Title: “Driving factors of aerosol acidity: a new hierarchical quantitative analysis framework and its application in Changzhou, China”

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Authors: Duan et al.

General Comments:

Aerosol acidity is one of the core parameters in atmospheric chemistry. In recent years, much interesting work has been done on the trends and driving factors of aerosol acidity changes. This article is pioneering in decomposing the trends of aerosol acidity changes into long-term, seasonal, diurnal, and random components, and decoupling the driving factors into meteorological and emission drivers. This research framework greatly simplifies the interpretation of the results from complex multiphase buffering theory. I believe that with minor revisions, this article can be published in Atmospheric Chemistry and Physics.

Here are my specific recommendations:

Responses:

We thank the referee for the valuable and constructive comments/suggestions on our manuscript. We have revised the manuscript accordingly, and please find our point-to-point responses below.

Specific comments:

1.Lines 35-36: The expression here is not very precise. Andrew Ault et al have focused on directly measuring aerosol pH. Although their methods have limitations and have not yet been widely applied in practical measurements, direct measurement methods do exist.

Responses:

We thank the reviewer for the comment. We've modified the expressions as:

"Current direct measurement methods of aerosol pH (Ault, 2020) are not yet applied in ambient observations due to limitations such as slow measurement speeds (Lei et al., 2020) or the targeting of single particles (Craig et al., 2017). Therefore, thermodynamic models are widely adopted to estimate aerosol acidity and investigate its influencing factors (Clegg et al., 2001; Fountoukis and Nenes, 2007; Tao and Murphy, 2021; Zaveri et al., 2008; Zuend et al., 2008)."

2.Lines 57-64: I hope to use highly concise language to summarize the differences between this study and previous research on chemical profiles and meteorological parameters driven pH changes, as well as highlight the most innovative and distinctive features of this article.

Responses:

We thank the reviewer for the comment. We've added this point as (see the last paragraph in Sect. 1):

"Combining this model with time series analysis, we proposed a novel hierarchical quantitative analysis framework, which can not only quantify the contribution of different influencing factors, but also reveal the underlying mechanisms and dominant pathways of the influences. Compared with previous studies, this framework can provide a more systematic, in-depth and quantitative understanding on how the meteorology or chemical profiles would affect aerosol pH over different time scales of interest. Applying this framework to the long-term observations in Changzhou, China, distinct driving factors and underlying mechanisms were quantified for different time series components, and future implications were also discussed."

3.Line 87: Can mathematical formulas be provided here? For example, linear fitting and Fourier curve fitting, as well as how to use mathematical methods to decouple the trends of 4 components.

Responses:

We thank the reviewer for the comment. We've added this point as (see Sect. 2.2 and Text S1 in SI):

"Linear-fitting ($y=a*t + b$, where t is defined as time hereinafter) is adopted to predict the long-term trends (Kang et al., 2020; Mudelsee, 2019), and one-term Fourier curve fitting ($y=a_0+a_1*\cos(\omega*t) +b_1*\sin(\omega*t)$) is adopted to fit the seasonal and diurnal cycles (Bloomfield, 2004; Singh et al., 2017)."

Sect 2.2, Line 105 in the revised manuscript: "See more details in SI Text S1-S2"

"**S1. Detailed description of decomposing parameters into 4 time series components**

The decomposition process consists of the following main steps: linear-fitting of the long-term trends, one-term Fourier curve fitting of seasonal and diurnal variations, and extraction of random residues. For parameter p, this process is expressed as Eq. S1a-d:

$$p_{yr} = a_1*t + b_1 \quad \text{(S1a)}$$

$$p_{seas} = a_2+ b_2*\sin(\omega_1*t)+ c_1 \times \cos(\omega_1*t) \quad \text{(S1b)}$$

$$p_{day} = a_3+ b_3*\sin(\omega_2*t)+ c_2 \times \cos(\omega_2*t) \quad \text{(S1c)}$$

$$p_{res} = p - p_{yr} - p_{seas} - p_{day} \quad \text{(S1d)}$$

where p, p_{yr}, p_{seas}, p_{day} and p_{res} are the values of actual observed, long-term trend, seasonal variation, diurnal cycle and residues, respectively. The t is the time, and a_i, b_i

and c_i are the coefficients of fitted curves during the corresponding time series, respectively. ω_1 and ω_2 are $2\pi/365$ days^{-1} and $2\pi/24$ hours^{-1}, respectively, to fixed the cycle period of Fourier curve as 1 year and 1 day in fitting the seasonal and diurnal variations."

