Significant contrasts in aerosol acidity between China and the United~~s~~ States

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Abstract. Aerosol acidity governs several key processes in aerosol physics and chemistry, thus affecting aerosol mass and composition, and ultimately the climate and human health. Previous studies have reported ~~the~~ aerosol pH values separately in China and the United States (US), implying ~~a~~ different aerosol acidity between these two countries. However, there is ~~a~~ debate about whether mass concentration or chemical composition ~~plays~~ is ~~a~~the more important ~~role in~~ driv~~inger~~ ~~such a~~of differences in aerosol acidity. A full picture of the pH difference and the underlying mechanisms responsible for ~~the pH difference~~it ~~are~~is hindered ~~not fully understood, limited by~~ by the scarcity of simultaneous measurements of ~~aerosol~~ particle composition and gaseous species~~composition and gas species~~, especially in China. Here we conduct a comprehensive assessment of ~~the~~ aerosol acidity in China and the US~~United States,~~ using extended ground-level measurements and regional chemical transport model simulations. We show that aerosol in China is~~is~~ significantly less acidic than ~~that~~ in the US~~United States~~, with pH values 1–2 units higher. Based on a proposed multivariable Taylor Series method and a series of sensitivity tests, we identify ~~several~~ major factors leading to the pH difference. Compared to the US~~United States~~, China ~~is associated with~~has much higher aerosol mass concentrations~~aerosol~~ (gas + particle, by a factor of 8.4 on average) and a higher fraction of ~~s in China are generally in more~~~~total~~ total ammonia (~~$TNH_3=NH_4^+$~~gas + particle~~$+NH_3$~~) in the aerosol composition ~~rich conditions~~~~s where particle phase ammonium (NH_4^+) concentrations are adequate enough to nearly neutralize major acidic inorganic anions such as sulfate, nitrate, and chloride, leading to a higher aerosol pH~~. Our assessment shows that such differences in mass concentrations and chemical composition play equally important roles in driving the aerosol pH difference between China and the US~~United States~~. Therefore, both the facts that China is more polluted than the US and is rich in ammonia together explain the aerosol pH difference. ~~Higher relative availability of the stronger acidic component, sulfate, compared with the weaker acidic component, total nitrate ($TNO_3=NO_3^-+HNO_3$), also contributes to the lower aerosol pH in the United States. As a response to higher aerosol pH, the higher nitrate to sulfate molar ratios in China indicates a~~

~~nitrate-rich condition, further leading to higher aerosol water uptake which will continually promote nitrate aerosol formation. Considering the historical emissions trends,~~ ~~especially the recent faster decline in SO_2 emissions than NO_x emissions in China, the nitrate to sulfate molar ratios in China is expected to further increase, and the difference in aerosol acidity between these two countries is expected to continue.~~~~the difference in aerosol acidity between these two countries is expected to continue as SO_2 and NO_x emissions are further controlled.~~ The difference~~s~~ in aerosol acidity highlighted in the present study ~~imply~~ implies potential differences in formation mechanisms, physicochemical properties, and toxicity of aerosol particles ~~between~~ in ~~China and the United States~~these~~se~~ two countries.

1 Introduction

As an intrinsic aerosol property, aerosol acidity (usually ~~measured~~ characterized by aerosol pH) plays an important role in a variety of aerosol physical and chemical processes (Pye et al., 2020). Aerosol acidity can modulate aerosol mass by controlling the gas-particle partitioning of volatile and semi-volatile acids (such as HCl-Cl^- and HNO_3-NO_3^-) (Guo et al., 2016) and can influence~~ing~~ production rates of secondary aerosol ~~from~~ through heterogeneous pathways (Jang et al., 2002; Surratt et al., 2010; Pathak et al., 2011). ~~It~~Acidity also affects aerosol optical properties via proton dissociation of organic functional groups (Mo et al., 2017) and the morphology or phase state of organic aerosols (Losey et al., 2016; Losey et al., 2018). Recent evidence links aerosol acidity to aerosol toxicity and health outcomes. For example, ~~H~~highly acidic aerosols~~,~~ ~~for example,~~ cause greater dissol~~ve~~ution ~~more~~of metals which can generate reactive oxygen species in vivo (Fang et al., 2017). High aerosol acidity is associated with increased risks of respiratory disease and cancer (Kleinman et al., 1989; Gwynn et al., 2000; Behera et al., 2015).

Due to the difficulties in directly measur~~ements~~ing ~~of~~ aerosol pH (Jang et al., 2002; Li and Jang, 2012), thermodynamic models, including ISORROPIA-II (Fountoukis and Nenes, 2007), E-AIM (Clegg et al., 1998), and SCAPE2 (Kim and Seinfeld, 1995), have been widely used to calculate aerosol pH ~~from~~ based on measured gaseous and ~~aerosol~~ particle composition and meteorological data such as relative humidity (RH) and temperature. ~~A large number of~~M~~any~~ultiple studies suggest that these models ~~are capable of~~ can reproduce~~ing~~ the partitioning of semi-volatile species including HNO_3-NO_3^- and NH_4^+-NH_3, which are sensitive to aerosol pH (Guo et al., 2015; Hennigan et al., 2015; Guo et al., 2016).

~~Field~~ Analyses of field observations in different regions of the United States (US) ~~United States~~ have indicated that ~~the~~ aerosol acidity ~~was~~ is typically high. For example, Weber et al. (2016) (Weber et al., 2016) showed that aerosol pH in the ~~S~~southeastern ~~United States~~US was buffered to be ~~nearly constant~~consistently in the range of –0-2 despite a substantial sulfate reduction~~s~~ over the past 15 years, and ~~this~~ the same trend may be applicable to ~~many~~ other regions. Studies in the ~~N~~northeastern ~~United States~~US and California also ~~indicated~~ found ~~a~~ highly acidic aerosols with mean pH values of 0.8 and 1.9, respectively (Guo et al., 2017a). ~~The a~~Aerosol pH in the ~~M~~midwestern ~~United States~~US was typically higher than other areas~~.~~, with an~~the~~ average ~~aerosol pH was~~ of 3.8 (Lawal et al., 2018). Studies in China, on the other hand, ~~showed~~ have found generally higher ~~levels of~~ aerosol pH~~, indicating a lower aerosol acidity~~. Several studies in the heavily polluted North China Plain (NCP) region~~,~~ reported average pH ~~values between~~of 3.5–5.2 (Shi et al., 2017; Ding et al., 2019; Shi et al., 2019; Song et al., 2019; Wang et al., 2020a). Xi'an, a city ~~located~~ in ~~N~~northwest China, had aerosol pH values up to 5 (Wang et al., 2016; Guo et al., 2017b). Some sites in ~~S~~southeast China ~~showed a~~had lower aerosol pH, such as the site in Guangzhou ~~with an~~which had an average ~~value~~ of 2.3 (Jia et al., 2020). A comprehensive, nationwide comparison of aerosol pH between China and the US ~~United States~~ can ~~give us~~provide a better understanding of the ~~driving~~ factors ~~of~~ driving aerosol pH and its effect ~~i~~on aerosol formation mechanisms and properties (Pathak et al., 2009; Guo et al., 2017a; Wang et al., 2020a). However, such comparisons are still scarce (Guo et al., 2017b; Nenes et al., 2020; Zheng et al., 2020), primarily ~~limited by~~because of a lack of extensive simultaneous measurements of aerosol composition and semi-volatile gaseous compounds in China.

In this study, we compared the aerosol mass concentrations, chemical composition~~,~~ and acidity between China and the US ~~United States~~ based on one-year ~~large-scale~~ measurements from 34 ground monitoring sites in the ~~United States~~US and 16 sites in China (mostly clustered in the NCP). In order to extend the spatial coverage to nationwide scales, we employed the Community Multiscale Air Quality (CMAQ) model to simulate the concentrations of gaseous and ~~aerosol~~ particle species which were used to calculate aerosol pH ~~in~~ across both countries. We proposed a new method to identify the factors driving ~~factors leading to~~ the pH difference between these two countries~~then carried out a series of sensitivity tests to identify~~ and discussed the causes and implications~~effects~~ ~~associated withof~~of the pH difference.

2 Data collection and method

2.1 Observational data

Measurements of ~~G~~gaseous species (including HNO_3, NH_3 and HCl) and~~,~~ ~~aerosol~~ particle components (including ~~$PM_{2.5}$ components of~~ SO_4^{2-}, NO_3^-, NH_4^+, ~~and~~ Cl^-~~)~~, and nonvolatile cations (NVCs)) ~~(including Na^+, Mg^{2+}, K^+, and Ca^{2+})~~ ~~collected~~ from monitoring networks in China and the ~~United States~~US ~~and~~ are used for analysis and comparison in this study. NVCs ~~include~~considered are Na^+, Mg^{2+}, K^+, and Ca^{2+}. The names and locations of the monitoring sites can be found in Tables S1 and S2. The sum of total observed aerosol ionic compounds is defined as water soluble ions (WSI), though it is recognized that not all of the ions are routinely measured~~, including~~ ~~such as~~ (e.g., trace species and organic ions). We also study the partitioning of semi-volatile species including NH_3--NH_4^+ and HNO_3-NO_3^- because they are sensitive to pH, especially when the partitioning ratios, ε(NH_4^+) and ε(NO_3^-), defined as the molar ratio of NH_4^+ to total ammonia ($TNH_3=NH_3+ NH_4^+$) and the molar ratio of NO_3^- to total nitrate ($TNO_3=HNO_3+NO_3^-$), are around 50% (Guo et al., 2017a; Chen et al., 2019).

In the ~~United States~~US, observational data are from ~~the~~ co-located~~ sites of the~~ Clean Air Status and Trends Network (CASTNET) (https://www.epa.gov/castnet) and Ammonia Monitoring Network (AMoN) (http://nadp.slh.wisc.edu/amon/) sites. ~~Two sites in~~ CASTNET and AMoN sites are assumed to be co-located if they are within 1km of one another.~~,~~

Observations from co-located sites ~~and~~are then combined for pH calculation. Weekly ambient concentrations of gases and ~~particles~~ particulate species, including HNO_3, SO_4^{2-}, NO_3^-, NH_4^+, Cl^- and NVCs, are available from CASTNET sites, while biweekly concentrations of NH_3 are available from AMoN sites. ~~In order to~~To match biweekly data of NH_3 from AMoN to weekly data of other species from CASTNET, ~~we assume concentrations of~~ The same NH_3 ~~in two adjacent consecutive weeks~~are used for both weeks of the CASTNET samples ~~to be the same~~. This assumption is expected to have a minor effect on pH ~~prediction~~estimates, as a previous study found that a 10 times increase in NH_3 is required to increase pH by one unit (Guo et al., 2017b). ~~and~~This assumption is also ~~confirmed in the~~supported in later discussion (Text~~.~~ S1~~Sect.3.2.3~~). HCl data is not available, so we ~~only~~ use particle phase Cl^- as total Cl ~~in~~ for pH calculations. Sensitivity tests ~~either~~ assuming HCl concentrations of~~e~~ ~~a~~ four times ~~of HCl vs.~~the Cl^- concentrations or us~~e~~ing ~~derived~~ HCl concentrations derived from CMAQ modeled HCl/Cl^- ratios show~~ed~~ little difference in aerosol pH~~,~~ compared to ~~that~~the pH estimated by using particle phase Cl^- as total Cl (Fig~~.~~ .~~ure~~ S1). Considering the small reported ~~little~~ change in aerosol pH in the ~~United States~~US over a long-term period (Weber et al., 2016; Lawal et al., 2018) and the configuration of the chemical transport model which is set up for the year 2011 (see the following section), we use observational data in 2011 to investigate the aerosol pH in the ~~United States~~US. Only ~~the~~ sites with measurements available for all species were selected ~~in~~for this study. ~~As a result, t~~There are 34 co-located CASTNET and AMoN sites, which are ~~evenly distributed~~scattered across the contiguous ~~United States~~US (Fig. S2a). The accuracy ~~for~~ of CASTNET measurements has been assessed through the analysis of reference and continuing calibration verification samples with a criterion of~~were all in~~ 95~~%~~-105% (except ~~for~~ NH_4^+, ~~which is in~~~~has an accuracy of~~whose accuracy criterion is 90~~%~~-110%)~~, while the accuracy of NH_3 data derived from AMoN was in 97%-103%, suggesting a good~~~~the high quality of this datasets~~the data. Detailed information about data quality ~~could be found~~is available ~~at~~in the CASTNET Quality Assurance Report-Annual 2011 (United States Environmental Protection Agency, 2012b)~~ and Quality Assurance Support for the NADP (National Atmospheric Deposition Program)~~. A previous study demonstrated that the NH_3 concentrations measured by the passive AMoN samplers ~~operated by AMoN~~ are comparable to annular denuder systems (as a reference system) with ~~the~~a mean relative percent difference of -9% (Puchalski et al., 2015).

In China, hourly observational data are extracted from the d~~D~~ata-sharing platform operated by the Comprehensive Observation Network for Air Pollution in Beijing-Tianjin-Hebei and i~~I~~ts ~~s~~Surrounding Areas (http://123.127.175.60:8765/siteui/index). This collaborative observation network ~~gathers information from~~is supported by ~~multi-source~~multiple institutions and ~~and~~ provides simultaneous observations of gaseous and ~~aerosol~~ particle species at individual monitoring sites (Wang et al., 2019). ~~In this study, w~~We derive daily average concentrations of gaseous species including NH_3, HNO_3 and HCl and of particle species including NH_4^+, NO_3^-, Cl^-~~-~~, and NVCs ~~for pH calculation~~ from hourly observational data at 16 monitoring sites for use in pH calculation. These monitoring sites are clustered in NCP in ~~the~~ eastern China (Fig. S2c). Due to the lack of data quality information, we first process~~ed~~ the data ~~before using them~~ by removing unreasonable data points ~~for quality control by removing unreasonable data~~. We define a set of valid data ~~of~~containing all the ~~the~~ measured components in one day as one case. We first remove ~~the~~ cases with one or more ~~any~~ missing component~~(s)~~. In this step, 2704 ~~out~~ of 5840 cases are removed ~~in this step~~. We then identify ~~the~~ data points ~~beyond the scope of~~that ~~is~~are more than three median absolute deviations from the median as outliers and remove ~~the~~ cases with any component identified as an outlier. Eventually, 1766 cases remain for subsequent analyses. Although we remove ~~a large number of~~many cases in this process, the remaining cases cover most of the days in a year and ~~distribute~~are evenly distributed by month~~s~~ (Table S3). ~~For example, data points showing extremely large values for certain species (e.g. [Ca^{2+}]>1000μg·m^{-3}) are removed. 16 monitoring sites with measurements available for all species are selected in this study. These sites cluster in NCP in eastern China (Fig. S2c).~~It should be noted that the weekly (or longer) duration of the CASTNET samples in the US may lead to biases in the measured concentrations especially for ~~those~~ volatile species such as ammonium nitrate. Sickles et al. (1999) conducted a comprehensive comparison of ~~the~~ measurements using the CASTNET weekly-duration sampling approach with those using a 24-h-duration sampling approach. Both approaches used filter packs. They found that compared to 24-h ~~duration~~sampling, weekly ~~duration~~sampling led to low biases of -5%, -5%, and -0.7%, on average, in measured HNO_3, NO_3^-, and NH_4^+, respectively, and high biases of 4% and 16%, on average, in SO_4^{2-} and SO_2, respectively. To evaluate the potential biases ~~pertaining to~~in the calculated aerosol pH due to the ~~long~~weekly-~~-~~duration sampling, we conduct a sensitivity test to adjust the CASTNET-measured concentrations based on the~~se~~ reported average differences between weekly-duration and 24-h-duration samples (Sickles et al., 1999) (Results and Discussion).

2.2 Model configuration

We use ~~the~~ CMAQ version 5.0.2 (United States Environmental Protection Agency, 2014) to simulate gaseous and ~~aerosol~~ particle species concentrations and aerosol pH in China and the ~~United States~~US. The model domains ~~of the two simulations~~ cover ~~the~~ mainland China and the contiguous ~~United States~~US with 124×184 and 112×148 horizontal grid cells, respectively.~~,~~ ~~and are b~~Both are resolved at the 36-km horizontal resolution ~~and~~with 13 vertical layers extending to ~16 km above the ground. In both simulations, gas-phase chemistry is modeled with the CB05 chemical mechanism (Yarwood et al., 2005), and the aerosol thermodynamic equilibrium is modeled with ISORROPIA II (Fountoukis and Nenes, 2007).

