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

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29 **Abstract**

30 Water-soluble organic nitrogen (WSON) in fine particulate matter (PM_{2.5}) were determined at
31 urban coastal environments in China based on one-year measurement. The WSON
32 concentrations were in a range of 14.3-257.6 nmol N m⁻³ and accounted for 22.0–61.2% of the
33 water-soluble nitrogen (WSN) in composition. The average total concentration of free amino
34 acid (FAA) was 1,264.5±393.0 pmol m⁻³, which was lower than those in continental urban
35 cities but nevertheless comparable to rural area of Pearl River Delta (PRD) in China. The total
36 quantified amines and amino compounds ranged from 223.8 to 806.0 pmol m⁻³ in which
37 methylamine, ethylamine and ethanolamine were the most abundant compounds. The average
38 concentration of urea was 7.8±3.0 nmol m⁻³ and at least one order of magnitude higher than
39 those in marine and rural areas but comparable to other continental cities in China during non-
40 dust period. Summer showed the highest average concentration of WSON (95.0±66.6 nmol N
41 m⁻³) and composition in WSN (49.3%) compared to other seasons (27.9-37.0%). The results
42 were consistent with previous findings that the inorganics can contribute more than the organics
43 in secondary aerosol formation. There was no distinctive seasonal variations of organic
44 compositions of FAA, amine and amino compounds, and urea. This observation was possibly
45 attributed to mix of original sources in urban and different prevailing wind directions. Fair
46 correlations ($r < 0.4$) between WSON compounds and atmospheric oxidants [ozone (O₃)
47 and nitrogen oxides (NO_x)] suggest that biogenic oxidation is possibly not a major contributing
48 factor in atmospheric coastal urban location.

52 **Keywords:**

53 *Water-soluble organic nitrogen; Amino acids; Amines; Urea; Coastal area; PM_{2.5}*

54 1. Introduction

55 Organic forms of nitrogen are widespread components in the atmosphere and their
56 deposition can constitute a substantive input of atmospheric nitrogen to terrestrial and aquatic
57 ecosystems (Neff et al. 2002). Organic nitrogen (ON) contributes ~10-50% of the total nitrogen
58 in the atmospheric deposition (Bencs et al. 2009; Benítez et al. 2009; Zhang et al. 2008). In
59 between, bioavailable nitrogen greatly affects our environments and human health. (Aber et al.
60 1989; Choi et al., 2018; Delfino et al., 2011; Samy et al. 2013). Water-soluble organic nitrogen
61 (WSON), composited of major fraction of bioavailable nitrogen, could influence physical and
62 chemical properties of aerosols and water droplets by altering their buffering capacity and
63 basicity (Zhang et al. 2002). A past study showed that participation of ON compounds could
64 participate secondary organic aerosol formation (SOA) in atmosphere (Facchini et al. 2008).
65 WSON can be emitted from either natural or anthropogenic sources. The common natural
66 inputs comprise mineral dust, bacteria, algal blooms, degraded proteins, sea salt, organic debris
67 and marine emissions (Luo et al. 2015b; Mace et al. 2003a; Violaki et al. 2015). In addition,
68 anthropogenic sources include high-temperature fossil fuel combustion, vehicle exhaust,
69 industrial activities, biomass burning, cooking, agricultural activities and atmospheric reactions
70 (Jiang et al., 2018; Ho et al. 2015; Rastogi et al. 2011; Violaki and Mihalopoulos 2010). In
71 some extent, ON was accounted for ~10-20% of the total fine particulate matter (PM) (Rastogi
72 et al. 2011; Zhang et al. 2002), while WSON was contributed >40% of ON for the samples
73 collected in Amazon Basin in dry season while biomass burning activities frequently occurred
74 (Mace et al. 2003b). In China, WSON was accounted for ~30% of the total nitrogen in Beijing
75 and ~40% of water-soluble nitrogen (WSN) in Xi'an, China (Duan et al. 2009; Ho et al. 2015).
76 Few studies have been conducted in Guangzhou, China. Li et al. (2012) found that WSON had
77 a composition of 17–21% of total nitrogen in precipitation samples. Besides, the compositions
78 of WSON were also found to be higher in rural (20–34%) than urban (12–13%) in this southern

79 Chines megacity (Yu et al. 2017). In marine environment, WSON could contribute ~84% of
80 the total dissolved nitrogen (TDN) in the aerosols (Violaki et al. 2015). The emissions of ON
81 species could be linked with high biological activities in surface ocean (Altieri et al. 2012). The
82 correlations between WSON in marine biogeochemical cycles and the roles in atmosphere were
83 well interpreted (Violaki et al. 2015). However, the investigation on the origins and chemical
84 compositions of WSON in PM were still restricted to marine environment (Kanakidou et al.
85 2012; Lesworth et al. 2010; Luo et al. 2015a).

