Exploring the Increasing Trend of Organic Carbon in the Atmospheric Aqueous Phase

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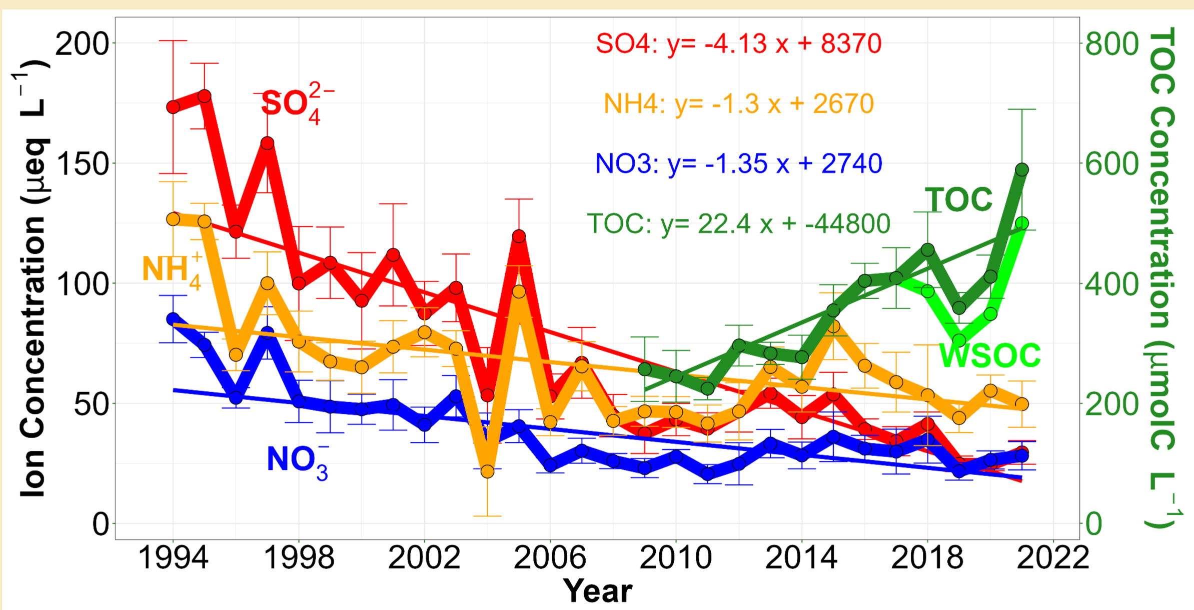
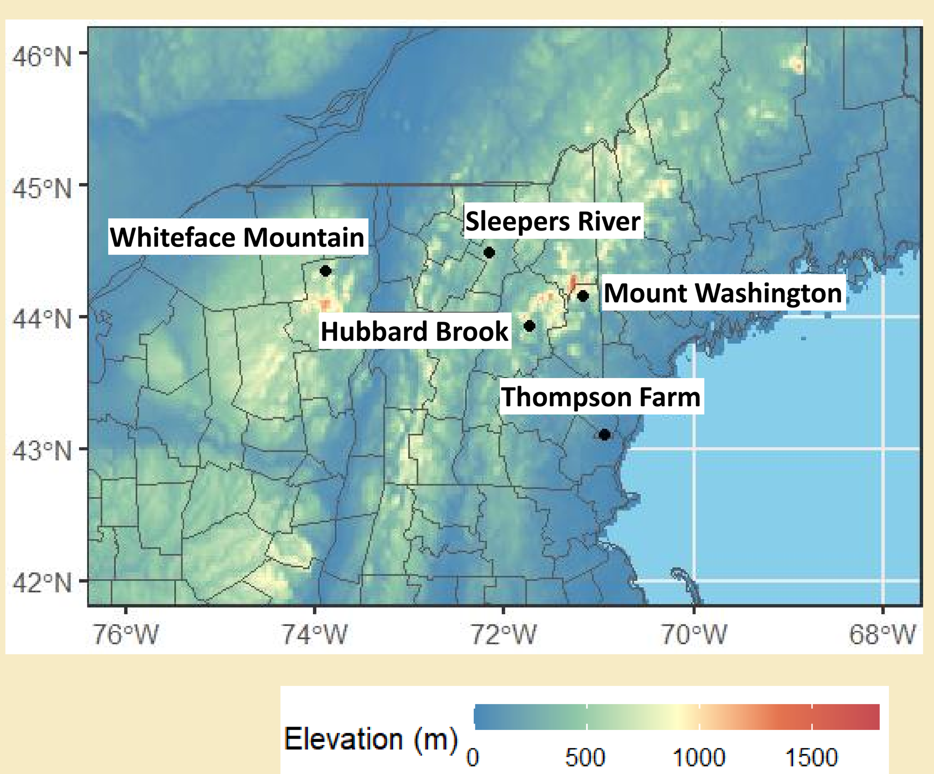
A Changing Chemical System



