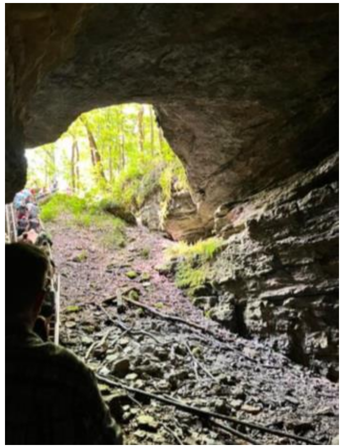




Southeastern US Winter Particle Nitrate Study

Continuing Progress Towards Natural Visibility Conditions

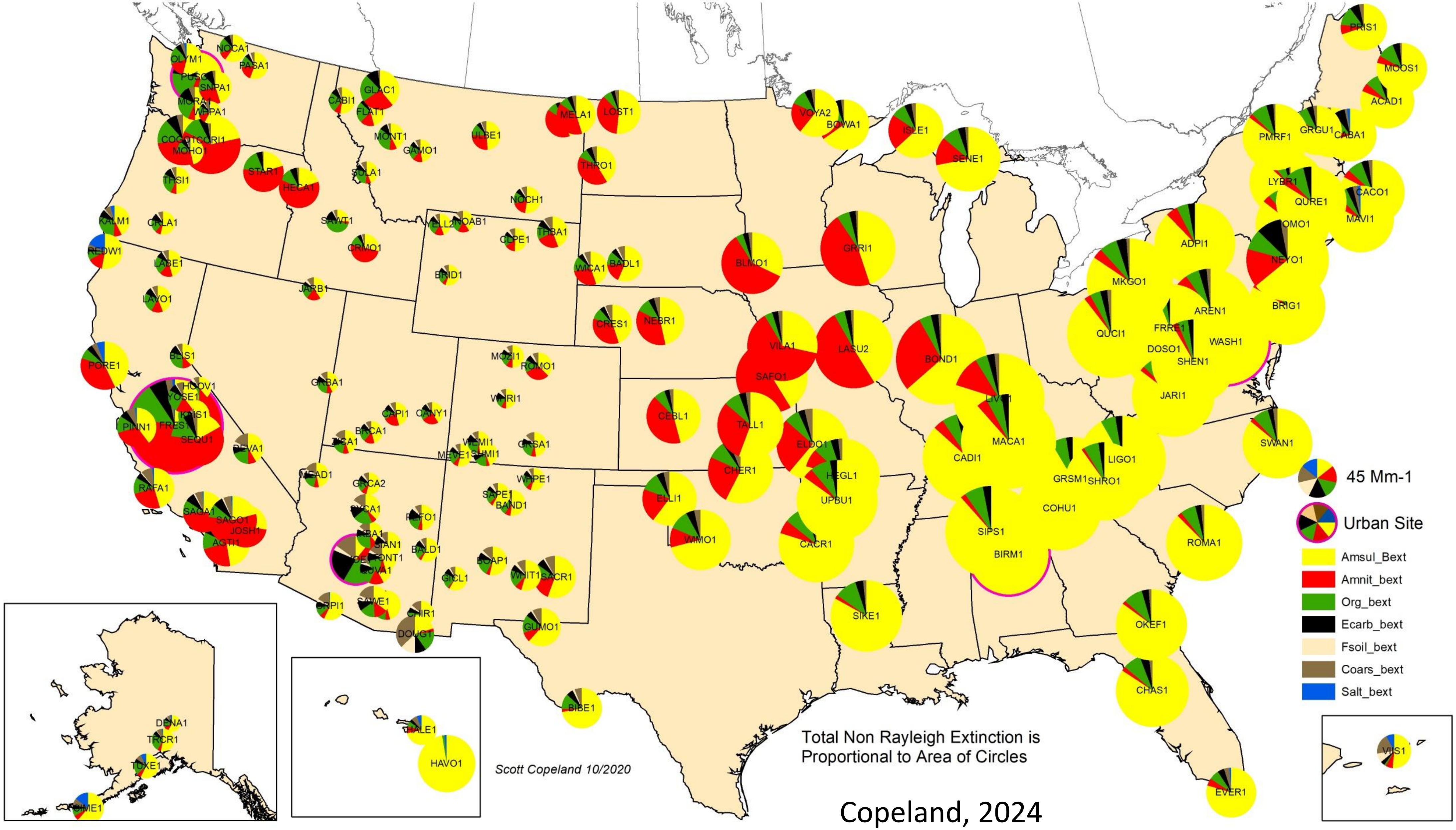


Participants

- National Park Service - Air Resource Division
  - Planning, oversite, analyze and interpret results
    - Bret Schichtel
    - Anthony Prenni
    - Mike Barna
- Colorado State University – Atmospheric Science Department
  - Planning, conduct field study and analyze and interpret results
    - Jeff Collett
    - Amy Sullivan
- Hankuk University Department of Environmental Science, Korea
  - Field work and analyze and interpret results
    - Taehyoung Lee
    - Taehyun Park
    - Jihee Ban

IMPROVE Data - 2005 Second IMPROVE Algorithm

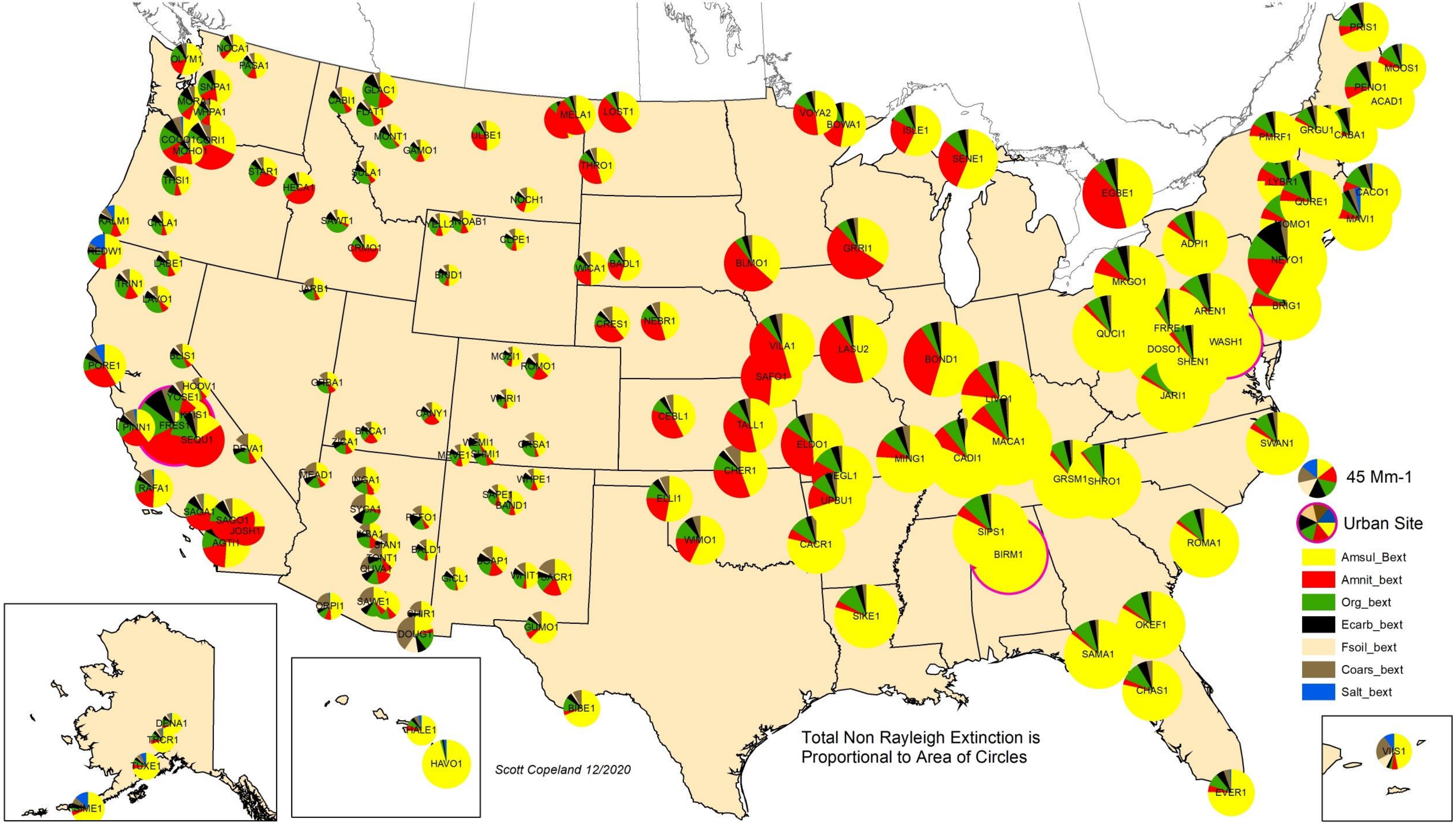
Non Rayleigh Mean of 20% Most Impaired



Copeland, 2024

IMPROVE Data - 2006 Second IMPROVE Algorithm

Non Rayleigh Mean of 20% Most Impaired



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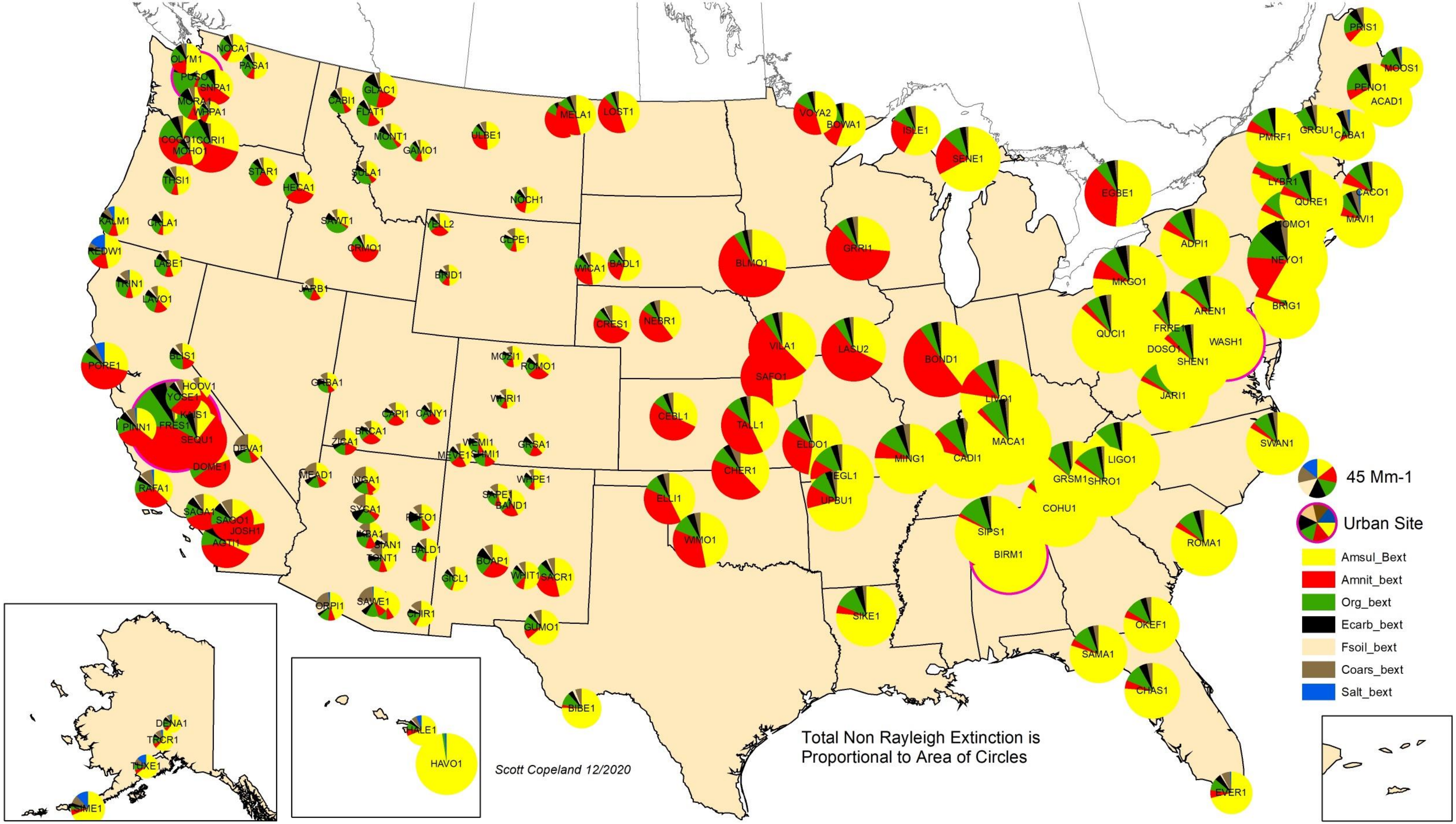
Non Rayleigh Mean of 20% Most Impaired



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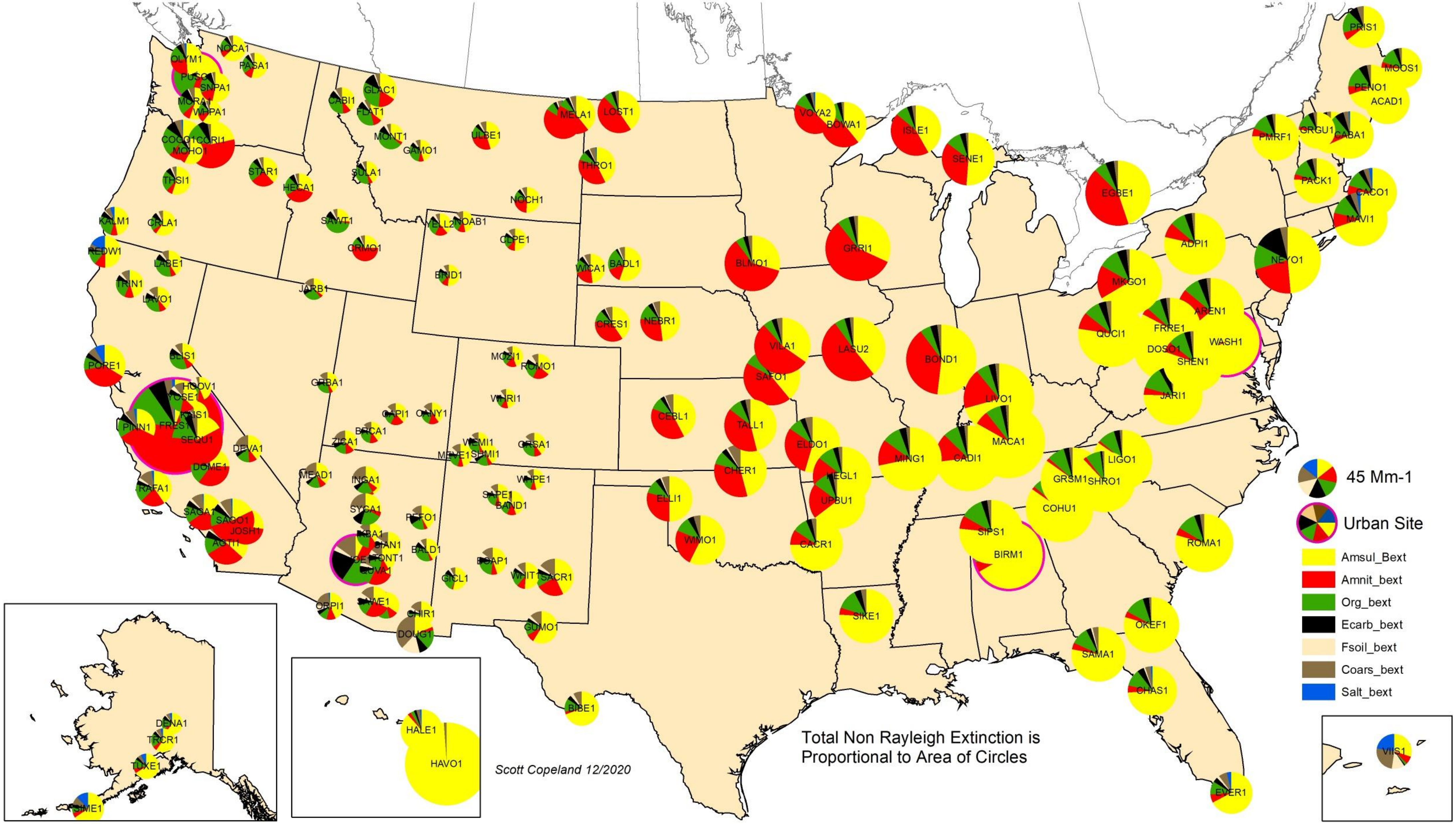

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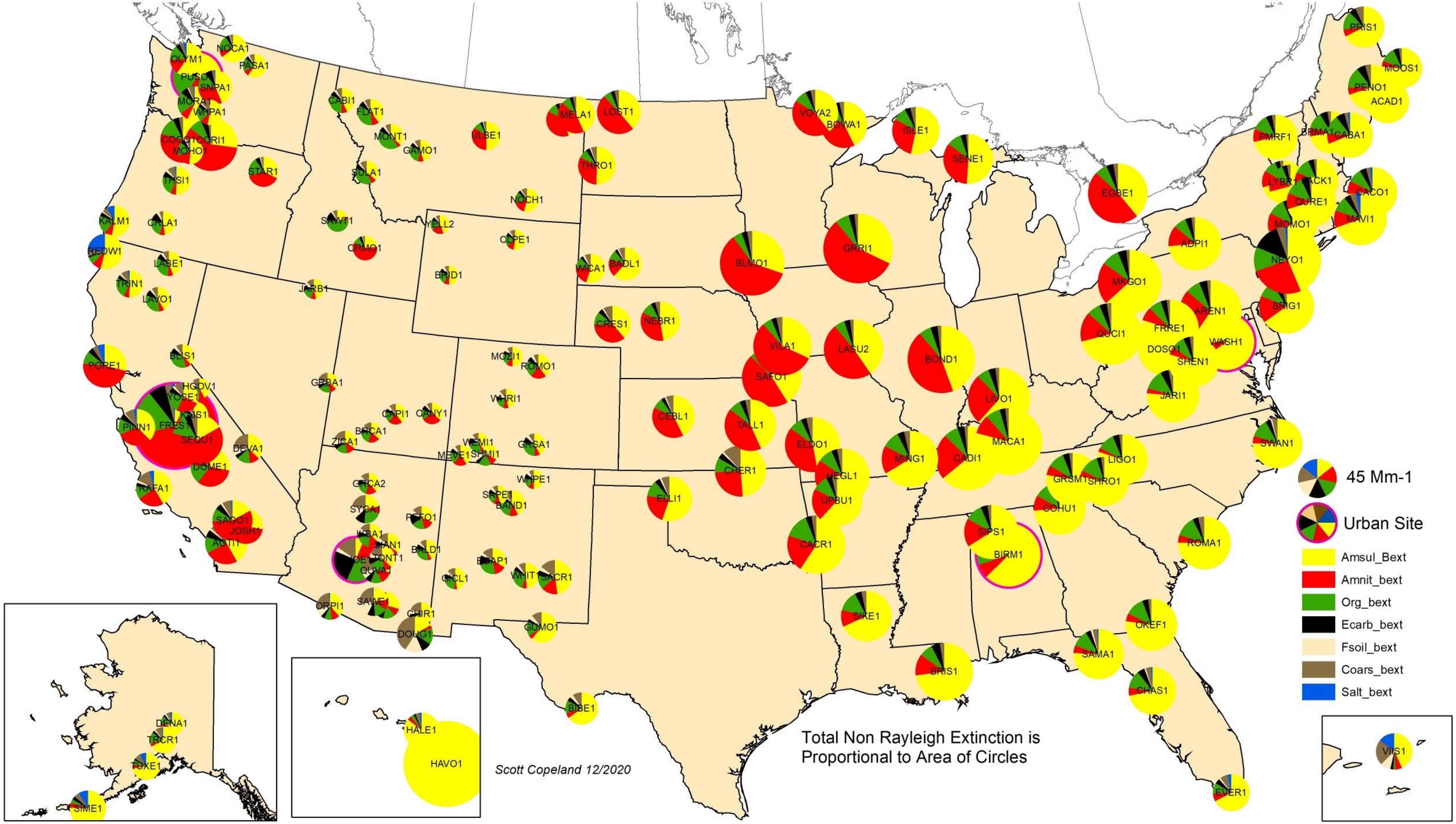

