Fine particle pH and its impact on PM$_{2.5}$ control in a megacity of Central China

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Abstract: Fine particle (PM$_{2.5}$) acidity greatly affects the formation of secondary aerosol, and the drivers of PM$_{2.5}$ pH variation are vital in understanding its effects. Moderate PM$_{2.5}$ acidity was found in Wuhan, a megacity of Central China, wherein 80% of PM$_{2.5}$ hold pH values ranging from 2-4. Total ammonia (NH$_x$) and sulfate contributed 79.1-93.7% to pH changes in spring and winter, while relative humidity was the largest contributor (33.7-36.3%) in summer and fall. By sensitivity simulations, PM$_{2.5}$ remained acidic with pH changes less than 0.5 units in spring, summer and fall in foreseeable future even when the concentration varied by two orders of magnitude. While pH changes in winter were three times those in the other seasons, and NH$_x$ changes was suggested as the indicator of PM$_{2.5}$ pH variation in winter. Furthermore, the impact of pH on PM$_{2.5}$ response to emissions control was evaluated. The pH has opposite influences on the effectiveness of SO$_2$ and NO$_x$ control in reducing PM$_{2.5}$, the former being more effective at low pH and the latter being more effective at high pH due to ammonium and nitrate gas-particle partitioning. The effect of NH$_x$ control on PM$_{2.5}$ reduction is nonlinearly affected by pH. It is directly effective at low pH, but more ammonia control is required before achieving effectiveness at high pH. For the current particulate pH of 3-4 in Wuhan, both SO$_2$ and NO$_x$ control are beneficial for PM$_{2.5}$ reduction. However, NH$_x$ control is less effective before it is reduced by approximately 20%.

Key words: Fine particle pH; Gas-particle partitioning; PM$_{2.5}$ reduction; ISORROPIA
1. Introduction

Fine particulate (PM$_{2.5}$) pH plays great influence on secondary aerosol formation and transformation through chemical kinetics and thermodynamics of gas-particle partitioning (Zheng et al., 2020; Cheng et al., 2016; Wang et al., 2016; Manktelow et al., 2010; Keene et al., 2004; Grassian, 2001; Underwood et al., 2001). Exploring the variations in atmospheric particle pH is essential for understanding the properties of atmospheric particles and their effects on the climate (Pye et al., 2020; Crumeyrolle et al., 2008; Watson et al., 2002), ecosystem (Johnson et al., 2008; Larssen et al., 2006; Schindler, 1988), and human health (Dockery et al., 1996). The PM$_{2.5}$ pH has garnered attention owing to its important role in haze formation in China (Zhou et al., 2018; Tian et al., 2018; Liu et al., 2017).

Fine particle pH is affected by precursor emissions (Shi et al., 2017) and meteorological conditions (He et al., 2012), resulting in different acidities at different sites. Many regions in China, such as Beijing (Ding et al., 2018; Wang et al., 2016; Cheng et al., 2016; Yang et al., 2015; He et al., 2012), Shanghai (Pathak et al., 2009), Guangzhou (Jia et al., 2018; Huang et al., 2011), Tianjin (Shi et al., 2017), Xi’an (Wang et al., 2018), Lanzhou (Pathak et al., 2009), Chongqing (He et al., 2012), Hong Kong (Yao et al., 2007; Yao et al., 2006; Pathak et al., 2004; Pathak et al., 2003), and Tai mountains (Zhou et al., 2012), have reported the fine particle acidity characteristics. There is a wide range of PM$_{2.5}$ pH in China, with values ranging between -2.5 (Yao et al., 2007) and 6.2 (Cheng et al., 2016), respectively. Previous studies investigated the impacts of particle chemical components (i.e., sulfate, nitrate and ammonium) on pH (Kakavas et al., 2021; Chen et al., 2019; Zheng et al., 2019; Ding et al., 2018; Liu et al., 2017; Guo et al., 2015), and highlighted the role of gas-particle partitioning in understanding the PM$_{2.5}$ pH (Guo et al., 2018; Guo et al., 2017; Liu et al., 2017). Additionally, aerosol water content (AWC) can also influence the particulate pH by H$^+$ production from aqueous reactions and the dilution of proton concentrations.
Few studies have quantified the contributions of different factors to the PM$_{2.5}$ acidity changes in different seasons.

