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Mist Cannon Trucks Can Exacerbate Secondary Organic Aerosol Formation and $PM_{2.5}$ Pollution in the Road Environment

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Abstract: Mist cannon trucks have been widely applied in megacities in China to reduce the road dust. Their practical effect on controlling the formation of secondary organic aerosol and fine particles remains unknown. We characterized the chemical composition variations in $PM_{2.5}$ collected on the road sides with the simulated operations of mist cannon truck and traditional sprinkling truck via Fourier transform ion cyclotron resonance mass spectrometry and ion chromatography. The mass concentrations of water-soluble organic carbon in $PM_{2.5}$ showed a significant increase (62-70%) after air spraying. Further, we found that secondary organic aerosols, particularly organic nitrates, increased significantly via the interactions of reactive gas-phase organics, atmospheric oxidants, and aerosol liquid water after air spraying, although the air spraying had a better effect on suppressing road dust than the ground aspersion. Moreover, the formation of $PM_{2.5}$ in the road segment where the mist cannon truck passed was promoted, with an increase of up to 13% in mass concentration after 25–35 minutes, on average. The application of mist cannon trucks undoubtedly worsens the road atmospheric environment and causes health hazards to walking residents. The overall results provide not only valuable insights to the formation processes of secondary organic aerosols associated with aerosol liquid water in the road environment but also management strategies to regulate the mist cannon truck operation in China.

Keywords: Mist cannon truck; Water mist; Secondary organic aerosols; $PM_{2.5}$; Process and mechanism

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1 Introduction

Over the past decade, the demand for effective road dust control has grown dramatically due to the upgraded environmental protection policies and quality of life. Traditionally, the sprinkling trucks with the ground aspersion work well for vehicle-generated road dust. The newly developed mist cannon trucks are able to spray water mist up to 120 meters away and 100 m high, with a droplet diameter of as small as 5 μm. They are considered to be more water-saving and efficient than the traditional sprinkling truck (the ground aspersion). Thus, the mist cannon trucks have been widely utilized by the local environmental bureau in recent years to achieve the target of strict emission control in megacities in China (Wang et al., 2022). Traffic-related emissions contribute a huge amount of volatile organic compounds (VOCs), nitrogen oxides (NO_x), ammonia (NH_3), and fine aerosol particles ($PM_{2.5}$) to the urban atmosphere, which exerts adverse impacts on human health and climate change (Deng et al., 2020; Yang et al., 2022). However, no study has investigated whether and how the water mist sprayed by mist cannon truck affects the road atmospheric environment in coordination with traffic emissions.

As we know, the mist cannon trucks can spray a large amount of fine water mist in a short time. It is expected that the air humidity of local road environment where the mist cannon truck passed will increase sharply. Aerosol liquid water (ALW) exists in the condensed phase as a function of particle chemical composition, particle concentration, temperature (T), and relative humidity (RH) (Nguyen et al., 2015; Xu et al., 2020a). Typically, an increase in RH can promote the rise in ALW concentration

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(Guo et al., 2015). ALW, as a ubiquitous and abundant medium, can not only facilitate partitioning of gas-phase water-soluble organics to the condensed phase but also drive the formation of secondary organic aerosol (SOA) (Carlton and Turpin, 2013; Sareen et al., 2017). The severe haze episodes in Beijing can even be partly attributed to the interactions between ALW (or high RH) and aerosol organic components (Li et al., 2019; Wang et al., 2021). In particular, 40–80% of fossil-fuel-derived primary organic aerosols were found to be water-soluble (Qiu et al., 2019). Undoubtedly, there are large knowledge gaps in our current understanding on ALW-related water-soluble SOA formation in the road environment with mist cannon truck operation.

Although few studies have systematically evaluated the ability of mist cannon truck to remove road dust, it is easy to understand that the tiny water droplets generated by mist cannon system can indeed capture coarse particles (i.e., dropping dust to the ground) more effectively than the water column sprayed by the traditional sprinkling truck. However, fine particles (e.g., $PM_{2.5}$) are a major threat to urban atmospheric environment and human health (Yue et al., 2020). Thus, it is necessary to understand the removal effect of mist cannon truck on fine particles in road environment. Assessing the impact of the mist cannon truck operation on road $PM_{2.5}$ pollution is also of great significance for guiding future environmental protection initiatives.

In this study, we simulated the operation scenes of mist cannon truck and traditional sprinkling truck on the sides of the urban road (Nanchang, eastern China) and collected ambient $PM_{2.5}$ samples in these scenes. The molecular compositions of water-soluble organic matter (WSOM) in $PM_{2.5}$ samples were resolved using ultrahigh-

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resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). We also present the measurements of the relevant chemical parameters in $PM_{2.5}$ samples and the predicted ALW concentration. Furthermore, the variations of $PM_{2.5}$ concentrations in the road segment where the mist cannon truck passed were monitored. The obtained results will clarify the impact of spraying water mist by mist cannon truck on SOA formation and $PM_{2.5}$ pollution control in the urban road environment for the first time.

2 Experimental Section

2.1 Study Site and Sample Collection.

A branch road (provincial capital north 2nd road) that was selected as study area was located in the centre of Nanchang (Eastern China) (**Figure S1a**). This area is characterized by heavy traffic and high population density. There are no typical pollution sources, such as factories and garbage treatment plants, within 30 km of the study area. The trees on both sides of the road are very high and luxuriant (**Figure S1a**), likely indicating that the atmosphere in this road environment is rarely disturbed by strong winds and is relatively stable. The dominant species of the trees at the area is camphor trees (*Cinnamomum Camphora*). Thus, the region is expected to be influenced by both anthropogenic (vehicle exhausts) and biogenic VOCs.

