Assessing Sources and Fluxes of Reactive Nitrogen Deposition to Urban Landscapes Using Ion Exchange Resins

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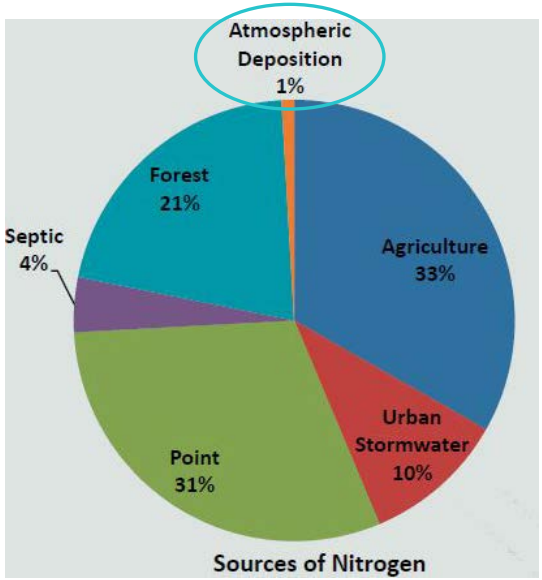
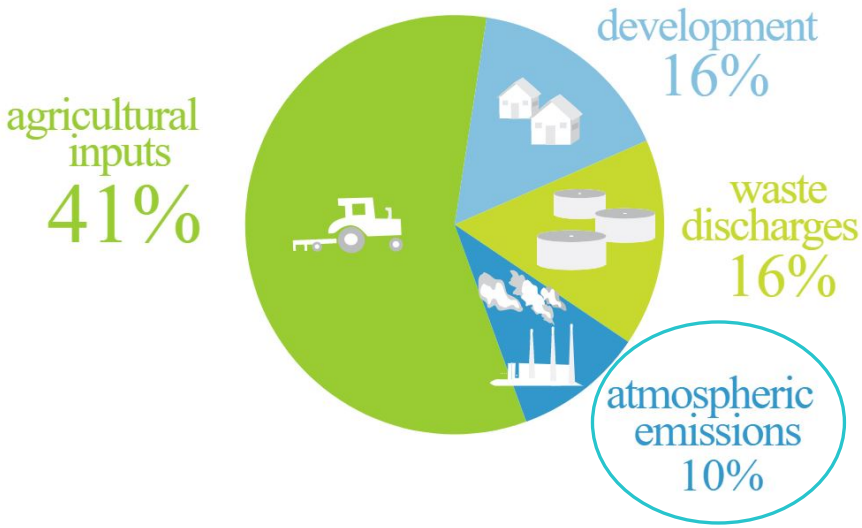
Why do we care about N deposition?

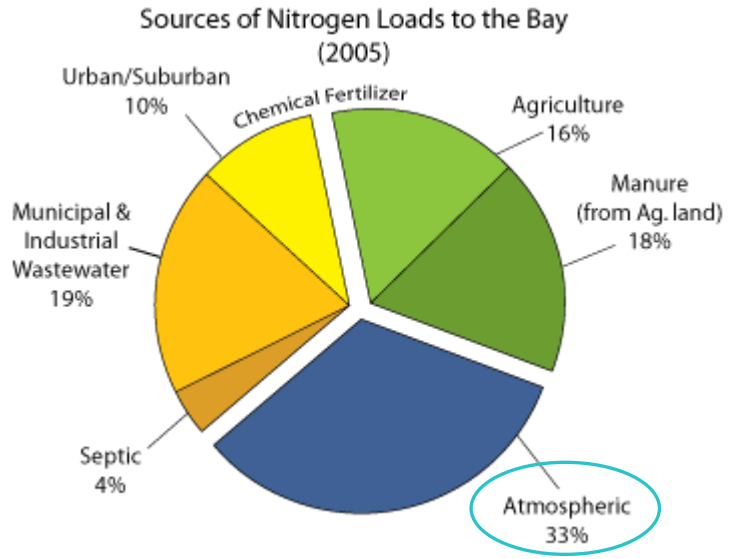
- Atmospheric deposition is a significant source to nitrogen budgets
  - Lack of consensus on how important this flux is