The meteorological and emission inputs used to drive the China~~'s~~ simulation are adopted from “AiMa”, an online operational air quality forecasting system (Lyu et al., 2017; AiMa Forecast, 2017). In the AiMa modeling system, the meteorological data ~~were~~ are generated with the Weather Research and Forecasting (WRF) model (William C. Skamarock 2008) driven by the 0.5-degree global weather forecast products produced by the National Centers for Environmental Prediction (NCEP) Global Forecast System (GFS) (Global Forecast System (GFS) Model). The AiMa emission inventory was compiled and derived by integrating a variety of inventories and utilizing various activity data and has been continuously updated since its establish~~ed~~ment (Lyu et al., 2017). The base year of the current AiMa emission inventory is 2017. For the ~~United States~~US simulation~~ in the United States~~, we use WRF-modeled meteorological fields downscaled from the North American Regional Reanalysis (NARR) data (Mesinger et al., 2006) as the meteorological input and the 2011 National Emissions Inventory provided by the ~~United States~~US Environmental Protection Agency as the emission input (United States Environmental Protection Agency, 2012a). The base year of the meteorology and emissions is consistent with the year of the measurements in each country (i.e., 2017 for China and 2011 for the ~~United States~~US).

In order to evaluate the model performance against observations, we calculate normalized mean bias (NMB) and normalized root-mean-square error~~s~~ (NRMSE) to evaluate the spatial variation of pH, species concentrations and partitioning ratios with following equations:~~,~~

$$\mathrm{NMB} = \frac{\sum_1^N (C_m - C_O)}{\sum_1^N C_O} \quad (1)$$

$$\mathrm{NRMSE} = \frac{\sqrt{\frac{\sum_1^N (C_m - C_O)^2}{N}}}{\overline{C_O}} \quad (2)$$

where C_m is the ~~CMAQ~~ modeled value, C_o is the ~~observational~~ observed value, N is the number of simulation-observation pairs~~ used in NMB and NRMSE calculations~~.

2.3 Aerosol pH calculation

In this study, we use the ISORROPIA-II thermodynamic model (Fountoukis and Nenes, 2007) to determine the composition in a K^+-Ca^{2+}-Mg^{2+}-NH_4^+-Na^+-SO_4^{2-}-NO_3^--Cl^--H_2O aerosol system under equilibrium conditions with gas phase precursors. Aerosol pH is calculated based on H^+_{air} and liquid water content ~~uptake by inorganic species~~ (LWC~~$_i$~~) from ISORROPIA-II output:

$$\mathrm{pH} = -log_{10}\left(\gamma_{H^+} \cdot H^+_{\mathrm{aq}}\right) = -log_{10}\left(\frac{1000\gamma_{H^+} \cdot H^+_{\mathrm{air}}}{\mathrm{LWC}}\right) \quad (3)$$

where γ_{H+} is the activity coefficient of the hydronium ion ~~and~~ which is assumed to be 1 in this study (~~note that,~~ the binary activity coefficients of ionic pairs, including H^+, are calculated in ISORROPIA-II), H^+_{aq} (mol·L^{-1}) is the hydronium ion concentration in ~~the~~ aerosol liquid water, H^+_{air} (μg·m^{-3}) is the equilibrium particle hydronium ion concentration per volume air. LWC (μg·m^{-3}) in this study only considers the water uptake by inorganic species. ~~includes LWC$_i$ and LWC$_o$, which means the water uptake by inorganic species and organic species (μg·m^{-3}) are modeled separately because both organic and inorganic species are hygroscopic. In this study, we only consider the effect of LWC$_i$~~ ~~since~~ ~~Note that t~~The effect of water uptake by organic species~~LWC$_o$~~ on aerosol pH has been found to be minor (Guo et al., 2015).

There are two modes in ISORROPIA-II's calculation, ~~i.e.~~ the forward mode and the reverse mode. In the forward mode, the inputs include total concentrations (i.e. gas+~~aerosol~~particle) of TNH_3, TNO_3, TCl (HCl+Cl^-), SO_4 and NVCs and meteorological parameters (temperature and~~,~~ ~~relative humidity~~RH); in the reverse mode, only the ~~aerosol~~ particle phase of compounds and meteorological parameters are needed (Fountoukis and Nenes, 2007). In this study, the ISORROPIA-II model is run in the forward mode for aerosol in metastable state because the concentrations of both gas and particle species are available and also because the reverse mode has been reported to be more sensitive to measurement errors (Hennigan et al., 2015; Song et al., 2018).

We ~~also~~ find that there are measurements with unrealistically high Ca^{2+} concentrations (such that Ca^{2+} is more than LWC×0.002, i.e., the solubility of Ca^{2+} in aerosol liquid water). This may be due to the measurement method of Ca^{2+} which ~~needs to~~ uses large amounts of water to dissolve filter-~~based~~ collected particles. This process will likely dissolve the waterinsoluble part of Ca^{2+} in aerosols which may cause higher bias ~~of~~in aerosol Ca^{2+} concentrations. In the existence of aerosol SO_4^{2-}, Ca^{2+} precipitates along with SO_4^{2-} as $CaSO_4$ because of the low solubility (Seinfeld and Pandis, 2006). Including the high Ca^{2+} concentration ~~or not causes a~~leads to large differences in ~~predicted~~estimated pH because of the high acidity of SO_4^{2-} (Text S2~~Sect. 3.2.4~~). In order to avoid th~~is~~ise potential bias, we use modified Ca^{2+} concentration for pH calculations while keeping SO_4^{2-} unchanged~~,~~. ~~t~~That is, we use the original Ca^{2+} concentration to calculate aerosol LWC and then use the concentration of Ca^{2+} that can dissolve in the LWC as the modified Ca^{2+} concentration ~~if~~in cases where the original Ca^{2+} ~~is in excess of~~ exceeds its solubility in the calculated LWC.

~~We evaluate the model performance by comparing the gas-particle partitioning of semi-volatile compounds between measured and simulated values such as $\varepsilon(NO_3^-)$ and $\varepsilon(NH_4^+)$.~~ We compare the directly measured gas-particle partitioning ratios of semi-volatile compounds with the ratios re-partitioned by ISORROPIA-II using measured total (gas+particle) concentrations as inputs. The purpose of this comparison, as conducted in previous studies (Guo et al., 2016; Guo et al., 2017a), is to examine the measurement data quality. This method is effective when the species have substantial fractions in both gas and particle phases (Guo et al., 2017a). The comparison results of $\varepsilon(NH_4^+)$ and $\varepsilon(NO_3^-)$ are shown in Fig. S3. The correlation coefficients and the slopes of linear regression are all close to 1, suggesting good agreement between ~~the~~ the measured and ISORROPIA-re-calculated partitioning ratios.~~simulations and observations.~~ In terms of these partitioning ratios, the model (ISORROPIA-II) performs better in the ~~United States~~US than in China, which may be attributable,~~e~~ in part~~ly,~~ to the ~~more even~~more balanced partitioning of the species between gas and particle phase in the ~~United States~~US.

2.4 Multivariable Taylor Series Method (MTSM)

~~In order T~~To separate the contribution of ~~each~~ individual components (~~8~~ eight species in total, includ~~e~~inge Na^+, SO_4, TNO_3, TNH_3, TCl, Ca^{2+}, K^+, and Mg^{2+}) and meteorological variables (~~relative humidity~~RH and temperature) to the pH difference between China and the ~~United States~~US, we ~~use~~ propose a multivariable Taylor Series ~~Method~~ method (MTSM). First, we derive the average conditions (i.e., species concentrations and meteorological conditions) across all the sites in the ~~United States~~US and China. We then use the ~~United States~~US as the starting point and China as the end point and decompose the contributions of individual compounds to the pH difference based on the following equations:

$$\Delta c_i = c_{i,China} - c_{i,US} \tag{4}$$

$$c_{i,\lambda} \cong c_{i,US} + \Delta c_i \cdot \lambda \tag{5}$$

$$\Delta pH = pH_{US} - pH_{China} = \int_0^1 \left(\sum_{i=1}^{8} \frac{\partial pH}{\partial c_{i,\lambda}} \cdot \Delta c_i\right) \cdot d\lambda \cong \sum_{s=1}^{100} \left(\sum_{i=1}^{8} \frac{\partial pH}{\partial c_{i,\frac{s}{100}}} \cdot \Delta c_i\right) \cdot 0.01 \tag{6}$$

$$\Delta pH_i \cong \sum_{s=1}^{100} \frac{\partial pH}{\partial c_{i,\frac{s}{100}}} \cdot \Delta c_i \cdot 0.01 \tag{7}$$

where subscript *i* denotes a specific species or meteorological variable; $c_{i,China}$ and $c_{i,US}$ represent the values of~~concentration species~~ *i*~~the concentration of compound i~~ in China and the ~~United States~~US, respectively; Δc_i is the difference in c_i between

China and the ~~United States~~US; $c_{i,\lambda}$ is an intervening c_i between $c_{i,China}$ and $c_{i,US}$ defined by λ , ~~-~~$\lambda \in [0, 1]$; when λ is 0, $c_{i,\lambda}$ is $c_{i,US}$ ~~when λ is 0~~; when λ is 1, $c_{i, ,\lambda}$ is $c_{i,China}$ ~~when λ is 1~~. ~~In this study we assume negligible interaction between species, therefore the increasing concentration of species *i* will not have the effect of changing the concentration of other species.~~ The pH difference between China and the ~~United States~~US (i.e., ΔpH) can be expressed as the sum of the partial derivatives of pH with respect to $c_{i,\lambda}$ which is then integrated from $c_{i,US}$ to $c_{i,China}$, as described by Eq. (6). In this study, we take 100 steps with equal intervals to gradually change λ from 0 to 1 (Eq. (6)) and record the partial derivatives of pH with respect to individual $c_{i,\lambda}$, and derive the contributions of all the species and meteorological variables to the pH change at every step. By summing up the contributions of individual variables at all ~~the~~ steps, we characterize the contributions of individual factors ~~components~~ to the overall pH difference (Eq. (7)). Based on the same method, we further quantify the contributions of individual factors to the differences in LWC and H_{air}^+, respectively, the two variables directly used to calculate aerosol pH (Results and Discussion).

3 Results and discussion

3.1 The pH difference between China and the ~~United States~~US

3.1.1 The pH difference based on observations

The sensitivity test to adjust the CASTNET-measured concentrations based on the reported average differences between weekly-duration and 24-h-duration samples shows little difference between the unadjusted and adjusted pH values in the US (2.69±0.85 and 2.74±0.83 on average for the unadjusted and adjusted pH, respectively), suggesting that the weekly duration of the CASTNET sampling has little impact on the calculated aerosol pH. Therefore, we proceed with our subsequent analyses using the unadjusted pH. The aerosol pH values calculated based on observational data show a significant difference between China (most observation sites are in NCP) and the ~~United States~~US. In China (mainly the NCP), the 2017 annual average pH ~~level~~ at monitoring sites is 4.3~~ and~~, rang~~es~~ing from 3.3 to 5.4 ~~by monitoring sites~~ with an interquartile range of 3.9–4.6. In the contiguous ~~United States~~US, the 2011 annual average pH ~~level~~ is 2.6, ranging from 1.9 to 3.9 with an inter-quartile range of 2.2–3.0 (Fig. 1). The t-test shows a statistically significant difference between the two groups ($p<0.0001$), suggesting that the aerosols are on average more acidic at the monitoring sites in the contiguous ~~United States~~US than in China (NCP).

The pH difference ~~can~~ is also ~~be~~ illustrated by the cumulative distribution function (CDF) curves (Fig. 2, solid lines). The shapes of the CDF curves are similar in these two countries with a slightly steeper slope in the contiguous ~~United States~~US (Fig.~~ ~~2a). The pH values, however, are 1–2 units higher in China (NCP) than in the contiguous ~~United States~~US ~~at~~ across varying levels of cumulative frequencies in the CDF curves. In some cases, ~~the~~ aerosols~~ acidities~~ could be completely neutral in China (NCP) (the frequency is 2% for pH ≥7), while in the contiguous ~~United States~~US, the pH values in all ~~the~~ cases are below 6.

Spatially, 14 out of the 16 sampling sites in China are in the NCP (~~Fig.~~~~Figure ~~Fig. S2c) which is one of the most populous and polluted regions in China (Hu et al., 2014; Cui et al., 2020). Our pH results in this region are consistent with other studies (ranging from 3.5 to 4.6) (Liu et al., 2017; Ding et al., 2019; Ge et al., 2019). The distribution of sampling sites in the ~~United States~~US, on the other hand, is more evenly distributed spatially. The pH values in the Midwest and California are higher than in other regions like the Southeast, in line with previous studies (Lawal et al., 2018; Chen et al., 2019). Overall, the pH level in the ~~ United States~~US is 1.7 units lower than ~~in ~~over the NCP of China.

3.1.2 The pH difference based on model simulations

To ~~solve the uneven spatial~~address the issue of insufficient spatial coverage of the observational data in China, we conduct simulations using CMAQ, in ~~company ~~conjunction with the observational data, to further ~~address ~~study the pH difference on a nation-wide scale. We evaluate the model performance by comparing the modeled and observed aerosol pH values (Fig. 3), major ~~aerosol ~~particle and gaseous species including SO_4^{2-}, NO_3^-, NH_4^+ and HNO_3, NH_3, and the partitioning ratios including $\varepsilon(NH_4^+)$ and $\varepsilon(NO_3^-)$, at monitoring sites (Figs. S4–S6).

Spatially, the model simulations generally capture the observed variations in pH, species concentrations, and partitioning ratios, although there are some notable biases~~ occurred~~ (Figs. S4 and S5). In both China (NCP) and the contiguous US, the modeled NH_4^+, NO_3^-, and NH_3 are biased low~~, compared to observations,~~ while modeled HNO_3 ~~are~~is biased high, ~~which ~~result~~s~~ing in low biases in the predicted $\varepsilon(NO_3^-)$ and $\varepsilon(NH_4^+)$. The modeled SO_4^{2-} in ~~the two~~both countries ~~are all~~is biased low.~~For SO_4^{2-}, the model captures the high concentration in the NCP and the eastern US, but it shows low biases in some sites in the southern NCP. This leads to a more negative NMB of the modelled SO_4^{2-} in China than in the United States, which can also be seen from Fig S5a& Fig S5i. Low biases are also found for other aerosol components, including NH_4^+, NH_3 and NO_3^-, in both countries.~~ Such low biases have been seen in previous studies (Fountoukis et al., 2013; Theobald et al., 2016)~~, which can be~~and have been attributed to the spatial mismatch between the observations and simulations due to the coarse resolutions of ~~the ~~model grid cells (usually ~~in the range of ~~20–50 km resolution~~s~~) (Shen et al., 2014; Wang et al., 2014a). Smaller NMBs in the US indicate~~d~~ a better performance, compared to China (NCP). Larger differences between observations and simulations in China (NCP) could also be caused by larger measurement uncertainties as the data in China are collected from different monitoring stations operated by individual research institutions (Wang et al., 2019) and thus lack a unified quality control, compared with data in the US, which come~~s~~ from national monitoring networks (United States Environmental Protection Agency;National Atmospheric Deposition Program). ~~Due to t~~The co-occurrence of ~~the ~~low biases in $\varepsilon(NO_3^-)$, which causes lower bias in aerosol pH, and low biases in $\varepsilon(NH_4^+)$ and SO_4^{2-}~~-~~, which cause higher bias in aerosol pH, likely offset each other, ~~the~~resulting in small biases ~~pertaining to~~in aerosol pH~~ likely offset each other,~~. Indeed, ~~and ~~the simulated average pH values ~~in~~at observation sites (3.8±0.2 in NCP, China and 1.8±0.5 in the contiguous US) are generally in line with the observed averages (4.3±0.5 in NCP, China and 2.6±0.5 in the contiguous US) (Fig. 3), although the model shows a moderate low bias in both countries. ~~-~~The larger pH difference in the US than in China is likely due to the low bias in TNH_3 to which the sensitivity of pH is found to be more pronounced in the US than in China (discussed in detail in Text S1).~~For ε(NO_3^-), the model performs generally well, with high ε(NO_3^-) in China and low ε(NO_3^-) in the United States (Fig. S4f&Fig. S4vi, Fig. S5f& Fig. S5vi), although ε(NO_3^-) in both countries are biased low (NMB is -28% in China and -30% in the United States) due to the lower bias in NO_3^- than in HNO_3. For ε(NH_4^+), the model reproduces the low levels in NCP and the high levels in the northeastern United States, but in China, ε(NH_4^+) levels are biased high (NMB=52%) because of the low bias in NH_3 (Fig. S4g&Fig. S4e, Fig.S5g&Fig.S5e). The pH values predicted by the model are reasonable justified because 90% of the cases have the absolute pH differences between observation and simulation smaller than 1.2 in China and 2.0 in the United States. Both the NMBs and NRMSEs for pH are smaller in China than in the United States (Fig. 3).~~

With respect to the temporal variation, the model captures the seasonal trends of pH, ε(NH_4^+), and ε(NO_3^-) in both countries, ~~all of which are~~with lower values in summer and higher values in winter (Fig. 4). The lower temperature in winter~~time~~ favors the partitioning toward particle ~~-~~phase for semi-volatile species. Comparison of the seasonal trends of the individual aerosol components shows a better agreement in the ~~United States~~US than in China. For example, the simulation in the US captures the trends of almost all ~~the~~ components, though it ~~shows~~is biased high~~er~~ ~~concentrations of~~for SO_4^{2-} and NH_4^+ ~~than the observed ones~~ in summer (Fig. S6~~.~~ b and~~,~~ h); the simulation in China misses the peaks of SO_4^{2-} in winter and NH_3 in summer, ~~-~~and has high biases for HNO_3 in summer (~~Fig.~~~~Figure~~ Fig. S6~~.~~ a, i, and e). ~~On the other hand, the simulation in the United States captures the trends of almost all the components though is biased low for SO_4^{2-} and NH_4^+in summer (Fig. S6b, h). These results indicate the need for better quantification of the monthly emission trends in China which are currently subject to high uncertainty.~~ Measurement-related biases may contribute to the disparity in the temporal trends between observed and modeled concentrations. The uncertainty in monthly profiles of emission estimates may also play an important role. For example, CASTNET's~~the~~ long ~~duration~~sampling period ~~of the CASTNET sampling system in the US~~ could lead to a larger measurement bias in summer than in winter (Sickles and Shadwick, 2008); ~~T~~the large uncertainty in the current estimates of NH_3 emissions in China, especially the reported underestimation of summertime emissions as indicated by an inversion analysis (Kong et al., 2019), may cause the absence of the summertime NH_3 peak in the simulated trend (~~Fig.~~~~Figure~~Fig. S6i). Further investigation is needed to better understand the factors underpinning the disparity between observations and model simulations. In spite of the various potential uncertainties, o~~O~~verall, the spatial and temporal evaluation suggests generally good agreement between the model simulations and observations in both countries.

