# **Response letter**

[Atmospheric Chemistry and Physics, MS ID: acp-2018-53] Title: Characteristics and mixing state of amine-containing particles at a rural site in the Pearl River Delta, China.

## **Comments to the Authors:**

Both referees of your revised manuscript are in favor of publication but have a few technical and minor revision requests. Please consider the referees' comments in revising your manuscript before publication of your work proceeds.

**Response**: Thank you for your comments and contribution to our manuscript. We have revised the whole manuscript according to the reports from two anonymous referees, and the point-by-point responses have been listed below. We appreciate these valuable and helpful comments and suggestions to our work and enable it to meet the high quality of the journal Atmos. Chem. Phys. All the revisions made in the manuscript have been highlighted with blue color. The marked-up manuscript has been uploaded.

Anything about our paper, please feel free to contact me at limei2007@163.com

Best regards! Sincerely yours

Mei Li June 17, 2018

### Response to the report #1 from anonymous referee #2

### **Comments:**

The corrections are satisfactory. The authors should use a smooth line instead of bins in Figure 5 because now it presents size distributions.

**<u>Response</u>**: Thank you for your comments. We have revised the Figure 5 according to your suggestion. The vertical lines have been replaced by log-normal fitting curves. The old Figure 5:



Figure 5. Unscaled size-resolved number distributions of total amine-containing particles and amine particles containing three marker ions of  ${}^{59}(CH_3)_3N^+$ ,  ${}^{74}(C_2H_5)_2NH_2^+$ , and  ${}^{86}(C_2H_5)_2NCH_2^+$  in summer and winter in Heshan.

The new Figure 5:



Figure 5. Unscaled size-resolved number distributions of total amine-containing particles and amine particles containing three marker ions of  ${}^{59}(CH_3)_3N^+$ ,  ${}^{74}(C_2H_5)_2NH_2^+$ , and  ${}^{86}(C_2H_5)_2NCH_2^+$  in summer and winter in Heshan.

### Response to the report #2 from anonymous referee #3

### **General comments:**

This paper has been significantly improved from the first version. I have a few comments that should be addressed before publication.

**<u>Response</u>**: Thank you for your comments. We have revised the manuscript according to your comments and suggestions, and the point-by-point responses are listed below.

### **Major Comments:**

1. Figure 8 is a bit problematic. Correlations between sulfate and nitrate on amine-containing particles is used to infer how amines are formed. Sulfate and nitrate should be separated out in this figure in order to determine the formation of different aminium salts. Also, the correlations are quite misleading since amine-containing particles were compared against each other instead of sulfate, nitrate, and amine markers on all particles.

**<u>Response</u>**: Thank you for your suggestion. The seasonal trends of the peak areas of sulfate and nitrate have been separated out in new Figure 8, and the related discussions have been revised. The linear regressions in old Figure S3 have also been revised to the linear regressions between amines and sulfate and nitrate separately in new Figure S4. In this work all the particles containing amines have been picked up as amine-containing particles, so no amine markers existed in the rest particles, thus, the correlations between sulfate, nitrate and amines on all particles were actually the correlations between them in amine-containing particles.

"The temporal variations of the peak areas of amines, ammonium, and the sum of sulfate and nitrate in amine-containing particles are shown in Figure 8. The peak areas of amines and the sum of nitrate and sulfate had similar variation patterns both in summer and winter. The linear regression between them showed robust correlations both in summer ( $r^2=0.74$ ) and winter ( $r^2=0.88$ ) (Figure S4), indicating the formation of aminium salts." have been revised to "The temporal variations of the peak areas of amines, ammonium, sulfate and nitrate in amine-containing particles are shown in Figure 8. The peak areas of amines and sulfate had similar variation patterns both in summer and winter, and the linear regression between them showed robust correlations both in summer ( $r^2=0.69$ ) and winter ( $r^2=0.72$ ) (Figure S4), indicating the formation of aminium sulfate salt during the entire sampling period. However, the peak areas of amines and nitrate only exhibited similar trends in winter, and the linear regression between them showed robust correlations both in summer ( $r^2=0.69$ ) and winter ( $r^2=0.72$ ) (Figure S4), indicating the formation of aminium sulfate salt during the entire sampling period. However, the peak areas of amines and nitrate only exhibited similar trends in winter, and the linear regression between them showed a better correlation in winter ( $r^2=0.78$ ) than in summer ( $r^2=0.52$ ) (Figure S4), suggesting the possible formation of aminium nitrate salt in winter." in lines 348-356.

