



Seasonal behavior of water-soluble organic nitrogen in fine particulate matter (PM_{2.5}) at urban coastal environments in Hong Kong

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Abstract

Water-soluble organic nitrogen (WSON) in fine particulate matter (PM_{2.5}) was determined at urban coastal environments in China based on 1-year measurement. The WSON concentrations were in a range of 14.3–257.6 nmol N m⁻³ and accounted for 22.0–61.2% of the water-soluble nitrogen (WSN) in composition. The average total concentration of free amino acid (FAA) was 1264.5 ± 393.0 pmol m⁻³, which was lower than those in continental urban cities but nevertheless comparable to the rural area of Pearl River Delta (PRD) in China. The total quantified amines and amino compounds ranged from 223.8 to 806.0 pmol m⁻³ in which methylamine, ethylamine, and ethanolamine were the most abundant compounds. The average concentration of urea was 7.8 ± 3.0 nmol m⁻³ and at least one order of magnitude higher than those in marine and rural areas but comparable to other continental cities in China during non-dust period. Summer showed the highest average concentration of WSON (95.0 ± 66.6 nmol N m⁻³) and composition in WSN (49.3%) compared to other seasons (27.9–37.0%). The results were consistent with previous findings that the inorganics can contribute more than the organics in secondary aerosol formation. There were no distinctive seasonal variations of organic compositions of FAA, amine and amino compounds, and urea. This observation was possibly attributed to a mix of original sources in urban and different prevailing wind directions. Fair correlations ($r < 0.4$) between WSON compounds and atmospheric oxidants [ozone (O₃) and nitrogen oxides (NO_x)] suggest that biogenic oxidation is possibly not a major contributing factor in atmospheric coastal urban location.

Keywords Water-soluble organic nitrogen · Amino acids · Amines · Urea · Coastal area · PM_{2.5}

Introduction

Organic forms of nitrogen are widespread components in the atmosphere and their deposition can constitute a substantive input of atmospheric nitrogen to terrestrial and aquatic ecosystems (Neff et al. 2002). Organic nitrogen (ON) contributes ~10–50% of the total nitrogen in the atmospheric deposition (Bencs et al. 2009; Benítez et al. 2009; Zhang et al. 2008). In between, bioavailable nitrogen greatly affects our environments and human health (Aber et al. 1989; Choi et al. 2018; Delfino et al. 2011; Samy et al. 2013). Water-soluble organic nitrogen (WSON), composited of a major fraction of bioavailable nitrogen, could influence physical and chemical properties of aerosols and water droplets by altering their buffering capacity and basicity (Zhang et al. 2002). A past study showed that participation of ON compounds could participate secondary organic aerosol formation (SOA) in atmosphere (Facchini et al. 2008). WSON can be emitted from either natural or anthropogenic sources. The common natural inputs comprise mineral dust, bacteria, algal blooms, degraded proteins, sea salt, organic debris, and marine emissions (Luo et al. 2015b;

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Mace et al. 2003a; Violaki et al. 2015). In addition, anthropogenic sources include high-temperature fossil fuel combustion, vehicle exhaust, industrial activities, biomass burning, cooking, agricultural activities, and atmospheric reactions (Jiang et al. 2018; Ho et al. 2015; Rastogi et al. 2011; Violaki and Mihalopoulos 2010). In some extent, ON was accounted for ~10–20% of the total fine particulate matter (PM) (Rastogi et al. 2011; Zhang et al. 2002), while WSON was contributed >40% of ON for the samples collected in Amazon Basin in dry season while biomass burning activities frequently occurred (Mace et al. 2003b). In China, WSON was accounted for ~30% of the total nitrogen in Beijing and ~40% of water-soluble nitrogen (WSN) in Xi'an, China (Duan et al. 2009; Ho et al. 2015). Few studies have been conducted in Guangzhou, China. Li et al. (2012) found that WSON had a composition of 17–21% of total nitrogen in precipitation samples. Besides, the compositions of WSON were also found to be higher in rural (20–34%) than urban (12–13%) in this southern Chinese megacity (Yu et al. 2017). In the marine environment, WSON could contribute ~84% of the total dissolved nitrogen (TDN) in the aerosols (Violaki et al. 2015). The emissions of ON species could be linked with high biological activities in surface ocean (Altieri et al. 2012). The correlations between WSON in marine biogeochemical cycles and the roles in the atmosphere were well interpreted (Violaki et al. 2015). However, the investigation on the origins and chemical compositions of WSON in PM were still restricted to the marine environment (Kanakidou et al. 2012; Lesworth et al. 2010; Luo et al. 2015a).

The aims of this study are to (1) investigate the compositions of free amino acids (FAAs), primary amines, amino compounds, and urea in atmospheric aerosols collected from urban coastal environments in Hong Kong, China, (2) identify seasonal variations of those WSON species in one-year samples, (3) identify correlations between the temporal variations and meteorological conditions and other air oxidants.

Materials and methods

Sampling locations and meteorological conditions

Hong Kong is located on the eastern side of the Pearl River Estuary and characterized by a subtropical climate dominated by the East Asian monsoon. The prevailing synoptic winds are the northerlies and northeasterlies in winter, the easterlies in spring and autumn, and the southwesterlies in summer. PM_{2.5} samples were collected at Tung Chung (TC, 22.289 °N, 113.943 °E), where the location is a residential town in southwest of Hong Kong (Fig. 1). TC is a new town and the Hong Kong International Airport is located ~3 km to the north of the sampling location. At TC, major pollution sources include vehicular emissions from the upwind urban areas to the east

and the northeast, emissions from marine vessels in the water channel to the north, and the power plants at Tap Shek Kok to the north and at Lamma Island to the east. The air sampler is located on the rooftop of a four-floor building, ~16 m above the ground level, in proximity of the heavily used North Lantau Highway (~60 m away).