Hampton Roads Planning District Commission ("Save the Bay" Virginiaplaces.org) 2010



Chesapeake Bay Story (University of Maryland Center for Environmental Science and State of Maryland)



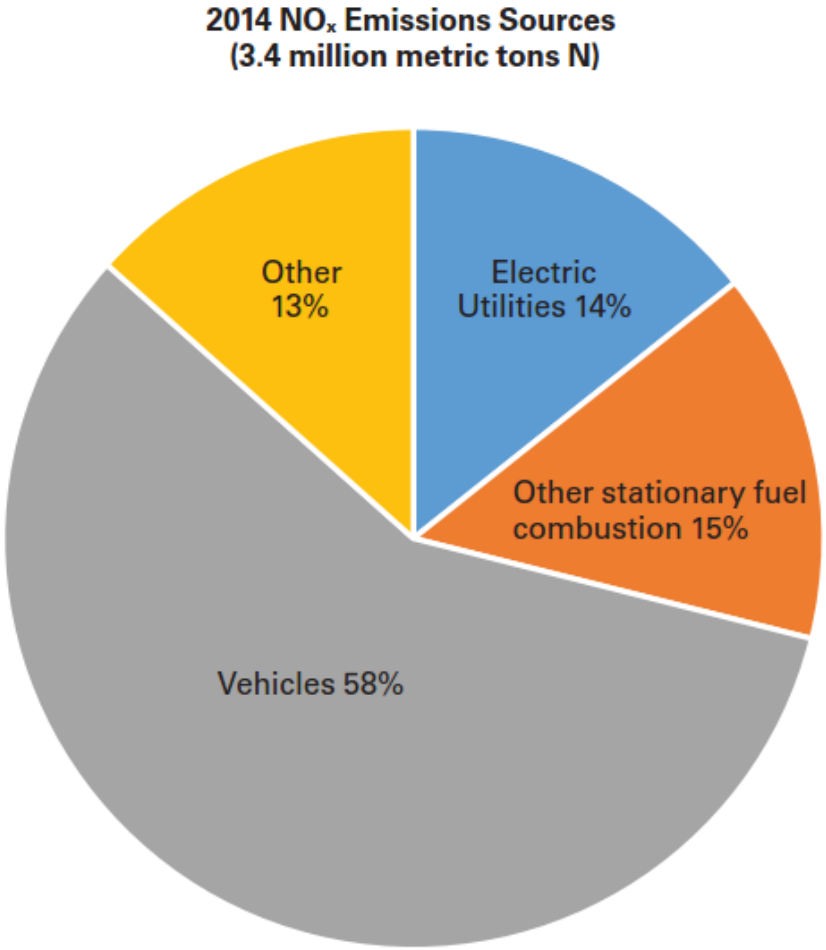
Source: Chesapeake Bay Program Phase 4.3 Model

Sources of N deposition

NO_x
- Fossil fuel combustion from vehicles and power plants
- NO_x is oxidized in atmosphere and returns to terrestrial environment as of NO_3^- in precipitation or dry particulate deposition

NH_3
- Catalytic converters on cars and soil volatilization

Vehicles are concentrated in urban areas but most national monitoring sites are in rural areas
- Interpolation models don't account for this



USA 2014 NO_x emissions by source from National Emissions Inventory (NEI).

Previous research on urban N deposition

Urban areas have higher deposition rates than rural areas

- local versus regional emissions?

Urban deposition is highly spatially variable

- could this be to different sources?
- different deposition velocities due heterogeneity of structures in the urban environment?

Highlights key knowledge gaps in understanding the sources, dynamics, and overall fluxes of reactive nitrogen deposition in urban areas

(Decina et al 2017, Bettez & Groffman 2013)

Goals of this study

Quantify urban deposition fluxes across Pittsburgh

- Expand on existing knowledge of urban N deposition fluxes
- Explore spatial and temporal variability

Narrow knowledge gaps on how spatial variability is related to NO_X and NH_3 emission sources.