"The sum of the sulfate and nitrate peak areas had a higher increase rate than the amine peak area from 6 to 8 February, which may have been caused by an increase of ammonium during this period." have been removed from the manuscript.

"Robust correlations between the peak intensities of amines and the sum of nitrate and sulfate were observed, suggesting the possible formation of aminium sulfate and nitrate salts." have been revised to "Robust correlations between the peak intensities of amines and sulfate and nitrate were observed, suggesting the possible

### formation of aminium sulfate and nitrate salts." in the abstract in lines 60-62.

The old Figure 8:



Figure 8. Temporal variations in the peak areas of amines, ammonium, and the sum of sulfate and nitrate in amine-containing particles during summer and winter. The relative acidity ratio ( $R_a$ ), which was calculated as the ratio of the total sulfate and nitrate peak areas to the ammonium peak area, is plotted as  $log(R_a)$ .

The new Figure 8:



Figure 8. Temporal variations of the peak areas of amines, ammonium, sulfate and nitrate in amine-containing particles during summer and winter. The relative acidity ratio ( $R_a$ ), which was calculated as the ratio of the total sulfate and nitrate peak areas to the ammonium peak area, is plotted as  $\log(R_a)$ .

The old Figure S3:



Figure S3. The linear regressions between peak area of amines and the peak area of sulfate and nitrate in summer and winter.



The new Figure S4:

Figure S4. The linear regressions between the peak areas of amines and sulfate in summer (a) and winter (c), and the linear regressions between the peak areas of amines and nitrate in summer (b) and winter (d) in amine-containing particles.

2. The conclusions could be significantly strengthened by moving the commentary on lines 382-398 that links sulfate formation in Chinese haze to mixing state and amines to the conclusions.

**<u>Response</u>**: Revision made. "In addition, the presence of aminium salts affects the water activities and osmotic coefficients of aqueous solutions, which may influence the calculation of pH using aerosol thermodynamic models (Sauerwein et al., 2015). Furthermore, it should be noted that the measured pH of bulk ambient aerosols may not be representative of the actual single particle acidity. As pointed out in Pratt et al.

(2009) and in this work, the mixing state of aerosols should be considered in order to comprehensively estimate the aerosol pH. Several recent studies have reported a 'missing' source of sulfate produced from the oxidation of SO<sub>2</sub> by NO<sub>2</sub> during haze episodes with high ambient relative humidity in northern China, and the neutralization of particulate ammonium is a key factor in this formation mechanism (Cheng et al., 2016; Wang et al., 2016). Our study reveals that amines have a potential influence on particle acidity, which could also impact this sulfate formation process during haze episodes. In order to discuss the potential role of amines in this sulfate formation pathway, real-time concentrations of amines, ammonium, sulfate, nitrate, and their precursors must be available. The results of this study suggest that amine chemistry involving particle acidity and mixing state with sulfate, nitrate and ammonium may have an important role in the aging process of particles in regions with high concentration of amines." have been moved to the conclusions in lines 425-441.

# Specific Comments:

## Introduction

1. I suggest adding one few more reference on amines on lines 89-90. Please add [Facchini et al., 2008].

**Response**: Revision made. [Facchini et al., 2008] has been cited and added in line 90.

2. Lines 111-113: Please also add [Gaston et al., 2013; Qin et al., 2012; Zauscher et al., 2013].

**<u>Response</u>**: Revision made. [Gaston et al., 2013; Qin et al., 2012; Zauscher et al., 2013] have been cited and added in lines 112-114.

# Methods

1. Was a silica gel drier used during sampling to reduce particle phase water?

**Response**: Yes, a silica gel drier was used to dry the ambient particles before arriving at the SPAMS. "The SPAMS was installed at the top of the main building, and aerosols were introduced to the SPAMS through a 2.5 m copper tube." have been revised to "The SPAMS was installed at the top of the main building, and aerosols were introduced to the SPAMS through a 2.5 m copper tube and a silica gel drier." in lines 156-157.