The reduction of atmospheric particulate matter has always been a concern, especially after frequent haze pollution events occurring in China (Zhou et al., 2022; An et al., 2019; Bai et al., 2019; Tian et al., 2018). Many studies have explored the responses of PM$_{2.5}$ to precursor emissions control, such as SO$_2$, NO$_x$, and NH$_3$ (Pinder et al., 2008; Blanchard et al., 2000; Ansari and Pandis, 1998). Recently, the sensitivity of particulate nitrate to ammonia or nitric acid has become a research hotspot (Xu et al., 2019; Guo et al., 2018; Wu et al., 2016). Nitrate in PM$_{2.5}$ could be effectively reduced by ammonia emission control in North China (An et al., 2019; Liu et al., 2019), but unsensitive in other regions such as South China (Liu et al., 2019), Sichuan Basin (Liu et al., 2019), and East China (Xu et al., 2018). Moreover, studies have also focused on the evaluation methods and indicators of the effectiveness of PM$_{2.5}$ reduction in emission control (Nenes et al., 2020; Zheng et al., 2019; Xu et al., 2019; Wu et al., 2016). However, the effect of particle pH on the sensitivity of PM$_{2.5}$ precursor emissions have not been considered widely. This may lead to the ineffectiveness of emission control measures for particles reduction.

Based on the hourly observations of water-soluble inorganic ions in PM$_{2.5}$ and precursor gases in 2014 and 2018 in Wuhan, the driving factors of particulate pH changes during this period were identified and their contributions were quantified using a thermodynamic model. The variations of future PM$_{2.5}$ pH for each season were predicted. Besides, the effect of particulate pH on the response of PM$_{2.5}$ to precursor reductions was explored. Results here can deepen the understanding of aerosol acidity properties and provide a reference for fine particle reduction policy making.

2. Materials and methods

2.1 Observations
The observation site (114.36° N, 30.53° E) is approximately 20 m above ground and is located in a commercial/residential mixed area without obvious industrial emission sources (Figure 1). Water-soluble ions (WSI), including NH$_4^+$, K$^+$, Ca$^{2+}$, Na$^+$, Mg$^{2+}$, SO$_4^{2-}$, NO$_3^-$, and Cl$^-$ in PM$_{2.5}$, and atmospheric HNO$_3$, NH$_3$, and HCl were synchronously observed hourly using an online ions analyzer (Marga ADI 2080). The details about the instrument can be found in Text S1 and previous research (Zheng et al., 2019). Continuous monitoring was conducted from January to December in 2014 and 2018, except for data missing due to equipment maintenance. Hourly temperature (Temp) and relative humidity (RH) were obtained from the local observatory (Text S1) (Zheng et al., 2019). At this observation site, SO$_2$ and NO$_2$ were monitored hourly by ultraviolet fluorescence and chemiluminescence online monitoring equipment from 2013, respectively.

2.2 Simulations

The fine particle pH and AWC were calculated using the thermodynamic model ISORROPIA-II (Fountoukis and Nenes, 2007; Nenes et al., 1998) (http://nenes.eas.gatech.edu/ISORROPIA), wherein the inputs were NH$_4^+$, K$^+$, Ca$^{2+}$, Na$^+$, Mg$^{2+}$, SO$_4^{2-}$, NO$_3^-$, Cl$^-$, gaseous precursors (HNO$_3$, HCl and NH$_3$) (Song et al., 2018), ambient RH, and Temp. Concentrations and existing forms of species (gas or particle phase) under chemical equilibrium can be predicted by the model (Guo et al., 2018). The metastable state with forward mode was applied in this study because of its better performance (Weber et al., 2016; Guo et al., 2016; Hennigan et al., 2015; Guo et al., 2015; Fountoukis and Nenes, 2007). Similar to previous studies at this observation site (Zheng et al., 2019), there were good agreements between the predicted and observed concentrations for major species, as shown in Figure 2. The minimum observed RH was 30%, satisfying the model assumptions of inorganic ions in the liquid phase (Guo et al., 2017; Bertram et al., 2011; Fountoukis and Nenes, 2007; Ansari and Pandis, 2000). Data with RH > 95% were excluded.
owing to the exponential changes in AWC with RH, which could lead to huge pH uncertainty due to the
propagation of RH uncertainties (Guo et al., 2016; Guo et al., 2015; Malm and Day, 2001) and issues
with inlet transmission losses (Guo et al., 2016).