In line with ~~the pH comparison based on observational data~~observations (Sect. 3.1.1), the nationwide model simulations show significant differences in aerosol acidity between the two countries. Almost all the areas in the ~~United States~~US have aerosol pH values lower than ~~3~~ 3 according to the CDF ~~plot~~ (Fig. 2b). Higher pH values are found in the middle and eastern ~~United States~~US, while in the western ~~United States~~US except California, the pH values are lower (Fig. 3). In China, a large portion of areas (87%) have aerosol pH values above ~~3~~ 3 according to the CDF~~ plot,~~. ~~which~~This is especially true in ~~the~~ eastern China ~~with~~which has the largest population (Fig. 3). Aerosol pH values in ~~the~~ western and southeastern China are generally lower than in the east. It should be noted that due to ~~limitations in~~~~in~~ the scarcity of observational data, the pH

~~predictions~~estimates in ~~the~~ southern and western China are not evaluated. The nationwide annual average pH values in China and the ~~United States~~US are 2.7±0.6 and 0.8±0.8 units, respectively, lower than the observation-based values due partly to the model bias but also because most of the monitoring sites are in ~~the~~ areas with high pH ~~areas~~ (Fig. 3) ~~and the bias in model simulation (Fig. 4a, Fig 4b)~~.

Given the adverse health impacts of ambient aerosols (Burnett et al., 2014; Freedman et al., 2019) and the potential linkage of aerosol acidity with aerosol toxicity through the solubility of redox-active metals (Oakes et al., 2012; Fang et al., 2015; Ye et al., 2018), we further calculate and compare the population-weighted averages of ~~the~~ aerosol pH in the two countries ~~in order~~ to highlight the pH levels in densely populated areas. The ~~calculation shows the~~ population-weighted pH values ~~of~~are 3.3±0.4 and 2.2±0.5 in China and the ~~United States~~US, respectively, both of which are higher than non-weighted averages, ~~which means~~indicating that aerosols in more populous areas tend to be less acidic (Fig. 2b). This finding is further confirmed by the statistically significant positive correlation ($\alpha=0.01$), within each country, between the aerosol pH and population density (China: $r=0.42$, $p<0.0001$; the ~~United States~~US: $r=0.28$, $p<0.0001$). Consistent with the observation-based results, the t-test for the model simulations shows a significant difference in ~~either~~ both the population-weighted ~~or~~and non-weighted aerosol pH values between the two countries ($p<0.001$).

3.2 ~~Potential c~~Causes ~~and effects of~~ of the aerosol pH difference~~s~~

3.2.1 Gaseous and ~~aerosol~~particle compound profiles between China (NCP) and the contiguous US~~nited States~~

We further investigate the factors leading to the pH difference. Although both observations and simulations are subject to uncertainty, we expect that ~~the observational data~~observations should provide more direct and reliable evidence for this investigation~~, when available~~. It should be noted that the monitoring sites in China were clustered in NCP and, thus, may not be representative of the ~~entire~~whole of China. Table 1 summarizes the annual average concentrations of gaseous and ~~aerosol~~ particle species measured in China (NCP) and the contiguous ~~United States~~US during the study period (China: 2017~~,~~ ; ~~the United States~~US: 2011). For all the gaseous and ionic species (except HNO_3), the average concentrations in China (NCP) are statistically significantly higher than those in the contiguous ~~United States~~US. The total concentrations of WSI species in China (NCP) (34.4 μg·m^{-3}) are on average six times the concentrations in the contiguous ~~United States~~US (5.7 μg·m^{-3}) and ~~present a larger~~have greater variation, ranging from 0.2–240 μg·m^{-3}, compared to ~~the~~ a range of 0.1–31 μg·m^{-3} in the contiguous ~~United States~~US. Similar to other studies in China (Yao et al., 2002; Pathak et al., 2009; Zhang et al., 2013; Liu et al., 2016) and the ~~United States~~US (Guo et al., 2015; Feng et al., 2020), NH_4^+, NO_3^- and SO_4^{2-}, contribute more than 80% of the total WSI concentrations in both countries. The mass fractions of individual WSIs, however, differ between the two countries (Fig. 5). In China (NCP), the dominant WSI was NO_3^- (34.6%), followed by SO_4^{2-} (26.3%) and NH_4^+ (25.5%). In the contiguous ~~United States~~US in 2011, SO_4^{2-} contributed nearly half of the total WSI concentration (49.4%), and the contributions of NO_3^- and NH_4^+ are comparable (NO_3^- 17.6%, NH_4^+ 18.8%)~~, though~~. Note that SO_4^{2-} and NO_3^- levels have been ~~found to~~ decreasing~~ed~~ dramatically ~~along~~over the years, leading to decreases in NH_4^+ ~~due to~~since there is less substrate to interact with NH_3 and form particulate ammonium species (Butler et al., 2016).

~~As t~~Two of the most predominant anions in aerosols, ~~the concentrations of~~ SO_4^{2-} and NO_3^- at the monitoring sites in China (NCP) are present at ~~4~~ four and 15 times the concentrations observed in the contiguous ~~United States~~US, respectively. ~~In particular, t~~The relative difference in NO_3^- between the ~~the~~ two countries is the most significant, compared with the differences in other WSI components. Hence, the difference of the nitrate to sulfate molar ratio (NO_3^-/SO_4^{2-}) is also significant ~~in~~ between the ~~the~~ two countries. The observational data show that the ratios at most monitoring sites in China (NCP) are larger than 1, and that only two sites have ~~the~~ ratios lower but close to 1 (0.81, 0.94)~~;~~. ~~o~~On the other hand, 27 out of the 34 sites in the contiguous ~~United States~~US ~~found~~ show a ratio lower than 1, ranging from 0.25–0.99~~, which are generally lower than in China (NCP)~~. High NO_3^-/SO_4^{2-}~~nitrate to sulfate~~ ~~ratio~~ in China (NCP) could be caused by more efficient oxidation of NO_x than SO_2 in China ~~to allow for larger amount of~~leading to greater nitrate formation as well as higher aerosol pH and availability of ~~ammonia~~ NH_3 which favor the formation process of particle nitrate (Guo et al., 2018b; Vasilakos et al., 2018). The varying ratios of NO_3^-/SO_4^{2-} on aerosol could further affect aerosol liquid water uptake, which ~~will be discussed~~is discussed in Supplementary Information ~~-~~(Text~~.~~ S2)~~in Sect. 3.2.4~~.

The most abundant cation in aerosols is NH_4^+, and the concentration difference of NH_4^+ between the two countries (by a factor of 11) is more significant than~~compared with~~ the difference of other cations (by factors of 2-7). ~~The average NH_4^+ level at the monitoring sites in China (NCP) is more than ten times the level in the contiguous United StatesUS.~~ In addition, ε(NH_4^+) in China (NCP) (0.13–0.48) is approximately 50% lower than in the contiguous ~~United States~~US (0.22-0.85), ~~which~~ mean~~s~~ing that compared to the ~~United States~~US, TNH_3 in China tends to be present more in the gas phase. Higher NH_4^+ and lower ε(NH_4^+) levels in China ~~indicate~~ amount to a higher level of TNH_3~~,~~ which ~~plays~~ has an important ~~role~~ influence on aerosol pH, partitioning of TNO_3 and even particulate mass (see Supplementary Information for more discussion)~~, discussed in Sect 3.2.3~~.

NVCs such as Na^+, Ca^{2+}, Mg^{2+}, and K^+ are often minor components of particles but are important because of their ability to neutralize acidic species in the atmosphere, such as sulfuric and nitric acids (Zhang et al., 2007). Neglecting NVCs would ~~makes~~cause low biases of pH, driving the NH_3-NH_4^+ equilibrium to shift~~ing~~ toward the particle phase because more ammonium would be ~~is~~ used to neutralize the aerosol~~ acidity~~ ~~than~~ that ~~sh~~would otherwise be neutralized by NVCs (Guo et al., 2018a). Therefore, NVCs are included in calculating aerosol pH in this study. High NVC concentrations usually occur at the sites near emission sources. For example, high concentrations of Na^+, mainly from sea salt (Zhang et al., 2011), occur at Sites 13, 27, and 30 in the ~~United States~~US, which are all coastal sites. ~~The~~High concentrations of Ca^{2+}, mainly from mineral dust, are found ~~in greater abundance~~ at Sites 6, 11, and 23 in the contiguous ~~United States~~US and at Site 5 in China (NCP), which ~~are~~ are in prairies impacted by sand and dust. Average NVC concentrations in China (NCP) are up to an order of magnitude higher than in the contiguous ~~United States~~US, although in both countries, most of the NVCs concentrations are small compared to SO_4^{2-}, NO_3^-, and NH_4^+. The predominant NVCs in China (NCP) are Ca^{2+} (2.8%), K^+ (2.1%), and Na^+ (2.0%)~~ and~~, ~~K^+ (2.1%), while~~ and in the contiguous ~~United States~~US, they are Ca^{2+} (5.9%) and Na^+ (3.7%).

3.2.2 Characterization of contributions to aerosol acidity by ~~each component~~individual factors

We use MTSM as described in Sect. 2.4 to characterize the contribution of each component to the pH difference between the ~~United States~~US and China. Three groups (i.e., observation, simulation non-weighted, simulation population-weighted) of the annual average concentrations in the ~~United States~~US and China listed in Table S4 are chosen as the starting (~~the United States~~US) and ending (China) points~~ and~~ to perform the analysis. ~~t~~The results are shown in Fig. 6.

The average concentrations based on the observational and simulated data are not completely consistent due to the representativeness of the monitoring sites and the discrepancy between the ~~model~~ simulations and observations. The MTSM analyses based on the three groups, however, show~~ed~~ similar results~~, such as that~~. For example, all~~ the~~ three groups suggest the high TNH_3 in China as an important factor leading to the difference in aerosol pH between the two countries (Fig. 6). The contribution of TNH_3 is the highest in the "observation" group due to the large difference in TNH_3 concentration. Other cations, mainly NVCs, have a relatively small effect (0.2, 0.2, and 0.3 in groups "observation", "simulation", "simulation-weighted", respectively), which is consistent with a previous study (Zheng et al., 2020). ~~The effects of other NVCs like Na^+, K^+, Mg^{2+} and Ca^{2+} on the pH difference are also considerable. The NVCs in aggregate show contributions of 0.8, 0.6, 1.0 in the "observation", "simulation", and "population-weighted simulation" groups, respectively, suggesting that the difference in NVCs explains approximately 1-unit difference in aerosol pH between the two countries. The higher NVC contribution in the "weighted simulation" group than in the "non-weighted" group may be explained by the interactions between NVCs and anthropogenic emissions which have been found to result in a larger control of NVCs over aerosol pH~~ (Guo et al., 2018a; Wong et al., 2020)~~.~~

Unlike TNH_3 and NVCs which lead to higher pH values in China than in the ~~United States~~US, SO_4^{2-} contributes in the opposite~~ly~~ direction to the pH difference~~ between the two countries~~. High SO_4^{2-} concentrations decrease aerosol pH in China by 0.6–1.3 units~~ (varying by group)~~, compared to the ~~United States~~US, although this effect is fully offset by TNH_3~~ and NVCs~~.

Compared to other species, the concentrations of TNO_3 are the most different between the two countries (by a factor of 15), but MTSM shows that the contribution of TNO_3 ~~on~~to the pH difference is relatively small (0.1, 0.1, and 0.2 in the observation, non-weighted, and population-weighted groups). This result is further confirmed by a sensitivity test of TNO_3 (Fig. S10) which shows that the change in pH from changing only TNO_3 is ~~subtle~~ small in ~~the two~~ both countries~~ with the~~a ~~change in TNO_3 only~~. More detailed analyses and discussions on the effects of TNH_3, TNO_3, and SO_4 on aerosol pH can be found in Supplementary Information.

Studies have identified an important role of temperature in driving aerosol pH (Battaglia et al., 2017; Tao and Murphy, 2019; Jia et al., 2020). Our MTSM analysis show~~ed~~s that temperature accounts~~ed~~ for 0.07–0.39 unit of pH difference between China and the US, which varies by group~~ (observation: -0.31; non-weighted: 0.39; population-weighted: -0.07)~~ (Fig. 6). Such relatively small contributions of temperature, compared to those of TNH_3 and ~~T~~SO_4, are mainly because of the small difference in temperature between these two countries ~~(they~~which are ~~located on~~at similar latitudes~~)~~. The difference in the annual average temperature between China and the ~~United States~~US is 1.4 K, -5.0 K, and 2.6 K in the observation, non-weighted, and population-weighted groups, respectively (Table S4~~3~~).

3.2.3 Two pathways ~~pertaining~~leading to the aerosol acidity difference

As aerosol pH is calculated as [log$_{10}$(LWC) ~~–~~– log$_{10}$(H_{air}^+) – 3]~~ (both LWC and H_{air}^+ are in the unit of μg·m^{-3})~~, all mechanisms ~~through which factors~~ affecting aerosol pH ~~are associated with either~~must be through the modification of LWC, ~~or that of~~ H_{air}^+~~–~~, or both (LWC and H_{air}^+ are expressed as mass per unit volume of air, μg m^{-3}).~~–~~ We ~~use MTSM to~~ quantitatively separate the contributions of individual factors to the China-US pH difference into the LWC-modifying pathway and the H_{air}^+-modifying pathway (Fig. 6). To achieve this, we use MTSM to quantify the contributions of individual factors to the differences in log$_{10}$(LWC) and [–log$_{10}$(H_{air}^+)−3], respectively, between the two countries, with the same approach as we did for pH (LWC and H_{air}^+ are two output variables directly predicted by ISORROPIA). The results show that both the changes in LWC and H_{air}^+ lead to increases in aerosol pH when ~~changing the~~ conditions change from those in the US to China.

~~Due primarily to the positive response of~~Given that LWC increases with~~to~~ aerosol mass concentration (Song et al., 2019), higher component concentrations in China than in the US increase LWC and, thus, increase aerosol pH (Fig. 6b). Through ~~such~~the LWC-modifying pathway, changes in SO_4, TNH_3, and TNO_3 lead to ~~compatible~~ increases in pH (0.15–0.3) (Fig. 6b)~~,~~ ~~while~~, which are consistent in all three groups. Compared to other groups, ~~t~~the observation group represents a ~~larger~~higher pH increase due to Cl and a higher pH decrease ~~induced by Cl and~~due to RH~~, respectively, than in the other groups~~ (Fig. 6b), mainly because of the larger differences in Cl concentrations and RH ~~indicated by~~for this group than ~~by~~for ~~the~~ other groups (Table S4).

