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Decision Tree Analysis to Identify Factors that Impact Methylmercury Fraction in Wet Deposition

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2016 Annual Meeting and Scientific Symposium of the National Atmospheric Deposition Program.
October 31 – November 4, 2016, La Fonda on the Plaza, Santa Fe, NM

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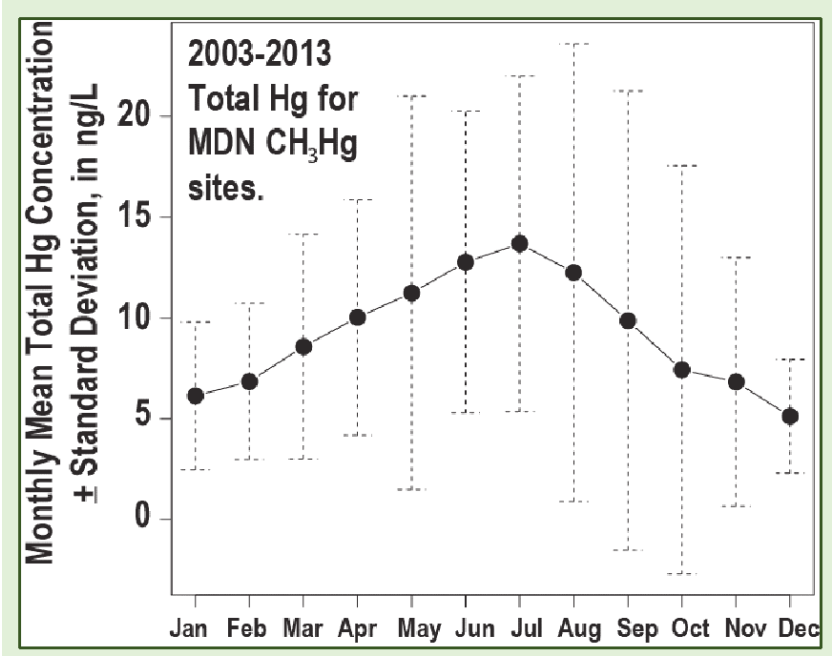
NADP'S MDN MethylImercury Dataset

RELEASED FALL 2015
6,050 OBSERVATIONS
61 NADP-MDN SITES
OCT 1996 → FEB 2015

Previous Assessments of the Methylmercury Dataset …

- Wetherbee, Rhodes, Gay, Brunette, Prestbo, & Risch – 2015
  a) Poster at the International Conference of Mercury as a Global Pollutant – Jeju, Korea
  b) Panel Presentation at the 2015 AGU-CGU Joint Meeting – Montreal, Canada

- Mean concentration of 0.122 ± 0.450 ng/L
- Median concentration of 0.050 ng/L
- Debris shifted the mean to 0.078 ± 0.254 ng/L and median of 0.019 ng/L
- 0.5 to 4.0% of Total Hg is Methyl species
- Seasonal variation exists with maximum concentrations occurring in the summer



(Wetherbee et al. 2015a)