In Section 3.2, a series of sensitivity simulations were conducted to explore the key factors and their
contribution in each season. The chemical and meteorological factors, including SO4^2-, NHx (NH3+NH4+),
TNO3 (NO3^-+HNO3), TCl (Cl^-+HCl), RH, and temperature were evaluated. Each factor was subject to
interannual replacement. For instance, firstly based on 2014 observation, a factor was imported by 2014
and 2018 seasonal average, respectively, while the other model inputs were unchanged with 2014,
obtaining pH2014-4 and pH2014-8. Then based on 2018 observation, the similar simulation was conducted,
obtaining pH2018-4 and pH2018-8. The ∆pH (pH changes) was the average of the difference between pH2014-
4 and pH2014-8 and the difference between pH2018-4 and pH2018-8. The same approach was applied to each
factor and the simulation of AWC changes (and ∆AWC).

3. Results and discussion

3.1 Fine particle pH in 2014 and 2018

The annual average PM2.5 concentration significantly decreased by 45.7% in Wuhan from 2014
(92.2±57.6 μg m^-3) to 2018 (50.4 ±33.6 μg m^-3), while both of them still exceeded the PM2.5 annual value
of the secondary air quality standard in China (35 μg m^-3). The proportion of SNA (sulfate, nitrate and
ammonium) in PM2.5 increased from 34% in 2014 to 47% in 2018, indicating the gradual dominance of
inorganic components in fine particles, which is consistent with other studies (Li et al., 2019). The strong
relationship among SO4^2-, NO3-, and NH4+ in 2014 (r^2(square of correlation coefficient) of SO4^2-^NO3^- =
0.73, r^2 of NH4+-NO3^- = 0.91, r^2 of SO4^2-^-NH4+= 0.86) (Table S1) exhibited partial homology (e.g.,
combustion emission). While the correlation among SO4^2-, NO3-, and NH4+ decreased in 2018 (r^2 values
of SO$_4^{2-}$-NO$_3^-$, NH$_4^+$-NO$_3^-$, and SO$_4^{2-}$-NH$_4^+$ were 0.40, 0.87 and 0.59, respectively) (Table S1). The variation of dominant emission sources was identified from the changes in the [NO$_3^-$]/[SO$_4^{2-}$] mass ratio (Xing et al., 2021), which increased from 0.85 in 2014 to 1.17 in 2018, implying the decrease in stationary source (mainly coal combustion) or increase in mobile source (mainly traffic emissions). Compared to SNA, the contributions of non-volatile cations (NVCs, including K$^+$, Na$^+$, Ca$^{2+}$, and Mg$^{2+}$) to PM$_{2.5}$ were only 3.0% and 4.0% in 2014 and 2018, respectively.

The aerosol acidity was moderate in Wuhan, exhibiting a decline of 0.25 units from 2014 (3.63) to 2018 (3.38). The difference of pH between 2014 and 2018 was 0.3 when NVCs were not included in the thermodynamic analysis. The largest component of NVCs is Ca$^{2+}$ (Table 1), which has the greatest effect on pH among NVCs and was mainly originated from sand or road dust and construction activities (Hegde et al., 2016). Considering the weak effect of NVCs on the aerosol acidity in Wuhan and the randomness of sand-dust event, the NVCs effect was subtracted from fine particle pH and AWC in the subsequent discussion.

Figure 3 showed the frequency proportions in different particle pH ranges during the four seasons. In both 2014 and 2018, the fine particle pH distribution was in accordance with the norm, and both of the peaks were at pH values of 3-3.5 with frequencies of 27.4% and 24.6%, respectively. In Wuhan, over 80% of the fine particulate was at a pH of 2-4. Higher pH mainly appeared in winter (3.5-4.5) and lower particulate pH was observed in summer (below 3.5) (Figure 3). Compared to the pH frequency distribution between 2014 and 2018, the particulate pH in each season dropped in Wuhan. Fine particle pH also changed hourly, with an early morning peak at approximately 07:00 (local time, pH up to 3.67 in 2014 and 3.27 in 2018), and a subsequent decrease during the daytime, reaching a minimum in the afternoon at around 16:00 (local time) (Figure S1), which was similar to the results of Guo. et al (2015).
There was a great consistency in the diurnal variation trend between particulate pH and AWC both in 2014 and 2018 (Figure S1). The following section explored the driving factors of pH variation in Wuhan during 2014-2018.