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

92 **2. Materials and methods**

93 *2.1 Sampling locations and meteorological conditions*

94 Hong Kong is located on the eastern side of the Pearl River Estuary and characterized by
95 a subtropical climate dominated by the East Asian monsoon. The prevailing synoptic winds are
96 the northerlies and northeasterlies in winter, the easterlies in spring and autumn, and the
97 southwesterlies in summer. PM_{2.5} samples were collected at Tung Chung (TC, 22.289 °N,
98 113.943 °E), where the location is a residential town in southwest of Hong Kong (Figure 1).
99 TC is a new town and the Hong Kong International Airport is located ~3 km to the north of the
100 sampling location. At TC, major pollution sources include vehicular emissions from the
101 upwind urban areas to the east and the northeast, emissions from marine vessels in the water
102 channel to the north, and the power plants at Tap Shek Kok to the north and at Lamma Island

103 to the east. The air sampler is located on the rooftop of a four-floor building, ~16 m above the
104 ground level, in proximity of the heavily used North Lantau Highway (~60 m away).

106 *2.2 Sample collection*

107 Sampling campaign was conducted in four non-consecutive months: August– September
108 2011 in late summer; November–December 2011 in late autumn; February–March 2012 in late
109 winter and May 2012 in late spring. PM_{2.5} samples were collected on pre-fired (900 °C for 4 h)
110 quartz-fiber filters (20.3 cm × 25.4 cm, Whatman Inc., UK) using high volume (hi-vol)
111 samplers manufactured by Graseby Andersen (Palatine, IL, USA). The hi-vol sampler was
112 operated at flow rates of 1.13–1.41 m³ min⁻¹. Background contamination was monitored by
113 processing operational blanks (unexposed filters) simultaneously with field samples. The field
114 blanks were collected at the sampling location by mounting filters in the samplers without
115 purging through the air. The PM_{2.5} mass loadings were determined by gravimetric method for
116 which all filters were equilibrated in a controlled chamber at a temperature of 22±2 °C and
117 relative humidity (RH) of 35-45% for 24 hours. Each sample was weighed in triplicate
118 (weighing differences were <15 and < 20 µg before and after sampling, respectively) using a
119 MC5 electronic microbalance (±1 mg sensitivity, Sartorius, Gottingen, Germany). All samples
120 were stored in freezer (<-10 °C) prior the analysis.

122 *2.3 Free amino acid and primary amine analysis*

123 Detailed sample treatment and analytical procedures for measurement of free amino acids
124 and primary amines were shown in our previous publication (Ho et al., 2015). In brief, each
125 filter sample was extracted with Milli-Q water (resistivity:18.2 MΩ-cm) twice in an ultrasonic
126 water bath. The water extracts were then combined, filtered and concentrated to a volume of
127 0.5 mL by rotary evaporator before analysis (Yang et al. 2005). The extracts were then

128 derivatized with 6-aminoquinolyl-*N*-hydroxysuccinimidyl carbamate [AccQ-Fluor reagent
129 (AQC)] and AccQ.Tag borate buffer (WAT052880, Waters Corporation, Milford, MA, USA).
130 The derivatization step used for the calibration standards was identical compared with the
131 samples. The extraction recovery for the target organic nitrogen species ranged from 79.6 to
132 96.8 %.

133 The derivatized sample extracts or standards were injected into a high performance liquid
134 chromatography (HPLC, 1200 Series, Agilent Technology) equipped with a fluorescence
135 detector. The column used for separation was a 3.9×150 mm AccQ.Tag Amino Acid Analysis
136 Silica base bonded with 4 μm C-18 reversed-phase column (Waters Corporation) at 37 °C in
137 operation. The calibrations were demonstrated to be linear [correlation coefficient (r^2) >0.999].
138 The minimum detection limit (MDL) was obtained by analyzing ten replicates of the lowest
139 concentrations of standard solution, ranging from 0.036 to 0.086 nmol mL⁻¹ (equivalent to
140 0.262-0.626 pmol m⁻³). The measurement precision was in a range of 3.6-8.5 %. The
141 measurement uncertainties ranged from ±3.2 to ±9.1% for the target amino acids.

143 *2.4 Urea and non-primary amines analysis*

144 For urea, identification and quantification were performed by direct injection of the extract
145 to the HPLC coupled with a photodiode array detector (DAD) (1200 Series; Agilent
146 Technology). The target compound was separated with an C18 column (Cogent Bidentate,
147 4.6×150 mm, 4 μm particles size; Microsolv Technology, Leland, NC, USA) and detected at
148 an absorption wavelength of 210 nm. The MDL was 0.05 ng mL⁻¹ and measurement precision
149 was 3%.