Sources of Methylmercury in Precipitation

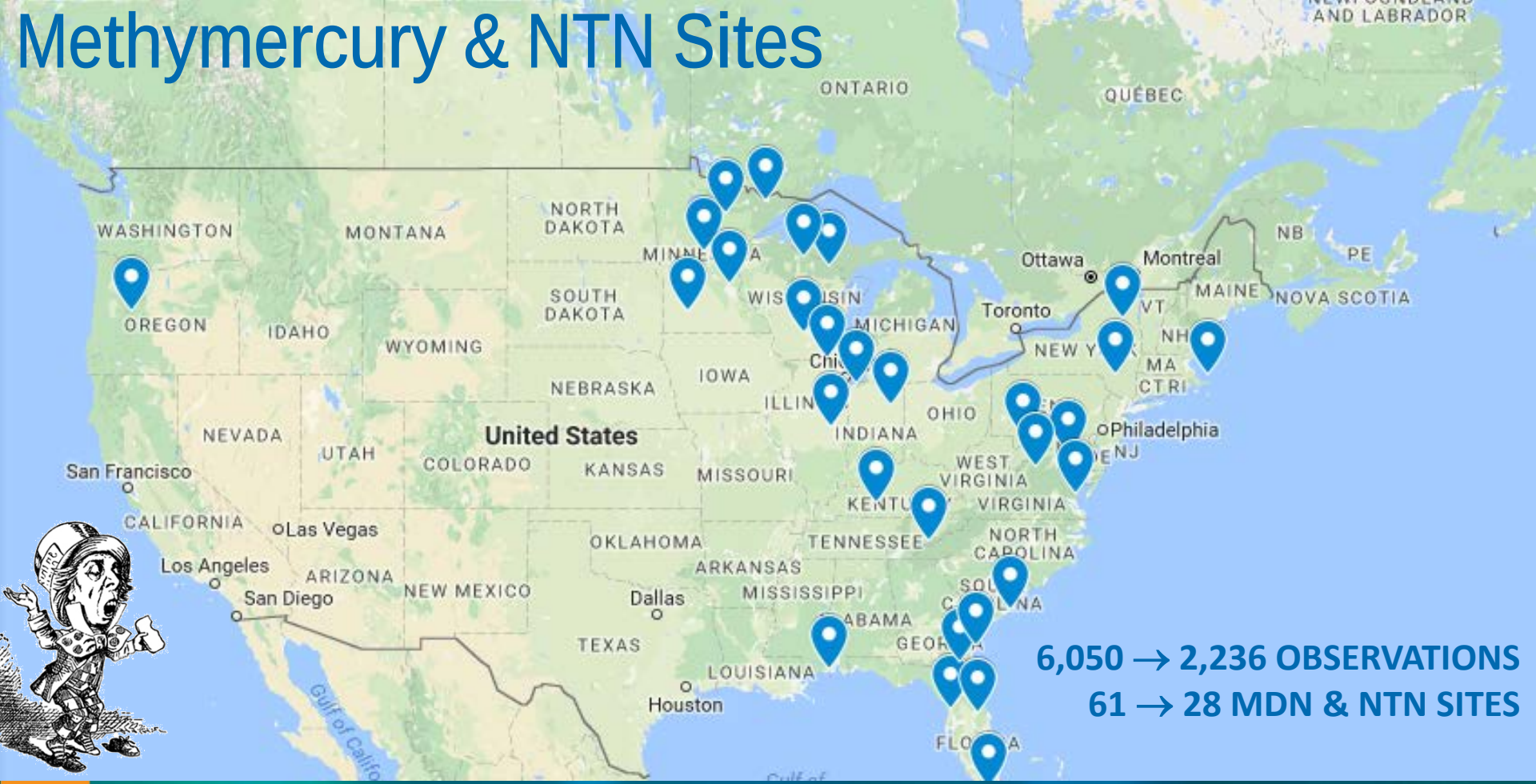
- Potential source(s) of methylmercury in wet deposition.
  - Volatilization of monomethylmercury,
  - Evasion and demethylation of dimethylmercury,
  - Direct methylation of Hg^0 in the atmosphere.

- Gardfedlt et al. (2003): Acetic acid as an abiotic methylating agent in atmospheric and surface waters. Presence of chloride, oxalate, and sulfite that may limit methylation rate due to competition between acetate and Hg(II).

- Celo et al. (2006): Contributions of various methyl donors (Co, Sn, I) on abiotic methylation. Methylation is dependent upon pH, temperature, and complexing agents – especially chloride.

Q: What is the role of major cations and anions on the presence of methymercury?

Methymercury & NTN Sites



6,050 → 2,236 OBSERVATIONS

61 → 28 MDN & NTN SITES

Methymercury & NTN Sites – with matched events

AVAILABLE MATCHED SAMPLES		
FL11	1X	4.27 ng/L
IN20	16X	0.34 ng/L
IN34	9X	0.44 ng/L
MD08	1X	0.62 ng/L
MS12	1X	0.11 ng/L

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Exploratory Statistics - Decision Tree Analysis (Learning)

Decision Tree Analysis recursively partitions data to create a tree of partitions.

