

Review 2 on the manuscript « Biogenic, urban, and wildfire influences on the molecular composition of dissolved organic compounds in cloud water” by Cook et al.

My main comments have been addressed in the author’s reply to Reviewer 1 and in the revised version of the manuscript. I only have a few more comments/questions which, depending on the answers, might require some additional small changes in the manuscript.

1. Acid-catalyzed reactions vs Fenton processes (radical generation)

As for Reviewer 1, my main concern was the conclusion that the correlation between O/C ratios and pH necessarily meant the occurrence of acid-catalyzed reactions. But such reactions are extremely slow over the range of pH of 4-5 reported here (typically $\ll 10^{-7} \text{ s}^{-1}$, thus take weeks or months). By contrast, radical production in aqueous media, which is controlled by Fenton processes, is strongly pH-dependent and a much more plausible explanation for these results. I saw that the authors have taken this comment into account by adding “and radical processes” next to “acid-catalyzed”. I would suggest writing “or” rather than “and”, or any other formulation pointing more strongly towards radical processes.

2. Acid-catalyzed reactions vs biological processes

Another explanation that was not considered is that the oligomeric material found in the cloudwater could be of microbial origin. There is now an extensive literature reporting the presence of microorganisms in cloud water, alive and in full capacity to metabolize (process) organic compounds at rates that are in competition with non-biological reactions (see for instance Vaitilingom et al., ACP 11, 8721, 2011). Microorganisms are also well-known to produce organic acids, which would affect the pH of the medium. Thus, the observed correlation O/C vs pH could be entirely biologically-driven. The presence of microorganisms and of their metabolites in cloud water might not be easy to link to specific sources as they are present in all kinds of environments.

Could the authors discuss to which extent this could be the case (or ruled out) ?

3. Potential formation of oligomers in the electrospray

The samples do not seem to be ran through a column before to be introduced into the electrospray of the spectrometer. Such direct injection (or infusion) has been known in the past to produce spurious oligomers (= not present in the initial samples) in the ionizing source. Could the author discuss the probability of this happening in their analyses ?

4. Aerosols: source or target of aqueous-phase processes ?

This comment addresses the argument given in introduction to justify the relevance of this study. I am not asking the authors to necessarily change their introduction at this point, but at least to keep this comment in mind in future works.

Indeed, the idea that aqueous-phase processes can affect aerosol composition and SOA formation has been circulating for some years. This is, however, difficult to justify as cloud (or fog) droplets are in very small numbers (a few 100 cm^{-3} at the most) compared to the number of aerosol particles in most regions (1000 to $100\,000 \text{ cm}^{-3}$). Thus only one in 10 to one in 1000 aerosol particle might be affected by aqueous-phase processes. This is far from affecting the composition of the entire aerosol population (for instance, it is hard to imagine any significant effects on the overall optical property), let alone SOA formation, which produces many 1000 's particles cm^{-3} .

Thus, a better argument for the study of the organic composition of cloudwater could be to explain the formation of specific compounds, that could be used as tracers for aqueous processes for instance, or that have specific properties.