150 Detailed sample preparation, derivatization steps, and instrumental parameters for
151 measurement of non-primary amines were shown in Ruiz-Jimenez et al. (2012). Dansyl
152 chloride in acetone (Sigma-Aldrich, St. Louis, MO, USA) was served as a derivatizing agent.

153 The derivatized products were then introduced to the HPLC (Series 1200; Agilent Technology)
154 was furnished with an Waters Sunfire C18 column (2.1×150 mm, 3.5 µm particle size) coupled
155 with an ion-trap mass spectrometer (Esquire 3000; Bruker Daltonics, Billerica, MA, USA).
156 The MDL for the non-primary amines ranged from 0.005-0.019 ng mL⁻¹. The precisions were
157 <6.9% by replicate analyses of standards.

159 *2.5 Other nitrogen analysis*

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

168 Determination of cations [i.e., potassium (K⁺), sodium (Na⁺), ammonium (NH₄⁺),
169 calcium (Ca²⁺) and magnesium (Mg²⁺)] and anions [nitrate (NO₃⁻), sulfate (SO₄²⁻) and chloride
170 (Cl⁻)] were followed the steps shown in Ho et al., (2015). The target ions were determined by
171 a Dionex-600 Ion Chromatograph (Dionex Inc., Sunnyvale, CA, USA). An IonPac AS14A
172 column (8 mM Na₂CO₃/1 mM NaHCO₃ as an eluent) was used for the anions analyses. For the
173 cation analyses, an IonPac CS12A column was used for separation (20 mM methanesulfonic
174 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
175 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
176 analysis. The certified values (within ±4 %) of reference materials (National Research Center
177 for Certified Reference Materials, China) were in good agreement for the five cations and three

178 anions. The measurement uncertainties ranged from ± 2.2 to $\pm 5.1\%$ for the targeted ions.

179 NH_4^+ , NO_2^- and NO_3^- were the major WSIN species in the aerosols, and WSON was
180 defined as the difference between WSN and WSIN. The concentrations of NO_2^- in all samples
181 were below the detection limit and thus considered as negligible. The calculation of WSIN and
182 WSON (nmol N m^{-3}) can be referred to the following equations:

$$183 \quad [\text{WSIN}] = [\text{NH}_4^+ - \text{N}] + [\text{NO}_2^- - \text{N}] + [\text{NO}_3^- - \text{N}] \quad (1)$$

$$184 \quad [\text{WSON}] = [\text{WSN}] - [\text{WSIN}] \quad (2)$$

186 3. Results and discussion

187 3.1 Concentrations of nitrogen fractions and other compounds

188 The abundances of major nitrogen fractions (i.e., WSN, WSIN and WSON) and
189 quantified individual compounds are tabulated on Table 1. The molar concentrations of WSN
190 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
191 concentrations of WSON and WSIN were in a range of 14.3-257.6 nmol N m^{-3} and 12.9-310.4
192 nmol N m^{-3} , respectively. The compositions of WSON in WSN were between 22.0 to 61.2%.
193 The average WSON in this study was >50% lower than in Qingdao (China) (Shi et al., 2010),
194 but higher than in Hawaii (U.S.), Keelung (Taiwan) and Tasmania (Australia) (Chen and Chen
195 2010; Mace et al. 2003a; Cornell et al. 2001). Although the levels in TC were lower than in
196 continental cities such as Xi'an and Beijing (China) (Shi et al. 2010; Duan et al., 2009; Wang
197 et al., 2013; Ho et al. 2015), they still exceeded those observed in Atlanta and Chapel Hill (U.S.)
198 (Rastogi et al. 2011; Lin et al. 2010). The average concentration of WSON in TC was consistent
199 with a study at East China Sea (Nakamura et al. 2006). The total concentrations of FAA ranged
200 from 779.7 to 2199.2 pmol m^{-3} , and its average of $1,264.5 \pm 393.0 \text{ pmol m}^{-3}$ was ~40% lower
201 than continental area in Xi'an (Zhang and Anastasio 2003; Ho et al. 2015), but ~4.0 times
202 higher than in Venice (Barbaro et al. 2011). The results in this study were consistent with

