



## RESEARCH ARTICLE

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### Key Points:

- Wet deposition of WSON increased significantly during fall with elevated WSON concentrations and WSON/WSTN ratios in rainwater
- Wet deposition of WSON was largely attributed to in-cloud scavenging
- Biomass burning in the harvest season was a significant source of in-cloud WSON

### Supporting Information:

- Supporting Information S1

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## Enhanced Wet Deposition of Water-Soluble Organic Nitrogen During the Harvest Season: Influence of Biomass Burning and In-Cloud Scavenging

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**Abstract** Globally water-soluble organic nitrogen (WSON) accounts for about one third of water-soluble total nitrogen in atmospheric deposition, yet the key factors influencing WSON deposition remain uncertain. In the present study, precipitation and aerosol samples were collected during 2016–2018 at a forest site in the Pearl River Delta, south China. Rainwater WSON concentrations were found to elevate significantly during fall, and wet deposition of WSON during fall could account for about 50% of its annual total wet deposition. The wet deposition and rainwater concentrations of K<sup>+</sup> and levoglucosan, which are tracers for biomass burning emissions, also increased substantially during fall. The average WSON/water-soluble total nitrogen ratio in precipitations (0.48) was over two times higher than that in aerosols (0.20) during fall, while during other seasons, the ratios in precipitations (0.17) and in aerosols (0.19) were comparable. Moreover, concentrations of WSON in rainwater, unlike that of inorganic N, did not decrease significantly with the increase of precipitation amount during fall. These results suggested that enhanced biomass burning during fall (harvest season) might be an important source of in-cloud WSON, and in-cloud scavenging, instead of below-cloud washout, likely contributed remarkably to the wet deposition of WSON.

## 1. Introduction

Atmospheric nitrogen (N) deposition is the pathway of ultimately scavenging reactive N species in the air (Duce et al., 2008; Galloway et al., 2004). The deposited N can act as the supplementary nutrition for ecosystems, while a surplus of N deposition may result in adverse ecological effects such as acidification of soils, water eutrophication, and reductions of biodiversity and plant production (Bleeker et al., 2011; Liu et al., 2011; Matson et al., 1999). Previous studies touching N deposition mostly focused on inorganic N deposition, although water-soluble organic N (WSON) typically accounts for 25–35% in water-soluble total N (WSTN) in wet/bulk deposition (Cornell, 2011; Cornell et al., 2003; Neff et al., 2002). The impacts of organic N deposition on ecosystems, though having not been well understood, should be similar to those of inorganic N deposition. On one hand, the uptake of low molecular weight organic N (e.g., amino acid) by plants occurs widely in low-N ecosystems (Andersen et al., 2017; Kielland, 1994; Kielland et al., 2006). On the other hand, N-containing polymers may be depolymerized by microbial extracellular enzymes to organic N-containing monomers, which can be utilized by plants directly or be transformed to soil inorganic N (Schimel & Bennett, 2004). Therefore, more studies are needed to address organic N deposition if we are to get a more holistic picture of N deposition and its impacts on the ecosystems.

Atmospheric WSON exists significantly in gaseous, particulate, and aqueous phases (Matsumoto et al., 2019; Weathers et al., 2000). They can be emitted directly from various anthropogenic and biogenic sources (i.e., primary sources) or produced secondarily via multiple atmospheric processes (i.e., secondary sources). The major primary sources include biomass burning (Mace, Artaxo, & Duce, 2003; Zamora et al., 2011), vehicle and ship emissions (Rastogi et al., 2011; Yu et al., 2017), agricultural activity (Song et al., 2017; Zhang et al., 2012), soil dust (Mace, Kubilay, & Duce, 2003; Shi et al., 2010), terrestrially biogenic emission (Miyazaki et al., 2014), and oceanic emission (Luo et al., 2018; Violaki et al., 2015). Reactions involving

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carbonyls and ammonia (Galloway et al., 2009), as well as hydrocarbons and  $\text{NO}_x$  (including  $\text{NO}_3$  radical) (Perring et al., 2013), are the typical pathways to form secondary organic N compounds. The complex sources and atmospheric processes of WSON may result in a great heterogeneity either spatially or temporarily in WSON deposition pattern. For example, WSON/WSTN ratios in precipitations ranged from below 10% to over 80% on a global scale without clear spatiotemporal patterns (Cornell, 2011). Based on multiple-site observations, Zhang et al. (2012) found significant correlation between the concentrations of inorganic N and WSON in bulk deposition, yet Cape et al. (2012) revealed that WSON was not correlated with  $\text{NO}_3^-$ -N or  $\text{NH}_4^+$ -N in wet/bulk deposition. The key factors influencing WSON deposition warrant further investigation.