Two sampling points with a distance of approximately 70 m were selected, which were respectively on the roadside effected by air spray and ground aspersion (**Figure S1b-e**). The air spraying 8 m above the ground was to simulate the water mist sprayed by the mist cannon truck. In contrast, the ground aspersion with a height of 0.4 m above

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the ground was designed to simulate the operation of traditional sprinkling truck. Typically, thousands of oral fluid droplets emitted by loud speech will disappear in the time range of 8 to 14 minutes in the stagnant air environment (Stadnytskyi et al., 2020). It implied that the residence time of the fine water mist sprayed by the mist cannon truck in the air may be longer than 8 min. As mentioned above, the luxuriant trees on both sides of the road cause the atmosphere in the road environment to be relatively stable with less disturbance by strong winds. Thus, the frequency of spraying water was set to 1 minute spraying every 8 minutes (lower limit) in this study. The spraying was controlled by an intelligent timing irrigation equipment (Nadster, China). It should be noted that the diameter of the pores in the nozzle for air spraying is less than 0.8 mm, while that in the nozzle for ground aspersion is approximately 6 mm.

Fine aerosol particles ($PM_{2.5}$) were collected onto the prebaked (500°C for ~10 hours) quartz fiber filters (Pallflex, Pall Corporation, USA) using a high-volume air sampler (Series 2031, Laoying, China). Sampling at the above-mentioned two sites was simultaneously performed from 23 March to 26 March, 2021. The duration of each aerosol sampling was approximately 4 h (9:00−13:00 LT) every day. We observed that the traffic flow on March 25 was higher than that on other days. The weather of sampling periods was cloudy to sunny, sunny, sunny, and shower (only one short precipitation event in the sampling period), corresponding an ambient average temperature (T) of approximately 21 °C. The ambient average relative humidity (RH) in those periods (23–25 March) ranged between 50% and 60%. The average RH can reach 84–87% after air spraying. The ambient average RH was as high as 80% during

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the period of 9:00−13:00 on 26 March. Thus, the water spraying operation was stopped when the samples were collected on 26 March. The samples were stored at −28 °C prior to the analysis. In addition, the mass concentrations of $PM_{2.5}$ were measured online (Thermo Scientific 5030i, USA) from July to August 2021 near the trunk road where the mist cannon truck frequently operated (**Figure S1a**). Specifically, $PM_{2.5}$ concentrations near road (81 road, Nanchang) were recorded at 5-minute intervals from 10 minutes before to 50 minutes after the mist cannon truck passed by.

2.2 Chemical Analysis.

A portion of each filter sample was ultrasonically extracted with Milli–Q water (MQW, 18.2 MΩ cm). WSOM in the extracting solution was further extracted using the typical solid phase extraction (SPE) method, as indicated by previous studies (Dittmar et al., 2008; Qiao et al., 2020; Xie et al., 2020). Briefly, the cartridge (PPL, 0.5 g, Agilent) was rinsed with 18 mL of methanol (LC-MS grade, Thermo Fisher) and 18 mL of HCl solution (pH = 2) in turn. Subsequently, the extracts with acidity adjusting (pH = 2) were injected into cartridge. Acidified MQW (18 mL) and normal MQW (6 mL) were added in turn to remove the salt and chloride ion trapped in the cartridge. After dryness under a stream of N_2, trapped OM was eluted using 15 mL of methanol. The eluted solution was concentrated to 4 mL and then preserved at −28 ℃ until analysis. The molecular compositions of WSOM in $PM_{2.5}$ samples were determined using a Bruker Apex Ultra Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) (Bruker, Germany) coupled to an Apollo II Electrospray ionization (ESI) (He et al.,

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2020). The samples were injected into the ionization sources at a speed of 250 μL h^{-1}. The instrument was operated in the negative-ion mode, with a spray shield voltage of 4.0 kV. The mass range was set to *m*/*z* 200–800. One hundred and twenty-eight continuous scans were acquired on each analysis to heighten the signal-to-noise ratio of the mass spectrum. Detailed methodologies and data quality control during the analysis were illustrated elsewhere (He et al., 2019; He et al., 2020).

Another filter cut was ultrasonically extracted with Milli–Q water for the determination of water-soluble organic carbon (WSOC), water soluble total nitrogen (WSTN), and inorganic ions. The mass concentrations of WSOC and WSTN in samples were measured with a total organic carbon/total nitrogen analyser (Elementar vario, Germany) (Xu et al., 2019). The mass concentration of WSOC was estimated to that of WSOM using a conversion factor of 1.8 (Finessi et al., 2012; Müller et al., 2017; Simon et al., 2011; Yttri et al., 2007). The mass concentrations of water-soluble inorganic ions, such as SO_4^{2-}, NO_3^-, NH_4^+, and K^+, were measured using an ion chromatography system (Dionex, Thermo, USA) (Xu et al., 2022; Xu et al., 2020b). The mass concentration of water-soluble organic nitrogen (WSON) was calculated as the difference in the concentrations between WSTN and inorganic nitrogen (i.e., NO_3^-_N + NO_2^-_N + NH_4^+_N) (Xu et al., 2020a). Ambient temperature and relative humidity were measured using a temperature and humidity monitor (CEM 9880M, China).

2.3 Data Processing and Statistical Analyses.

The molecular formulas assigned from FT-ICR MS were classified into four main

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compound groups in this study. These identified groups include CHO (containing only C, H, and O), CHON (containing C, H, O, and N), CHOS (containing C, H, O, and S), and CHONS (containing C, H, N, O, and S) (Song et al., 2018). The double-bond equivalent (DBE) was calculated to describe the unsaturation degree of organic compounds (**Supplementary Information**) (Qiao et al., 2020; Schmidt et al., 2017). The modified aromaticity index (AI_{mod}) was also calculated to reflect the aromaticity of organic molecules (**Supplementary Information**) (Koch and Dittmar, 2006; Schmidt et al., 2017). The carbon oxidation state (OSc) can be used to indicate the evolving composition of aerosol organics that underwent oxidation processes (Kroll et al., 2011). The calculation of OSc was detailed in the **Supplementary Information.** According to the oxygen-to-carbon (O/C) and hydrogen-to-carbon (H/C) elemental ratios, the identified molecular formulas were further classified into five compound categories, including unsaturated aliphatic-like, highly unsaturated-like, highly aromatic-like, polycyclic aromatic-like, and saturated-like molecules (Sihui et al., 2021). These classified compound categories were visualized in the van Krevelen diagram (**Supplementary Information**).