3.2 Driving factors of pH decline during 2014-2018

The annual average concentrations of atmospheric SO$_2$ and NO$_x$ (Figure S2) obviously decreased from 2014 to 2018 for implementing control measures (Jin et al., 2016), while the particle pH still continued to decline. There were other driving factors affecting the pH variation during 2014-2018.

Figure 4 showed the sensitivity results of the driving factors affecting the pH variation in Wuhan between 2014 and 2018 (please refer to Section 2.2 for the simulation details). NH$_x$ mainly contributed to the pH decline during 2014-2018 both in spring and winter. RH was the most important factor leading to the pH decreases in summer and fall. The contribution of NH$_x$ to pH variation were 44.2%-48.9% in spring and winter, and the RH contribution to pH changes was 33.7-36.3% in summer and fall (Figure 4, pie chart). This differed from the North China Plain, where SO$_4^{2-}$ + Ca$^{2+}$, NH$_x$ + RH, NH$_x$ + Temp, and SO$_4^{2-}$ + NH$_x$ were the driving factors of pH corresponding to spring, summer, fall and winter, respectively (Ding et al., 2019). Compared with North China, the higher RH (CSY, 2019) and relatively lower ammonia emission (Huang et al., 2012) in Central China resulted in the higher sensitivity of RH and NH$_x$ to particulate pH (Liu et al., 2019; Ding et al., 2019).

Sulfate decline in Wuhan raised the particulate pH as expected (Fu et al., 2015), wherein the pH increased by 0.07-1.0 units corresponding to the 12-63% decrease in sulfate. Similar to previous research (Ding et al., 2019), the sensitivity of fine particulate pH to TNO$_3$ variation was less than that of SO$_4^{2-}$, owing to the low volatility of the latter. In spring, summer, and winter, the particulate pH almost unchanged when TNO$_3$ decreased (7-12%). The pH in fall slightly decreased by 0.05 units with a 61%
TNO$_3$ increase. The insensitivity of pH to TNO$_3$ reduction partly resulted from the decrease in AWC (Figure S3) and the gas-particle partitioning. Moreover, the removal of nitrate released ammonium to the gas phase, leading to hydroxyl decline and buffering changes in PM$_{2.5}$ pH (Blanchard et al., 2000; Dennis et al., 2008).

NH$_x$ decreased by 22.3% and 44.1% in spring and winter, respectively, resulting in pH decrease by 0.2 and 1.0 units, respectively. The difference of pH decline between the two seasons was partly due to the discrepancy in AWC changes (Figure S3). Lower particle phase distribution in spring (below 0.4 in both 2014 and 2018) compared to winter (about 0.7 in both 2014 and 2018) contributed to the low AWC changes in former. NH$_x$ reduction in the season with higher particle phase distribution caused a greater decline in NH$_4^+$ water uptake (Guo et al., 2018). The negligible effect of NH$_x$ on pH changes in summer and fall was mainly due to the small NH$_x$ concentration variation and relatively low NH$_x$ particle phase distribution (Table 1).

Unlike SO$_4^{2-}$ and TNO$_3$, decreasing TCl in summer and fall reduced the particle pH, partly due to the decline in AWC (Figure S3). TCl showed a negligible impact on the pH changes in winter, even though the AWC in winter also obviously decreased. Compared to the other seasons, TCl in winter was mostly distributed in the particle phase, with $\varepsilon$(Cl$^-$) (particulate Cl$^-$ fraction, $\varepsilon$(Cl$^-$)= Cl$^-$/TCl) of 0.95 in 2014 (Table 1). Cl$^-$ in particle phase was in the form of NH$_4$Cl, owing to excessive ammonia in the observation city (Zheng et al., 2019). Reduction of TCl released associated ammonium to the gas phase, buffering the particulate pH changes.