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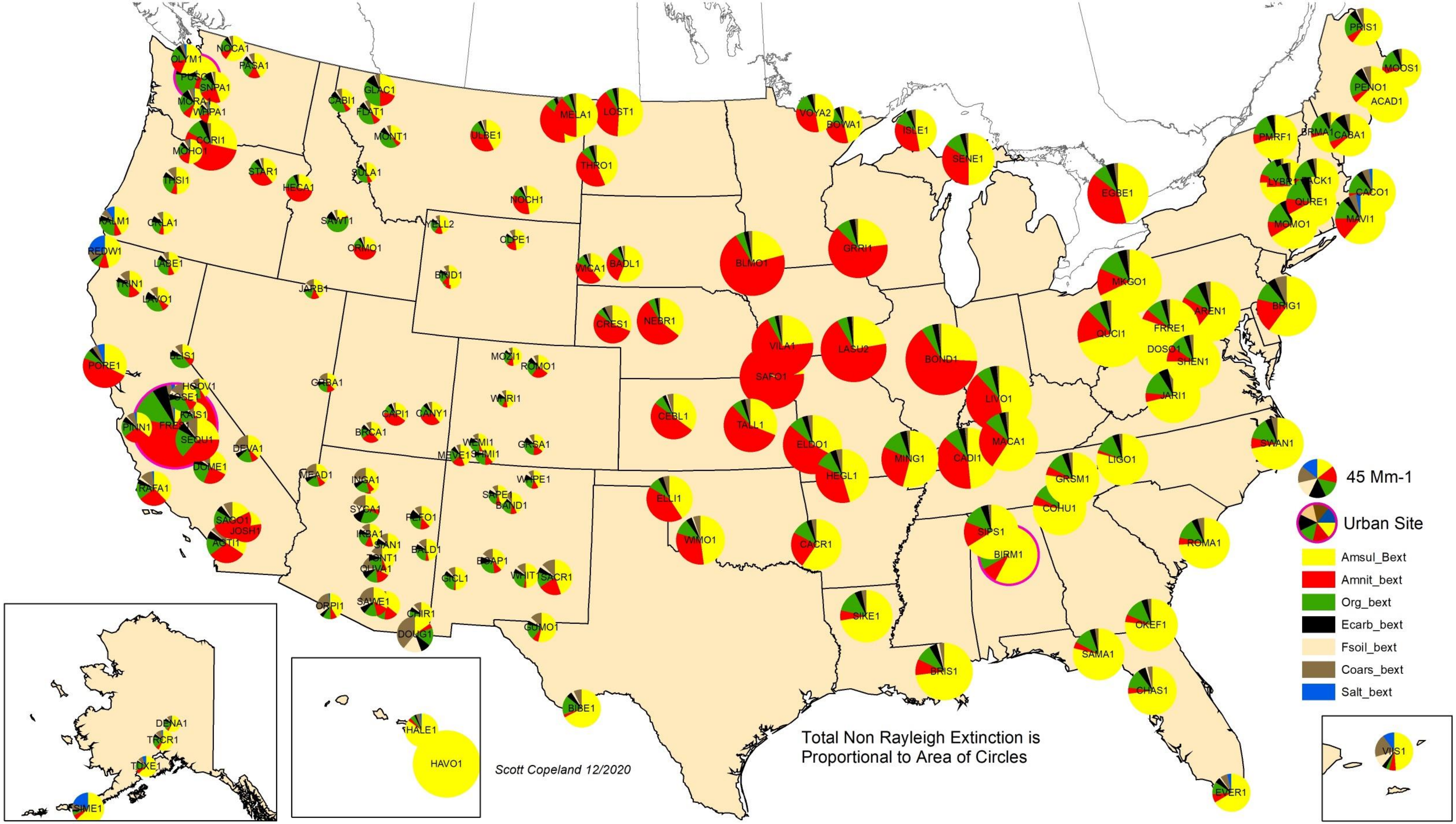
Non Rayleigh Mean of 20% Most Impaired



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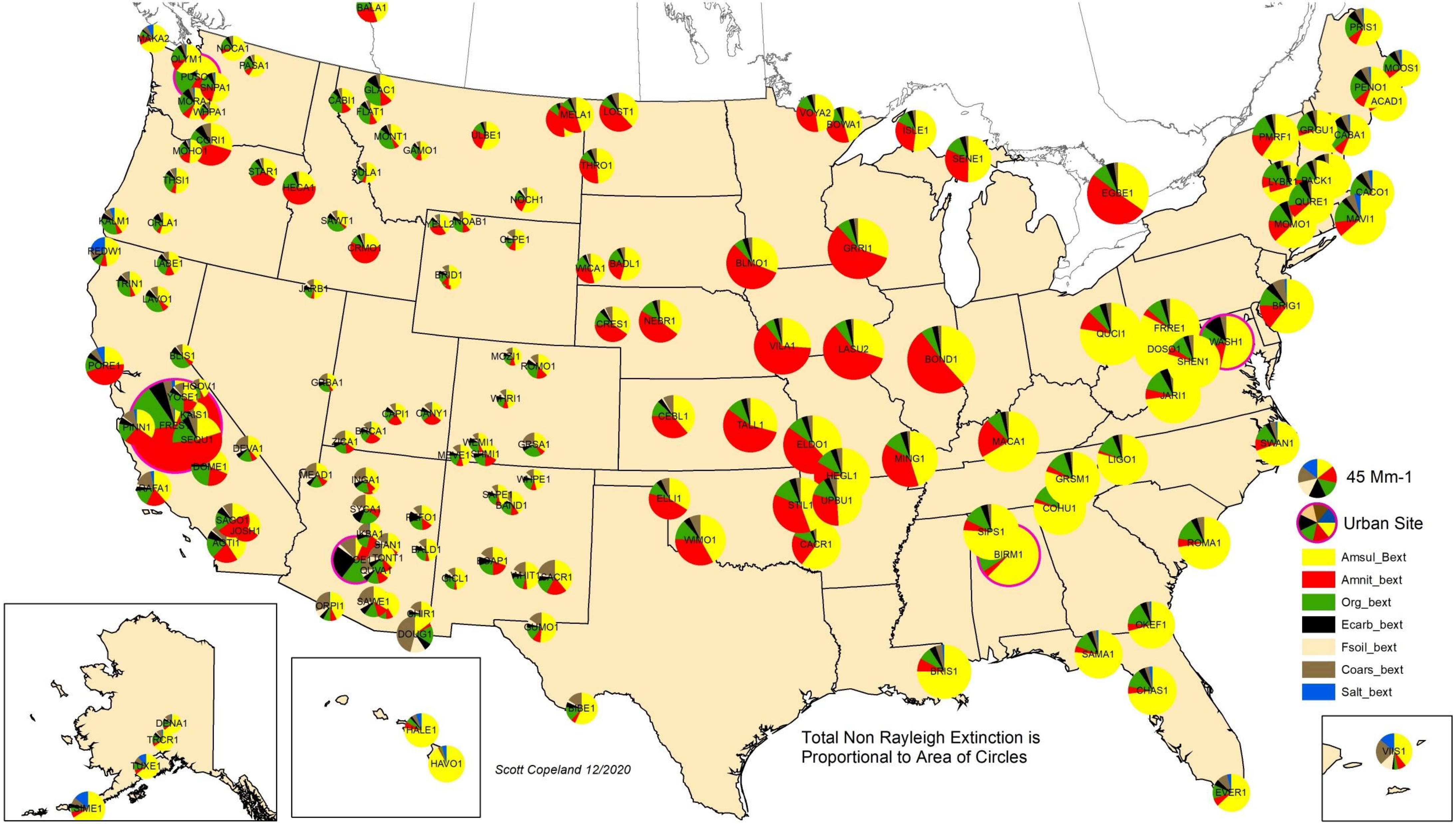

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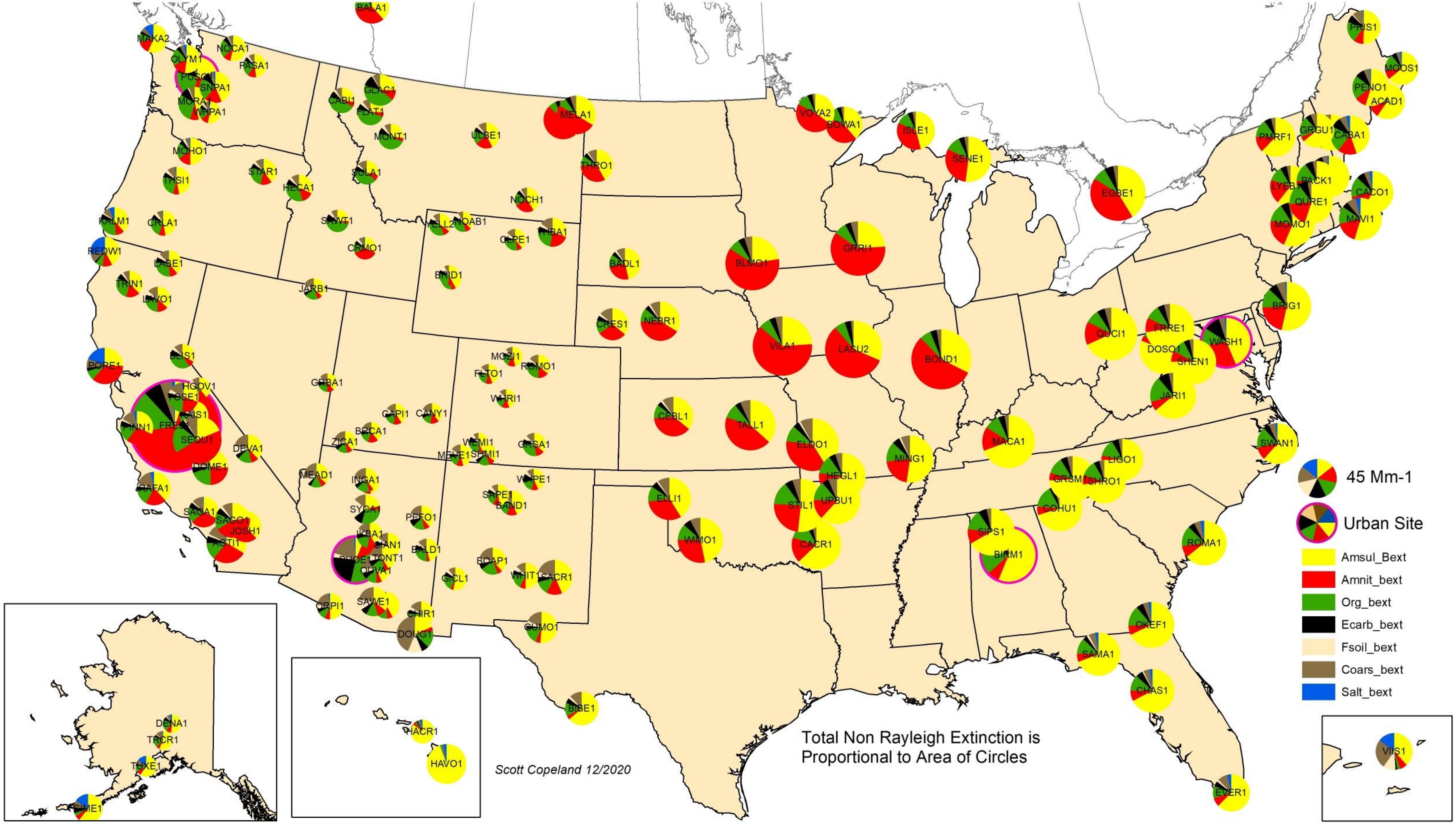

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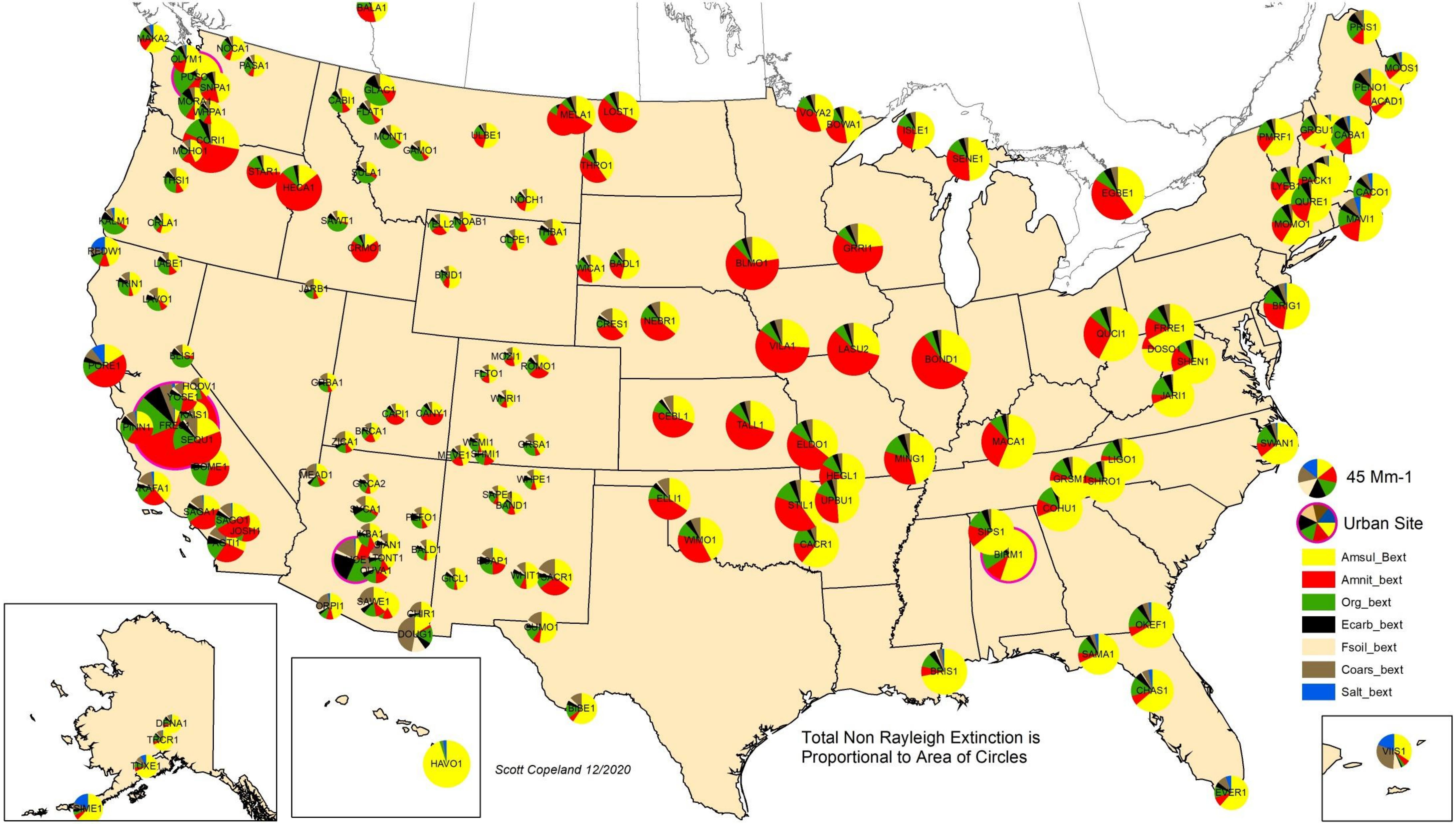
Non Rayleigh Mean of 20% Most Impaired



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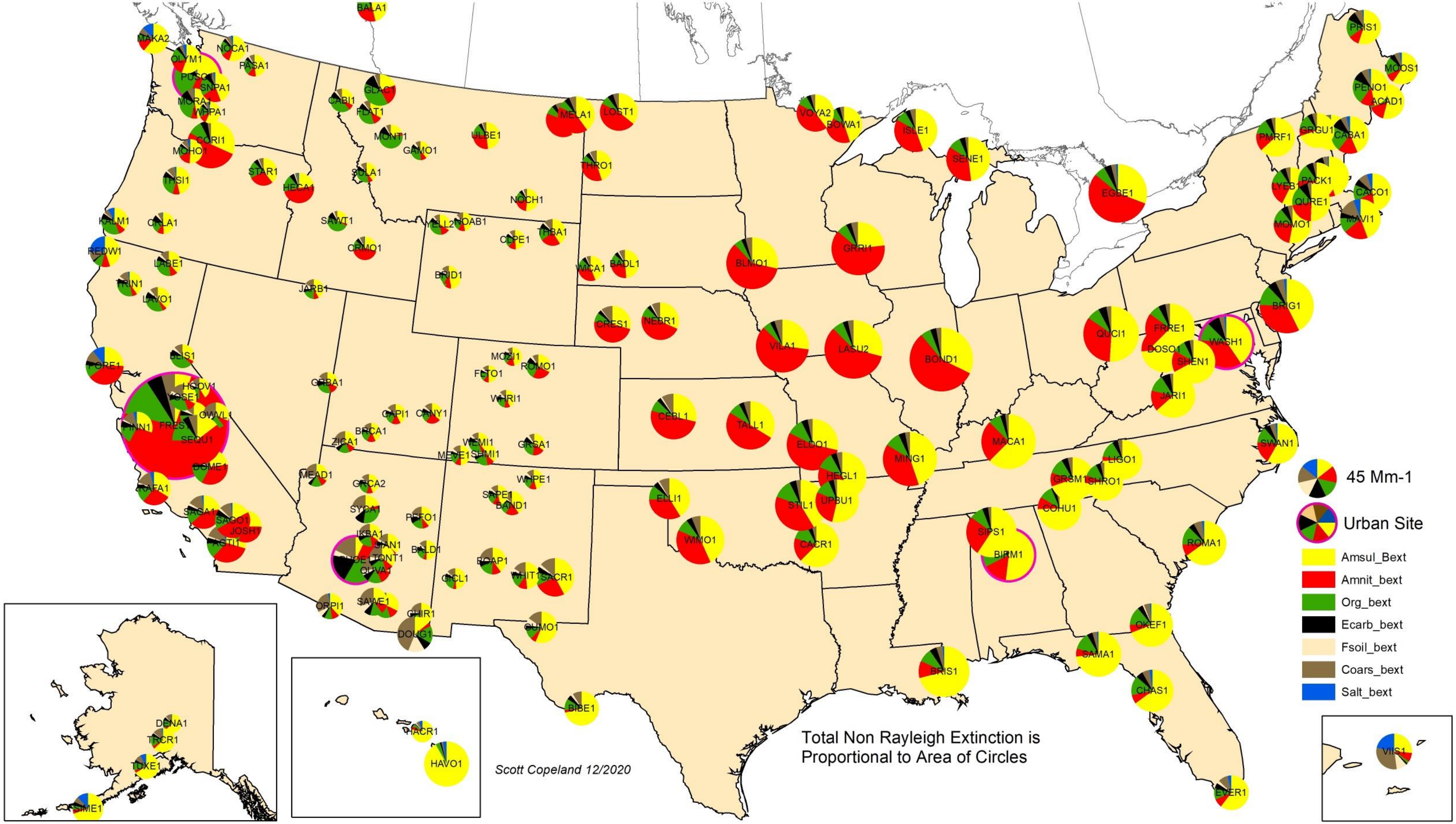
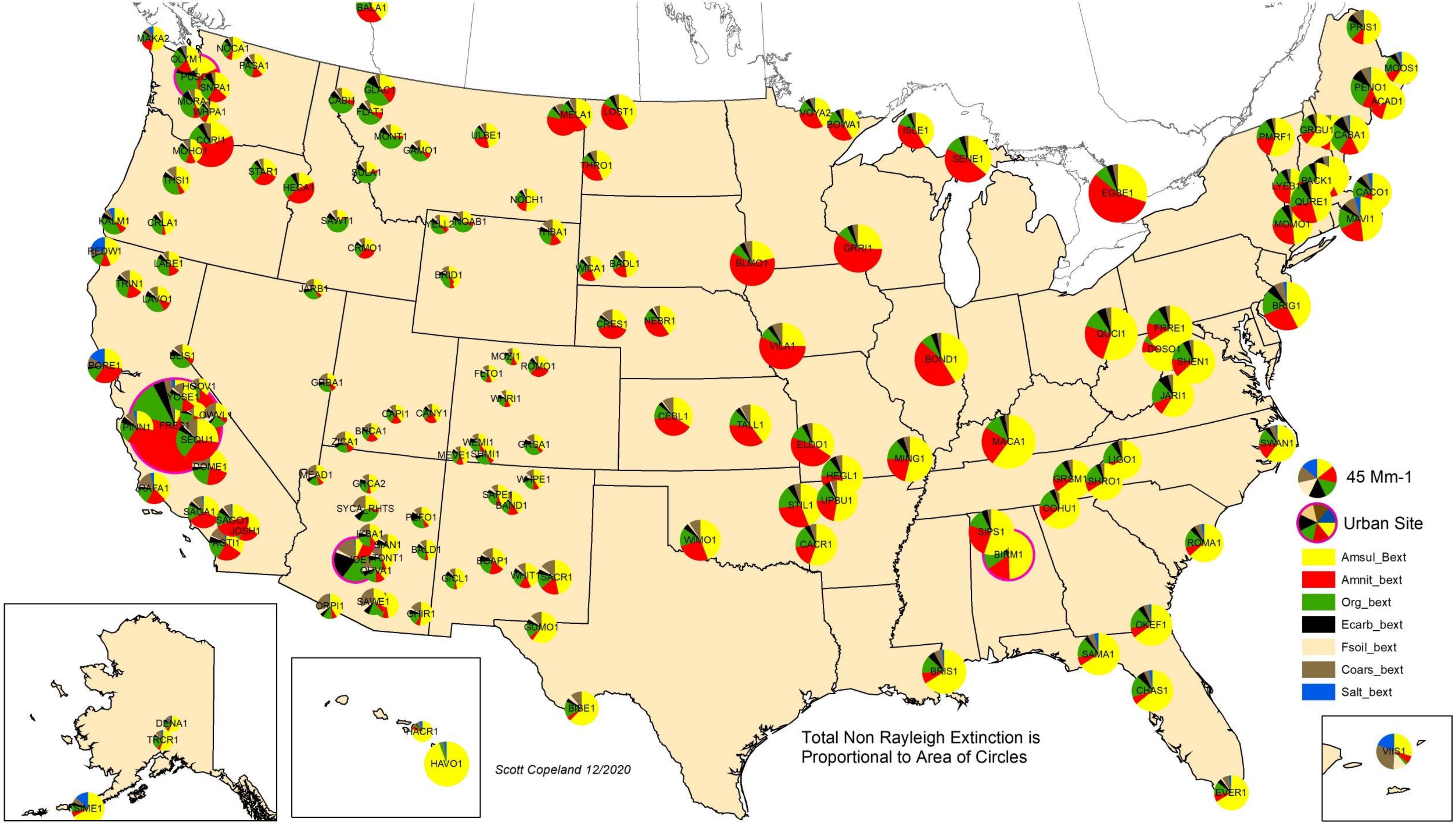
Non Rayleigh Mean of 20% Most Impaired