The thermodynamic model ISORROPIA-II was applied to calculate the mass concentrations of ALW driven by inorganic components (Guo et al., 2015; Tan et al., 2017; Xu et al., 2022). The model predicts the inorganic ALW based on particle mass concentrations of inorganic species, RH, and ambient T (**Supplementary Information**). Particle hygroscopicity is also influenced by organics in aerosol particles (Cruz and Pandis, 2000; Sareen et al., 2013). The impact of organic faction on aerosol water is

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complex and depends on the composition of organic matter (Nguyen et al., 2016). In this study, the mass concentration of water associated with aerosol organic fraction was predicted according to a previously reported model with the Zdanovskii−Stokes−Robinson mixing rule (**Supplementary Information**) (Nguyen et al., 2015; Nguyen et al., 2016).

3 Results and Discussion

3.1 Chemical Characteristics of $PM_{2.5}$ in Different Road Segments.

Figure 1 compares the differences in the chemical composition of $PM_{2.5}$ collected in the air spray road segment and ground aspersion road segment. WSOM was the dominant component irrespective of the weather and road section where the samples were collected, which accounted for 30–40% of the water-soluble aerosols (**Figure1a–c**). From March 23 to March 25, the mass concentrations and fractions of WSOM (/WSOC) were higher in the air spray road segment than in the ground aspersion road segment. For the case without water spray treatment (as reference group), the chemical composition characteristics of $PM_{2.5}$ samples collected from those two adjacent road segments only showed small differences (**Figure1d,h,i**). Obviously, these variations in the mass concentrations and fractions of WSOM can be attributed to the difference in water-soluble SOA yield or formation pathway caused by different water spray treatments.

The variation pattern of ALW was similar to that of WSOC during the study periods (**Figure1e–h**). Moreover, the mass concentrations of WSON also tended to

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224 decrease from the air spray road segment to the ground aspersion road segment. Linear
225 regression analysis for all data showed that the mass concentrations of ALW were
226 significantly positively ($P < 0.01$) correlated with those of WSOC and WSON, with R^2
227 of 0.84 and 0.75, respectively. The results were consistent with those obtained by the
228 previous studies conducted in an agriculture area in Italy (Hodas et al., 2014) and a
229 suburban forest site in Tokyo (Xu et al., 2020a). Those studies suggested that the ALW
230 dependence of reactive gas uptake and subsequent aqueous reactions significantly
231 contributed the production of WSOC and WSON. Thus, the increase in ALW
232 concentration after air spraying can promote the formation of aqueous SOA in the road
233 environment.

234 Nitrate and sulfate were the most abundant inorganic components (**Figure1a–d**),
235 which have been identified as typical factors controlling ALW (Hodas et al., 2014).
236 From the air spray road segment to the ground aspersion road segment, the decrease in
237 nitrate concentration was more significant than that in sulfate concentration (**Figure1e–**
238 **f**). Moreover, the concentration of nitrate significantly correlated with that of ALW (P
239 < 0.01, $R^2 = 0.7$). In contrast, the sulfate did not show a strong correlation with ALW
240 ($R^2 = 0.3$). In the region with large NO_x and ammonia emissions (traffic-related) (Yang
241 et al., 2022), the formation of nitrate could be promoted by enhanced RH (24–43% of
242 increase) caused by air spraying. This is partly consistent with the thermodynamics of
243 ammonium nitrate formation (Hodas et al., 2014; Mozurkewich, 1993). Thus, the
244 increase in ALW concentration after air spraying was mainly driven by RH and locally
245 (traffic emissions) formed nitrate aerosol. It also implied that the formation of nitrate

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and ALW is mutually reinforcing (Chen et al., 2022).

Interestingly, Ca^{2+} and Mg^{2+} showed a significant increase in the concentration from the air spray road segment to the ground aspersion road segment (**Figure1i–k**), which was contrary to the case of other components (e.g., WSOC, ALW and nitrate). In addition, during March 26 without water spray treatment, the differences in both Ca^{2+} and Mg^{2+} concentrations between those two adjacent road segments were almost negligible (**Figure1f**). It is well known that Ca^{2+} and Mg^{2+} are typical crustal materials and are mainly enriched in atmospheric coarse particles (Chen and Chen, 2008). Thus, a decrease in Ca^{2+} and Mg^{2+} concentrations after air spraying implied that the water mist sprayed by mist cannon truck had a better effect on suppressing road dust than the ground aspersion by traditional sprinkling truck.

3.2 General Molecular Characteristics of Water-Soluble Organic Aerosols.

Thousands of molecular formulas (5966–8102) were observed in WSOM in $PM_{2.5}$ collected from road environment (**Table 1**). The CHO molecular formulas (1089–2037) accounted for 20–25% in all molecular formulas. CHO compounds were classified by the number of oxygen atoms in their molecules, according to which the subgroups ranged from O_2 to O_{15} (**Figure 2**). The number and intensity of dominated O_5–O_{10} subgroups accounted for 72–85% and 71–86% of the total compounds, respectively; moreover, these percentages were higher than the results reported for aerosols in Beijing (Xie et al., 2020). The average H/C and O/C ratios of CHO compounds varied from 1.08 to 1.24 and from 0.42 to 0.49, respectively (**Table S1**). The average O/C ratios

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were higher than the value (0.03 ± 0.11) obtained from typical unban aerosols (Beijing, China), while the H/C ratios showed relatively small differences between our results and observation results in Beijing (1.14 ± 0.37) (Xie et al., 2020). These dissimilarities might be attributed to the more complex sources of urban aerosols compared to aerosols collected from road environment.

