Update on EPA's Aquatic Acidification Index (AAI) and supporting studies.

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Secondary NOx/SOx Process

Why a NAAQS?

- Clean Air Act Acid Rain Program (Title IV) has reduced emissions of SO_2 and NO_x from utilities, but was not designed to fully address aquatic acidification in sensitive ecoregions across the country
  - Basically an emissions-based program – lacks a linkage between emissions and effects – in contrast to air quality-based standards
  - Despite observed improvement, many reports (e.g., NAPAP) find continuing adverse effects exist in many acid sensitive areas
  - Sampled lakes exhibit improved water quality trends -- 12% in the Northeast and 56% in the Adirondack mountains
  - Recovery significantly lagging in southern Appalachian mountains

Background – Secondary N/S NAAQS

- EPA sets NAAQS for primary and secondary standards for 6 criteria pollutants {O3, Pb, PM (2.5 and 10), oxides of S and N}
  - Primary address human health
  - Secondary address environmental welfare relevant to human benefits
- Current secondary standards set to protect against direct effects of gaseous NO_2 and SO_2 on vegetation, not deposition-related effects:
  - Annual NO_2 standard set at 0.053 ppm
  - 3-Hour SO_2 standard set at 0.5 ppm
- EPA secondary NOx/SOx NAAQS review 2006 – 2012
  - Focused on deposition related effects (nutrient enrichment, aquatic and terrestrial acidification) as a more ecologically relevant approach
  - Resulting in a focus on aquatic acidification effects (dominant role of man made atmospheric inputs; strong science base)
    - Note: Assume directional benefits for terrestrial acidification indicators (e.g., ↓ Al/BC ratios)

Background

- The extent to which emissions NOx/SOx lead to aquatic acidification depends on:
  - Ability of the water body to neutralize acidifying inputs from atmospheric deposition
  - Ambient concentration NOx/SOx and resulting level of acidifying deposition
- Critical load (CL) represents the amount of acidifying deposition that a water body can receive and maintain a specified level of protection
  - Level of protection is often link to maintaining a level of Acid-neutralizing Capacity (ANC) in drainage waters
  - ANC level is selected to support of healthy aquatic ecosystems
  - Steady-state, mass balance biogeochemistry approach

- Aquatic ecological effects occur when:
  - *CL exceeds the acidifying (wet and dry) deposition*

Conceptual model of an aquatic acidification standard

Ecological effects and ecological indicator → Linking atmospheric oxides of S and N deposition to ecological indicator → Linking "allowable" deposition to "allowable" concentrations of ambient air indicators of oxides of N and S

Standard Design: anchored by steady state critical load modeling which enables linking of aquatic acidification effects (ANC) to ambient air indicators through atmospheric deposition

Elements of the standard:

•**Indicators**: NOy and SOx to be measured by States to determine if the standard is met

•**Form**: Aquatic Acidification Index (AAI) equation

- •Ambient air concentrations are input to the equation
- •Equation parameters are calculated from well-accepted critical loads models and CMAQ modeled deposition velocities.
- •Equation parameters vary spatially across the U.S., so that "allowable" NOy and SOx concentrations also vary across the U.S. (to account for ecosystems variation in sensitivity to NOy and SOx) while affording all ecosystems the same amount of protection

•**Level**: the target AAI value that, in combination with the other elements of the standard, is judged to provide requisite protection

•**Averaging time**

Translating a linked atmospheric-biogeochemical construct in NAAQS terminology

AAI derivation

Start with CL expression:
Define a potential ANC based on the relative difference between CL and deposition

$$CL_{N+S} = ([BC]_0^* - [ANC_{lim}])Q + Neco$$

{modification of SSWC model}

Ambient indicators

$$[ANCp] = [BC]_0 + Neco/Q - Dep_{NHx}/Q - T_{NOy}Conc_{NOy}/Q - T_{SOx}Conc_{SOx}/Q == AAI_{WB}$$

Translating a linked atmospheric-biogeochemical construct in NAAQS terminology

$$AAI_{WB} = [BC]_0 + Neco/Q - Dep_{NHx}/Q - T_{NOy}Conc_{NOy}/Q - T_{SOx}Conc_{SOx}/Q$$

Water quality

Air observations of NOy/SOx

LEVEL, FORM

$$AAI = F1^* - F2 - F3Conc_{NOy} - F4Conc_{SOx}$$

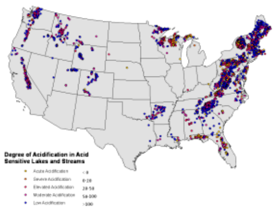
Biogeochemical
Base cation supply
Nitrogen neutralization