Through the H_{air}^+-modifying pathway, the effects of individual factors on pH changes ~~are divided~~vary (Fig. 6c). Increases in acidic components (SO_4 and TNO_3) ~~in China~~ increase H_{air}^+ ~~concentrations~~ and thus decrease aerosol pH (Fig. 6c). Increases in TNH_3, TCl, and NVCs, on the other hand, decrease H_{air}^+ ~~concentrations~~ and increase aerosol pH (Fig. 6c). By increasing H_{air}^+ ~~concentrations~~, increased SO_4 decreases pH by 0.7–1.2 units, showing a much stronger acidic capacity than another acidic component, TNO_3, which only decreases pH by 0.17–0.27 units (Fig. 6c). Compared to the ~~United States~~US, China is in a TNH_3-rich condition. The molar ratios of [TNH_3] / (2×[SO_4]+[TNO_3]+[TCl]) in China vs. in the ~~United States~~US are 3 vs. 1.4, 2.0 vs. 1.0, and 2.4 vs. 1.5 in the observation, non-weighted, and population-weighted groups, respectively. Changing the conditions from the ~~United States~~US to China, TNH_3 plays the most important role in neutralizing the acidic components and driving the pH increase in the~~is~~ H_{air}^+-modifying pathway (~~Figure~~ Fig. 6c).

For individual factors, the net changes in pH are a result of the combination of the two pathways. For example, ~~I~~increased SO_4 increases LWC and H_{air}^+ simultaneously. The increase in LWC increases aerosol pH, while the increase in H_{air}^+ decreases aerosol pH. All ~~the~~ three groups suggest that the effect of H_{air}^+ on pH overwhelms that of LWC on pH, leading to a net decrease in pH from ~~the~~an SO_4 increase (Fig. 6). Increased TNH_3 increases pH in both pathways, adding up to a larger ~~final~~ increase in pH (Fig. 6). Increased TNO_3 through these two pathways, however, is associated with opposite effects on pH which are comparable in magnitude and thus tends to offset each other (especially in the observation group) (Fig. 6). This explains the aforementioned small change in pH from the TNO_3 increases. Combining all the factors, both pathways ~~enhance~~increase aerosol pH (Fig. 6b and c), resulting in the large difference in aerosol acidity between these two countries (Fig. 6a).

To facilitate a follow-up sensitivity test to link the two pathways with mass concentration and chemical composition, we define the total mass concentration as the sum of the mass concentrations of all the seven input components (i.e., Na^+, SO_4, TNH_3, TNO_3, TCl, Ca^{2+}, K^+, and Mg^{2+}), including both gas and particle phases, and the chemical composition as the composition of the seven components in the aerosol (gas + particle) system. The observation group shows that the total mass concentration in China is 8.4 times that in the US, and the chemical composition in China is richer in TNH_3 than that in the US (as illustrated by the ratios of $[TNH_3] / (2\times[SO_4]+[TNO_3]+[TCl])$ mentioned above). It has been found that both LWC and H_{air}^+ are affected by mass concentration and aerosol composition (Guo et al., 2015; Xie et al., 2019; Zheng et al., 2020). To investigate how the differences in mass concentration and composition between China and the US is associated with the LWC- and H_{air}^+-modifying pathways and consequently the pH difference, we first increase the mass concentrations of individual input components in the US case by a constant factor of 8.4, whereby we get an intervening case representing the overall pollution level as in China but with the chemical composition feature as in the US (Table S4, sensitivity test). From the intervening case, we then shift the composition of the US case to that of China (Table S4, sensitivity test). Note that throughout this sensitivity test, meteorological conditions are held constant. The first step by increasing the mass concentration yields an increase of 1.02 units in the aerosol pH which is mainly achieved through the LWC-modifying pathway (1.06 units) instead of the H_{air}^+-modifying pathway (-0.04 unit) (Fig. S7 (a), (b), (c)). The second step by changing the chemical composition shows a further increase of 0.76 units in the aerosol pH which is mainly achieved through the H_{air}^+-modifying pathway (0.88 units), whereas the LWC-modifying pathway (-0.11 unit) plays a minor role (Fig. S7 (d), (e), (f)). This sensitivity test reveals that the LWC-modifying pathway is mainly associated with the change in mass concentration, and the H_{air}^+-modifying pathway is mainly associated with the change in chemical composition.

The increased pH in the first step is surprising as we initially thought that the pH should be unchanged before and after multiplying the concentration of each component with a constant factor. Further investigation shows that, during the first step, increased aerosol concentration drives more fractions of TNO_3 and TNH_3 partitioning into particle phases—$\varepsilon(NH_4^+)$ and $\varepsilon(NO_3^-)$ increase from 0.4 and 0.6 to 0.6 and 0.98, respectively. Therefore, although the chemical composition of the aerosol system keeps constant, the particle composition changes. This repartitioning can be explained by the Henry's Law, $[A_{aq}]=H_A \cdot p_A$, where $[A_{aq}]$ is the aqueous-phase concentration of A in the unit of moles per liter water, p_A is the partial pressure of A in the gas phase, and H_A is the Henry's law coefficient (Seinfeld and Pandis, 2006). In the first step after multiplying the constant factor, assuming no repartitioning, p_A increases due to the increased concentration of A in the gas phase, while $[A_{aq}]$ remains largely constant because of the simultaneous increases in LWC and particle-phase A concentration (c_A), given that $[A_{aq}]$ is proportional to $c_A \cdot LWC^{-1}$ (note that LWC and c_A are expressed as mass per unit volume of air, and $[A_{aq}]$ is expressed as moles per unit volume of water). According to the Henry's Law, more gas-phase A will dissolve in water, and thus, the total A in the system shift toward the particle phase after the multiplication of the constant factor. Due likely to the weak acidic capacity of NO_3^- which is overwhelmed by NH_4^+, the particle is ultimately neutralized by the increased NH_4^+ in the first step.

We find that by increasing the concentration of every component by a constant factor, the magnitude and direction of the resulting change in pH are sensitive to the fraction of TNH_3 in the aerosol system while insensitive to the ratio of SO_4 to TNO_3. Based on an NH_4^+-SO_4^{2-}-NO_3^--H_2O system, we conduct a series of sensitive tests to investigate the change in aerosol pH in response to the multiplication of a constant factor of 8.4 (Fig. S8). The change in pH reduces gradually from 1.2 units to 0.8 unit when the TNH_3 mass fraction of the system decreases from 67% to 27% (Fig. S8). With further decreases in the TNH_3 fraction, the increase in pH diminishes rapidly, becomes negative when the TNH_3 mass fraction is lower than 25%, and is -0.6 when the TNH_3 mass fraction is 17% (Fig. S8). Under a constant TNH_3 mass fraction, the change in pH remain generally constant across a wide range of the mass ratios of SO_4 to TNO_3 (from 5:1 to 1:5) (Fig. S8). In populated continental regions, mass fractions of TNH_3 are often found high (Bencs et al., 2008; Behera and Sharma, 2010; Zheng et al., 2015; Cheng et al., 2016; Guo et al., 2017b), and the pH increase rather than decrease in response to the multiplication is thus expected.

Such an assessment by tracking pathway- and step-specific contributions ~~gains~~provides a better understanding of the pH difference between China and the US. We show that through the LWC-modifying pathway, the increases in aerosol components consistently lead to increases in pH, and that through the H_{air}^+~~–~~-modifying pathway, the effects of different components on pH vary in ~~sign~~direction. If~~–~~ the LWC-modifying pathway dominated the pH changes over the H_{air}^+-modifying pathway, aerosol mass concentrations would be the main factor driving the aerosol acidity difference between China and the US, and one could simply attribute ~~such a~~the difference in aerosol acidity to the fact that China ~~were~~is more polluted than the US. In contrast, if the H_{air}^+-modifying pathway dominated, chemical composition would be the dominant factor, and the compound profiles of precursors emissions, which affect the availability of the corresponding aerosol components in the air, would play an important role. While there has been ~~a~~ debate about~~,~~ ~~between~~whether mass concentration ~~and~~or chemical composition plays a more important role in determining aerosol pH (Cheng et al., 2016; Guo et al., 2017a; Pye et al., 2020; Zheng et al., 2020), our results suggest that both are important in explaining the China-US pH difference (Fig. 6b and c). The three groups are not consistent with each other in which pathway contributes more than the other to the pH difference, but they all suggest that ~~effects on pH associated with~~ the two pathways are comparable in terms of their effects on aerosol pH (Fig. 6b and c).

Our results, showing the importance of both mass concentration associated with LWC and chemical composition associated with H_{air}^+ and a minor role of temperature, seem in some aspects to contradict a previous study (Zheng et al., 2020) which highlighted LWC and temperature instead of chemical composition as the most important factors explaining the pH difference between China (NCP) and the ~~United States~~US. We note that the difference in the conclusions is reasonable when considering the differences in the specific ~~settingsparameters~~cases examined in these two studies~~y cases~~ies. The pre~~r~~vious study compared the conditions in NCP in winter with those in the southeastern ~~United States~~US in summer (SE-US).

Because of the differences in latitude (north for China vs south for the ~~United States~~US) and season (winter for China vs summer for the ~~United States~~US), the difference in temperature between their scenarios (29 K) was ~~one~~an order of magnitude greater than those in our study which has ~~larger~~greater spatial and temporal coverage~~s~~ (2.6 K in the observation group, 5 K in the non-weighted group, and -1.4 K in the population-weighted group). Using MTSM, we evaluate the pH difference between NCP and SE-US scenarios ~~adopted~~considered in the previous study. The results show that temperature accounts for 1.3 units of difference in aerosol pH between their two scenarios (Fig. S9), in line with what was previously reported (1.6 units).

In addition, ISORROPIA simulations show a LWC difference of 8.2 $\mu g \cdot m^{-3}$ between China (NCP) and the contiguous US in the ~~group~~ “observation” group in our study and 340 $\mu g \cdot m^{-3}$ between the scenarios ~~adopted~~considered in the previous study. The much larger LWC difference in the previous study ~~than that in~~compared to ours is mainly driven by the differences in pollutant~~s~~ concentrations. For example, the SO_4 concentration is as high as 156 $\mu g \cdot m^{-3}$ in the NCP scenario in the previous study~~, while~~ but only 9.2 $\mu g \cdot m^{-3}$ in our~~s~~ study. Such differences in concentrations are reasonable, given that the previous study selected a severe haze event occurring in Beijing in winter 2013 as the scenario for China (NCP), while we use annual average levels over NCP in 2017 as our case for China (NCP). Note that winter 2013 was a period when air pollution reportedly reached record high levels across ~~the~~ northern China (Wang et al., 2014b; Li et al., 2016). Since 2013, China has launched strict controls on air pollutant emissions, and $PM_{2.5}$ levels have decreased significantly between 2013 and 2017 (Zhang et al., 2019). Therefore, the NCP scenario in the previous study should be more representative of short-term haze events in the pre-2013 period, while our China (NCP) case should be more representative of annual average levels in recent years.

4 Conclusion and implications

Based on extended ground-level measurements and regional air quality model simulations, we find significant differences in aerosol pH between China and the ~~United States~~US. Aerosols in the ~~United States~~US are on average more acidic with pH generally 1–2 units lower than in China. We propose an MTSM method to identify the key factors leading to the pH difference. The MTSM analysis reveals the important role of TNH_3 in causing the pH difference and an opposi~~te~~ng effect from SO_4 which partially offsets the positive effect of TNH_3 on the pH change. Other factors play relatively minor roles. Further investigation highlights two pathways, one associated with changes in LWC and the other with changes in H_{air}^+~~, respectively~~, linking to the pH difference. The increased mass concentration in China, compared to the ~~United States~~US, enhances LWC, and the change in chemical composition toward a TNH_3-rich condition reduces H_{air}^+. Both pathways facilitate the increases in aerosol pH in China and are comparable in terms of driving the pH increase.

~~Our results, showing the importance of both LWC and chemical composition and a minor role of temperature, seem in some aspects to contradict a previous study (Zhang et al., 2019) which highlighted LWC and temperature instead of aerosol composition as the most important factors explaining the pH difference between China (NCP) and the United States. We note that the difference in conclusion is reasonable considering the difference in the specific settings of the study cases. The~~

~~pervious study compared the conditions in NCP in winter with those in the southeastern United States in summer (SE-US). Because of the differences in latitude (north for China vs south for the United States) and season (winter for China vs summer for the United States), the difference in temperature between their scenarios (29 K) was one order of magnitude larger than those in our study (2.6 K in the observation group, 5 K in the non-weighted group, and -1.4 K in the population-weighted group). Using MTSM, we evaluate the pH difference between the scenarios adopted in the previous study (i.e., NCP and SE-US). The results show that temperature account for 1.3 units of difference in aerosol pH between their two scenarios (see SX below), which is in line with what was reported (1.6 units)."~~

~~In addition, ISORROPIA simulations show a LWC difference of 8.2 μg·m^{-3} between China (NCP) and the contiguous United States in group "observation" in our study and 340 μg·m^{-3} between the scenarios adopted in the previous study. The much larger LWC difference in the previous study than that in ours is mainly driven by the differences in pollutants concentrations. For example, the TSO_4 concentration is as high as 156 μg·m^{-3} in the NCP scenario in the previous study, while only 9.2 μg·m^{-3} in ours. Such differences in concentrations are reasonable, given that the previous study selected a severe haze event occurring in Beijing in winter 2013 as the scenario for China (NCP), while we use annual average levels over NCP in 2017 as our case for China (NCP). Note that winter 2013 was a period when air pollution reportedly reached record high levels across the northern China (Wang et al., 2014b; Li et al., 2016). Since 2013, China has launched strict controls on air pollutant emissions, and $PM_{2.5}$ levels decreased significantly between 2013 and 2017 (Zhang et al., 2019). Therefore, the NCP scenario in the previous study should be more representative of short-term haze events in pre-2013 period, while our China (NCP) case should be more representative of annual average levels in recent years.~~

~~3.2.3 Effects of ammonium on aerosol pH~~

~~The result of MTSM indicates that the difference in TNH_3 is one of the predominant reasons causing the pH difference. In order to study the effect of TNH_3, we conduct sensitivity tests for China and the United States separately to investigate the responses of aerosol pH to changing TNH_3. We change the TNH_3 concentrations from 0.1 to 1000 μg·m^{-3} while keep all other components constant at their annual average levels based on observation data (Table 2). We also use simulation data with population as the weight to study the effects, which consider other areas in China where TNH_3 concentration is not as high as in NCP. The results are shown in Fig. 7. It is clearly illustrated that, over a large range of TNH_3 concentrations, aerosol pH increases with the increase in TNH_3 because the production process of NH_4^+ from NH_3 consumes aqueous H^+. However, in both countries, aerosol pH has a small decrease with the increase in TNH_3 when TNH_3 concentration is very low, this could be due to higher biases in H^+ concentration by ISORROPIA in ammonia poor conditions (Ansari and Pandis, 1999). The local sensitivity of pH to TNH_3, expressed as the pH increase per tenfold increase in TNH_3 at current TNH_3 level, is higher in the United States (3.0 based on observational data and 1.59 based on simulation data) than in China (0.4 based on observational data and 1.21 based on simulation data), indicated a higher sensitivity of~~

~~aerosol pH to TNH_3 in the United States than in China. Besides, we find that the responses of pH to TNH_3 are nonlinear and anisotropic. With all others equal, pH in the United States could be closer to the level in China if the TNH_3 increases to the level in China. On the other hand, the pH in China would be lower than the United States if the TNH_3 decreases to the United States level because of the relative higher abundances of acidic components (SO_4, TNO_3, TCl) than basic ions (TNH_3, NVCs) (Fig. 7a). In both countries, the sensitivities would quickly diverge from the original values toward higher values as TNH_3 decreases, with the sensitivities in China changing at a faster pace. As TNH_3 increases, however, the sensitivities in these two countries would gradually become constant, stabilizing at comparable levels (0.002 pH unit per TNH_3 increase in both two countries). Results based on simulation data are similar with results based on observational data, especially the sensitivity of aerosol pH at high level of TNH_3 (represented by similar slope). Higher pH values in China based on simulation data at low TNH_3 level (1-10 $\mu g \cdot m^{-3}$) could be caused by lower SO_4^{2-} concentrations. However, lower value of aerosol pH at high level of TNH_3 (> 50 $\mu g \cdot m^{-3}$) based on simulation data even with lower SO_4^{2-} concentrations indicates the limit effect of TNH_3 at this level and potential effect of other components.~~

~~The effects of TNH_3 on the gas-particle partitioning of NH_3-NH_4^+ and HNO_3-NO_3^- are illustrated in Fig. 7b and 7c, showing a decreasing trend of $\varepsilon(NH_4^+)$ and an increasing trend of $\varepsilon(NO_3^-)$ as TNH_3 increases. In the range of observation cases the value of $\varepsilon(NH_4^+)$ in China is smaller than in the United States, suggesting excess presence of TNH_3 compared to other aerosol components (e.g., TNO_3 and SO_4). $\varepsilon(NO_3^-)$ increased with increased TNH_3, due to higher aerosol pH which promote TNO_3 shifting to the particle phase as well as increased NH_4^+ promote the condensation of HNO_3 to form NH_4NO_3. Higher $\varepsilon(NO_3^-)$ in China than in the United States with an average $\varepsilon(NO_3^-)$ in China being close to 1 confirmed the excess presence of TNH_3. Both the lower $\varepsilon(NH_4^+)$ and higher $\varepsilon(NO_3^-)$ in China estimated by the sensitivity curves are consistent with observations.~~