IMPROVE Data - 2015 Second IMPROVE Algorithm

Non Rayleigh Mean of 20% Most Impaired



IMPROVE Data - 2016 Second IMPROVE Algorithm

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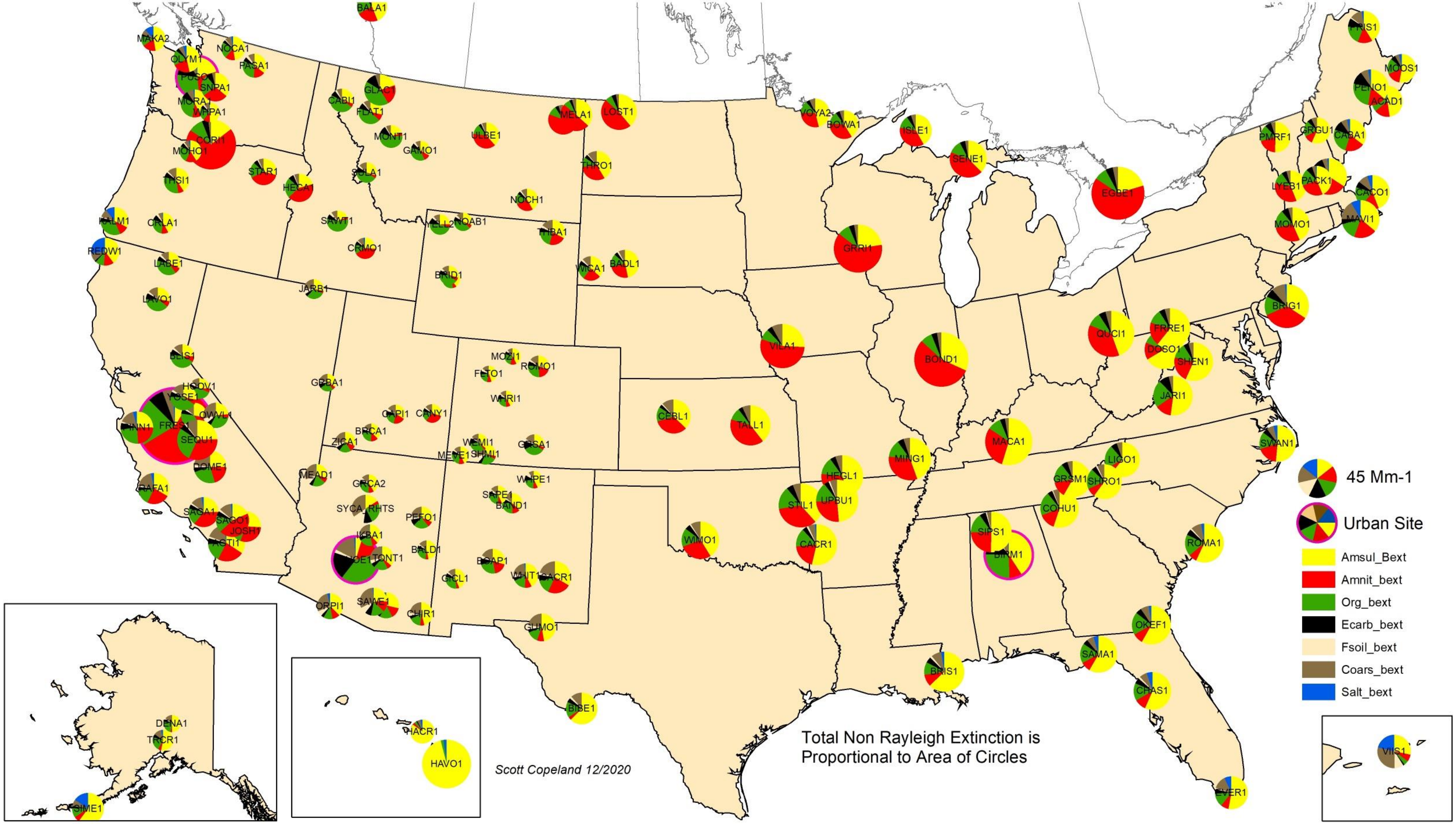

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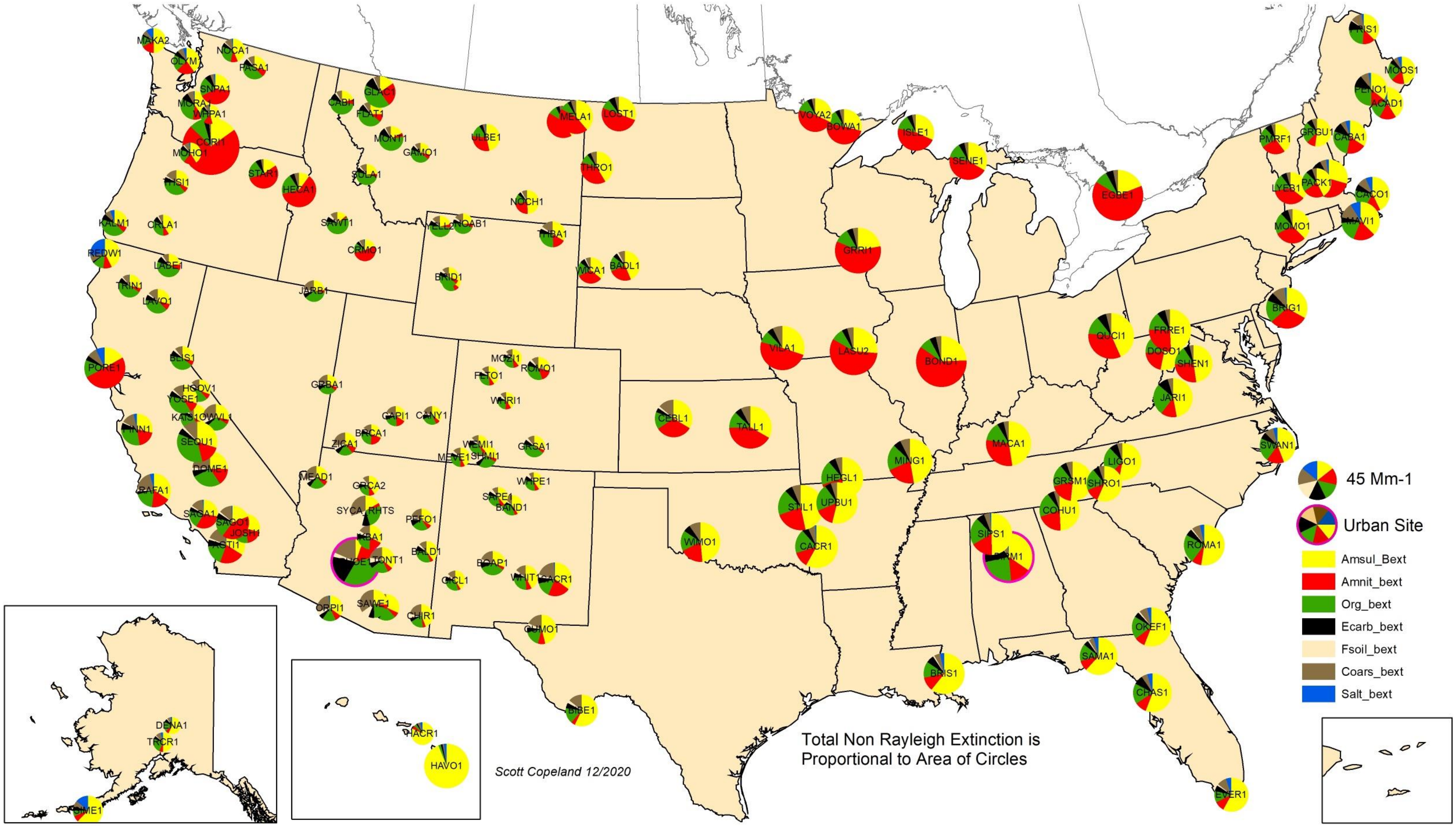

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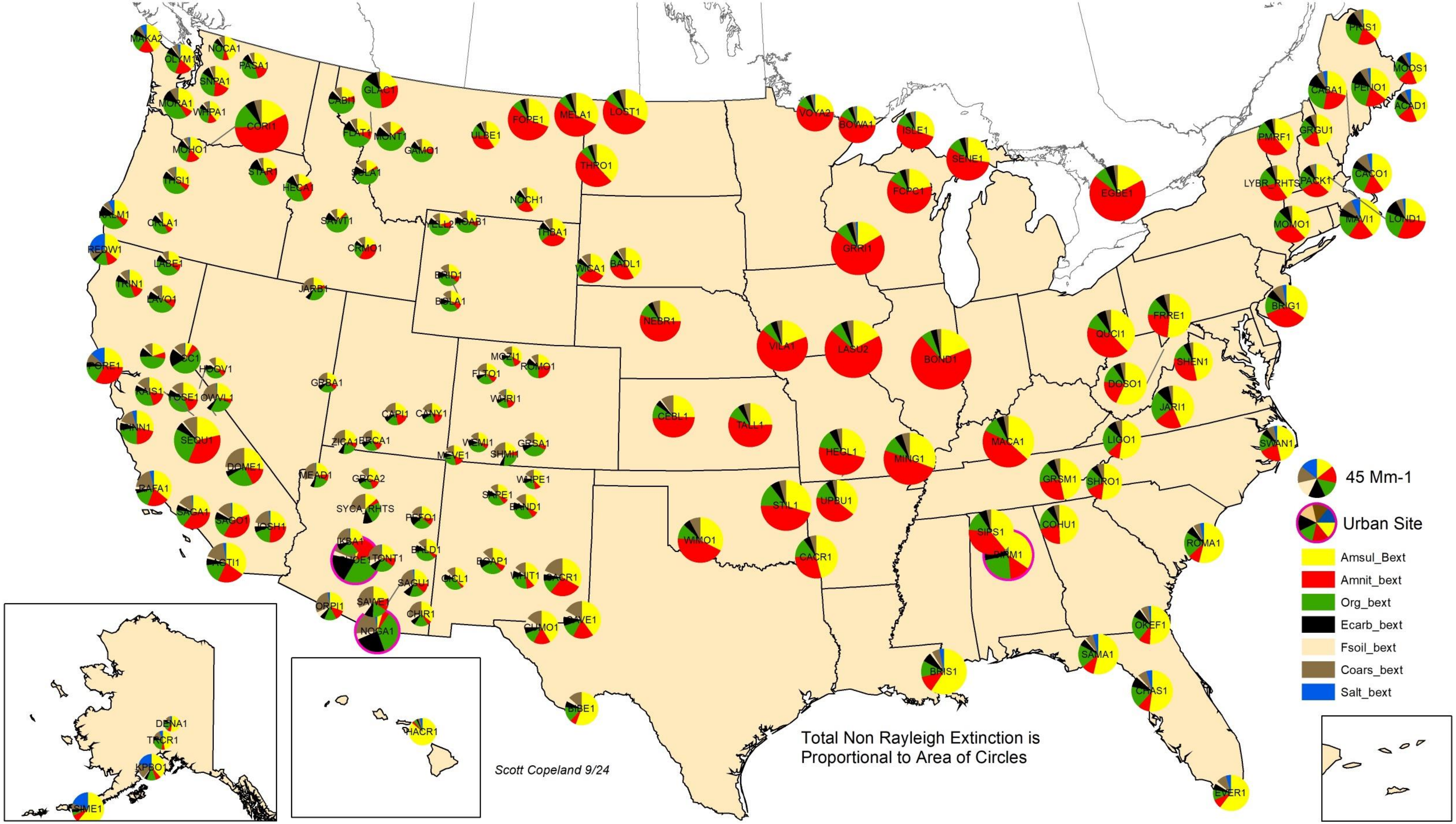
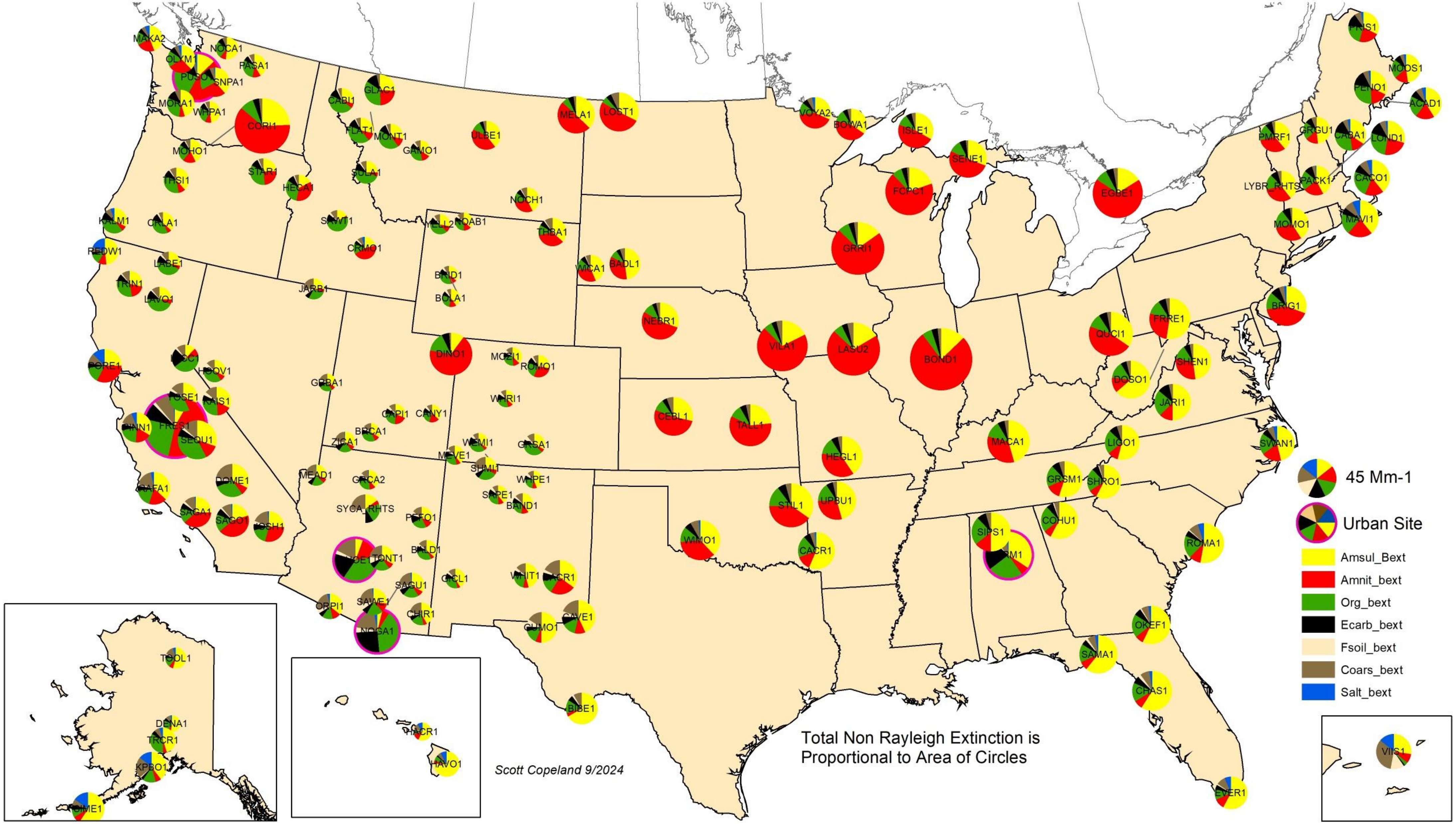


