

C1-C2 alkyl aminiums in urban aerosols: Insights from ambient and fuel combustion emission measurements in the Yangtze River Delta region of China[☆]

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Abstract

We measured low molar-mass alkyl aminiums (methylaminium, dimethylaminium, ethylaminium and diethylaminium) in urban aerosols in the Yangtze River Delta region of eastern China in August 2014 and from November 2015 to May 2016. After examining artifact formation on sample filters, methylaminium, dimethylaminium and ethylaminium concentrations were quantified. The three C1-C2 aminiums exhibited a unimodal size distribution that maximized between 0.56 and 1.0 μm . Their concentrations in $\text{PM}_{2.5}$ were $5.7 \pm 3.2 \text{ ng m}^{-3}$, $7.9 \pm 5.4 \text{ ng m}^{-3}$ and $20.3 \pm 16.6 \text{ ng m}^{-3}$, respectively, with higher concentrations during the daytime and in warm seasons. On new particle growth days, amine uptake to particles larger than 56 nm was barely enhanced. The molar ratios of individual aminium/ NH_4^+ in $\text{PM}_{2.5}$ were on the order of 10^{-4} and 10^{-3} . Aminiums were thus far less to out-compete ammonium (NH_4^+) in neutralizing acidic species in particle sizes down to 56 nm. Abundant nitrate ($\text{NO}_3^-/\text{SO}_4^{2-}$ molar ratio = ~ 3) and its correlation to methylaminium and ethylaminium implied that nitrate might be more important aminium salt than sulfate in urban aerosols of this area. Direct measurement of particle-phase amine emission from coal and biomass burning showed that coal burning is an important atmospheric

amine source, considering coal burning is top-ranked particulate matter source in China.

Aminiums cannot out-compete ammonium in neutralizing acidic species in particle sizes down to 56 nm. Their uptake to particles >56 nm was barely enhanced on new particle growth days. Coal burning is an important atmospheric amine source.

Keywords: Atmospheric amines; Urban aerosol composition; New particle growth; Fuel combustion emission

1 Introduction

Amines are highly hydrophilic basic compounds like ammonia (NH₃). Atmospheric amines are emitted from a variety of anthropogenic and natural sources, including animal husbandry, industry activities, combustion, automobiles, sewage treatment, oceanic emission, vegetation, etc. (Ge et al., 2010). The contribution of amines to the total reduced nitrogen in the atmosphere was estimated to be around one-third (Neff et al., 2002). The most common atmospheric amines are C1-C6 alkylamines.

As semi-volatile reactive compounds, amines are likely to contribute to aerosols via (a) acid-base chemistry (Murphy et al., 2007; Wang et al., 2010), (b) displacement reaction with ammonium (Bzdek et al., 2010; Chan and Chan, 2012; Qiu et al., 2011), (c) condensation of gas phase oxidation products (Tang et al., 2013), (d) partitioning into atmospheric aqueous phase (Chan and Chan, 2013; McGregor and Anastasio, 2001; Sellegri et al., 2005) or (e) direct emission in particle phase (Sodeman et al., 2005; Tran and Marriott, 2008). Particle-phase amines may further react with carbonyl compounds (De Haan et al., 2009) or oxidants (Zahardis et al., 2008), leading to more oxidized compounds. Comprehensive review of the thermodynamic properties and multiphase chemistry of amines can be found in Ge et al. (2011) and Qiu and Zhang (2013). Recently, many attentions were paid to atmospheric amines because of their potential importance in atmospheric new particle formation (NPF) (Almeida et al., 2013; Glasoe et al., 2015; Kirkby et al., 2011; Kulmala et al., 2013; Kurtén et al., 2008; Loukonen et al., 2010; Smith et al., 2010; Yu et al., 2012; Zhao et al., 2011).

Global modeling suggested that amine-driven nucleation is most important in the boundary layer of polluted source areas (Bergman et al., 2015; Dunne et al., 2016). Being potential source area, heavily polluted urban regions are recently becoming hotspots of NPF studies (Herrmann et al., 2014; Kanawade et al., 2014; Kulmala et al., 2016; Nie et al., 2014; Stanier et al., 2004; Wang et al., 2014, 2015; Xiao et al., 2015; Yu et al., 2016a). There are just a few measurements of particle-phase amine in urban aerosols around the world (Huang et al., 2014, 2016; Tao et al., 2015; VandenBoer et al., 2011; Yang et al., 2005; Youn et al., 2015; Zhang et al., 2002). The measurements on amine emissions from fuel combustion sources are even scarcer. So far, there is no direct measurement of amines from coal or biomass burning emissions, which are top-ranked particulate matter (PM) sources in China. The absence of amine emission inventories, in either gas phase or particle phase, leads to high uncertainties of present global/regional models in simulating their atmospheric distribution and aerosol contribution (Yu and Luo, 2014).

Due to their low concentrations, particle-phase aminiums were most commonly measured with filter collection and subsequent off-line analysis using gas chromatography (GC), liquid chromatography (LC) and ion chromatography (IC) combined with mass spectrometers (MS) or fluorescence detectors. A review of these sampling and analysis techniques for airborne amines could be found in Szulejko and Kim (2014). Two inherent problems of such off-line methods are unresolved aminium peaks due to co-elution and possible sampling artifacts (Mäkelä et al., 2001; Yu et al., 2016b). Particle or gas phase amines have also been measured successfully using online IC coupled with Particle-Into-Liquid Sampler (PILS) or URG Ambient Ion Monitor system (Sorooshian et al., 2008, 2009; VandenBoer et al., 2011). Other techniques like electrospray ionization MS (Roach et al., 2010), selective-ion-flow-tube MS (Nosedá et al., 2010), ion-mobility spectrometry (Karpas et al., 2013), Fourier transform infrared spectroscopy (FTIR, Mertens et al. (2012)), time-of-flight aerosol MS (Healy et al., 2015) were rarely used, because of their limitation to speciate and quantify amines or relatively high cost.