Reduced N (NHx) deposition

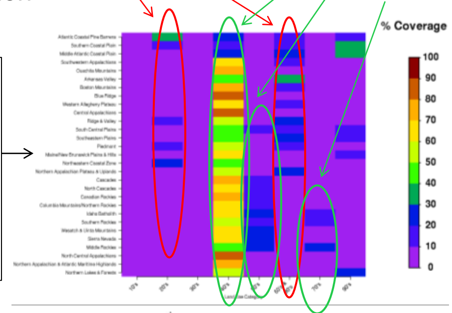
Concentration to deposition translators, Tratios

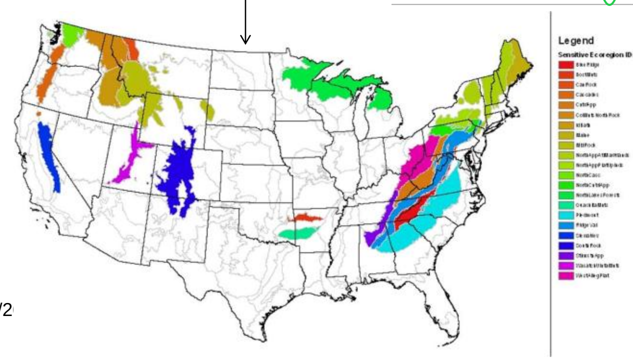
Charge balance between major cations supplied by ecosystem and acidifying anions contributed by deposition: interpreted as the potential ANC water bodies would realize from an atmospheric state.

Accommodating homogeneity and heterogeneity in a national application – spatial aggregation



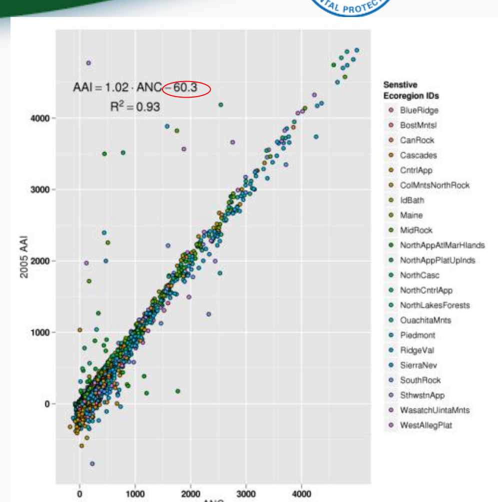
Objective - to focus on sensitive areas (based on ANC –left panel) and are likely to benefit (using NLCD rt. panel) from reductions in deposition segregated into similar biogeochemical attributes (Omernik ecoregions – below)

