Assessment of Smoke-Influence and Regional Trends of Organic Carbon Concentrations in Cloud & Rain Water Samples

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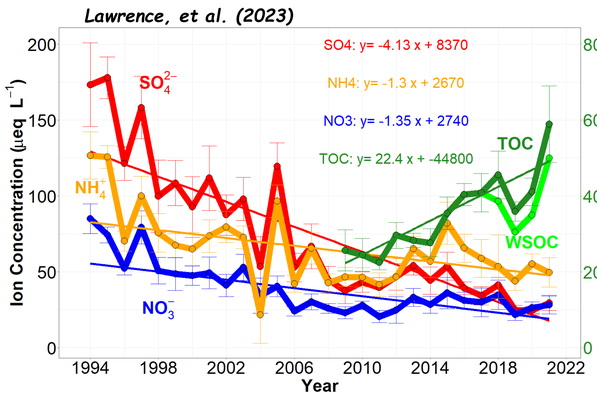
Cloud Water Long-Term Trends at WFM

Decades of cloud water composition measurements have been obtained at Whiteface Mountain (WFM) in northern NY State. Historical observations have largely focused on inorganic ions, but organics now dominate the cloud and aerosol composition. Carbon comprises the "backbone" of organic molecules. On an annual basis, Total Organic Carbon (TOC) concentrations in cloud water have doubled since measurements began in 2009 through 2021.



Samples since 2018 were filtered during collection. Thus, WSOC was measured rather than TOC starting in 2018.

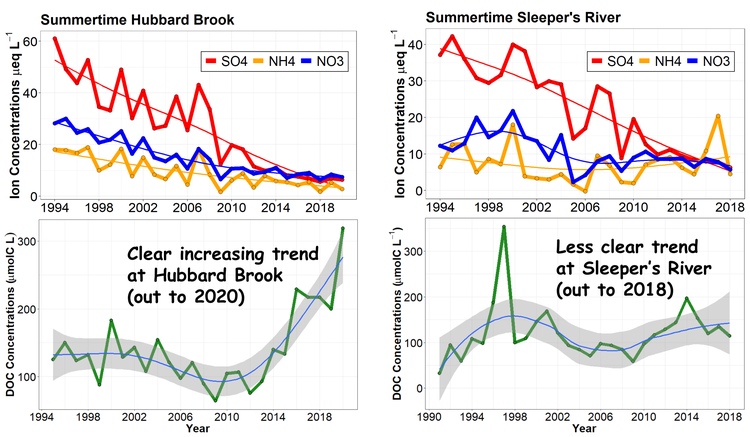
Tests for a small subset of samples in 2018 and 2019 indicated that 85% TOC ~ WSOC

WSOC: Water Soluble Organic Carbon

TOC: Total Organic Carbon

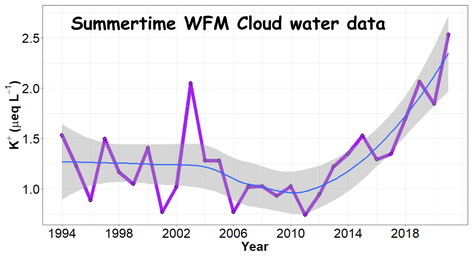
Comparison to Rain Long-Term Trends (at Sleepers River & Hubbard Brook)

Preliminary evaluation of rain water chemical composition data at two other locations in the northeastern United States (Hubbard Brook in New Hampshire, and Sleeper's River in Vermont) suggest that the increasing organic carbon trend observed at WFM may be reflecting a broader regional trend.



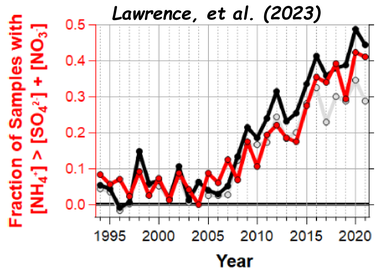
Dissolved Organic Carbon (DOC) in precipitation samples is measured the same way as Water Soluble Organic Carbon (WSOC) in cloud water samples, and they can thus be compared directly. However, rain water samples are generally more dilute than cloud water due to the higher moisture conditions under which rain forms. We may need to weight by sample volume for better direct comparisons.

Hypotheses for Increasing Organic Carbon



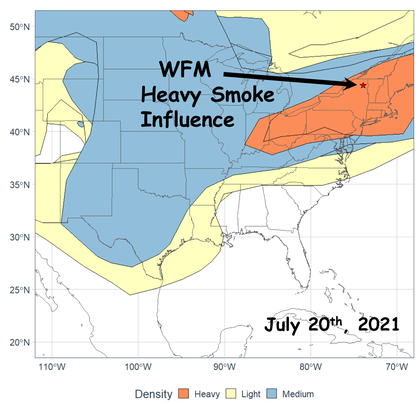
Increasing trend in annual median cloud water potassium ion (K^+) concentrations is coincident with increasing organic carbon trend since 2010, suggesting an important contribution from wood burning smoke.