RH hold different impacts on the fine particulate pH in different seasons. Decreased RH reduced the PM$_{2.5}$ pH in summer and fall, but nearly exhibited no effect in spring. Moreover, increased RH in winter also presented a negligible impact on the pH changes. The effect of RH on fine particulate pH
was determined by the competition of RH’s impact on protons and AWC (Ding et al., 2019 ACP),
including the process of water uptake, gas-to-particle conversion and liquid phase reaction (Seinfeld et
al., 2006; Guo et al., 2018). The Temp in summer and autumn in 2018 increased by 1.5-1.7 °C compared
with 2014, contributing to the decline in particulate pH. High Temp promote the conversion of semi-
volatile components, such as ammonium nitrate and ammonium chloride, to the gas phase (Seinfeld et
al., 2006). Additionally, high Temp could also reduce the AWC (Figure S3), further leading to the
decrease in PM2.5 pH (Guo et al., 2015).

3.3 Future pH

Based on the most significant positive and negative drivers of particulate pH changes, we expanded
the ranges of NH₃ and SO₄²⁻ in spring and winter, and RH and SO₄²⁻ in summer and fall, for more
sensitivity analyses by ISORROPIA-II. Total ammonia and sulfate were independently varied in steps
of 0.1 μg m⁻³ in spring and winter. In summer and fall, RH and sulfate independently changed in steps
of 1% and 0.1 μg m⁻³, respectively. Other inputs were under the seasonal average conditions. The
corresponding prediction results were shown in Figure 5.

It showed that PM2.5 remained acidic even with the significant reduction of sulfate (from 35 to 0.1
μg m⁻³), in consistent with Weber et al. (2016)’s study in the U.S. Moreover, the pH variations in summer
and fall were smaller than those in spring and winter, which agreed well with the above section.

According to the changes during 2014-2018, the sulfate concentration decreased in each season, and
all values were lower than 10 μg m⁻³ in 2018. In the springs of foreseeable future, within a sulfate
concentration of 10 μg m⁻³, the particulate pH will still be above 2.5, even if NH₃ is reduced by half from
2018. Furthermore, assuming an increase of sulfate in future spring, although this probability is low due
to the continuous SO₂ control policy in China, the particulate pH would still be close to 2 (1.83) with a
50% increase in sulfate and a 50% decrease NH₄ reduction. Additionally, assuming that the NH₄ increases by half in the future and the sulfate changes by +50%, 0% and -50%, the changes in pH are +0.19, +0.47, and +0.62, respectively. As mentioned in last section, sulfate and NH₄ were the most important factors affecting the pH in spring. While the particulate pH in future spring is generally less affected by sulfate and NH₄. This shows that in the foreseeable future, the pH of aerosols in Wuhan will not change considerably (within 0.5) in spring.

In winter, at the sulfate level observed in 2018, the pH decreased by 1.7 units when NH₄ decreased by half. Even if NH₄ drops by 20%, the pH changes will still be more than 0.5 units. However, if NH₄ remains at its 2018 level, the pH only increases by 0.29 units when the sulfate decreases by half. The pH decreased by 1.28 units when both sulfate and NH₄ decreased by half. Clearly, the particulate pH was sensitive to NH₄ changes in winter, and NH₄ variation might be an indicator of fine particle pH in winter.

In the foreseeable future, one may directly deduce the decline in wintertime particulate pH from the reducing NH₄ in Wuhan.

In fall, the pH value decreased by 0.7 units when the RH decreased to 30%, and it increased by 0.27 units when the RH increased to 95%. When RH was at the 2018 annual value, the pH increased and decreased by 0.3 and 0.46 units when sulfate was halved and increased by half, respectively. The results showed that although sulfate and RH were the most important components and meteorological parameters affecting the particulate pH in fall, fine particle pH in future fall was less affected by them.

In the foreseeable future, the particulate pH in this megacity of Central China will not change significantly (within 0.5 units), similar to that in spring.