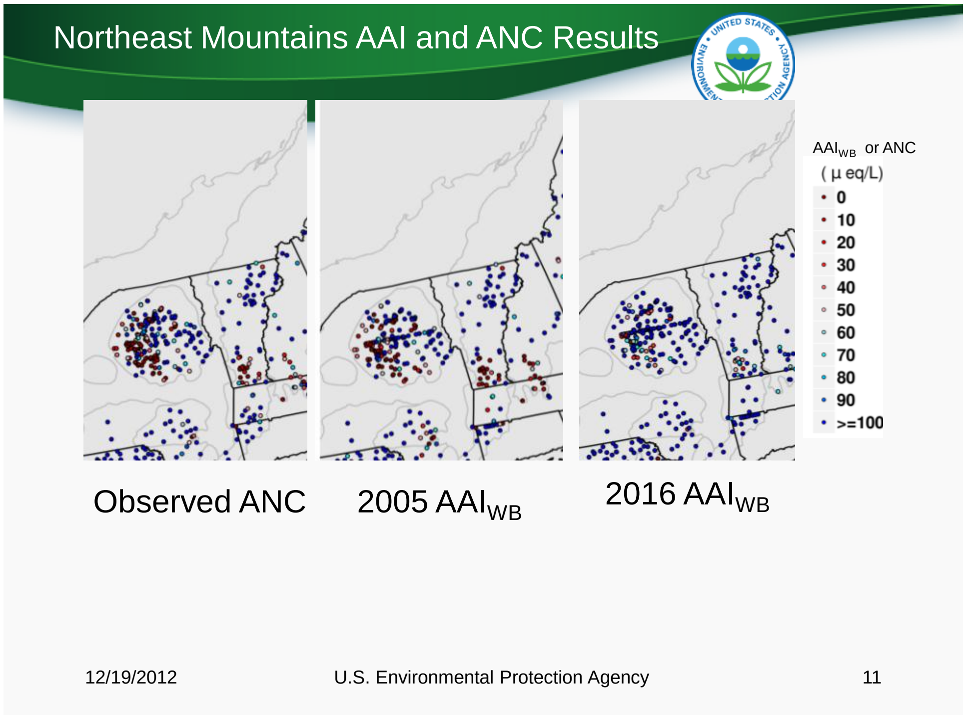


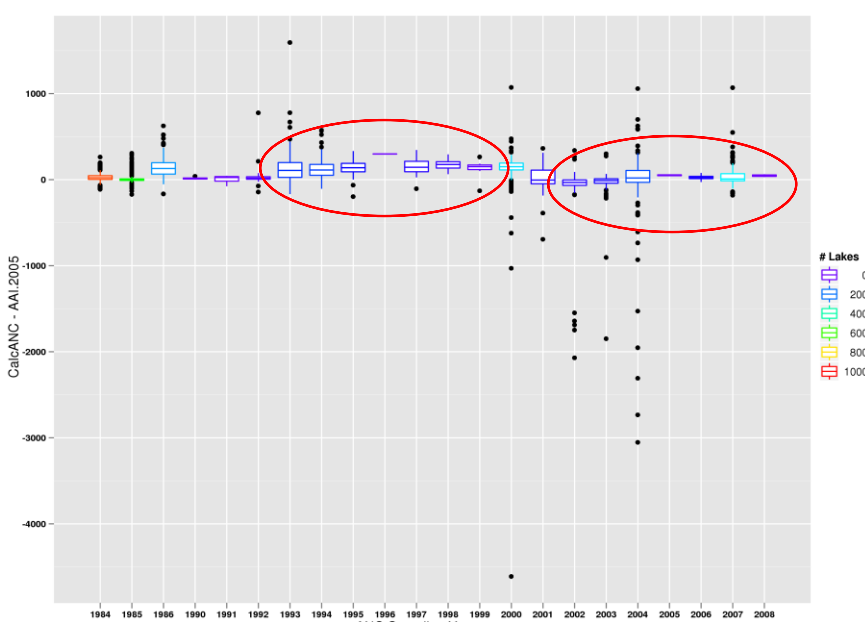


Does this work?

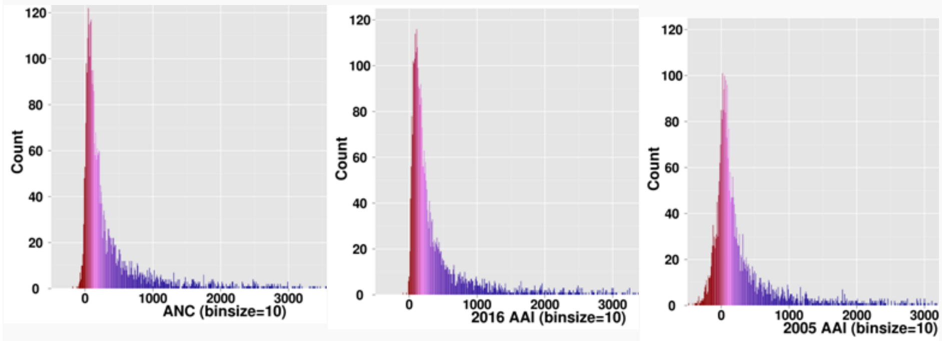
Comparison of calculated AAI values with
observed ANC. Offset due to possible deposition bias and SS assumptions – lag in cation leaching rates, sulfate adsorption/release, possibly associated with water quality sampling periods