2. Lines 191-195: Please also cite [Gaston et al., 2013; Qin et al., 2012]. **Response**: Revision made. [Gaston et al., 2013; Qin et al., 2012] have been cited and added in lines 192-193.

3. In table 1, include references for each ion peak. **Response**: Revision made. The new Table 1:

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Marker ion	Alkylamine assignment
<sup>59</sup> (CH <sub>3</sub> ) <sub>3</sub> N <sup>+</sup>	Trimethylamine (TMA) <sup>a</sup>
$^{74}(C_2H_5)_2NH_2^+$	Diethylamine (DEA) <sup>b</sup>
$^{86}(C_2H_5)_2NCH_2^+$	DEA, TEA, DPA <sup>c</sup>
$^{101}(C_2H_5)_3N^+$	Triethylamine (TEA) <sup>d</sup>
$^{102}(C_{3}H_{7})_{2}NH_{2}^{+}$	Dipropylamine (DPA) <sup>e</sup>
$^{143}(C_{3}H_{7})_{3}N^{+}$	Tripropylamine (TPA) <sup>f</sup>

Table 1. Marker ions chosen for the amine-containing particles

References are as follows: <sup>a</sup>Zhang et al., 2012, Gaston et al., 2013; <sup>b</sup>Angelino et al., 2001; <sup>c</sup>Huang et al., 2012, Zauscher et al., 2013, Qin et al., 2012; <sup>d</sup>Gaston et al., 2013; <sup>e</sup>Pratt et al., 2009; <sup>f</sup>Healy et al., 2015.

4. Line 220: Please also add to the end of the sentence "and are likely sea salts". This will help avoid confusion.

**<u>Response</u>**: Revision made. "and are likely sea salts" have been added in lines 220-221.

### Results

1. Line 231: From Figure 1, it looks like the open ocean trajectory has the fewest amines. Perhaps your amines aren't "marine sources" per say but are derived from coastal emissions.

**<u>Response</u>**: Revision made. "suggesting that the majority of amine-containing particles came from anthropogenic and marine sources" has been revised to "suggesting that the majority of amine-containing particles came from anthropogenic sources and coastal emissions" in lines 231-232.

2. Line 232: Cluster 4 for the winter is very stagnant. I would guess that those stagnant conditions also facilitate the partitioning of amines.

**<u>Response</u>**: Revision made. "Besides, the stagnant meteorological conditions associated with Cluster 4 also facilitated the partitioning of amines from gas to particle phase in winter." have been added in lines 238-239.

## 3. Line 263-266: What about the role of temperature?

**<u>Response</u>**: Thank you for your suggestion. No significant diurnal temperature differences were found both in summer and winter, and the related discussions "Although lower temperature facilitates the partitioning of gaseous amines into the particulate phase (Huang et al., 2012), no significant temperature differences were found both in summer (day:  $32\pm1.1$  °C; night:  $27.5\pm1.1$  °C) and winter (day:  $15\pm1.4$  °C; night:  $13\pm0.8$  °C), which suggests a minor influence of temperature on the diurnal pattern of amine-containing particles." have been added in lines 268-273.

4. Figure 4 needs to have actual m/z values on the ion peaks. For example, instead of CH3NH, show 30CH3NH+.

**<u>Response</u>**: We have revised the Figure 4 according to your suggestion. Besides, the old Figure 6 has also been revised due to the same reason. The new Figure 4:



Figure 4. Average ion mass spectra of amine-containing particles in summer and winter. The color bars represent each peak area corresponding to a specific ion in individual particles.



The new Figure 6:

Figure 6. Mass spectra of total ammonium-containing ( $NH_4^+$ -containing) particles in summer and winter. The color bars represent each peak area corresponding to a specific fraction in individual particles.

5. Lines 287-291: was the size distribution for amines any different than the size distribution for all particles? If not, then this figure and discussion is not very important.

**<u>Response</u>**: The unscaled size-resolved number distributions of total detected particles and amine-containing particles in summer and winter are shown as follows. In

summer, the total detected particles and amine-containing particles exhibited similar unimodal distributions in the submicron mode from 0.4 to 1.5  $\mu$ m. However, in winter, the peak of total detected particles shifted to a larger size range from 0.6 to 0.9  $\mu$ m compared with the size range of amine-containing particles from 0.5 to 0.8  $\mu$ m. Therefore, the size distributions of amine-containing particles were different from the size distributions of total detected particles. Thus, we believe the related discussions about amine-containing particles are useful to infer the sources and possible formation process of amines in particles.