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203 findings in rural area of Guangzhou (China) (Song et al. 2017). Previous studies showed that
204 FAA could be separated as protein-type and non-protein-type amino acid (AA). The average
205 molar concentrations of total protein-type AA ($1147.5 \pm 358.6 \text{ pmol m}^{-3}$) were ~ 9.8 times higher
206 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
207 most abundant component, followed by alanine (Ala, $169.0 \pm 57.0 \text{ pmol m}^{-3}$), cysteine (Cys,
208 $161.1 \pm 55.9 \text{ pmol m}^{-3}$) and valine (Val, $117.6 \pm 37.1 \text{ pmol m}^{-3}$). These protein-type AA
209 accounted for $\sim 70\%$ of the total quantified FAAs. The results are consistent other studies that
210 Gly and Ala are the two most abundant FAAs (Barbaro et al. 2011; Violaki and Mihalopoulos
211 2010). Gly is a fundamental component in fibrous proteins in animals and intermediates in
212 products (Voet et al. 2008). However, Song et al. (2017) reported the four most abundant FAA
213 was in descending order: Gly > Val > methionine (Met) > phenylalanine (Phe) in rural area of
214 Guangzhou. Met is a unique constituent in protein for all living organism and potentially
215 attributed to biological origins (Song et al. 2017). The composition differences of FAA can be
216 used to distinguish source of origin (urban or rural area). β -alanine (β -Ala) (97.7 pmol m^{-3}) was
217 the most abundant non-protein AA component.

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218 The total concentrations of amine compounds ranged from $223.8\text{-}806.0 \text{ pmol m}^{-3}$.
219 Methylamine, ethylamine, and ethanolamine were the most abundant primary amines with
220 average concentrations of 263.6 ± 97.3 , 108.4 ± 28.2 , and $42.0 \pm 13.6 \text{ pmol m}^{-3}$, respectively. The
221 concentrations were lower than other studies in Xi'an and Guangzhou (China) (Ho et al. 2015;
222 Liu et al. 2017). The concentration of N-methylformamide was in a range of $13.6\text{-}57.1 \text{ pmol}$
223 m^{-3} and N-methylformamide was an abundant compound in TC. This compound can be
224 identified in solvents used in oil refineries and as precursor in amidation reactions (Sahoo and
225 Sit 2017). The concentration of urea ranged from 2.8 to 14.5 nmol m^{-3} . A previous study
226 showed that urea could be originated from natural and anthropogenic sources. The compound
227 is a commonly-used nitrogen fertilizer (Glibert et al. 2005). Further applications can be found

228 in different industrial processes such as manufacture of resins, glues, solvents, medicines,
229 cleaning products and cosmetics (Francis et al. 2002). The natural occurrence of urea could be
230 identified in marine and land environments as the compound is considered as final metabolite
231 of nitrogenous matter in mammals and marine species (Song et al. 2017). The levels in TC
232 were at least one order of magnitude higher than samples collected from marine environments
233 at Crete (Greece) and Tasmania (Australia) (Mace et al. 2003a; Violaki and Mihalopoulos,
234 2011) and rural areas such as Rondonia (Brazil) (Mace et al. 2003b). Nevertheless, the results
235 in this study were close to Qingdao (China) during non-dust period (Shi et al. 2010).

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237 3.2 Seasonal variations of WSON

238 Figure 2 illustrates seasonal variations of WS fractions. The highest average
239 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
240 observed in winter, coupled with highest average $\text{PM}_{2.5}$ concentration ($47.0 \pm 11.0 \text{ ug m}^{-3}$).
241 However, WSON showed highest average concentration ($95.0 \text{ nmol N m}^{-3}$) in summer and
242 WSN composition (49.3%) compared to other seasons (27.9-37.0%). The results were
243 consistent with other studies that inorganic species (e.g., nitrate) could have more contributions
244 to secondary aerosol formation compared to organic compounds (Cheng et al. 2016). This
245 observation could possibly be attributed to prevailing northerly winds transport the air
246 pollutants from mainland China in winter. The origins of WSON were due to dominant
247 southwesterly winds from marine in summer (Matsumoto et al. 2017). Seasonal emission
248 sources and meteorological factors (i.e., temperature, relative humidity, radiation and mixing
249 layer height) could influence formation and fate of organic nitrogen in atmospheric reactions
250 (Zhang et al. 2002). The total FAA concentration was $1548.3 \pm 331.5 \text{ pmol m}^{-3}$ in winter and in
251 a range of 19.3-42.4% higher than other seasons. The trend is, in descending order:
252 winter>autumn>spring> summer. No distinct variations of organic profiles (protein and non-

253 protein types) were observed in FAA. These could be attributed to complexity of marine
254 sources in urban areas. Song et al. (2017) reported the seasonal trend
255 (autumn>winter>summer>spring) on proteinaceous matters in PRD in China. A previous study
256 showed that biomass burning can be a major contributing source for FAA enrichment (Ho et
257 al. 2014). However, prevailing easterly wind in autumn could deter regional transport of
258 biomass burning products such as FAAs to TC sampling location. The highest concentrations
259 of amine ($564.1 \pm 124.9 \text{ pmol m}^{-3}$) and urea ($10.7 \pm 2.4 \text{ nmol m}^{-3}$) were observed in winter and
260 both compounds showed similar seasonal trends compared to FAA. Urea can be transferred
261 from sea surface via bubble-bursting processes and also evaporated from soil as part of
262 windblown materials. This compound can further be emitted from industrial activities (Violaki
263 and Mihalopoulos 2011). The above trends suggest that anthropogenic sources due to regional
264 transport could be a dominant factor under northerlies and north easterlies winds during winter.