China is suffering from severe atmospheric PM pollution in recent years. In this study we investigated particle-phase aminiums in the urban aerosol of the Yangtze River Delta (YRD) region, one of the most populated and industrialized areas in eastern China. The results of size distribution, temporal variations and relations to major aerosol components were presented. Particle-phase aminium emissions from coal and biomass burning were measured and their importance in atmospheric amine was firstly discussed.

2 Methods

Ambient aerosols were collected from two urban sites in the YRD region, which covers 2.1×10^5 km² with 170 million residents. Urban site 1 (32.33°N, 119.33°E) is a national air monitoring station in downtown area of Yangzhou. Urban site 2 (32.30°N, 118.72°E) is 68 km to the east of urban site 1 and located in a university campus that is about 15 km to the northwest of the downtown area of Nanjing. Details of ambient and laboratory sample

collections are present in [Table 1](#).

Table 1 Summary of sample collections and analyses in the atmosphere and from coal and biomass burning emissions.

alt-text: Table 1

Number of samples or sample sets	Sampling site, duration and period	Sampler	Chemical analysis	Purposes
103	Urban site 1, 23 h, 11/13/2015–4/6/2016	hi-volume air sampler, PM _{2.5} inlet (QG-1000, Qingdao Jingcheng Ltd., China, flow rate: 1.05 m ³ min ⁻¹)	aminium, ECOC, cation and anions	monthly variation, relations to major components
72	Urban site 2, 3 h/daytime sample and 11.5 h/nighttime sample, 4/12/2016–5/11/2016	medium-volume air sampler (TH-150C, Wuhan Tianhong Ltd., China, flow rate: 100 L min ⁻¹)	aminium, ECOC	diurnal variation
21	Urban site 2, 23 h, 8/11/2014–9/2/2014	nano-MOUDI (122R, MSP Corp., Shoreview, MN, flow rate: 30 L min ⁻¹), SMPS (DMA3081 and CPC3775, TSI Inc., St. Paul, MN, scan range: 8–350 nm)	aminium, ECOC, cation and anions	size distribution, growth event analysis
31	laboratory controlled coal and biomass burning	Dekati Fine Particle Sampler (FPS-4000, Dekati Ltd., Finland)	aminium, ECOC, cation and anions	Particle-phase aminiums from coal and biomass burning

2.1 Ambient sample collections

A total of 103 daily PM_{2.5} samples were collected using a high-volume air sampler at site 1 from November 2015 to April 2016. PM_{2.5}, trace gases and environmental variables (e.g., temperature and RH) were routinely monitored during this period by local air monitoring station. In order to investigate the diurnal variations of aminiums, a median-volume air sampler was deployed at site 2 from April to May 2016 to collect 4 p.m.-2.5 samples each day for 18 days. The four samples represent morning (sampling time: 8:00–11:00), noon (11:30–14:30), afternoon (15:00–18:00) and nighttime (20:00–7:30), respectively.

21 sets of size-resolved daily samples were collected at site 2 in August 2014 using a nano micro-orifice uniform deposit impactor (nano-MOUDI, [Marple and Olson \(1999\)](#)). The nominal cutoff diameters are 18, 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.1, 0.056, 0.032, 0.018 and 0.01 μm. A scanning mobility particle sizer (SMPS) with a size scan range of 8–350 nm was deployed in parallel to the nano-MOUDI to monitor NPF in the atmosphere. Quartz fiber filter (Whatman, Maidstone, England) was used as collection substrates for both filtration (hi-vol or medium-vol sampler) and impactor (nano-MOUDI) samples. Possible amine background in the filters were prebaked at 450 °C for 4 h. All samples were stored at –4 °C before chemical analysis.

2.2 Collection of particles from coal and biomass burning emissions

We purchased 5 types of coal briquettes of different origins from local market and collected 4 types of local biomass fuels (pine wood, cedar wood, straw and bamboo). Known amount of coal or biomass fuel was burned in a constant exhaust flow in a residential stove. A dilution sampling system (FPS-4000, DEKATI, Finland) draw a sample flow of 1 L per minute (L min⁻¹). The FPS-400 system was designed to provide sufficient dilution, cooling and residence time to mimic real-world fuel burning emission of all condensable products. After dilution with particle-free air to about ~20 L min⁻¹, PM_{2.5} in the sample flow was filtered onto a quartz fiber filter. A SMPS sampled a split flow of ~1.5 L min⁻¹, for a short period, to measure particle number size distribution. It showed the emissions were characterized by a condensation mode with peak diameter around 50–300 nm. A total of 31 samples were collected for 9 fuel types. Aminium emission factor (mg kg⁻¹) can be estimated from aminium amounts on the sample filter, the exhaust flow rate, the sample flow rate and fuel consumption.

2.3 Chemical analysis

Chemical analyses for all types of samples are also summarized in [Table 1](#). Elemental Carbon (EC) and Organic Carbon (OC) were measured using a thermal-optical carbon analyzer (DRI, 2001A, Atmoslytic Inc. Calabasas, CA) on filter punches. The rest of a filter was ultrasonically extracted with known amount of deionized water (18.2 MΩ cm). The extract was then filtered through a 0.45 μm PTFE syringe filter. Cation (NH₄⁺) and anions (SO₄²⁻, NO₃⁻ and Cl⁻) in the filtrate were analyzed for hi-vol, nano-MOUDI and fuel combustion samples using an IC system (DX500, Dionex, Sunnyvale, CA). The IC analysis procedure followed [Yang et al. \(2005\)](#) and [Yu et al. \(2010\)](#). Ion concentration in the air was calculated base on the observed mass in the filtrate, extract volume, sampling air volume and the difference between punch area and aerosol-deposit area.