- Groupings of X values are identified that best predict the Y value,
- All possible cuts are searched to optimize statistical parameters,
- Splits are done recursively forming a decision tree until an optimal fit is reached,
- Process chooses optimum splits from a large number of possible splits.

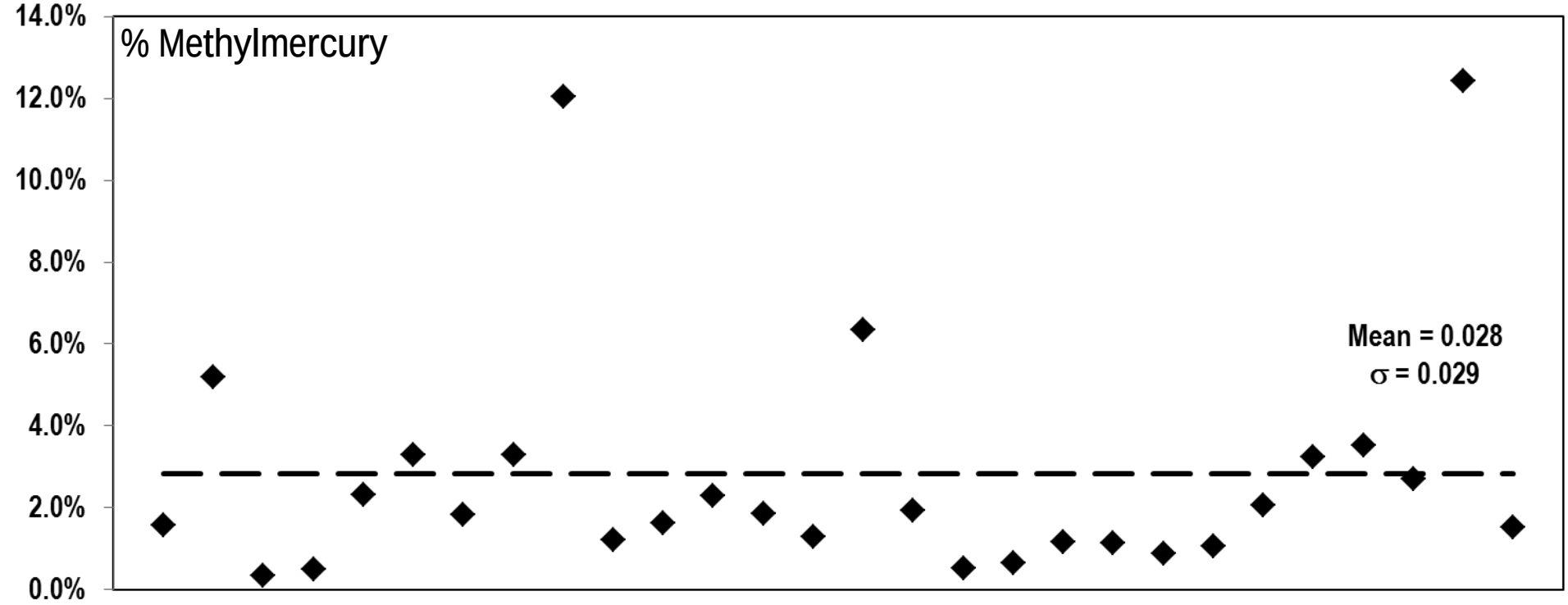
Goal is to identify inorganic constituents that are associated with methylmercury in precipitation.

jmp® Statistical Discovery.™ From SAS. Version 11

Advantages of the Approach:

- Explore relationships without a good model,
- Process handles large problems easily, and
- Results are very interpretable.