3.3. Correlation between FAAs and oxidants

267 Figure 3 shows the correlations between FAAs and atmospheric oxidants (O_3 ,
268 NO and NO_x). Only a fair correlation ($r = 0.38$, $p < 0.01$) was observed between total FAAs and
269 O_3 . Ozone can promote release of FAAs from vegetation and enhance rate of chemical
270 oxidation, nitration and oligomerization of protein in atmosphere (Shiraiwa et al. 2012; Kampf
271 et al. 2015). In addition, second-order rate of reaction mechanism was identified between
272 protein and atmospheric oxidants. This observation could be due to reaction was dependent on
273 the abundances of precursor and O_3 (Liu et al. 2017; Shiraiwa et al. 2012; Kampf et al. 2015).
274 The results in this study are different from the rural area of PRD in China (Song et al.
275 2017). This observation points to possibly high local contribution for FAAs from plant
276 materials and living organisms. Fair correlations ($r = 0.32$, $p < 0.01$ and $r = 0.33$, $p < 0.01$,
277 respectively) were identified between Gly/Met and O_3 (Figure 3). The results imply that

278 biomass emissions and bioactivities were not the dominant sources for urban atmosphere under
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3 279 different wind directions. Fair correlations ($r < 0.32, p < 0.01$ and $r < 0.25, p < 0.01$, respectively)
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5 280 were also observed between total quantified amine/urea and O_3 (Figure 3). The
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7 281 observations suggest non-significant association between amine/urea compounds and
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9 282 the atmospheric oxidants in urban area. Aliphatic amines can be oxidized in the
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11 283 atmosphere by hydroxyl radicals ($\bullet OH$), nitrate radicals ($\bullet NO_3$) and O_3 , leading to the
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13 284 formation of secondary aerosol formation (Murphy et al. 2007). Highest concentration
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15 285 of total quantified amines was observed in TC during winter, and this can be used to
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17 286 explain higher potential contribution to the SOA formation (Huang et al. 2014).

287 The molar compositions of ON groups in WSON are shown in Figure 4. Highest
288 contribution of FAAs (4.7%) and amines (1.7%) were identified in spring. The result is
289 consistent with previous findings in urban area of Xi'an in China. The results could be
290 due to higher proteinaceous matter emissions from spores and pollens, and further lead
291 to possibly higher FAA formations from hydrolysis of combined amino acids (Ho et al.
292 2015). Moderate correlation ($r = 0.64$) was identified between urea and FAA (Figure 5).
293 Shi et al. (2010) reported that ~50% of urea existed in fine particulate matter ($< 2.1 \mu m$)
294 composition. These particles can undergo gas-particle conversion processes (Cornell et
295 al. 1998). Agricultural activities and particles from crustal origins were identified as
296 major contributors for urea (Chen and Chen 2008). The above-mentioned correlation
297 suggests that these groups of ON compounds can possibly be originated from the same
298 sources in TC sampling location.

300 3.4. Potential health impacts of WSON species

301 Referred to our previous work (Chuang et al 2015), we found that the increases of
302 inflammatory response in mice evidently related to particulate OC and free amino acids.

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303 The non-protein type amino acids could be among the environmental determinants of
304 the inflammatory allergic potency of PM_{2.5} on human respiratory system. Even though
305 the average concentrations of amino acids in TC were lower than those heavy-polluted
306 cities such as Xi'an, the widespread sources from urban and marine may have a mix of
307 contribution on the toxicity. In addition, the effects of the physicochemistry of amines
308 (e.g., nitroamines) on bioreactivity should be further investigated in such coastal urban
309 environments.

