

Author responses in blue. Planned additions to the manuscript are underlined.

Anonymous Referee #1

This is an excellent and thorough review of the current state-of-science on the acidity of atmospheric aerosols and droplets. Below are some comments intended to improve the manuscript:

We thank the reviewer for the supportive comments.

1. The Abstract is focused on the electrolytes and does not discuss the organic fraction and its contribution. Something should be mentioned about organic bases, such as amines, and organic acids such as carboxylics and dicarboxylics.

We revised a sentence in the abstract to explicitly mention organic acid/base partitioning. The role of organic species in driving pH is beginning to be examined, so we highlighted the well-known role of pH on organic acid/base partitioning.

In the atmosphere, the acidity of condensed phases (aerosol particles, cloud water, and fog droplets) governs the phase partitioning of semi-volatile gases such as  $\text{HNO}_3$ ,  $\text{NH}_3$ ,  $\text{HCl}$ , and organic acids and bases as well as chemical reaction rates.

2. Same in section 1 around line 22.

A list of specific organic acids/bases were added:

Semi-volatile species, for which significant fractions typically exist in both the gas and condensed phases, include ammonia ( $\text{NH}_3$ ), nitric acid ( $\text{HNO}_3$ ), hydrochloric acid ( $\text{HCl}$ ), and low molecular weight organic acids (formic, acetic, oxalic, malonic, succinic, glutaric, and maleic acids) and/or bases (e.g. amines).

3. The use of the word "occult" is completely foreign to me. It should at least be defined, but better would be to use a word more familiar.

Occult is now defined (we keep the term for compactness in the figure):

The acidity of atmospheric deposition for dry, wet, and occult (wind-driven cloud-water) pathways is directly affected by aerosol and cloud pH (Fig. 1).

4. Page 4, line 32. Nicotine (and cocaine for that matter) are organic bases. increasing pH partitions these compounds to the gas phase (so-called free-basing). The gaseous compounds have a much higher deposition efficiency to the respiratory tract than particles increasing the dose.

We clarified the statement to indicate the role of particle acidity was to drive nicotine off surfaces and into the indoor air. We also added a reference to the partitioning mechanism for alkaloids to indicate the behavior may apply to other species as well.

Aerosol acidity was also recently shown to enhance airborne nicotine levels and resulting thirdhand smoke exposure by promoting volatilization from surfaces (such as clothes) and allowing distribution throughout a building's indoor air (DeCarlo et al., 2018). Similar behavior may be possible for other alkaloids (Pankow, 2001).

5. section 3, page 17, line 26. Change The to This.

Updated

6. Section 5, page 30, line 17: Why do you say that cloud liquid water is not in equilibrium with the gas phase? Well, nothing is completely in equilibrium but the surface area in a cloud is huge so equilibrium is nearly attained.

In a relative sense, aerosols are in much more equilibrium that clouds can ever be. This is because their size, hence equilibration times, is orders of magnitude smaller. For this reason you can always assume thermodynamic equilibrium for submicron, but not supermicron aerosol. Droplets are 10s of microns, so the equilibrium assumption is even less satisfied (Seinfeld and Pandis, 1998).

The comment “water is not in equilibrium with the gas phase” refers to the effect of perturbing the RH of the air surrounding the sample. For aerosol, even a 10% change in RH can profoundly impact liquid water, as equilibration with RH is almost instantaneous. Cloud liquid water, on the other hand, is not driven by RH but by the cooling rate that generates them. After sampling, the evaporation biases have a much smaller effect precisely because the liquid volume is so large. We have removed the reference to “water equilibration” to avoid unnecessary confusion.

**Sentence to be modified from:**

The same limitations do not exist for fog/cloud water or precipitation, where larger sample volumes can be collected from accessible clouds, the associated water is not in equilibrium with the gas phase (although evaporation artifacts may still cause biases), and solutions are dilute enough to allow for a direct pH measurement. The latter has been done with electrochemical pH probes for decades (Sect. 5.2).

**To:**

The sample volumes for fog/cloud water or precipitation are orders of magnitude larger than for aerosols and can be collected from clouds using well established instrumentation. This, together with their dilute concentration allow for a direct pH measurement, which has been done with electrochemical pH probes for decades (Sect. 5.2).

7. The authors may not be aware of the work by Beverly Cohen published in 2000 using a metal plate to assess aerosol acidity.

We were not aware but have located a report and article:

1. Field Evaluation of Nanofilm Detectors for Measuring Acidic Particles in Indoor and Outdoor Air  
By: Beverly S Cohen, Maire SA Heikkinen, Yair Hazi, Hai Gao, Paul Peters, and Morton Lippmann, <https://www.healtheffects.org/system/files/Cohen.pdf>
2. Cohen et al., Detecting H<sup>+</sup> in ultrafine ambient aerosol using iron nano-film detectors and scanning probe microscopy, <https://doi.org/10.1080/104732200301881>.

The technique is used to determine the number of acidic vs nonacidic particles. It provides some qualitative information (e.g. H<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>HSO<sub>4</sub> are more acidic than (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>). We have not added a reference due to the qualitative nature of the study.

8. Page 33, section 5.1.3, line 31: Comment should be common.

Updated

9. Page 58, lines 22-27: Something should be said here about the role of volatile acids (HCl, HNO<sub>3</sub>) and bases (NH<sub>3</sub>, amines). If these exist in the gas phase, they serve to equilibrate acidity across the particle size distribution. If the particles are so acidic that the volatile bases are depleted from the gas phase, I can see how there could be a gradient in acidity with particle size. Likewise for the particles being alkaline and the volatile acids being depleted. As the authors discuss elsewhere, these gases are key to understanding the acidity of particles but unfortunately they are infrequently measured. I encourage a simple discussion of this logic.

We added a new sentence in the paragraph highlighting the role for semivolatile acids and bases:

Overall, atmospheric particle pH is size dependent and generally higher for coarse mode particles due to variations in inorganic composition with particle size. Differences as large as 4 pH units have been reported between fine and coarse particles (Fang et al., 2017; Young et al., 2013). Bulk PM<sub>1</sub> and PM<sub>2.5</sub> acidity is more similar than fine vs coarse mode acidity (pH<sub>F</sub> within 1 – 2 units, e.g., Bougiatioti et al., 2016; Guo et al., 2017b), but submicron (diameter < 1 μm) particles still show higher acidity than bulk PM<sub>2.5</sub>. The reason for this is the strong enrichment of aerosol with NVCs from dust and sea salt at the larger sizes (even in the fine mode) and role of sulfate in new particle formation and surface-area driven condensation at the small sizes (Fig. 2). While semivolatile acids and bases act to homogenize acidity across the size distribution, mass transfer limitations (next section) and the heterogeneity of emission composition lead to variation in pH with size. Significant pH changes can occur in the 1 to 2.5 μm size range (Fang et al., 2017; Ding et al., 2019). The size dependent pH is also seen for sea salt aerosol (Fridlind and Jacobson, 2000) as well as in urban aerosols in China (Ding et al., 2019) where the fine mode is consistently 2-3 pH units lower than the coarse mode. The implications of this acidity gradient are considerable, for

metal solubility and their impacts on public health and ecosystem productivity, as well as chemistry and semi-volatile partitioning of pH-sensitive species.