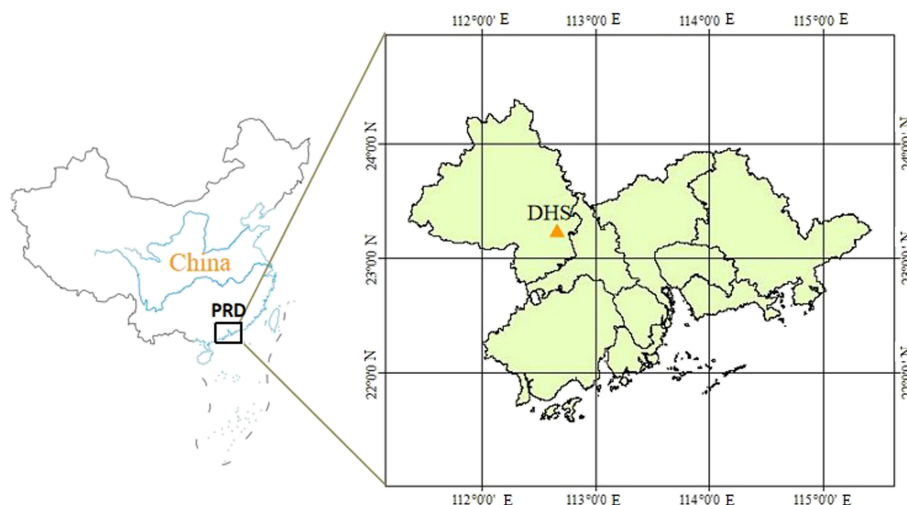
Wet deposition involves in-cloud scavenging (rainout) and below-cloud scavenging (washout) processes. Cape et al. (2011) suggested that organic N averagely accounts for about 30% in total N in ambient aerosol with an interquartile range of 17–35%. This range is analogous to the typical proportion of organic N in total N in rainwater, which is 25–35% (Cornell, 2011). These results suggest that below-cloud scavenging of aerosol N may contribute substantially to the deposited N in rainwater. A study by Mace, Kubilay, and Duce (2003) in eastern Mediterranean indicated that aerosol WSON might be an important contributor to WSON in rainwater, yet the relationships between urea and ion species in rainwater and aerosol were quite different. Another study conducted in Tampa Bay, however, suggested below-cloud scavenging of aerosol WSON was a very minor contributor to WSON in rainwater, although a larger contribution of aerosol inorganic N to wet inorganic N deposition was found, especially for  $\text{NO}_3^-$ -N (Calderon et al., 2007). Altieri et al. (2016) studied the concentrations and chemical compositions of rainwater and aerosol WSON collected on the island of Bermuda and found that the WSON in marine rain is compositionally different from that in concurrently collected aerosols, suggesting that in-cloud scavenging, instead of below-cloud washout, is the main contributor to rain WSON. The available studies imply that more studies should further compare the chemical compositions in rainwater and aerosol to uncover the fate of atmospheric organic N, particularly in-cloud and below-cloud scavenging of WSON.

In the remote marine atmosphere, the increase of WSON concentration seems to associate closely with enhanced oceanic biogenic activities (Altieri et al., 2016; Luo et al., 2018; Violaki et al., 2015), and in-cloud scavenging of WSON may contribute dominantly to its wet deposition (Altieri et al., 2016). In continental areas, WSON can derive from various anthropogenic and natural sources, and the key sources and scavenging processes contributing to wet WSON deposition remain unclear. The Pearl River Delta (PRD) city cluster is located in south China and considered as one of the largest megacities in the world with an area of  $5.6 \times 10^4 \text{ km}^2$  and a population of ~43 million and has experienced rapid industrialization in the last several decades. Previous studies found that WSON deposition rates at some sites of this region could reach  $8\text{--}18 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  in 2005–2009 (Fang et al., 2008; Li et al., 2012; Wang et al., 2013), and a recent study revealed that deposition rates of WSON at three contrasting sites were still as high as  $9\text{--}17 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  in 2016–2018 (Yu et al., 2020), which are among the highest levels of WSON deposition rates in developed regions worldwide (Cape et al., 2012; Cornell, 2011; Jiang et al., 2013; Neff et al., 2002). In the present study, we selected one station in this region, compared the chemical compositions in concurrently collected rainwater and aerosol samples, to explore the key sources and scavenging processes influencing wet WSON deposition in continental areas.

## 2. Methodology

### 2.1. Sampling Site

The geographical location of the sampling site is shown in Figure 1. DingHuShan (DHS) ( $112^\circ 33' \text{ E}$ ,  $23^\circ 11' \text{ N}$ ) is a forest site around the tropic of cancer. The sampling site is on the top of a small hill and is not shaded by trees. This site is located in Dinghushan Biosphere Reserve in the northwest of the PRD. The reserve is ~90 km west of the metropolitan city of Guangzhou (~12 million inhabitants) and ~180 km northwest of Hong Kong (~7 million inhabitants). In addition, this place is surrounded by paddy fields several kilometers away (Wang et al., 2013), and agricultural activity is an important local source of atmospheric reactive N.



**Figure 1.** Geographical location of the sampling site. DHS is a forest site in the northwest of the PRD. In addition, this site is surrounded by large areas of paddy fields.

## 2.2. Sample Collection

### 2.2.1. Collection of Deposition Samples

Deposition samples were collected using an automatic wet-dry sampler (ZR-3901, Qingdao Junray Intelligent Instrument Inc., China) with a funnel to collect wet deposition and a cylinder to collect dry deposition. When there is no rain, the funnel is covered by a lid, and dry deposition is collected. When rainfall is detected by the rain sensor, the lid is automatically switched to cover the cylinder, and wet deposition (rainwater) is collected. The rainwater flows from the funnel into an 18 L plastic bottle. The lid is automatically switched back when rainfall ceases and the rainwater on the rain sensor surface is evaporated quickly since the sensor is always heated. Normally, event-based rainwater was collected. However, if it rained in consecutive days, rainwater was collected every 5 days. The collection system was cleaned with ultrapure water after each sampling. Teflon bottles were used to save the samples. The Teflon bottles were first soaked by mixture of organic solvent including dichloromethane, hexane, and methanol for a week and then soaked by dilute nitric acid (~10%) for another week. Then, the bottles were thoroughly cleaned by ultrapure water and dried before use. All samples were transferred to a refrigerator as soon as possible after collection. They were frozen at  $-20^{\circ}\text{C}$  and analyzed within a month.

We regularly tested (twice a month) the sampler to ensure it works normally. The container used to collect rainwater was cleaned at least three times with dilute nitric acid (~10%) and then ultrapure water after each sampling. No target species can be detected in the washing water after the container was cleaned. Also there is no detectable species in the clean Teflon bottles before they were used to save the deposition samples. Field blanks were also collected each week to detect contamination that may occur in the sample transport process. The blank sample was ultrapure water and placed in the clean Teflon bottle, which is used to collect the deposition samples. The blank samples were transported to the laboratory and analyzed in the same manner with the deposition samples. Across the sampling period, the blank samples were found not to be contaminated, suggesting the deposition samples were also not contaminated. Our sampling protocols are similar to those in previous studies investigating N deposition (e.g., Karthikeyan et al., 2009; Kuang et al., 2016; Nadim et al., 2001; Wang et al., 2019; Xu et al., 2015).