In summer, Figure 5 showed that the changes in RH could lead to significant changes in particulate pH. The pH decreased by 1.05 units when RH dropped to 30%, and it increased 0.63 units when RH
increased to 95%. The decrease and increase by half in sulfate resulted in a pH increase of 0.15 and a
decrease of 0.22 units, respectively. Compared to RH, the effect of sulfate on summertime PM$_{2.5}$ pH was
less than that in the former. The pH changed by 0.2-0.3 units when the summertime RH changed by 10%.
This implies that RH can be used as an indicator of fine particle pH in summer. However, considering
the modest interannual variation of atmospheric RH, the future summer pH will not deviate considerably
from the current levels. For the diurnal and hourly PM$_{2.5}$ variations in summer, the RH indicator might
be more useful.

3.4 Effect of pH on PM$_{2.5}$

Here, we assessed the effect of pH on PM$_{2.5}$ response to SO$_2$, NO$_x$, and NH$_3$ control in Wuhan using
a thermodynamic model. The observation data were divided into four groups according to particulate pH:
pH>4, pH 3-4, pH 2-3 and pH<2. Changes in the SNA were assessed when the SO$_4^{2-}$, TNO$_3$, and NH$_x$
were changed in each pH group, representing the control of SO$_2$, NO$_x$, and NH$_3$ emissions, respectively
(Guo et al., 2018). Each of them was individually changed in steps of 20%, while the other inputs
remained constant.

The effect of SO$_4^{2-}$ reduction on SNA changes at different pH groups in Figure 6 indicated that SO$_2$
control was more beneficial to SNA reduction at lower particulate pH. This was mainly contributed from
the increasing NH$_4^+$ decrease owing to relatively higher ammonia particle phase partitioning at low pH.
The loss of associated NH$_4^+$ was attributed to both the decrease in sulfate and the volatilization caused
by reduced AWC (Guo et al., 2018). This implied that the efficiency of reducing SNA by SO$_2$ control in
winter was lower than that in other seasons. It also showed that the particulate pH changed slightly
(within 0.5 units) when SO$_4^{2-}$ changed by 80% (Figure S4), partly due to buffering by ammonia gas-
particle partitioning (Guo et al., 2017; Weber et al., 2016).
Compared to SO$_4^{2-}$, there was a contrary effect of pH on the reduction of SNA from TNO$_3$ control.

At higher particulate pH, TNO$_3$ control was more effective for SNA reduction. A linear reduction in TNO$_3$ at high pH caused a linear decrease in SNA concentrations, owing to $\varepsilon$(NO$_3^-$)

($\varepsilon$(NO$_3^-$)=$\frac{[\text{NO}_3^-]_{\text{mol}}}{([\text{NO}_3^-]_{\text{mol}}+[\text{HNO}_3]_{\text{mol}})}$) close to 1. Thus, NO$_3^-$ was approximately equal to TNO$_3$ (Figure 7). Additionally, more ammonia was released with the reduction of nitrate at higher pH, from the significant $\varepsilon$(NH$_4^+$) ($\varepsilon$(NH$_4^+$)=$\frac{[\text{NH}_4^+]_{\text{mol}}}{([\text{NH}_4^+]_{\text{mol}}+[\text{NH}_3]_{\text{mol}})}$) decline (Figure 7). At low pH (lower than 2, Figure 6), TNO$_3$ reduction slightly influenced the SNA concentration, since most of the TNO$_3$ was in the gas phase, implying that NO$_3^-$ control might barely reduce strong acidic inorganic aerosols.

In the case of NH$_x$ reduction, at low pH (nearly pH<3, Figure 6), NH$_x$ reduction was directly effective for the decline in SNA. At higher particulate pH, NH$_x$ control was not immediately effective for SNA reduction, and more NH$_x$ reduction was required. For instance, considering a pH greater than 4, it could be seen that a 20% reduction in NH$_x$ had little effect on the SNA concentration. While the reduction of SNA was almost linear with NH$_x$ control when the NH$_x$ reduction reduced by more than 40%. At low pH, NH$_x$ reduction resulted in more NO$_3^-$ shifting to the gas phase, partly due to the decrease in $\varepsilon$(NO$_3^-$). At high pH, TNO$_3$ remained in the particle phase at 40% reduction of NH$_x$.

