Anthropogenic Influence on Reactive Chlorine in the Troposphere

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1. Introduction

Reactive halogens are important for atmospheric chemistry because they act as a sink for organic pollutants and greenhouse gases such as methane, as well as contribute to the formation of particulate matter. One form of reactive Cl, the Cl radical, is a small sink for methane (CH_4) that results in a large isotopic fractionation. The main source of reactive halogens is from acid-catalyzed reactions between ozone and sea-salt aerosol and the ocean surface. Based on modeling studies, it is thought that anthropogenic activity has increased the atmospheric abundance of reactive halogen concentrations due to anthropogenic increases in ozone and atmospheric acidity [Sherwen et al., 2016]. Here, we use a Greenland ice-core record of chloride (Cl^-) to investigate if these observations are consistent with this hypothesis.

2. Does a Greenland ice-core record reactive Cl?

$$xsCl = \frac{conc\ Cl}{conc\ Na \times 1.8}$$

Equation 1. Calculates xsCl ratio by using the measured concentration of Cl divided by the measured concentration of Na multiplied by the standard mass? ratio of Cl / Na of seawater (= 1.8)

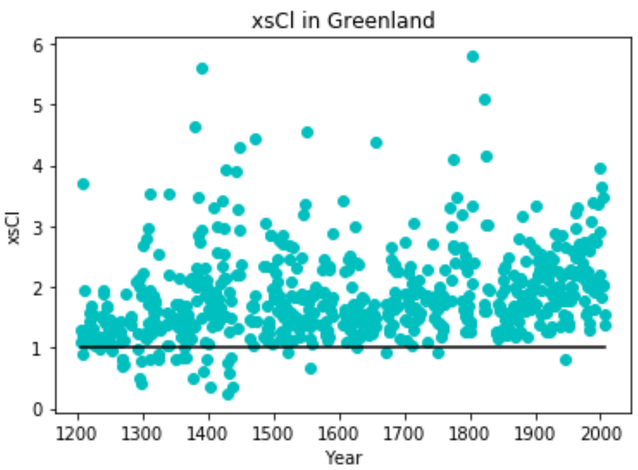


Fig. 1 Concentration xsCl plotted against year across entire Greenland Ice Core record, with a line showing when the value is equal to 1. xsCl > 1 indicates reactive Cl.

3. Has reactive Cl increased in the Industrial Era?

The formation of reactive chlorine from sea salt aerosol will increase the atmospheric lifetime of chlorine, allowing it to be transported farther from it's source, leading to an excess of Cl^- relative to Na^+.

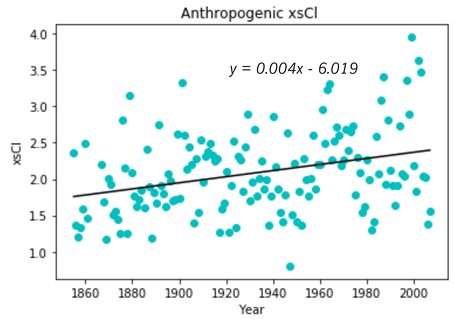
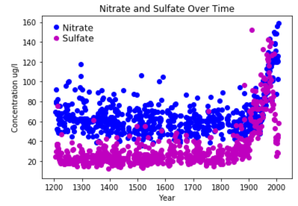


Fig. 2 Plot of xsCl vs. time over the anthropogenic era (1850 – present). The small increase in xsCl over the 157 year period is smaller than the interannual variability, suggesting an insignificant influence of anthropogenic activity.

4. Is there a relationship between xsCl and acidity?



$$Acidity = 2 \times Sulfate + Nitrate$$

Equation 2. Acidity is defined as the sum of 2 times sulfate and nitrate in mol/l

Fig. 3 Nitrate, and Sulfate plotted together over the entirety of the Greenland Ice Core record, with volcanic years (Cole-Dai et. al 2013) ± 2 removed.

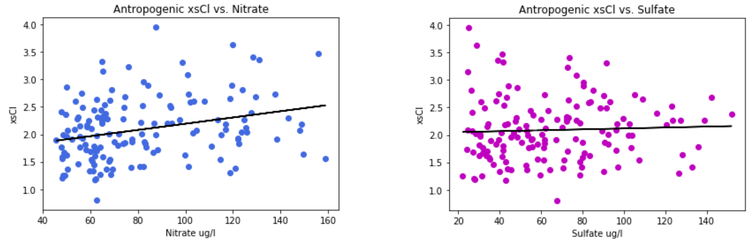


Fig. 4 Plots of nitrate and sulfate vs xsCl. The slope of the linear regression for nitrate vs xsCl is 0.0057 and the slope of the linear regression for sulfate vs xsCl is 0.0008.

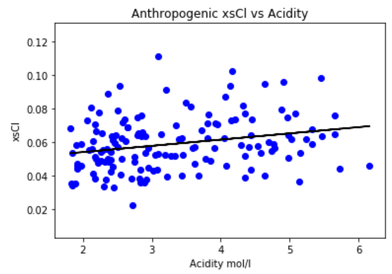


Fig. 5 Plot of xsCl vs Acidity with a linear regression slope of 0.0037. This plot also demonstrates an insignificant increase in xsCl's impact on acidity.

5. Conclusions

- xsCl > 1 is recorded throughout the entirety of the Greenland Ice Core record (1200 – 2006 C.E.)
- The observations of ice-core xsCl suggest an insignificant increase in reactive Cl during the anthropogenic era.
- Although the formation of reactive Cl is acid-catalyzed, the observations do not show a significant relationship between xsCl and acidity, suggesting other factors are limiting it's formation in the atmosphere.
- The xsCl observations suggest that although reactive Cl is highly variable over time, there are no significant trends in the anthropogenic era. This suggests that any observed trends in the CH_4 growth rate or CH_4 isotopes are not influenced by changes in reactive Cl.

References

- Cole-Dai J., Ferris D. G., Lanciki A. L., Savarino J., Thiemens M. H. and McConnell J. R. (2013) Two likely stratospheric volcanic eruptions in the 1450s C.E. found in a bipolar, subannually dated 800 year ice core record. *Journal of Geophysical Research: Atmospheres* **118**, 7459–7466.
- Stanford Mineral Makeup of Seawater. (n.d.). Retrieved from https://web.stanford.edu/group/Urchin/mineral.html
- Sherwen, T., et al. (2017). "Halogen chemistry reduces tropospheric O_3 radiative forcing." Atmos. Chem. Phys. **17: 1557-1569**.