The average H/C and O/C ratios of CHON compounds ranged from 1.05 to 1.21 and 0.42 to 0.51, respectively (**Table S1**). The H/C ratio ranges of CHON compounds in this study overlapped with those measured in previous studies (Sihui et al., 2021; Xie et al., 2020). However, the O/C ratios of CHON compounds were relatively higher in road-derived aerosols than in aerosols or snow collected in urban areas (building roof) (Sihui et al., 2021; Xie et al., 2020), which implied the importance of source strength (e.g., vehicle emissions) to aerosol chemical composition. The number of CHON formulas (1501–2685) was much higher than that of CHO formulas (**Table 1**). The assigned CHON formulas were further divided into $CHON_1$ (N_1O_2–N_1O_{16}), $CHON_2$ (N_2O_2–N_2O_{13}), and $CHON_3$ (N_3O_2–N_3O_{13}) groups (**Figure 2**). $CHON_1$ was found to be the dominant nitrogen-containing species in all samples, which was consistent with previous reports on urban aerosols and snow (Sihui et al., 2021; Xie et al., 2020). Moreover, the $CHON_1$ compounds with O/N > 2 contributed 99.2% – 100.0% to total $CHON_1$ species in all samples. The $CHON_2$ compounds with O/N > 2 accounted for 90.2–100.0% of CHON species containing two nitrogen atoms. For $CHON_3$ group, the proportion of nitrogen-containing compounds with O/N > 2 was 53.0–61.8%. The CHON species with O/N > 2, which allows an assignment of oxidized-form nitrogen,

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290 are preferentially ionized in negative electrospray ionization mode (Lin et al., 2015;
291 Sihui et al., 2021). Studies on the compositions of organic matter in urban rainwater
292 and aerosols have suggested that numerous CHON compounds contained oxidized
293 nitrogen function groups (e.g., $–ONO_2$) and that NO_x-related oxidation processes are
294 responsible for the formation of these CHON compounds (Altieri et al., 2009; Lee et
295 al., 2016). Thus, the CHON compounds with O/N > 2 in our $PM_{2.5}$ samples can be
296 assumed to be substantially in an oxidized form (e.g., organic nitrates).

297 **Figure 2** also shows the differences in the number of CHO and CHON species
298 between the air spray road segment and ground aspersion road segment. The abundance
299 of each O_n subgroup in CHO compounds considerably enhanced after air spraying,
300 especially the subgroups of O_5–O_{11}. In contrast, the number of CHO species for these
301 two cases without water spray treatment showed a considerably small difference
302 (**Figure 2d**). In general, the total number of CHO compounds increased significantly
303 after air spraying (**Table 1** and **Figure 2**). However, there was no significant change for
304 the total number of CHO species between the two cases without water spray treatment.
305 These findings implied that increased ALW via the air spraying can contribute
306 substantially to the formation of CHO compounds with a more oxygenated state.

307 The number of CHON compounds decreased significantly from the air spray road
308 segment to the ground aspersion road segment, a variation pattern of which was similar
309 to that of CHO compounds (**Figure 2** and **Table 1**). Furthermore, the decrease in
310 number from the air spray road segment to the ground aspersion road segment was more
311 remarkable for $CHON_1$ compounds than for $CHON_2$ compounds. In contrast, the

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312 variation in the number of $CHON_3$ after air spraying was less significant than that of
313 $CHON_{1-2}$ compounds. In addition, insignificant change in the number of CHON
314 compounds was found in $PM_{2.5}$ collected in the two road segments without water spray
315 (**Figure 2d**). As mentioned above, the potentially high abundance of organic nitrates
316 has been suggested in these road-derived aerosols. Thus, an increase in nitrogen-
317 containing compounds after air spraying indicated that the interactions among ALW,
318 traffic-derived reactive nitrogen and ambient VOCs play an important role in organic
319 nitrogen compound formation in aerosol fine particles. The current result can be partly
320 supported by that obtained by Xu et al. (2020a) in a suburban forest in Tokyo, Japan.
321 The authors suggested that ALW is a key driver for the formation of aerosol WSON
322 through secondary processes associated with atmospheric reactive nitrogen and
323 biogenic VOCs. For the sulfur-containing compounds, their molecular number just
324 showed a relatively small change after air spraying (**Figure S2**). It suggested that the
325 impact of ALW on sulfur-containing compound formation was weaker than that of ALW
326 on the formation of CHO and CHON compounds in this road environment.
327
328 **3.3 Newly Emerging CHO and CHON Species under the Influence of High ALW.**
329 The molecular compositions of CHO compounds in $PM_{2.5}$ in the van Krevelen
330 diagram were scattered across wider ranges in the air spray road segment than in the
331 ground aspersion road segment, particularly in the sunny days (24 and 25 March)
332 (**Figure 3**). The result may be attributed to the increasing molecular diversity caused by
333 ALW-related atmospheric processes. It also implied the importance of photochemical

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334 reactions in CHO compound formation. Further, the unique CHO compounds were
335 identified between $PM_{2.5}$ samples in the air spray road segment (/no water spray road
336 segment (A)) and the ground aspersion road segment (/no water spray road segment (B))
337 (**Figure S3**). On 23 March and 24 March, the newly emerging CHO compounds after
338 air spraying were dominated by unsaturated aliphatic-like and highly unsaturated-like
339 compounds. However, both unsaturated-like species (unsaturated aliphatic-like and
340 highly unsaturated-like) and aromatic-like species (highly aromatic-like and polycyclic
341 aromatic-like) contributed significantly to the newly emerging CHO compounds after
342 air spraying on 25 March when the ALW and traffic flow were higher than other days
343 (**Figure S3**). Obviously, the formation of those unique CHO compounds was tightly
344 associated with increased ALW.

345 **Figure 4** shows the OSc of identified unique CHO molecules. The OSc values of
346 these CHO molecules were higher than those of primary vehicle exhausts (–2.0 to –1.9)
347 (Aiken et al., 2008). The OSc values of the secondary organic aerosol formed via the
348 reactions of anthropogenic and biogenic VOCs (e.g., isoprene, monoterpene, toluene,
349 alkane, and alkene) and oxidants (e.g., O_3 and/or •OH) varied from –1.1 to +1.0 (Kroll
350 et al., 2011; Li et al., 2021), which was within the OSc value ranges of CHO molecules
351 measured in this study. In addition, hydrocarbon-like organic aerosol (HOA) likely
352 linked with primary fresh vehicle exhausts (Sun et al., 2016) only accounted for less
353 than 6% of total unique CHO compounds (**Figure 4**). As mentioned previously, there
354 are dense trees on both sides of the road. Thus, these newly emerging CHO compounds
355 can be largely attributed to secondary processes associated with oxidation of vehicle

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356 exhausts and biogenic VOCs by O_3 and/or •OH. In addition, we also observed an
357 oligomerization trend (e.g., methylglyoxal ($C_3H_4O_2$) to form oligomers ($C_{4-7}H_{6-10}O_5$)
358 in particle phase) for CHO compounds after air spraying, particularly on 25 March with
359 a high ALW and a large traffic flow (**Figure S4c**). The overall results implied that the
360 water mist sprayed by mist cannon trucks can indeed enhance the abundance and
361 diversity of CHO compounds in fine aerosol particles via promoting gas-to-particle
362 partitioning of gas-phase oxidation products of VOCs and subsequent aqueous-phase
363 reactions.