Aminiums in the filtrate were analyzed for all samples. The derivatization and analysis of aminiums followed the method of Asif Iqbal et al. (2014); Cháfer-Pericás et al. (2005); Herráez-Hernández et al. (2006). To 8.6 mL of filtered extract, 1 mL of borate buffer (pH 8.5) and 0.4 mL of 9-fluorenylmethyl chloroformate solution (FMOC) were added. The extract reacted at room temperature for 30 min prior to injection into a HPLC (Waters e2695, Milford, MA, USA) with a fluorescence detector (Waters 2475). Excitation and emission wavelengths were 264 and 313 nm, respectively. Aminium separation was accomplished using an optimized acetonitrile-water gradient elution program in an Athena C18-WP analytical column (4.6 × 250 mm, 5 μm). Five calibration solutions of different concentrations were prepared using a mixture of aminium standards (hydrochloride salts of methylamine, dimethylamine, trimethylamine, ethylamine and diethylamine). The calibration standards were analyzed as their derivatives in triplicate to obtain calibration curves. All chemicals including the buffer solution (NaOH, H₃BO₃), FMOC chloride, acetonitrile and aminium standards were HPLC grade or the highest grade commercially available from Aldrich.

Fig. 1 is the chromatogram of a mixture of aminium standards. The relative ordering of retention times of FMOC, methylaminium (MA), dimethylaminium (DMA), ethylaminium (EA) and diethylaminium (DEA) derivatives is the same as that reported by Cháfer-Pericás et al. (2005). Trimethylaminium-FMOC reaction is very slow, especially in aqueous solution where trimethylaminium is protonated (Asif Iqbal et al. (2014); Szulejko and Kim, 2014). As a result, trimethylaminium peak is absent from the chromatogram and cannot be identified in this study. Detection limits were 0.01–0.03 ng mL⁻¹ for MA and DMA and 0.12–0.14 ng mL⁻¹ for EA and DEA. The recoveries determined by analyzing laboratory blank filters spiked with known amounts of aminium standards ranged from 84.3% to 97.1%.

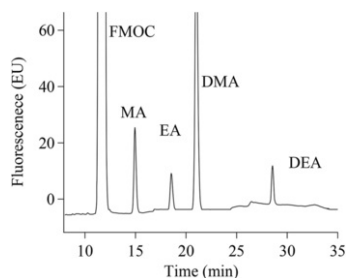


Fig. 1 HPLC chromatogram of standard solution containing FMOC and aminium derivatives.

alt-text: Fig. 1

2.4 Amine artifact formation on sample filters

Low molar-mass alkyl aminiums are semi-volatile compounds. There are two possible artifact sources (1) amine background may form on quartz fiber filters due to gas adsorption or nitrate and chloride salt formation (with HNO₃ and HCl) when air is drawn through or impinges on the filters. (2) Particle bounce-off from upper MOUDI stages to lower stages may create artificial aerosol loading on the lower stages. The bounce-off issue may be severe for the lowest 3 stages (10–18 nm, 18–32 nm and 32–56 nm) of nano-MOUDI, considering the low aerosol loading on these 3 stages. Furthermore, 90-mm quartz fiber filters mounted on these 3 stages may suffer from more adsorption background than 47-mm filters on the upper 10 stages (surface area: 63.59 cm² vs. 17.34 cm²). Therefore, unreliable data from the lowest 3 stages were discarded in this study. That is, we simply used the nano-MOUDI as a regular MOUDI. In future, we recommend greased aluminum foil as impaction substrate for sub-56 nm particle collection to minimize adsorption and bounce-off, as well as more sensitive amine analytical method.

To correct adsorption/salt formation artifact, a backup filter was mounted below a front sample filter for all the filtration samples (hi-vol or medium-vol samplers). The field adsorption/salt formation background on the front and backup filters was assumed to occur to an equal extent. For the MOUDI samples, a different artifact correction approach was used: additional 5 sets of field blank filters were collected by drawing air through the MOUDI for 24 h with particles being removed by a HEPA filter installed in the upstream of MOUDI inlet. These blank filters were supposed to be saturated with amines from the gas phase (field background), just like real sample filters. When collecting real samples, the HEPA filter was not installed. The amount of amine on the filter was thus the sum of particle-phase amine and field background.

Chemical analysis showed that for the filtration samples, MA, DMA, EA and DEA amounts detected on the backup filters were on average 14% (range: 4–26%), 21% (4–50%), 1.6% (0–6%) and 68% (20–120%) of those on the front filters. Fig. 2 shows a comparison between aminiums (and OC) detected on real MOUDI sample filters on August 17, 2014 (red squares) and the adsorption/salt formation background (black dots). These results thus indicated that the DEA detected on filtration samples and impactor samples was mostly due to gas adsorption or salt formation. i.e., particle-phase DEA amount was negligible.