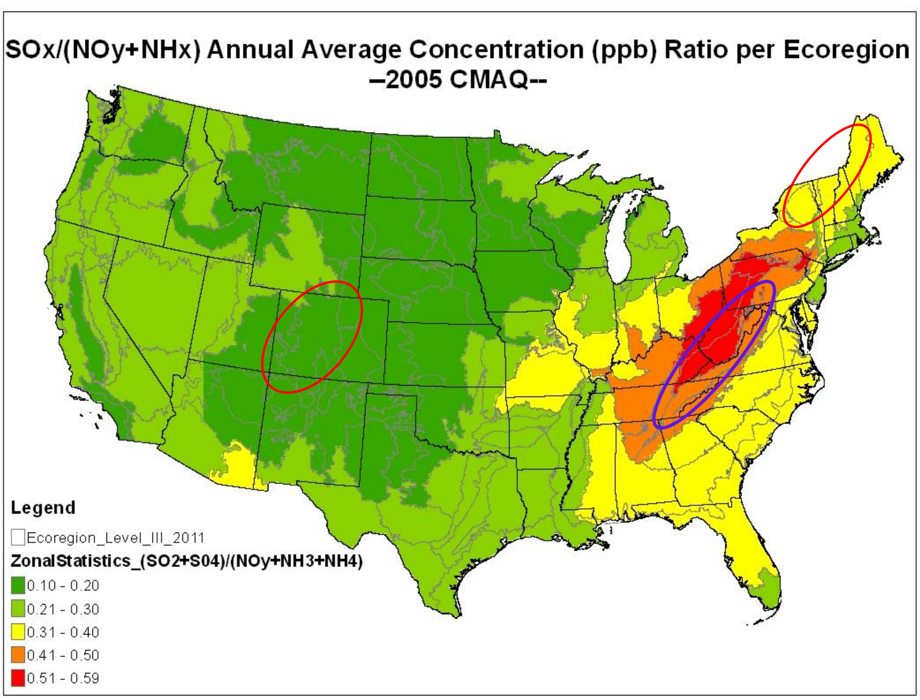




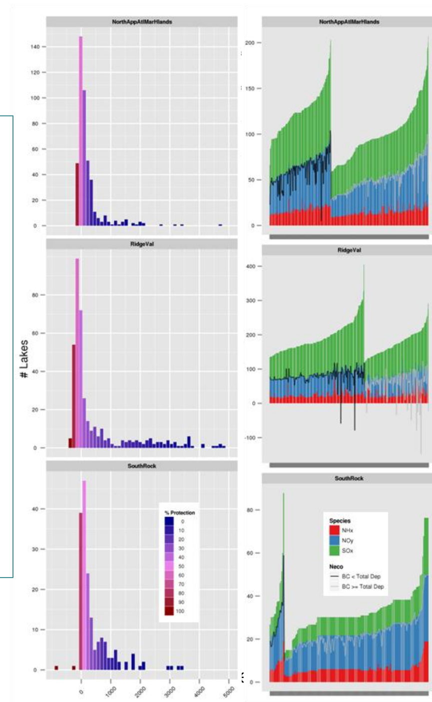
Differences (ANC-AAI) segregated by water quality sampling year



National distributions of observed ANC, 2005 AAI_{WB} and 2016 AAI_{WB}.



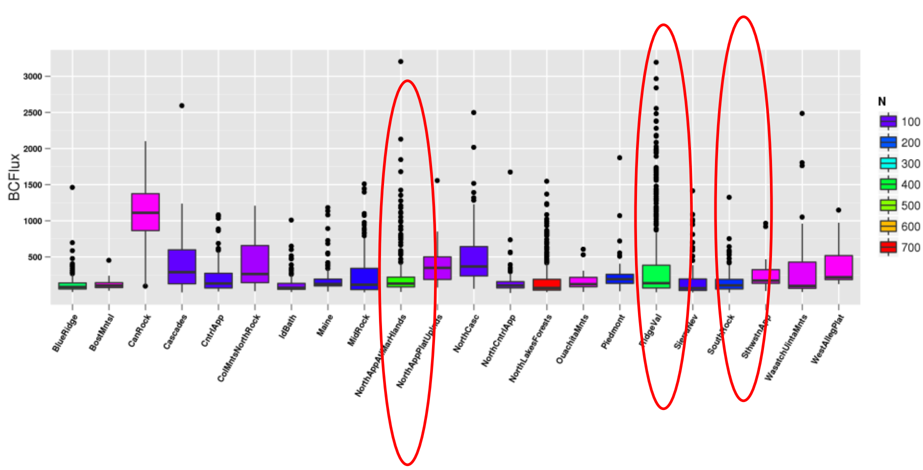
Example AAI_{WB} Distributions (left) for 3 regions and deposition and base cation flux components (right).
The black/grey lines on the right panels are Neco values for each water body. The black to grey transition reflects a negative to positive balance of major ions based on base cation flux - total acidifying deposition flux, an indicator of relative acidification. Note the high variability of Neco relative to atmospheric deposition indicating greater heterogeneity in surface features



Adirondacks/NE

Central Appalachians
(Ridge and Valley)