364 For the CHON compounds, their molecular compositions were scattered across an
365 increased ranges in the van Krevelen diagram after air spraying (**Figure S5**). Moreover,
366 these newly emerging CHON molecules after air spraying showed a high diversity, as
367 shown in **Figure S6**. The group of $CHON_1$ was the dominant nitrogen-containing
368 compound in the identified unique CHON compounds. On 23 March and 24 March, the
369 mainly unique CHON compounds emerged during air spraying were unsaturated
370 aliphatic-like and highly unsaturated-like nitrogen-containing species. The number of
371 highly aromatic-like and polycyclic aromatic-like compounds that newly emerged also
372 increased significantly following increased traffic flow and ALW (25 March). The
373 results suggested that increases in ALW after air spraying can facilitate the formation
374 of particle-phase nitrogen-containing compounds (Hallquist et al., 2009; Xu et al.,
375 2020a).

376 Organic nitrates have been supposed to be abundant in our $PM_{2.5}$ samples collected
377 from road environment. It is well documented that atmospheric organic nitrates are

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primary, secondary, and tertiary byproducts of anthropogenic and biogenic VOCs with O_3 (/•OH) under the influence of NO_x or nitrate radicals (Lee et al., 2016; Sihui et al., 2021; Yeh and Ziemann, 2014). In addition, numerous organic nitrates are known as semivolatile compounds, with a partition between the gas and particle phases when they are oxidized or photolyzed (Bean and Hildebrandt Ruiz, 2016). Recently, an oxidation and hydrolysis mechanism associated with the atmospheric organic nitrates formation has been proposed to interpret the potential origins or precursors of CHON compounds (Sihui et al., 2021). In this study, we found that 68–82% of newly emerging $CHON_1$ compounds after air spraying can be explained by oxidation (e.g., R_1OH)-product (e.g., R_1ONO_2) pair (**Figure 5a-c**). It indicated that these newly emerging $CHON_1$ compounds were largely derived from the oxidation of CHO species under existence of NO_x. A similar pattern was also observed in the newly emerging $CHON_2$ compounds (**Figure S7**). The number of unique $CHON_1$ and $CHON_2$ compounds in the two cases without water spray treatment was much less than that in the cases with air spraying and ground aspersion (**Figure 5** and **Figure S7**). However, a significant oligomerization trend for CHON compounds after air spraying was not observed after air spraying (**Figure S8**). It should be pointed out that vehicle exhausts and roadside vegetation are important sources for VOCs and NO_x in this road environment. These results suggested that increased ALW caused by air spraying can serve as an abundant medium for the formation of organic nitrates via CHO compounds as potential precursors.

3.4 Environmental Implication.

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Misting cannon sprayers are commonly applied in greening maintenance and conventional agriculture for the distribution of fertilizers, pesticides, and herbicides. In recent years, misting cannon trucks are developed and serve as an excellent option for road dust control due to the production of tiny water droplets that can drop dust to the ground. In particular, it is a high-performance system of spraying disinfection in the road environment during the COVID-19 epidemic period. For the first time, we provide a detailed characterization of chemical compositions in road-derived $PM_{2.5}$ under the influence of air spraying. Recent study conducted in a rural site (China) has suggested that gaseous water-soluble organic compounds mainly partitioned to the organic phase under the condition of RH less than 80% (relatively low ALW) but to ALW under the humid condition (RH > 80%, as air spraying operation), highlighting the importance of high ALW in SOA formation processes (Lv et al., 2022). Our results verified the formation of numerous new CHO and CHON compounds by ALW-related promoting effect (**Figure 6**). In particular, the mass concentrations of WSOC in $PM_{2.5}$ increased by 62–70% after air spraying. Clearly, although the air spraying by mist cannon system could exert a better effect on suppressing road dust than the ground aspersion, as discussed previously, air pollution induced by increased SOA will be exacerbated in the road environment.

To further reveal the influence of air spraying on $PM_{2.5}$ pollution on the roadside, we investigated the time series of percentage variation in $PM_{2.5}$ mass concentrations after mist cannon truck operation at a low-speed (< 30 km/h) (**Figure 7**). At 25–35 minutes after the mist cannon truck passed, the increase proportion of $PM_{2.5}$

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concentration on the roadside gradually reached the maximum (~13%, on average). Subsequently, the proportion of increase in $PM_{2.5}$ concentration gradually decreased, reaching ~6% at 50 min after the mist cannon truck was operated. It should be noted that the width of the road segment (81 road, Nanchang, China) where $PM_{2.5}$ was monitored is very large (~43 m). Thus, on conventional urban roads, the water mist sprayed by mist cannon truck should exert a greater promoting effect on the formation of $PM_{2.5}$. The overall results suggested that mist cannon truck cannot effectively reduce the $PM_{2.5}$ level in the road environment, but lead to aggravation of $PM_{2.5}$ pollution.

The chemical composition of fine aerosol particles in the urban road atmosphere is highly complex, including a lot of harmful organic compounds (polycyclic aromatic hydrocarbons and nitro-aromatics), as indicated by our measurements and previous study (Tong et al., 2016). Emissions from vehicles and roadside greening vegetation are important anthropogenic and biogenic sources of reactive gas-phase OC and key precursors to form SOA in urban areas (Gentner et al., 2012; Tong et al., 2016; Xu et al., 2020a). In particular, organic aerosol composition in the road environment can be strongly impacted by vehicle emissions (e.g., VOCs and NO_x) (Tong et al., 2016). Inhalation of the particles containing harmful organics can be responsible for a number of adverse health effects (Künzli et al., 2000). However, the wide application of mist cannon truck by local environmental protection department undoubtedly accelerates the formation processes of SOA and $PM_{2.5}$ associated with ALW, which will further worsen the urban road environment and cause health hazards to walking residents. Thus, the present study provides the crucial information for the decision makers to regulate the

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444 current mist cannon truck operation in many cities in China.