Sample collection

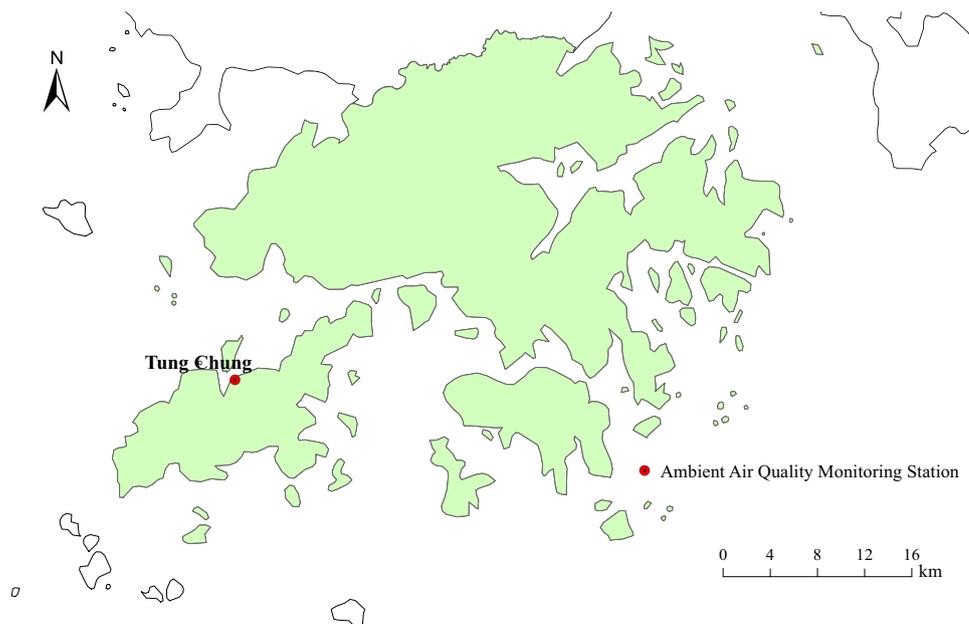
Sampling campaign was conducted in four non-consecutive months: August–September 2011 in late summer; November–December 2011 in late autumn; February–March 2012 in late winter; and May 2012 in late spring. PM_{2.5} samples were collected on pre-fired (900 °C for 4 h) quartz-fiber filters (20.3 cm × 25.4 cm, Whatman Inc., UK) using high-volume (hi-vol) samplers manufactured by Graseby Andersen (Palatine, IL, USA). The hi-vol sampler was operated at flow rates of 1.13–1.41 m³ min⁻¹. Background contamination was monitored by processing operational blanks (unexposed filters) simultaneously with field samples. The field blanks were collected at the sampling location by mounting filters in the samplers without purging through the air. The PM_{2.5} mass loadings were determined by a gravimetric method for which all filters were equilibrated in a controlled chamber at a temperature of 22 ± 2 °C and relative humidity (RH) of 35–45% for 24 h. Each sample was weighed in triplicate (weighing differences were < 15 and < 20 µg before and after sampling, respectively) using a MC5 electronic microbalance (± 1 mg sensitivity, Sartorius, Gottingen, Germany). All samples were stored in the freezer (< -10 °C) prior the analysis.

Free amino acid and primary amine analysis

Detailed sample treatment and analytical procedures for the measurement of free amino acids and primary amines were shown in our previous publication (Ho et al. 2015). In brief, each filter sample was extracted with Milli-Q water (resistivity, 18.2 MΩ-cm) twice in an ultrasonic water bath. The water extracts were then combined, filtered, and concentrated to a volume of 0.5 mL by rotary evaporator before analysis (Yang et al. 2005). The extracts were then derivatized with 6-aminoquinolyl-*N*-hydroxysuccinimidyl carbamate [AccQ-Fluor reagent (AQC)] and AccQ.Tag borate buffer (WAT052880, Waters Corporation, Milford, MA, USA). The derivatization step used for the calibration standards was identical compared with the samples. The extraction recovery for the target organic nitrogen species ranged from 79.6 to 96.8%.

The derivatized sample extracts or standards were injected into a high-performance liquid chromatography (HPLC, 1200 Series, Agilent Technology) equipped with a fluorescence detector. The column used for separation was a 3.9 × 150 mm AccQ.Tag Amino Acid Analysis Silica base bonded with 4-µm C-18 reversed-phase column (Waters Corporation) at

Fig. 1 Map of sampling location at Tung Chung, Hong Kong



37 °C in operation. The calibrations were demonstrated to be linear [correlation coefficient (r^2) > 0.999]. The minimum detection limit (MDL) was obtained by analyzing ten replicates of the lowest concentrations of standard solution, ranging from 0.036 to 0.086 nmol mL⁻¹ (equivalent to 0.262–0.626 pmol m⁻³). The measurement precision was in a range of 3.6–8.5%. The measurement uncertainties ranged from ± 3.2 to ± 9.1% for the target amino acids.

Urea and non-primary amines analysis

For urea, identification and quantification were performed by direct injection of the extract to the HPLC coupled with a photodiode array detector (DAD) (1200 Series; Agilent Technology). The target compound was separated with a C18 column (Cogent Bidentate, 4.6 × 150 mm, 4-μm particle size; Microsolv Technology, Leland, NC, USA) and detected at an absorption wavelength of 210 nm. The MDL was 0.05 ng mL⁻¹ and measurement precision was 3%.