~~The gas to particle partitioning of NH_3 produces inorganic ammonium salt of ammonium bisulfate (NH_4HSO_4) and ammonium sulfate ($(NH_4)_2SO_4$) first because the affinity of sulfuric acid for NH_3 is much larger than that of nitric and hydrochloric acid for NH_3, especially when TNH_3 concentration is relatively low (Behera et al., 2013). The excess TNH_3 may also react with nitric acid and hydrochloric acid to form salt of NH_4NO_3 and NH_4Cl which will dissolve in the aerosol liquid water (Zhao et al., 2016). Therefore, the ratio of $[NH_4^+]$ to different acid ions ($[SO_4^{2-}]$, $[NO_3^-]$, $[Cl^-]$) can be used to indicate the relative abundance of ammonia. To further investigate the effects of TNH_3 on pH at different levels of abundance, we divide the observation data into three groups based on neutralization condition of particle phase NH_4^+. Group A contains the observations when $[NH_4^+] < 2\times[SO_4^{2-}]$, when available NH_4^+ cannot completely balance aerosol SO_4. Group B consists of the data points when $2\times[SO_4^{2-}] < [NH_4^+] < 2\times[SO_4^{2-}]+[NO_3^-]+[Cl^-]$ when most of the aerosol TSO_4 is in the form of SO_4^{2-} and excess $[NH_4^+]$ is available to stabilize nitrate and chloride driving the gas phase to shift to the particle phase. Group C contains the data points when $[NH_4^+] > 2\times[SO_4^{2-}]+[NO_3^-]+[Cl^-]$, where available NH_4^+ is enough to balance particle phase anions. We then investigate the sensitivities of pH to TNH_3 in these three groups for China and the United States separately by changing the input TNH_3 from a median variation range (i.e. 55% to 150%) in each group in the two countries, respectively, and keeping all other components (i.e., concentrations and meteorological conditions) unchanged.~~

~~Note that no data in the United States fall in Group C, making up only two groups in the United States (i.e., Groups A and B). The results with average values of each group are shown in Fig. 8.~~

~~The aerosol pH increases with the increases in TNH$_3$ in all groups, which consist with the result of the sensitivity test in Fig. 7, but the increasing rates (i.e., the sensitivities of pH to TNH$_3$) and the pH levels vary among different groups (Fig. 8a). In China, Group C that represents aerosol systems with largest amount of excess NH$_4^+$ shows the highest pH levels and the flattest slopes of pH with TNH$_3$, suggesting a relatively low sensitivity of pH to the change in TNH$_3$ when TNH$_3$ is abundant. Group A that represents aerosol systems with insufficient NH$_4^+$, shows the lowest pH levels with the slopes slightly steeper than in Group C. As TNH$_3$ decreases to 55%, the average pH in China in Group A can be as low as 2.3, closer to the pH level in the United States, consist with the conclusion in sensitivity test using average value only (Fig. 7a). Group B can be regarded as an intermediate group between Groups A and C. But the sensitivities of pH to TNH$_3$ changes in group B are the highest among the three groups when reducing TNH$_3$, which could be due to the rapid increase in ε(NH$_4^+$) in this group as TNH$_3$ decreases (Fig. 8b), that leads to a faster loss of NH$_4^+$ (Zheng et al., 2019). Note that although the relative abundance of NH$_4^+$ in group B is smaller than in group C, the transition from group B to group C due to TNH$_3$ increase does not always happen. Because if TNH$_3$ increase in an aerosol system with $2\times[SO_4^{2-}] < [NH_4^+] < 2\times[SO_4^{2-}]+[NO_3^-]+[Cl^-]$, [NH$_4^+$] would increase, and more TNO$_3$ and TCl would shift into the particle phase, leading to the increase of WSI concentration. However, the average WSI concentration in group B is 55.03±46.79 μg·m^{-3} in China, significantly higher than that in group C in China (31.60±20.29 μg·m^{-3}). LWC in group B (22.90±7.38 μg·m^{-3}) is also higher than that in group C (14.37±16.85 μg·m^{-3}). We find that most of the cases in group B could be identified as highly polluted cases where large amount of NH$_4$NO$_3$ is formed and dissolves in the aerosol water. As a result, despite the higher abundance of NH$_4^+$ in group B than group A, ε(NH$_4^+$) in group B is the highest among all the groups (Fig. 8b).~~

~~Throughout the observed cases, 85% in China are in Group C (i.e., aerosol systems with excess NH$_4^+$), and 55% in the United States are in Group A (i.e., aerosol systems with insufficient NH$_4^+$). The higher sensitivity of pH to TNH$_3$ in group A than in group C explains why the pH sensitivity to TNH$_3$ increases more significantly in the United States than in China as TNH$_3$ decreases (Fig. 7a). Overall, the positive sensitivity of pH to TNH$_3$ and the different dominant groups in these two countries (Group C in China, Group A in the United States) suggest that the high abundance of TNH$_3$ in China increases the aerosol pH and is one of the major reasons for the pH difference between the two countries.~~

~~3.2.4 The relationship between sulfate/nitrate and aerosol pH~~

~~Besides the effect of TNH$_3$ on aerosol pH discussed in Sec 3.2.3, other species, especially the acidic species which mainly include SO$_4$ and TNO$_3$, could also affect aerosol pH because of their effects on H$^+_{air}$ concentration as well as on LWC (Ding et al., 2019). This effect is investigated in a sensitivity test by changing TNO$_3$ or SO$_4$ concentration while keeping other inputs constant as the average levels (Fig. 9). Similar to the MSTM results as shown in Fig. 6, elevated SO$_4$ significantly increases aerosol pH by increasing H$^+_{air}$. On the other hand, elevated TNO$_3$ only slightly increases H$^+_{air}$, indicating a weaker acidity than that of TSO$_4$, in line with the result in a previous study (Guo et al., 2017b). This is partially due to the semi-~~

~~volatile property of TNO_3 (Ding et al., 2019). Notably, even in China where $\varepsilon(NO_3^-)$ are mostly close to 1, the variation of aerosol pH with TNO_3 (roughly equals to NO_3^- in this case) is also subtle. Therefore, for two systems with different moles of SO_4^{2-} and NO_3^- neutralized by same moles of NH_4^+, the system with more SO_4^{2-} will likely have a lower pH. This result indicates that higher aerosol acidity is associated with higher availability of TSO_4 rather than TNO_3, which can be confirmed by observed data in Fig. 10.~~

~~Compared to the difference in TNO_3/TSO_4, the difference in NO_3^-/SO_4^{2-} molar ratio is more significant due to higher aerosol pH and ammonium in China promotes TNO_3 shift in particle phase as NH_4NO_3, leading to a higher NO_3^-/SO_4^{2-} molar ratio, while low pH in the United States promotes TNO_3 stay in gas phase, leading to a lower NO_3^-/SO_4^{2-} ratio. Based on observation data, 74.5% of the cases in China have NO_3^-/SO_4^{2-} molar ratio larger than one, while only 22.3% in the United States. The different NO_3^-/SO_4^{2-} ratios, as a result of the pH difference as well as TNO_3/SO_4 difference in two countries, could subsequently affect other aerosol properties, such as aerosol water uptake ability, which is one of the important reasons causing haze events in China during winter time (Xie et al., 2019; Wang et al., 2020b). Although nitrate aerosol and sulfate aerosol absorbs similar amounts of water per mass (Fig. S7), heavy haze events in China are usually associated with increased LWC with enhanced RH levels under nitrate-dominate condition (Wang et al., 2020b). In order to study this effect, we categorize the observation data into a nitrate-rich group (Group N, where $[NO_3^-]/[SO_4^{2-}] > 3$) and a sulfate-rich group (Group S, where $[NO_3^-]/[SO_4^{2-}] < 1$) and compare these two groups under different RH conditions. The ratio 3 in group N is mentioned in lab studies and is a more typical value of nitrate-rich conditions in field observations (Ge et al., 1998; Xie et al., 2019).~~

~~The results in Fig. 11 show that aerosol pH values in the same groups in China and the United States have similar responses to the changes in RH. In both countries, as RH increases, the pH in group N decreases, and the pH in group S increases (Fig. 11a). Both the values and the increasing rate of LWC in group N is larger than in group S, suggesting a higher water uptake ability in nitrate-rich condition, which is likely due to higher aerosol mass compared with group S as shown in Fig. 11f. The nearly two times aerosol mass in group N as in group S indicates the co-condensation effect of nitrate aerosol and LWC (Guo et al., 2017a), which suggests that NO_3^- formed in aerosol leads to a higher LWC due to the increase in aerosol mass, while higher LWC dilutes H^+_{air} and increases pH, which is favorable for more HNO_3 shifting from gas phase to particle phase and thus continually increases particle NO_3^- concentration. This effect will reach a balance when most of the gas phase HNO_3 is in the particle phase with enough NH_4^+, and, therefore, $\varepsilon(NO_3^-)$ is close to 100% in group N in the two countries (Fig. 11e). Besides, water uptake by hygroscopic aerosols increases the aerosol surface area and volume, enhancing the hydrolysis of N_2O_5 across particles and forming NO_3^- (Tian et al., 2018; Wang et al., 2020b).~~

~~The condition in group N usually has a higher LWC and aerosol mass, due to the mutual promotion between LWC and particle nitrate. And such a condition in group N occurs more often in China than in the United States, which is probably one of the reasons leading to high particle concentrations on hazy days in China.~~

~~4 Discussions and implications~~

~~Based on extended ground-level measurements and regional air quality model simulations, we find significant differences in aerosol pH between China and the United States. Aerosols in the United States are on average more acidic with pH generally 1–2 units lower than in China. We use two independent methods, i.e., the MTSM method and sensitivity tests, to identify the key factors leading to the pH difference. These two methods consistently reveal the important role of TNH_3 in causing the pH difference. The MTSM method further shows a significant contribution of NVCs on the pH difference, and tThe sensitivity tests highlight the high nitrate/sulfate ratios as one of the important responses to the pH difference, and high nitrate aerosol in China will further lead to higher aerosol water uptake, which may have other effects to aerosol conditions.~~

~~The nitrate/sulfate ratio depends on the emission ratio of NO_x/SO_2, the availability of cations due to the dependency of $\varepsilon(NO_3^-)$ on TNH_3 (Fig. 8c, Fig. 9c), and other factors such as the atmospheric oxidizing capacity. Further investigation into the total emissions shows that the emission molar ratios of $[NO_x]/[SO_2]$ are close to 3:1 in both countries (2.92 In China in 2017 and 3.12 in the United States in 2011 when assuming the emission NO_x is in the form of NO_2), indicating that the emission difference is not the major factor leading to the nitrate/sulfate ratio difference. On the other hand, the emission molar ratio of $[NH_3]/([NO_x]+2\times[SO_2])$ in China (0.75) is 1.6 times higher than that in the United States (0.46), which is consistent with the measured high relative abundance of TNH_3 in China and confirms that high availability of cations (mainly NH_4^+ caused by high NH_3 emission) is one of the causes for the high nitrate/sulfate ratio in China.~~

~~Will the aerosols in China be as acidic as in the United States as emissions are further controlled without significant reductions in TNH_3? Unlikely. Although both countries have been taking actions to cut down pollutant emissions (Pinder et al., 2007; Hand et al., 2012; Zhang et al., 2019), the reduction rates of NO_x and SO_2 emissions are quite different between the two countries (Fig. 12). In the United States, the reduction rates of NO_x and SO_2 emissions (mainly from mobile and power sectors) were similar during the past two decades, while the emission of NH_3 (mainly from the agricultural sector) kept relatively constant (Fig. 12, https://www.epa.gov/air-emissions-inventories/air-pollutant-emissions-trends-data). The data in the monitoring sites in the United States showed a decreasing SO_4^{2-} concentration over the years due to the SO_2 emission reduction, but the reduction of NO_3^- is not obvious compared with SO_4^{2-} (Fig. S8). Lower SO_4^{2-} concentration could lead to a higher aerosol pH in the United States, but this effect could be buffered by partitioning of TNH_3, leading to a lower aerosol pH than expected (Weber et al., 2016). Overall, significant higher SO_4^{2-} concentration compared with relative stable NO_3^- concentration still led to nitrate to sulfate ratio smaller than one. This ratio, however, reached a value higher than 1 in 2015, four years after the period of this study (2011). In China, on the other hand, SO_2 emission reduction rate has been higher than NO_x reduction rate especially after the year 2012 (Fig. 12), which could lead to a higher nitrate to sulfate ratio (Wang et al., 2020b). Although we don't have yearly aerosol concentration data in China, the shift from sulfate dominant aerosol to nitrate dominant aerosol has been already observed and reported by previous studies (Wang et al., 2011; Xie et al., 2019). We also collected the $PM_{2.5}$, SO_4^{2-}, NO_3^- and NH_4^+ concentrations in different years from many other studies in three major cities (Beijing, Shanghai, Guangzhou), which illustrate the increasing trend of the NO_3^-/SO_4^{2-} ratio along the years (Table S4). As~~

~~emissions of SO_2 and NO_2 are being controlled in China, NH_3 is becoming relatively more abundant, which is evident from the historical emission trends (decreasing SO_2 and NO_x emissions vs. steady NH_3 emission, (Zheng et al., 2018)), neutralizing the aerosol. Hence, aerosol pH in China will unlikely decrease as further emission control of NO_x and SO_2 is implemented.~~

Previous studies have suggested that low aerosol pH is associated with increased toxicity because of the increased ~~dis~~solubility of transition metals in aerosol LWC, which induce airway injury and inflammation through the production of reactive oxygen species in vivo (Kim et al., 2015). The lower aerosol pH in the ~~United States~~US than in China implies that aerosols in the ~~United States~~US may be more toxic than in China~~ after being inhaled by humans~~. However, this implication should be interpreted with caution because there are other known pathways through which particulate matter can harm ~~the human body~~humans, and the mechanisms of how particulate matter affects health ~~have~~ are not ~~been~~ completely understood (Armstrong et al., 2004). More studies are needed to ~~address~~ assess the health outcomes associated with the disparity in aerosol pH between the two countries.

Author contribution

HS initiated the research project. HS ran the model. HS and BZ designed the experiments, analysed results, and wrote the initial draft of the manuscript. YH, SX, and ZX helped with data preparation. All co-authors commented on and contributed to the writing of the paper.

Competing interests

The authors declare that they have no conflict of interest.

Data availability

The data presented in this manuscript and the observational data in China can be obtained from the corresponding author upon request. The observational data in China can also be obtained from the Data-sharing platform by Comprehensive Observation Network for Air Pollution in Beijing-Tianjin-Hebei and i~~I~~ts ~~s~~Surrounding Areas (http://123.127.175.60:8765/siteui/index). The observational data in the ~~United States~~US can be obtained from Clean Air Status and Trends Network (CASTNET) (https://www.epa.gov/castnet) and Ammonia Monitoring Network (AMoN) (http://nadp.slh.wisc.edu/amon/)

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References

AiMa Air Quality Forecasting System: http://www.aimayubao.com/wryb_eval.php?movie=no, 2017.

Ansari, A. S., and Pandis, S. N.: An Analysis of Four Models Predicting the Partitioning of Semivolatile Inorganic Aerosol Components, Aerosol Science and Technology, 31, 129-153, 10.1080/027868299304200, 1999.

Armstrong, B., Hutchinson, E., Unwin, J., and Fletcher, T.: Lung cancer risk after exposure to polycyclic aromatic hydrocarbons: a review and meta-analysis, Environ Health Perspect, 112, 970-978, 10.1289/ehp.6895, 2004.

Battaglia, M. A., Douglas, S., and Hennigan, C. J.: Effect of the Urban Heat Island on Aerosol pH, Environ Sci Technol, 51, 13095-13103, 10.1021/acs.est.7b02786, 2017.

Behera, S. N., and Sharma, M.: Investigating the potential role of ammonia in ion chemistry of fine particulate matter formation for an urban environment, Science of The Total Environment, 408, 3569-3575, https://doi.org/10.1016/j.scitotenv.2010.04.017, 2010.

Behera, S. N., Betha, R., and Balasubramanian, R.: Insights into Chemical Coupling among Acidic Gases, Ammonia and Secondary Inorganic Aerosols, Aerosol and Air Quality Research, 13, 1282-1296, 10.4209/aaqr.2012.11.0328, 2013.