445

446 **4 Conclusions**

447 We investigated the changes in chemical compositions of $PM_{2.5}$ collected from the
448 road sides of the urban road (Nanchang, eastern China) with the simulated operations
449 of mist cannon truck and traditional sprinkling truck. Moreover, we also conducted
450 online measurement of $PM_{2.5}$ concentration in the urban road segment where the mist
451 cannon truck passed by. The mass concentrations of WSOC in $PM_{2.5}$ increased
452 significantly (62-70%) from the ground aspersion road segment to the air spray road
453 segment. Similarly, ALW, mainly driven by RH and locally formed nitrate aerosol, also
454 showed a significant increase after air spraying. Moreover, we found that the mass
455 concentration of ALW in $PM_{2.5}$ was significantly ($P < 0.01$) correlated with that of
456 WSOC and WSON. Thus, the increase of ALW after air spraying can promote the
457 formation of particle-phase water-soluble organics in the road environment. In addition,
458 a decrease in Ca^{2+} and Mg^{2+} concentrations after air spraying suggested that the water
459 mist sprayed by mist cannon truck exerted a better effect on suppressing road dust than
460 the ground aspersion by traditional sprinkling truck.

461 A comparison in the number of CHO and CHON species between the air spray
462 road segment and ground aspersion road segment suggested that the increase of ALW
463 after air spraying can enhance the abundance and diversity of CHO and CHON
464 compounds in fine aerosol particles. The newly emerging CHO compounds after air
465 spraying can be largely attributed to secondary processes associated with oxidation of

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vehicle exhausts and biogenic VOCs by oxidants and oligomerization. Organic nitrates were considered to be the abundant nitrogen-containing compounds in the $PM_{2.5}$ samples. Furthermore, we found that the newly emerging organic nitrates were largely derived from the oxidation of CHO species under existence of NO_x.

At 25–35 minutes after the mist cannon truck passed, $PM_{2.5}$ concentration on the roadside increased by up to 13%, on average. The proportion of increase in $PM_{2.5}$ concentration gradually decreased to ~6% at 50 min after the mist cannon truck was operated. The overall results suggested that although mist cannon truck could exert a better effect on suppressing road dust than the traditional sprinkling truck, air pollution induced by increased SOA and $PM_{2.5}$ level will be exacerbated in the urban road environment. Our findings provide new insights into the formation processes of SOA associated with the water mist sprayed by mist cannon truck in the road atmospheric environment.

Data Availability

The data presented in this paper can be accessed at zenodo (DOI:10.5281/zenodo.7113675).

Supporting Information

Additional 1 table and 8 figures and details about parameter calculation, compound categorization, and ALW prediction.

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Competing interests

The authors declare no competing financial interest.

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Table 1. The number of compounds in different subgroups in different samples and the number fractions of common molecules in the same subgroup in different samples.

Sample type (Date: Mar. 23–26)	Total	CHO	Common (CHO)	Common fraction (CHO)	CHON	Common (CHON)	Common fraction (CHON)
Air spray (23)	7069	1766	1104	63%	2375	1308	55%
Ground aspersion (23)	6166	1233		90%	1803		73%
Air spray (24)	7317	1861	990	53%	2447	1225	50%
Ground aspersion (24)	6067	1098		90%	1501		82%
Air spray (25)	8102	2037	804	39%	2685	1209	45%
Ground aspersion (25)	5966	845		95%	1464		83%
No water spray (A) (26)	6998	1621	1315	81%	2120	1579	74%
No water spray (B) (26)	6990	1539		85%	1963		80%

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Figures 1–7

Figure 1.

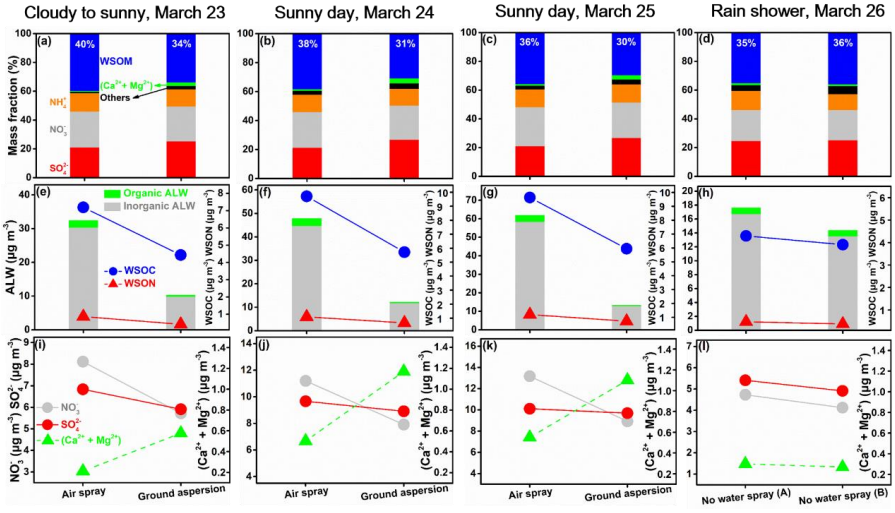

Figure 1. The mass fractions of the chemical components in $PM_{2.5}$: (a, b, and c) air spray road segment vs ground aspersion road segment and (d) no water spray road segment (A) vs no water spray road segment (B). The mass concentrations of nitrate, ammonium, and the sum of calcium and magnesium in $PM_{2.5}$: (e, f, and g) air spray road segment vs ground aspersion road segment and (h) no water spray road segment (A) vs no water spray road segment (B). The mass concentrations of ALW, WSOC, and WSOM in $PM_{2.5}$: (i, j, and k) air spray road segment vs ground aspersion road segment and (l) no water spray road segment (A) vs no water spray road segment (B).

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Figure 2.