IMPROVE Data - 2019 Second IMPROVE Algorithm

Non Rayleigh Mean of 20% Most Impaired



IMPROVE Data - 2020 Second IMPROVE Algorithm

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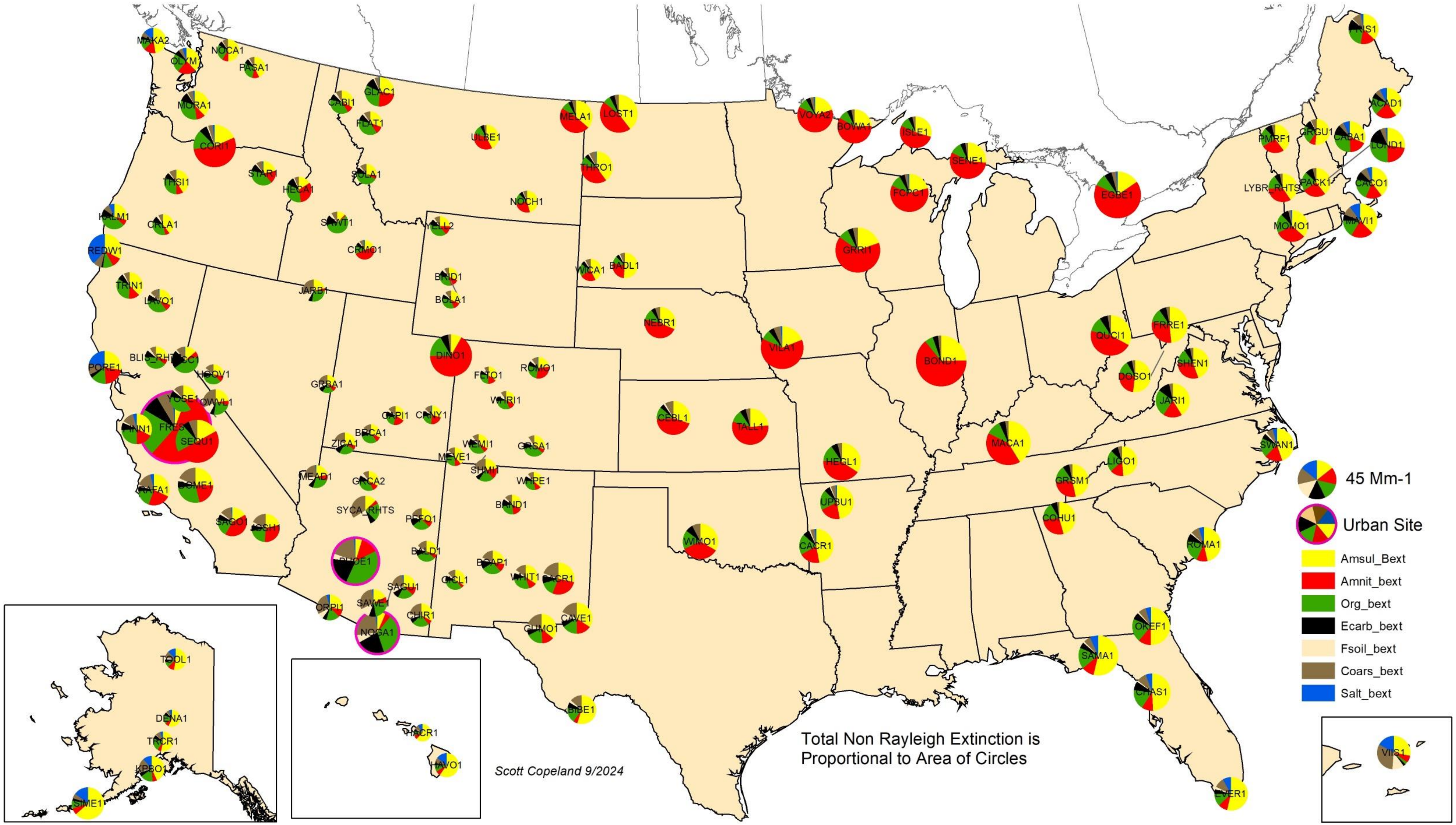
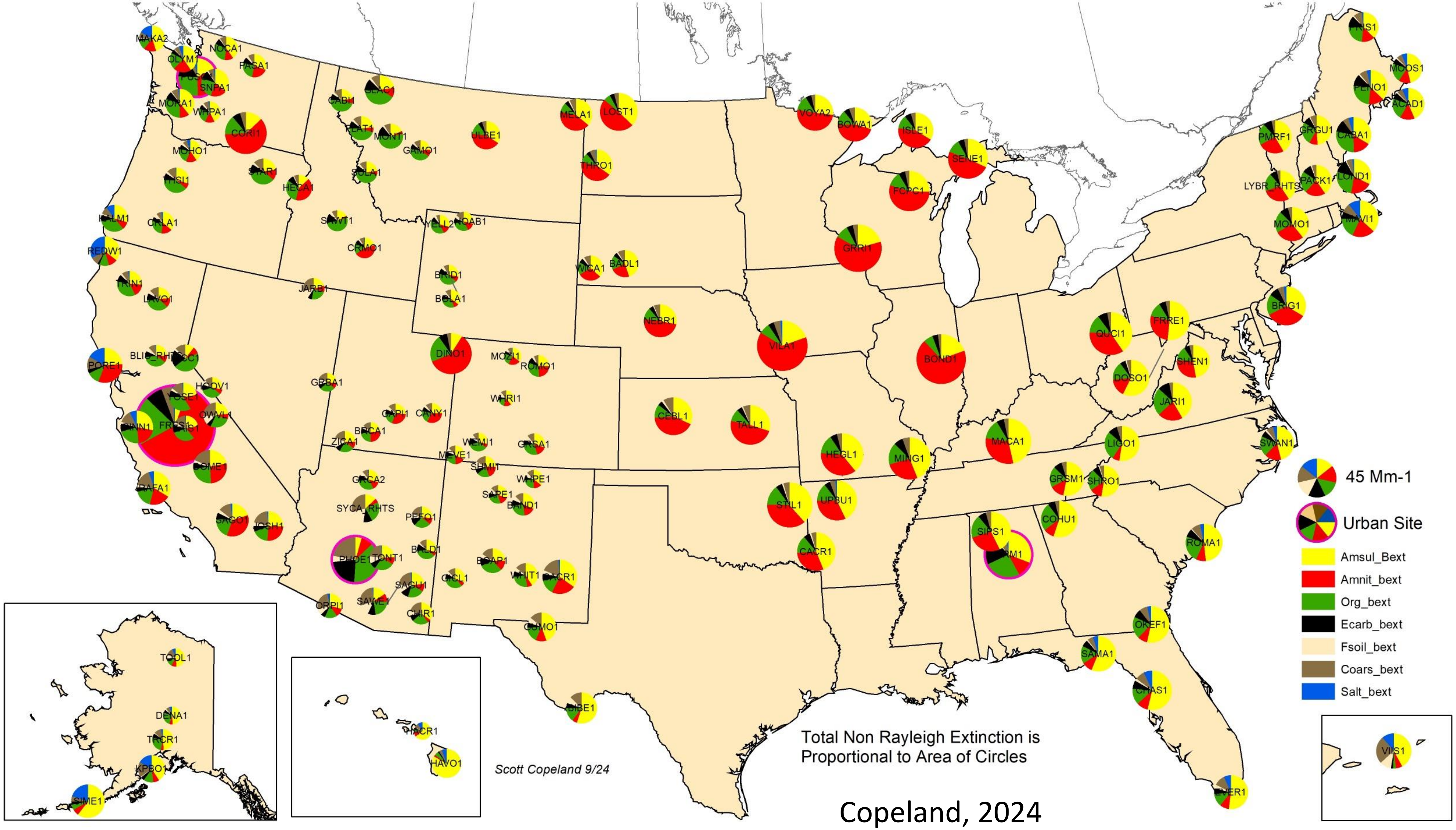


IMPROVE Data - 2021 Second IMPROVE Algorithm

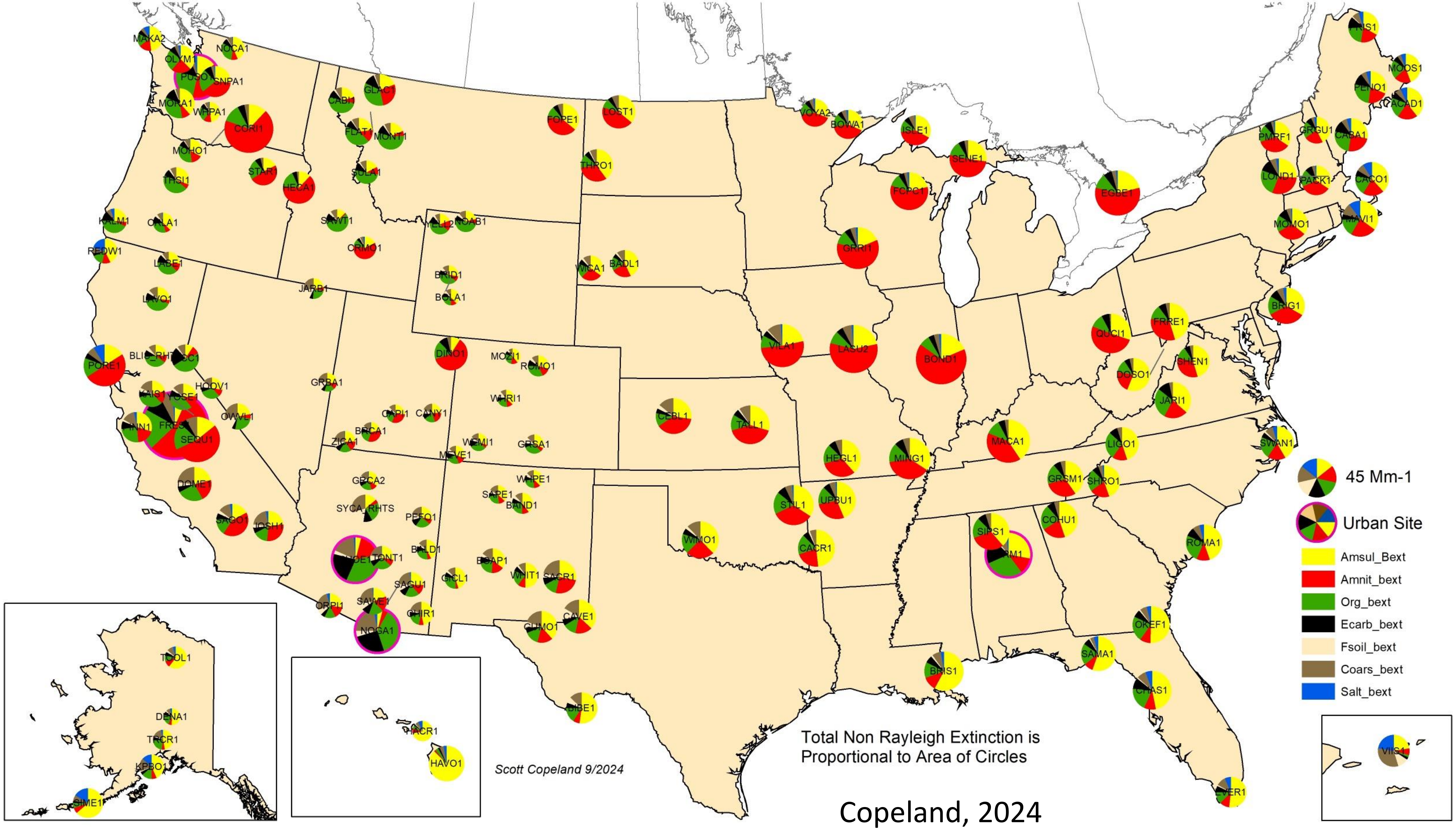
Non Rayleigh Mean of 20% Most Impaired



Copeland, 2024

IMPROVE Data - 2022 Second IMPROVE Algorithm

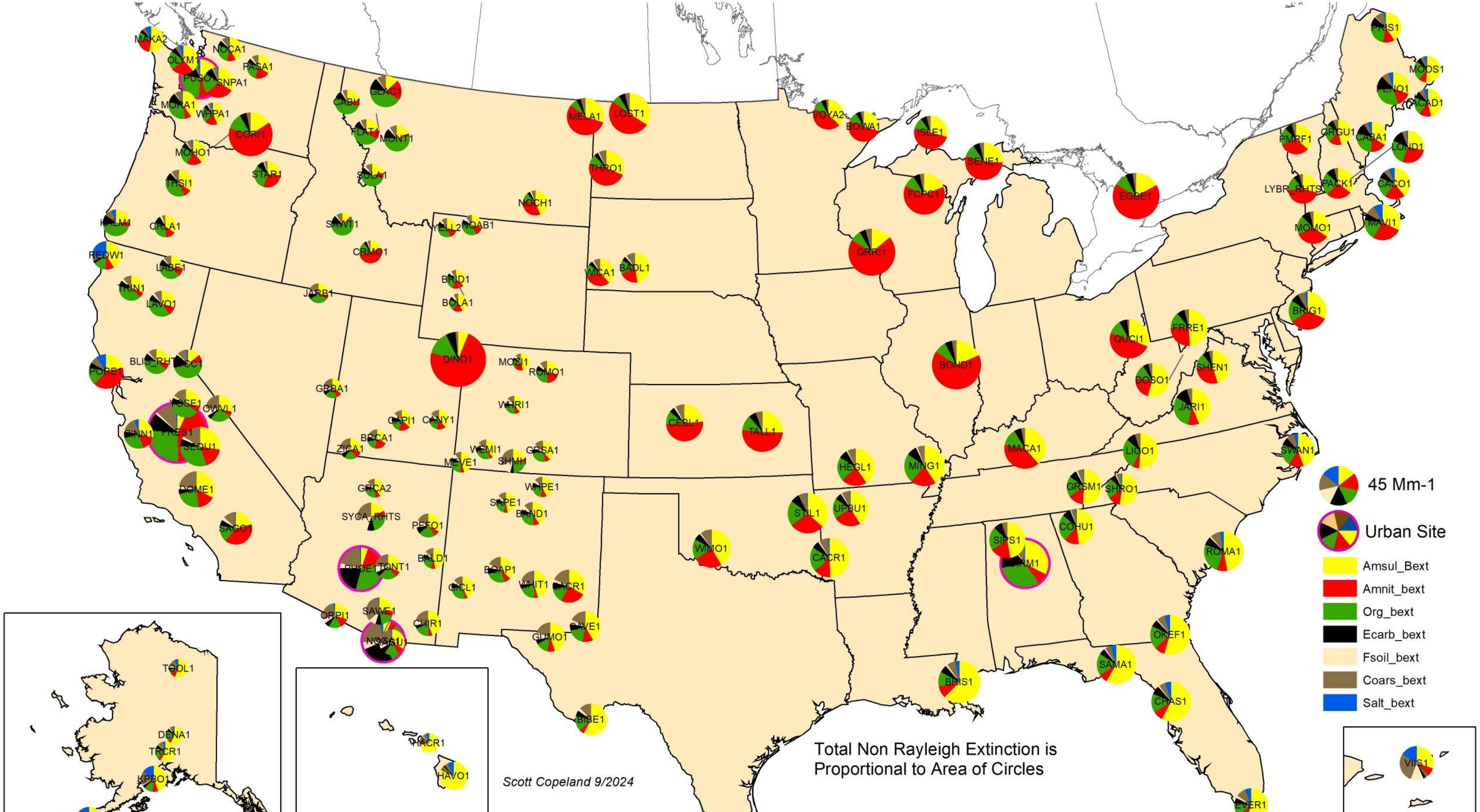
Non Rayleigh Mean of 20% Most Impaired



Copeland, 2024

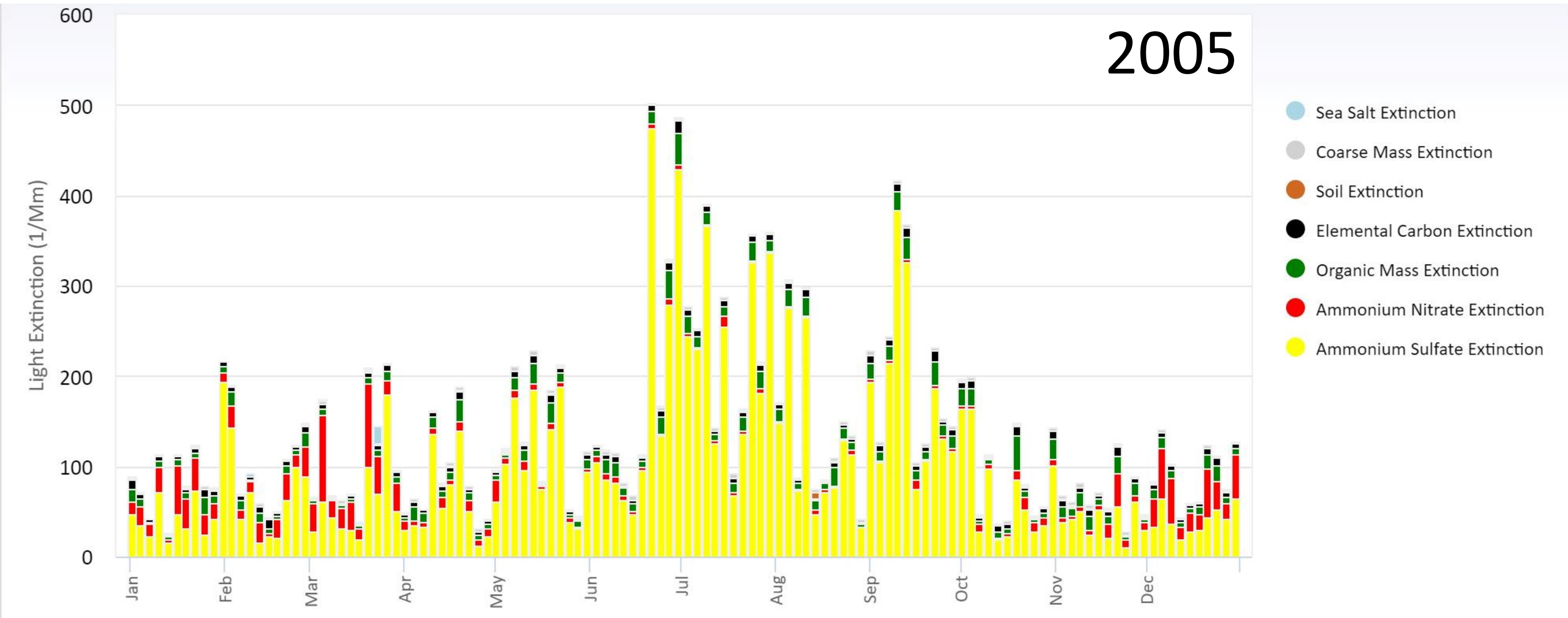
IMPROVE Data - 2023 Second IMPROVE Algorithm