Illustration of Method – Matched NTN & MDN Weekly Samples



ALL DATA (n=28)

Illustration of Method – First Split

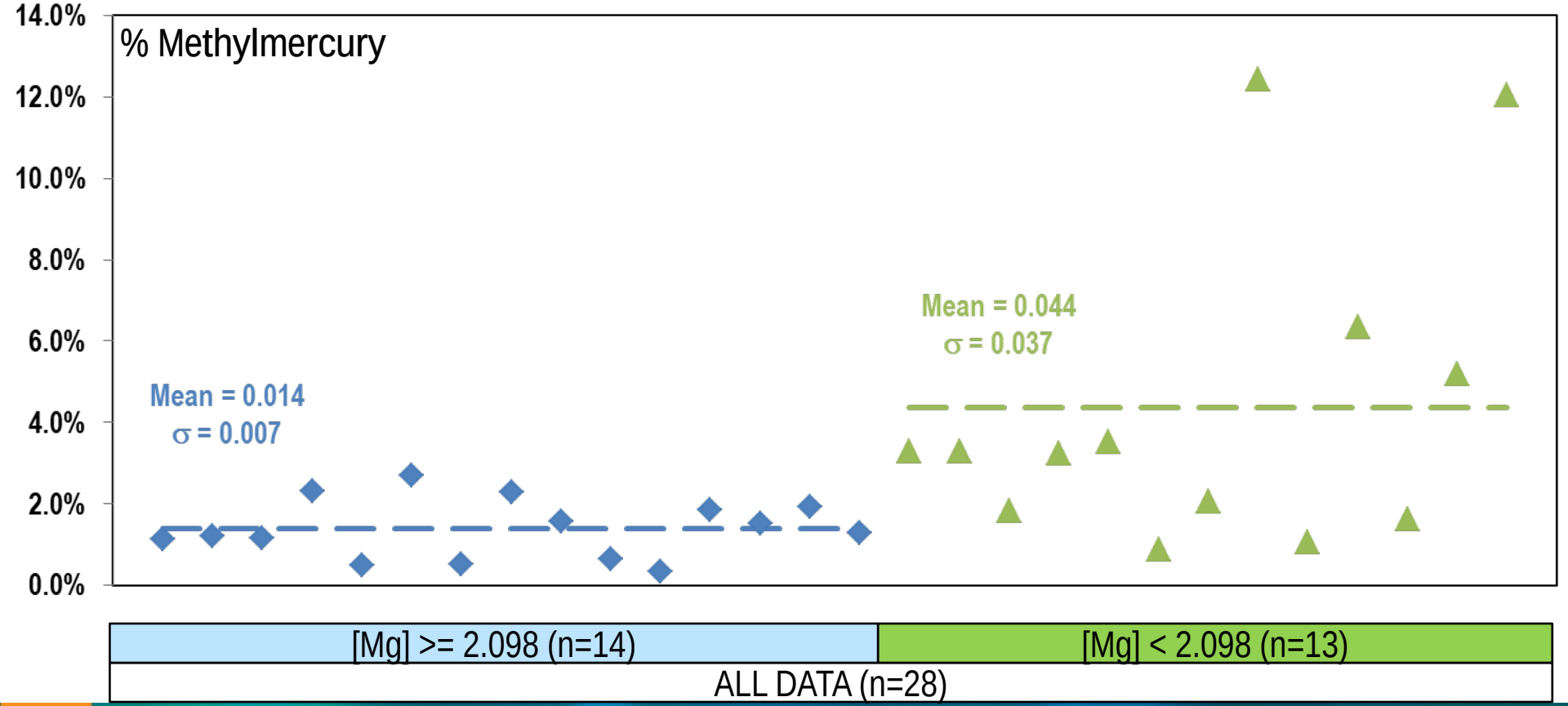
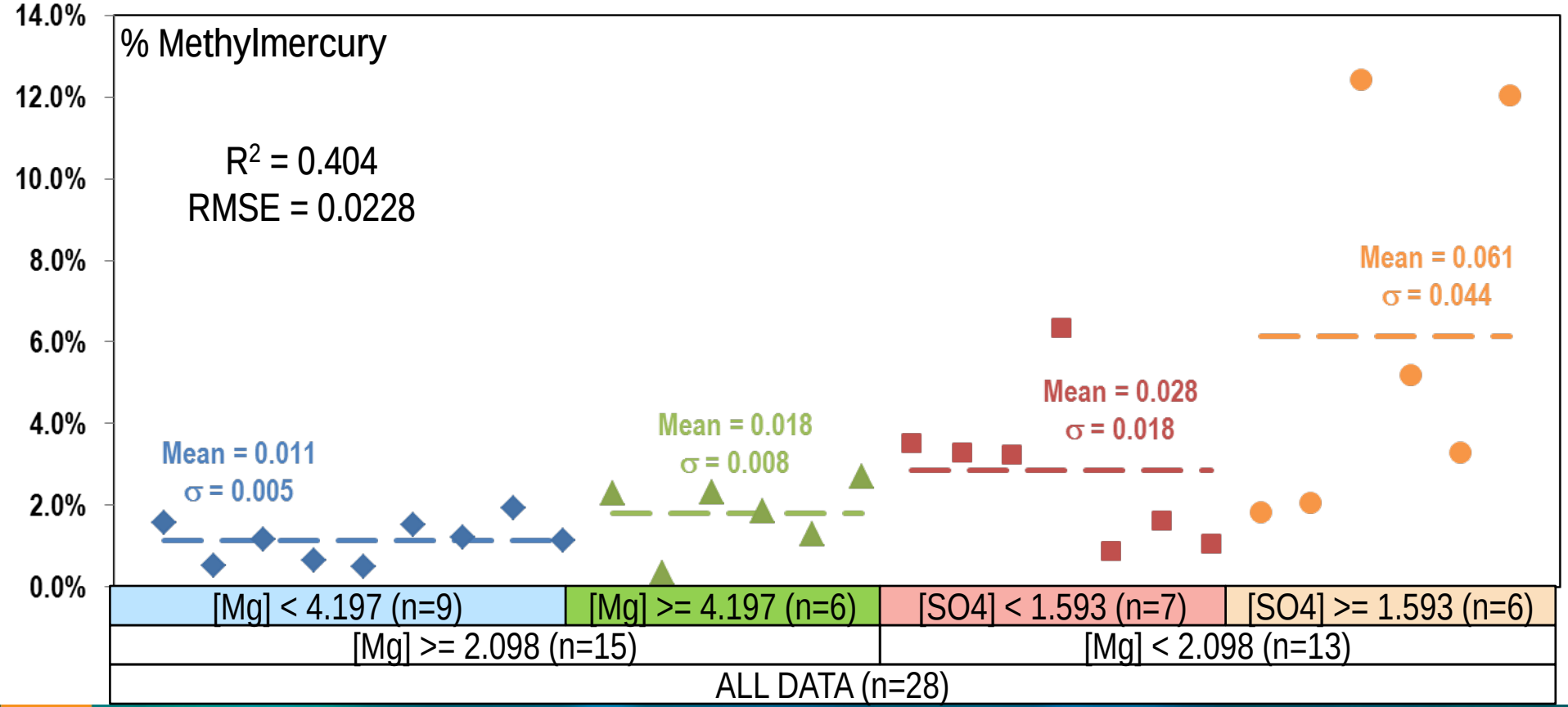


