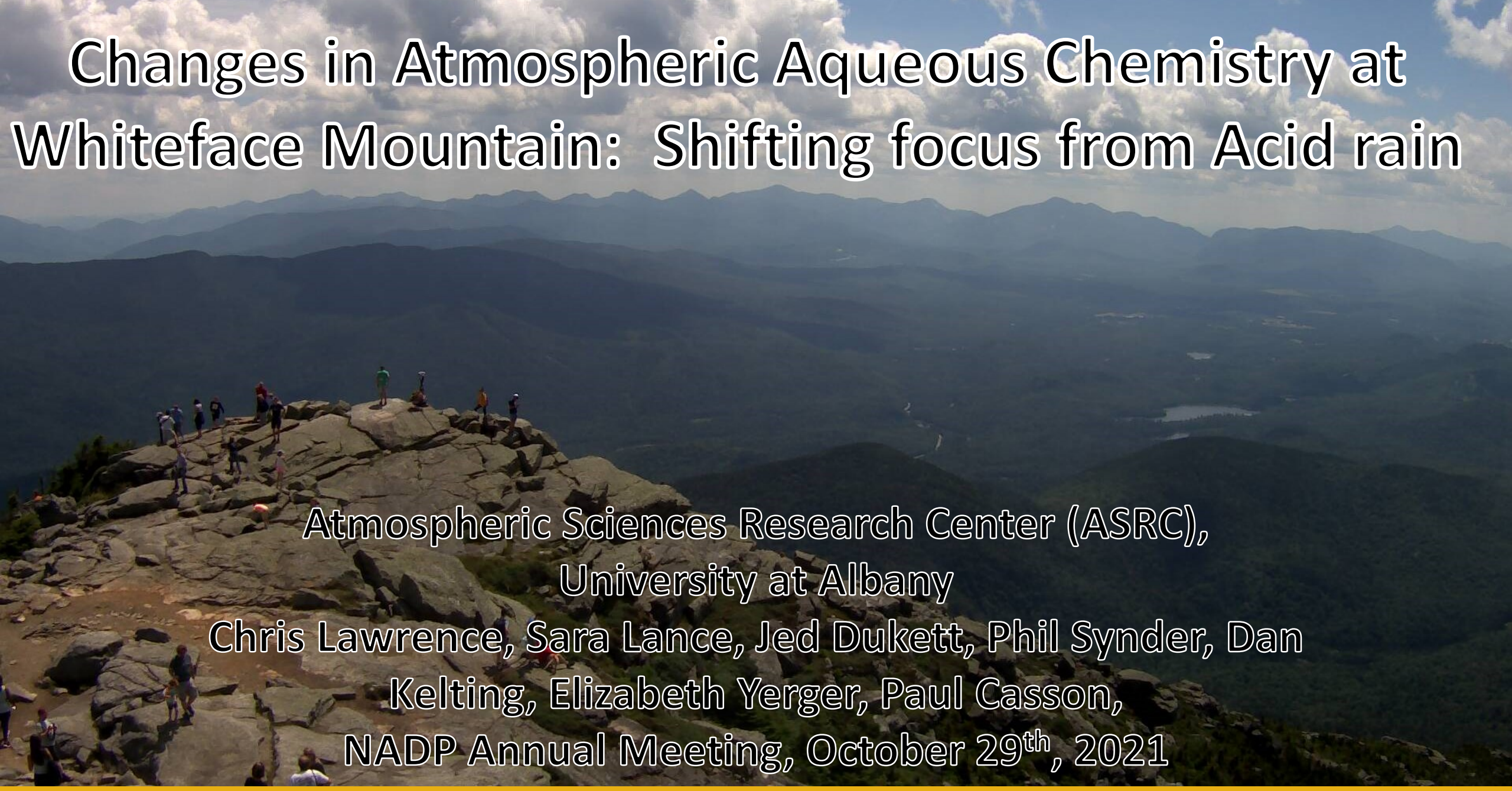
Changes in Atmospheric Aqueous Chemistry at Whiteface Mountain: Shifting focus from Acid rain

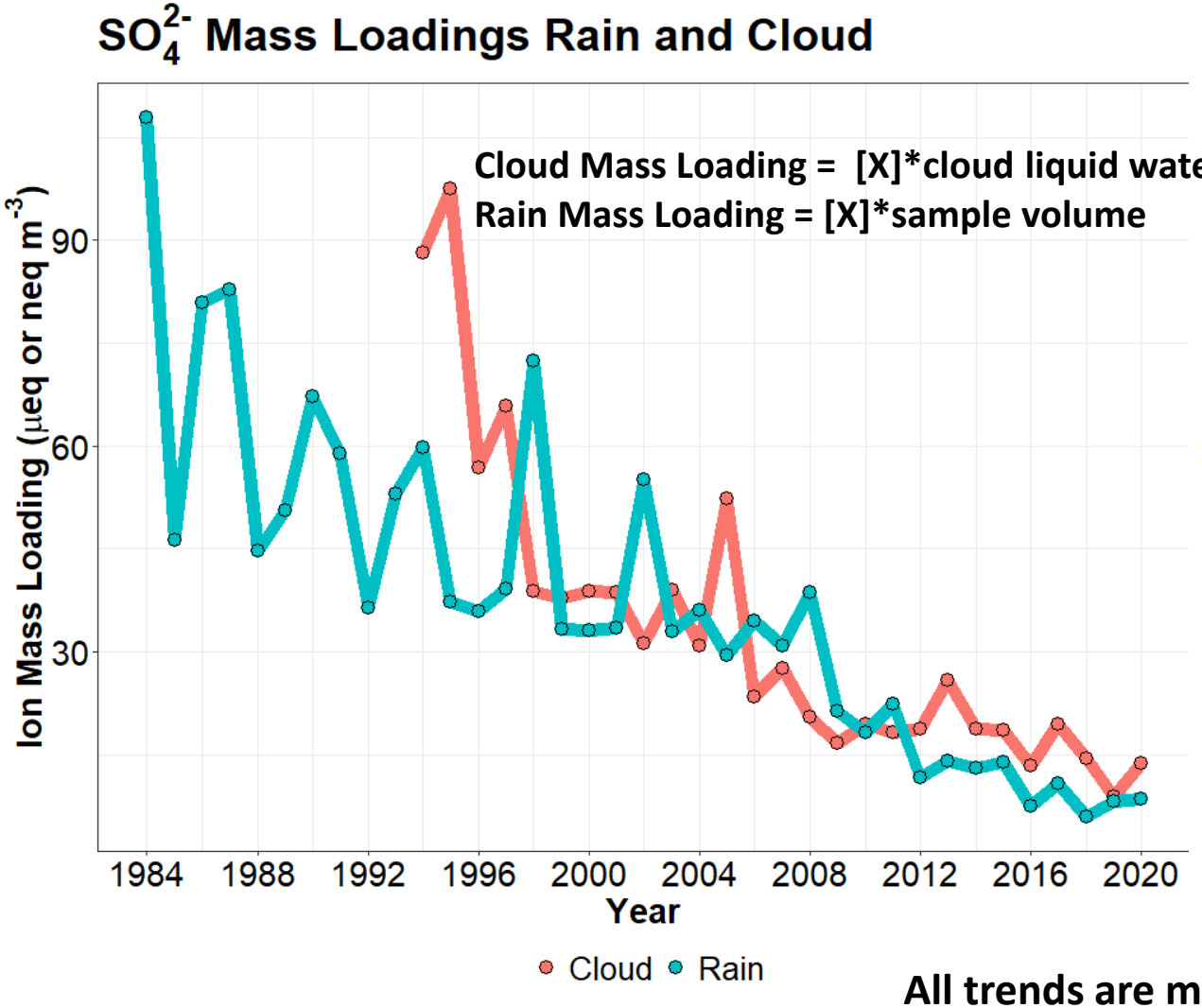


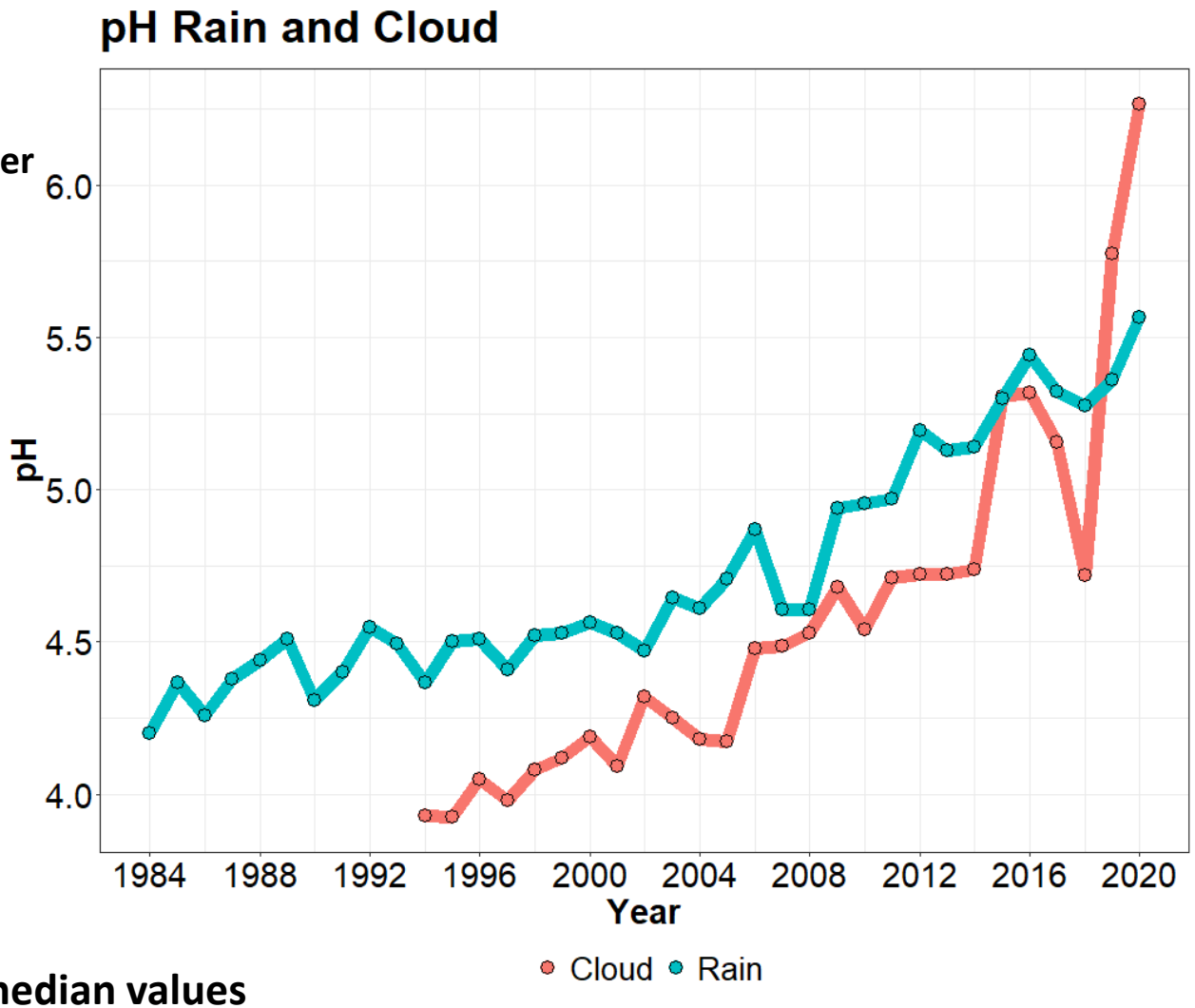
Atmospheric Sciences Research Center (ASRC),
University at Albany
Chris Lawrence, Sara Lance, Jed Dukett, Phil Synder, Dan Kelting, Elizabeth Yerger, Paul Casson,
NADP Annual Meeting, October 29th, 2021