Detailed sample preparation, derivatization steps, and instrumental parameters for measurement of non-primary amines were shown in Ruiz-Jimenez et al. (2012). Dansyl chloride in acetone (Sigma-Aldrich, St. Louis, MO, USA) was served as a derivatizing agent. The derivatized products were then introduced to the HPLC (Series 1200; Agilent Technology) and were furnished with a Waters Sunfire C18 column (2.1 × 150 mm, 3.5-μm particle size) coupled with an ion-trap mass spectrometer (Esquire 3000; Bruker Daltonics, Billerica, MA, USA). The MDL for the non-primary amines ranged from 0.005 to 0.019 ng mL⁻¹. The precisions were < 6.9% by replicate analyses of standards.

Other nitrogen analysis

WSN [i.e., sum of water-soluble organic nitrogen (WSO_N) and water-soluble inorganic nitrogen (WSIN)] was quantified in the analysis. The extraction procedures were referred to our previous study (Ho et al. 2015). Total nitrogen (TN) in the filtrates was measured by thermo-catalytic oxidation approach using a total organic carbon (TOC)/TN analyzer (TOC-L, Shimadzu, Kyoto, Japan). The nitrogen content was analyzed by measuring the oxides of nitrogen with using chemiluminescence detector. The detection limit was 5 μg L⁻¹ with a precision of ± 8.8%. The measurement uncertainties ranged from ± 4.4 to ± 9.7%. The results reported in this study were all corrected by the field blanks of 60 μg L⁻¹.

Determination of cations [i.e., potassium (K⁺), sodium (Na⁺), ammonium (NH₄⁺), calcium (Ca²⁺), and magnesium (Mg²⁺)] and anions [nitrate (NO₃⁻), sulfate (SO₄²⁻), and chloride (Cl⁻)] followed the steps shown in Ho et al. (2015). The target ions were determined by a Dionex-600 Ion Chromatograph (Dionex Inc., Sunnyvale, CA, USA). An IonPac AS14A column (8 mM Na₂CO₃/1 mM NaHCO₃ as an eluent) was used for the anions analyses. For the cation analyses, an IonPac CS12A column was used for separation (20 mM methanesulfonic acid as an eluent) purpose. The MDL were 0.5 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⁻ in the analysis. The certified values (within ± 4%) of reference materials (National Research Center for Certified Reference Materials, China) were in good agreement for the five cations and three anions. The measurement uncertainties ranged from ± 2.2 to ± 5.1% for the targeted ions.

NH₄⁺, NO₂⁻, and NO₃⁻ were the major WSIN species in the aerosols, and WSON was defined as the difference

between WSN and WSIN. The concentrations of NO_2^- in all samples were below the detection limit and thus considered as negligible. The calculation of WSIN and WSON (nmol N m^{-3}) can be referred to the following equations:

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

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

Results and discussion

Concentrations of nitrogen fractions and other compounds

The abundances of major nitrogen fractions (i.e., WSN, WSIN, and WSON) and quantified individual compounds are tabulated in Table 1, 2. The molar concentrations of WSN ranged from 33.3 to 513.5 nmol N m^{-3} , with an average of $178.7 \pm 128.4 \text{ nmol N m}^{-3}$. The molar concentrations of WSON and WSIN were in a range of 14.3–257.6 nmol N m^{-3} and 12.9–310.4 nmol N m^{-3} , respectively. The compositions of WSON in WSN were between 22.0 and 61.2%. The average WSON in this study was > 50% lower than that in Qingdao (China) (Shi et al. 2010), but higher than that in Hawaii (USA), Keelung (Taiwan), and Tasmania (Australia) (Chen and Chen 2010; Mace et al. 2003a; Cornell et al. 2001). Although the levels in TC were lower than those in continental cities such as Xi'an and Beijing (China) (Shi et al. 2010; Duan et al. 2009; Wang et al. 2013; Ho et al. 2015), they still exceeded those observed in Atlanta and Chapel Hill (USA) (Rastogi et al. 2011; Lin et al. 2010). The average concentration of WSON in TC was consistent with a study at East China Sea (Nakamura et al. 2006). The total concentrations of FAA ranged from 779.7 to 2199.2 pmol m^{-3} , and its average of $1264.5 \pm 393.0 \text{ pmol m}^{-3}$ was ~40% lower than continental area in Xi'an (Zhang and Anastasio 2003; Ho et al. 2015), but ~4.0 times higher than that in Venice (Barbaro et al. 2011). The results in this study were consistent with findings in the rural area of Guangzhou (China) (Song et al. 2017). Previous studies showed that FAA could be separated as protein-type and non-protein-type amino acid (AA). The average molar concentrations of total protein-type AA ($1147.5 \pm 358.6 \text{ pmol m}^{-3}$) were ~9.8 times higher than the total non-protein AA ($117.0 \text{ pmol m}^{-3}$). Glycine (Gly, $434.3 \pm 154.6 \text{ pmol m}^{-3}$) was the most abundant component, followed by alanine (Ala, $169.0 \pm 57.0 \text{ pmol m}^{-3}$), cysteine (Cys, $161.1 \pm 55.9 \text{ pmol m}^{-3}$), and valine (Val, $117.6 \pm 37.1 \text{ pmol m}^{-3}$). These protein-type AA accounted for ~70% of the total quantified FAAs. The results are consistent other studies that Gly and Ala are the two most abundant FAAs (Barbaro et al. 2011; Violaki and Mihalopoulos 2010). Gly is a fundamental component in fibrous proteins in animals and intermediates in products (Voet et al. 2008). However, Song et al. (2017) reported that the four most abundant FAA were in descending order: Gly > Val > methionine (Met) >

phenylalanine (Phe) in rural area of Guangzhou. Met is a unique constituent in protein for all living organism and potentially attributed to biological origins (Song et al. 2017). The composition differences of FAA can be used to distinguish source of origin (urban or rural area). β -Alanine (β -Ala) (97.7 pmol m^{-3}) was the most abundant non-protein AA component.