Southern Rockies

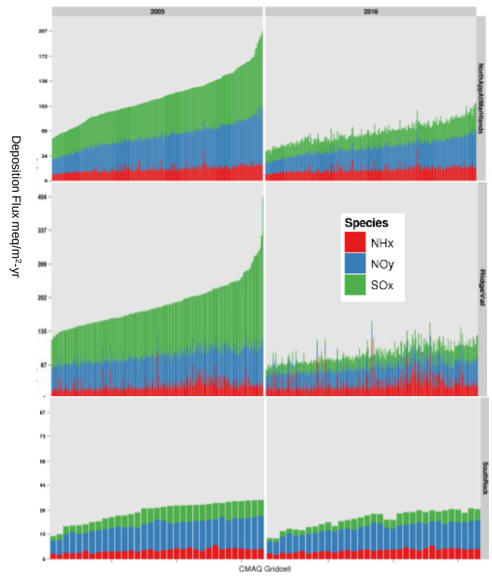


Variations in pre-industrial base cation flux

Deposition components – across regions and time

Deposition components for Northeast mtns. (top), Appalachian (middle) and Rocky Mtn. regions for 2005 (left) and 2016. Note different scales.

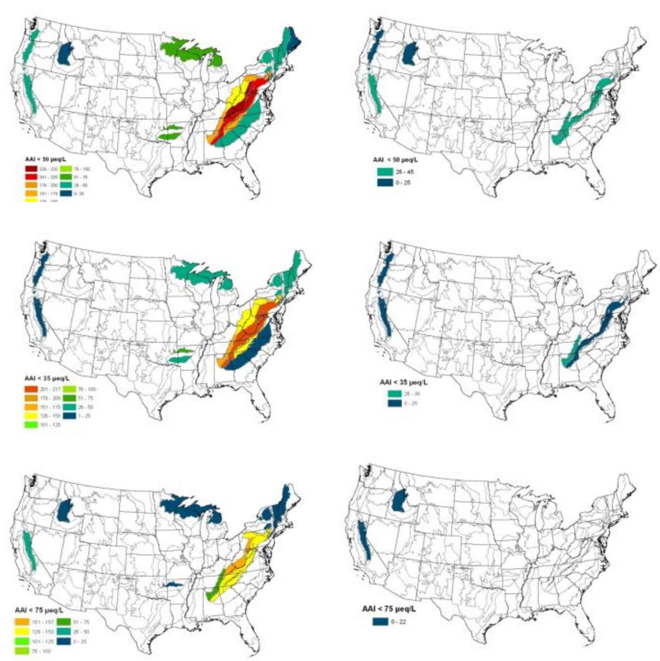
Transition from S –N contribution in East. Elevated importance of NHx everywhere



<u>NAAQS relevant application</u>

Combining Level (target ANC) and Form (% lakes protected)

2005 (left) and 2016 (right) AAI Exceedances for cases 50/90 (top); 35/90 (middle) and (75/70).



Summarize National Future Implications

- The potential of air contributions to aquatic acidification is projected to decrease markedly across the eastern U.S.
  - Largely due to continued projected reductions in SOx emissions associated with Mercury and Air Toxics Standards (MATS) rule
  - Historically, northeast systems respond more rapidly to changing deposition
    - SS models do not account for response times
- Perception of adverse aquatic acidification should equilibrate East to West, again due to dominance of S change in eastern systems
- Nitrogen rises in importance everywhere
  - Active NOx reductions programs from mobile source/fuel and EGU transport rules
    - Although Cross-state Air Pollution Rule (CSAPR), which was rejected, projected further decrease in NOx emissions
  - Lacking regulatory drivers, influence of reduced nitrogen (ammonia emissions) gains in relative importance to NOx and SOx
  - Nutrient enrichment may replace acidification as primary deposition concern in pristine environments (especially mountainous West)
- Increasing CO_2 levels /climate change
  - Clear impact on ocean system chemistry
  - Chemistry influence on freshwater system likely a minor player relative to hydrologic cycle and subsequent ecosystem alteration effects, in turn modify deposition

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Policy Background

NAAQS Secondary Standard NOx/SOx: EPA's Final Rule "after a 5 plus year science review and assessment"

- *Current secondary standards afford inadequate protection*
- *Decision not to move forward with a new standard based on AAI concept*
- *Conduct a pilot studies field program in 3-5 ecoregions:*
  - *"to collect and analyze data so as to enhance our understanding of the degree of protectiveness that would likely be afforded by a standard based on the AAI…"*