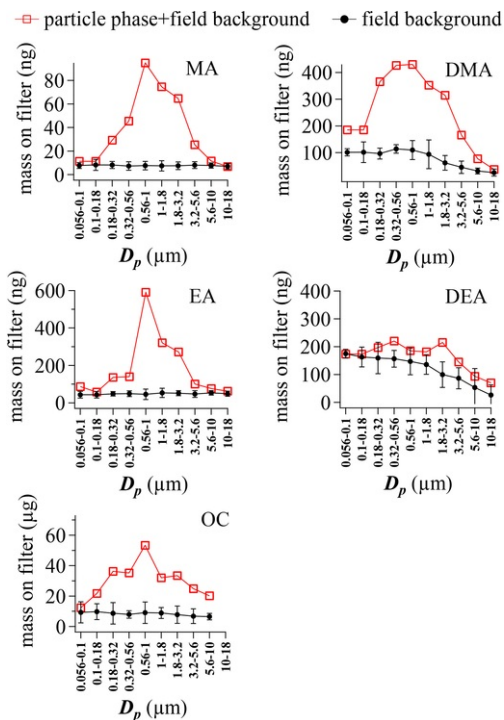


Fig. 2 A comparison of amine or OC amount that deposited on quartz fiber filters of nano-MOUDI stages (particle phase + field background) and gas adsorption or salt formation background that formed on the filters (field background) on August 17, 2014.

alt-text: Fig. 2

By analyzing laboratory blanks, we excluded the possibility that DEA background on the filters came from prebaked clean filter, DI water, acetonitrile, buffer solution or contamination in the glassware or HPLC. Our observations thus led to a conclusion that particle-phase DEA is almost negligible in comparison to the gas phase, while MA, DMA and EA have higher particle-phase fractions than DEA. This seems to contradict with the understanding that DEA is less volatile and its nitrate or chloride salt has smaller dissociation equilibrium constant than MA, DMA and EA (Ge et al., 2011; Murphy et al., 2007). There may be two possibilities to explain our observations. First, ambient DEA was below the detection limit of our HPLC method. The DEA peak in the samples was in fact from another unknown co-eluting species that predominately resides in the gas phase. Second, DEA in the particles was displaced by some other amine molecules (Bzdek et al., 2010; Chan and Chan, 2012; Qiu et al., 2011) and thus resided mainly in the gas phase. In either possibility, the observed DEA was largely due to sampling artifact. Therefore, only MA, DMA and EA were quantified in this study after correcting the adsorption/salt formation background. DEA concentration was also not reported in previous studies using HPLC derivatization methods; or DEA co-eluted with TMA in the studies using IC method (see Table 2 and references therein).

Table 2 Summary of low MW amine concentrations in urban, marine/coastal or forest aerosols, measured using offline sampling and subsequent HPLC, IC or GC/MS analysis. AQC: 6-Aminoquinolyl-N-hydroxysuccinimidyl carbamate, OPA: o-Phthalaldehyde.

alt-text: Table 2

Location	Concentration in aerosols (ng m ⁻³)	Method and detection limits	References
Nanjing and Yangzhou, China	MA 5.7 ± 3.2, DMA 7.9 ± 5.4, EA 20.3 ± 16.6	FMOC derivatization-HPLC fluorescence	This work
Nanjing, China	MA 0.5–54.4, EA 1.3–20.9, ethanolamine 0.3–14.4	AQC derivatization-HPLC fluorescence	Yang et al. (2005)
Shanghai, China	DEA + TMA 38.8 ± 17.0, EA 11.5 ± 17.4, DMA:15.7 ± 7.9, MA 8.9 ± 6.1 in PM _{1.8}	IC	Tao et al. (2015)

Shanghai, China	EA 0.24, MA 2.35	online OPA derivatization in HPLC auto-sampler	Huang et al. (2016)
Hong Kong, China	MA 10–30, DMA 20–90, EA 3–7, DEA 40–140	GC/MS, IC	Huang et al. (2014)
Davis, CA, USA	MA 1.8–5.5, ethanolamine 0.4–6.7	OPA derivatization-HPLC fluorescence	Zhang et al. (2002)
Tucson, USA	DMA 9.3–20.5	IC	Youn et al. (2015)
Toronto, Canada	16–81, mainly DMA and TMA + DEA	IC	VandenBoer et al. (2011)
Boreal forest, Finland	DMA 20–100	IC	Mäkelä et al. (2001)
Eastern China sea	Summer: DMA 34.2 ± 5.4 , TMA 55.8 ± 7.8 ; spring: DMA 9.9 ± 5.4 , TMA 16.8 ± 9.6	IC	Yu et al. (2016)
Remote tropical east Atlantic Ocean	MA 0–0.03, DMA 0.13–0.36, DEA 0.005–0.11 during spring algal bloom; MA 0.002–0.52, DMA 0.1–1.4, DEA 0.09–0.76 during winter algal bloom	AQC derivatization- HPLC/ESI-ITMS	Müller et al.(2009)
Marine aerosol over the North Atlantic	DMA 2–24, DEA 4–32 during high biological activity periods	IC	Facchini et al. (2008)
Airborne sampling in Asia Pacific region	MA, EA and ethanolamine 3.4–24.5 totally	AQC derivatization-HPLC fluorescence	Mader et al. (2004)

3 Results and discussion

3.1 Monthly and diurnal variations of aminiums in urban aerosols

Aminium concentrations in the hi-volume PM_{2.5} samples were MA: 4.9 ± 1.9 ng m⁻³, DMA: 4.3 ± 2.4 ng m⁻³ and EA: 15.4 ± 8.1 ng m⁻³ from November 2015 to April 2016 at site 1. Aminium concentrations in the medium-volume PM_{2.5} samples collected at site 2 during April–May 2016 were 7.6, 4.2 and 21.7 ng m⁻³ on average for MA, DMA, and EA respectively, which were quite close to those in April at site 1. [Table 2](#) summarizes recent publications of aminium concentrations in urban aerosols, as well as marine/coastal/forest aerosols. To facilitate comparison, we selected only the measurements using offline sampling and subsequent HPLC, IC or GC/MS analysis. The observed concentrations of low molar-mass aminiums (e.g., MA, DMA, TMA, EA, DEA, ethanolaminium) in urban aerosols are on the order of a few to tens of ng m⁻³. An exception is [Huang et al. \(2016\)](#) who reported ethylaminium of sub-ng m⁻³ level in Shanghai, China. Similar particle-phase concentrations were also observed in boreal forest and marine/coastal air masses ([Facchini et al., 2008](#); [Mäkelä et al., 2001](#); [Mader et al., 2004](#); [Yu et al., 2016b](#)), except that [Müller et al. \(2009\)](#) observed sub-ng m⁻³ MA, DMA and DEA over remote tropical east Atlantic Ocean.

