biomass burning have significant contribution to WSON at the continental urban site. Additionally, WSON exhibited fair relationships with EC ($r = .54$), which indicated that the contribution of the fossil fuel combustion/industrial emission cannot be ruled out.

Table 3
Correlation coefficients (r) of selected species.

	WSON	TONS	Protein AA	Non-protein AA	Primary amines	OC	EC	WSOC	NH ₄ ⁺	NO ₂ ⁻	NO ₃ ⁻	SO ₄ ²⁻	K ⁺	WS	Temp	RH	
WSON	1																
TONS	.592**	1															
Protein AA	.585**	.999**	1														
Non-protein AA	.631**	.964**	.959**	1													
primary amines	.586**	.973**	.963**	.930**	1												
OC	.412**	.582**	.595**	.563**	.491**	1											
EC	.542**	.488**	.497**	.463**	.426**	.820**	1										
WSOC	.417**	.621**	.632**	.574**	.547**	.819**	.664**	1									
NH ₄ ⁺	.856**	.506**	.499**	.529**	.511**	.318**	.453**	.294*	1								
NO ₂ ⁻	-.206	-.033	-.025	-.112	-.048	-.132	-.208	-.171	-.228	1							
NO ₃ ⁻	.788**	.579**	.571**	.591**	.592**	.406**	.468**	.392**	.936**	.194	1						
SO ₄ ²⁻	.762**	.380**	.376**	.405**	.372**	.430**	.512**	.462**	.853**	-.390*	.760**	1					
K ⁺	.717**	.672**	.677**	.656**	.622**	.816**	.750**	.752**	.715**	-.214	.751**	.767**	1				
WS	-.296*	-.248*	-.258*	-.265	-.174	-.435**	-.495**	-.424**	-.266*	.240	-.264*	-.214	-.442**	1			
Temp	-.385**	-.749**	-.761**	-.694**	-.672**	-.716**	-.534**	-.716**	-.263*	.070	-.355**	-.239	-.675**	.329**	1		
RH	.258*	.013	.007	.063	.023	-.345**	-.258*	-.301*	.338**	.093	.266*	.029	-.099	-.052	.020	1	

**Correlation is significant at the .01 level (2-tailed).

*Correlation is significant at the .05 level (2-tailed).

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