4.Line 142: It is recommended to use percentiles for RH.

Responses:

We thank the reviewer for the comment. We've used percentiles for RH throughout manuscript (see the paragraph before Sect. 4.1 and second paragraph in Sect. 4.3), and we also modified the axis labels in figures about RH (Fig. S4d and S7d).

5.Lines 144-145: The decomposition of pH into the three factors can be understood mathematically. However, is it appropriate to plot these three factors as time series? From the perspective of aerosol physicochemical properties, especially the meaning of H^+, plotting them as time series may not be easily interpretable.

Responses:

We thank the reviewer for the comment. We've adopted a bottom-up method to quantify the time series components of pH. Each input parameter *p* in ISORROPIA v2.3 is subdivided into 4 time series components, which are further used in ISORROPIA v2.3 to obtain the pH at corresponding time series. We've performed time-series decomposition of all influencing factors. This process clarifies how the fluctuations of different factors affect pH levels. The underlying principle of such decompositions in time series analysis is that some influencing factors present periodic variation, with the most common period being seasons or days (Anderson, 2011; Wei, 2013). For example, one important influencing factor of aerosol acidity, the temperature, exhibits significant seasonal and diurnal variations; in comparison, emission profile of some species may show relatively small diurnal variations but stronger seasonally variations. Thus, we consider it reasonable to plot these factors as a time series. We've clarified these points in the revised manuscript and SI text S2 as:

Sect 2.2, Line 105 in the revised manuscript: "See more details in SI Text S1-S2".

"S2. Detailed descriptions of quantitative analysis of each factor based on ISM and time series analysis

Here we adopted a bottom-up method to quantify the time series components of upper-level factors in the ISM model and its driving factors. That is, based on the decomposition of time series analysis, each input parameter p in ISORROPIA v2.3 is subdivided into 4 time series components. The underlying principle of such decompositions is that most influencing factors of aerosol acidity, such as temperature and emissions, are influenced by long-term variations, periodical variations (i.e., seasonally and diurnally) and random fluctuations (Anderson, 2011; Wei, 2013). For example, temperature can be decomposed into long-term trend (T_{yr}), seasonal variations (T_{seas}), diurnal cycles (T_{day}) and residuals (T_{res}), respectively."

6.Lines 149-152: The colors are unclear. It is recommended to increase the thickness of the lines in the legend.

Responses:

We thank the reviewer for the comment. We've increased the thickness of the lines in the legend of Fig. 2.

7.Lines 178-179: There seems to be an error here.

Responses:

We're sorry for this mistake. There is a citation of Fig. 4, and we've corrected it.

8.Lines 239-241: What are the percentage changes in pKa^*, c_{ni} and X_{gp} relative to? The difference in pH or the original pH? This could be expressed more clearly in the figure caption.

Responses:

We thank the reviewer for the comment. The percentage variations in pKa^*, c_{ni} *and* X_{gp} is relative to the pH variations. We've clarified this point in the figure caption of Fig. 6 as:

"**Figure 6: Hierarchical relationship among major influencing factors of aerosol pH variations for the 4 time series components, respectively.** Here, the percentage variations are derived by the variations due to factor X to overall variations. For example, the contribution of pK_a^* variations to seasonal variations of pH is derived by $\Delta pK_a^*{}_{,\ seas} / \Delta pH_{,\ seas} * 100\%$, where the overall pH variations $\Delta pH_{,\ seas} = \Delta pK_a^*{}_{,\ seas} + \Delta c_{ni,\ seas} + \Delta X_{gp,\ seas}$. Factors contributing less than |10%| are not shown."

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