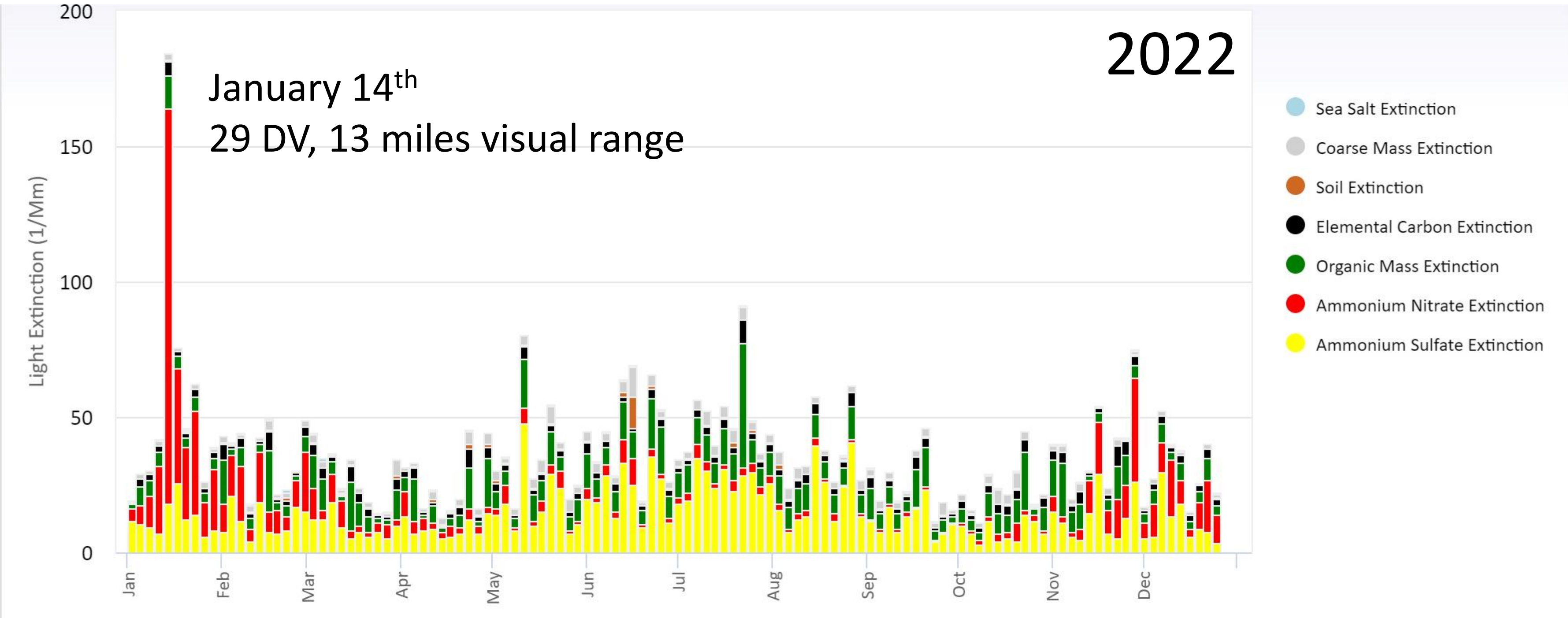
Non Rayleigh Mean of 20% Most Impaired



Copeland, 2024

Mammoth Cave Daily Haze Budgets

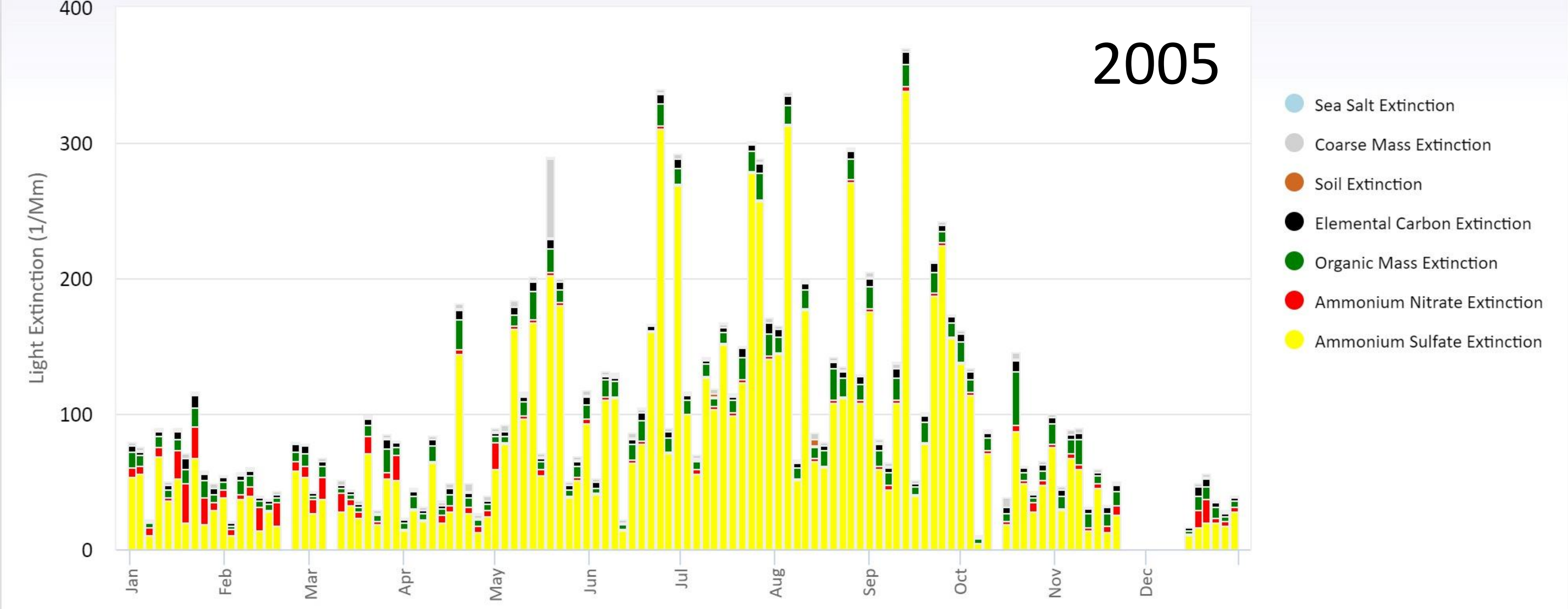


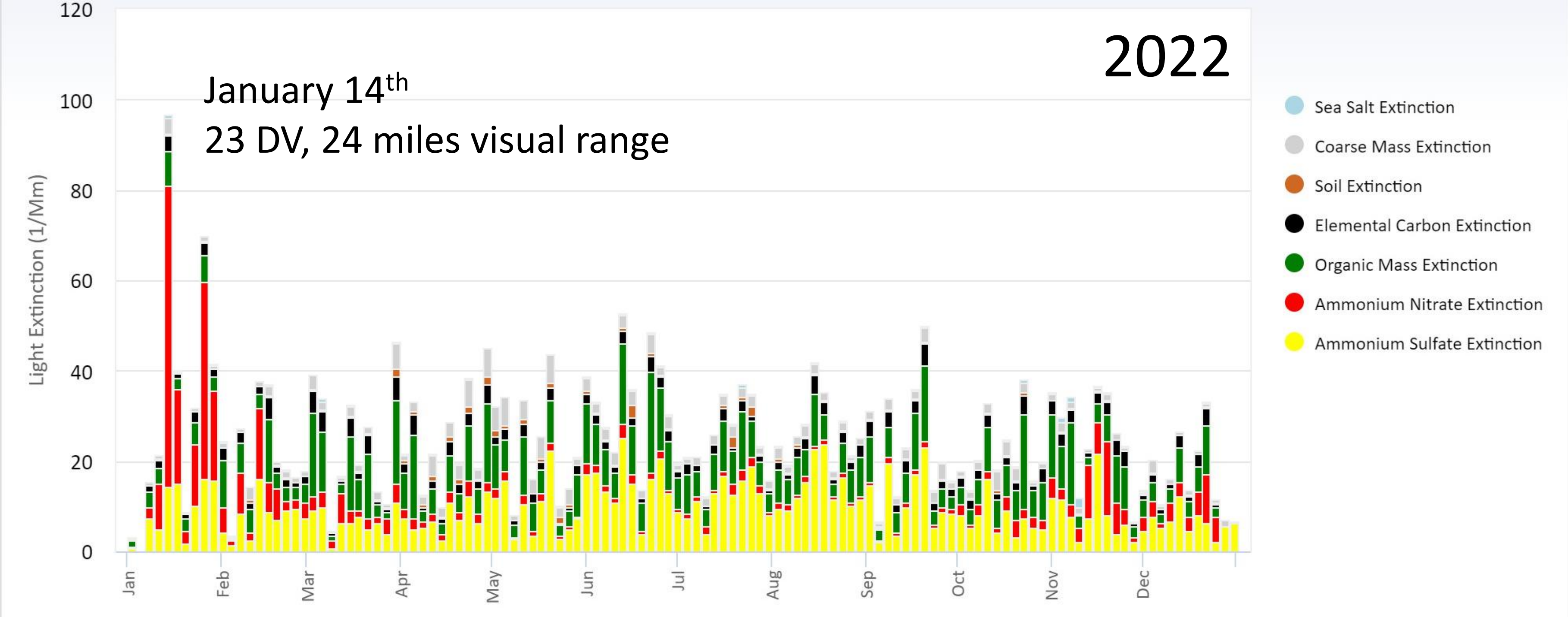


Note:

- large decreases in summer haze
- Smaller decreases in winter haze
- Winter episodes are similar between years

Great Smoky Mtn. Haze Budgets





Note:

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- Smaller decreases in winter haze
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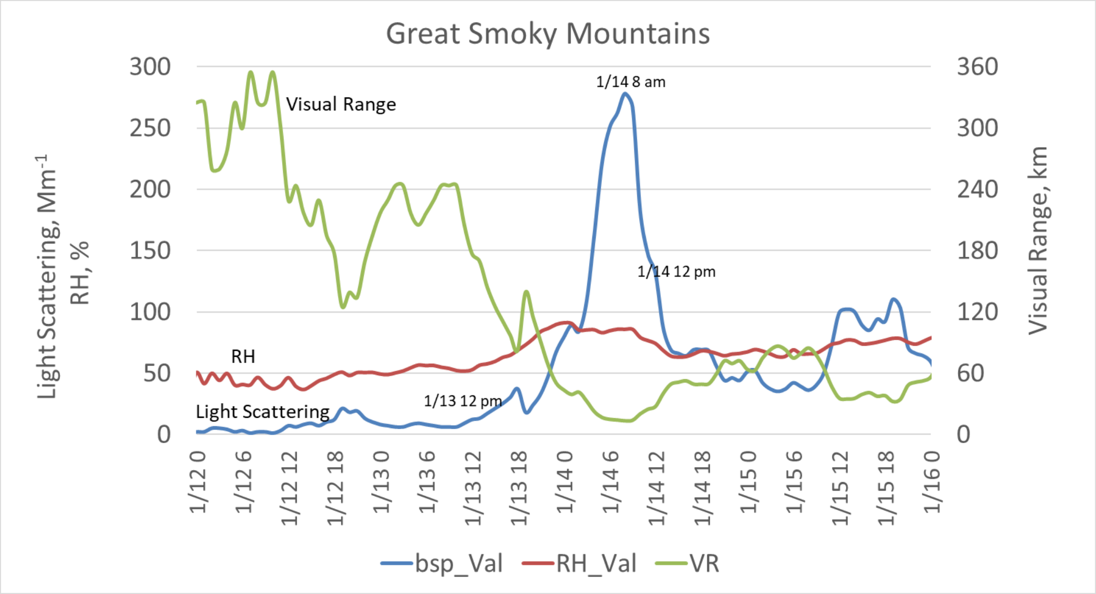
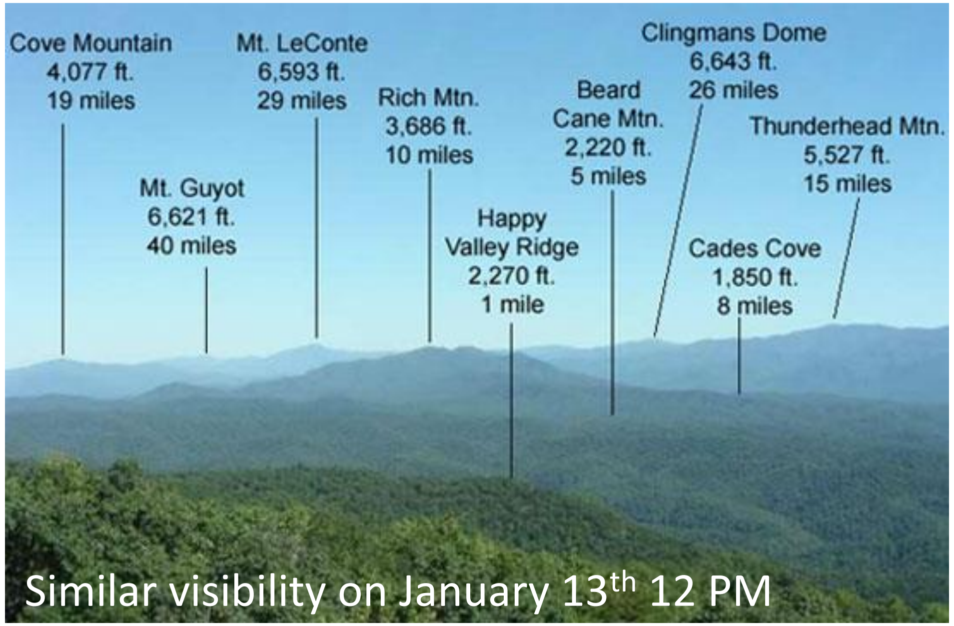
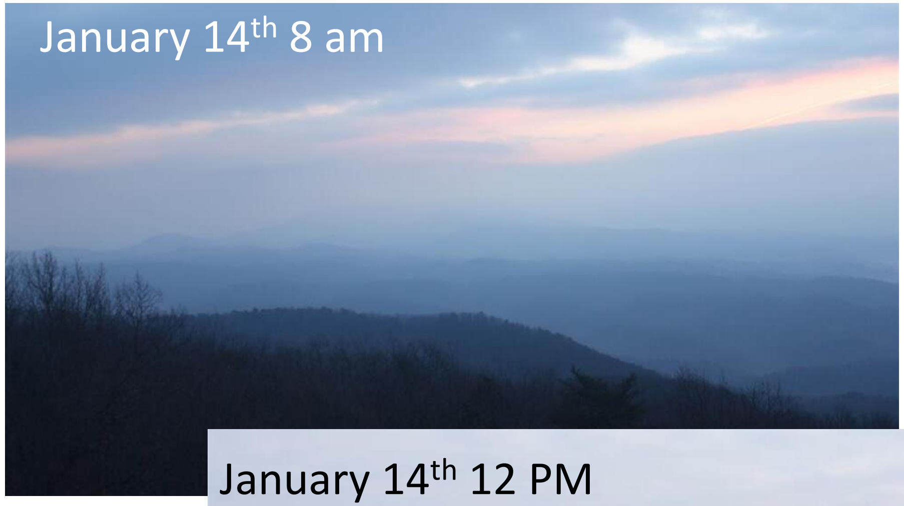


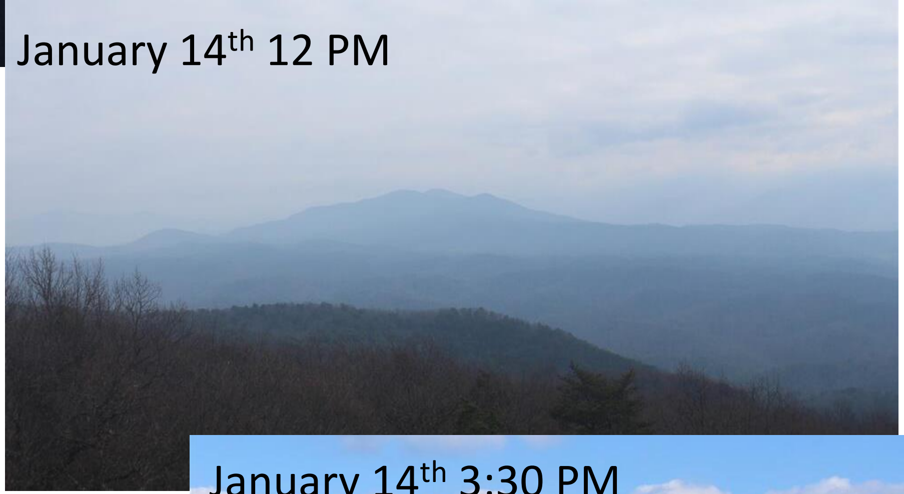
Great Smoky Mountains
Light Scattering, Mm^{-1}
RH, %
Visual Range, km
300
250
200
150
100
50
0
360
300
240
180
120
60
0
Visual Range
1/14 8 am
1/14 12 pm
RH
1/13 12 pm
Light Scattering
1/12 0
1/12 6
1/12 12
1/12 18
1/13 0
1/13 6
1/13 12
1/13 18
1/14 0
1/14 6
1/14 12
1/14 18
1/15 0
1/15 6
1/15 12
1/15 18
1/16 0
bsp_Val
RH_Val
VR



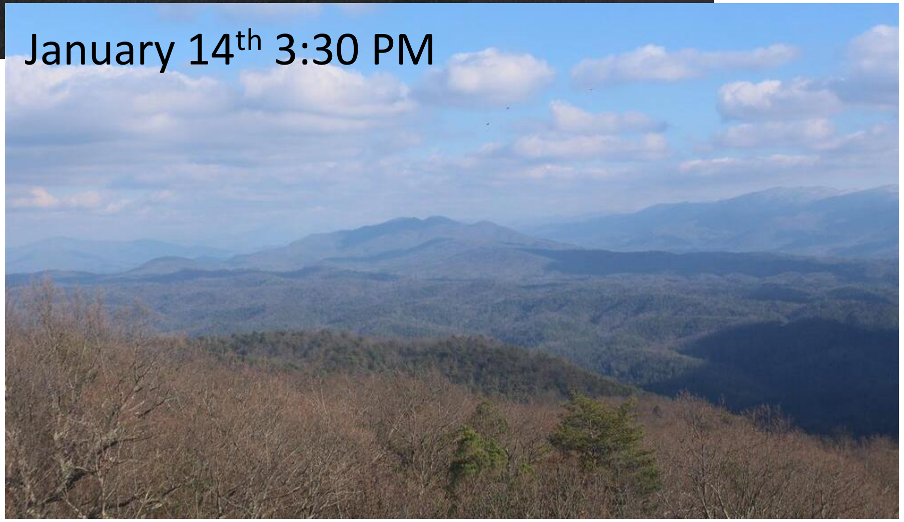
Cove Mountain
4,077 ft.
19 miles
Mt. LeConte
6,593 ft.
29 miles
Clingmans Dome
6,643 ft.
26 miles
Rich Mtn.
3,686 ft.
10 miles
Beard
Cane Mtn.
2,220 ft.
5 miles
Thunderhead Mtn.
5,527 ft.
15 miles
Mt. Guyot
6,621 ft.
40 miles
Happy
Valley Ridge
2,270 ft.
1 mile
Cades Cove
1,850 ft.
8 miles
Similar visibility on January 13th 12 PM



January 14th 8 am



January 14th 12 PM

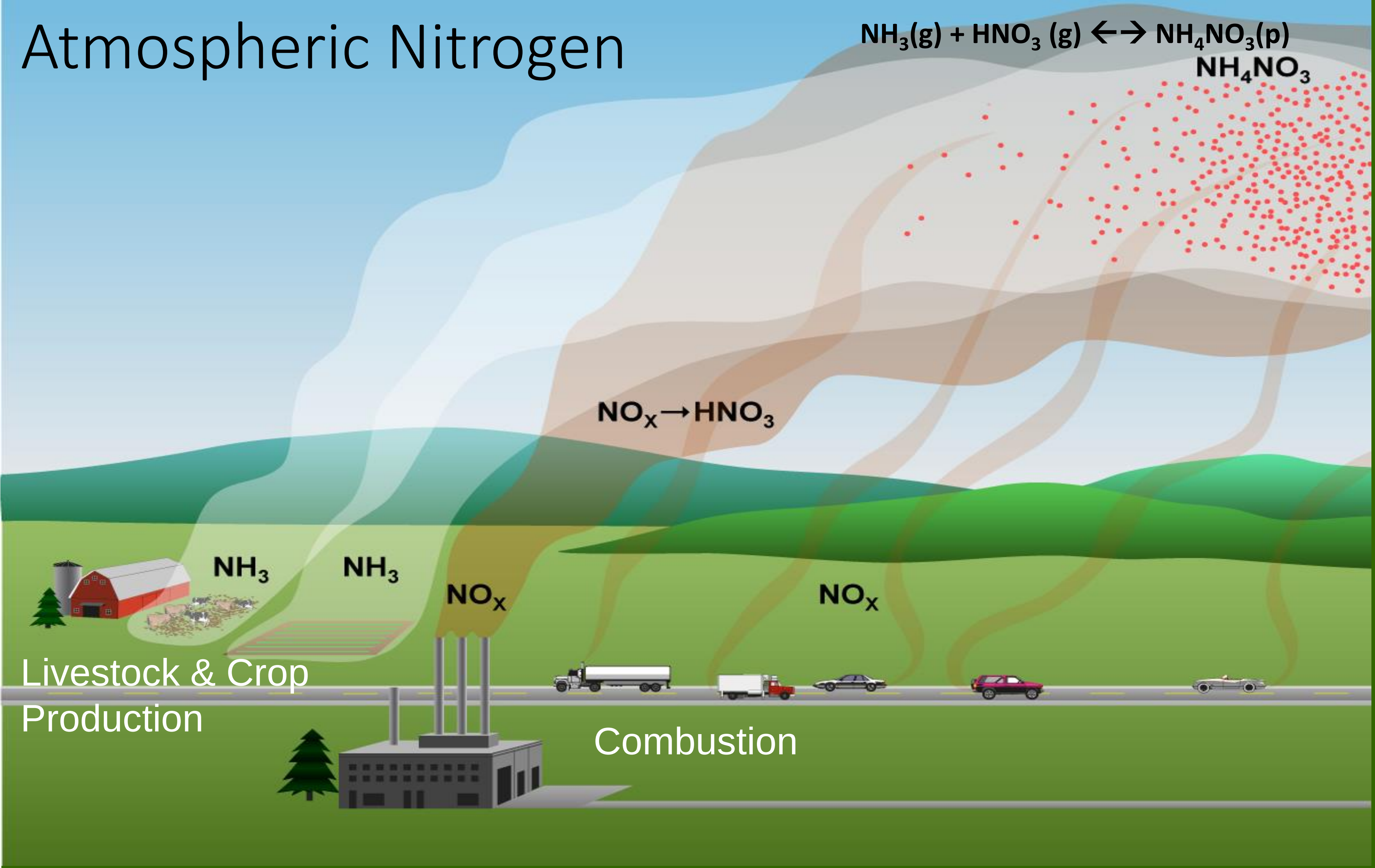


January 14th 3:30 PM

Issue

- Ammonium nitrate is becoming a larger fraction of human caused haze impairment in the southeastern US (and other regions)
  - Winter haze is decreasing at slower rate than summer
- Why?
  - Sulfate has decreased, but what else is happening?
- How might it change in the future?
- What can we do about it?