Field Pilot Program

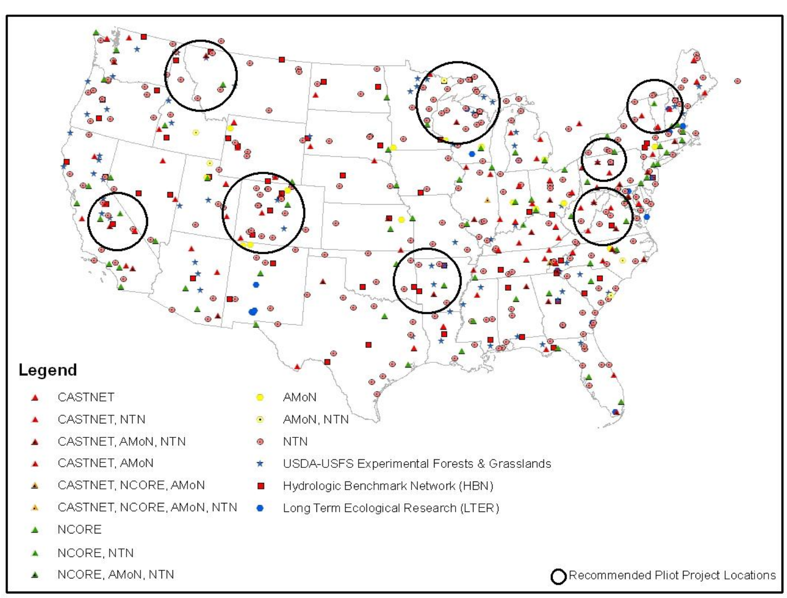
Pilot Program Objectives

- Proof-of-concept for AAI approach
  - Use of actual ambient air measurements to define level of protection
    - *AAI target and nth % protection*
    - examine the extent to which the sample ecoregions would meet a set of alternative AAI-based standards
- Improve understanding of AAI components, variability, and uncertainty
  - improve characterization of concentration and deposition patterns of NO_y ,SO_x, reduced forms of nitrogen
  - explore alternative approaches for estimating F1 through F4 factors for the AAI equations
  - expanded critical load data bases
- Enhance atmospheric measurements and models
  - total nitrate measurements as a potential alternative indicator for No_y
  - evaluation of modeled dry deposition algorithms
- Demonstrate implementation
  - Air monitoring network design
  - Spatial aggregation and uncertainty
  - Various SIP requirements
- Strengthen linkages between atmospheric deposition and water quality

Measurements

- Focus on 3-5 ecoregions
- Existing CASTNET, rural Ncore, NADP NTN infrastructure
  - at least 2-3 sites with minimum suite of measurements
- Atmospheric measurements:
  - Weekly SO2, SO4, NO3 NH4, HN03 (CASTNET)
  - Continuous NOy (Ncore)
  - Passive NH3 (AMoN),
  - Precipitation chemistry SO4, NO3, NH4 (NADP's NTN)
- Possible Atmospheric measurements enhancements:
  - Continuous SO2, NH3, SO4
  - Speciated NOy (PAN, true NO2), HNO3, NH4,
  - Organic-N
  - Site specific direct measurement of dry deposition flux(coordination between ORD and AmeriFlux/LTER)
- Collaboration with ongoing long-term water quality monitoring
  - TIME/LTM, NPS/USFSUSGS/EPA experimental studies
- Rely on ongoing improvements to FOCUS National Critical Load Data Base

General Areas of Focus



Proctor Maple - Underhill, VT site

- NCore
- Existing NADP – NTN
- Addition of CASTNET Filter Pack (CFP) and passive Ammonia