The total concentrations of amine compounds ranged from 223.8 to 806.0 pmol m^{-3} . Methylamine, ethylamine, and ethanolamine were the most abundant primary amines with average concentrations of 263.6 ± 97.3 , 108.4 ± 28.2 , and $42.0 \pm 13.6 \text{ pmol m}^{-3}$, respectively. The concentrations were lower than other studies in Xi'an and Guangzhou (China) (Ho et al. 2015; Liu et al. 2017). The concentration of N-methylformamide was in a range of 13.6–57.1 pmol m^{-3} and N-methylformamide was an abundant compound in TC. This compound can be identified in solvents used in oil refineries and as precursor in amidation reactions (Sahoo and Sit 2017). The concentration of urea ranged from 2.8 to 14.5 nmol m^{-3} . A previous study showed that urea could be originated from natural and anthropogenic sources. The compound is a commonly used nitrogen fertilizer (Glibert et al. 2005). Further applications can be found in different industrial processes such as the manufacture of resins, glues, solvents, medicines, cleaning products, and cosmetics (Francis et al. 2002). The natural occurrence of urea could be identified in marine and land environments as the compound is considered as final metabolite of nitrogenous matter in mammals and marine species (Song et al. 2017). The levels in TC were at least one order of magnitude higher than samples collected from marine environments at Crete (Greece) and Tasmania (Australia) (Mace et al. 2003a; Violaki and Mihalopoulos 2011) and rural areas such as Rondonia (Brazil) (Mace et al. 2003b). Nevertheless, the results in this study were close to Qingdao (China) during non-dust period (Shi et al. 2010).

Seasonal variations of WSON

Figure 2 illustrates seasonal variations of WS fractions. The highest average concentrations of WSN ($234.4 \pm 103.8 \text{ nmol N m}^{-3}$) and WSIN ($164.9 \pm 73.6 \text{ nmol N m}^{-3}$) were observed in winter, coupled with highest average $\text{PM}_{2.5}$ concentration ($47.0 \pm 11.0 \text{ } \mu\text{g m}^{-3}$). However, WSON showed the highest average concentration ($95.0 \text{ nmol N m}^{-3}$) in summer and WSN composition (49.3%) compared to other seasons (27.9–37.0%). The results were consistent with other studies that inorganic species (e.g., nitrate) could have more contributions to secondary aerosol formation compared to organic compounds (Cheng et al. 2016). This observation could possibly be attributed to prevailing northerly winds that transport the air pollutants from mainland China in winter. The origins of WSON were due to dominant southwesterly winds from marine in summer (Matsumoto et al. 2017). Seasonal emission sources and meteorological factors (i.e., temperature, relative humidity, radiation, and mixing layer height) could influence formation and fate of

Table 1 Concentrations of chemical compounds in sampling location (TC)

Species	Min	Max	Mean ± SD	Species	Min	Max	Mean ± SD
PM mass ($\mu\text{g m}^{-3}$)	8.47	68.7	33.1±16.2	WSON/WSN	22.0%	61.2%	36.4±8.7%
WSN (nmol N m^{-3})	33.3	513.5	178.7±128.8	WSN/PM	2.7%	10.6%	6.8±3.5%
WSON (nmol N m^{-3})	10.6	257.6	64.3±56.7	WSIN/PM	1.6%	6.7%	4.4±2.7%
WSIN (nmol N m^{-3})	12.9	310.4	114.4±78.5	WSON/PM	0.9%	5.3%	2.5±1.2%
O ₃ ($\mu\text{g m}^{-3}$)	10.0	120.7	50.7±31.6				
NO ($\mu\text{g m}^{-3}$)	1.1	43.7	12.4±11.3				
NO _y ($\mu\text{g m}^{-3}$)	18.2	142.4	65.3±31.5				
Free Amino Acids (FAA) (pmol m^{-3})				Amines (pmol m^{-3})			
<i>Protein type FAA</i>							
Alanine (Ala)	78.7	311.3	169.0±57.0	Methanolamine	120.9	547.5	263.6±97.3
Arginine (Arg)	nd	nd	nd	Ethylamine	52.2	161.6	108.4±28.2
Aspartic acid (Asp)	9.7	39.1	23.0±8.2	Ethanolamine	18.3	68.1	42.0±13.6
Cysteine (Cys)	70.7	279.3	161.1±55.9	Dipropylamine	0.44	2.1	1.2±0.4
Glutamine (Gln)	7.5	33.2	20.3±7.4	Tripropylamine	0.52	2.7	1.3±0.5
Glutamic acid (Glu)	4.8	24.0	12.0±4.0	iso-Butylamine	0.14	1.0	0.43±0.23
Glycine (Gly)	176.5	842.6	434.3±154.6	sec-Butylamine	0.21	1.2	0.53±0.25
Histidine (His)	4.0	21.0	10.4±4.3	Dimethylamine	0.62	3.7	1.7±0.78
Isoleucine (Ile)	9.5	42.7	25.4±9.2	Diethylamine	0.38	1.8	0.84±0.35
Leucine (Leu)	12.6	41.8	26.6±8.7	Ethylenediamine	0.12	0.57	0.29±0.12
Lysine (Lys)	23.7	71.1	45.7±12.5	Phenylamine	0.94	5.3	2.6±1.1
Methionine (Met)	2.9	12.4	6.7±2.4	N-Methylphenylamine	0.14	0.58	0.35±0.14
Phenylalanine (Phe)	10.1	53.1	22.2±9.0	2-Methylphenylamine	0.05	0.23	0.12±0.05
Proline (Pro)	12.1	52.6	25.8±9.9	4-Methylphenylamine	0.05	0.25	0.14±0.07
Threonine (Thr)	16.3	77.0	40.0±14.7	4-Ethylphenylamine	0.05	0.23	0.14±0.05
Tyrosine (Tyr)	1.0	3.9	2.3±0.8	iso-Propylphenylamine	0.06	0.26	0.15±0.06
Serine (Ser)	12.3	36.2	25.5±7.0	3-Propylphenylamine	0.08	0.38	0.19±0.08
Valine (Val)	51.0	180.3	117.6±37.1	p-Aminophenol	0.16	1.1	0.46±0.25
<i>Total Protein FAA</i>	<i>531.2</i>	<i>2000.4</i>	<i>1147.5</i>	2-Amino-1-butanol	0.08	0.27	0.16±0.05
<i>Non-protein type FAA</i>				N-Methylformamide	13.6	57.1	31.8±11.3
β -alanine (β -Ala)	39.6	163.4	97.7±30.9	4-Aminobenzoic acid	0.07	0.33	0.17±0.07
γ -aminobutyric acid (γ -Aba)	3.4	19.6	8.1±3.5	Total Amines	223.8	806.0	456.6
Ornithine (Orn)	4.7	20.4	11.2±3.7				
<i>Total Non-protein FAA</i>	<i>49.5</i>	<i>198.8</i>	<i>117.0</i>	Urea (nmol m^{-3})	2.8	14.5	7.8
Total FAA (Protein + Non-Protein)	580.8	2199.2	1264.5				