- The chemical composition of cloud water collected at Whiteface Mountain (WFM) has changed since the 1990s, as the major constituents responsible for acid deposition have decreased dramatically (*Lawrence et al., 2023)*
- Simultaneously, median concentrations of total organic carbon (TOC) have approximately doubled from 2009, with the causes behind this trend remaining unclear.
- While the trends in sulfate (SO_4^{2-}) and nitrate (NO_3^-) observed at WFM have been seen throughout the region, it is unknown if organic carbon follows a similar regional pattern. Few sites have long-term measurements of organic carbon.

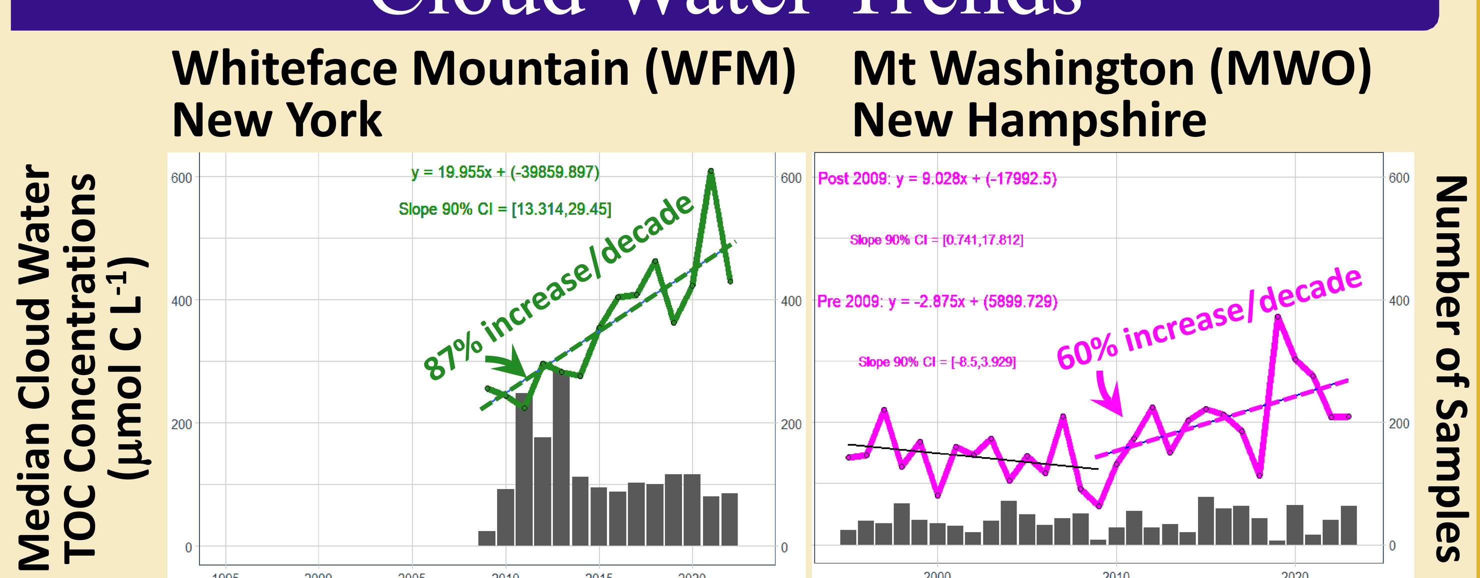
Site Locations & Analysis Methods

- Five datasets that measured either organic carbon (TOC) or Dissolved Organic Carbon (DOC) in cloud water or precipitation were compiled for this trend analysis
- Summertime median values (June-September) were used for cloud water trends, starting in 2009 (first year TOC was measured at WFM).
- Monthly precipitation volume weighted mean concentrations were used for the wet deposition collection sites.