Behera, S. N., Cheng, J., Huang, X., Zhu, Q., Liu, P., and Balasubramanian, R.: Chemical composition and acidity of size-fractionated inorganic aerosols of 2013-14 winter haze in Shanghai and associated health risk of toxic elements, Atmospheric Environment, 122, 259-271, https://doi.org/10.1016/j.atmosenv.2015.09.053, 2015.

Bencs, L., Khaiwal, R., Hoog, J., Rasoazanany, E., Deutsch, F., Bleux, N., Berghmans, P., Roekens, E., Krata, A., and Van Grieken, R.: Mass and ionic composition of atmospheric fine particles over Belgium and their relation with gaseous air pollutants, Journal of Environmental Monitoring, 10, 1148-1157, 10.1039/B805157G, 2008.

Burnett, R. T., Pope, C. A., 3rd, Ezzati, M., Olives, C., Lim, S. S., Mehta, S., Shin, H. H., Singh, G., Hubbell, B., Brauer, M., Anderson, H. R., Smith, K. R., Balmes, J. R., Bruce, N. G., Kan, H., Laden, F., Prüss-Ustün, A., Turner, M. C., Gapstur, S.

M., Diver, W. R., and Cohen, A.: An integrated risk function for estimating the global burden of disease attributable to ambient fine particulate matter exposure, Environ Health Perspect, 122, 397-403, 10.1289/ehp.1307049, 2014.

Butler, T., Vermeylen, F., Lehmann, C. M., Likens, G. E., and Puchalski, M.: Increasing ammonia concentration trends in large regions of the USA derived from the NADP/AMoN network, Atmospheric Environment, 146, 132-140, https://doi.org/10.1016/j.atmosenv.2016.06.033, 2016.

Chen, Y. L., Shen, H. Z., and Russell, A. G.: Current and Future Responses of Aerosol pH and Composition in the US to Declining SO2 Emissions and Increasing NH3 Emissions, Environ Sci Technol, 53, 9646-9655, 10.1021/acs.est.9b02005, 2019.

Cheng, Y., Zheng, G., Wei, C., Mu, Q., Zheng, B., Wang, Z., Gao, M., Zhang, Q., He, K., Carmichael, G., Pöschl, U., and Su, H.: Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China, Science Advances, 2, e1601530, 10.1126/sciadv.1601530, 2016.

Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: Thermodynamic Model of the System H+−NH4+−SO42-−NO3-−H2O at Tropospheric Temperatures, The Journal of Physical Chemistry A, 102, 2137-2154, 10.1021/jp973042r, 1998.

Cui, Y., Yin, Y., Chen, K., Zhang, X., Kuang, X., Jiang, H., Wang, H., Zhen, Z., and He, C.: Characteristics and sources of WSI in North China Plain: A simultaneous measurement at the summit and foot of Mount Tai, Journal of Environmental Sciences, 92, 264-277, https://doi.org/10.1016/j.jes.2020.02.017, 2020.

Ding, J., Zhao, P., Su, J., Dong, Q., Du, X., and Zhang, Y.: Aerosol pH and its driving factors in Beijing, Atmos. Chem. Phys., 19, 7939-7954, 10.5194/acp-19-7939-2019, 2019.

Fang, T., Guo, H., Verma, V., Peltier, R. E., and Weber, R. J.: PM2.5 water-soluble elements in the southeastern United States: automated analytical method development, spatiotemporal distributions, source apportionment, and implications for heath studies, Atmos. Chem. Phys., 15, 11667-11682, 10.5194/acp-15-11667-2015, 2015.

Fang, T., Guo, H., Zeng, L., Verma, V., Nenes, A., and Weber, R. J.: Highly Acidic Ambient Particles, Soluble Metals, and Oxidative Potential: A Link between Sulfate and Aerosol Toxicity, Environ Sci Technol, 51, 2611-2620, 10.1021/acs.est.6b06151, 2017.

Feng, J., Chan, E., and Vet, R.: Air quality in the eastern United States and Eastern Canada for 1990–2015: 25 years of change in response to emission reductions of SO2 and NOx in the region, Atmos. Chem. Phys., 20, 3107-3134, 10.5194/acp-20-3107-2020, 2020.

Fountoukis, C., and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K^+-Ca^{2+}-Mg^{2+}-NH^{4+}-Na^+-SO_4^{2-}-NO_3^--Cl^--H_2O aerosols, Atmos. Chem. Phys., 7, 4639-4659, 10.5194/acp-7-4639-2007, 2007.

Fountoukis, C., Koraj, D., Van Der Gon, H. D., Charalampidis, P., Pilinis, C., and Pandis, S.: Impact of grid resolution on the predicted fine PM by a regional 3-D chemical transport model, Atmos. Environ., 68, 24-32, 2013.

Freedman, M. A., Ott, E.-J. E., and Marak, K. E.: Role of pH in Aerosol Processes and Measurement Challenges, The Journal of Physical Chemistry A, 123, 1275-1284, 10.1021/acs.jpca.8b10676, 2019.

Ge, B., Xu, X., Ma, Z., Pan, X., Wang, Z., Lin, W., Ouyang, B., Xu, D., Lee, J., Zheng, M., Ji, D., Sun, Y., Dong, H., Squires, F. A., Fu, P., and Wang, Z.: Role of Ammonia on the Feedback Between AWC and Inorganic Aerosol Formation During Heavy Pollution in the North China Plain, Earth and Space Science, 6, 1675-1693, 10.1029/2019EA000799, 2019.

Ge, Z., Wexler, A. S., and Johnston, M. V.: Deliquescence Behavior of Multicomponent Aerosols, The Journal of Physical Chemistry A, 102, 173-180, 10.1021/jp972396f, 1998.

NCEP Product Inventory - Global Products: https://www.nco.ncep.noaa.gov/pmb/products/gfs/#GFS.

Guo, H., Xu, L., Bougiatioti, A., Cerully, K. M., Capps, S. L., Hite Jr, J. R., Carlton, A. G., Lee, S. H., Bergin, M. H., Ng, N. L., Nenes, A., and Weber, R. J.: Fine-particle water and pH in the southeastern United States, Atmos. Chem. Phys., 15, 5211-5228, 10.5194/acp-15-5211-2015, 2015.

Guo, H., Sullivan, A. P., Campuzano-Jost, P., Schroder, J. C., Lopez-Hilfiker, F. D., Dibb, J. E., Jimenez, J. L., Thornton, J. A., Brown, S. S., Nenes, A., and Weber, R. J.: Fine particle pH and the partitioning of nitric acid during winter in the northeastern United States, Journal of Geophysical Research: Atmospheres, 121, 10,355-310,376, 10.1002/2016jd025311, 2016.

Guo, H., Liu, J., Froyd, K., Robert, J., Veres, P., Hayes, P., Jimenez, J., Nenes, A., and Weber, R.: Fine particle pH and gas-particle phase partitioning of inorganic species in Pasadena, California, during the 2010 CalNex campaign, Atmospheric Chemistry and Physics Discussions, 1-33, 10.5194/acp-2016-1158, 2017a.

Guo, H., Weber, R. J., and Nenes, A.: High levels of ammonia do not raise fine particle pH sufficiently to yield nitrogen oxide-dominated sulfate production, Scientific Reports, 7, 12109, 10.1038/s41598-017-11704-0, 2017b.

Guo, H., Nenes, A., and Weber, R. J.: The underappreciated role of nonvolatile cations in aerosol ammonium-sulfate molar ratios, Atmos. Chem. Phys., 18, 17307-17323, 10.5194/acp-18-17307-2018, 2018a.

Guo, H., Otjes, R., Schlag, P., Kiendler-Scharr, A., Nenes, A., and Weber, R. J.: Effectiveness of ammonia reduction on control of fine particle nitrate, Atmos. Chem. Phys., 18, 12241-12256, 10.5194/acp-18-12241-2018, 2018b.

Gwynn, R. C., Burnett, R. T., and Thurston, G. D.: A time-series analysis of acidic particulate matter and daily mortality and morbidity in the Buffalo, New York, region, Environ Health Perspect, 108, 125-133, 10.1289/ehp.00108125, 2000.

Hand, J. L., Schichtel, B. A., Malm, W. C., and Pitchford, M. L.: Particulate sulfate ion concentration and SO2 emission trends in the United States from the early 1990s through 2010, Atmos. Chem. Phys., 12, 10353-10365, 10.5194/acp-12-10353-2012, 2012.

Hennigan, C. J., Izumi, J., Sullivan, A. P., Weber, R. J., and Nenes, A.: A critical evaluation of proxy methods used to estimate the acidity of atmospheric particles, Atmos. Chem. Phys., 15, 2775-2790, 10.5194/acp-15-2775-2015, 2015.

Hu, J., Wang, Y., Ying, Q., and Zhang, H.: Spatial and temporal variability of PM2.5 and PM10 over the North China Plain and the Yangtze River Delta, China, Atmospheric Environment, 95, 598-609, https://doi.org/10.1016/j.atmosenv.2014.07.019, 2014.

Jang, M., Czoschke, N. M., Lee, S., and Kamens, R. M.: Heterogeneous Atmospheric Aerosol Production by Acid-Catalyzed Particle-Phase Reactions, Science, 298, 814, 10.1126/science.1075798, 2002.

Jia, S., Chen, W., Zhang, Q., Krishnan, P., Mao, J., Zhong, B., Huang, M., Fan, Q., Zhang, J., Chang, M., Yang, L., and Wang, X.: A quantitative analysis of the driving factors affecting seasonal variation of aerosol pH in Guangzhou, China, Science of The Total Environment, 725, 138228, https://doi.org/10.1016/j.scitotenv.2020.138228, 2020.

Kim, K.-H., Kabir, E., and Kabir, S.: A review on the human health impact of airborne particulate matter, Environment International, 74, 136-143, https://doi.org/10.1016/j.envint.2014.10.005, 2015.

Kim, Y. P., and Seinfeld, J. H.: Atmospheric Gas–Aerosol Equilibrium: III. Thermodynamics of Crustal Elements Ca2+, K+, and Mg2+, Aerosol Science and Technology, 22, 93-110, 10.1080/02786829408959730, 1995.

Kleinman, M. T., Phalen, R. F., Mautz, W. J., Mannix, R. C., McClure, T. R., and Crocker, T. T.: Health effects of acid aerosols formed by atmospheric mixtures, Environ Health Perspect, 79, 137-145, 10.1289/ehp.8979137, 1989.

Kong, L., Tang, X., Zhu, J., Wang, Z., Pan, Y., Wu, H., Wu, L., Wu, Q., He, Y., Tian, S., Xie, Y., Liu, Z., Sui, W., Han, L., and Carmichael, G.: Improved Inversion of Monthly Ammonia Emissions in China Based on the Chinese Ammonia Monitoring Network and Ensemble Kalman Filter, Environ Sci Technol, 53, 12529-12538, 10.1021/acs.est.9b02701, 2019.

Lawal, A. S., Guan, X., Liu, C., Henneman, L. R. F., Vasilakos, P., Bhogineni, V., Weber, R. J., Nenes, A., and Russell, A. G.: Linked Response of Aerosol Acidity and Ammonia to SO2 and NOx Emissions Reductions in the United States, Environ Sci Technol, 52, 9861-9873, 10.1021/acs.est.8b00711, 2018.

Li, J., and Jang, M.: Aerosol Acidity Measurement Using Colorimetry Coupled With a Reflectance UV-Visible Spectrometer, Aerosol Science and Technology, 46, 833-842, 10.1080/02786826.2012.669873, 2012.

Li, S., Ma, Z., Xiong, X., Christiani, D. C., Wang, Z., and Liu, Y.: Satellite and Ground Observations of Severe Air Pollution Episodes in the Winter of 2013 in Beijing, China, Aerosol and Air Quality Research, 16, 977-989, 10.4209/aaqr.2015.01.0057, 2016.

Liu, M., Song, Y., Zhou, T., Xu, Z., Yan, C., Zheng, M., Wu, Z., Hu, M., Wu, Y., and Zhu, T.: Fine particle pH during severe haze episodes in northern China, Geophysical Research Letters, 44, 5213-5221, 10.1002/2017GL073210, 2017.

Liu, P., Zhang, C., Mu, Y., Liu, C., Xue, C., Ye, C., Liu, J., Zhang, Y., and Zhang, H.: The possible contribution of the periodic emissions from farmers' activities in the North China Plain to atmospheric water-soluble ions in Beijing, Atmos. Chem. Phys., 16, 10097-10109, 10.5194/acp-16-10097-2016, 2016.

Losey, D. J., Parker, R. G., and Freedman, M. A.: pH Dependence of Liquid–Liquid Phase Separation in Organic Aerosol, The Journal of Physical Chemistry Letters, 7, 3861-3865, 10.1021/acs.jpclett.6b01621, 2016.

Losey, D. J., Ott, E.-J. E., and Freedman, M. A.: Effects of High Acidity on Phase Transitions of an Organic Aerosol, The Journal of Physical Chemistry A, 122, 3819-3828, 10.1021/acs.jpca.8b00399, 2018.

Lyu, B., Zhang, Y., and Hu, Y.: Improving PM2.5 Air Quality Model Forecasts in China Using a Bias-Correction Framework, Atmosphere, 8, 10.3390/atmos8080147, 2017.

Mesinger, F., DiMego, G., Kalnay, E., Mitchell, K., Shafran, P. C., Ebisuzaki, W., Jović, D., Woollen, J., Rogers, E., Berbery, E. H., Ek, M. B., Fan, Y., Grumbine, R., Higgins, W., Li, H., Lin, Y., Manikin, G., Parrish, D., and Shi, W.: North

American Regional Reanalysis, Bulletin of the American Meteorological Society, 87, 343-360, 10.1175/bams-87-3-343, 2006.

Mo, Y., Li, J., Liu, J., Zhong, G., Cheng, Z., Tian, C., Chen, Y., and Zhang, G.: The influence of solvent and pH on determination of the light absorption properties of water-soluble brown carbon, Atmospheric Environment, 161, 90-98, https://doi.org/10.1016/j.atmosenv.2017.04.037, 2017.

National Atmospheric Deposition Program: Ammonia Monitoring Network (AMoN), in, http://nadp.slh.wisc.edu/AMoN/.

Quality Assurance Support for NADP: http://nadp.slh.wisc.edu/QA/.

Nenes, A., Pandis, S. N., Weber, R. J., and Russell, A.: Aerosol pH and liquid water content determine when particulate matter is sensitive to ammonia and nitrate availability, Atmos. Chem. Phys., 20, 3249-3258, 10.5194/acp-20-3249-2020, 2020.

Oakes, M., Ingall, E. D., Lai, B., Shafer, M. M., Hays, M. D., Liu, Z. G., Russell, A. G., and Weber, R. J.: Iron Solubility Related to Particle Sulfur Content in Source Emission and Ambient Fine Particles, Environ Sci Technol, 46, 6637-6644, 10.1021/es300701c, 2012.

Pathak, R. K., Wu, W. S., and Wang, T.: Summertime PM2.5 ionic species in four major cities of China: nitrate formation in an ammonia-deficient atmosphere, Atmos. Chem. Phys., 9, 1711-1722, 10.5194/acp-9-1711-2009, 2009.

Pathak, R. K., Wang, T., Ho, K. F., and Lee, S. C.: Characteristics of summertime PM2.5 organic and elemental carbon in four major Chinese cities: Implications of high acidity for water-soluble organic carbon (WSOC), Atmospheric Environment, 45, 318-325, https://doi.org/10.1016/j.atmosenv.2010.10.021, 2011.

Pinder, R. W., Adams, P. J., and Pandis, S. N.: Ammonia Emission Controls as a Cost-Effective Strategy for Reducing Atmospheric Particulate Matter in the Eastern United States, Environ Sci Technol, 41, 380-386, 10.1021/es060379a, 2007.

Puchalski, M. A., Rogers, C. M., Baumgardner, R., Mishoe, K. P., Price, G., Smith, M. J., Watkins, N., and Lehmann, C. M.: A statistical comparison of active and passive ammonia measurements collected at Clean Air Status and Trends Network (CASTNET) sites, Environmental Science: Processes & Impacts, 17, 358-369, 10.1039/C4EM00531G, 2015.

Pye, H. O. T., Nenes, A., Alexander, B., Ault, A. P., Barth, M. C., Clegg, S. L., Collett Jr, J. L., Fahey, K. M., Hennigan, C. J., Herrmann, H., Kanakidou, M., Kelly, J. T., Ku, I. T., McNeill, V. F., Riemer, N., Schaefer, T., Shi, G., Tilgner, A., Walker, J. T., Wang, T., Weber, R., Xing, J., Zaveri, R. A., and Zuend, A.: The acidity of atmospheric particles and clouds, Atmos. Chem. Phys., 20, 4809-4888, 10.5194/acp-20-4809-2020, 2020.