^aBelow minimum detection limit

organic nitrogen in atmospheric reactions (Zhang et al. 2002). The total FAA concentration was $1548.3 \pm 331.5 \text{ pmol m}^{-3}$ in winter and in a range of 19.3–42.4% higher than other seasons. The trend is, in descending order: winter > autumn > spring > summer. No distinct variations of organic profiles (protein and non-protein types) were observed in FAA. These could be attributed to complexity of marine sources in urban areas. Song et al.

(2017) reported the seasonal trend (autumn > winter > summer > spring) on proteinaceous matters in PRD in China. A previous study showed that biomass burning can be a major contributing source for FAA enrichment (Ho et al. 2014). However, prevailing easterly wind in autumn could deter regional transport of biomass burning products such as FAAs to TC sampling location. The highest concentrations of amine ($564.1 \pm 124.9 \text{ pmol m}^{-3}$) and

Table 2 Seasonal variations of WSON compounds in sampling location (TC)

ON species	Spring		Summer		Autumn		Winter	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Free amino acids (FAA) (pmol m ⁻³)								
Protein-type FAA								
Alanine (Ala)	169.2	48.3	166.6	96.9	152.6	47.1	189.8	47.1
Arginine (Arg)	bd ^a	bd	bd	bd	bd	bd	bd	bd
Aspartic acid (Asp)	17.7	5.01	17.8	7.41	24.2	6.18	31.5	6.18
Cysteine (Cys)	132.1	34.1	135.3	62.0	172.2	56.2	198.8	56.2
Glutamine (Gln)	16.1	4.28	12.9	5.46	21.7	5.07	28.9	5.07
Glutamic acid (Glu)	10.4	2.70	9.3	3.53	12.4	3.14	15.4	3.14
Glycine (Gly)	341.4	107.9	339.8	142.9	469.5	117.3	564.8	117.3
Histidine (His)	11.9	3.1	12.4	6.0	8.7	3.70	9.1	3.70
Isoleucine (Ile)	21.3	6.4	21.4	14.2	26.5	7.53	31.4	7.53
Leucine (Leu)	28.4	7.1	26.5	13.4	24.2	6.93	27.7	6.93
Lysine (Lys)	49.8	10.9	46.6	18.1	39.3	9.75	48.2	9.75
Methionine (Met)	5.28	1.67	5.88	3.04	7.00	2.04	8.44	2.04
Phenylalanine (Phe)	19.3	5.71	16.1	6.17	23.7	6.68	28.3	6.68
Proline (Pro)	22.9	5.47	24.1	12.5	27.2	10.2	28.6	10.2
Threonine (Thr)	35.2	12.1	30.5	13.9	41.0	11.8	51.4	11.8
Tyrosine (Tyr)	2.19	0.65	2.10	1.06	2.16	0.78	2.54	0.78
Serine (Ser)	26.3	6.98	22.6	9.68	25.2	7.31	27.4	7.31
Valine (Val)	89.4	26.5	111.8	49.2	124.0	33.1	143.4	33.1
Total protein FAA	982.8	263.7	988.7	450.9	1179.8	300.3	1406.8	300.3
Non-protein-type FAA								
β-Alanine (β-Ala)	86.8	21.6	79.1	37.2	100.7	28.5	120.6	28.5
γ-Aminobutyric acid (γ-Aba)	8.8	2.2	7.5	3.6	7.3	2.7	9.0	2.7
Ornithine (Orn)	11.7	2.9	11.8	6.0	9.6	3.4	12.0	3.4
Total non-protein FAA	107.4	26.2	98.4	46.8	117.6	33.3	141.6	33.3
Total FAA (protein + non-protein)	1090.1	289.7	1087.2	497.0	1297.4	331.5	1548.3	331.5
Amines (pmol m ⁻³)								
Methanolamine	229.3	61.8	228.8	109.8	267.2	89.8	322.7	89.8
Ethylamine	98.5	25.6	97.5	36.8	105.7	23.7	130.4	23.7
Ethanolamine	39.8	11.0	37.9	20.5	38.5	12.8	51.8	12.8
Dipropylamine	0.95	0.21	1.30	0.45	1.11	0.42	1.48	0.42
Tripropylamine	1.00	0.27	1.48	0.74	1.11	0.38	1.59	0.38
iso-Butylamine	0.25	0.06	0.34	0.20	0.40	0.19	0.70	0.19
sec-Butylamine	0.33	0.08	0.39	0.21	0.53	0.17	0.84	0.17
Dimethylamine	1.39	0.33	1.13	0.57	1.62	0.55	2.73	0.55
Diethylamine	0.60	0.14	0.65	0.22	0.85	0.35	1.21	0.35
Ethylenediamine	0.20	0.05	0.24	0.10	0.32	0.13	0.40	0.13
Phenylamine	2.29	0.70	1.97	0.83	2.63	1.42	3.34	1.42
N-Methylphenylamine	0.29	0.11	0.28	0.14	0.33	0.11	0.49	0.11
2-Methylphenylamine	0.09	0.02	0.11	0.04	0.11	0.04	0.16	0.04
4-Methylphenylamine	0.09	0.03	0.14	0.06	0.14	0.06	0.19	0.06
4-Ethylphenylamine	0.13	0.04	0.11	0.05	0.13	0.06	0.19	0.06
iso-Propylphenylamine	0.10	0.03	0.13	0.07	0.15	0.06	0.20	0.06
3-Propylphenylamine	0.13	0.04	0.14	0.04	0.18	0.07	0.28	0.07
p-Aminophenol	0.26	0.07	0.27	0.07	0.48	0.20	0.78	0.20
2-Amino-1-butanol	0.15	0.06	0.13	0.06	0.15	0.04	0.20	0.04