Atmospheric Nitrogen

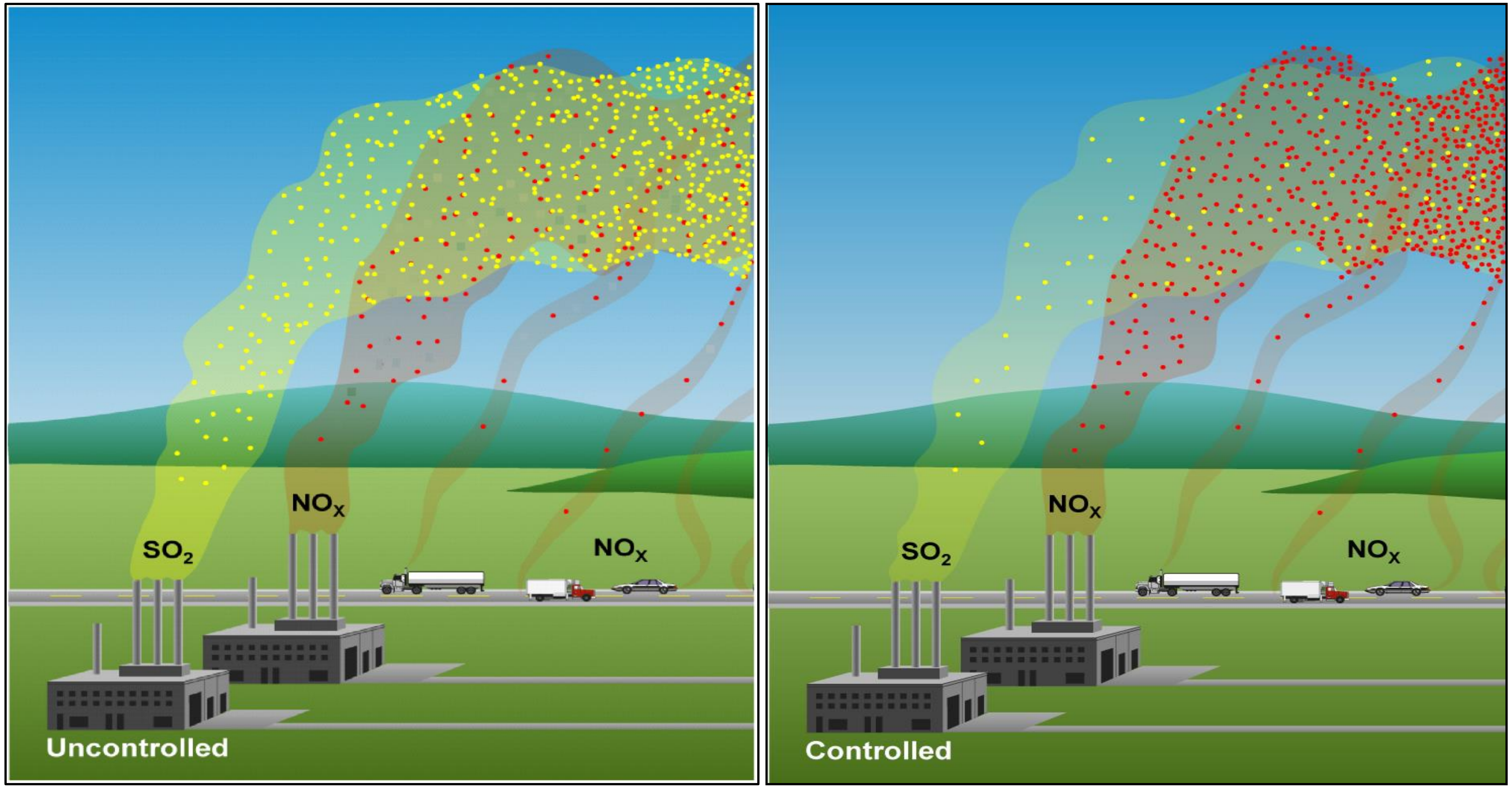


- Excess NO_x/HNO_3
  - NH_3 limited
  - NH_3 reductions result in PM2.5 reductions
- Excess NH_3/NH_4
  - HNO_3 limited
  - NH_3 reduction result in $PM_{2.5}$ reduction

- **NOx is oxidized forming nitric acid (HNO_3) gas**
- **Nitric acid is generally neutralized by ammonia forming particulate ammonium nitrates. This reaction is temperature and humidity dependent**

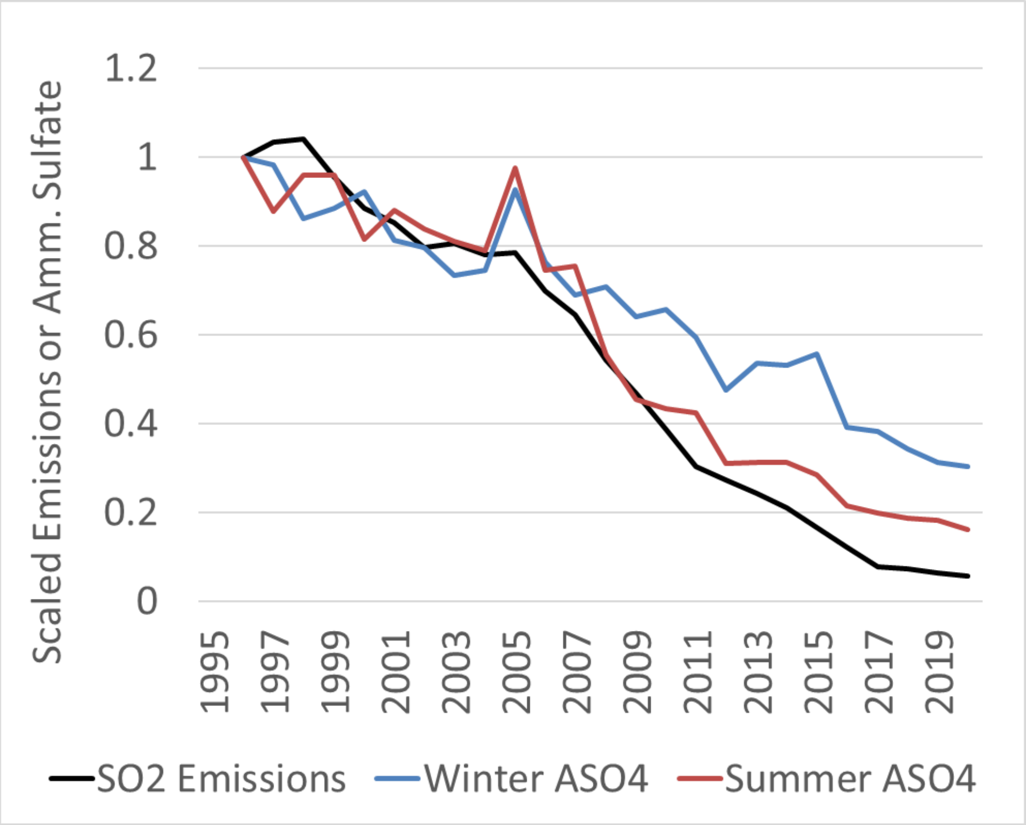
Relationship of Sulfates and Nitrates

Ammonia limited conditions



- Ammonia preferentially neutralized sulfate acids over nitric acid
- In a NH3 limited regime, reductions in SO_2 or increases in NH_3 can increase the formation of ammonium nitrate particles

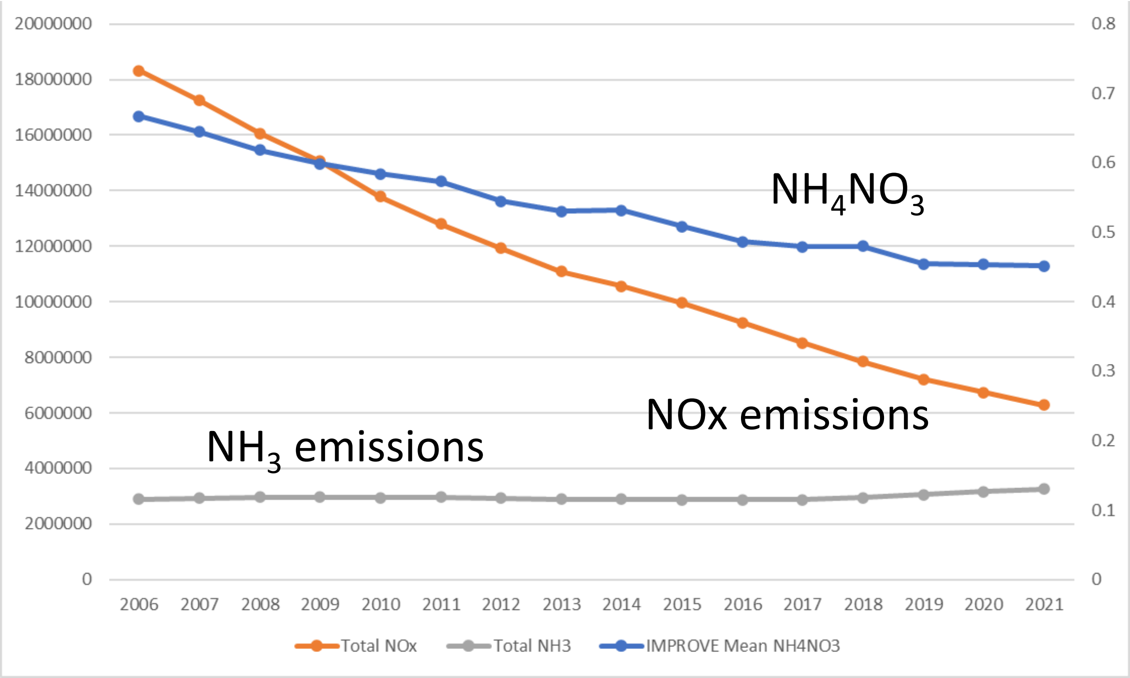
Eastern US SO_2 Emissions and Sulfate Trends



- Steep declines in annual SO_2 emission rates since 1995
- Near linear response in sulfate from 1995 – 2007 (Malm et al., 2002; Hand et al., 2012)
- Since 2007 winter sulfate decreased as a smaller rate than during the summer causing the change in the sulfate seasonality

Eastern US NOx Emissions and Nitrate Trends

Trends in 5-Yr Average Eastern US Total NH_3 and NO_x Emissions and IMPROVE NH_4NO_3



Copeland, 2022

- Ambient Nitrate and NOx emissions have had large reduction, while NH3 emission have increased
- Nitrate has decreased at less than half the rate of NOx

Shift in Secondary Inorganic Aerosol Formation in the Rural CONUS from 2011-2020

Is particulate nitrate formation NH_3, NOx limited or both?

Da Pan, Denise L. Mauzerall, Lillian E. Naimie, John T. Walker, Amy P. Sullivan, Aleksandra Djurkovic, Rui Wang, Xuehui Guo, Melissa Puchalski, Bret A. Schichtel, Mark A. Zondlo, Jeffrey L. Collett Jr.

Da et al., (2023) Nature Geoscience

Operated by Battelle

Colorado State University

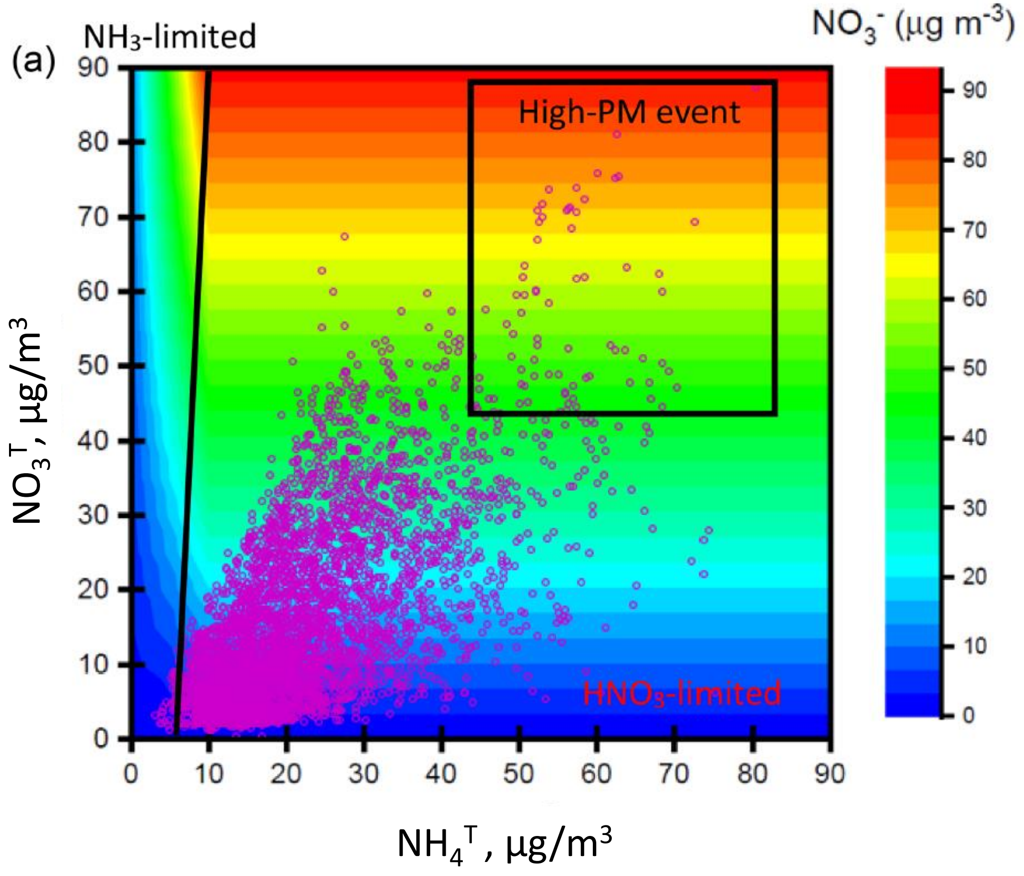
Definitions

- Total ammonium (NH_4^T) = NH_3 (g) + NH_4^+ (P)
- Total Nitrate (NO_3^T) = HNO_3 (g) + NO_3^- (P)
- $\varepsilon(\mathrm{NH_4^+})$ fraction of NH_4^+ in NH_4^T
- $\varepsilon(\mathrm{NO_3^-})$ fraction of particulate NO_3^- in NO_3^T

Measured Data Driven Aerosol Thermodynamic Modeling

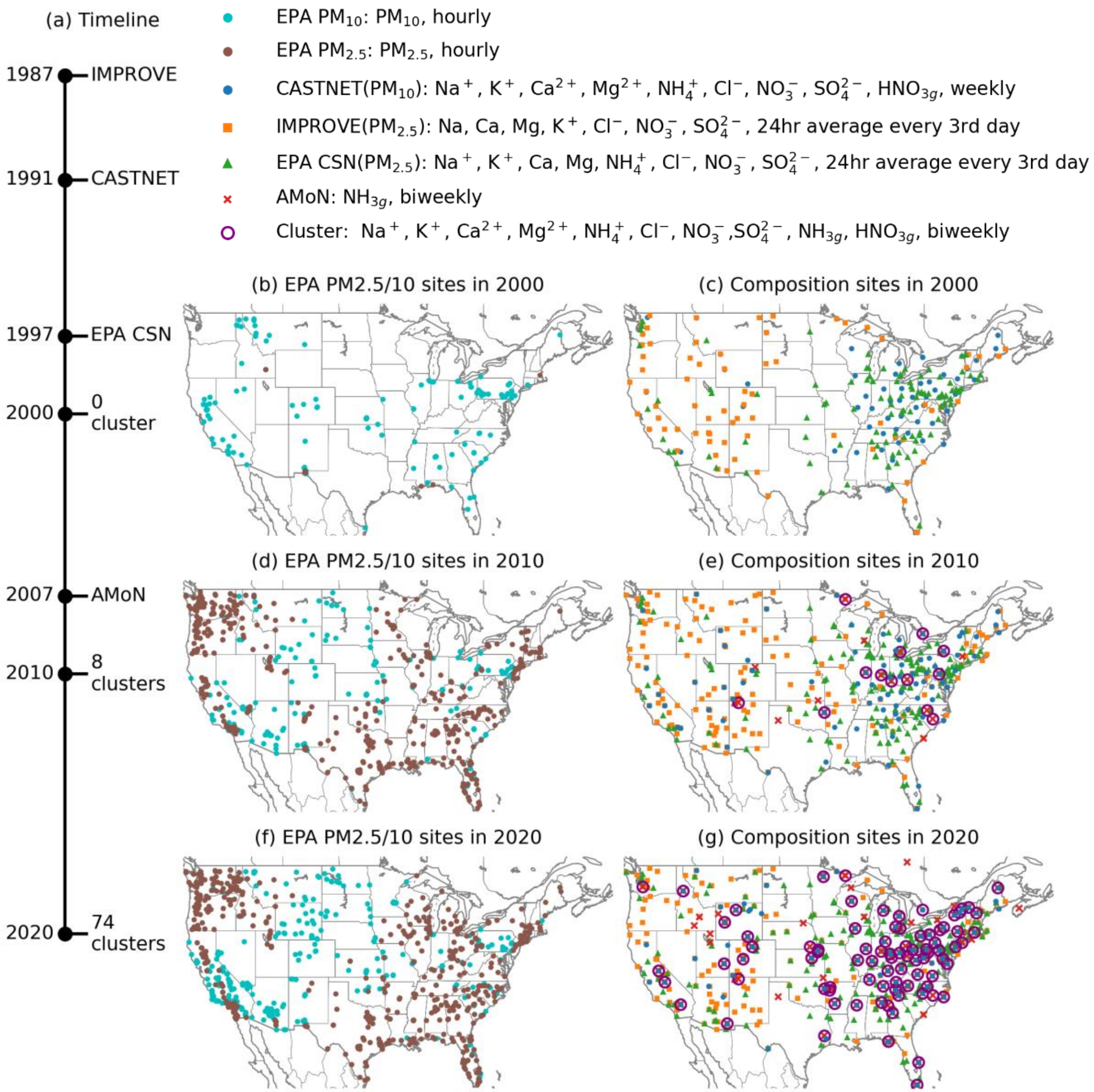
What is the sensitivity of particulate nitrate to changes in NH_4^T and NO_3^T?

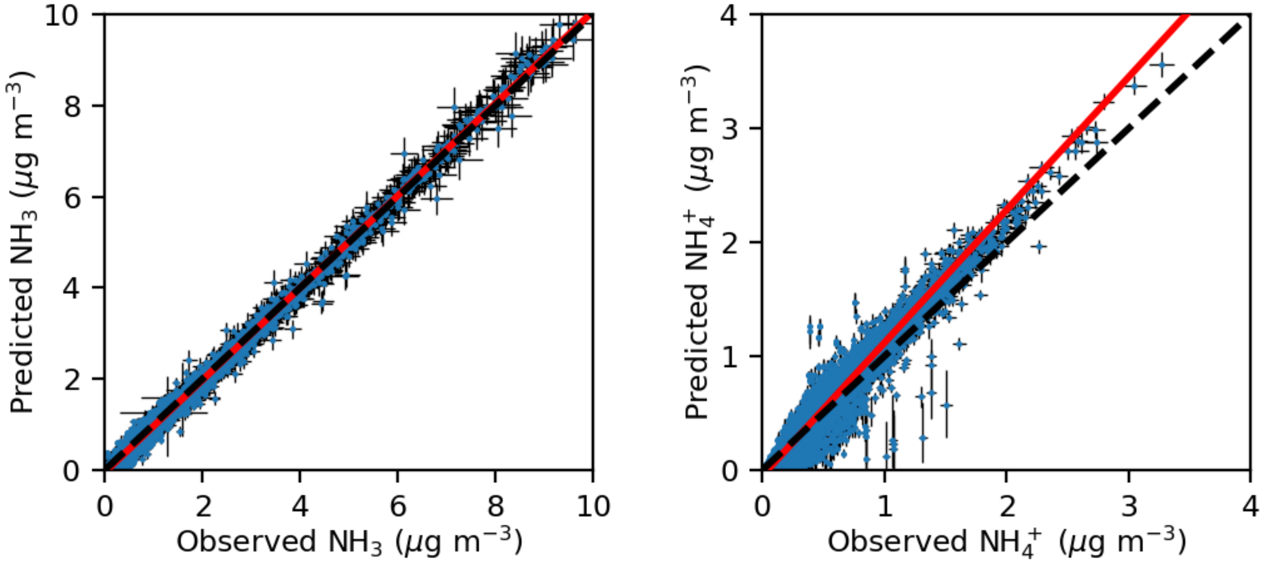
- ISORROPIA-II thermodynamic model
- The model partitions total nitrate (HNO3 and PNO_3) and total ammonia (NH_3 and NH_4) between the gas and aerosol phases.
- Inputs include measured NO_3^T and NH_4^T, temperature, RH and other gaseous precursors and aerosol data
- Same thermodynamic model used in Chemical transport models, e.g. CMAQ and CAMx.



Ammonium nitrate concentrations simulated by ISORROPIA II depending on NO_3^T and NH_4^T with SO_4 = 10 μg/m³ (Lin et al., 2020).