Seinfeld, J. H., and Pandis, S. N.: Atmospheric chemistry and physics: from air pollution to climate change, John Wiley & Sons, Inc., Hoboken, xxviii + 1203 pp. pp., 2006.

Shen, H. Z., Tao, S., Liu, J. F., Huang, Y., Chen, H., Li, W., Zhang, Y. Y., Chen, Y. C., Su, S., Lin, N., Xu, Y. Y., Li, B. G., Wang, X. L., and Liu, W. X.: Global lung cancer risk from PAH exposure highly depends on emission sources and individual susceptibility, Scientific Reports, 4, 10.1038/srep06561, 2014.

Shi, G., Xu, J., Peng, X., Xiao, Z., Chen, K., Tian, Y., Guan, X., Feng, Y., Yu, H., Nenes, A., and Russell, A. G.: pH of Aerosols in a Polluted Atmosphere: Source Contributions to Highly Acidic Aerosol, Environ Sci Technol, 51, 4289-4296, 10.1021/acs.est.6b05736, 2017.

Shi, X., Nenes, A., Xiao, Z., Song, S., Yu, H., Shi, G., Zhao, Q., Chen, K., Feng, Y., and Russell, A. G.: High-Resolution Data Sets Unravel the Effects of Sources and Meteorological Conditions on Nitrate and Its Gas-Particle Partitioning, Environ Sci Technol, 53, 3048-3057, 10.1021/acs.est.8b06524, 2019.

Sickles, I. J. E., Hodson, L. L., and Vorburger, L. M.: Evaluation of the filter pack for long-duration sampling of ambient air, Atmospheric Environment, 33, 2187-2202, https://doi.org/10.1016/S1352-2310(98)00425-7, 1999.

Sickles, J. E., and Shadwick, D. S.: Comparison of particulate sulfate and nitrate at collocated CASTNET and IMPROVE sites in the eastern US, Atmospheric Environment, 42, 2062-2073, https://doi.org/10.1016/j.atmosenv.2007.11.051, 2008.

Song, S., Gao, M., Xu, W., Shao, J., Shi, G., Wang, S., Wang, Y., Sun, Y., and McElroy, M. B.: Fine-particle pH for Beijing winter haze as inferred from different thermodynamic equilibrium models, Atmos. Chem. Phys., 18, 7423-7438, 10.5194/acp-18-7423-2018, 2018.

Song, S., Nenes, A., Gao, M., Zhang, Y., Liu, P., Shao, J., Ye, D., Xu, W., Lei, L., Sun, Y., Liu, B., Wang, S., and McElroy, M. B.: Thermodynamic Modeling Suggests Declines in Water Uptake and Acidity of Inorganic Aerosols in Beijing Winter Haze Events during 2014/2015–2018/2019, Environmental Science & Technology Letters, 6, 752-760, 10.1021/acs.estlett.9b00621, 2019.

Surratt, J. D., Chan, A. W. H., Eddingsaas, N. C., Chan, M., Loza, C. L., Kwan, A. J., Hersey, S. P., Flagan, R. C., Wennberg, P. O., and Seinfeld, J. H.: Reactive intermediates revealed in secondary organic aerosol formation from isoprene, Proceedings of the National Academy of Sciences, 107, 6640, 10.1073/pnas.0911114107, 2010.

Tao, Y., and Murphy, J. G.: The sensitivity of PM2.5 acidity to meteorological parameters and chemical composition changes: 10-year records from six Canadian monitoring sites, Atmos. Chem. Phys., 19, 9309-9320, 10.5194/acp-19-9309-2019, 2019.

Theobald, M. R., Simpson, D., and Vieno, M.: Improving the spatial resolution of air-quality modelling at a European scale–development and evaluation of the Air Quality Re-gridder Model (AQR v1. 1), Geoscientific Model Development, 9, 4475-4489, 2016.

Tian, S., Pan, Y., and Wang, Y.: Ion balance and acidity of size-segregated particles during haze episodes in urban Beijing, Atmospheric Research, 201, 159-167, https://doi.org/10.1016/j.atmosres.2017.10.016, 2018.

United States Environmental Protection Agency: Clean Air Status and Trends Network (CASTNET), in, https://www.epa.gov/castnet.

2011 National Emissions Inventory (NEI) Data: https://www.epa.gov/air-emissions-inventories/2011-national-emissions-inventory-nei-data, 2012a.

United States Environmental Protection Agency: CASTNET Quality Assurance Quarterly Report, United States Environmental Protection Agency, 2012b.

Vasilakos, P., Russell, A., Weber, R., and Nenes, A.: Understanding nitrate formation in a world with less sulfate, Atmos. Chem. Phys., 18, 12765-12775, 10.5194/acp-18-12765-2018, 2018.

Wang, G., Zhang, R., Gomez, M. E., Yang, L., Levy Zamora, M., Hu, M., Lin, Y., Peng, J., Guo, S., Meng, J., Li, J., Cheng, C., Hu, T., Ren, Y., Wang, Y., Gao, J., Cao, J., An, Z., Zhou, W., Li, G., Wang, J., Tian, P., Marrero-Ortiz, W., Secrest, J., Du, Z., Zheng, J., Shang, D., Zeng, L., Shao, M., Wang, W., Huang, Y., Wang, Y., Zhu, Y., Li, Y., Hu, J., Pan, B., Cai, L., Cheng, Y., Ji, Y., Zhang, F., Rosenfeld, D., Liss, P. S., Duce, R. A., Kolb, C. E., and Molina, M. J.: Persistent sulfate formation from London Fog to Chinese haze, Proceedings of the National Academy of Sciences, 113, 13630-13635, 10.1073/pnas.1616540113, 2016.

Wang, R., Tao, S., Balkanski, Y., Ciais, P., Boucher, O., Liu, J., Piao, S., Shen, H., Vuolo, M. R., Valari, M., Chen, H., Chen, Y., Cozic, A., Huang, Y., Li, B., Li, W., Shen, G., Wang, B., and Zhang, Y.: Exposure to ambient black carbon derived from a unique inventory and high-resolution model, Proceedings of the National Academy of Sciences, 111, 2459-2463, 10.1073/pnas.1318763111, 2014a.

Wang, S., Xing, J., Jang, C., Zhu, Y., Fu, J. S., and Hao, J.: Impact Assessment of Ammonia Emissions on Inorganic Aerosols in East China Using Response Surface Modeling Technique, Environ Sci Technol, 45, 9293-9300, 10.1021/es2022347, 2011.

Wang, S., Wang, L., Li, Y., Wang, C., Wang, W., Yin, S., and Zhang, R.: Effect of ammonia on fine-particle pH in agricultural regions of China: comparison between urban and rural sites, Atmos. Chem. Phys., 20, 2719-2734, 10.5194/acp-20-2719-2020, 2020a.

Wang, Y., Ying, Q., Hu, J., and Zhang, H.: Spatial and temporal variations of six criteria air pollutants in 31 provincial capital cities in China during 2013–2014, Environment International, 73, 413-422, https://doi.org/10.1016/j.envint.2014.08.016, 2014b.

Wang, Y., Gong, Z., Liu, Z. L., Tang, G., Cheng, L., Che, F., Gao, J., and Ji, D.: Construction and Application of Comprehensive Observation Network for Air
Pollution in Beijing-Tianjin-Hebei and Its Surrounding Areas(In Chinese), Environmental Science Research, 32, 1651-1663, 10.13198/j.issn.1001-6929.2019.09.12, 2019.

Wang, Y., Chen, Y., Wu, Z., Shang, D., Bian, Y., Du, Z., Schmitt, S. H., Su, R., Gkatzelis, G. I., Schlag, P., Hohaus, T., Voliotis, A., Lu, K., Zeng, L., Zhao, C., Alfarra, M. R., McFiggans, G., Wiedensohler, A., Kiendler-Scharr, A., Zhang, Y., and Hu, M.: Mutual promotion between aerosol particle liquid water and particulate nitrate enhancement leads to severe nitrate-dominated particulate matter pollution and low visibility, Atmos. Chem. Phys., 20, 2161-2175, 10.5194/acp-20-2161-2020, 2020b.

Weber, R. J., Guo, H. Y., Russell, A. G., and Nenes, A.: High aerosol acidity despite declining atmospheric sulfate concentrations over the past 15 years, Nat Geosci, 9, 282-+, 10.1038/Ngeo2665, 2016.

William C. Skamarock , J. B. K., Jimy Dudhia , David O. Gill , Dale M. Barker , Wei Wang , Jordan G. Powers: A description of the Advanced Research WRF version 3. NCAR Technical note -475+STR, 2008.

Wong, J. P. S., Yang, Y., Fang, T., Mulholland, J. A., Russell, A. G., Ebelt, S., Nenes, A., and Weber, R. J.: Fine Particle Iron in Soils and Road Dust Is Modulated by Coal-Fired Power Plant Sulfur, Environ Sci Technol, 10.1021/acs.est.0c00483, 2020.

Xie, Y., Wang, G., Wang, X., Chen, J., Chen, Y., Tang, G., Wang, L., Ge, S., Xue, G., Wang, Y., and Gao, J.: Observation of nitrate dominant PM2.5 and particle pH elevation in urban Beijing during the winter of 2017, Atmos. Chem. Phys. Discuss., 2019, 1-25, 10.5194/acp-2019-541, 2019.

Yao, X., Chan, C. K., Fang, M., Cadle, S., Chan, T., Mulawa, P., He, K., and Ye, B.: The water-soluble ionic composition of PM2.5 in Shanghai and Beijing, China, Atmospheric Environment, 36, 4223-4234, https://doi.org/10.1016/S1352-2310(02)00342-4, 2002.

Ye, D., Klein, M., Mulholland, J. A., Russell, A. G., Weber, R., Edgerton, E. S., Chang, H. H., Sarnat, J. A., Tolbert, P. E., and Ebelt Sarnat, S.: Estimating Acute Cardiovascular Effects of Ambient PM(2.5) Metals, Environ Health Perspect, 126, 027007, 10.1289/ehp2182, 2018.

Zhang, Q., Streets, D. G., He, K., and Klimont, Z.: Major components of China’s anthropogenic primary particulate emissions, Environmental Research Letters, 2, 045027, 10.1088/1748-9326/2/4/045027, 2007.

Zhang, Q., Zheng, Y., Tong, D., Shao, M., Wang, S., Zhang, Y., Xu, X., Wang, J., He, H., Liu, W., Ding, Y., Lei, Y., Li, J., Wang, Z., Zhang, X., Wang, Y., Cheng, J., Liu, Y., Shi, Q., Yan, L., Geng, G., Hong, C., Li, M., Liu, F., Zheng, B., Cao, J., Ding, A., Gao, J., Fu, Q., Huo, J., Liu, B., Liu, Z., Yang, F., He, K., and Hao, J.: Drivers of improved PM2.5 air quality in China from 2013 to 2017, Proceedings of the National Academy of Sciences, 116, 24463, 10.1073/pnas.1907956116, 2019.

Zhang, R., Jing, J., Tao, J., Hsu, S. C., Wang, G., Cao, J., Lee, C. S. L., Zhu, L., Chen, Z., Zhao, Y., and Shen, Z.: Chemical characterization and source apportionment of PM2.5 in Beijing: seasonal perspective, Atmos. Chem. Phys., 13, 7053-7074, 10.5194/acp-13-7053-2013, 2013.

Zhang, T., Cao, J., Tie, X., Shen, Z., Liu, S. X., Ding, H., Han, Y., Wang, G., Ho, K. F., Qiang, J., and Li, W. T.: Water-soluble ions in atmospheric aerosols measured in Xi'an, China: Seasonal variations and sources, Atmospheric Research, 102, 110-119, 10.1016/j.atmosres.2011.06.014, 2011.

Zhao, M., Wang, S., Tan, J., Hua, Y., Wu, D., and Hao, J.: Variation of Urban Atmospheric Ammonia Pollution and its Relation with PM2.5 Chemical Property in Winter of Beijing, China, Aerosol and Air Quality Research, 16, 1390-1402, 10.4209/aaqr.2015.12.0699, 2016.

Zheng, B., Tong, D., Li, M., Liu, F., Hong, C., Geng, G., Li, H., Li, X., Peng, L., Qi, J., Yan, L., Zhang, Y., Zhao, H., Zheng, Y., He, K., and Zhang, Q.: Trends in China's anthropogenic emissions since 2010 as the consequence of clean air actions, Atmos. Chem. Phys., 18, 14095-14111, 10.5194/acp-18-14095-2018, 2018.

Zheng, G., Su, H., Wang, S., Andreae, M. O., Pöschl, U., and Cheng, Y.: Multiphase buffer theory explains contrasts in atmospheric aerosol acidity, Science, 369, 1374, 10.1126/science.aba3719, 2020.

Zheng, G. J., Duan, F. K., Su, H., Ma, Y. L., Cheng, Y., Zheng, B., Zhang, Q., Huang, T., Kimoto, T., Chang, D., Pöschl, U., Cheng, Y. F., and He, K. B.: Exploring the severe winter haze in Beijing: the impact of synoptic weather, regional transport and heterogeneous reactions, Atmos. Chem. Phys., 15, 2969-2983, 10.5194/acp-15-2969-2015, 2015.

Zheng, M., Wang, Y., Bao, J., Yuan, L., Zheng, H., Yan, Y., Liu, D., Xie, M., and Kong, S.: Initial Cost Barrier of Ammonia Control in Central China, Geophysical Research Letters, 46, 14175-14184, 10.1029/2019gl084351, 2019.

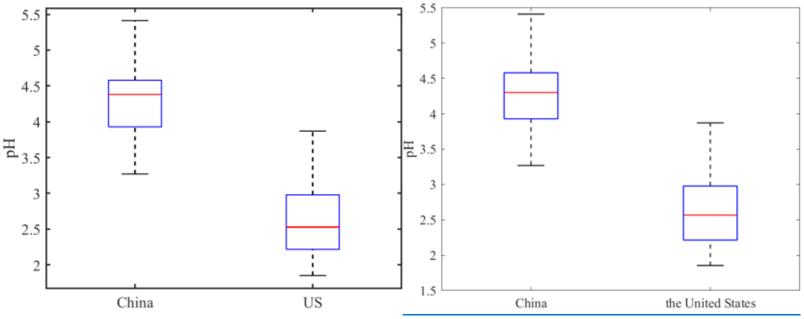


Figure 1.~~:~~ Annual average aerosol pH at each monitoring site in China and the United States based on observational data. The arithmetic mean (midline), the interquartile range (box), and the minimum-maximum range (whiskers) are shown in the box plot.

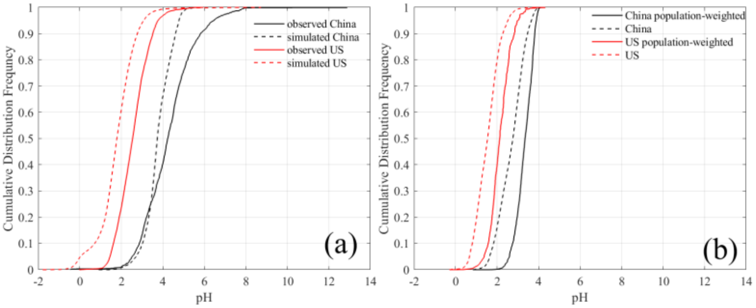


Figure 2.~~:~~ The cumulative distribution function (CDF) curves of aerosol pH in China and the United States based on (a) observed particulate and gaseous composition (solid lines) and CMAQ simulations collocated with observation sites (dashed line); (b) simulated data nationwide. In panel (b), both average and population weighted CDFs are shown.

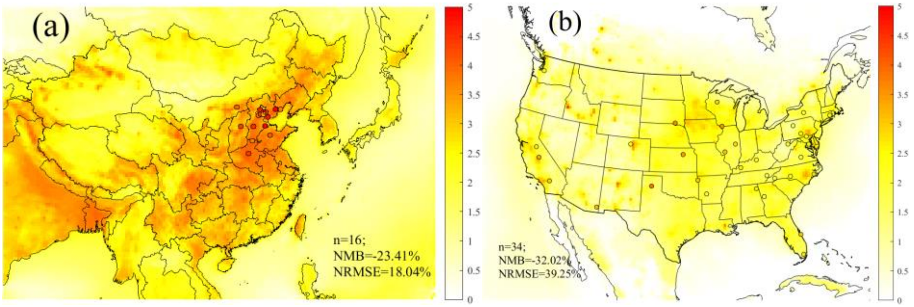


Figure 3.~~:~~ Overlay of annual mean pH calculated based on simulated concentrations (colored map) and observed concentrations (colored dots) over the study domain in (a) China and (b) the United States. Number of sites (N), normalized mean bias (NMB) and normalized root-mean-square error (NRMSE) are provided in each figure.