- Compare urban and rural fluxes and sources with dual nitrate isotopes

Hypothesize higher N fluxes from vehicular-sourced emissions at urban sites

- Based on preliminary data, predict that urban N deposition fluxes are 2-3x higher than those measured at rural monitoring sites

- Urban sites will be more heavily influenced by local vehicular NO_x emissions relative to rural sites where regional power plant NO_x emissions have been shown to dominate deposition.

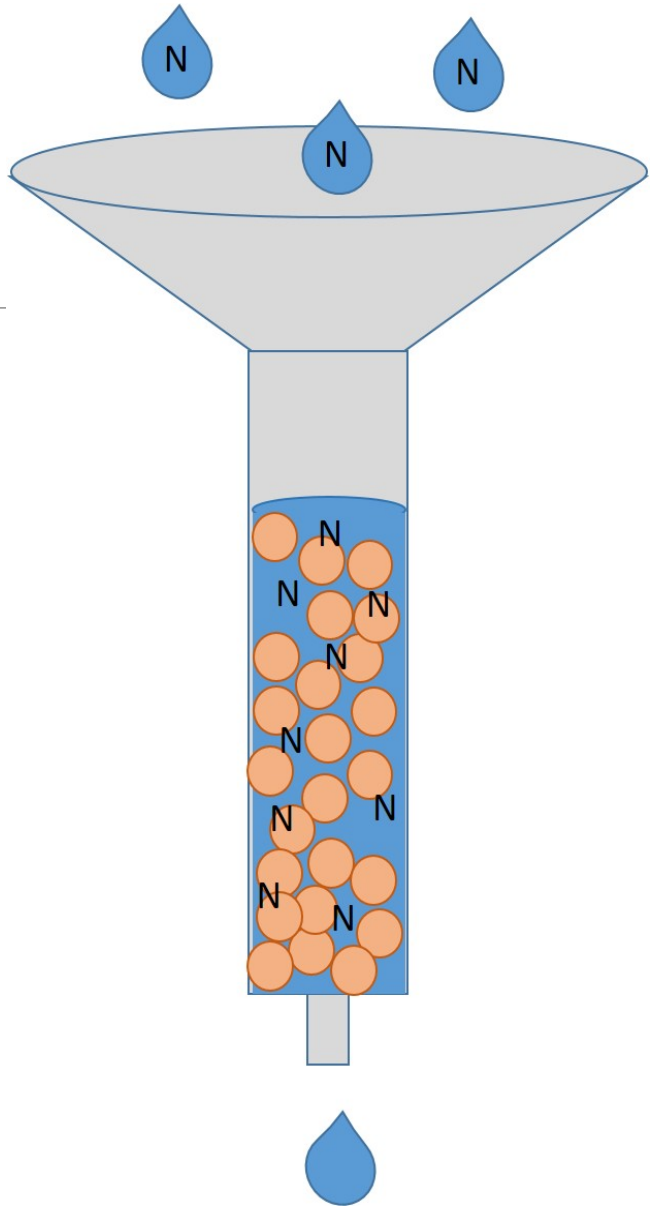
(Elliott et al. 2009, Elliott et al. 2007)

Ion Exchange Resins (IERs)

Need enough sites to capture high spatial variability

- NADP NTN and EPA CASTNET sites require considerable cost to establish and maintain,
- Ion Exchange Resins are a good alternative
  - relatively inexpensive
  - integrate fluxes over many weeks without requiring exact precipitation volume
  - can be used for isotopic analyses of resin eluents without fractionation

Polyethylene polymer beads selectively bind NO_3^- or NH_4^+ and it remains in the column until it is eluted back at the lab



(Templer & Weathers 2011, Fenn & Poth 2007)

Methods

Ion Exchange Resin columns
- Separate anion (NO_3^-, NO_2^-) and cation (NH_4^+) columns