Deposition samples were concurrently collected at three contrasting sites (one urban, one rural, and one forest) from September 2016 to August 2018. Detailed descriptions of sampling can be found elsewhere (Yu et al., 2020). Wet and dry deposition rates of  $\text{NO}_3^-$ -N,  $\text{NH}_4^+$ -N, and WSON, as well as spatiotemporal patterns of  $\text{NO}_3^-$ -N,  $\text{NH}_4^+$ -N, and WSON in wet and dry deposition at the three sites, were presented previously (Yu et al., 2020). Wet WSON deposition was found to represent a major fraction of total WSON deposition, and remarkably, there was a substantial increase of the wet deposition rate of WSON during fall at all the three sites. In the present study, we used a subset of the data, which is the result of wet N deposition at

the forest site (named DHS, and description of the site is presented above), combining the data of aerosol N collected at the site from September 2016 to August 2017, to further investigate the factors resulting in a largely enhanced wet WSON deposition during fall.

### 2.2.2. Collection of Aerosol Samples

Ambient PM<sub>2.5</sub> samples were collected from September 2016 to August 2017 at the DHS site. Daily samples were collected every 5 days using a high-volume sampler (Tisch Environmental Inc., Ohio, USA) with a constant flow rate of 1.1 m<sup>3</sup> min<sup>-1</sup> at the site. Quartz fiber filter (20.32 cm × 25.40 cm, Whatman, Mainstone, Shropshire, UK), used as collection substrate, was prebaked for 6 hr at 450°C to remove potential organics. The detailed descriptions of sampling processes can be found elsewhere (Yu et al., 2016; Yu et al., 2017). The flow rate was calibrated before and after sampling using a flowmeter (Dwyer Instruments Inc., Michigan, USA). Field blanks were also collected in a sampling campaign for data correction.

### 2.3. Laboratory Analysis

Inorganic N species (NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>) and other major ions (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>) in precipitation samples were measured by ion chromatography (Metrohm, 883 Basic IC plus, Switzerland) after filtering through a 0.22 μm pore size PTFE filter (ANPEL Inc., Shanghai, China). Water soluble organic carbon (WSOC) and WSTN in precipitation were determined by TOC/TN analyzer (Vario TOC select, Elementar Inc., Germany) using a thermo-catalytic oxidation approach (Miyazaki et al., 2011; Yu et al., 2017).

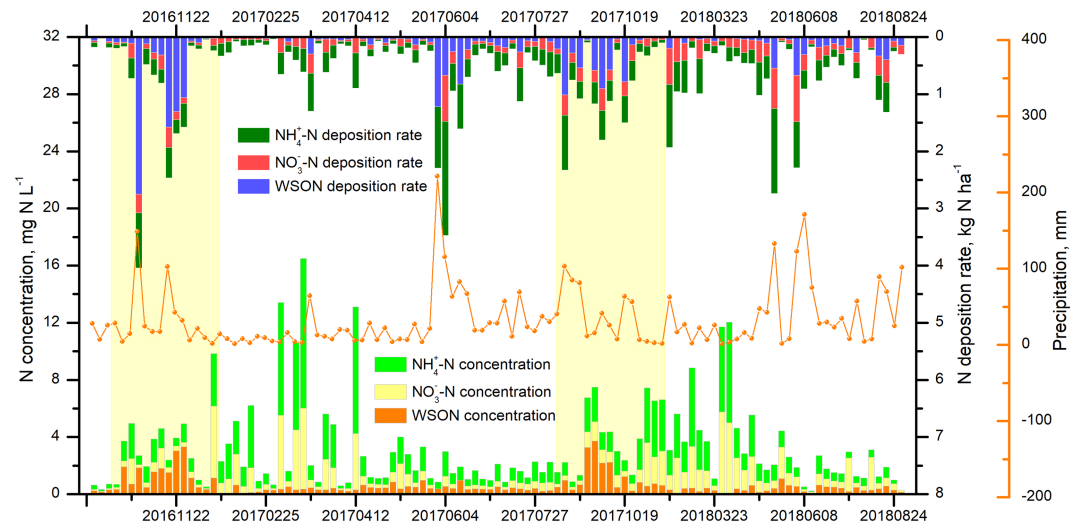
The concentrations of levoglucosan and mannosan in precipitation were measured by high-performance anion-exchange chromatography with a pulsed amperometric detection method after filtering through a 0.45 μm Teflon filter (Millipore, Billerica, MA, USA). The measurement was carried out on a Dionex DX-500 series ion chromatograph (Sunnyvale, CA, USA), consisting of an LC30 Chromatography Oven, a GP40 Gradient Pump, and an ED40 Electrochemical Detector (with an electrochemical cell and a conventional gold electrode). The separation was achieved on a Dionex CarboPac PA10 analytical column (4 × 250 mm) with aqueous sodium hydroxide (NaOH) as eluent at a flow rate of 0.5 ml min<sup>-1</sup>. Detailed description about the determination can be found elsewhere (Kuang et al., 2015).

To determine the species in aerosol, a punch (5.06 cm<sup>2</sup>) of the filter was extracted twice with 10 ml (a total of 20 ml) ultrapure Milli-Q water (18.2 MΩ·cm) and each for 20 min using an ultrasonic ice-water bath (Fu et al., 2014). The 20 ml water extracts were used to measure water-soluble ions, WSOC, and WSTN with the same method as that of the deposition samples described above. WSON is calculated as the difference of WSTN and inorganic nitrogen (NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>). Negative WSON values (about 6%) were set as zero, as addressed by previous studies (Fang et al., 2009; Mace, Artaxo, & Duce, 2003; Nakamura et al., 2006). The detection limits for WSTN, NH<sub>4</sub><sup>+</sup>, and NO<sub>3</sub><sup>-</sup> were 0.02, 0.01, and 0.02 mg L<sup>-1</sup>. N species were not detected in the ultrapure water and blank aerosol samples.