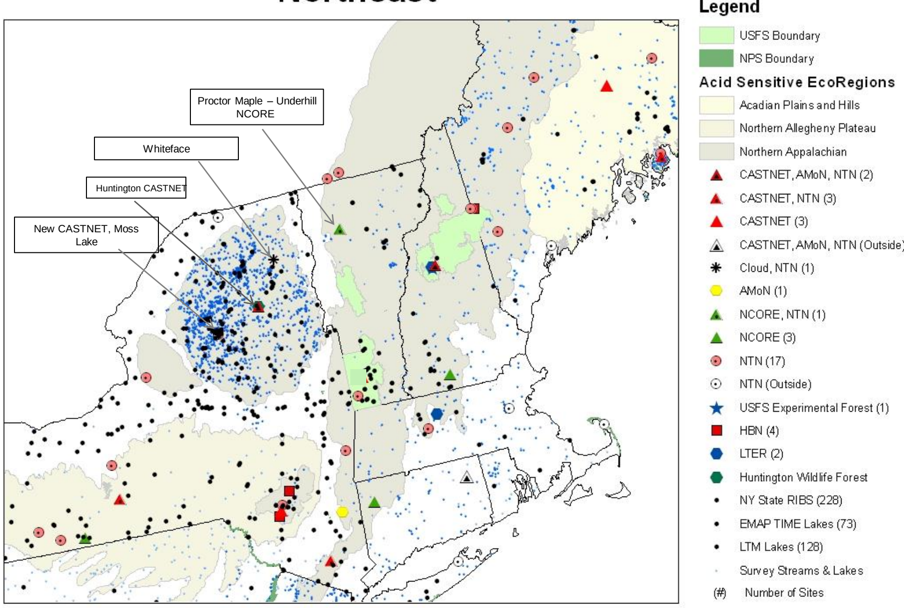
Ecoregion & Site Selection

- Site selection based on:
  - Building partnerships with other agencies and research groups (including private sector)
  - Leverage current and planned aquatic and atmospheric measurement programs
  - A mix of different atmospheric characteristics (high/low concentrations; N vs S drivers) and adversity/effects sensitivity (minimal to high impact)
  - National representativeness
- Focus on three ecoregions/areas
  - Adirondacks/New England mountains (Northeastern Highlands; 58)
    - Moderate acidification impacts; roughly equal N and S loading
  - Mid Appalachian Highlands (Blue Ridge, 66; Ridge and Valley, 67; Central Appalachians, 69; Western Allegheny Plateau, 62; Southwestern Appalachians, 68)
    - Severe acidification impacts; relatively greater S loadings
  - Colorado Rockies (Southern Rockies, 21) with NW Wyoming extension (Middle Rockies, 17)
    - Mild acidification impacts; relatively greater N loading

Adirondacks/New England

- Acidification impacted ecoregions
- Rich database, moderately impacted, observed improvements, S-dominated
- Existing air monitoring sites
  - NCore at Underhill, VT and Pack Monandack, NH
  - CASTNET sites at Huntington Wildlife, NY and Woodstock, NH
  - Whiteface mtn.
- Proximity to LTER/AmeriFlux sites
  - Bartlett Forest and Hubbard Brook, NH
  - Harvard Forest, MA
  - Howland, ME
- Strong partnership with NYDEC and NYSERDA
  - NY DEC is in the process of converting to NADP NTN samplers
    - adding CFP samplers
  - Providing direct capital and operational resources
  - NYSERDA supporting related research
  - SU – water quality
  - NY ASRC (Whiteface mtn. observatory includes cloud chemistry and deposition measurements)

Monitoring Locations Northeast



ADKs/New England – gaps in measurements are highlighted

Site Name	Lat/long	Elev. (m)	NTN	AMoN	CFP	NOy	Cont. SO2	O3	IMPROVE	CSN	Cont PM2.5	Other
Huntington Wildlife Forest CASTNET HWF187; NTN NY20	43.9731 -74.2232	765	NY20	EPA/CAMD – funding from OAR	EPA/CAMD	EPA/CAMD – funding from OAR		EPA/CAMD				Install NOy fall 2012
Akwesasne Mohawk-Fort Covington NTN NY22	44.9226 -74.4806	70	NY22									
Whiteface Mountain NTN NY98	44.3933 -73.8594	610	NY98 – not collocated with CFP	NYDEC/ NYSERDA – funding from R2 to CAMD	NYDEC/ NYSERDA – funding from R2 to CAMD	ASRC NY	NY DEC (base)	NY DEC (base + summit)		NY DEC (base)	NY DEC (base)	Install CFP fall 2012?
Moss Lake NTN NY29	43.7868 -74.8429	566	NY29									Install CFP fall 2012?
Nick's Lake	43.6858 -74.9854	525	NY wet deposition network?	NYDEC/ NYSERDA – funding from R2 to CAMD	NYDEC/ NYSERDA - funding from R2 to CAMD		NY DEC	NY DEC				If NY converts the current wet deposition network to NADP
Bennett Bridge NTN NY52	43.5282 -75.9492	247	NY52									
Paul Smith's	44.4343 -74,2493	560	NY wet deposition network?				NY DEC					If NY converts the current wet deposition network to NADP
Wanakena	44.1500 -74.8998	458	NY wet deposition network?									If NY converts the current wet deposition network to NADP
Piseco Lake	43.4496 -74.5162	519	NY wet deposition network?				NY DEC	NY DEC				If NY converts the current wet deposition network to NADP
Proctor Maple Research Center NCore 50-007-0007 NTN VT99	44.52839 -72.8688	399	VT99	CAMD will add AMoN if additional funds are available	EPA/CAMD – funding from OAR	State of VT	State of VT	State of VT			State of VT	Pending approval from VT for CFP install
Pack Monadnock Summit NCore 33-011-5001	42.86175 -71.8783					State of NH	State of NH	State of NH			State of NH	
Woodstock CASTNET WST109 NTN NH02	43.945 -71.7008	258	NH02	EPA/CAMD – funding from OAR	EPA/CAMD	CAMD will add NOy if additional funds are available		EPA/CAMD				$80K needed for equipment/install.
Bridgton NTN ME02	44.1075 -70.7289	222	ME02									
Gilead NTN ME08	44.4003 -71.0098	212	ME08									