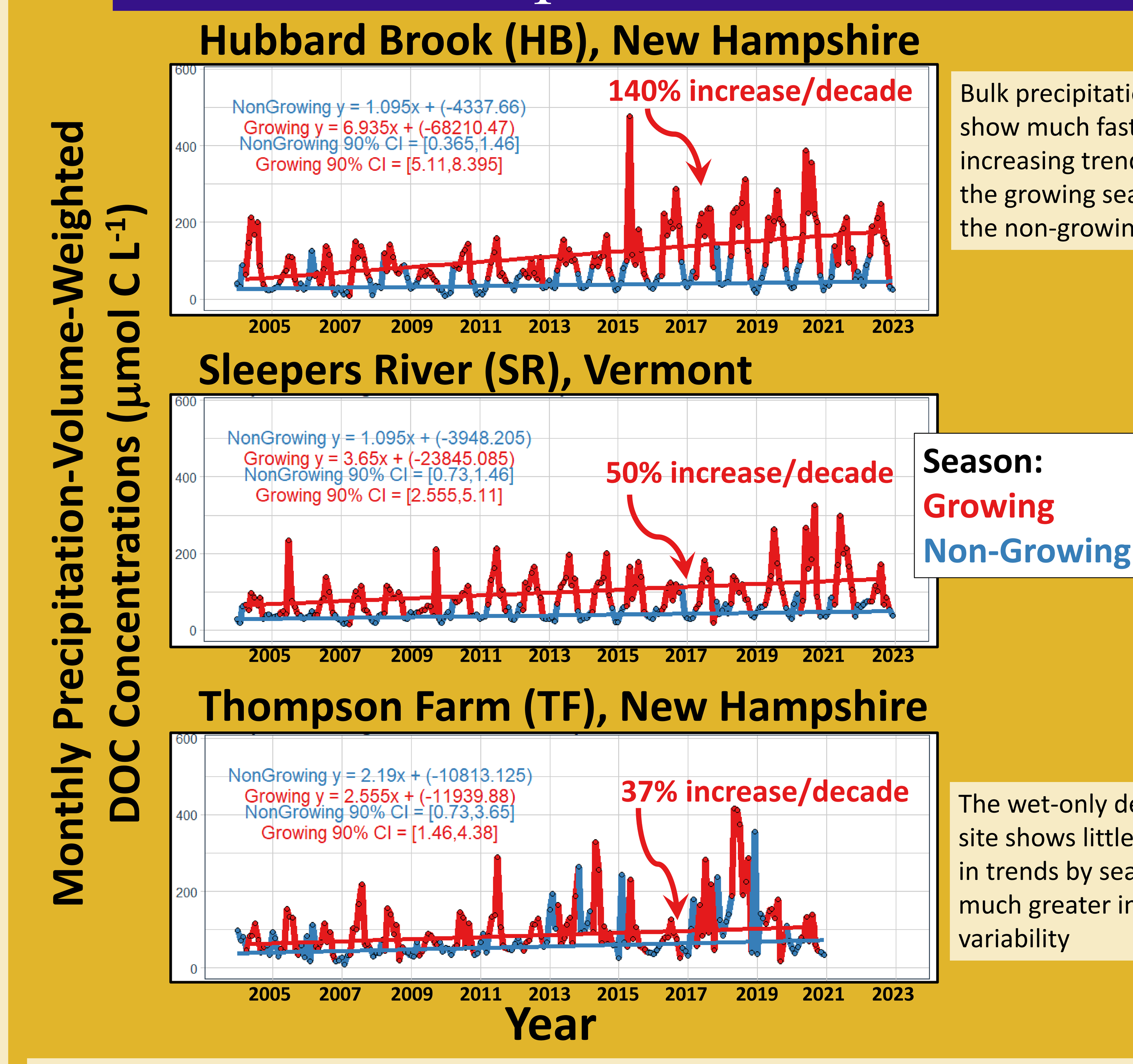
- Trends were estimated using a Theil-Sen regression with 90% confidence intervals.

Cloud Water Trends



- Median summertime cloud water concentrations of TOC have increased since 2009 at both WFM and Mountain Washington.
- There is little evidence of a trend at Mount Washington before 2009, but concentrations since 2009 increased at a similar relative rate as at WFM (approximately doubling from 2009-2022).
- The trends at Mount Washington are more uncertain due to high year-to-year variability in the number of samples collected and fewer samples generally.