On a daily basis there was no correlation between temperature and aminium concentration (Pearson's correlation coefficient $R = 0.18$ – 0.2 , $n = 103$, [Table 3](#)), however, aminiums and temperature followed a similar monthly variation from November to April ([Fig. 3](#)), as opposite to PM_{2.5} and NH₄⁺. That is, aminiums were lowest in the coldest January 2016 and increased with temperature in warm months. In August 2014 aminiums in the MOUDI-reconstructed PM_{1.8} were MA 7.2 ± 4.1 ng m⁻³, DMA 18.0 ± 11.7 ng m⁻³, and EA 36.4 ± 18.6 ng m⁻³ at site 2. The highest concentration in summer was consistent with the positive temperature dependence of particle-phase aminiums.

Table 3 Aminium/NH₄⁺ molar ratios, aminium/OC mass ratios and Pearson's correlation coefficients between aminiums and ions, trace gases and environmental variables at urban site 1 from November 2015 to April 2016 (103 samples). Correlation coefficients >0.6 are shown in bold.

alt-text: Table 3

	MA	DMA	EA
Concentration (ng m ⁻³)	4.9 ± 1.9	4.3 ± 2.4	15.4 ± 8.1
Aminium/NH ₄ ⁺ molar ratio (10 ⁻⁴)	2.7 ± 1.2	1.6 ± 0.9	5.4 ± 2.2
Aminium/OC mass ratio (10 ⁻⁴)	4.0 ± 2.1	3.7 ± 2.8	11.9 ± 6.0

Aminium	MA	1	0.62	0.81
	DMA	0.62	1	0.55
	EA	0.81	0.55	1
Aerosol	PM _{2.5}	0.51	0.28	0.48
	OC	0.59	0.24	0.58
	EC	0.43	0.15	0.48
	SO ₄ ²⁻	0.46	0.31	0.52
	NO ₃ ⁻	0.67	0.38	0.67
	NH ₄ ⁺	0.62	0.39	0.66
	K ⁺	0.46	0.21	0.43
	Ca ²⁺	-0.06	-0.07	-0.08
	Na ⁺	-0.00	-0.08	-0.14
	Cl ⁻	0.50	0.30	0.59
	Trace gas	NO ₂	0.72	0.41
SO ₂		0.43	0.14	0.50
CO		0.56	0.25	0.60
O ₃		-0.14	-0.09	0.08
Environmental variables	Temperature	0.18	0.19	0.20
	RH	0.26	0.32	0.12

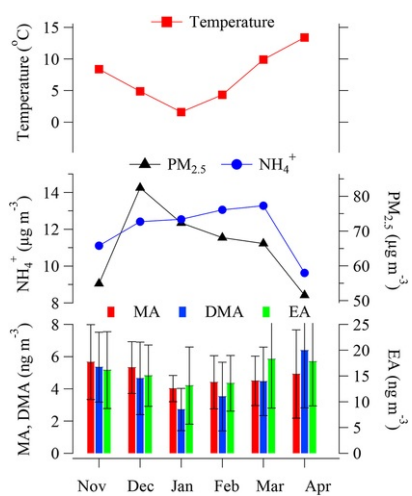


Fig. 3 Monthly variation of temperature, NH₄⁺, PM_{2.5} and aminiums (MA, DMA and EA) from November 2015 to April 2016.

alt-text: Fig. 3

Fig. 4 shows the diurnal variations of aminiums, EC, OC and temperature. Daytime concentrations were first normalized over nighttime concentration. Normalized C/C_{night} ratios were then averaged for 18 days during April-May 2016. Both EC and OC had lower daytime concentrations than nighttime, probably as a result of the lift of mixing height during the daytime. In contrast, aminiums had higher daytime concentrations than nighttime. However, aminiums did not follow exactly the same pattern as temperature: temperature was highest in the afternoon (15:00-18:00), whereas aminiums were highest in the morning (8:00-11:00).

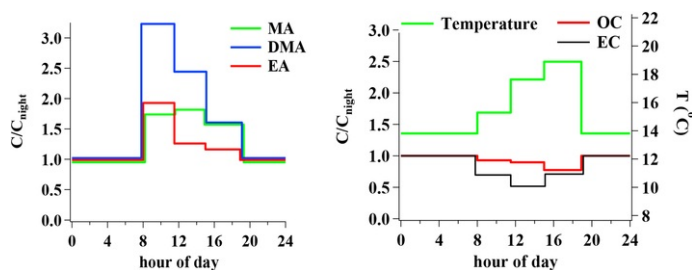


Fig. 4 Average diurnal variations of aminiums (MA, DMA and EA), EC, OC and temperature at urban site 2 from April to May 2016. Concentrations were normalized over nighttime concentrations.

alt-text: Fig. 4

The mechanism behind such diurnal and seasonal variations of aminiums is unknown. It is clearly that temperature was not the only dictating factor of aminium variations. An explanation could be like this: on a seasonal basis, amine emissions and aminium concentrations are higher in warm seasons than cold seasons. On a diurnal basis, higher level of human and biological activities in the morning, such as industry, combustion, automobiles, sewage treatment, and vegetation, triggers amine emission into the atmosphere. However, further increase of temperature in the afternoon drives amine to repartitioning from particles to gas phase, which results in a decreasing aminium trend from the morning to the afternoon.