Historic Cloud and Rain Water Monitoring Sites

- Contains historic NADP NTN site founded in 1984 and cloud water monitoring site with monitoring beginning in 1994
- Largely has investigated acid deposition
- Clean air act amendments have led to significant reductions in acid deposition, contributing to changes in the chemical system
- This work focuses on the trend in the changing chemical system at Whiteface and its implications with emphasis on species besides SO_4^{2-} and NO_3^-

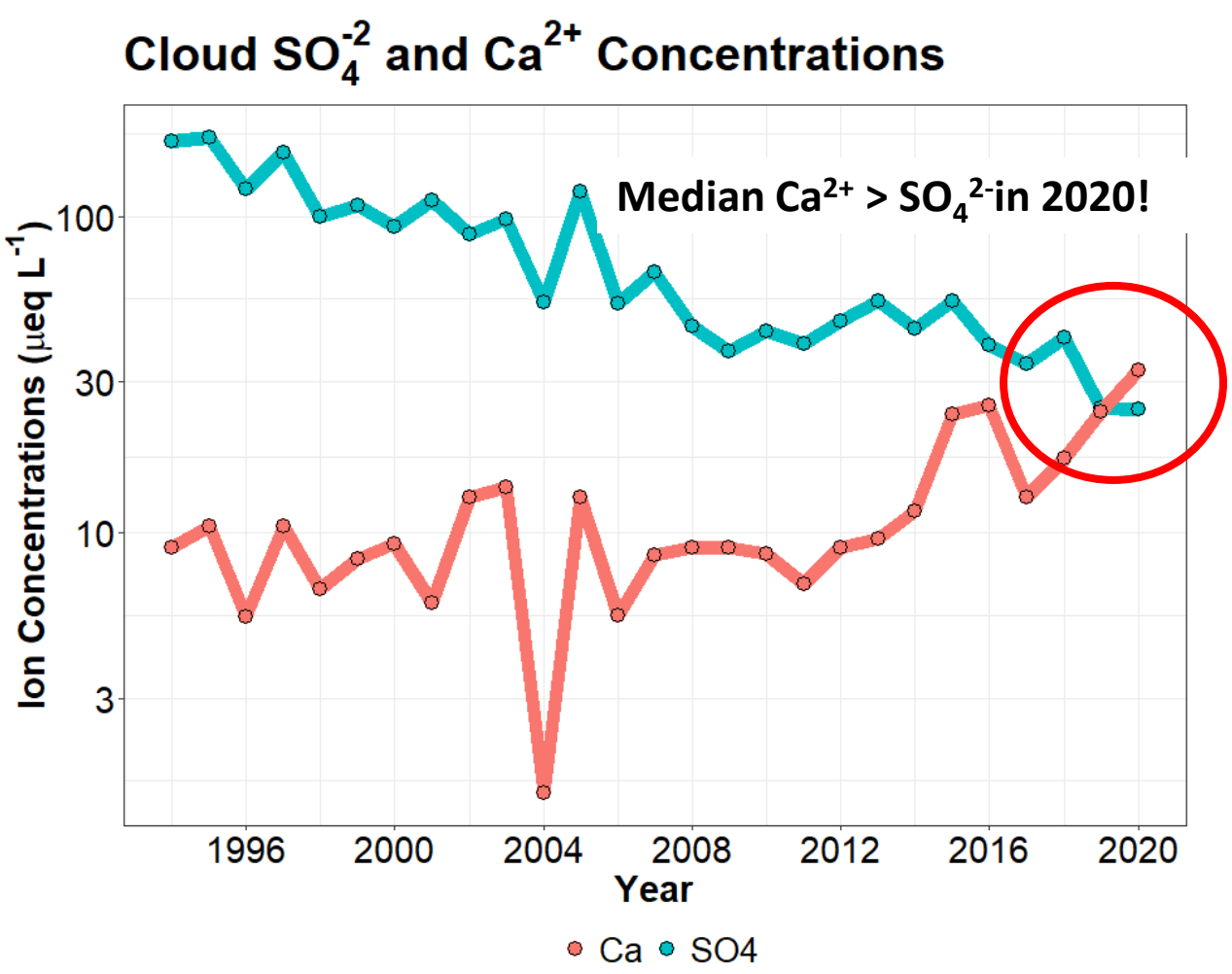
Significant Progress on Acid Deposition at WFM