## 3. Results

Figure 2 shows the temporal variations of the concentrations of NO<sub>3</sub><sup>-</sup>-N, NH<sub>4</sub><sup>+</sup>-N, and WSON in precipitation and their wet deposition rates at the sampling site across two study years. NO<sub>3</sub><sup>-</sup>-N and NH<sub>4</sub><sup>+</sup>-N concentrations showed similar variation patterns with high levels from fall to early spring, especially in winter when the precipitation amount was lower (Figures 2 and S1 in the supporting information). The deposition rates of NO<sub>3</sub><sup>-</sup>-N and NH<sub>4</sub><sup>+</sup>-N, however, showed higher levels in summer, mainly due to the high precipitation amount in the period (Figure 2), as demonstrated by the significant correlation between inorganic N deposition rates and precipitation amounts (Figure S2).

WSON in precipitation exhibited different seasonal pattern with inorganic N at DHS. WSON concentration increased substantially during fall at the site (Figures 2 and S1). The average of monthly precipitation-weighted concentration of WSON during fall was 1.17 mg N L<sup>-1</sup> at DHS, which was about three times higher than (*p* < 0.01) that in other seasons when WSON concentration averaged 0.43 mg N L<sup>-1</sup> (Table 1). Annual wet WSON deposition rate at DHS was 11.2 kg N ha<sup>-1</sup> yr<sup>-1</sup>, which was among the highest level of WSON deposition in the world (Cape et al., 2012; Cornell, 2011; Zhang et al., 2008; Zhang et al., 2012). Notably, the wet WSON deposition in fall accounted for about 50% of annual wet WSON deposition at the DHS site (Table 1). Analogous to WSON concentration, the WSON/WSTN ratio in



**Figure 2.** Time series of the concentrations of  $\text{NH}_4^+$ -N,  $\text{NO}_3^-$ -N, and WSON in precipitation and their wet deposition rates at the sampling site across the whole sampling period. The variation of precipitation amounts was also presented with yellow line. Shaded in faint yellow covers harvest season (fall).

precipitation also increased significantly in fall. Annual average WSON/WSTN ratio at DHS was 0.25; and it was 0.48 during fall, much higher than ( $p < 0.05$ ) the average value of 0.17 in other periods (Table 1).

The concentrations of  $\text{NO}_3^-$ -N and  $\text{NH}_4^+$ -N in ambient  $\text{PM}_{2.5}$  also showed high levels during fall to spring (Figures 3 and S1), similar to their counterparts in precipitation. However, WSON concentration showed more consistent seasonal variations with inorganic N in  $\text{PM}_{2.5}$  than in precipitation (Figure S1), as demonstrated by the much stronger correlation between inorganic N and WSON in  $\text{PM}_{2.5}$  than in precipitation (Figure S3). Average aerosol WSON concentration was  $0.67 \mu\text{g m}^{-3}$  at DHS during fall, and it was  $0.58 \mu\text{g m}^{-3}$  in other period (Table 1). Although average aerosol WSON concentration during fall was higher than that in other period at the site, the increase was not statistically significant ( $p > 0.05$ ), different from the result in precipitation. Average WSON/WSTN ratio in aerosol was 0.20 at DHS during fall, comparable to the average of 0.19 in other seasons. It is worth noting that average WSON/WSTN ratio in ambient  $\text{PM}_{2.5}$  was significantly smaller than that in precipitation at the site during fall ( $p < 0.05$ ).

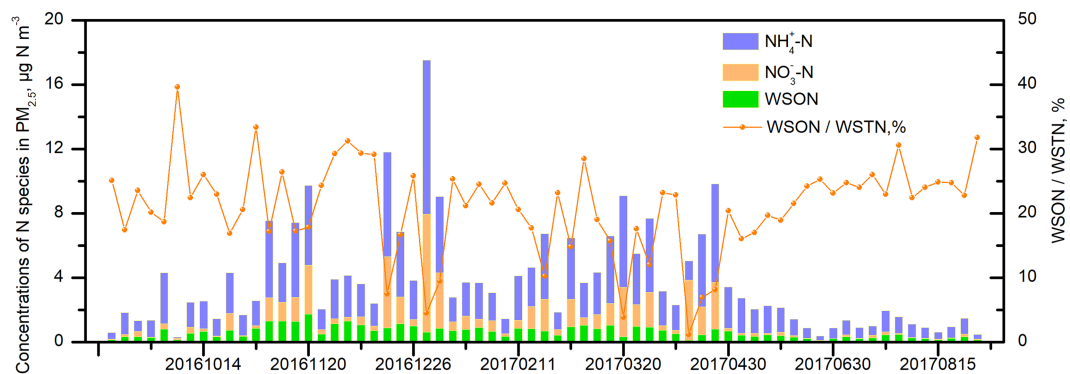
**Table 1**

Concentrations of  $\text{NO}_3^-$ -N,  $\text{NH}_4^+$ -N, and WSON in Precipitation ( $\text{mg N L}^{-1}$ ) and in Aerosol ( $\mu\text{g N m}^{-3}$ ), the Monthly Wet Deposition Rates of  $\text{NO}_3^-$ -N,  $\text{NH}_4^+$ -N, and WSON, and the Percent Contribution of WSON to WSTN in Precipitation and Aerosol at the DHS Site

Seasons	Months	Concentration in precipitation ( $\text{mg N L}^{-1}$ )			Wet deposition rate ( $\text{kg N ha}^{-1} \text{ month}^{-1}$ )			Concentration in aerosol ( $\mu\text{g N m}^{-3}$ )			% of WSON in precipitation	% of WSON in aerosol
		$\text{NO}_3^-$ -N	$\text{NH}_4^+$ -N	WSON	$\text{NO}_3^-$ -N	$\text{NH}_4^+$ -N	WSON	$\text{NO}_3^-$ -N	$\text{NH}_4^+$ -N	WSON		
Fall	Sep.	0.3	0.5	0.8	0.3	0.5	0.8	0.2	1.1	0.3	50.0	18.8
	Oct.	0.5	1	1.6	0.8	1.7	2.8	0.3	1.6	0.6	51.6	24.0
	Nov.	0.6	0.9	1.1	0.8	1.2	2.3	1.8	4.1	1.1	42.3	15.7
Winter	Dec.	7.0	4.7	1.1	0.1	0.1	0.02	0.7	2.5	1.1	8.6	25.6
	Jan.	1.1	1.9	0.2	0.7	1.1	0.1	2.2	3.7	0.8	6.3	11.9
	Feb.	0.8	1.6	0.3	0.2	0.5	0.1	1.0	2.5	0.7	11.1	16.7
Spring	Mar.	1.0	1.7	0.3	1.0	1.7	0.3	1.6	3.7	0.9	10.0	14.5
	Apr.	1.3	1.8	0.4	0.8	1.2	0.3	1.5	3.0	0.6	11.4	11.8
	May	0.4	0.8	0.4	0.9	1.9	0.9	0.1	1.7	0.4	25.0	18.2
Summer	Jun.	0.4	0.7	0.4	1.4	2.8	1.7	0.04	0.6	0.2	26.7	25.0
	Jul.	0.5	0.6	0.4	0.8	1.2	0.7	0.1	0.9	0.3	26.7	23.1
	Aug.	0.4	0.6	0.4	1.0	1.7	1.2	0.1	0.6	0.2	28.6	22.2