3.2 Relations to major aerosol components

Molar ratios of individual aminium to ammonium (aminium/ NH_4^+) were on the order of 10^{-4} from November 2015 to April 2016 (Table 3). In the summer of August 2016 DMA/ NH_4^+ and EA/ NH_4^+ increased to the order of 10^{-3} due to higher aminium concentrations. These ratios are generally much lower than those reported in the literature, in which DMA/ NH_4^+ ratio was up to 0.04 in sub-micron particles in Tucson, USA (Youn et al., 2015) and total aminium/ NH_4^+ was up to 0.17 in $\text{PM}_{1.8}$ in Toronto, Canada (VandenBoer et al., 2011). Since aminium levels are on similar order of magnitude at different urban sites, the variation of ratios depends mainly on the mass loading of NH_4^+ . In our area low aminium/ NH_4^+ most likely resulted from significantly higher ambient NH_3 concentration than amines. For example, Zheng et al. (2015) reported that NH_3 mixing ratio at urban site 2 was 3 orders of magnitude higher than the sum of C2-amines (1.7 ppbv vs. 3.9 pptv).

Our measurement showed that NH_4^+ was the dominant cation and balanced 90% of the sum of SO_4^{2-} , NO_3^- , and Cl^- . Molar ratios of $2 \times \text{SO}_4^{2-}/\text{NH}_4^+$, $\text{NO}_3^-/\text{NH}_4^+$ and $\text{Cl}^-/\text{NH}_4^+$ were 0.4, 0.6 and 0.11, respectively. This indicates that gas phase NH_3 was excessive in neutralizing aerosol H_2SO_4 and ~60% of NH_4^+ existed in the form of nitrate or chloride (mostly nitrate) in the particles. These ratios again imply that amine played a very minor role in neutralizing aerosol acidic species in this area. Our observation is thus different from other urban (Tao et al., 2015) or airborne measurements (Lee et al., 2003), which showed that acidic fine particles were not fully neutralized by NH_3 and the presence of high concentration amines contribute significantly to the neutralizing capacity of particles.

HNO_3 played more important role than H_2SO_4 in neutralizing NH_3 ($\text{NO}_3^-/\text{SO}_4^{2-}$ molar ratio: ~3). Considering amines are basic compounds like ammonia, nitrate may also be important salt form of amines. Correlation analysis showed that Pearson's correlation coefficients are highest between aminiums and NO_3^- (MA vs. NO_3^- : 0.664, EA vs. NO_3^- : 0.672, Table 3), followed by those between aminium and NH_4^+ (MA vs. NH_4^+ : 0.619, EA vs. NH_4^+ : 0.661). These correlation coefficients are higher than those with SO_4^{2-} . Aminiums also showed high correlation coefficients with NO_2 (0.717 and 0.705 for MA and EA, respectively). Similarly, a high Pearson's correlation coefficient of 0.728 between nitrate and DEA was observed in the Gulf of Mexico by Sorooshian et al. (2007), who suggested the presence of DEA nitrate in aerosols. Therefore, the correlation analysis also supports that nitrate was more important aminium salt than sulfate in the particles.

3.3 Size distributions

Fig. 5 shows the histograms of mass percentages in nine size bins between 0.056 and 10 μm for three aminiums, NH_4^+ , SO_4^{2-} , NO_3^- , EC and OC. All species exhibited a unimodal distribution that maximized between 0.56 and

1.0 μm . Coarse mode DMA, NO_3^- and OC were also seen. The predominance of droplet mode suggests that aminium formation probably experienced similar processes like NH_4^+ , SO_4^{2-} and NO_3^- . The peak diameter of 0.56-1.0 μm at our urban sites was the same as the measurement in Shanghai (Tao et al., 2015), but larger than those between 180 and 560 nm in the urban aerosols of North America (VandenBoer et al., 2011; Youn et al., 2015) and in marine aerosols (Facchini et al., 2008; Mäkelä et al., 2001; Müller et al., 2009; Maudlin et al., 2015; Miyazaki et al., 2010; Violaki and Mihalopoulos, 2010; Yu et al., 2016b). Yu et al. (2016b) reported an additional mode between 0.01 and 0.1 μm for DMA and TMA in marine aerosols using nano-MOUDI. In our study, we did not quantify aminiums below 56 nm due to high adsorption/salt formation background on stage 11-13 of the nano-MOUDI.

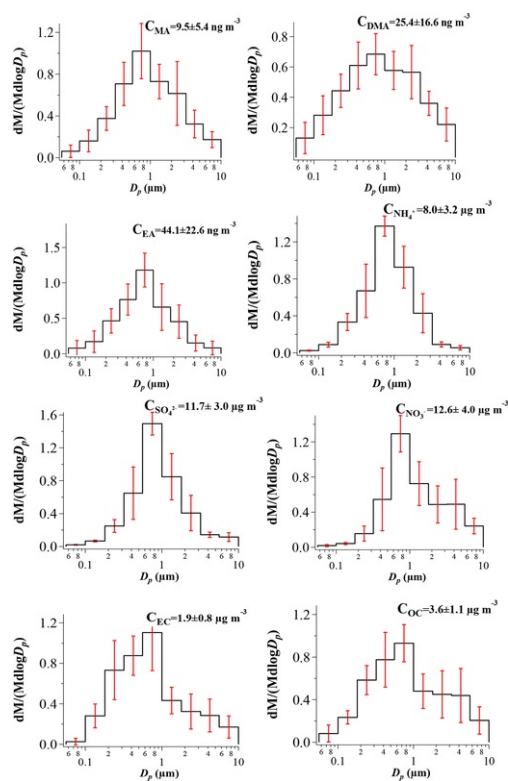


Fig. 5 Histograms of mass percentages in the nine MOUDI size bins between 0.056 and 10 μm for three aminiums, NH_4^+ , SO_4^{2-} , NO_3^- , EC and OC. Total concentrations and standard deviations are also shown.

alt-text: Fig. 5

Size-dependent aminium/ NH_4^+ molar ratios measured by Tao et al. (2015); Yu et al. (2016b) and VandenBoer et al. (2011) showed a strong enhancement of aminium over NH_4^+ in <200 nm particles. When looking at our size-resolved data, aminium/ NH_4^+ molar ratios in 56-100 nm particles increased by a factor of 2.6-5.6 (relative to $\text{PM}_{2.5}$) to 1.8×10^{-3} , 7.2×10^{-3} and 8.9×10^{-3} for MA, DMA and EA, respectively. Although aminiums were still far less to out-compete NH_4^+ , aminiums contributed more importantly, in a relative sense, to the reduced nitrogen composition of particles of 56-100 nm.