Table 2 (continued)

ON species	Spring		Summer		Autumn		Winter	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
N-Methylformamide	22.48	6.29	27.01	6.40	32.66	9.60	44.14	9.60
4-Aminobenzoic acid	0.11	0.02	0.14	0.06	0.18	0.06	0.24	0.06
Total amines	398.4	96.1	400.2	172.9	454.5	124.9	564.1	124.9
Urea (nmol m ⁻³)	6.8	1.7	7.2	3.7	6.6	2.4	10.7	2.4

^a Below minimum detection limit

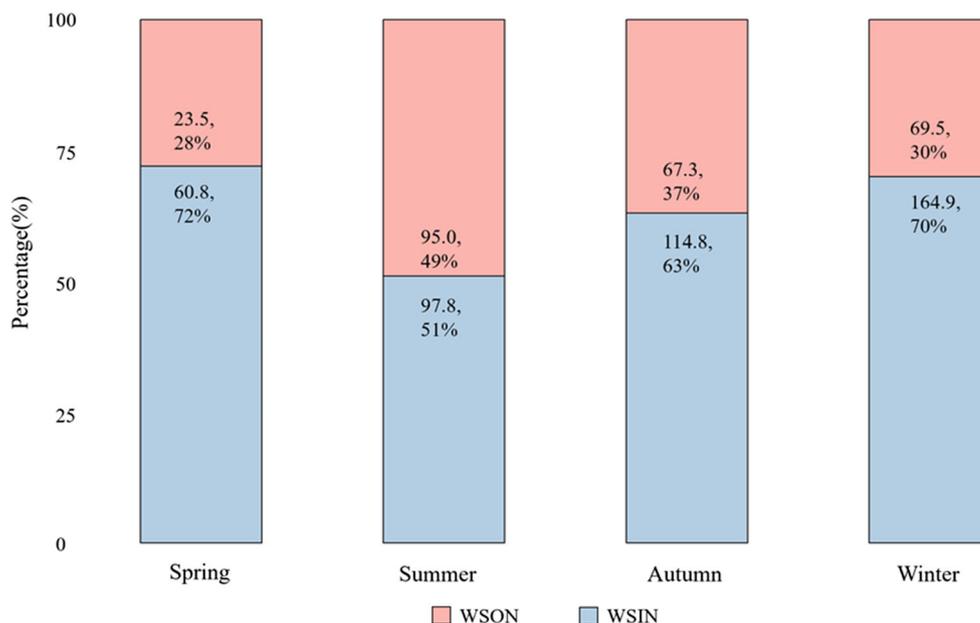
urea ($10.7 \pm 2.4 \text{ nmol m}^{-3}$) were observed in winter and both compounds showed similar seasonal trends compared to FAA. Urea can be transferred from sea surface via bubble-bursting processes and also evaporated from soil as part of windblown materials. This compound can further be emitted from industrial activities (Violaki and Mihalopoulos 2011). The above trends suggest that anthropogenic sources due to regional transport could be a dominant factor under northerlies and north easterlies winds during winter.