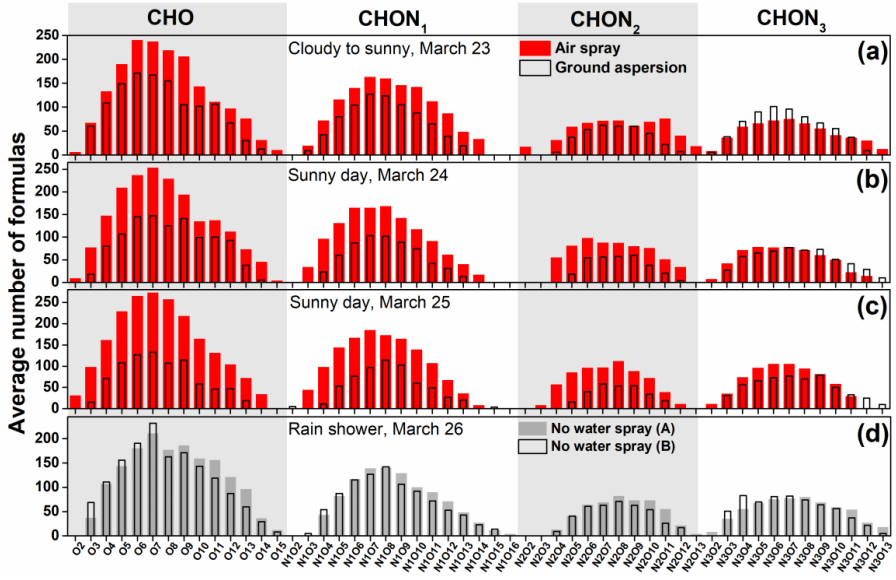

Figure 2. Classification of CHO and CHON species into subgroups according to the number of O atoms in their molecules in WSOM in $PM_{2.5}$ collected from different cases: (a, b, and c) air spray road segment vs ground aspersion road segment and (d) no water spray road segment (A) vs no water spray road segment (A).

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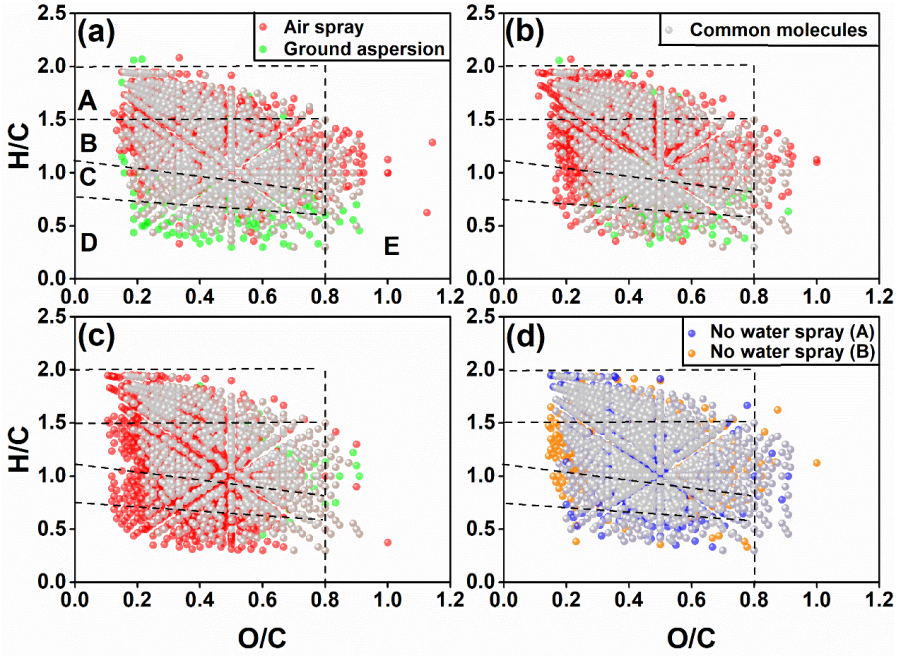
25 **Figure 3**



26

27 **Figure 3.** Van Krevelen diagrams of CHO compounds in WSOM in $PM_{2.5}$ collected
28 from different cases: air spray road segment vs ground aspersion road segment on (a)
29 March 23, (b) March 24, and (c) March 25 and two road segments without water spray
30 (A vs B) on (d) March 26. The circles of different colors indicate the unique organic
31 compounds identified in the above cases of paired comparison. Common molecules
32 identified in different cases are shown as gray circles. The classifications of compounds
33 include (A) unsaturated aliphatic-like, (B) highly unsaturated-like, (C) highly aromatic-
34 like, (D) polycyclic aromatic-like, and (E) saturated-like molecules.

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37 **Figure 4.**

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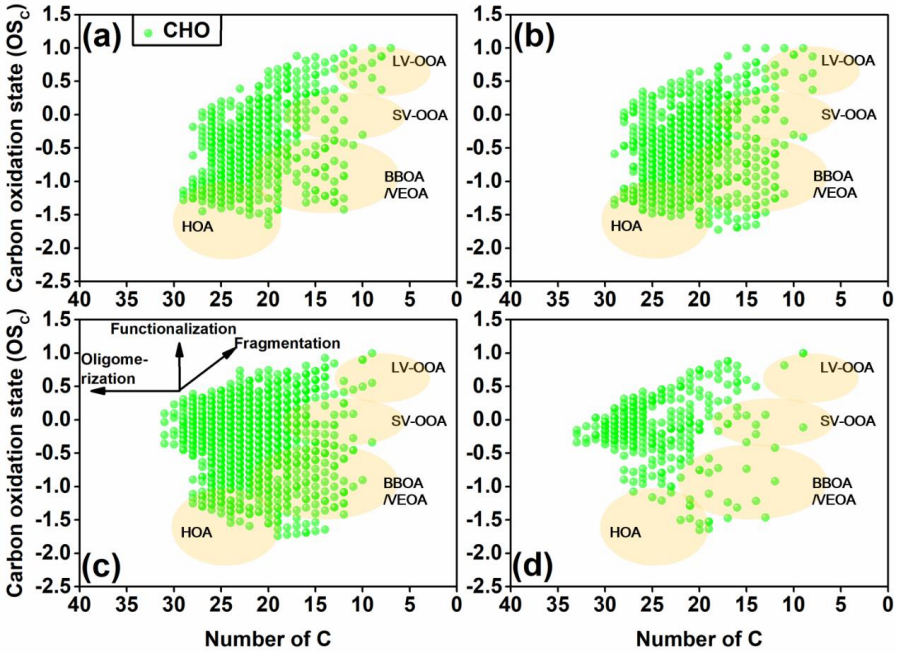