Figure R1. Unscaled size-resolved number distributions of total detected particles and amine-containing particles in summer and winter in Heshan.

6. Line 298: I suggest removing "formation processes" in the title of section 3.3. I am not completely convinced that you can completely deduce this information.

**<u>Response</u>**: Revision made. "3.3 Mixing state and formation processes of amine-containing particles" has been revised to "3.3 Mixing state of amine-containing particles" in line 305.

7. Lines 299-308: I suggest comparing your seasonal trends of amines and ammonium to Qin et al., 2012, which also contains observations of ammonium nitrate and amines.

**<u>Response</u>**: Revision made. "The high abundances of sulfate and nitrate in amine-containing particles suggest the possible formation of aminium sulfate and nitrate salts." have been revised to "The internal mixing state of amines with sulfate

and nitrate had also been found in Qin et al. (2012), which reported that the amine-rich particles consisted of  $18\pm10\%$  amines by mass in the form of aminium sulfate and nitrate salts in summer in Riverside, California. In this work, the high abundances of sulfate and nitrate in amine-containing particles suggest the possible formation of aminium sulfate and nitrate salts." in lines 310-315.

8. I find Figure 7 to be very interesting. What is the R2 between amines and ammonium-rich particles? It looks high in the winter.

**<u>Response</u>**: The linear regressions between amine-containing particles and ammonium-containing particles in summer and winter are shown in the Supplement as Figure S3:



Figure S3. The linear regressions between amine-containing particles and ammonium-containing particles in summer and winter.

"and the  $NH_4^+$ -containing particles and amine-containing particles showed a robust linear correlation in winter (r<sup>2</sup>=0.63) (Figure S3)." have been added in lines 337-338.

9. Lines 333-335: RH has been shown to exert an influence on compounds such as ammonium nitrate. I suggest revising this sentence to reflect that your findings indicate that source seems more important than RH for explaining seasonal trends. **Response**: Thank you for your suggestion. We have revised "RH does not seem to exert a major influence on particulate  $NH_4^+$  (Huang et al., 2012), because lower abundance of  $NH_4^+$  was observed in summer (RH = 72 ± 13%) than in winter (RH = 63 ± 11%)." to "In this work the lower abundance of  $NH_4^+$  was observed in summer (RH = 63 ± 11%), suggesting a more important influence of sources than RH on the seasonal trends of  $NH_4^+$ -containing particles." in lines 344-347.

10. Figure 8 just shows a peak area comparison on amine comparing particles. The trends reported in lines 339-341 are misleading because only amine-containing particles were selected so if these particles also had sulfate, the correlation would be high. How do the correlations hold if you compare the ion peak areas for all particles

### instead?

**<u>Response</u>**: In this work all the particles containing amines have been picked up as amine-containing particles, so no amine markers existed in the rest particles, thus, the correlations between sulfate, nitrate and amines on all particles were actually the correlations between them in amine-containing particles. As we have made the revisions in the response to Major Comment 1, the seasonal trends of the peak areas of sulfate and nitrate have been separated out in new Figure 8 to illustrate the formation of aminium sulfate and nitrate salts. In addition, the linear regressions in old Figure S3 have also been revised to the linear regressions between amines and sulfate and nitrate separately in new Figure S4.

"The temporal variations of the peak areas of amines, ammonium, and the sum of sulfate and nitrate in amine-containing particles are shown in Figure 8. The peak areas of amines and the sum of nitrate and sulfate had similar variation patterns both in summer and winter. The linear regression between them showed robust correlations both in summer ( $r^2=0.74$ ) and winter ( $r^2=0.88$ ) (Figure S4), indicating the formation of aminium salts." have been revised to "The temporal variations of the peak areas of amines, ammonium, sulfate and nitrate in amine-containing particles are shown in Figure 8. The peak areas of amines and sulfate had similar variation patterns both in summer and winter, and the linear regression between them showed robust correlations both in summer ( $r^2=0.69$ ) and winter ( $r^2=0.72$ ) (Figure S4), indicating the formation of aminium sulfate salt during the entire sampling period. However, the peak areas of amines and nitrate only exhibited similar trends in winter, and the linear regression between them showed robust correlations both in summer ( $r^2=0.69$ ) and winter ( $r^2=0.72$ ) (Figure S4), indicating the formation of aminium sulfate salt during the entire sampling period. However, the peak areas of amines and nitrate only exhibited similar trends in winter, and the linear regression between them showed a better correlation in winter ( $r^2=0.78$ ) than in summer ( $r^2=0.52$ ) (Figure S4), suggesting the possible formation of aminium nitrate salt in winter." in lines 348-356.