Note. Concentrations of N species in precipitation are 2 year averages of monthly precipitation-weighted concentrations.





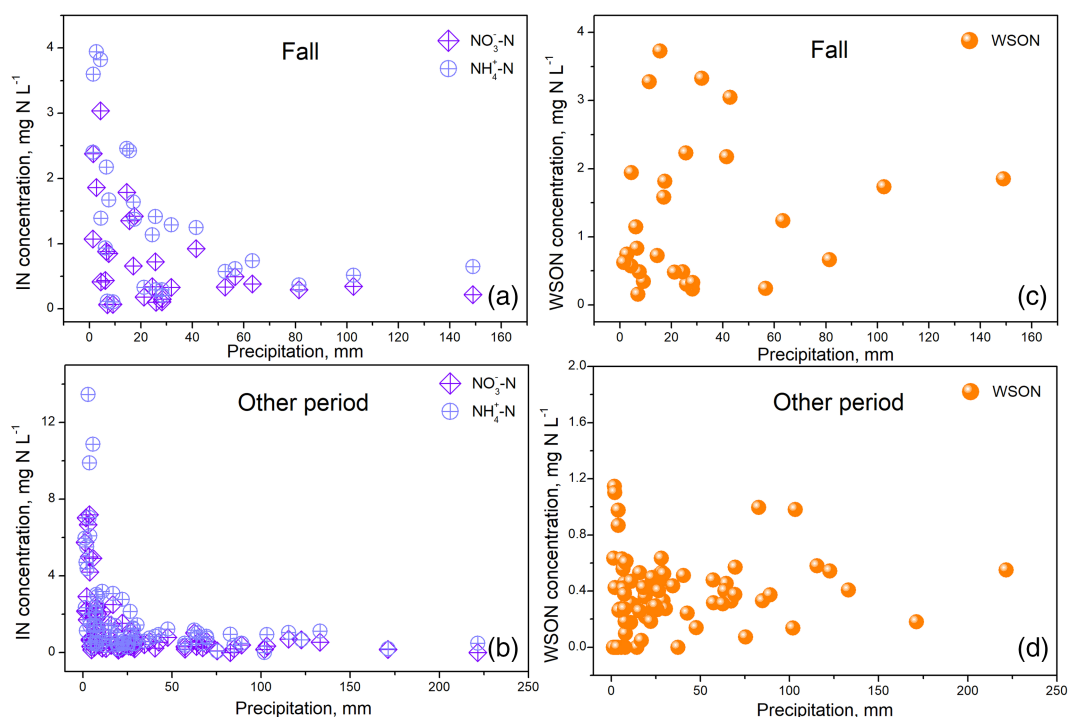
**Figure 3.** Time series of the concentrations of  $\text{NH}_4^+\text{-N}$ ,  $\text{NO}_3^-\text{-N}$ , and WSON in  $\text{PM}_{2.5}$  at the DHS site across the sampling year. Yellow line shows the variation of the proportion of WSON in WSTN in  $\text{PM}_{2.5}$ .

## 4. Discussions

### 4.1. In-Cloud Scavenging of WSON

Wet deposition of WSON involves in-cloud scavenging (rainout of aerosols/gases during the formation of cloud droplets) and below-cloud scavenging (washout of aerosols/gases present below the cloud base by raindrops during their fall), and the latter can be further divided into three parts: fine-mode particle scavenging, coarse-mode particle scavenging, and gas scavenging. Above results suggested the inconsistent seasonal variations of WSON in the collected precipitations and fine-mode particles ( $\text{PM}_{2.5}$  samples). In particular, for the precipitation and  $\text{PM}_{2.5}$  samples collected on the same day in fall, WSON/WSTN ratio in precipitation was two to three times higher than that in  $\text{PM}_{2.5}$ , suggesting that below-cloud scavenging of  $\text{PM}_{2.5}$  by rainfall could not explain the higher proportion of WSON in wet N deposition during fall. Previous studies also revealed that WSON/WSTN proportions in fine-mode aerosols observed at several sites in the PRD region ranged 10–30% (Liu et al., 2017; Yu et al., 2017), largely smaller than that observed in precipitation during fall from this study. Below-cloud scavenging of coarse particulate N may not be the reason either. Matsumoto et al. (2014) collected size-resolved particles at an urban and a forest site in Japan over 3 years and revealed that >90% of particulate WSON existed in fine mode and the average WSON/WSTN ratio in coarse particles was only 0.12. Aerosol collected in Guangzhou in the PRD region suggested that the WSON/WSTN ratio in coarse particle could be high (>0.5), but the studies also suggested that major part of WSON occurred in fine mode (Liu et al., 2017; Lu et al., 2019).