3.4 Aminiums on new particle growth days

Smith et al. (2010) observed that aminiums contributed 10-47% of the positive ions in nanoparticles (8-10 nm) using thermal desorption chemical ionization MS (TD-CIMS) during NPF events. Since new particles will eventually grow to the sizes of >56 nm (Aitken mode) during a typical NPF event, it is thus expected that aminium should also have higher concentrations on NPF days than non-NPF days in the Aitken mode of 56-100 nm and perhaps also submicron particles of 100 nm - 1.0 μm due to enhanced gas phase amine partitioning. To investigate this hypothesis, we singled out the 8 days with new particle growth events out of total 21 observation days in August 2014 (Fig. S1). We used the term "new particle growth event" here, because our SMPS scanned down to 8 nm, which is much larger than critical cluster size of 1-2 nm. We reconstructed aminium, OC and EC concentrations in 56-100 nm and 100 nm-1.0 μm on event days ($n = 8$) and non-event days ($n = 13$), respectively.

Fig. 6 shows that MA and DMA concentrations in 56-100 nm particles on the event days were on average a factor of ~1.2 higher than those on the non-event days, while EA on the event days was only 77% of that on the non-event days. Fig. 6b shows that in 100 nm - 1.0 μm particles, MA on the event days was on average a factor of 1.1 higher than that on the non-event days, while DMA and EA on the event days were lower than the non-event days. Considering the relatively large standard deviations of aminium concentrations (shown in Fig. 6), we did not see significantly higher aminium concentrations during the event days than the non-event days, in either Aitken-mode particles or sub-micron particles. This is different from the measurement at a southern Finland boreal forest site (Mäkelä et al., 2001), where a 30-fold enhancement of DMA in sub-micrometer particles was observed during NPF days (n = 3) compared with nonevent days (n = 2).

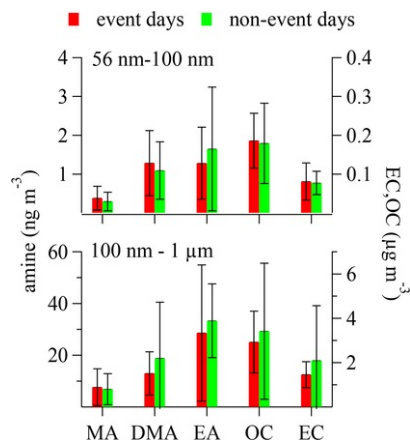


Fig. 6 Average concentration and standard deviation of three aminiums and EC and OC on new particle growth event days (n = 8) and non-event days (n = 13), reconstructed for 56-100 nm and 100 nm-1 μm , respectively, from nano-MOUDI size bins.

alt-text: Fig. 6

We can also see that new particle growth events barely enhanced OC concentration in 56-100 nm on the event days compared to the non-event days (Fig. 6, upper panel). One possibility is that new particles of 56-100 nm were largely composed of inorganic species. This is supported by our measurement that mass ratios of $m_{(\text{SO}_4^{2-} + \text{NO}_3^- + \text{NH}_4^+)}/m_{\text{OC}}$ were ~10 in average in this size range. In summary, amine uptake to Aitken-mode particles of 56-100 nm or submicron particles of 100 nm-1.0 μm was barely enhanced on the event days at out sites, although we cannot exclude the important role of amines in nucleation and early growth of new particles.

3.5 Particle-phase aminiums emitted from coal and biomass burning

Fig. 7 shows aminiums, OC, NH_4^+ and their mass ratios in freshly emitted particles from coal and biomass burning, as well as in urban aerosols. It can be seen that with identical fuel mass consumption and combustion conditions, biomass burning emitted more OC but less aminiums than coal burning (1st column, Fig. 7). Although coal briquettes (or biomass fuels) were of different origins, aminium concentrations were roughly proportional to OC concentrations ($R^2 = 0.38-0.87$), with aminium/OC mass ratios on the order of 10^{-3} for coal burning and $10^{-5}-10^{-4}$ for biomass burning. That is, primary OC emission from coal burning was rich in aminiums with a factor of ~15 (for MA and DMA) or ~60 (for EA) higher than biomass burning. Aminium/OC ratios in coal burning emission were also much higher than those in ambient aerosols (2nd column, Fig. 7). On the basis of our particle-phase aminium emission factors from coal burning (MA, EA and DMA: $18.0 \pm 16.4 \text{ mg kg}^{-1}$, $30.1 \pm 25.6 \text{ mg kg}^{-1}$ and $14.6 \pm 10.1 \text{ mg kg}^{-1}$, respectively) and annual coal assumption of $6.7 \times 10^{12} \text{ kg}$ in the world in 2015 (BP Statistical Review, 2016), we estimated that global fluxes of particulate MA, EA and DMA emissions from coal burning were $52 \pm 48 \text{ Gg N a}^{-1}$, $62 \pm 53 \text{ Gg N a}^{-1}$ and $30 \pm 21 \text{ Gg N a}^{-1}$, respectively. These numbers are comparable with annual global gaseous amine emissions from animal husbandry, marine and biomass burning (MA and DMA: 83 ± 26 and $33 \pm 19 \text{ Gg N a}^{-1}$, Ge et al. (2010)). Considering the high abundance of aminium in coal burning primary OC emission, our data suggested that coal burning emission could be an important atmospheric amine source.