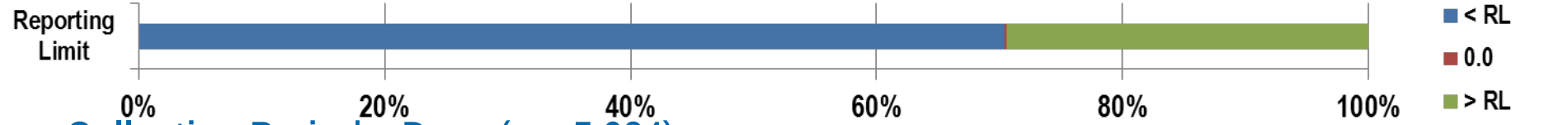
Illustration of Method – Second Split



Nuisances of the NADP Methylmercury Dataset…

- Quality Code (n = 5,995)

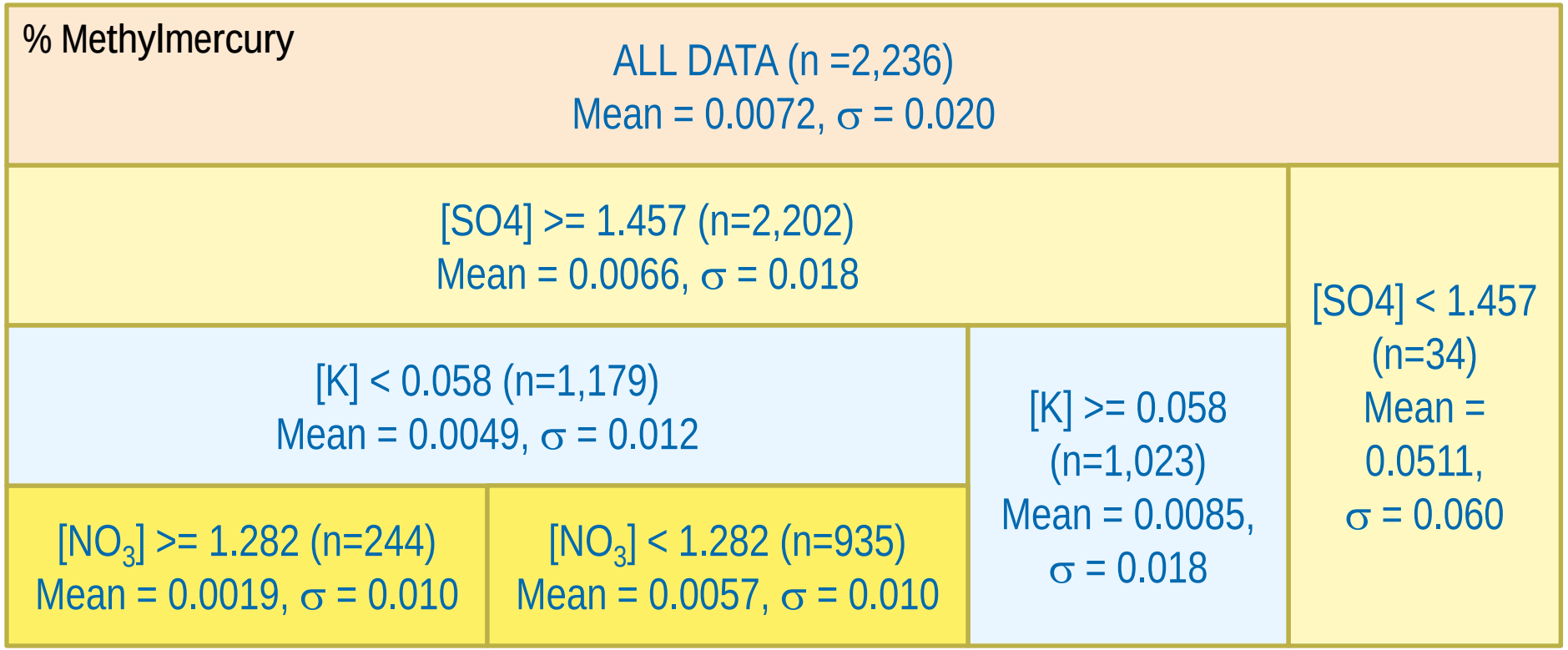
- Reporting Limit {0.005, 0.0025} (n = 5,995)



- Collection Period – Days (n = 5,984)