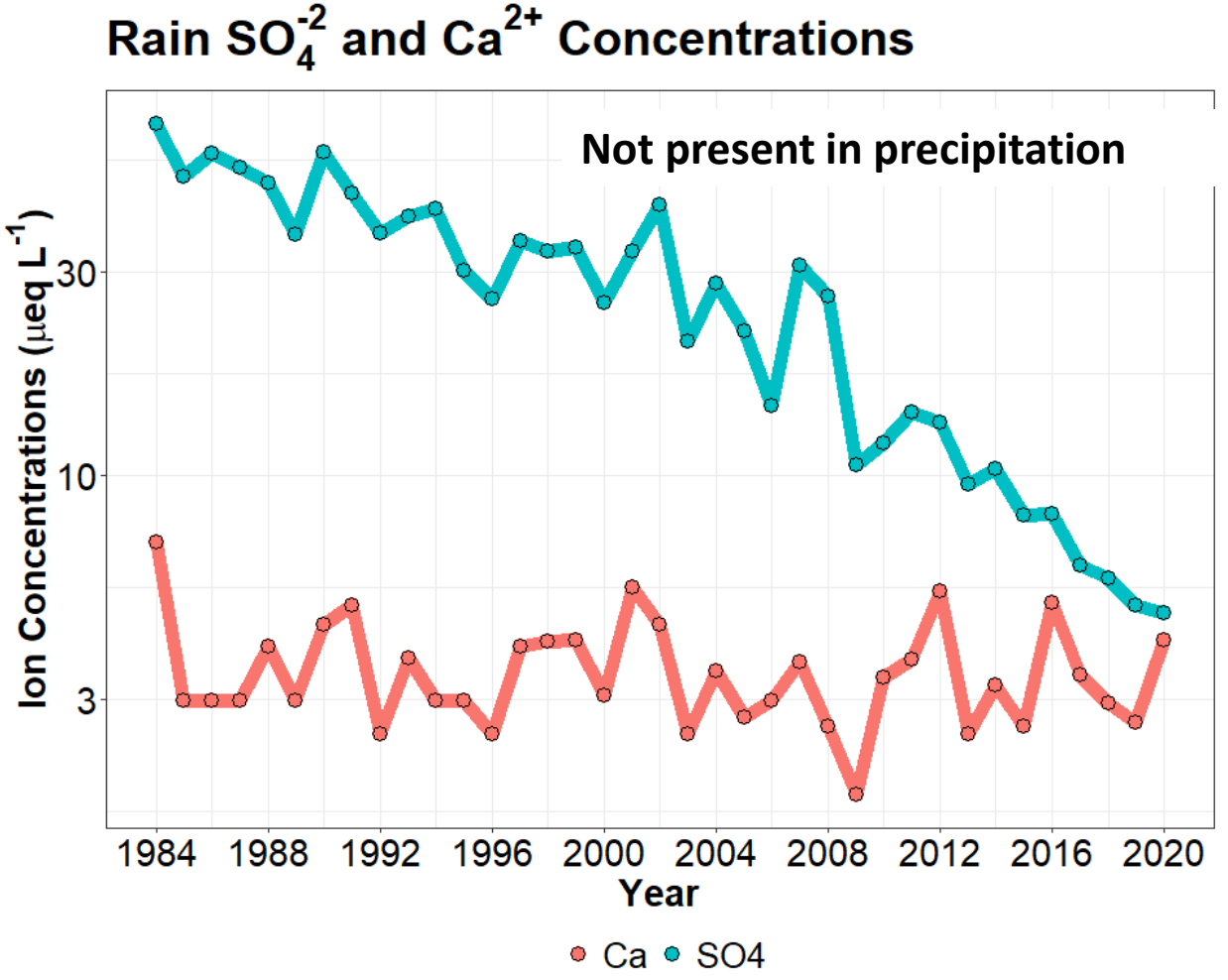




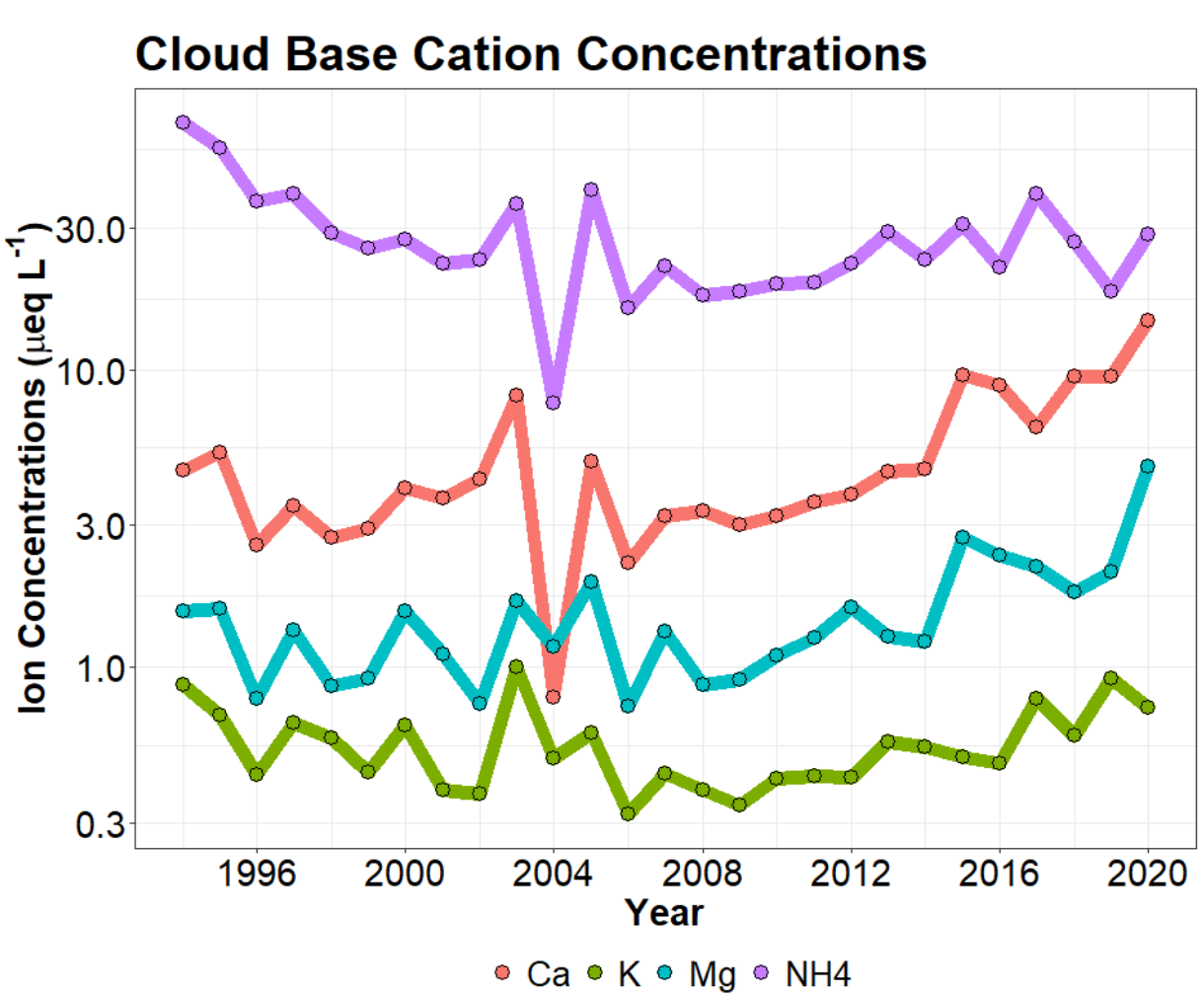
All trends are median values

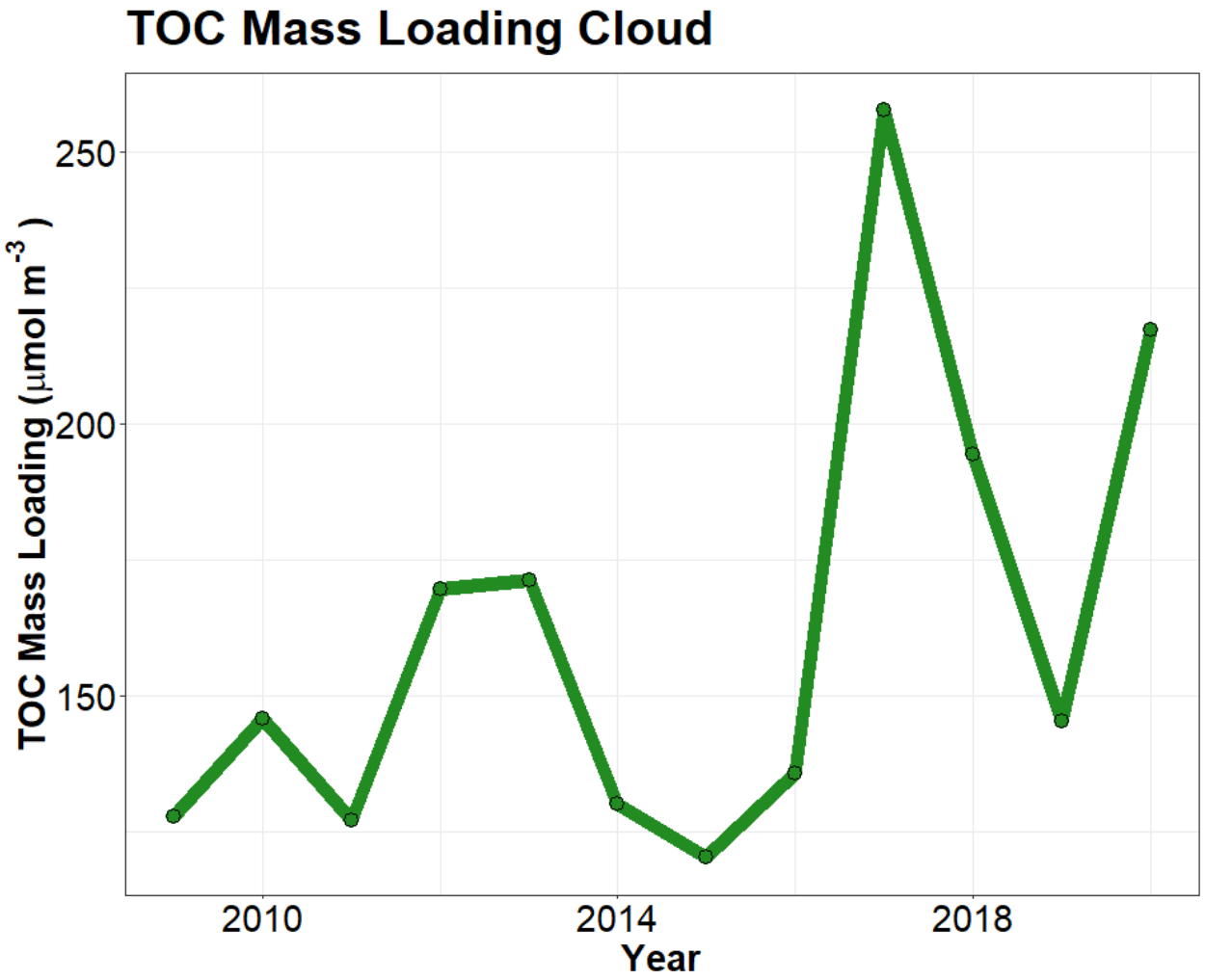
A Changing Chemical System: Ca^{2+}





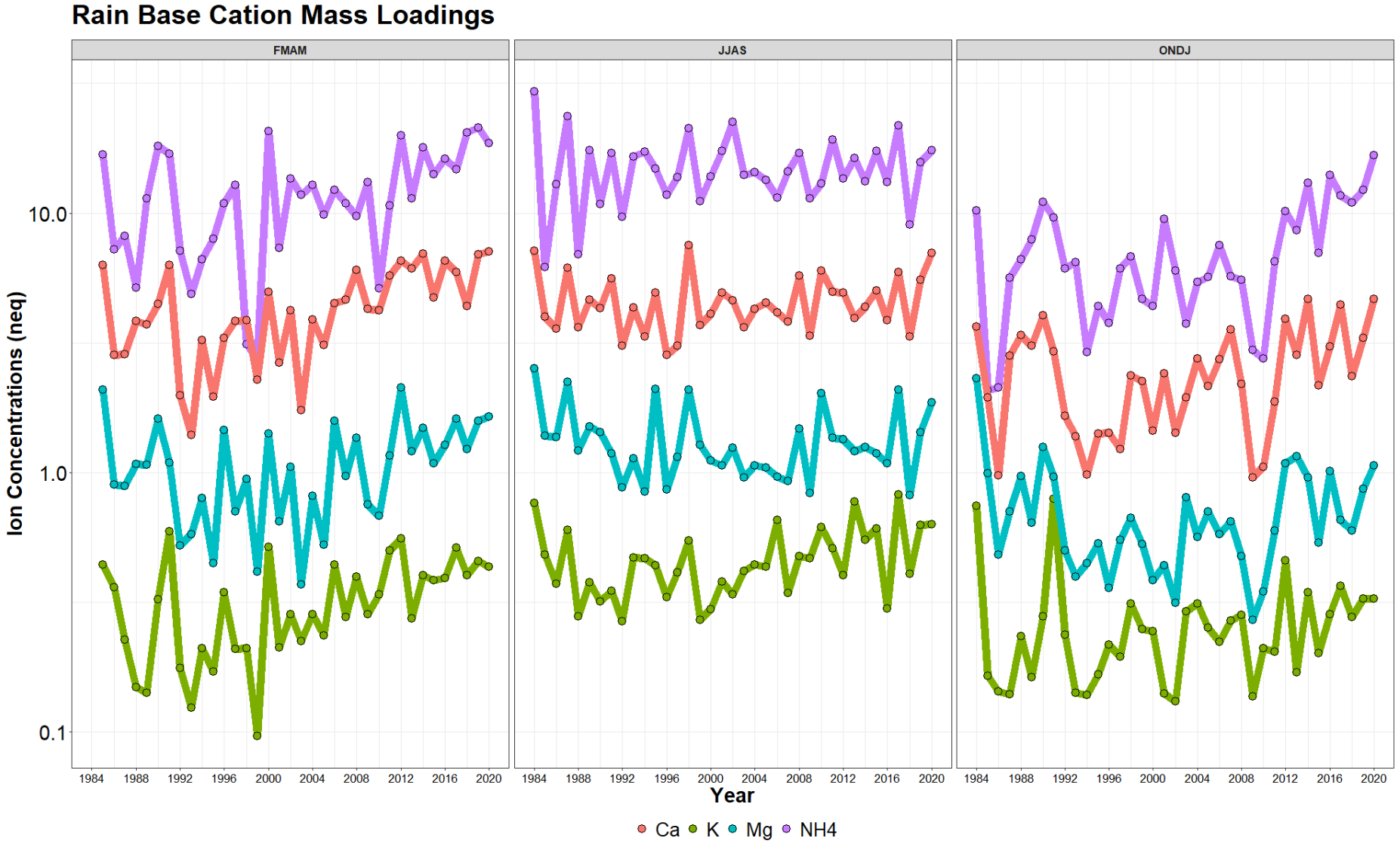
A Changing Chemical System: Base Cations and TOC