311 **4. Conclusion**

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

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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	WSN/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
Total Protein FAA	531.2	2000.4	1147.5	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				
Total Non-protein FAA	49.5	198.8	117.0	Urea (nmol m^{-3})	2.8	14.5	7.8
Total FAA (Protein + Non-Protein)	580.8	2199.2	1264.5				

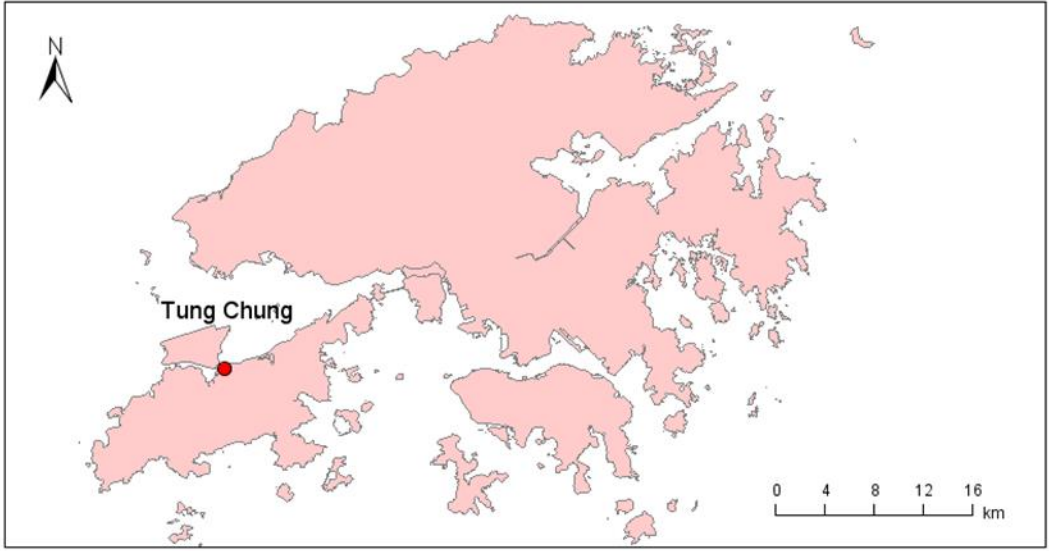
^a Below minimum detection limit.

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)								
<i>Protein type FAA</i>								
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
<i>Total Protein FAA</i>	982.8	263.7	988.7	450.9	1179.8	300.3	1406.8	300.3
<i>Non-protein type FAA</i>								
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
<i>Total Non-protein FAA</i>	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
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.

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

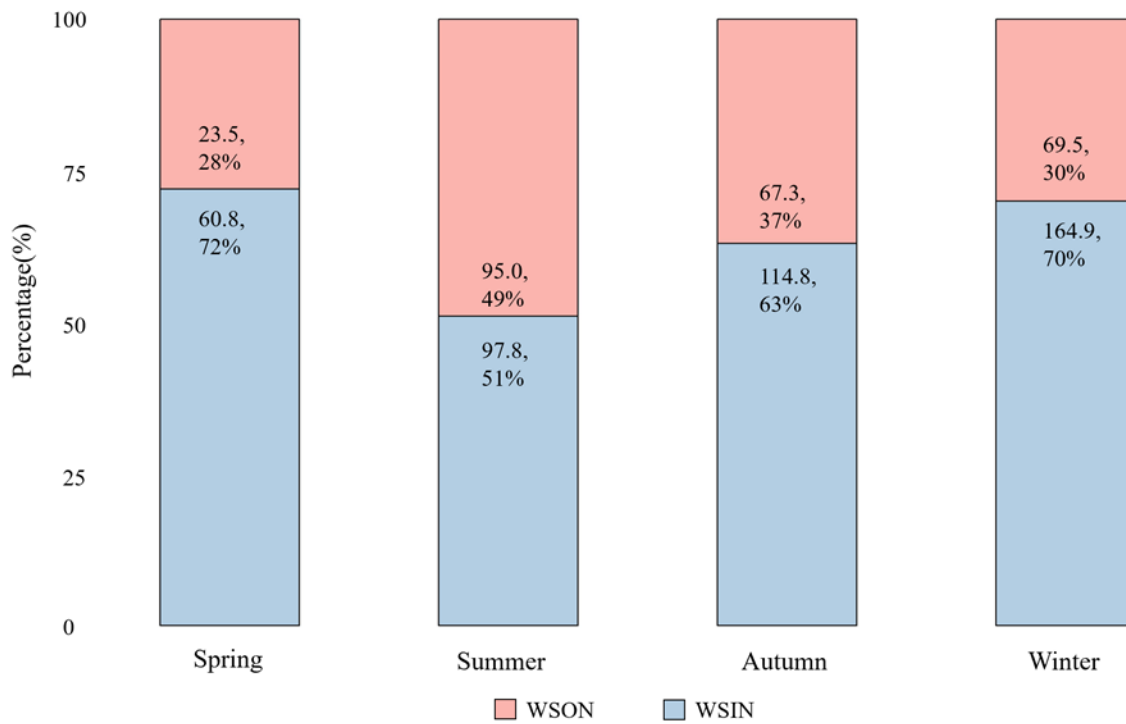


Figure 2. Seasonal variations of WSON and WSIN fractions. The values denote molar concentration (nmol N m⁻³) and molar composition (%).