Precipitation Trends

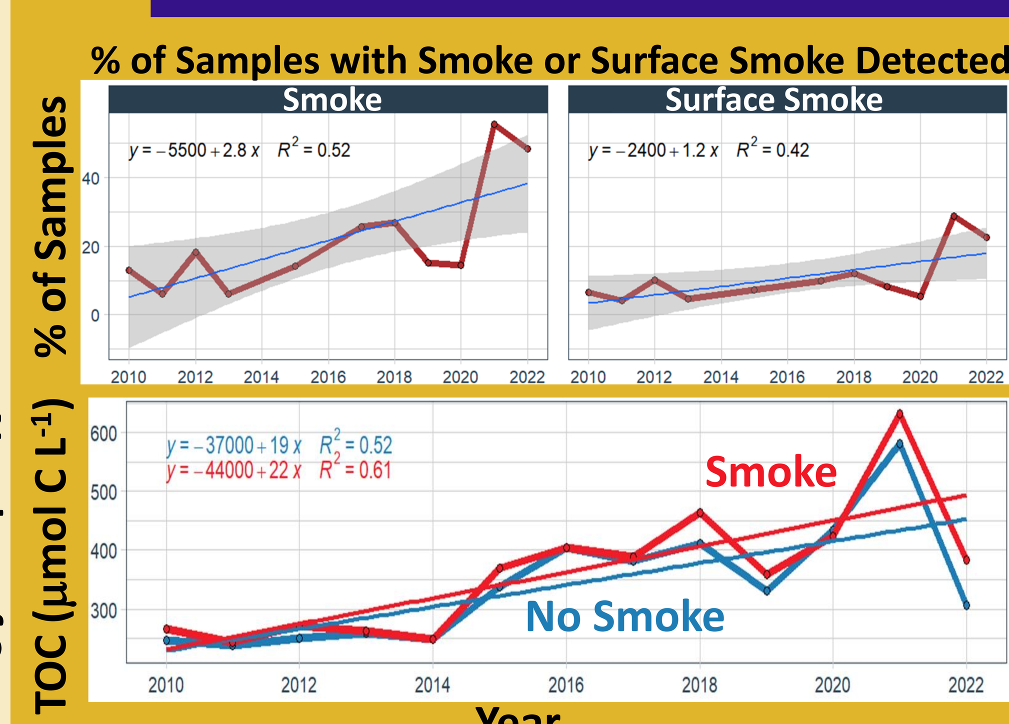


Bulk precipitation sites show much faster increasing trends during the growing season than the non-growing season

The wet-only deposition site shows little difference in trends by season, and much greater intraseasonal variability

- Trend analysis of precipitation chemistry data is separated into "growing" (April-October) and "non-growing" (November-March) seasons to investigate seasonal changes in overall trends in DOC deposition.
- At HB and SR, DOC trends are 3-7x greater during the growing season compared to the non-growing season, while TF shows little difference in trends by season.
- HB and SR measure bulk deposition, meaning the collector remains exposed to the atmosphere during both dry and wet periods, while TF only deploys during precipitation events.
- *Liptzin et al.(2022)* found that bulk deposition had 1.8-3.2x greater DOC than wet only deposition
- These findings could suggest that dry deposition of organic gases and particles may have a substantial contribution to the increasing organic carbon trends.

Wildfire Smoke Influence



- Wildfire smoke can release large amounts of organic carbon into the atmosphere.
- The NOAA Hazard Mapping System satellite smoke product was used to detect the presence of smoke over WFM (Schroeder et al., 2008).
- While smoke can lead to high TOC concentration for individual cloud water samples, the trend in median TOC concentrations does not change substantially when removing cloud samples expected to have been influenced by smoke.