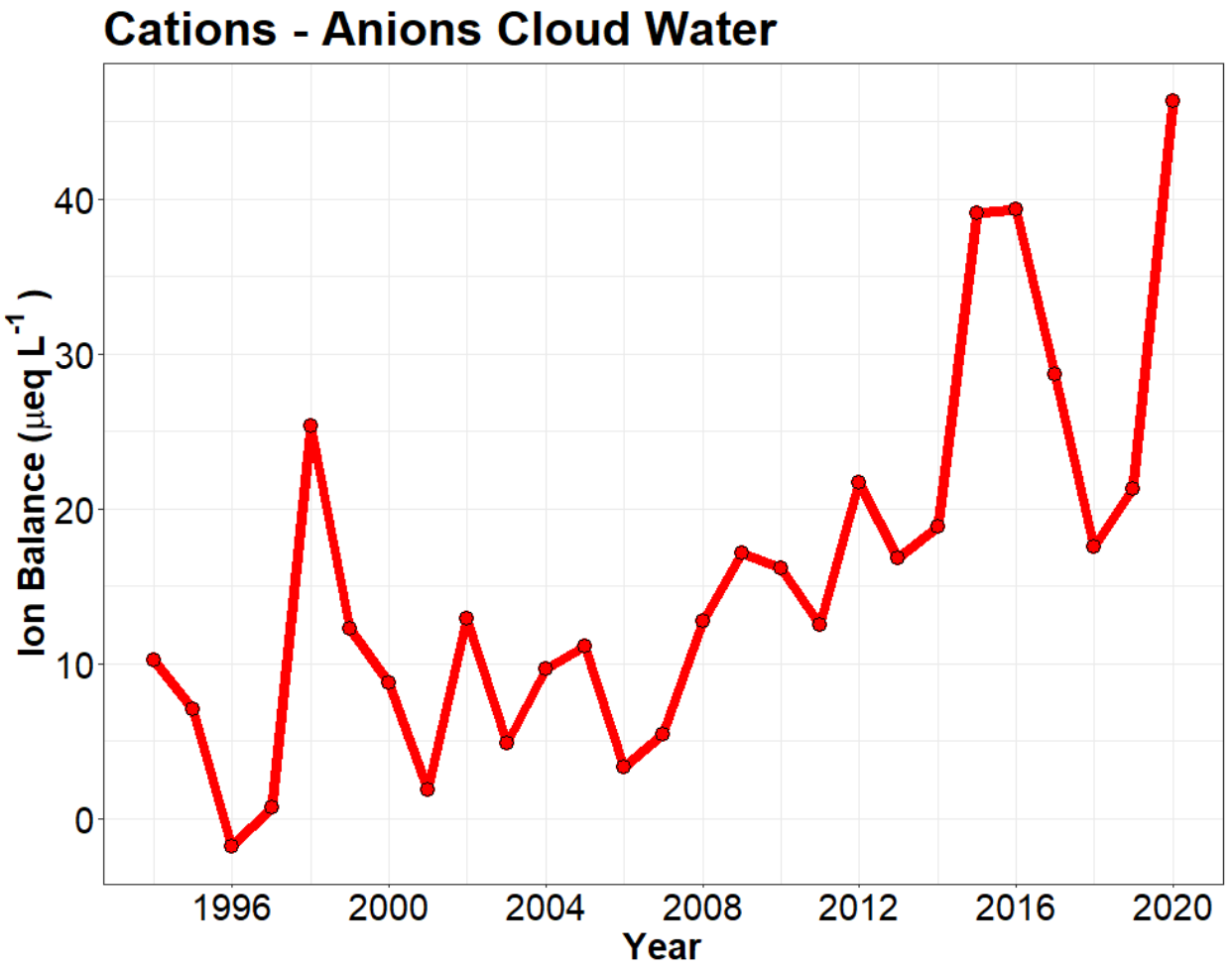


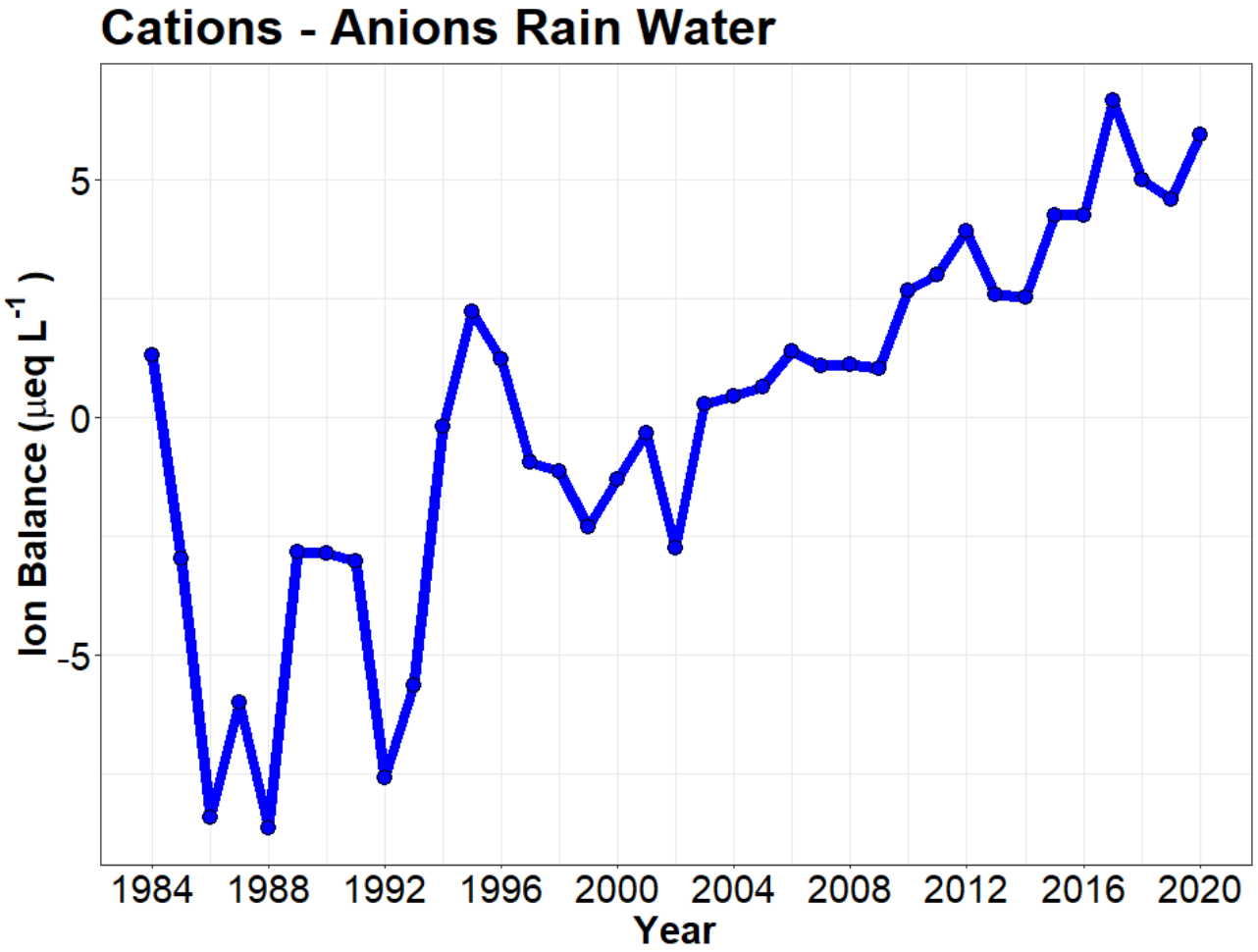
A Changing Chemical System: Base Cations

- No trends in Ca, Mg, and NH_4^+ in NTN data for cloud collection season
- Other season however show strong increasing trends for base cations, particular FMAM
- Additionally, K^+ may be increasing during cloud collection, implying different sources than Ca, Mg and K.
- Seasonality needs to be considered during trend analysis