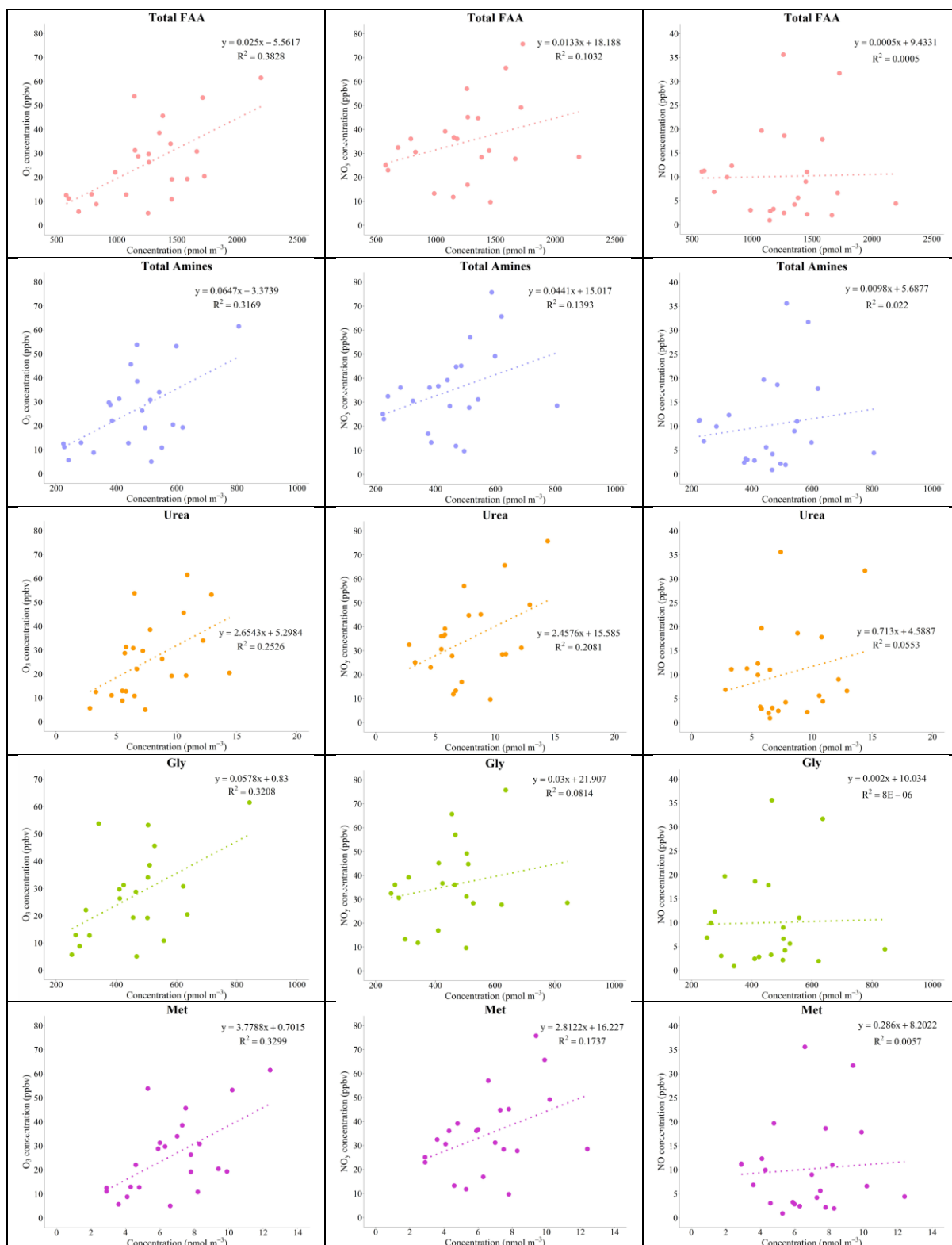


Figure 3. Relationships between concentrations of total FAA, total amines, urea, glycine (Gly) and methionine (Met) in relation to O₃, NO and NO_y.