Acknowledgements

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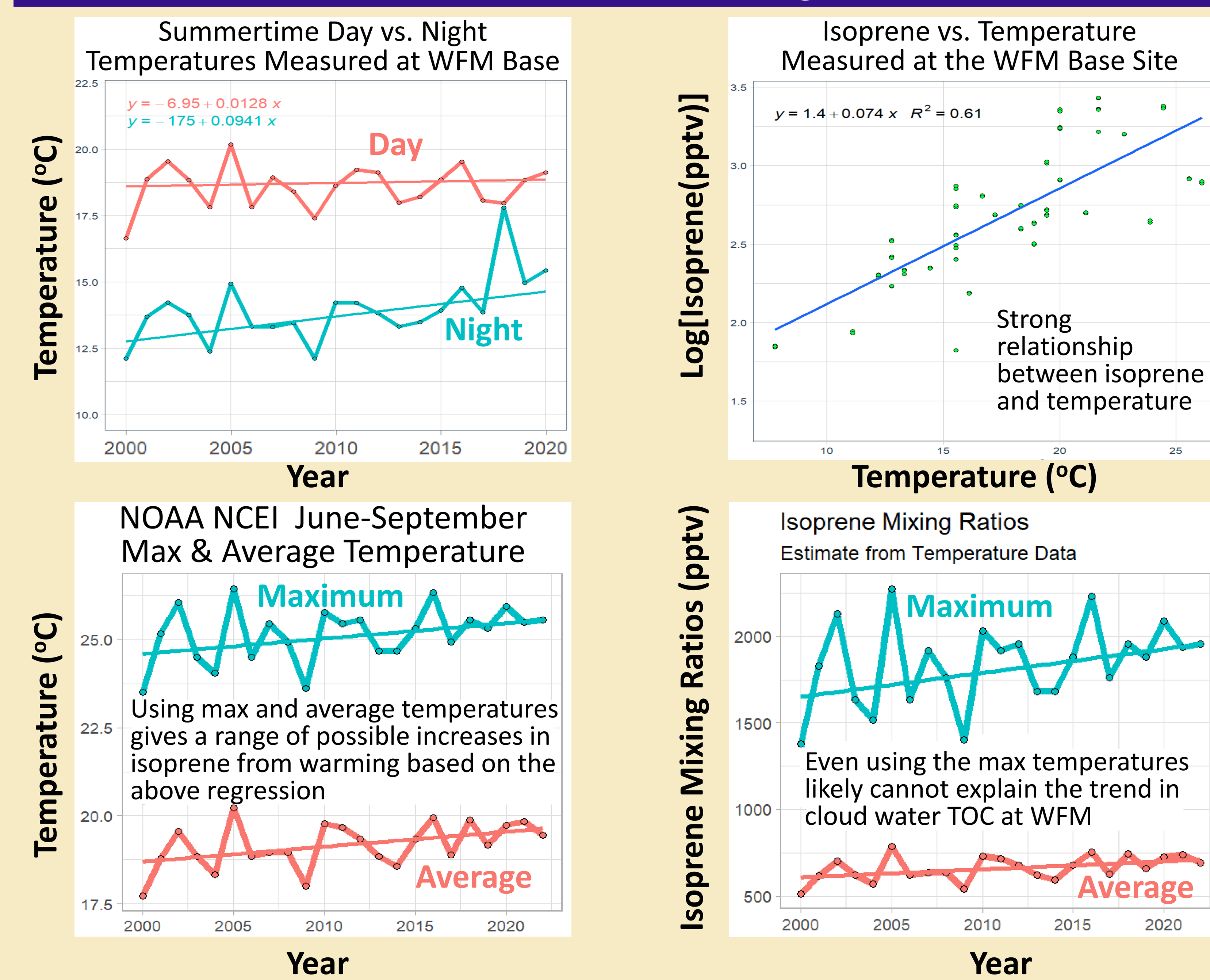
- 2022-2023 temperature data for the WFM Base site was obtained from the NYS Mesonet
- NOAA for their Hazard Mapping System and NCEI regional temperature trend analyses
- As current stewards of the cloud water chemistry program at WFM we honor the long-time stewards: the Mohawk and Haudenosaunee Nations

Increased Influence of Biogenic Emissions?



- Long-term measurements of Biogenic Volatile Organic Compounds (BVOCs) are sparse in the Northeast U.S. making it difficult to confidently estimate how BVOC emissions may have changed.
- Measurements of isoprene (typically the most abundant BVOC) were obtained at the WFM base site during the summer of 2022 and 2023 via whole air canister sampling.
- Isoprene concentrations measured in 2022 & 2023 show an exponential relationship with temperature very similar to measurements at WFM from the 1990s (*Gong & Demerjian,1997*) and TF from 2004-2008 (*Russo et al., 2010*), suggesting both a temporal and spatial robustness in the temperature/isoprene relationship.
- While temperatures have warmed at WFM, the bulk of this warming occurred at night. As isoprene is thought to be only emitted during periods of photosynthesis, it is unlikely that increased isoprene emissions in close proximity to WFM are responsible for the observed TOC trend.
- Long-term temperature datasets compiled by the NOAA National Centers for Environmental Information shows ~0.4°C/decade warming over the region (corresponding to an estimated 7-8% increase in isoprene concentrations/decade), which likely cannot explain the observed organic carbon trends on its own.

Conclusions

- There is a clear regional signal in atmospheric aqueous organic carbon in the Northeast U.S.
- The larger positive trends during the growing season in the bulk deposition sites suggest that changes in biogenic emissions are responsible for the majority of the observed trends.
- There is little evidence that increasing wildfire smoke influence is the major cause behind the trend in median TOC concentrations at WFM.
- While the Northeast has warmed since the 1990s, the warming likely isn't sufficient to explain the rate of increase in TOC or DOC in cloud water or precipitation.
- The lack of long-term datasets, particularly BVOC measurements in forested regions, creates a challenge for deeper investigation into the driving factors for the observed organic carbon trends in the Northeastern U.S.

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