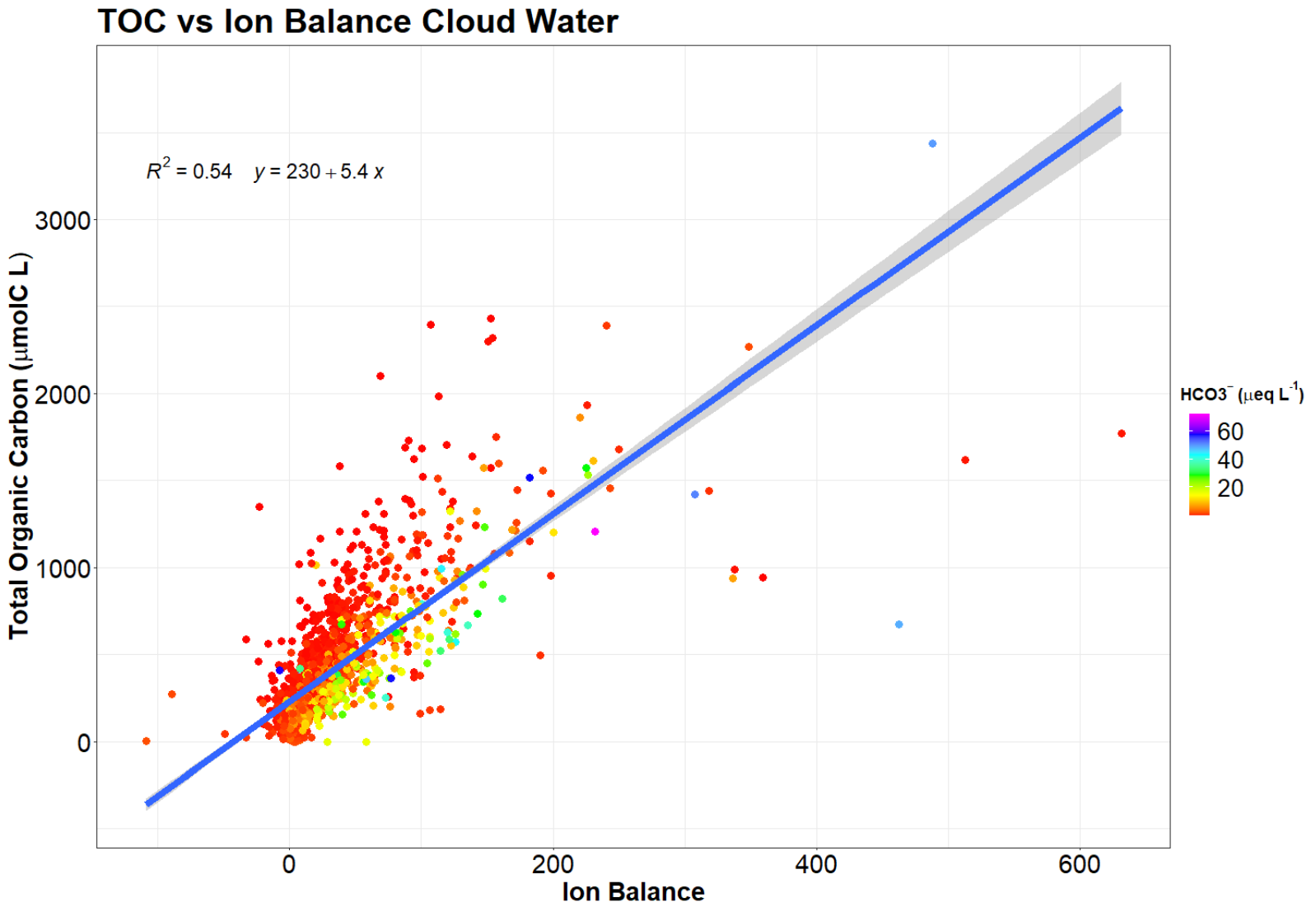


A Changing Chemical System



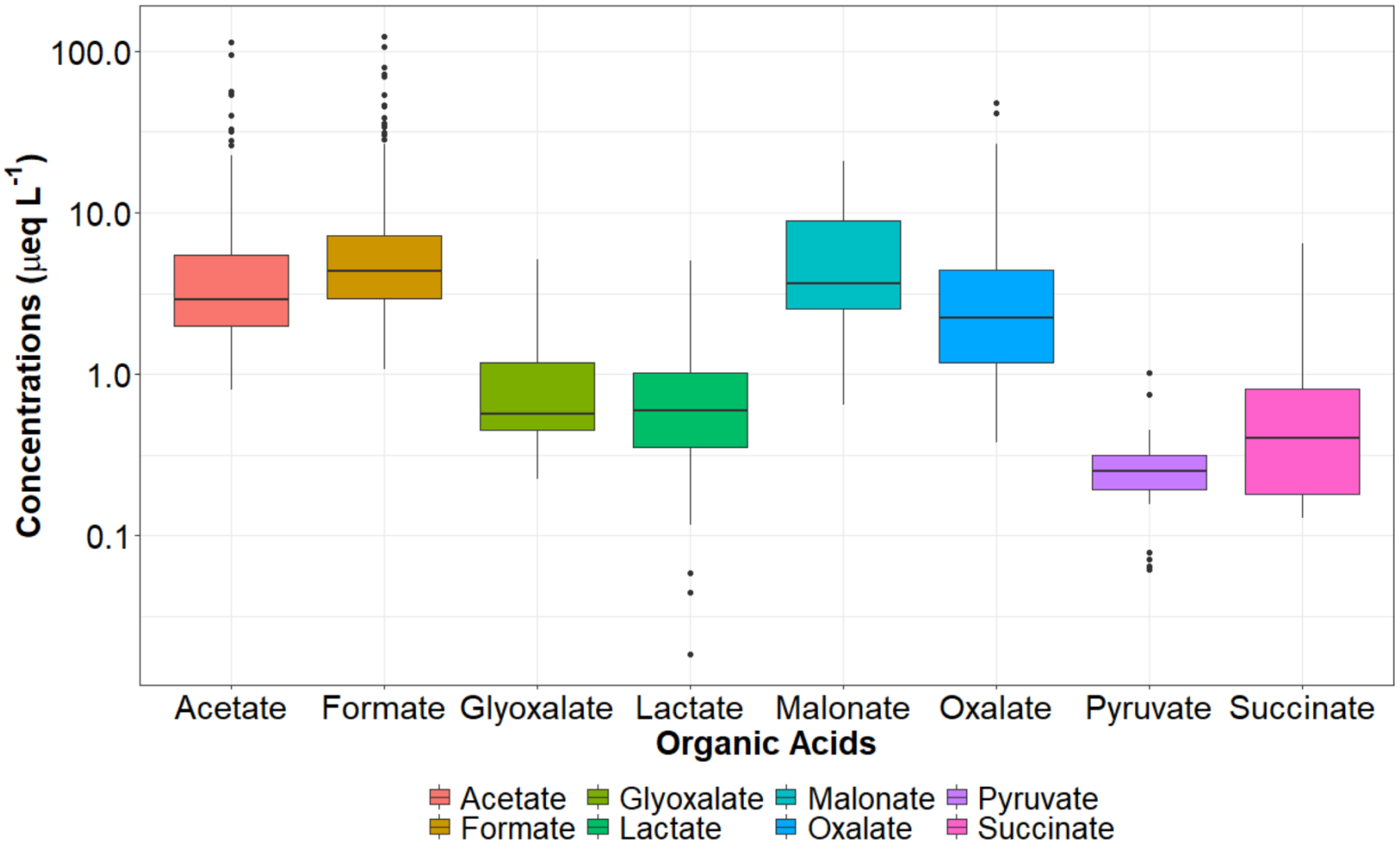


TOC and Ion Balance

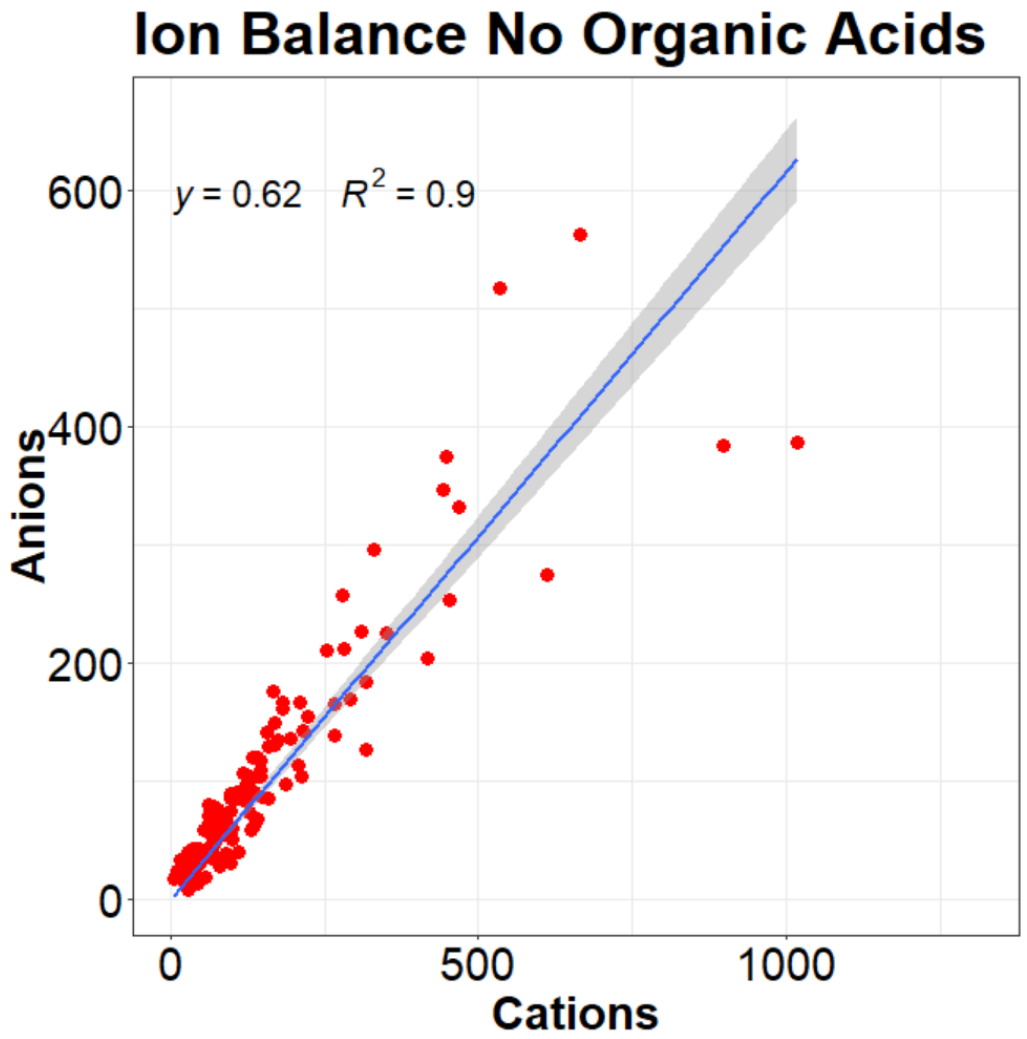


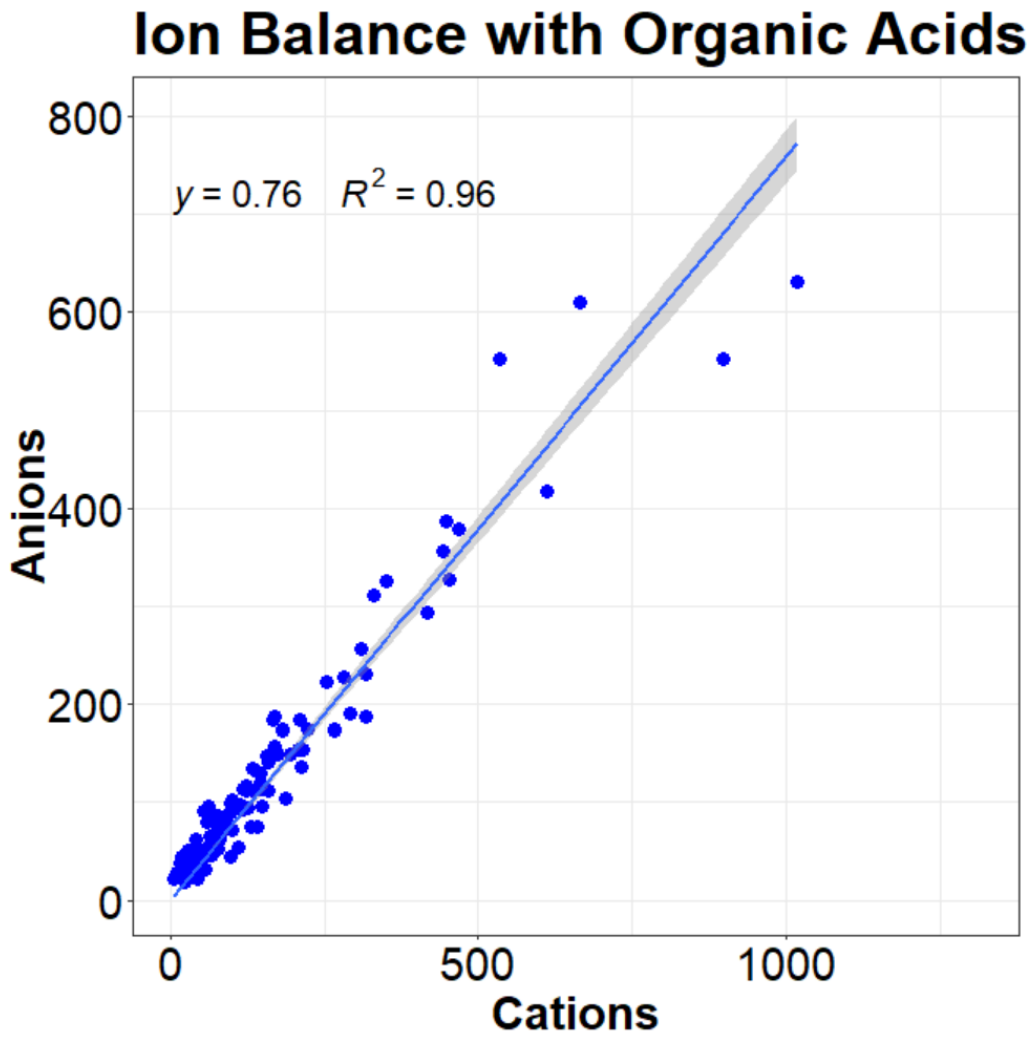
Measured Organic Acids

- Organic Acids measured in 2018 and 2019
- Formate, Acetate, Malonate and Oxalate highest concentrations
- Sources of organic acid complicated and highly uncertain



TOC and Ion Balance





So Far:

- Major Reductions in SO_4^{2-} with a corresponding increase in pH
- Increasing Concentrations in Ca^2, Mg^{2+}, and K+ and TOC, in cloud water, but not in rain water during the summer.
- Becoming clear the current measurements can't characterize the chemical system
- What are the major sources of these analytes and how are these trends changing over time?

Positive Matrix Factorization (PMF)

- Statistical receptor model commonly used in air quality for source apportionment
- Can split an observation (x_{ij}) into species profile (f_{kj}), the contribution of factor (g_{ik}) and a residual term (e_{ij}).

  - i = sample, j = chemical species, k = factor

- Factors are created by using weighted least squares method to minimize term Q. Terms weighted by measurement uncertainty.
- Used EPA PMF 5.0 Software for model calculations
- Ran analysis for 1994-2020 cloud data and summer-time 1984-2020 rain data. Cl and TOC not included in cloud water (CL inconsistent for 2018 and 2019, TOC only available from 2009-2020)

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \qquad Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}}\right]^2$$

PMF Results Cloud Water:

Factor 1: Crustal

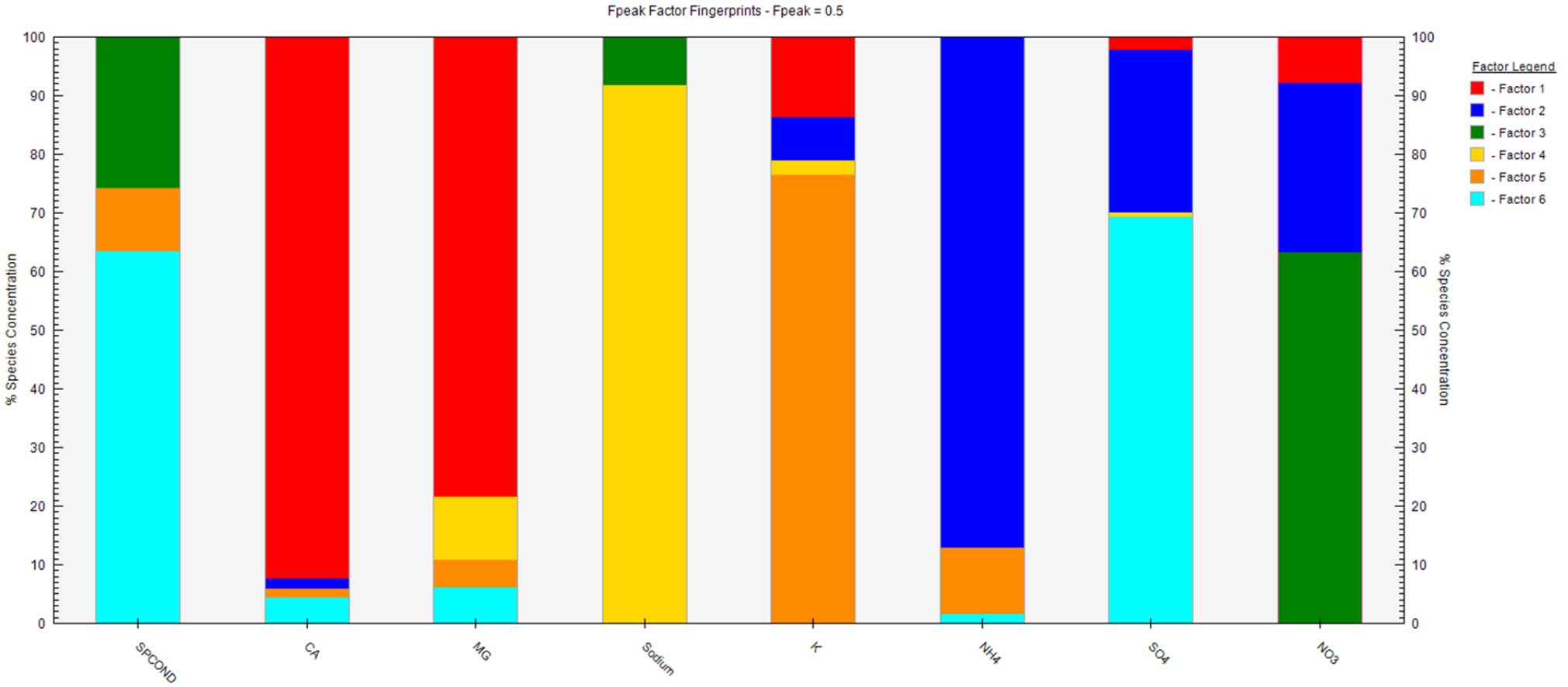
Factor 2: Agriculture

Factor 3: Motor Vehicles

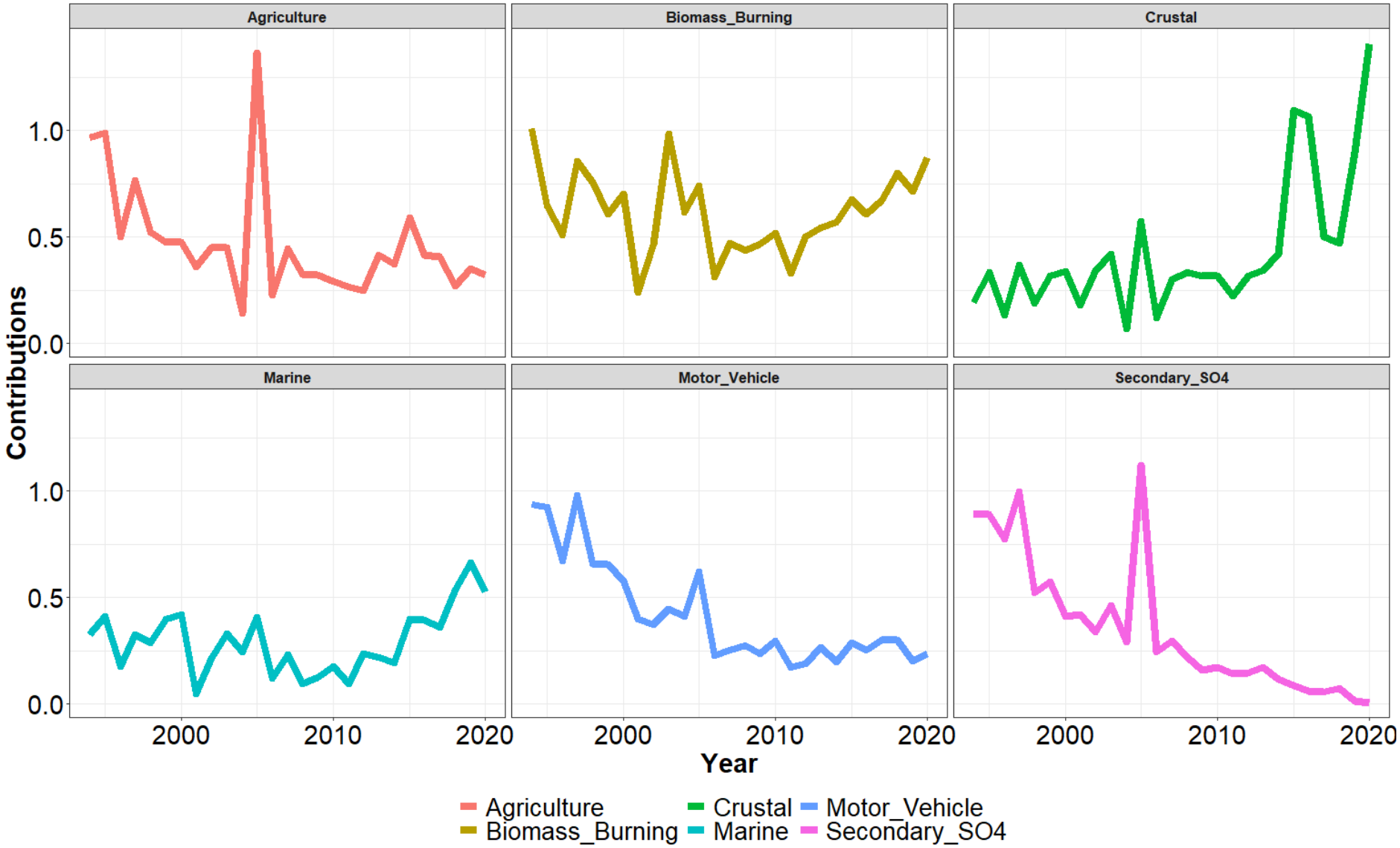
Factor 4: Marine

Factor 5: Biomass Burning

Factor 6: Secondary SO_4^{2-}



Trends in Factor Contributions: Clouds



Can the Cloud Water Factors Explain TOC?

$$TOC = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_5 x_1 x_2$$

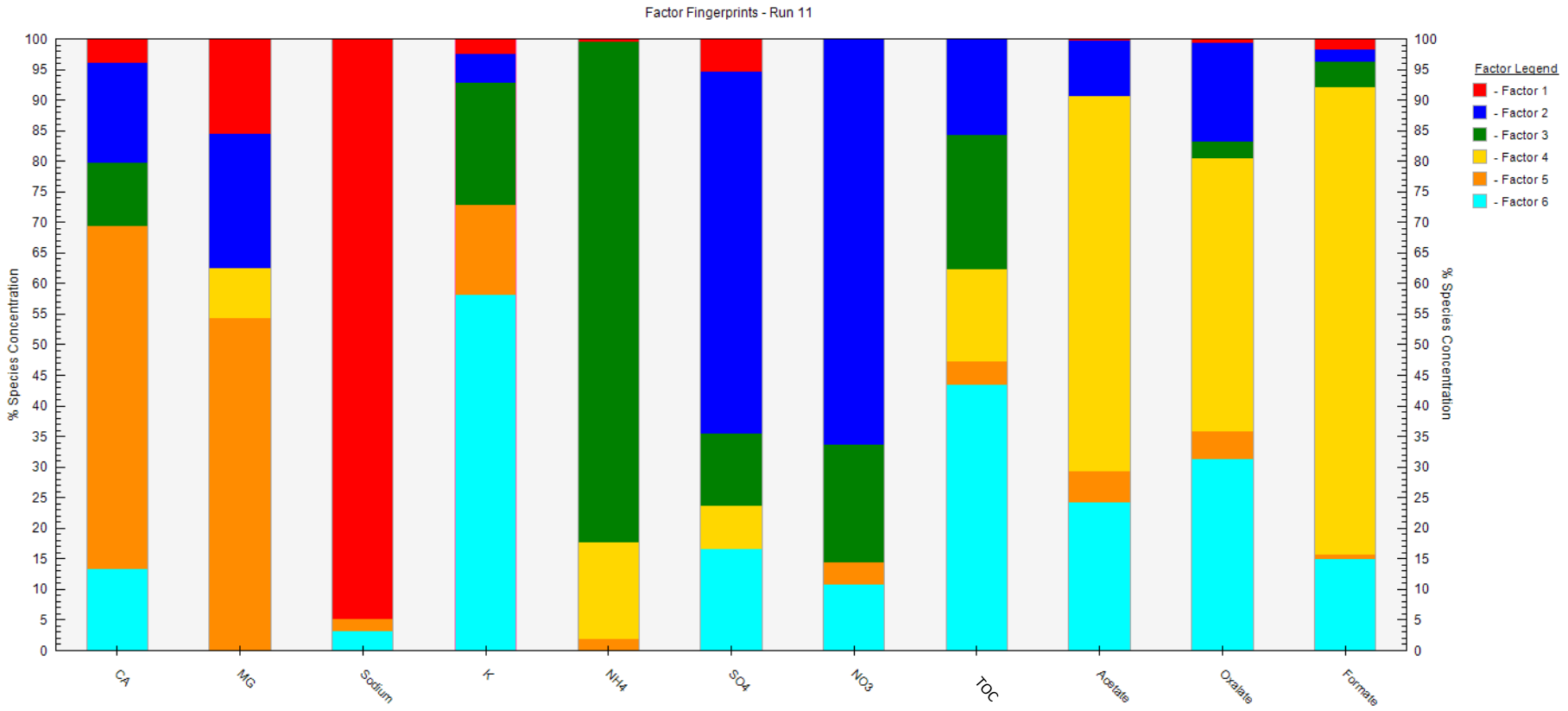
term	estimate	std.error	statistic	p.value
(Intercept)	0.4089388	0.0404256	10.115831	0.0000000
Biomass_Burning	0.7211921	0.0312868	23.050973	0.0000000
Agriculture	0.6579855	0.0461090	14.270210	0.0000000
Secondary_SO4	0.2559209	0.0969919	2.638581	0.0084132
Crustal	0.1153735	0.0315749	3.653965	0.0002673
Biomass_Burning_x_Agriculture	-0.1885260	0.0158799	-11.872015	0.0000000

r.squared	adj.r.squared	sigma	statistic	p.value	df	logLik	AIC	BIC	deviance	df.residual	nobs
0.6677017	0.666573	0.5774314	591.551	0	5	-1282.518	2579.036	2616.126	490.8046	1472	1478

- Multiple linear regression with standardized regression coefficients finds that Biomass Burning and Agriculture show major connections to TOC (though also correlate with each other
- Model only can explain ~67% of the variation, implying a missing factor for TOC not covered in the PMF analysis
- We have organic acid data, maybe that can tell us a little bit more information

PMF Results with Organic Acids

- Organic acids might be able to give us more info
- Secondary SO_4^{2-} and Motor Vehicle factors seem to disappear and become a fossil fuel factor instead
- Organic acids (particularly Formate) could be an indication of local biogenic influence
- TOC largely coming from biomass burning, biogenic, fossil fuel and agriculture



Factor 1: Marine Factor 2: Fossil Fuel Factor 3: Agriculture Factor 4: Biogenic? Factor 5: Crustal Factor 6: Biomass Burning