Correlation between FAAs and oxidants

Figure 3 shows the correlations between FAAs and atmospheric oxidants (O_3 , NO , and NO_x). Only a fair correlation ($r = 0.38$, $p < 0.01$) was observed between total FAAs and O_3 . Ozone can promote the release of FAAs from vegetation and enhance rate of chemical oxidation, nitration, and oligomerization of protein in the atmosphere (Shiraiwa et al. 2012; Kampf et al. 2015). In addition, the second-order rate of

reaction mechanism was identified between protein and atmospheric oxidants. This observation could be due to reaction was dependent on the abundances of precursor and O_3 (Liu et al. 2017; Shiraiwa et al. 2012; Kampf et al. 2015). The results in this study are different from the rural area of PRD in China (Song et al. 2017). This observation points to possibly high local contribution for FAAs from plant materials and living organisms. Fair correlations ($r = 0.32$, $p < 0.01$ and $r = 0.33$, $p < 0.01$, respectively) were identified between Gly/Met and O_3 (Fig. 3). The results imply that biomass emissions and bioactivities were not the dominant sources for urban atmosphere under different wind directions. Fair correlations ($r < 0.32$, $p < 0.01$ and $r < 0.25$, $p < 0.01$, respectively) were also observed between total quantified amine/urea and O_3 (Fig. 3). The observations suggest a non-significant association between amine/urea compounds and the atmospheric oxidants in the urban area. Aliphatic amines can be oxidized in the atmosphere by hydroxyl radicals ($\cdot\text{OH}$), nitrate radicals (NO_3) and O_3 , leading to the formation of secondary aerosol formation (Murphy et al. 2007). The highest concentration of

Fig. 2 Seasonal variations of WSON and WSIN fractions. The values denote molar concentration (nmol N m⁻³) and molar composition (%)



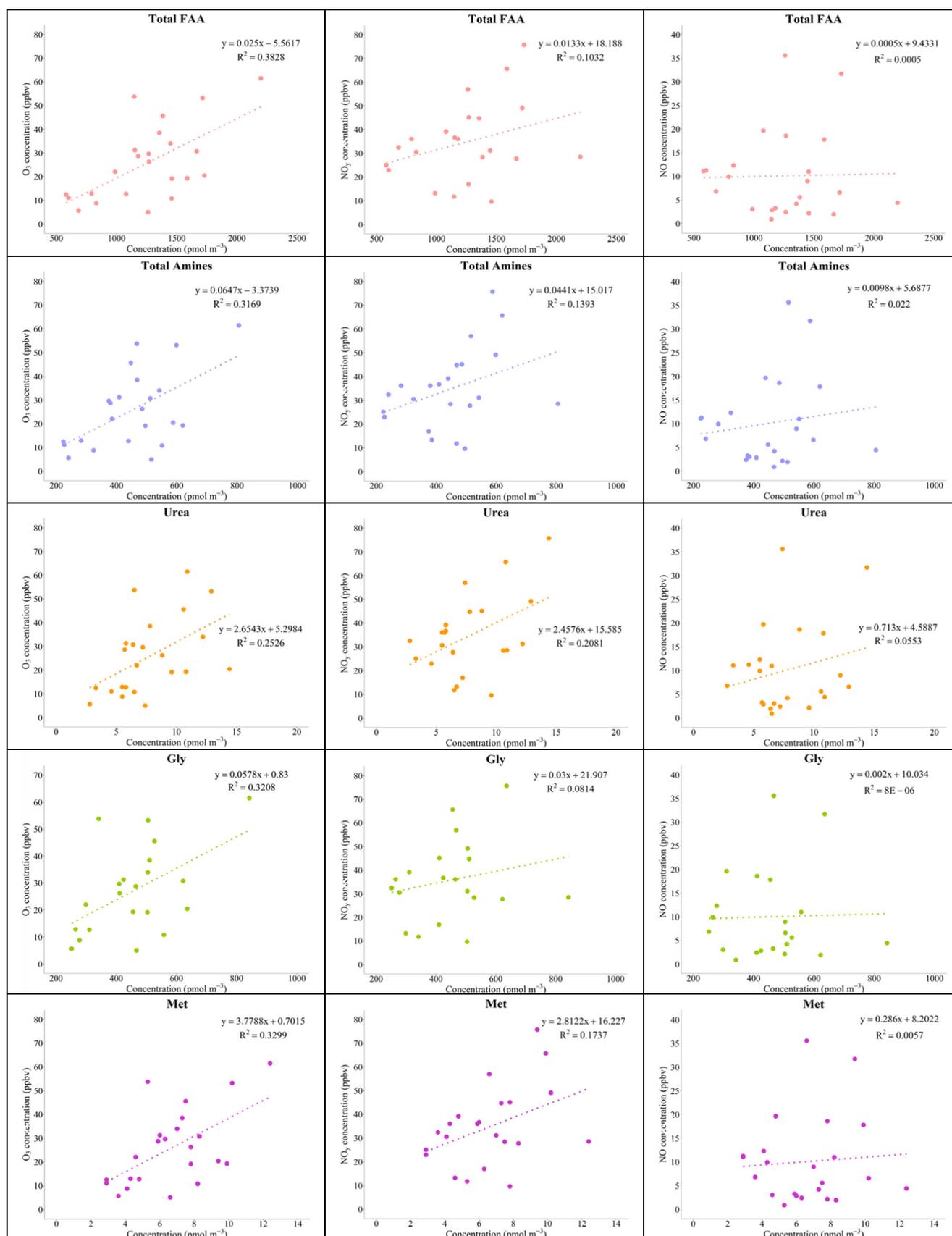
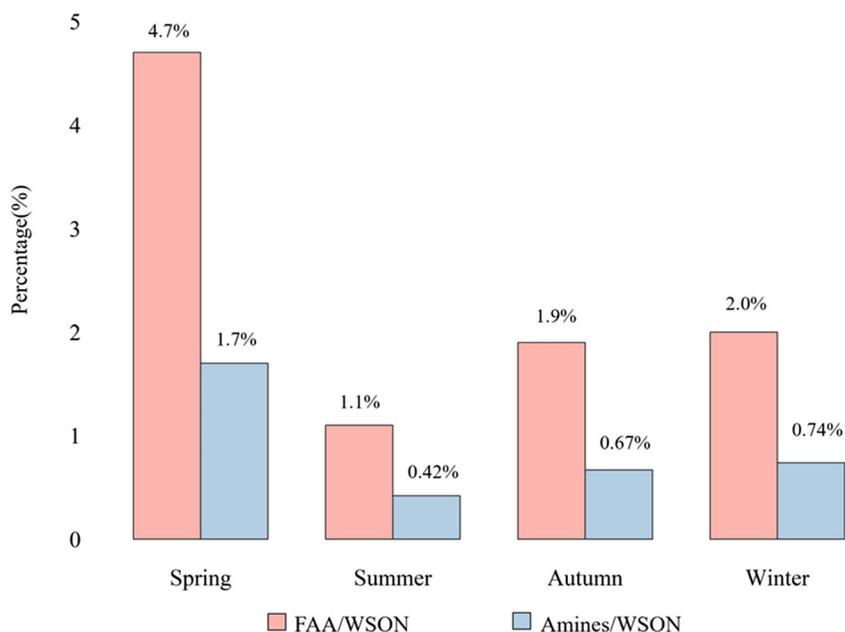