However, once the partitioning between NO$_3^-$ and HNO$_3$ was noticeably toward the gas phase due to the decline in pH and AWC since more NH$_x$ reduction, NO$_3^-$ sharply decreased (Figure S5). Simultaneously, NH$_4^+$ also rapidly declined as the $\varepsilon$(NH$_4^+$) value close to 1.

Fine particle pH is an objective condition that cannot be ignored when implementing strategies to reduce inorganic fine particles. For current observation with a pH of 3-4, both SO$_2$ and NO$_x$ control are effective for fine particle reduction. However, NH$_x$ control is less effective before approximately 20% NH$_x$ reduction in Wuhan, which almost consistent with previous studies (Zheng et al., 2019) suggesting...
4. Conclusions

Using hourly chemical composition observation data collected in a megacity of Central China, the driving factors of fine particle pH changes between 2014 and 2018 were analyzed. Moderate aerosol acidity was observed in Wuhan, with mean pH values of 3.63 and 3.38 in 2014 and 2018, respectively, showing a slight decline. In both 2014 and 2018, over 80% of particulate pH was at 2-4, with the largest frequency proportion occurring at a pH of 3-3.5. NHx mainly contributed to the pH decline during 2014-2018 in both spring and winter. RH was the most important factor leading to a decrease in pH in summer and fall. Further evaluation of the contribution of each factor to particulate pH changes showed that the contribution of NHx+SO4²⁻ was 79.1-93.7% in spring and winter, and RH was the largest contributor (33.7-36.3%) in summer and fall.

Sensitivities simulations of exploring the future particulate pH were conducted by expanding the concentration ranges of driving factors in each season. PM₂.₅ will remain acidic even when concentrations varied by two orders of magnitude. The interannual pH fluctuation in future spring, summer and fall (within 0.5 units in the foreseeable future) is less than that in winter. NHx can be suggested as an indicator of the changes of PM₂.₅ pH in winter. The decline of wintertime particulate pH can be inferred from the decrease of NHx in Wuhan.

Owing to higher NHx particle phase partitioning at low pH leading to a higher NH₄⁺ decrease, SO₂ control is more beneficial to SNA reduction at lower particulate pH. In contrast, NOₓ control is more effective for SNA reduction at higher particulate pH owing to high ε(NO₃⁻) (close to 1). NHx reduction is directly effective for SNA decline at low pH (nearly pH<3). At higher particulate pH, more NHx reduction will be required before effectiveness is achieved. For an observation city with a pH of 3-4, both
SO₂ and NOₓ control are effective for fine particle reduction, while NHₓ control is less effectiveness before approximately 20% NHₓ reduction.

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Table 1: Comparisons of the particulate composition and meteorological parameters in Wuhan in 2014 and 2018.

Figure 1: Location of the observation site in Wuhan, a megacity of Central China.

Figure 2: Comparisons of the measured SO$_4^{2-}$, NO$_3^-$, NH$_4^+$ and NH$_3$ with the predictions by thermodynamic model ISORROPIA-II.

Figure 3: Frequency proportions of different pH ranges in four seasons.

Figure 4: Factors contributing to pH changes between 2014 and 2018. Notably, the pie chart does not consider positive or negative changes, but represents the amplitude of pH change. The factors include SO$_4^{2-}$, TNO$_3$ (NO$_3^-$ + HNO$_3$), NH$_x$ (NH$_3$ + NH$_4^+$), TCl (Cl$^-$ + HCl), RH, and Temp, respectively.

Figure 5: Sensitivity of the pH to total ammonia (NH$_x$) and sulfate (SO$_4^{2-}$) concentrations in spring and winter, and that to the RH and SO$_4^{2-}$ in summer and fall.

Figure 6: The effect of fine particle pH on the SNA response to sulfate, total nitrate, and total ammonia changes.

Figure 7: Changes of $\varepsilon$(NO$_3^-$) and $\varepsilon$(NH$_4^+$) as functions of $\Delta$NO$_3^-$ at different pH ranges (particulate NO$_3^-$ fraction $\varepsilon$(NO$_3^-$) = [NO$_3^-$]/([NO$_3^-$]+[HNO$_3$]), NH$_4^+$ fraction $\varepsilon$(NH$_4^+$) = [NH$_4^+$]/([NH$_4^+$]+[NH$_3$])).
Table 1: Comparisons of the particulate components and meteorological parameters in Wuhan in 2014 and 2018.