39

40 **Figure 4.** OS_c of unique CHO molecules in WSOM in $PM_{2.5}$ collected from different
41 cases: air spray road segment vs ground aspersion road segment on (a) March 23, (b)
42 March 24, and (c) March 25 and two road segments without water spray (A vs B) on (d)
43 March 26. For the above cases of paired comparison, the unique CHO compounds
44 indicate the CHO molecules identified in $PM_{2.5}$ collected from the air spray (/no water
45 spray-A) road segments. The light orange background represents areas of HOA
46 (hydrocarbon-like organic aerosol), BBOA and VEOA (biomass burning and vehicle
47 emission organic aerosols) (Kroll et al., 2011; Tong et al., 2016), SV-OOA (semivolatile
48 oxidized organic aerosol), and LV-OOA (low-volatility oxidized organic aerosol) (Kroll
49 et al., 2011).

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Figure 5.

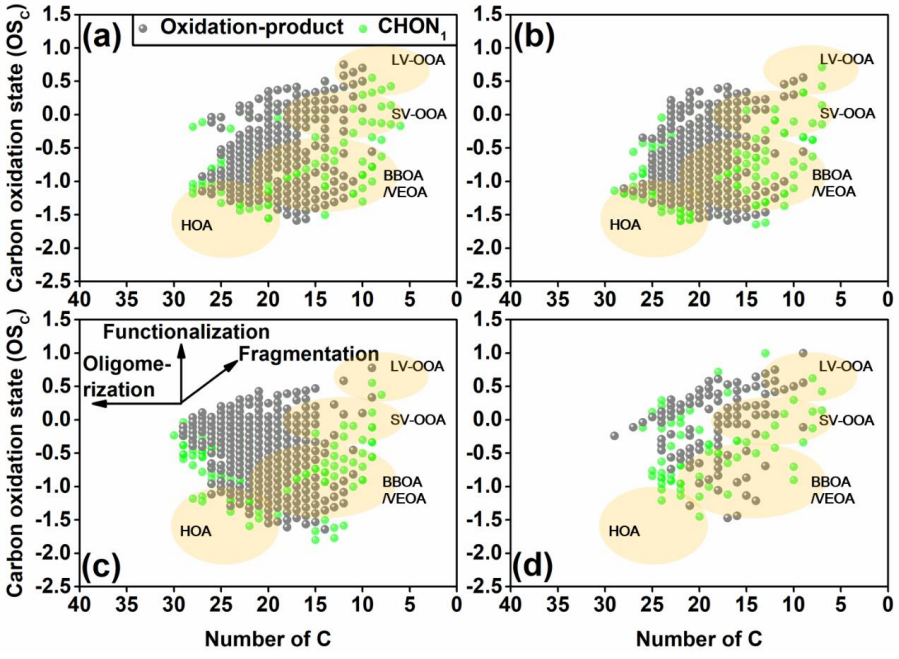

Figure 5. OS_c of unique $CHON_1$ molecules in WSOM in $PM_{2.5}$ collected from different cases: air spray road segment vs ground aspersion road segment on (a) March 23, (b) March 24, and (c) March 25 and two road segments without water spray (A vs B) on (d) March 26. For the above cases of paired comparison, the unique $CHON_1$ compounds indicate the $CHON_1$ molecules identified in $PM_{2.5}$ collected from the air spray (/no water spray-A) road segments. The light orange background represents areas of HOA, BBOA and VEOA, SV-OOA, and LV-OOA. The grey circles refer to the identified oxidation-product pairs.

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66 **Figure 6.**
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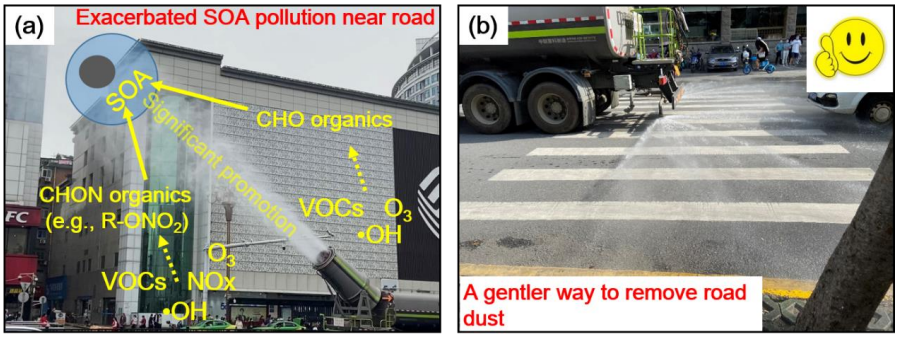

68

69 **Figure 6.** Conceptual picture showing the influence of (a) mist cannon truck and (b)
70 traditional sprinkling truck on SOA formation in the urban road environment.
71
72

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73 **Figure 7.**

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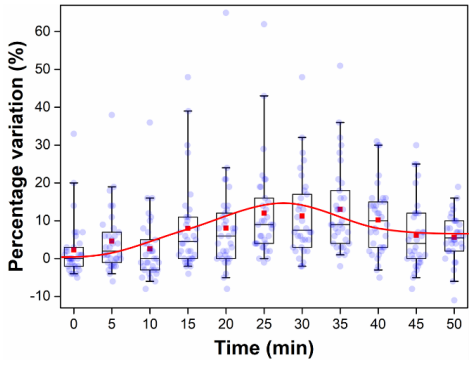

75

76 **Figure 7.** The time series of percentage variations in $PM_{2.5}$ mass concentrations after
77 mist cannon truck operation. Each box encompasses the 25th−75th percentiles.
78 Whiskers are the 5th and 95th percentiles. The solid lines and squares inside boxes
79 indicate the median and mean. All individual data are also presented as circles.

80