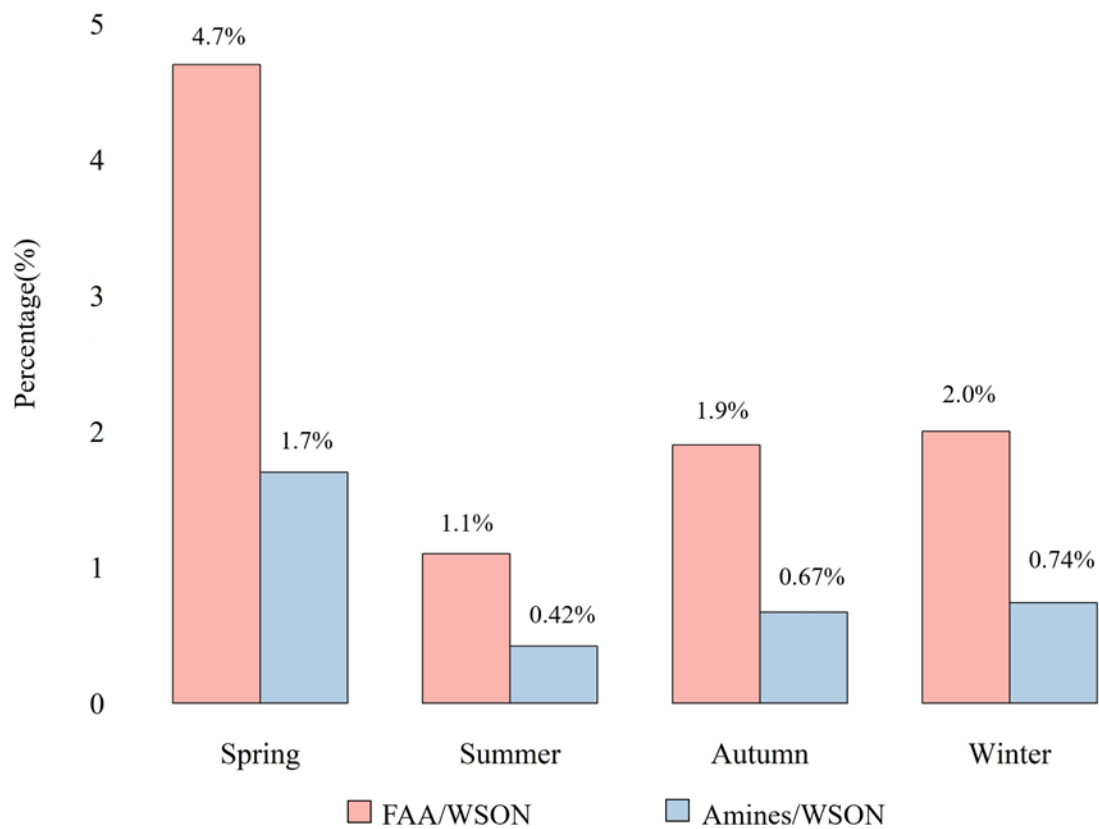
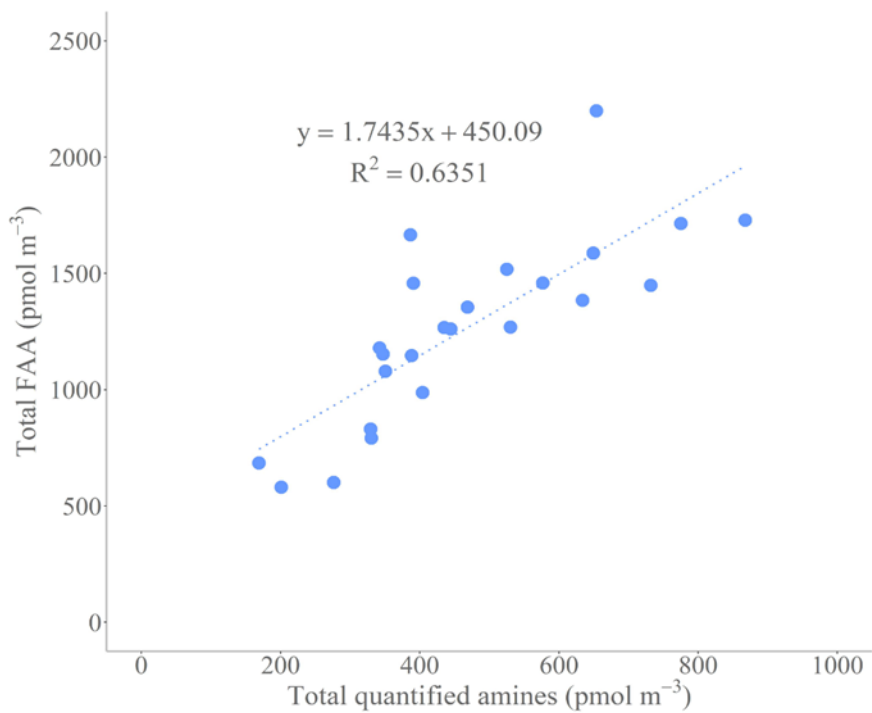


Figure 4. Molar compositions of total FAA and total quantified amines in WSON in different seasons.

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

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