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<th>Spring 2014</th>
<th>Summer 2014</th>
<th>Fall 2014</th>
<th>Winter 2014</th>
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<tr>
<td>SO$_4^{2-}$</td>
<td>11.6±5.73</td>
<td>10.6±5.92</td>
<td>7.85±4.11</td>
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<tr>
<td>NO$_3^-$</td>
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<td>5.58±4.18</td>
<td>4.68±3.16</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>1.36±1.68</td>
<td>0.91±0.91</td>
<td>1.24±0.82</td>
<td>0.3±0.37</td>
</tr>
<tr>
<td>K$^+$</td>
<td>0.66±0.73</td>
<td>0.64±0.42</td>
<td>0.22±0.17</td>
<td>0.36±0.22</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.84±1.48</td>
<td>1.08±0.95</td>
<td>0.37±0.24</td>
<td>0.3±0.11</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.27±0.14</td>
<td>0.59±0.64</td>
<td>0.18±0.11</td>
<td>0.19±0.10</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.11±0.23</td>
<td>0.11±0.09</td>
<td>0.04±0.03</td>
<td>0.03±0.02</td>
</tr>
<tr>
<td>NVCs</td>
<td>1.88±2.02</td>
<td>2.52±3.29</td>
<td>0.81±0.40</td>
<td>0.88±0.36</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>14.2±7.07</td>
<td>11.0±7.64</td>
<td>12.5±5.20</td>
<td>13.9±4.72</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>0.93±0.91</td>
<td>1.74±1.20</td>
<td>1.01±1.19</td>
<td>1.42±0.65</td>
</tr>
<tr>
<td>HCl</td>
<td>0.28±0.23</td>
<td>0.76±0.70</td>
<td>1.15±0.69</td>
<td>0.4±0.16</td>
</tr>
<tr>
<td>Temp (°C)</td>
<td>21.2±4.88</td>
<td>19.9±7.03</td>
<td>29.0±3.16</td>
<td>30.5±3.51</td>
</tr>
<tr>
<td>RH</td>
<td>0.72±0.16</td>
<td>0.7±0.17</td>
<td>0.78±0.11</td>
<td>0.73±0.13</td>
</tr>
</tbody>
</table>

NVCs: non-volatile cations, including K$^+$, Na$^+$, Ca$^{2+}$, and Mg$^{2+}$. 
Figure 1 Location of the observation site in Wuhan, a megacity of Central China.
Figure 2 Comparisons of the measured SO$_4^{2-}$, NO$_3^-$, NH$_4^+$ and NH$_3$ with the predictions by thermodynamic model ISORROPIA-II.
Figure 3 Frequency proportions of different pH ranges in four seasons (the number of data n = 4173 in 2014 and n = 5123 in 2018).
Figure 4 Factors contributing to pH changes during 2014-2018. Notably, the pie chart does not consider positive or negative changes, but represents the amplitude of pH change. The factors include $SO_4^{2-}$, $TNO_3$ ($NO_3^- + HNO_3$), $NH_x$ ($NH_3 + NH_4^+$), $TCl$ ($Cl^- + HCl$), RH, and Temp, respectively.
Figure 5 Sensitivity of the pH to total ammonia (NH₃) and sulfate (SO₄²⁻) concentrations in spring and winter, and that to RH and SO₄²⁻ in summer and fall.
Figure 6 The effect of fine particle pH on the SNA response to sulfate, total nitrate and total ammonia changes.
Figure 7 Changes of $\varepsilon(\text{NO}_3^-)$ and $\varepsilon(\text{NH}_4^+)$ as functions of $\Delta T_{\text{NO}_3}$ at different pH ranges (particulate $\text{NO}_3^-$ fraction $\varepsilon(\text{NO}_3^-) = [\text{NO}_3^-]/([\text{NO}_3^-]+[\text{HNO}_3])$, $\text{NH}_4^+$ fraction $\varepsilon(\text{NH}_4^+)= [\text{NH}_4^+]/([\text{NH}_4^+]+[\text{NH}_3]]$).