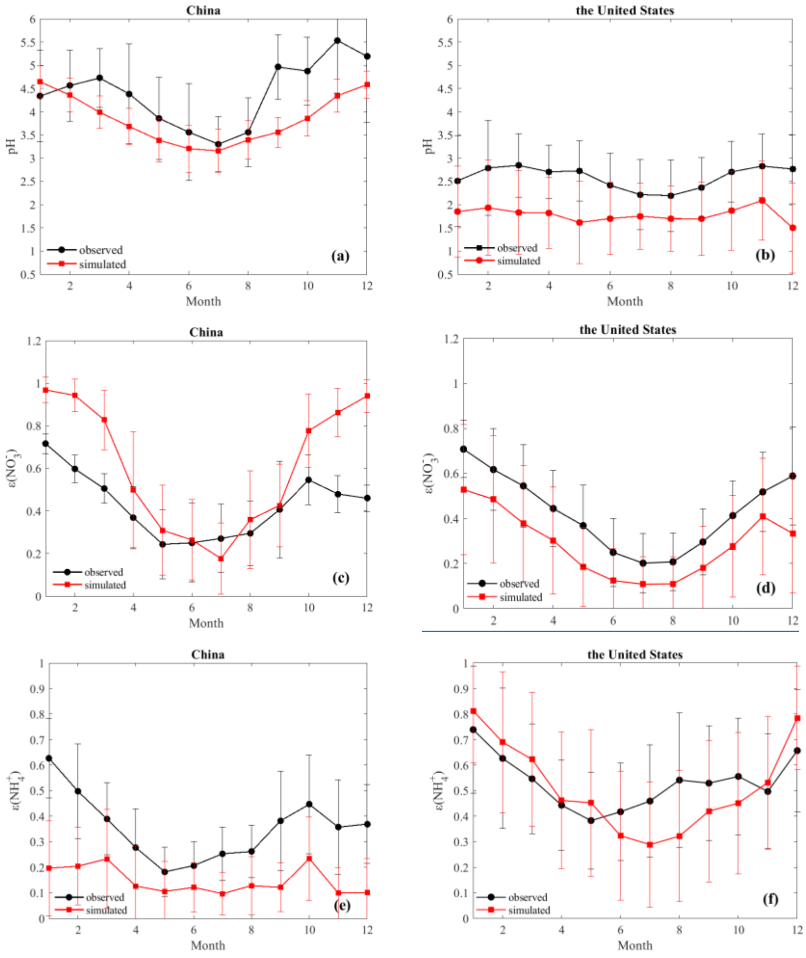


Figure 4.~~:~~ Monthly average values of pH, ε(NO_3^-) and ε(NH_4^+) based on observed and CMAQ simulated data in China (a, c, e) and in the United States (b, d, f). The error bars represent the standard deviation of all the cases in each month.

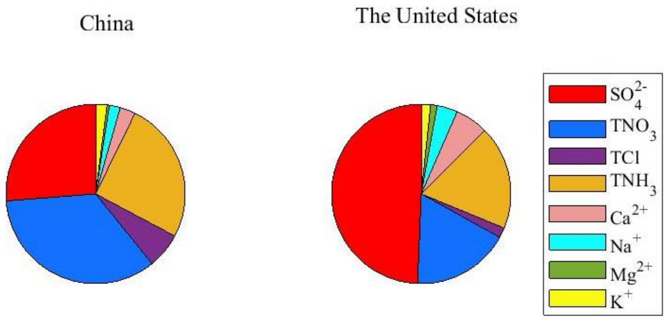
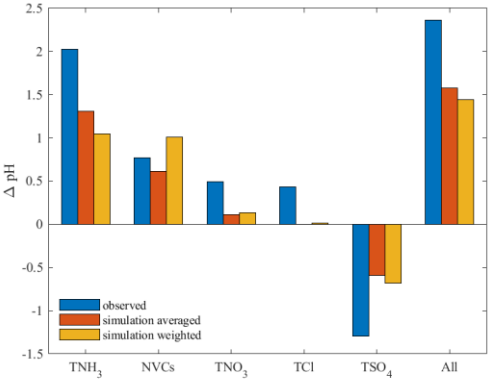


Figure 5.~~:~~ Annual average values of water-soluble ions (WSI) concentrations profiles in China (left) and in the United States (right).



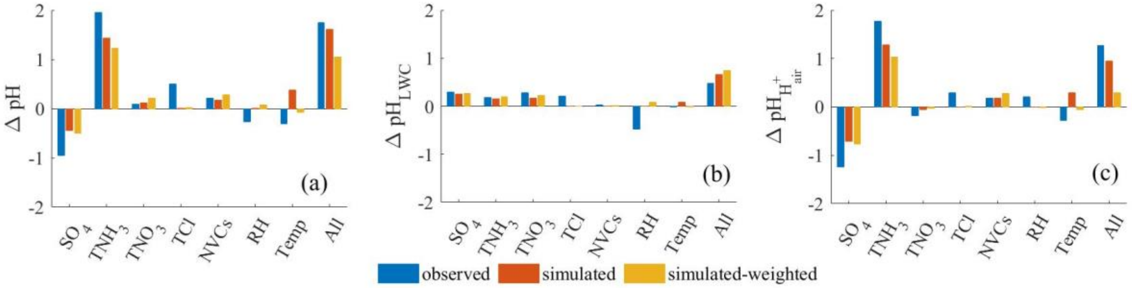
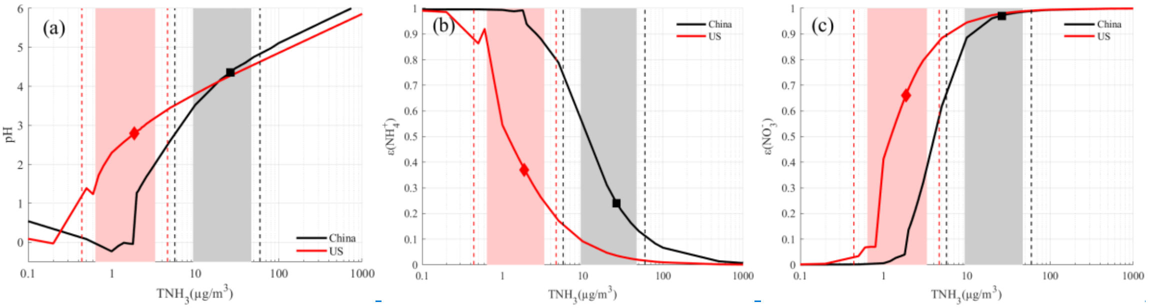
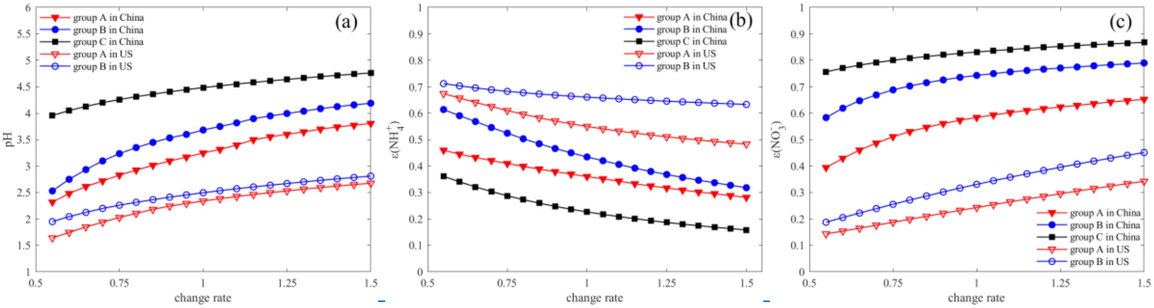


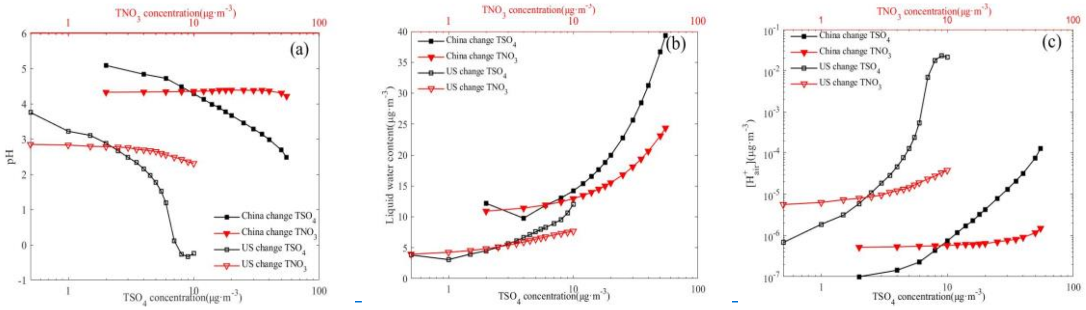
Figure 6.~~:~~ Contributions of individual~~each~~ components~~compounds~~s and meteorological factors~~s~~ to (a) total difference of aerosol pH (ΔpH), (b) the aerosol pH difference through the pathway of LWC (ΔpH_{LWC}), and (c) the aerosol pH difference through the pathway of H^+_{air} ($\Delta pH_{H^+_{air}}$) ~~aerosol pH difference~~ between China and the United States calculated by multi-variable Taylor series method (MTSM) in Sect. 2.4. For each factor, ~~T~~the sum of the contributions through the two pathways yields~~is~~ the net contribution of this factor to the aerosol pH. The case in the United States is chosen as the starting point, and China as the ending point.



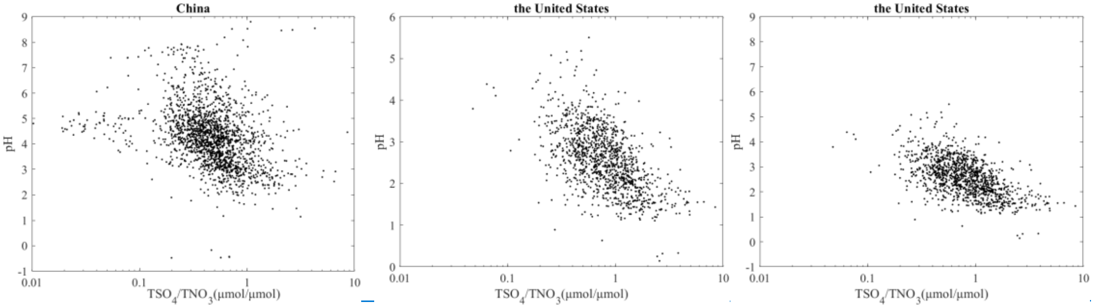
~~**Figure 7: Values of pH, ε(NH_4^+) and ε(NO_3^-) to the change of TNH_3 from 0.1 to 1000 μg·m^{-3} while keep all other components constant at their annual average levels.** The shaded areas show the TNH_3 concentration ranges that covers 75% of the observed cases in the countries, the black square and the red diamond mark the average TNH_3 levels in China and the United States, respectively.~~



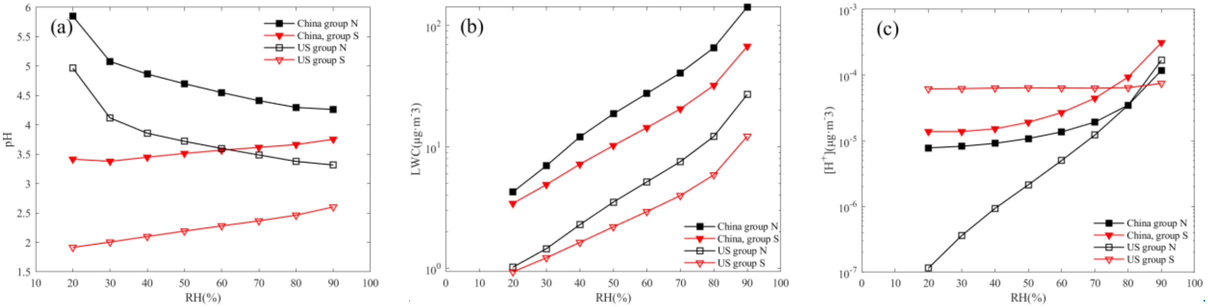
~~**Figure 8: Average values of pH, ε(NH_4^+) and ε(NO_3^-) when changing TNH_3 concentration from 55% to 150% in different groups.**~~ ~~Group A: China: pH=3.25±1.16, n=141; US: pH=2.41±0.72, n=651; Group B: China: pH=3.68±1.13, n=240; US: pH=2.75±0.69, n=540;Group C: China: pH=4.22±1.57, n=1312; US: n=0.~~

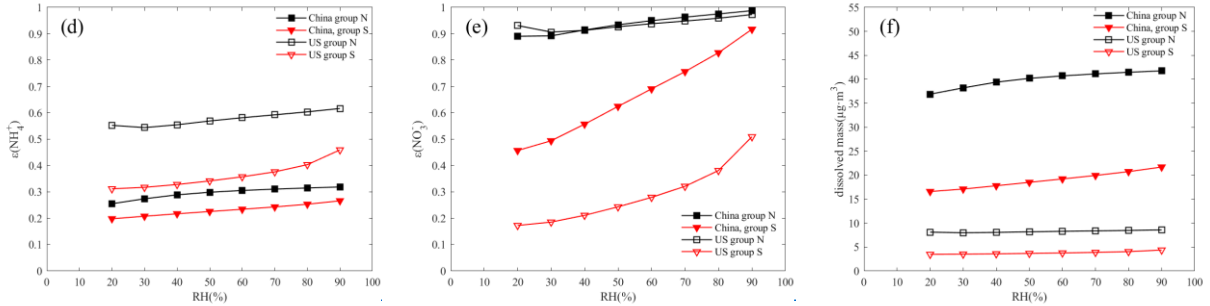


~~**Figure 9: Values of pH, liquid water content and H^+_{air} to the change of TSO_4 and TNO_3 concentration in China and the United States.**~~

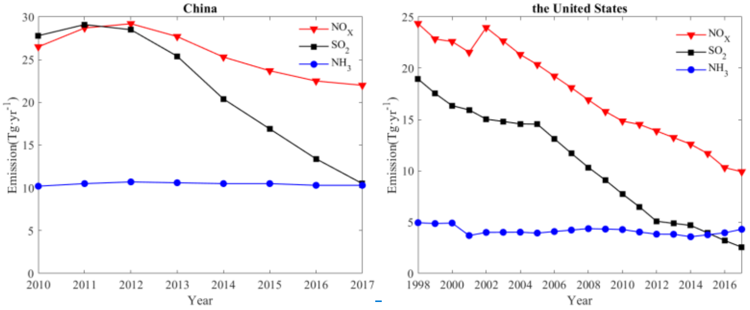


~~**Figure 10: The relation between aerosol pH and TSO_4/TNO_3 molar ratio in China (left) and the United States (right) based on observational data.**~~





~~**Figure 11: Values of pH, LWC, H^+_{air}, ε(NH_4^+), ε(NO_3^-) and dissolved mass in group N and group S under different RH conditions in China and the United States.** China: group N, n=410; group S, n=470; US: group N, n=72; group S, n=1119.~~



~~**Figure 12: Yearly trend of the emissions of NH_3, NO_x and SO_2 in China (left) and the United States (right).** The data in China are from studies by Zheng et al.(Zheng et al., 2018). The data in the United States are from Air Emissions Inventories by United States Environmental Protection Agency (https://www.epa.gov/air-emissions-inventories/air-pollutant-emissions-trends-data).~~

Table 1.~~:~~ Summary of the one-year average values of mass concentration of water~~-~~soluble ions (WSI), gaseous and aerosol species, aerosol pH and meteorological parameters (as average ± standard deviation) in China and the United States during the~~ir~~ study periods (i.e., 2017 for China and 2011 for the United States).

	China(n=1845)	US(n=1191)
WSI (μg·m^{-3})	34.4±25.5	5.7±2.2
Temperature (K)	284.8±11.7	287.4±10.0
RH (%)	45.1±17.6	71.4±20.9
pH	4.3±1.2	2.6±0.7
Particle phase (μg·m^{-3})		
SO_4^{2-}	9.2±7.1	2.2±1.3
NO_3^-	12.1±11.1	0.8±0.9
NH_4^+	8.9±8.0	0.8±0.5
Cl^-	2.2±2.3	0.4±0.1
Na^+	0.7±1.0	0.2±0.2
K^+	0.7±0.6	0.1±0.1
Ca^{2+}	1.0±0.1	0.3±0.2
Mg^{2+}	0.2±0.1	0.1±0.1

Gaseous phase (µg·m^{-3})		
NH$_3$	18.0±12.6	1.1±1.7
HCl	1.9±3.4	-
HNO$_3$	1.0±1.1	1.0±0.6
Total (µg·m^{-3})		
TNH$_3$	26.5±17.2	1.9±1.8
TCl	4.1±4.5	-
TNO$_3$	13.1±11.2	1.8±1.1