Complete (mostly) monitoring of Nitrogen Compounds

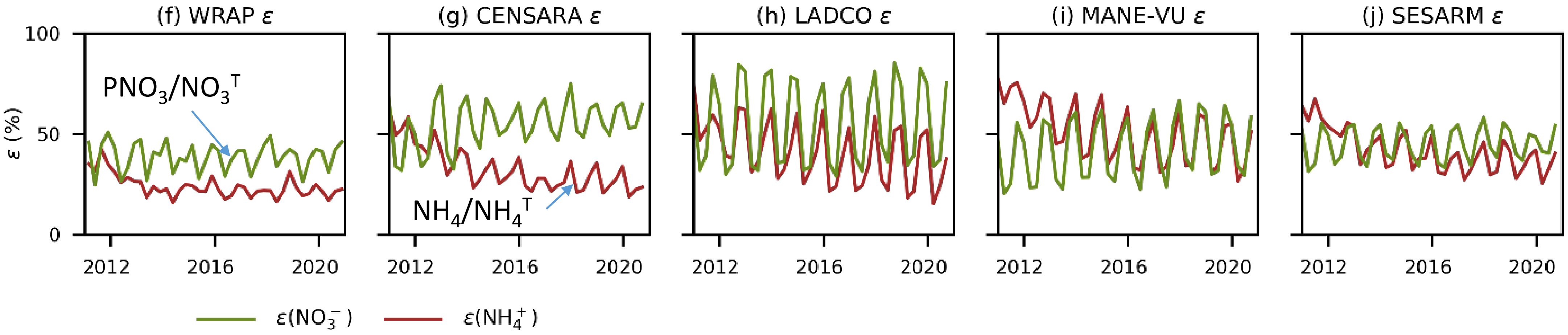




2 week averages

- In the last two decades, monitoring networks have gone through tremendous improvements
- With AMoN, multiple networks can be integrated at sites (purple circles) in rural regions
- Observations of precursor concentrations, aerosol composition, and meteorological conditions are available → Improved aerosol formation modeling and uncertainty estimates

Changing SIA (NO_3+SO_4) formation regime



$\varepsilon(NH_4^+)$ decreased by 20 – 50% → More gaseous NH_3 that can deposit near emission hotspots

SIA formation became less sensitive to NH_4^T changes → NH_3 controls became less effective than NO_x controls

$\frac{\Delta SIA}{\Delta NH_4^T}$ or $\frac{\Delta SIA}{\Delta NO_3^T}$ (40% reduction)	WRAP	CENSARA	LADCO	MANE-VU	SESARM
2011 NH_4^T	0.3	1.1	1.0	1.5	0.8
2011 NO_3^T	0.2	0.5	0.6	0.5	0.4
2020 NH_4^T	0.2	0.3	0.6	0.8	0.5
2020 NO_3^T	0.4	0.6	0.9	0.6	0.6

Changing SIA (NO_3+SO_4) formation regime in SESARM

$\frac{\Delta SIA}{\Delta NH_4^T}$ or $\frac{\Delta SIA}{\Delta NO_3^T}$ (40% reduction)	SESARM	Mammoth Cave	Great Smokey Mtn	Shenandoah 2015	Dolly Sods WV, 2012
2011 NH_4^T	0.8	0.98	1.16	0.66	1.36
2011 NO_3^T	0.4	0.37	0.14	0.29	0.26
2020 NH_4^T	0.5	0.53	0.47	0.57	0.62
2020 NO_3^T	0.6	0.73	0.42	0.55	0.38

- Throughout the Southeastern US particulate nitrate formation is more sensitive to changes in NO_3^T today than in the early to mid 2000's
- NOx controls today should be more effective than in past years
- At most sites, SIA is equally sensitive to changes in NH_4^T and NO_3^T, but sites like Dolly Sods, WV are still more sensitive to changes in NH_4^T
- Additional research is needed to understand the changing sensitivity and interplay of SIA to NH3 and NOx emissions

Southeastern US Nitrate Pilot Field Study

Primary Objective:

- Assess the sensitivity of particulate matter, haze and reactive nitrogen to changes ambient concentrations of NH_3 + NH_4, HNO_3 + pNO_3 at Southeastern NP
- Assess the sensitivity of ammonium nitrate to the total regional NO_x and NH_3 emissions and, where possible, to point, mobile, and agricultural sources

Other Objectives

- Assess the changes in aerosol hygroscopicity and affect on haze
- Assess the impact of changing emissions on nitrogen chemistry and reactive nitrogen deposition
    - Reduction in ammonium sulfate and nitrate will redistribute the deposition of reduced and oxidized N

Southeaster US Winter Nitrate Pilot Field Study

Field study Monitoring sites

- Mammoth Cave, KY will be the primary monitoring site
  - Deploy the mobile monitoring lab at the Mammoth Cave Air Quality Site
- Great Smoky Mountain, TN will be the secondary site
  - Look Rock air quality sites

Deployment: January 8th to February 14th 2025

Mammoth Cave, KY

Great Smoky Mountain, TN

Current Measurements

Mammoth Cave Houchin Meadow Site

- NADP mercury in litterfall sampling
- **NADP NTN and MDN**
- Nephelometer
- **IMPROVE**
- Ozone
- **CASTNET**
- RAWS fire weather
- National Park Service meteorology
- National Park Service all-in-one meteorology
- NASA AERONET
- PM sampling using Purple Air and QuantAQ devices

Other monitoring in Mammoth Cave

- Visibility camera
- NOAA Climate Reference Network
- Soil Climate Analysis Network

Great Smoky Mtns Look Rock Site

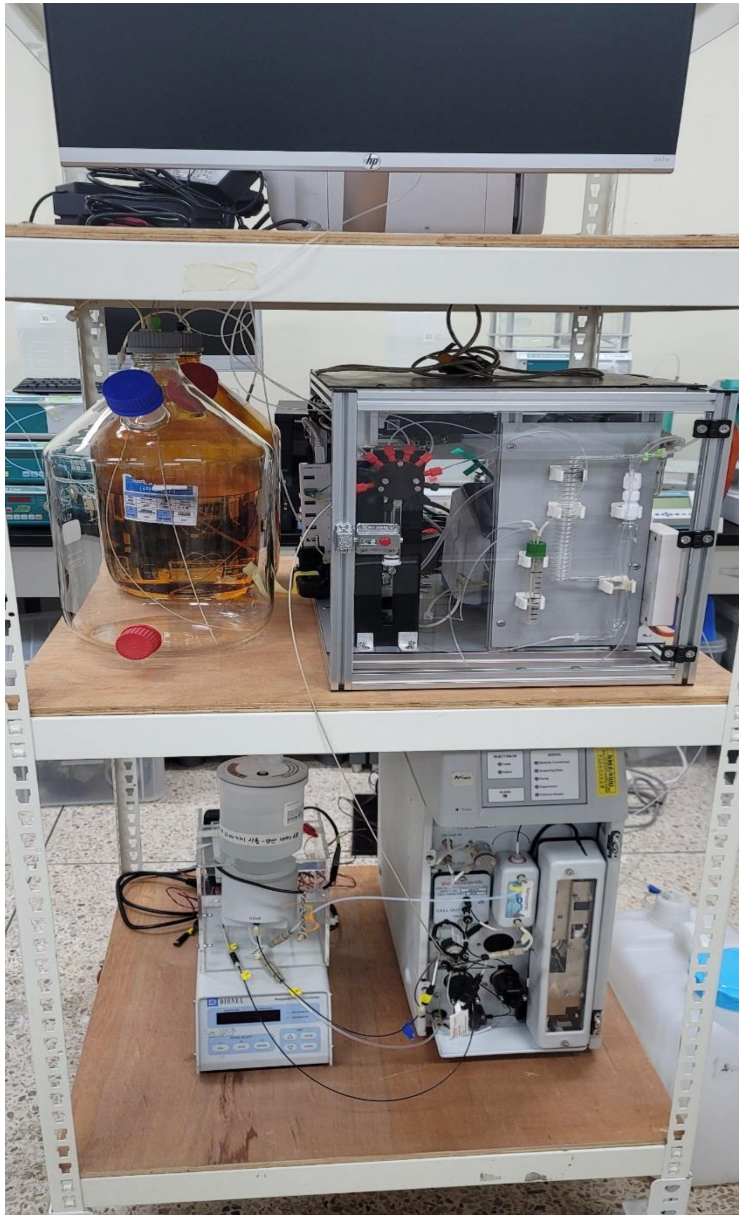
- Same as MACA, including
  - NADP NTN and MDN
  - IMPROVE
  - CASTNET
  - NPS GPMP – ozone and NOx
- NADP-AMON (2-week passive NH_3)
- ASCENT
  - Monitoring site with detailed high time resolution aerosol physical and chemical monitoring
- National Ecological Observatory Network (NEON)
- Ncore

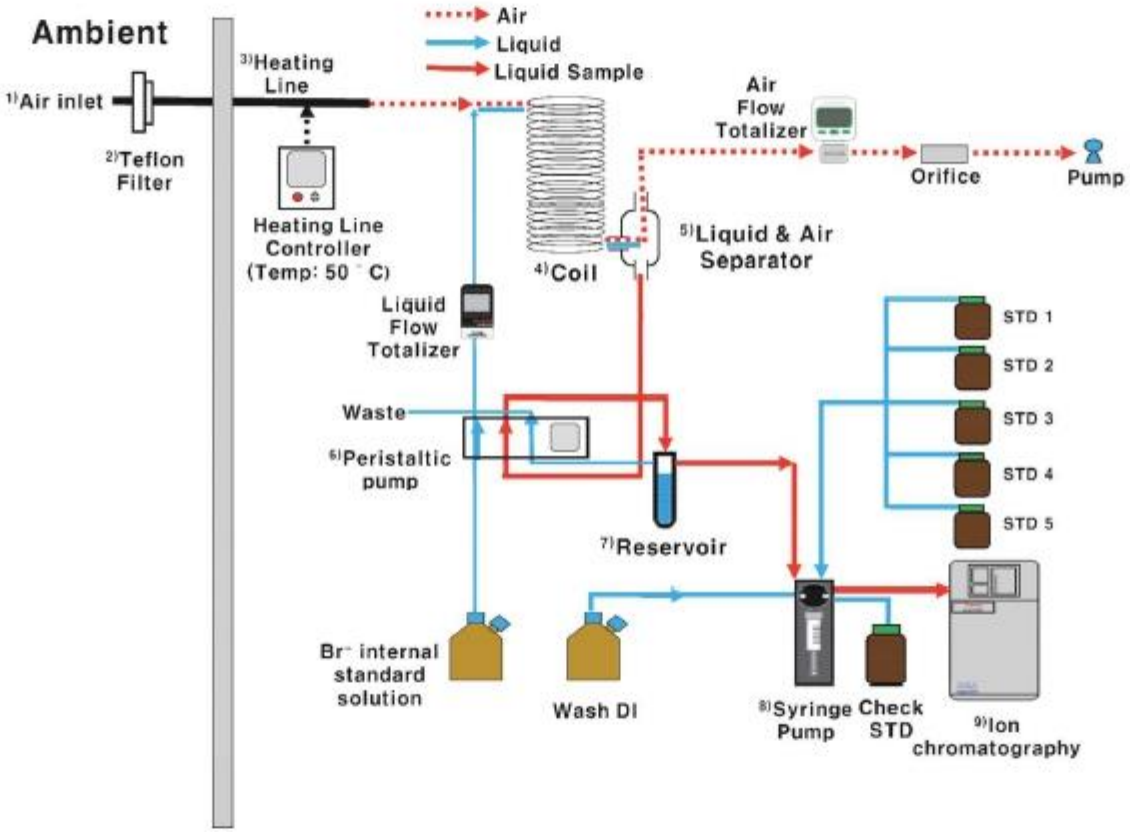
New Measurements

- Mammoth Cave
  - PILS – 15-minute particulate ions, e.g. sulfate and nitrate
  - URG – 24-hr gaseous and particulate concentrations
    - Ammonia, ammonium, nitric acid, nitrate, sulfur dioxide, sulfate
  - NOx
  - Continuous nitric acid (HNO_3)
    - wet scrubber (Taehyoung Lee's group)
  - Continuous ammonia
    - Air Sentry or Picarro instrument

- Great Smoky Mountains
  - URG – 24-hr gaseous and particulate concentrations, 4 days a week
  - Continuous ammonia
  - Continuous nitric acid

Nitric Acid Wet Scrubber





Lee et al.,

Analyses

- Standard data analyses
  - explore known and unknown relationships
- High time resolution thermodynamic modeling, similar to Da Pan’s work
  - Assess the sensitivity of particulate nitrate formation to ammonia and oxidized N availability
- Back trajectory analyses
  - Link sources to the measured concentrations and look for relationship in nitrate formation
    - urban areas
    - agricultural activities
    - Industrial activities
- Potential for using chemical transport model’s, e.g. CAMx and CMAQ in diagnostic data assessments

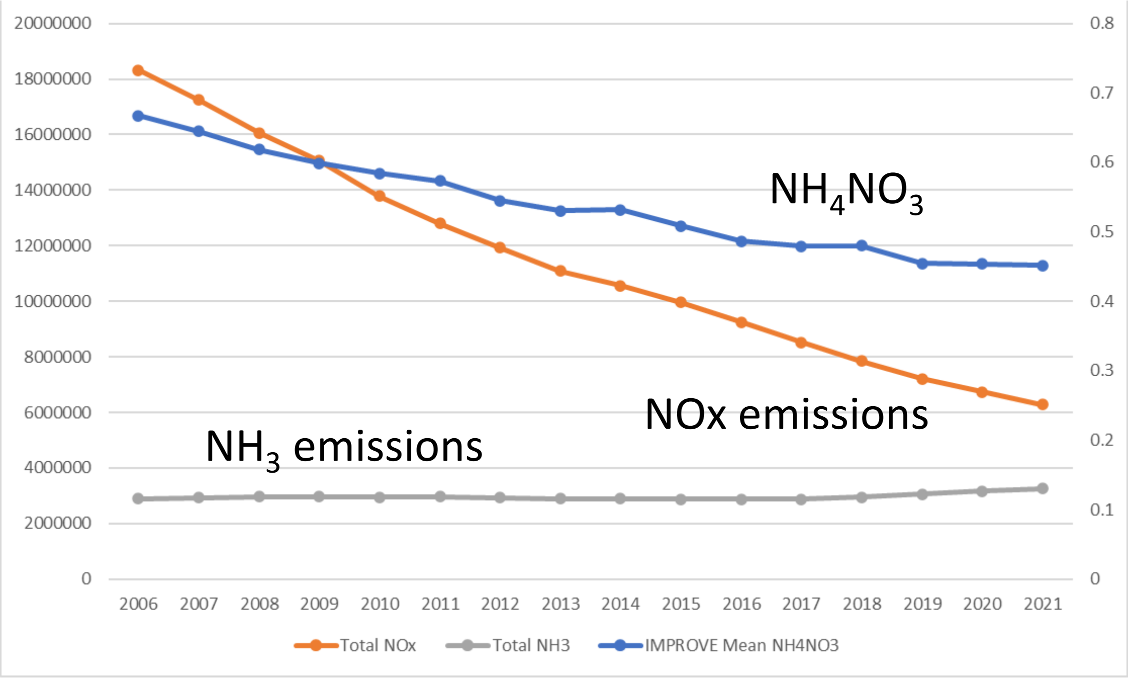
Collaboration and Sharing of Results

- Data and interpretations will be made available to the regulatory and scientific community
- Collaborations welcomed
  - Will not address all important questions, e.g. particle nitrate formation in urban settings
- Depending on results a larger scale collaborative study could be conducted in following years.

questions

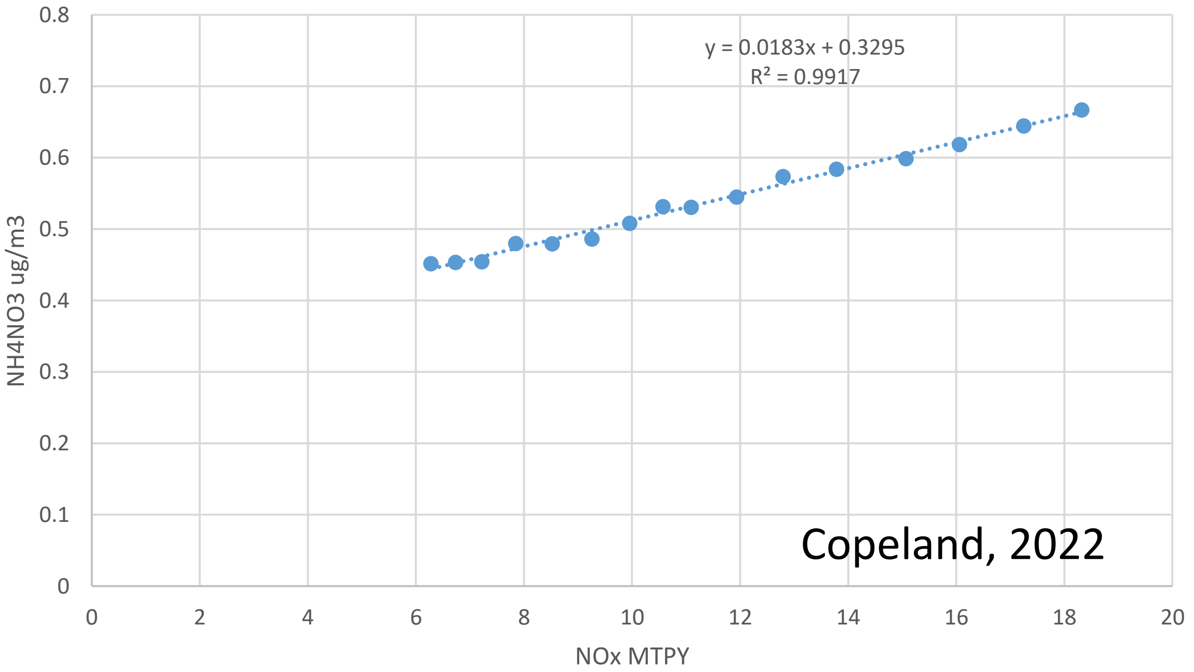
Eastern US NOx Emissions and Nitrate Trends

Trends in 5-Yr Average Eastern US Total NH_3 and NO_x Emissions and IMPROVE NH_4NO_3



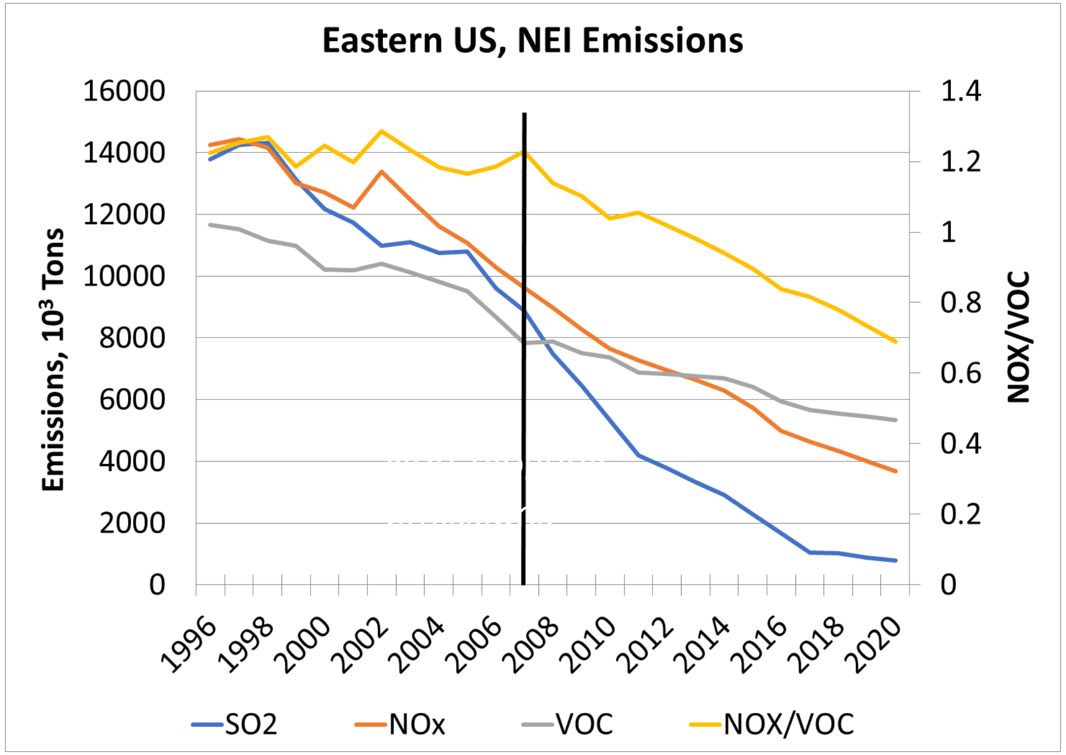
Ambient Nitrate and NOx emissions have had large reduction, while NH3 emission have increased

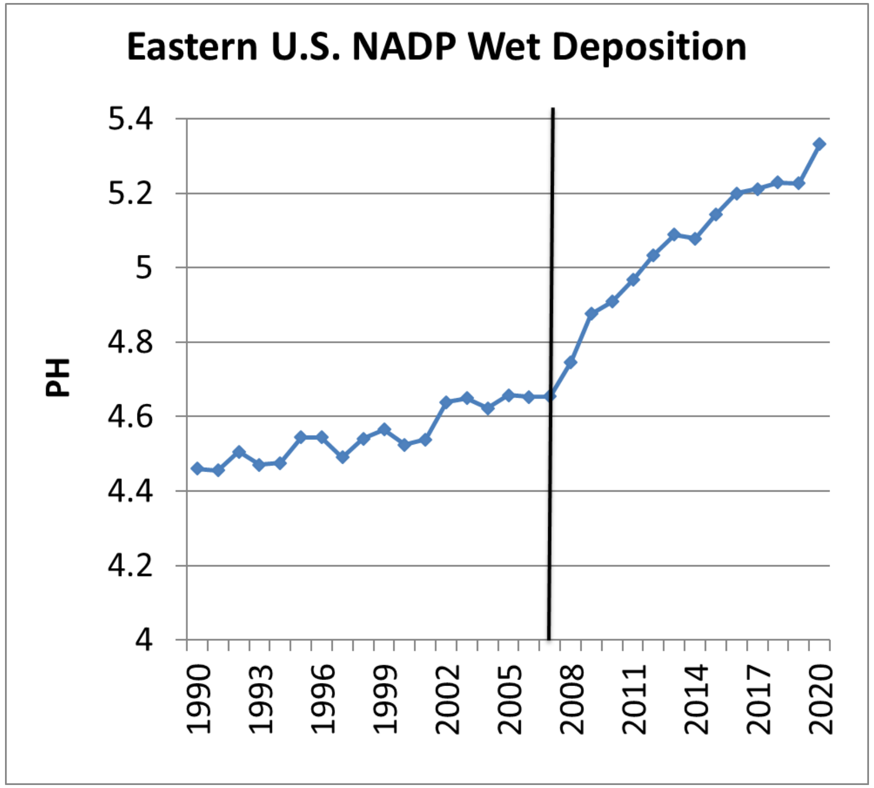
5-Year Average Eastern State Total NOx Emissions vs 5-Year Average IMPROVE NH_4NO_3



Eastern US NOx emissions have reduced at twice the rate of nitrate concentrations