PMF Result: Rain

Factor 1: Agriculture

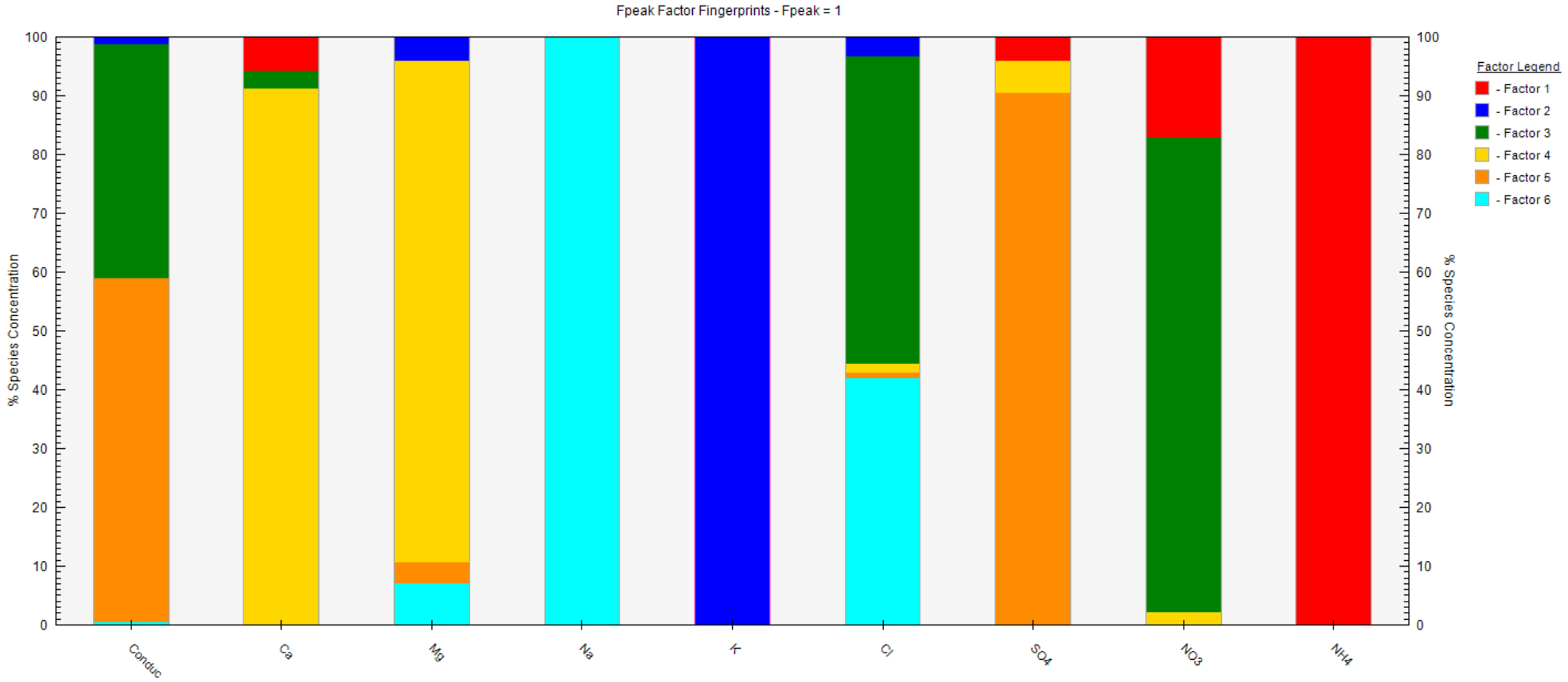
Factor 2: Biomass Burning

Factor 3: Motor Vehicles

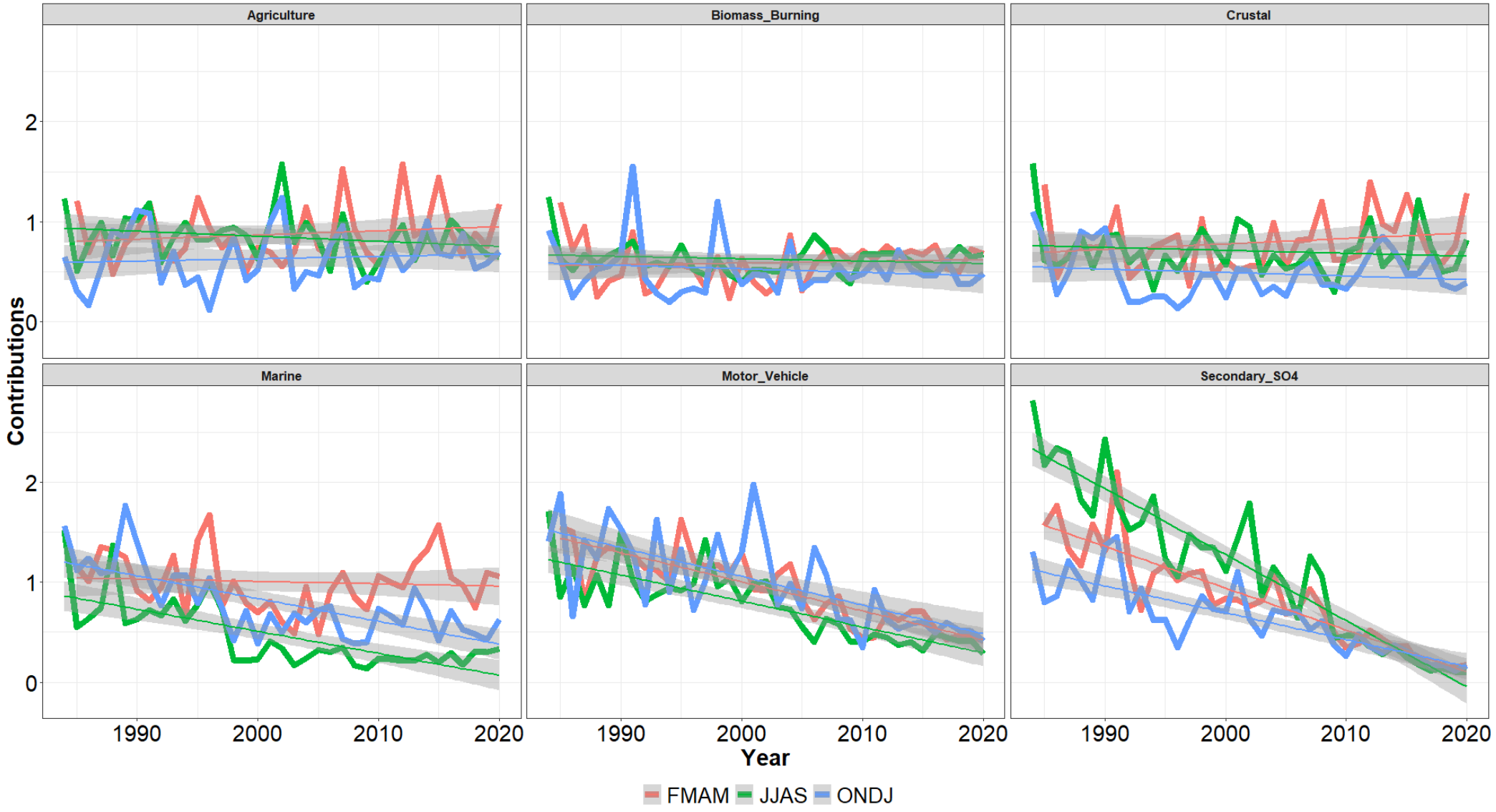
Factor 4: Crustal

Factor 5: Secondary SO_4^{2-}

Factor 6: Marine

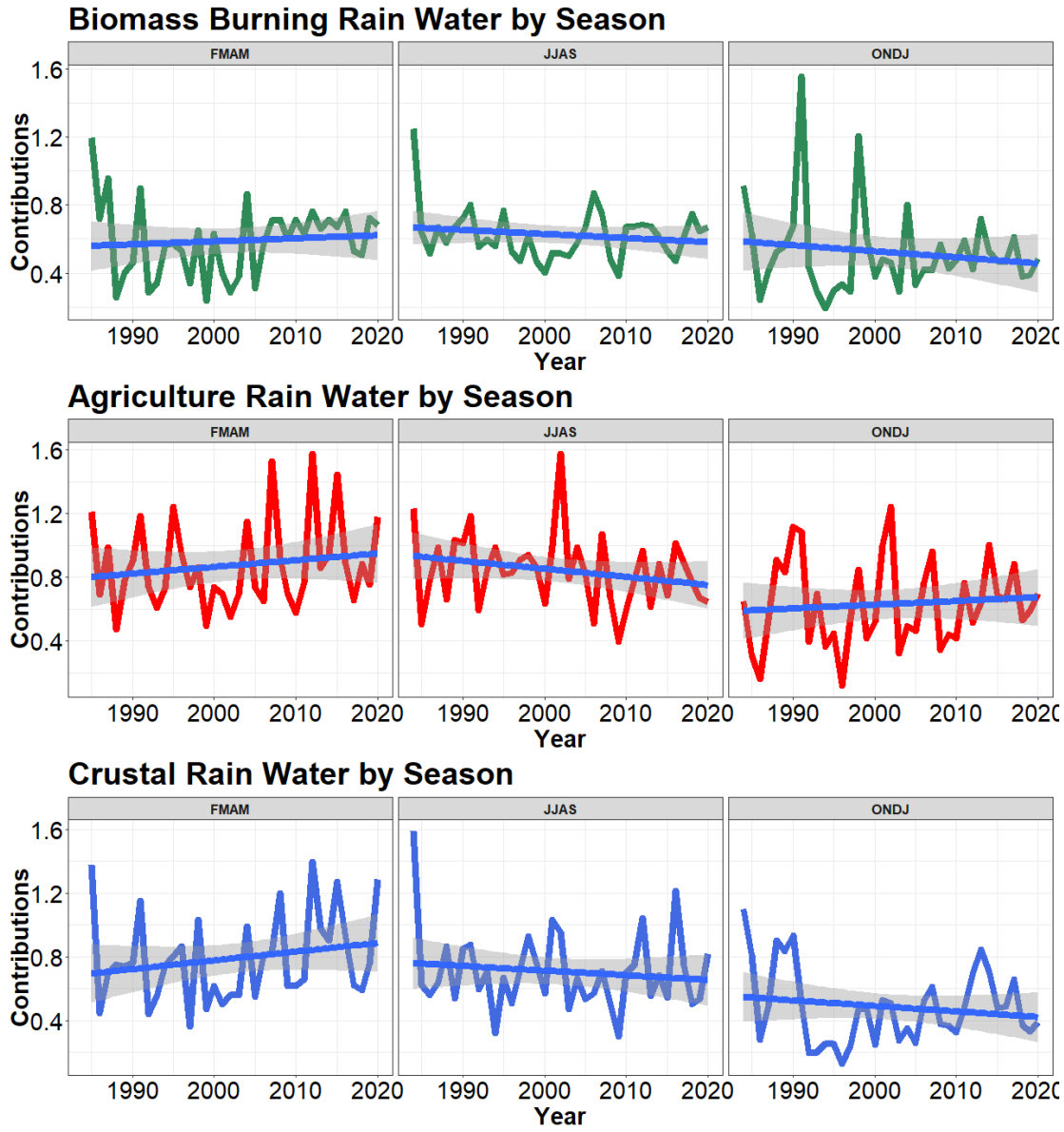


Trends in Factor Contributions: Rain



Factor Contributions in 3 Major Factors

- Season makes a big difference in the trends in factor contribution
- Virtually no change for Biomass, Agriculture or Crustal during summer
- Possible increasing trend for all 3 factors in FMAM
- Significant variation in precipitating vs non-precipitating clouds



Implications

- Changes in emissions and climate change are dramatically changing the chemical system in both rain and cloud water at WFM (and likely much of the Northeastern United States)
- Clear increasing trend in base cations in cloud water, but not rain water. Where are they depositing?
- SO_4^{2-} is no longer the dominate chemical species in the system, with unmeasured organic carbon species playing a increasing role.
- Reductions of SO_4^{2-} but no changes in NH_4^+ imply changes in how NH_3/NH_4^+ is interacting in the atmosphere with important implications for nitrogen deposition
- Changes in cloud pH can change partitioning of soluble gases and the chemistry of both inorganic and organic species (SO_4^{2-} formation, secondary organic aerosol formation)
- Changes in aerosol mass and chemical composition can have large (and highly uncertain) effects on direct and indirect (cloud formation) radiative forcings.

Acknowledgements

Extra Slides (1) Bicarbonate Estimates