If we further examine the relationships between deposited inorganic and organic N concentrations and precipitation amounts, we could found that, as shown in Figure 4, inorganic N concentrations decreased rapidly with the increase of precipitation amounts at the site, showing a washout process of atmospheric inorganic N by rainwater; in contrast, WSON concentrations remained relatively stable when the precipitation amounts increased, particularly in fall, suggesting that the high WSON concentrations in precipitation during fall should be not resulted from below-cloud scavenging of coarse particles, since coarse particles can be efficiently removed from the air by rainfall (Calderon et al., 2007). In gaseous phase, oxidized organic N species (e.g., peroxyacetyl nitrates and monofunctional alkyl nitrates) are barely water soluble (Perring et al., 2013; Roberts et al., 2007). Reduced organic N species are mainly amines, which are water soluble (Ge et al., 2011b). However, the typical concentration of amines is about 1–2 orders of magnitude lower than that of ammonia ( $\text{NH}_3$ ) in ambient air (Qiu & Zhang, 2013). Ge et al. (2011a) revealed that low-molecular weight aliphatic amines with one to six carbon numbers are the most common and abundant among amines. In south China, gas phase small amines in ambient air were totally several to tens of pptv (Liu et al., 2018), over 2 orders of magnitude lower than that of  $\text{NH}_3$ , which was typically about several ppbv (Pan et al., 2018). Liu et al. (2017) revealed that the sum of N in nine amines was only about 1% of  $\text{NH}_4^+\text{-N}$  in aerosol collected at an urban site in south China, suggesting a small ratio of amine-N to  $\text{NH}_3\text{-N}$  in gaseous phase at the site, since amines can be more readily partitioning to particle phase than  $\text{NH}_3$  (Qiu et al., 2011; You et al., 2014). Previous studies revealed that WSON represented <20% of WSTN in gas phase (Benítez et al., 2010; Matsumoto et al., 2019). Therefore, below-cloud scavenging of N species, both in particulate and gaseous



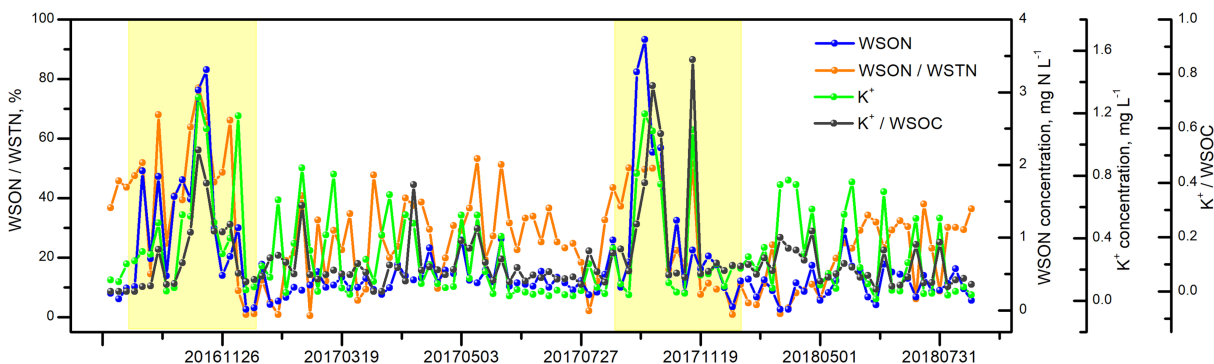
**Figure 4.** The relationships between the concentrations of N species in precipitation and precipitation amounts. (a) Inorganic N concentration versus precipitation amount during fall; (b) inorganic N concentration versus precipitation amount during other period; (c) WSON concentration versus precipitation amount in fall; and (d) WSON concentration versus precipitation amount during other period; the concentration of WSON did not decrease significantly along with the increase of precipitation amount at the site during fall.

phases, could not result in the observed high WSON/WSTN ratio in precipitation during fall. There might be a large amount of WSON already existing in cloud so that WSON concentrations in rainwater did not significantly decrease with the increase of precipitation amounts.

Our results suggest that the wet deposition of inorganic N might be largely attributed to below-cloud scavenging, while in-cloud scavenging may contribute remarkably to the wet deposition of WSON. Weathers et al. (2000) observed that organic N accounted for 15–97% (median: 73%) of total N in 16 cloud water samples collected in southern Chile. Recent statistics demonstrated that on a global scale, average WSON/WSTN ratio was about two times higher in rainwater than in aerosol (Luo et al., 2016), suggesting WSON might be enriched in cloud in comparison with inorganic N. In addition, WSON/WSTN ratio in precipitation is diffusive with a range of below 10% to over 80% (Cornell, 2011; Luo et al., 2016), and the correlation between WSON and inorganic N in precipitation differed much among studies (e.g., Cape et al., 2012; Zhang et al., 2012). However, in ambient aerosol, WSON and inorganic N were normally well correlated, and the WSON/WSTN ratios were normally lower than 25% (Luo et al., 2016). Differential scavenging processes (in-cloud and below cloud) for WSON and inorganic N might be an important factor of resulting in a complex relationship between them in precipitation. Cape et al. (2011) also argued that WSON concentration in cloud was normally higher than that in precipitation, with few correlations with inorganic N. Notably, larger range of WSON/WSTN ratio in precipitation than in aerosol suggested the compositions of N species in cloud might be much discrepant in different cloud events (i.e., WSON/WSTN ratio in cloud is not always high).

#### 4.2. Contribution of Biomass Burning to In-Cloud WSON

It is worthwhile to figure out the reasons for elevated levels of WSON in cloud during fall. Possible emission sources, including industrial emissions, power plant, and on-road mobile sources, showed very small seasonal variations in the PRD region (Zheng et al., 2009). However, biomass (straw) burning was much more intensive during fall-winter period in the PRD region (Ding et al., 2012; He et al., 2014; Yu et al., 2016; Yu