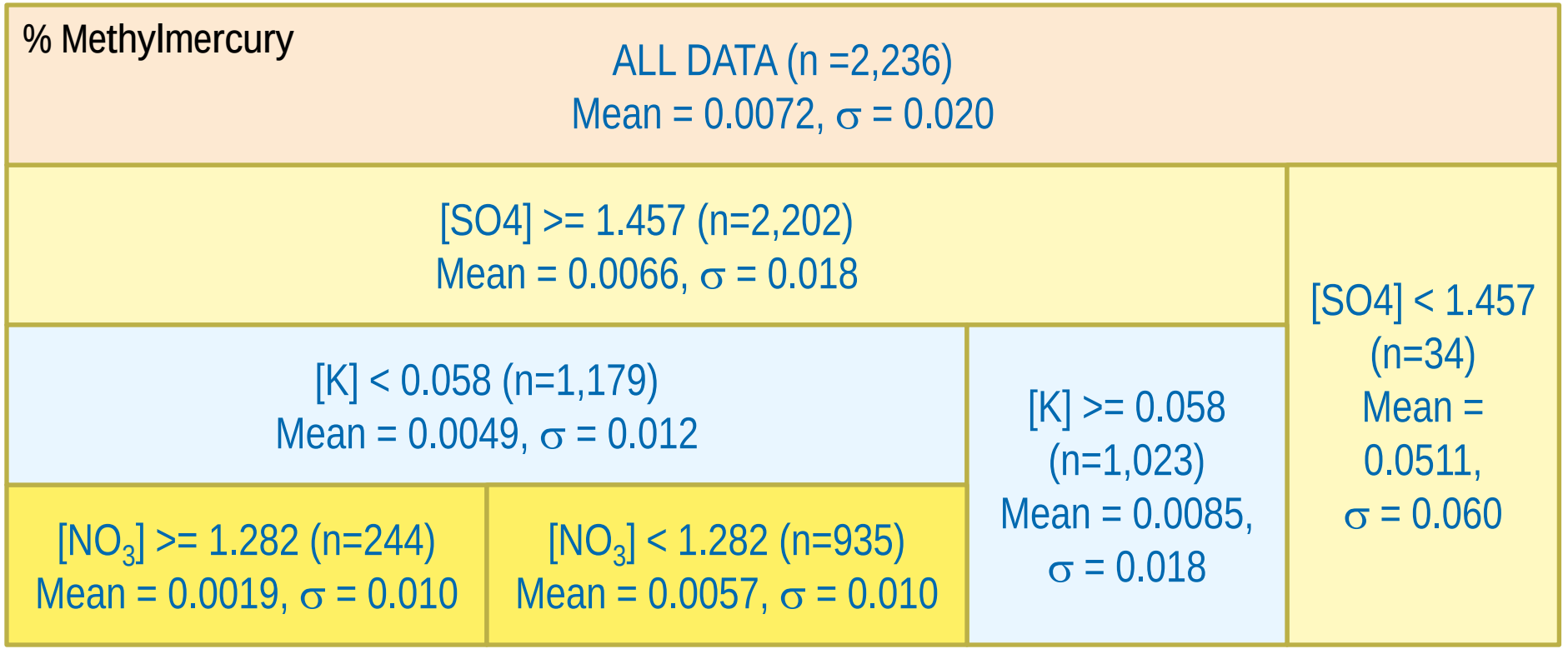
- Number of Samples in Composites (n = 3,354; 56%)

Decision Tree for Volume Weighted Dataset (n=2,236)



Molar Concentrations (E-06)

Decision Tree for Volume Weighted Dataset (n=2,236)



Molar Concentrations (E-06)

R^2 = 0.083; RMSE = 0.019

Summary & Conclusions

- NTN Constituents associated with Methylmercury are - Inconclusive
- Advantages of the Approach
  - Leverage observations from multiple NADP networks to gain insight on variables that may influence methylmercury in precipitation.
- Improvement Opportunities
  - Heavily censored Methyl data – appropriate analysis techniques?
  - Consider Site Location, Season, and Debris as components,
  - Compositing masks details associated with weekly extreme events,
  - Use of total mercury vs. reactive mercury (Hammerschmidt et al., 2007)

Questions & Acknowledgements

Advice, counsel, and commiserating from Greg Wetherbee, David Gay, and Mark Rhodes

Select Illustrations – Sir John Tenniel