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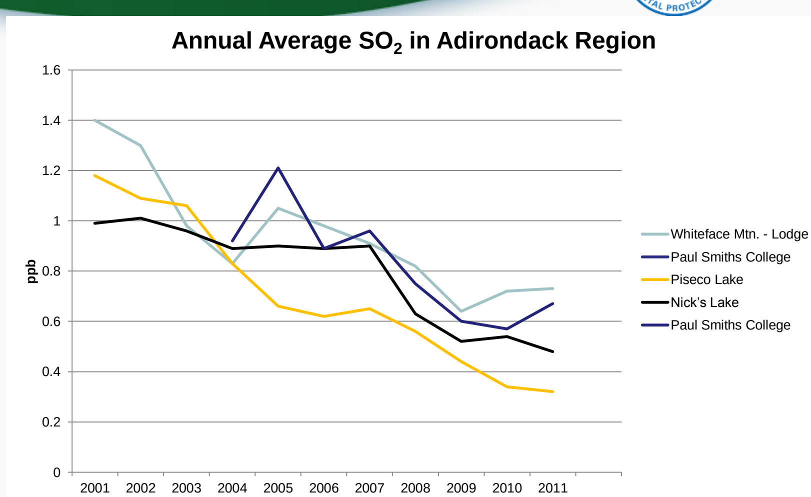
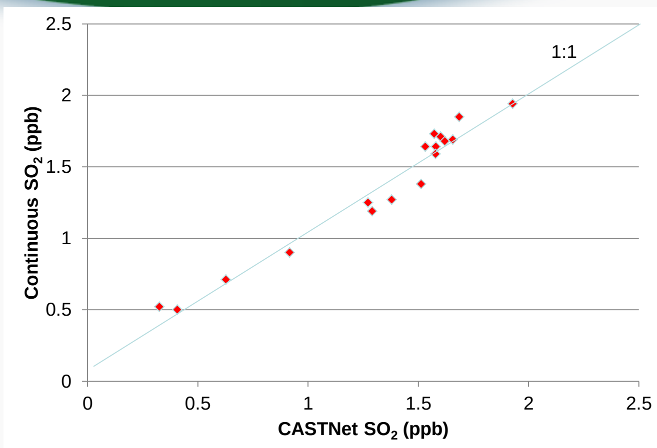
SO_2: Air Quality Indicator
(courtesy D. Felton)



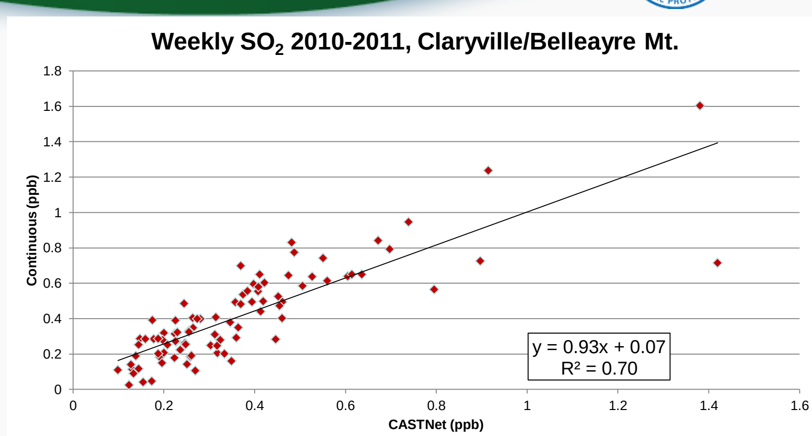
Continuous SO_2 and CFP SO_2 Comparison (courtesy D. Felton)



Annual comparisons are encouraging

Annual average SO2 at Belleayre Mountain (NYSDEC continuous) and Claryville (CASTNet integrated), 1995-2011.
The monitors are ~14 mi apart in the Catskill Mountains, NY

Continuous SO_2 and CFP SO_2 Comparison (courtesy D. Felton)



Weekly comparisons are not as encouraging and have a seasonal bias

Discussion and Questions