The new Figure 8:



Figure 8. Temporal variations of the peak areas of amines, ammonium, sulfate and nitrate in amine-containing particles during summer and winter. The relative acidity ratio ( $R_a$ ), which was calculated as the ratio of the total sulfate and nitrate peak areas to the ammonium peak area, is plotted as  $log(R_a)$ .

### The new Figure S4:



Figure S4. The linear regressions between the peak areas of amines and sulfate in summer (a) and winter (c), and the linear regressions between the peak areas of amines and nitrate in summer (b) and winter (d) in amine-containing particles.

11. Lines 347-349: The authors should explicitly state that this method was developed by Pratt et al., 2009 for single particle work since the authors use the exact same methodology.

**<u>Response</u>**: Revision made. "In this work the particle acidity of amine-containing particles is represented by the relative acidity ratio ( $R_a$ ), which is defined as the ratio of the sum of the sulfate and nitrate peak areas divided by the ammonium peak area (Denkenberger et al., 2007;Pratt et al., 2009;Cheng et al., 2017)." have been revised to "In this work the particle acidity of amine-containing particles is represented by the relative acidity ratio ( $R_a$ ), which is developed by Denkenberger et al. (2007) and Pratt et al. (2009), defined as the ratio of the sum of the sulfate and nitrate peak areas divided by the ammonium peak area (Denkenberger et al., 2007), and Pratt et al. (2009), defined as the ratio of the sum of the sulfate and nitrate peak areas divided by the ammonium peak area (Denkenberger et al., 2007;Pratt et al., 2009;Cheng et al., 2017)." in lines 360-363.

# 12. Lines 386-398 should be moved to the conclusions section.

**<u>Response</u>**: Revision made. "In addition, the presence of aminium salts affects the water activities and osmotic coefficients of aqueous solutions, which may influence the calculation of pH using aerosol thermodynamic models (Sauerwein et al., 2015). Furthermore, it should be noted that the measured pH of bulk ambient aerosols may not be representative of the actual single particle acidity. As pointed out in Pratt et al. (2009) and in this work, the mixing state of aerosols should be considered in order to comprehensively estimate the aerosol pH. Several recent studies have reported a

'missing' source of sulfate produced from the oxidation of SO<sub>2</sub> by NO<sub>2</sub> during haze episodes with high ambient relative humidity in northern China, and the neutralization of particulate ammonium is a key factor in this formation mechanism (Cheng et al., 2016;Wang et al., 2016). Our study reveals that amines have a potential influence on particle acidity, which could also impact this sulfate formation process during haze episodes. In order to discuss the potential role of amines in this sulfate formation pathway, real-time concentrations of amines, ammonium, sulfate, nitrate, and their precursors must be available. The results of this study suggest that amine chemistry involving particle acidity and mixing state with sulfate, nitrate and ammonium may have an important role in the aging process of particles in regions with high concentration of amines." have been moved to the conclusion in lines 425-441.

#### **Conclusions:**

1. I recommend removing the sentence on lines 417-419. Correlation does not equal causation.

**Response**: Revision made. "Robust correlations between the peak intensities of amines and the sum of nitrate and sulfate suggested the possible formation of aminium sulfate and nitrate salts." have been removed from the conclusion.

2. This section has conclusions but no implications. I recommend removing lines 429-436 and replacing it with lines 386-398.