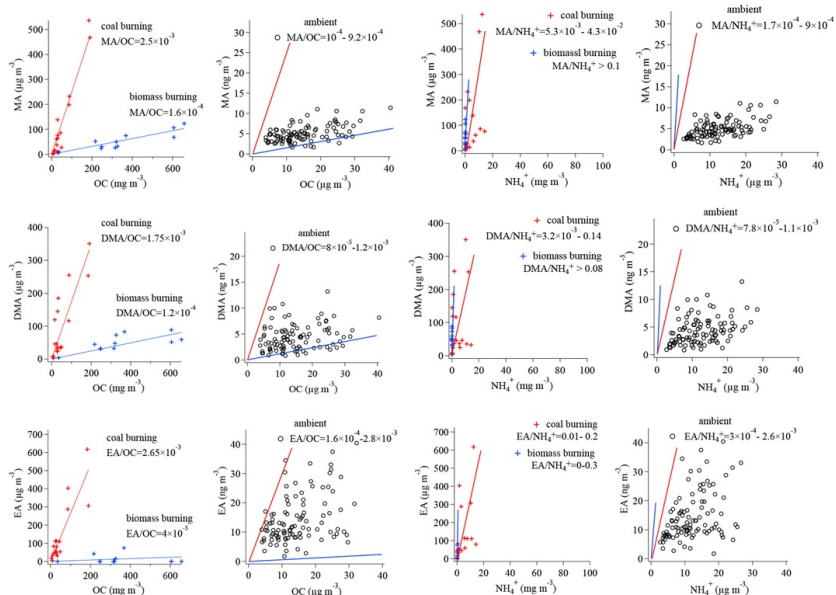


Fig. 7 Particle-phase aminiums vs. OC in coal burning and biomass burning emissions (1st column) and ambient aerosols (2nd column). Particle-phase aminiums vs. NH_4^+ in coal burning and biomass burning emissions (3rd column) and ambient aerosols (4th column).

alt-text: Fig. 7

In comparison to ambient aminium/ NH_4^+ mass ratios (10^{-5} - 10^{-3} , 4th column, Fig. 7), NH_4^+ was also relatively poor in coal burning aerosols (aminium/ NH_4^+ mass ratio: 5.3×10^{-3} -0.2, 3rd column, Fig. 7) and almost absent from biomass burning aerosols (aminium/ NH_4^+ mass ratios > 0.08). This implied that primary emission of NH_4^+ from coal or biomass burning aerosols is not likely an important contributor to NH_4^+ in the atmosphere, which is basically a secondary product from gaseous NH_3 conversion.

4 Conclusions

We used a FMOC derivatization-HPLC fluorescence method to measure C1-C2 alkyl aminiums in urban aerosols in the YRD region, one of the most populated and industrialized areas of eastern China. The concentrations of MA, DMA and EA in $\text{PM}_{2.5}$ were $5.7 \pm 3.2 \text{ ng m}^{-3}$, $7.9 \pm 5.4 \text{ ng m}^{-3}$ and $20.3 \pm 16.6 \text{ ng m}^{-3}$ at our urban sites, respectively, with higher concentrations during the daytime and in warm seasons. Based on our measurements and a survey of the literature, C1-C2 alkyl aminium concentrations in particles were found to be on similar order of a few to tens of ng m^{-3} in urban, marine/coastal and forest locations around the world, except remote marine atmosphere. This seemed to imply that either these aminiums could be emitted from a variety of continental and marine sources, or the lifetime of particle-phase aminiums was long enough to be transported far away from their source regions.

Recent modeling studies suggested that amine-driven nucleation may be important only near amine source regions, due to short amine lifetime of a few hours in the gas phase. Our measurement showed that even in polluted urban areas like the YRD region, aminiums were far less to out-compete NH_4^+ in particles down to 56 nm, because of strong NH_3 sources collocated in the urban areas. Abundant nitrate and its correlation to MA and DMA implied that nitrate might be more important aminium salt than sulfate. Our study also found that amine uptake to Aitken mode particles of 56-100 nm or submicron particles of 100 nm-1.0 μm were barely enhanced on the new particle growth days.

In the emission inventories of present global modeling work, only gas-phase amine was roughly estimated using scaling factors from NH_3 emission sources. Our measurement showed that particle-phase aminium emission from coal burning may also be an important source. Considering coal burning is top-ranked PM source in China, ignoring particle-phase aminium emission from coal burning will underestimate the concentration and misrepresent spatial distribution of amines in the atmosphere.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2017.06.034>.

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Appendix A. Supplementary data

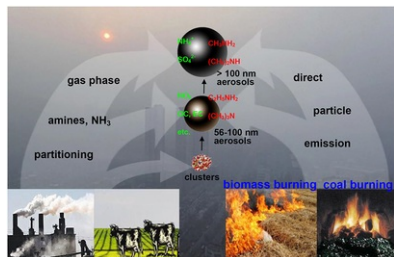
The following is the supplementary data related to this article:

[Multimedia Component 1](#)

Supplementary

alt-text: Supplementary

Graphical abstract



alt-text: Image 1

Highlights

- Ammonium concentration showed seasonal and diurnal variations in urban aerosols of our area.
- Nitrate was more important ammonium salt than sulfate in urban aerosols of our area.
- Particle-phase amine emission from coal burning is an important atmospheric amine source.
- Amine uptake to particles larger than 56 nm was barely enhanced on new particle growth events.
- Even in polluted urban areas in China, the contribution of amines to particle growth is weakened by the competition from co-located ammonia emission.