Fig. 3 Relationships between concentrations of total FAA, total amines, urea, glycine (Gly), and methionine (Met) in relation to O₃, NO, and NO₂

Fig. 4 Molar compositions of total FAA and total quantified amines in WSON in different seasons

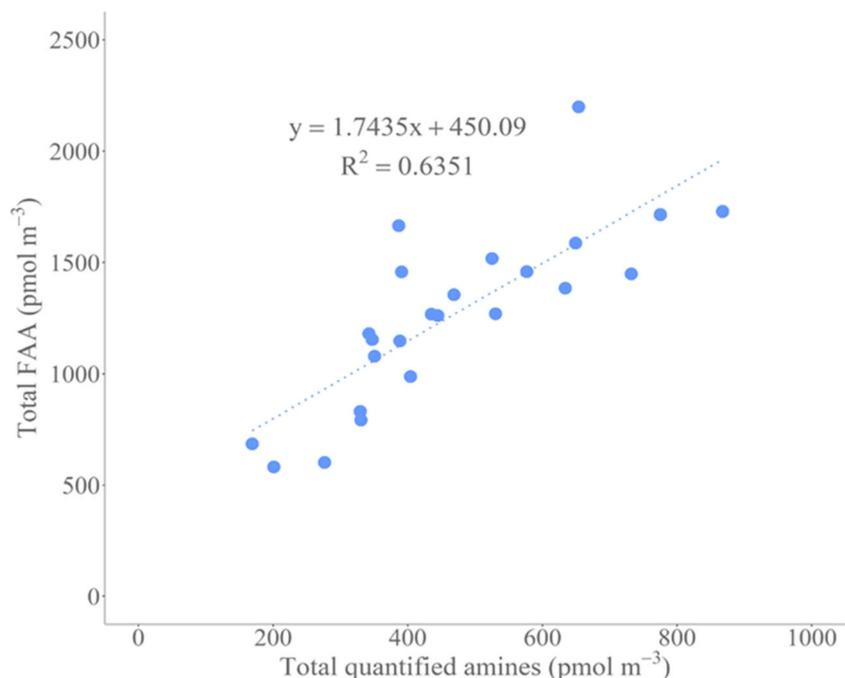


total quantified amines was observed in TC during winter, and this can be used to explain higher potential contribution to the SOA formation (Huang et al. 2014).

The molar compositions of ON groups in WSON are shown in Fig. 4. Highest contribution of FAAs (4.7%) and amines (1.7%) were identified in spring. The result is consistent with previous findings in the urban area of Xi'an in China. The results could be due to higher proteinaceous matter emissions from spores and pollens, and further lead to possibly higher FAA formations from hydrolysis of combined amino

acids (Ho et al. 2015). Moderate correlation ($r = 0.64$) was identified between urea and FAA (Fig. 5). Shi et al. (2010) reported that ~50% of urea existed in fine particulate matter ($< 2.1 \mu\text{m}$) composition. These particles can undergo gas-particle conversion processes (Cornell et al. 1998). Agricultural activities and particles from crustal origins were identified as major contributors for urea (Chen and Chen 2008). The above-mentioned correlation suggests that these groups of ON compounds can possibly be originated from the same sources in TC sampling location.

Fig. 5 Relationships between concentrations of total FAAs and total quantified amines



Potential health impacts of WSON species

Referred to our previous work (Chuang et al. 2015), we found that the increases of inflammatory response in mice evidently related to particulate OC and free amino acids. The non-protein-type amino acids could be among the environmental determinants of the inflammatory allergic potency of PM_{2.5} on human respiratory system. Even though the average concentrations of amino acids in TC were lower than those heavy-polluted cities such as Xi'an, the widespread sources from urban and marine may have a mix of contribution on the toxicity. In addition, the effects of the physicochemistry of amines (e.g., nitroamines) on bioreactivity should be further investigated in such coastal urban environments.

Conclusion

Characteristics of water-soluble organic nitrogen in PM_{2.5} at a coastal urban environment (TC) were investigated. The origins of WSN were demonstrated to be from a mix of natural and anthropogenic sources. The prevailing winds were shown to have implications towards the concentrations of WSON compounds. Biomass emissions and bioactivities from marine environments were not the dominant sources at this coastal sampling location. Further investigation on the emission sources determination in urban areas will be necessary to elucidate the roles of SOA formation in future analysis.

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