Response: Revision made. "In order to estimate the particle acidity, the relative acidity ratio  $(R_a)$ , defined as the ratio of the sum of the sulfate and nitrate peak areas divided by the ammonium peak area, was calculated and showed higher values in summer  $(326 \pm 326)$  than  $(31 \pm 13)$  in winter, suggesting the amine-containing particles were more acidic in summer than in winter. However, after including amines along with the ammonium in the acidity calculation, the new Ra' values showed no distinct seasonal change (summer:  $11 \pm 4$ ; winter:  $10 \pm 2$ ), suggesting that it is reasonable to consider amines when estimating particle acidity." have been replaced by "In addition, the presence of aminium salts affects the water activities and osmotic coefficients of aqueous solutions, which may influence the calculation of pH using aerosol thermodynamic models (Sauerwein et al., 2015). Furthermore, it should be noted that the measured pH of bulk ambient aerosols may not be representative of the actual single particle acidity. As pointed out in Pratt et al. (2009) and in this work, the mixing state of aerosols should be considered in order to comprehensively estimate the aerosol pH. Several recent studies have reported a 'missing' source of sulfate produced from the oxidation of SO<sub>2</sub> by NO<sub>2</sub> during haze episodes with high ambient relative humidity in northern China, and the neutralization of particulate ammonium is a key factor in this formation mechanism (Cheng et al., 2016; Wang et al., 2016). Our study reveals that amines have a potential influence on particle acidity, which could also impact this sulfate formation process during haze episodes. In order to discuss the potential role of amines in this sulfate formation pathway, real-time concentrations of amines, ammonium, sulfate, nitrate, and their precursors must be available. The results of this study suggest that amine chemistry involving particle acidity and mixing state with sulfate, nitrate and ammonium may have an important role in the aging process of particles in regions with high concentration of amines." in lines 425-441.

### **Technical Comments:**

1. Line 49: change "count" to "counts"

**<u>Response</u>**: Revision made. "Although the increase of amine-containing particle count mostly occurred at night" has been revised to "Although the increase of amine-containing particle counts mostly occurred at night" in lines 48-49.

2. Line 214: change "ion of m/z" to "an ion peak at m/z"

**<u>Response</u>**: Revision made. "Ion of m/z + 46 was detected in the ambient single particles" has been revised to "An ion peak at m/z + 46 was detected in the ambient single particles" in lines 214-215.

3. Line 250: change "similar variation pattern" to "a similar pattern"

**<u>Response</u>**: Revision made. "The amine particles containing <sup>74</sup>( $C_2H_5$ )<sub>2</sub>NH<sub>2</sub><sup>+</sup> and <sup>86</sup>( $C_2H_5$ )<sub>2</sub>NCH<sub>2</sub><sup>+</sup> both exhibited similar variation pattern with total amine-containing particles" has been revised to "The amine particles containing <sup>74</sup>( $C_2H_5$ )<sub>2</sub>NH<sub>2</sub><sup>+</sup> and <sup>86</sup>( $C_2H_5$ )<sub>2</sub>NCH<sub>2</sub><sup>+</sup> both exhibited a similar pattern with total amine-containing particles" in lines 252-254.

4. Line 255 and 412: remove "special"

**<u>Response</u>**: Revision made. "the special emission sources of trimethylamine (TMA)." has been revised to "the emission sources of trimethylamine (TMA)." in line 258. "the special sources of trimethylamine." has been revised to "the emission sources of trimethylamine." in line 410.

### 5. Line 258: change "count" to "counts"

**<u>Response</u>**: Revision made. "both showed higher count at night" has been revised to "both showed higher counts at night" in line 260.

6. Line 299: change "aging" to "mixing"

**Response**: Revision made. "To investigate the aging state of amine-containing particles" has been revised to "To investigate the mixing state of amine-containing particles" in line 306.

7. Line 316: change "During entire" to "During the entire"

**Response**: Revision made. "During entire sampling period" has been revised to "During the entire sampling period" in line 326.

8. Line 319: change "aging" to "mixing"

**<u>Response</u>**: Revision made. "indicating an aging state of  $NH_4^+$ -containing particles" has been revised to "indicating an mixing state of  $NH_4^+$ -containing particles" in lines

329-330.

9. Line 379: remove "Besides"

**Response**: Revision made. "Besides" has been removed in line 393.

10. Line 386: change "hence the mixing state..." to "As pointed out in Pratt et al., 2009 and in this work, the mixing state..."

**<u>Response</u>**: Revision made. "Hence, the mixing state of aerosols should be considered in order to comprehensively estimate the aerosol pH" has been revised to "As pointed out in Pratt et al. (2009) and in this work, the mixing state of aerosols should be considered in order to comprehensively estimate the aerosol pH." in lines 429-431.

### **References:**

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