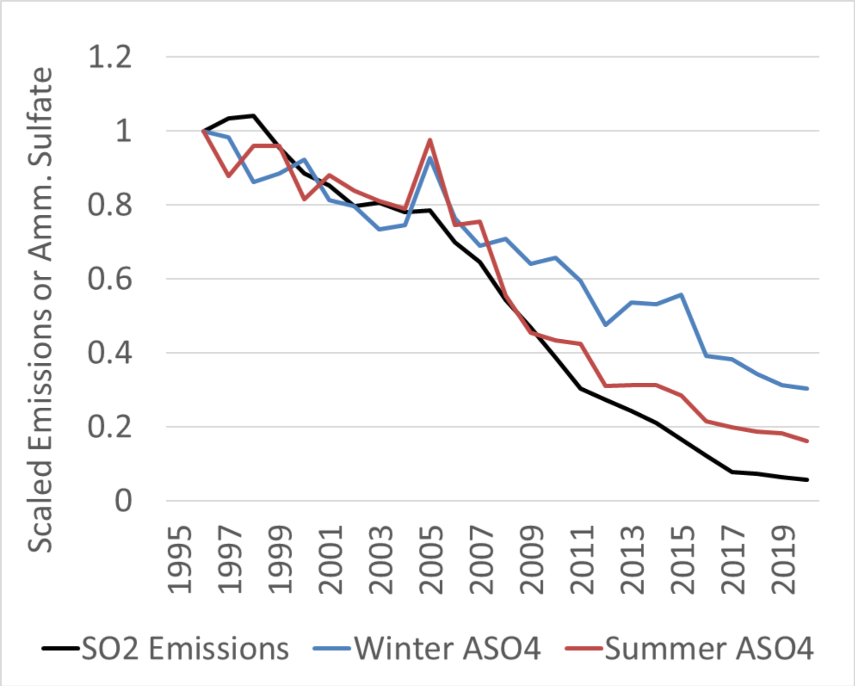
Changing Emissions and Atmospheric Chemistry

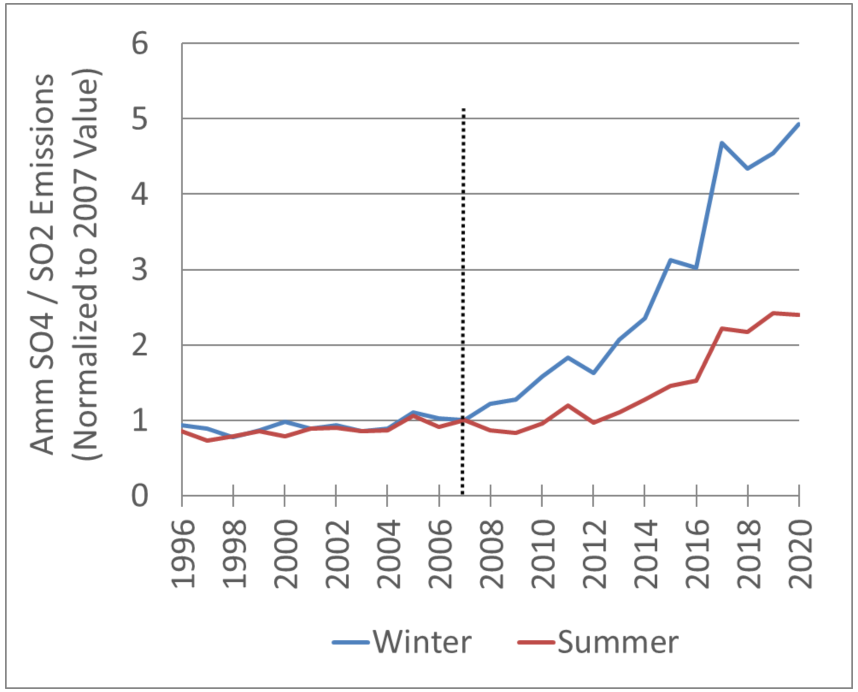




- H_2O_2 (peroxide) and O_3 are important in-cloud SO_2 and NOx to SO_4 and NO_3 oxidants
- As NOx/VOC ratio decrease, H_2O_2 (peroxide) formation tends to increases
- As cloud PH increases O_3 oxidation rates and SO_2 absorption increase
- High PH favors particulate nitrate formation

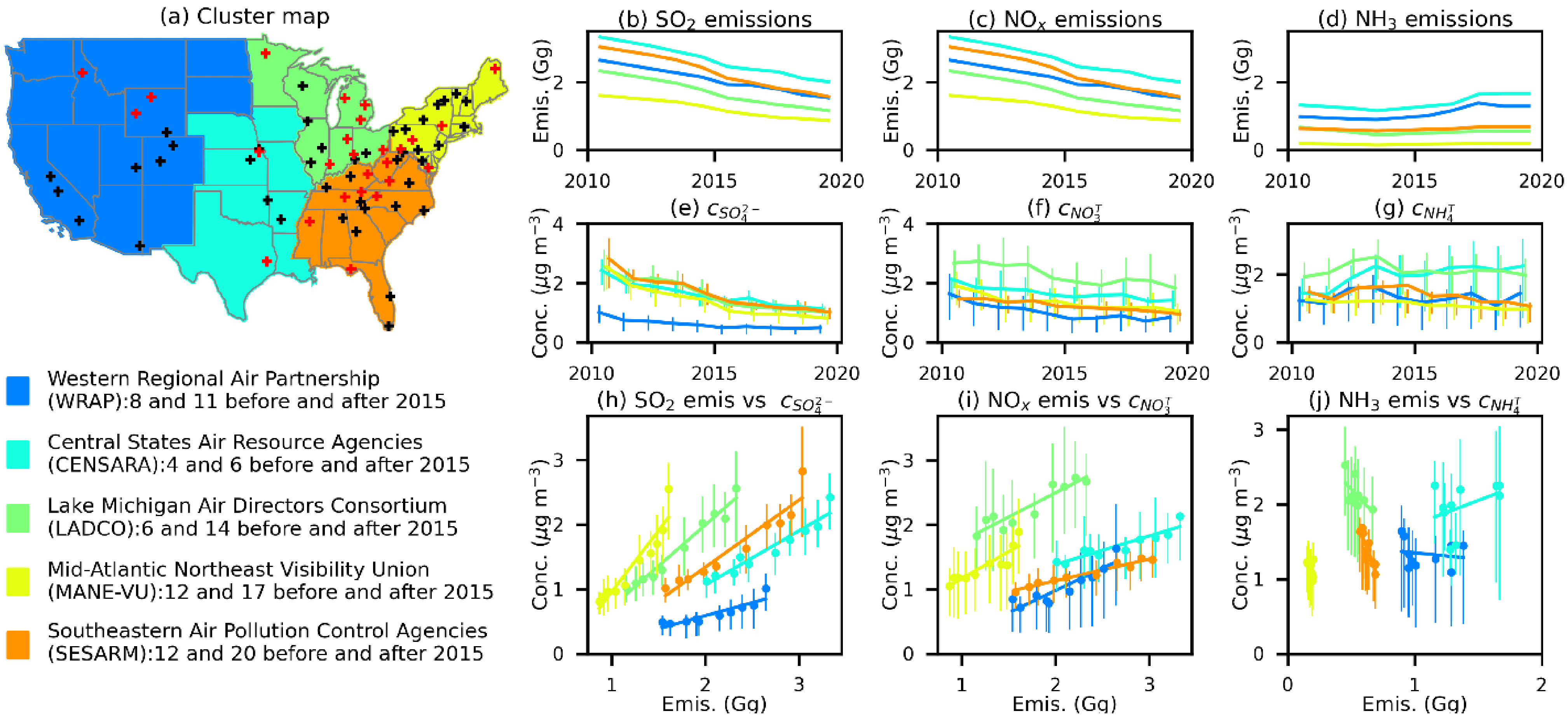
Eastern US SO_2 Emissions and Sulfate Trends





- Steep declines in annual SO_2 emission rates since 1995
- Near linear response in sulfate from 1995 – 2007 (Malm et al., 2002; Hand et al., 2012)
- Since 2007 winter sulfate decreased as a smaller rate than during the summer causing the change in the sulfate seasonality

Rapid changes in emissions and aerosol composition



SO_2 and NO_x emissions decreased by 70% and 50%

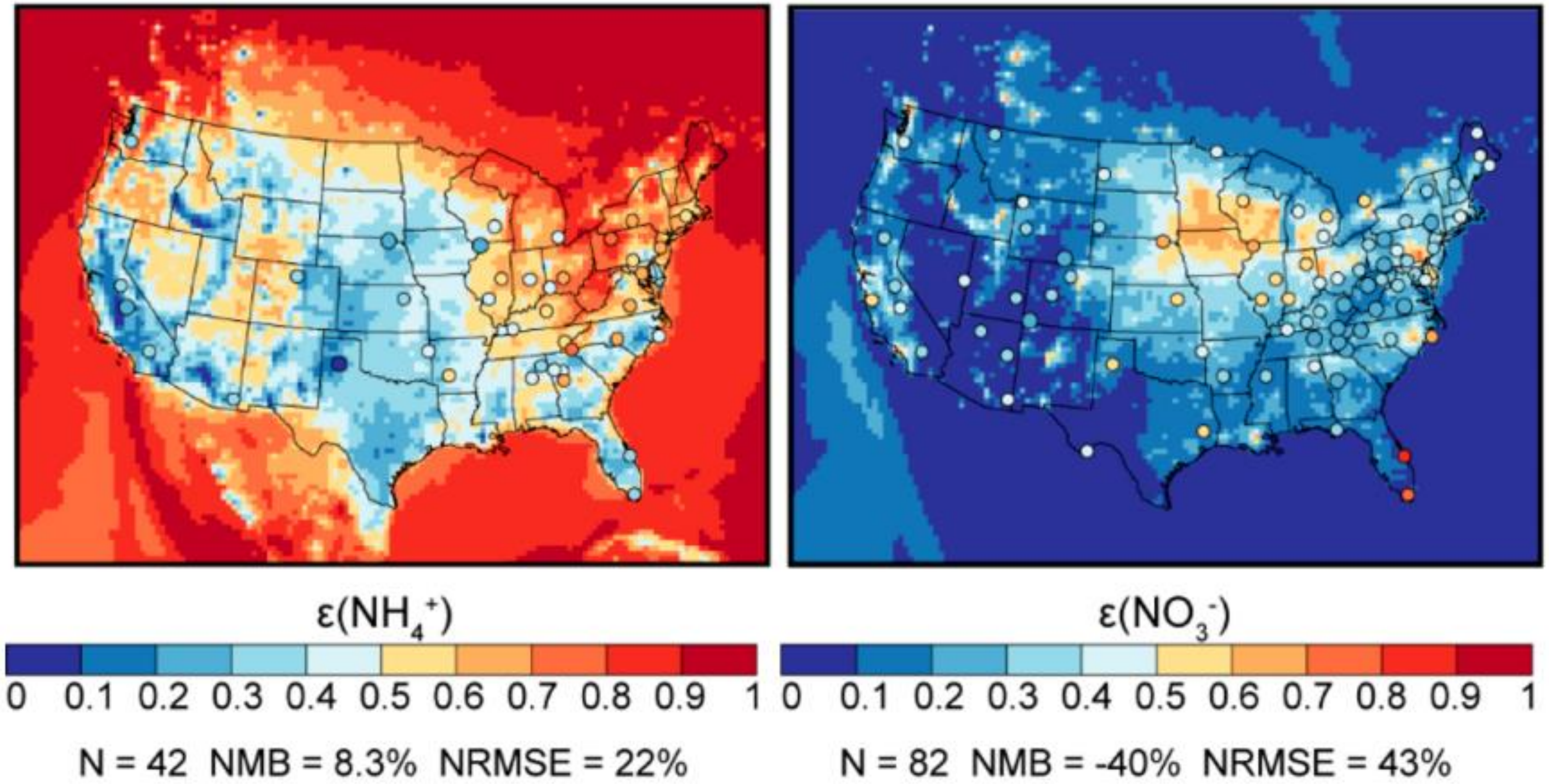
Conc. of SO_4^{2-} and NO_3^T decreased and correlated with emissions[2]

No clear or even inverse correlation between NH_4^T and NH_3 emissions

- Rapid changes in aerosol composition because of SO_2 and NO_x emission reductions
- Large uncertainties in NH_3 emissions and contributions of NH_3 to SIA formation

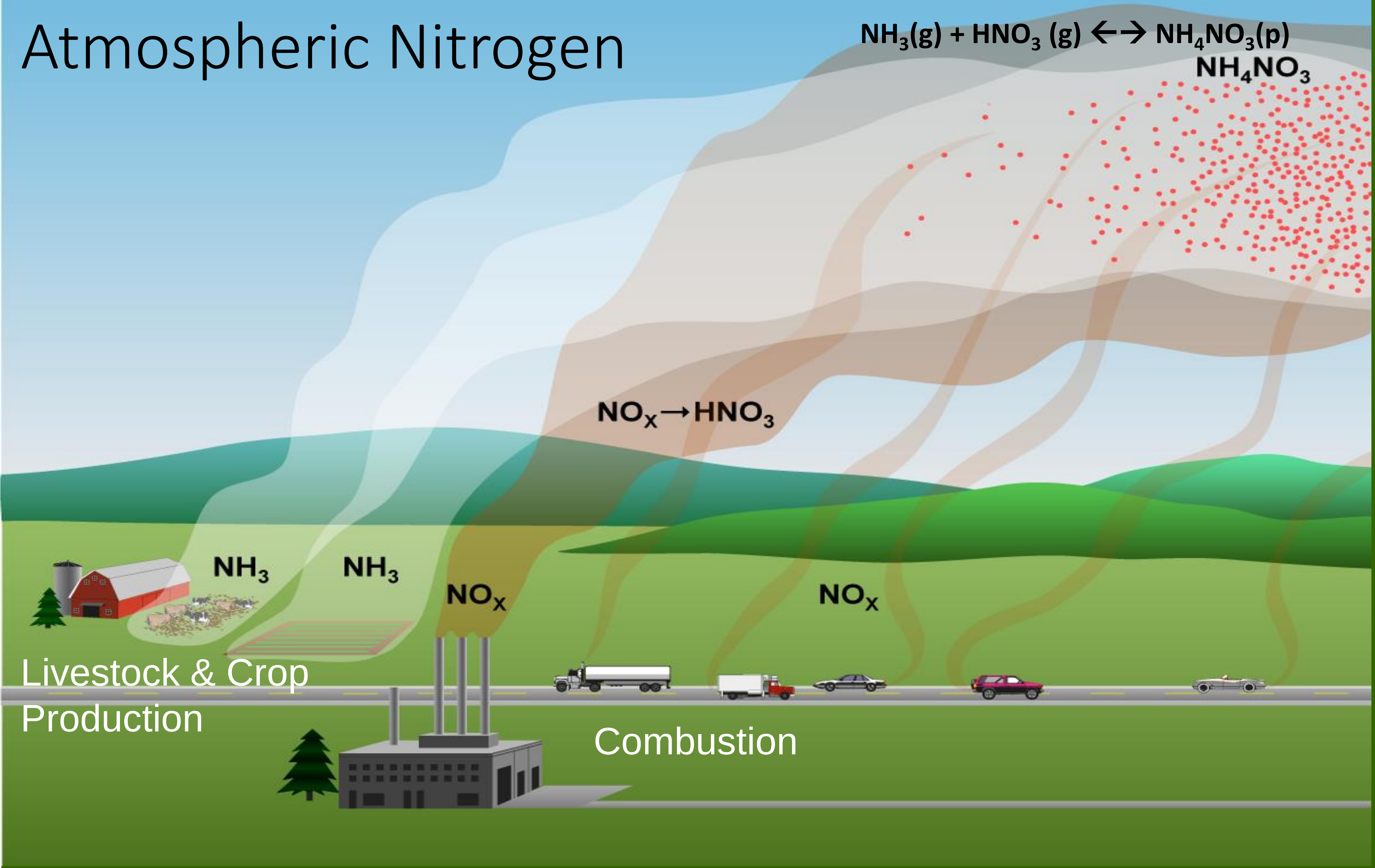
[1]Emission data from NEI Trend; [2]Mean annual observations from CASTNET and AMoN.

Large uncertainties in N_r simulations



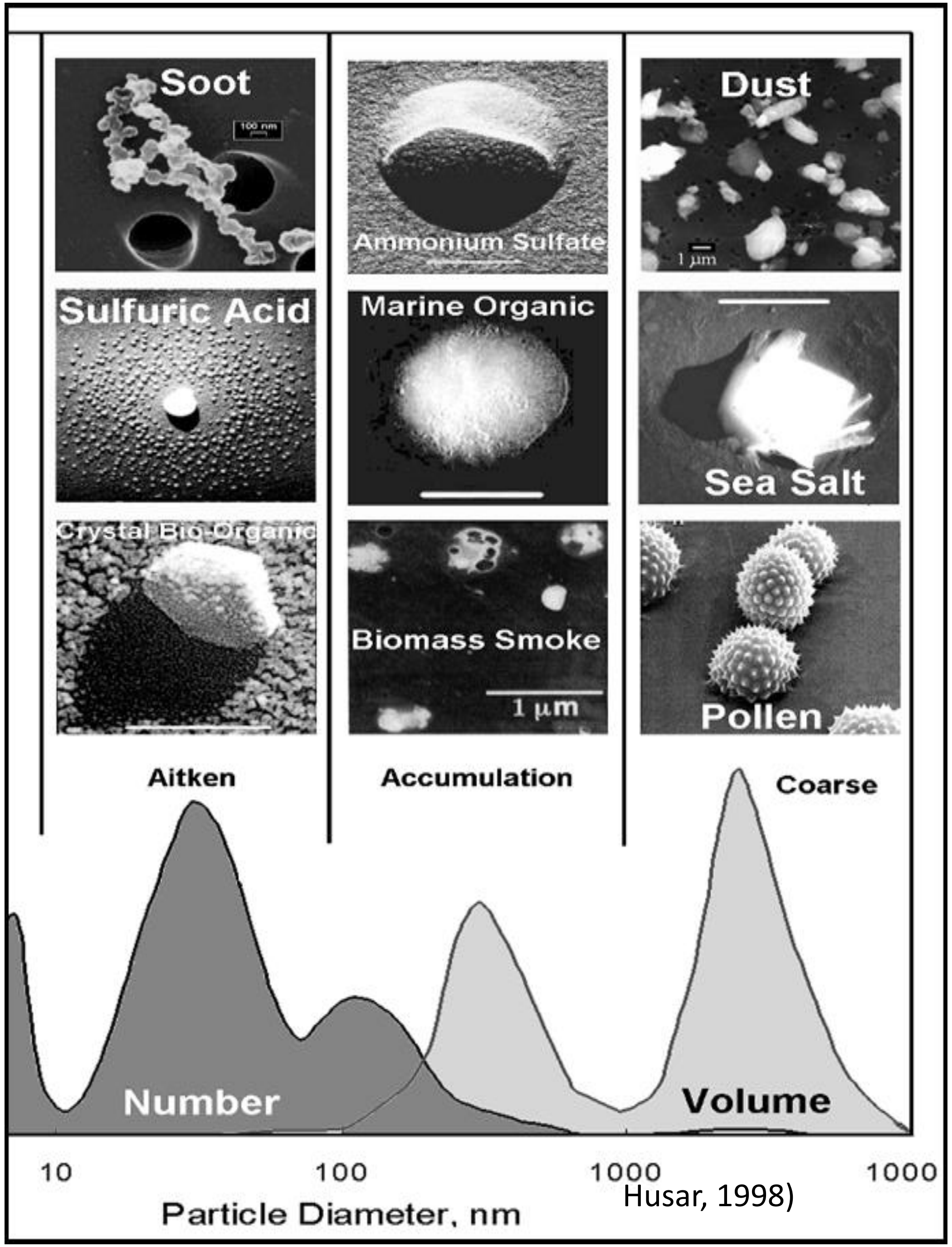
- Chemical transport models have large uncertainties in emission inventories and deposition processes
- Chen et al. (2019) found large differences between simulated (CMAQ) and observed (CASTNET + AMoN) fractions of NH_4^+ in NH_4^T ($\varepsilon(\mathrm{NH_4^+})$) and fractions of NO_3^- in NO_3^T ($\varepsilon(\mathrm{NO_3^-})$)
- We can better constrain SIA formation and Nr partitioning using in-situ observations, but do we have enough observations?

Atmospheric Nitrogen



- Excess NO_x/HNO_3
  - NH_3 limited
  - NH_3 reductions result in PM2.5 reductions
- Excess NH_3/NH_4
  - HNO_3 limited
  - NH_3 reduction result in $PM_{2.5}$ reduction

- **NOx is oxidized forming nitric acid (HNO_3) gas**
- **Nitric acid is generally neutralized by ammonia forming particulate ammonium nitrates. This reaction is temperature and humidity dependent**



Particulate nitrate

- Secondary aerosol from NOx emissions
- Usually in the form of ammonium nitrate (similar to ammonium sulfate)
- In the fine mode making it very efficient at scattering light and creating haze.