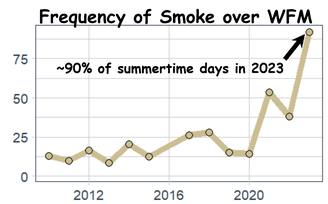
However, other dramatic changes, like a growing number of samples with surplus NH_4^+ relative to NO_3^- and SO_4^{2-}, could also indicate that changing heterogeneous chemical reactions or greater partitioning from the gas phase to the particle and/or aqueous phases (also known as "secondary processes") are playing an important role driving the recent trends in organic carbon.



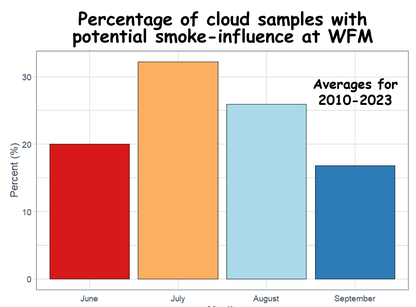
NOAA Hazard Mapping System (Fire and Smoke Product)

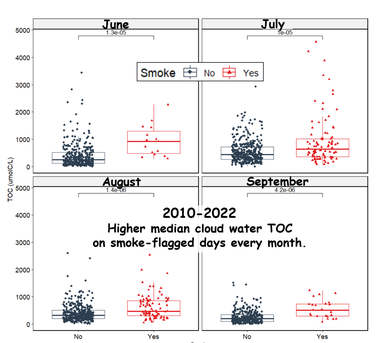
To evaluate the impact of smoke-influence on the increasing cloud water organic carbon trend at WFM, we used NOAA HMS, which uses multiple satellite observations to characterize fire events and smoke plumes on a routine basis.





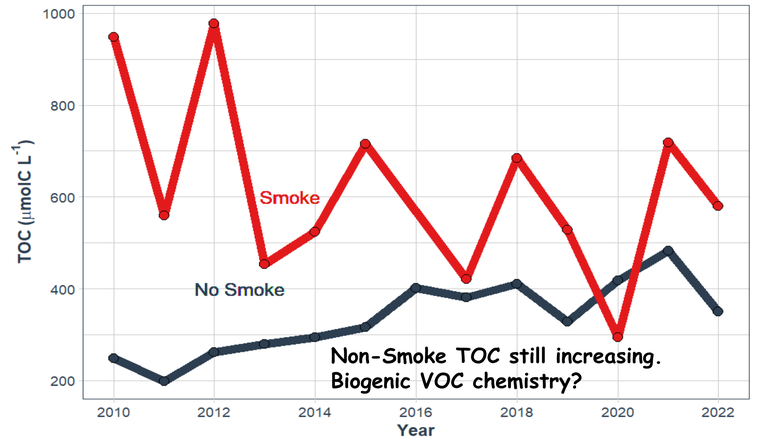
- Evidence of increasing smoke influence during cloud sampling periods at Whiteface Mountain (in terms of event frequency).
- Greater cloud water TOC on smoke-influenced days.



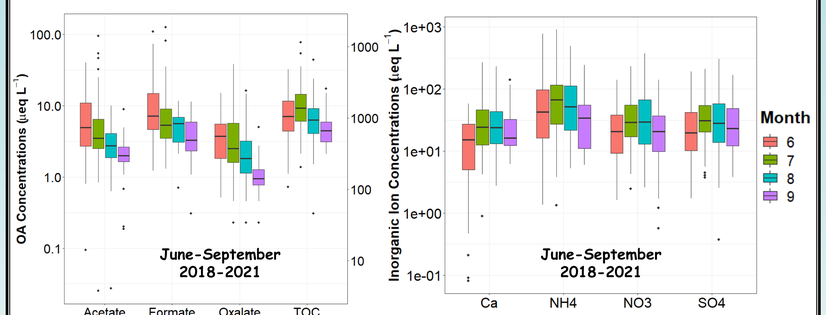


Quantifying Smoke-Influence

Comparing the cloud water chemical observations for smoke-influenced days versus non-smoke-influenced days (as determined with the NOAA HMS analysis), we find that, while the number of days with smoke-influence at WFM has grown, the median TOC for the smoke-influenced samples has decreased or remained the same between 2010 and 2022. Meanwhile, there is a strong increasing trend in TOC for samples collected on days not classified as smoke-influenced, suggesting that two very different processes are driving the increasing TOC trend.



Growing ion imbalance in rain water in the eastern US & Canada has been discussed previously by Feng et al. (2021) and was attributed to increased influence of organic acids. The cloud and rain water datasets shown here also demonstrate increasing ion imbalance (i.e. cations > anions, when including the traditional suite of inorganic ion measurements only). In 2018, we began measuring organic acids in WFM cloud water. The four year dataset analyzed thus far (2018-2021) does not display substantial evidence of an increasing trend but does exhibit a clear seasonal cycle that differs from the seasonal cycle of TOC and the major inorganic analytes.



We continue to refine these analyses and will collect additional data in the coming years to better quantify the role of these two independent processes on the long-term organic carbon trends observed in the northeastern United States.

References

Feng et al., Vol. 254, 118367, Atmospheric Environment, 2021
Lawrence et al., *ACP*, https://acp.copernicus.org/articles/23/1619/2023/, 2023

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