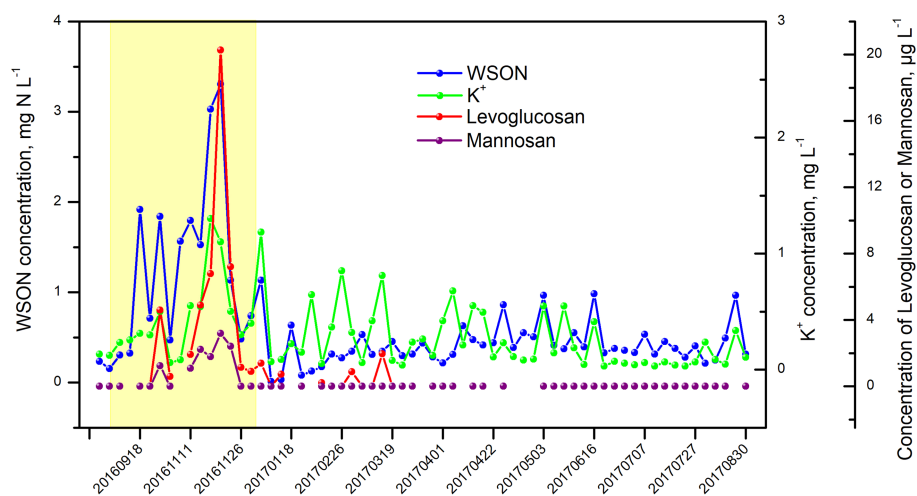
**Figure 5.** Time series of WSON concentration, WSON/WSTN ratio,  $K^+$  concentration, and  $K^+$ /WSOC ratio in precipitation at the sampling site. Shaded in faint yellow covers harvest season (fall).

et al., 2017; Zhang et al., 2013). Additionally, biomass burning has been recognized as an important source of particulate WSON (Mace, Artaxo, & Duce, 2003; Yu et al., 2017; Zamora et al., 2011). The enhanced biomass burning during fall (harvest season) might be a primary factor resulting in the high level of WSON in cloud.

Ambient potassium ( $K^+$ ) was normally regarded as a tracer of biomass burning (Andreae, 1983; Chen & Chen, 2010; Liu et al., 2016; Shi et al., 2010; Wang et al., 2017). As shown in Figure 5, there was a substantial enhancement of  $K^+$  concentrations in precipitation during fall, consistent with the enhanced WSON concentrations and WSON/WSTN ratios during the period, suggesting possible contribution of biomass burning to WSON deposition.  $K^+$  may be also derived from sea salt, soil dust, and biogenic emission other than biomass burning (Chen et al., 2010; Pöhlker et al., 2012). However, sea salt  $K^+$  was negligible (<5%) in our samples according to the calculation using sodium ( $Na^+$ ) tracer (Chen et al., 2010). Also higher  $K^+$  concentrations occurred when air masses came from continental regions in the present study. Calcium ( $Ca^{2+}$ ) concentrations were found to not increase during fall with  $K^+$ , indicating the enhanced  $K^+$  during fall was not attributed to soil dust either. Biological particles (e.g., fungal spore), containing  $K^+$  and organic N, are expected to contribute  $K^+$  and organic N in precipitation since they are known to avaiably serve as ice nucleators (Christner et al., 2008; Pöschl et al., 2010). However, the elevated wet deposition of WSON and  $K^+$  during fall should be attributed to biomass burning rather than biogenic emission, as evidenced by several facts.

First, the  $K^+$ /WSOC ratios in precipitation also increased substantially during fall (Figure 5). However, the ratio of  $K^+$  to organic carbon for biological particles is quite low. For example, Zhang et al. (2015) observed that average  $K^+$  to organic carbon ratio was about 0.05 in biological aerosol collected at a tropical rainforest site. In contrast, Wang et al. (2017) found that  $K^+$  to organic carbon ratio in aerosol heavily influenced by straw burning could be as high as 0.25. In the present study, average  $K^+$ /WSOC ratio in precipitation was 0.22 during fall and 0.08 during other periods. The largely elevated  $K^+$ /WSOC ratios in precipitation during fall might suggest the contribution to WSON deposition by biomass burning instead of biological particles. Second, the ratio of organic carbon to organic nitrogen (organic C/N ratio) may be also different between biological and biomass burning particles. Mace, Artaxo, and Duce (2003) collected aerosols in Amazon basin during wet (biogenic emission) and dry (biomass burning) seasons, which provides a good case to compare the chemical compositions of aerosols from biogenic emission and biomass burning. The results suggested in aerosol associated with biogenic emission, WSON concentration was low, and the organic C/N ratio was quite high, while the reverse was true for aerosol collected in biomass burning season. Mace, Artaxo, and Duce (2003) reported that tropical forests typically have a C/N ratio of 150. Descolas-Gros and Schölzel (2007) revealed that the mean C/N ratio for evergreen trees pollen grains was about 50. Bulk C/N ratio for biomass burning particles remains uncertain. However, available studies suggested that there are large amounts of N-containing molecules with low C/N ratio emitted from biomass burning. For example, with application of ultrahigh-resolution mass spectrometer, Laskin et al. (2009) and Wang et al. (2017) found that biomass burning would release lots of alkaloid compounds with C/N ratio of 2.5–10. In the present study, we found that both in precipitation and aerosol, WSON concentration was high, and WSOC/WSON ratios were relatively low during fall, and the WSOC/WSON ratios were largely elevated in





**Figure 6.** Variations of WSON concentration,  $K^+$  concentration, levoglucosan, and mannosan concentrations in precipitation at the DHS site from September 2016 to August 2017. Shaded in faint yellow covers harvest season (fall).

spring and summer (Figure S4). Third, in precipitation, the concentrations of levoglucosan and mannosan, two widely used biomass burning organic tracers (Ding et al., 2012; Kuang et al., 2015), also increased substantially during fall at the DHS site, as shown in Figure 6. Levoglucosan and mannosan in most of our rainwater samples were undetectable. However, levoglucosan and mannosan in rainwater collected in fall 2016 were detectable and showed much higher concentrations than in other seasons (Figure 6).  $K^+$  showed consistent enhancement with levoglucosan and mannosan (Figure 6), reinforcing that the elevated  $K^+$  in precipitation during fall was derived from biomass burning. Fourth, biogenic emission might be more intensive in spring and summer (growing seasons) than in fall in south China (Ho et al., 2005). Therefore, the largely enhanced wet WSON deposition during fall might be ascribed to the elevated biomass (straw) burning during harvest season. In fact, biomass burning particles might also serve as ice nucleators which induce rain formation (Szyrmer & Zawadzki, 1997). MODIS data also show that across the sampling period, there were many fire points around the DHS site, especially during fall (Figure S5). Note that a biomass burning event will not necessarily result in an enhanced WSON concentration in rainwater collected at a certain site due to meteorological conditions, while biomass burning tracers in collected rainwater samples clearly signaled the influence of biomass burning on rainwater compositions.

$K^+$  concentration in precipitation did not decrease significantly with the increase of precipitation amount at DHS during fall (Figure S6), similar to the deposition pattern of WSON, suggesting significant amount of  $K^+$  might also exist in cloud during the period. Meanwhile,  $Ca^{2+}$  concentrations decreased sharply with the increase of precipitation amounts at DHS (Figure S6), reinforcing that the sources of  $K^+$  and  $Ca^{2+}$  were different during fall. Significant amount of  $K^+$  and WSON in cloud might suggest that biomass burning particles containing  $K^+$  and WSON might be an important source of in-cloud  $K^+$  and WSON. We previously found that the WSON/WSTN ratio could be over 0.8 in particles directly emitted from biomass burning (Yu et al., 2017), supporting the simultaneous occurrences of high  $K^+$  level and WSON/WSTN ratio in the cloud influenced by biomass burning.

It is noticeable that enhanced biomass burning during the harvest season largely increased WSON concentration and WSON/WSTN ratio in cloud but not in the collected ambient aerosol, although WSON concentration in the surface aerosols marginally increased during fall at the site. Hot biomass burning smoke is readily lofted, and significant impacts of biomass burning plumes on the physicochemical properties of clouds have been demonstrated by reanalysis of remote sensing data (Brioude et al., 2009; Fromm et al., 2000; Fromm & Servranckx, 2003) as well as direct airborne characterization based on aircraft measurements (Mardi et al., 2018). Lofted biomass burning plumes might enhance in-cloud WSON and thereby wet WSON deposition. Abundant WSON species can be primarily emitted from biomass burning (Laskin et al., 2009; Mace, Artaxo, & Duce, 2003; Wang et al., 2017) or secondarily formed during upward transport of biomass burning plumes and in-cloud processing. The detailed mechanisms associated with the secondary

formation of WSON remain unclear, but several pathways may exist. The atmospheric aging of biomass burning plumes would yield abundant carbonyls (e.g., glyoxal and methylglyoxal), which can react with ammonia ( $\text{NH}_3$ ) and/or ammonium ( $\text{NH}_4^+$ ) to form organic N-containing compounds such as imidazole (Ervens et al., 2011; Galloway et al., 2009; Noziere et al., 2009). This pathway is a nonradical reaction and occurs dominantly in aqueous phase (Ervens et al., 2011). Ito et al. (2015) estimated that WSON deposition to the ocean due to biomass burning from the secondary formation involving aqueous phase reaction of glyoxal and methylglyoxal with ammonium is close to that from the primary emissions. Meanwhile, Lim et al. (2016) proposed that in aqueous phase, organic nitrates may be formed via nonradical reactions of glyoxal hydrate and nitric acid (esterification reaction) based on laboratory experiments. Organic nitrates can also be formed from the reactions between organic peroxy radicals and nitric oxide (NO), as well as alkenes with the nitrate radical ( $\text{NO}_3$ ) (Perring et al., 2013). Abundant organics,  $\text{NH}_3$ , and  $\text{NO}_x$  are emitted from biomass burning (Fang et al., 2017). The above pathways are expected to occur along with aged biomass burning plumes with large amounts of carbonyls, especially when the plumes go upward with close proximity to clouds, where more humid air would facilitate the aqueous formation of organic nitrogen compounds.

In the present study, the collected ambient aerosols seemed to be less influenced by the lofted biomass burning plumes in the harvest season, which might suggest that there was a certain distance between the locations of biomass burning and our sampling site, so that the collected surface aerosols were not heavily influenced by biomass burning emissions. The sources of aerosol WSON was apportioned by positive matrix factorization analysis. The results show that dominant part of aerosol WSON is secondarily formed (Figure S7). The contribution of biomass burning to aerosol WSON did not enhance during fall (Figure S7), suggesting the enhanced biomass burning during fall failed to heavily influence the compositions of collected aerosol. These results are consistent with above discussions that biomass burning emission enhanced the wet deposition of WSON by significantly contributing to in-cloud WSON rather than aerosol WSON. However, further research should be conducted to better understand the influences of biomass burning on the sources and sinks of atmospheric WSON.

## 5. Conclusions

In the present study, precipitation and aerosol samples were collected at a forest site of the PRD, south China, to explore the key factors influencing wet WSON deposition in continental areas. We found that the wet WSON deposition and rainwater WSON concentration increased substantially during fall. Correspondingly, WSON/WSTN ratio in precipitation also much increased during fall and could be as high as 0.48 compared with 0.17 in other period. WSON/WSTN ratio in concurrently collected aerosol was 0.20 at the site during fall (other period: 0.19), over two times lower than that in precipitation during the period. In addition, during fall, WSON concentration in precipitation did not decrease significantly along with the increase of precipitation amount. These results suggested that in-cloud scavenging of WSON contributed remarkably to its wet deposition. In keeping with WSON concentration and WSON/WSTN ratio, the concentrations of  $\text{K}^+$ , levoglucosan, and mannosan, as well as  $\text{K}^+$ /WSOC ratio in precipitation, also largely increased during fall, indicating an important contribution of biomass burning to wet WSON deposition. Similar to WSON,  $\text{K}^+$  should also exist significantly in cloud, particularly in fall. Our results suggested that biomass burning should be an important source of in-cloud WSON and significantly influence the regional wet deposition rate and pattern of WSON.

Globally biomass burning (including natural wildfire and anthropogenic prescribed burning) is a primary source of atmospheric organic pollutants. Primary and secondary in-cloud WSON derived from biomass burning would influence cloud properties. On the other hand, results presented here is helpful to explain the deposition patterns, sources, and removal processes of atmospheric WSON. Future studies should focus on the speciation of WSON in cloud water, rainwater, and aerosols to better constrain the compositions, atmospheric processes, and environmental effects of WSON.

## Data Availability Statement

Data supporting this paper can be found in SKLOG Data Repository (<http://www.sklog-1.cn/wp-content/uploads/2020/02/wet-deposition-of-WSON-at-DHS.xlsx>).

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