Eluted after 1-2 months of deployment

Flux calculations

Dual nitrate isotopes

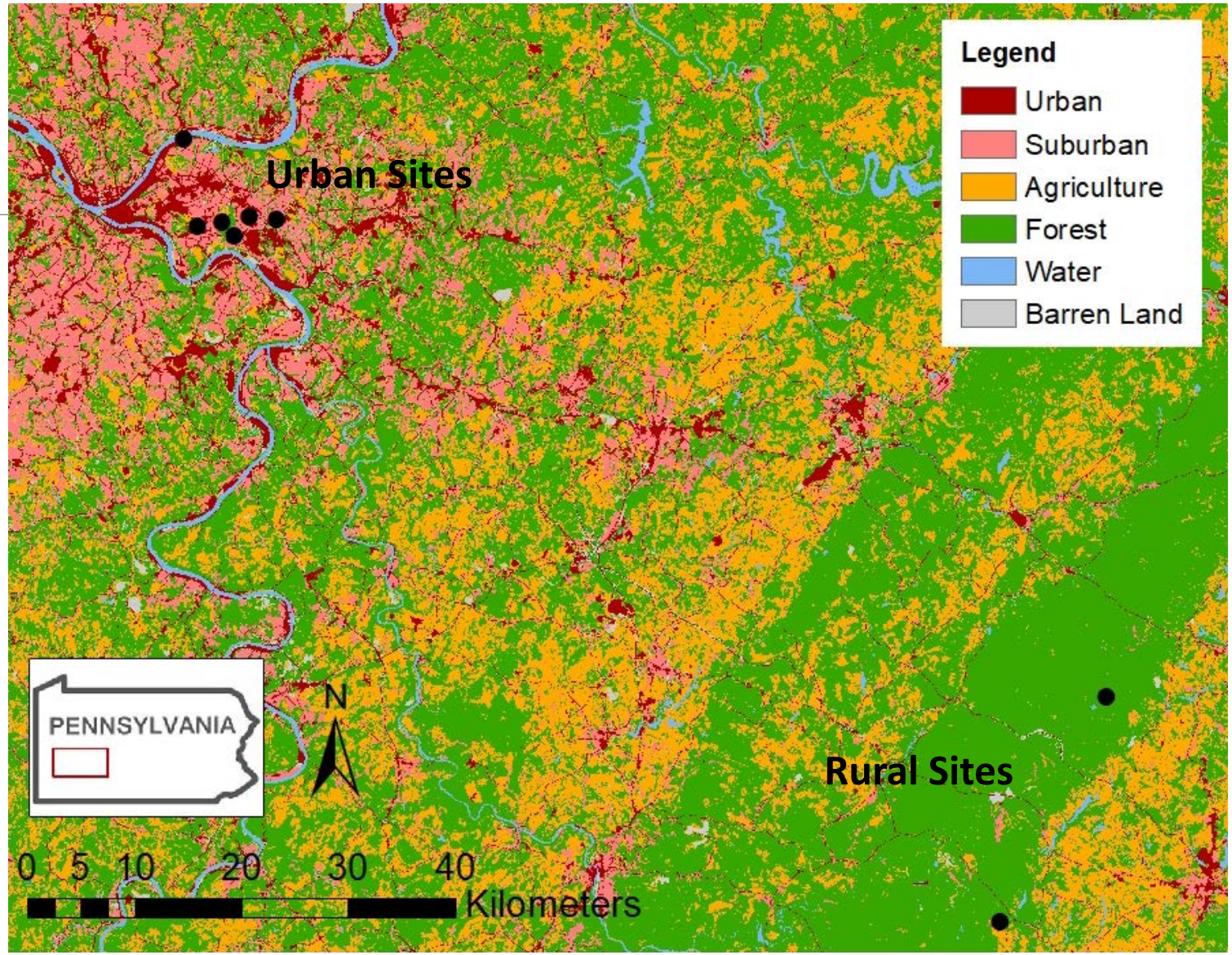
One year period
- July 2016 – July 2017

Site Selection

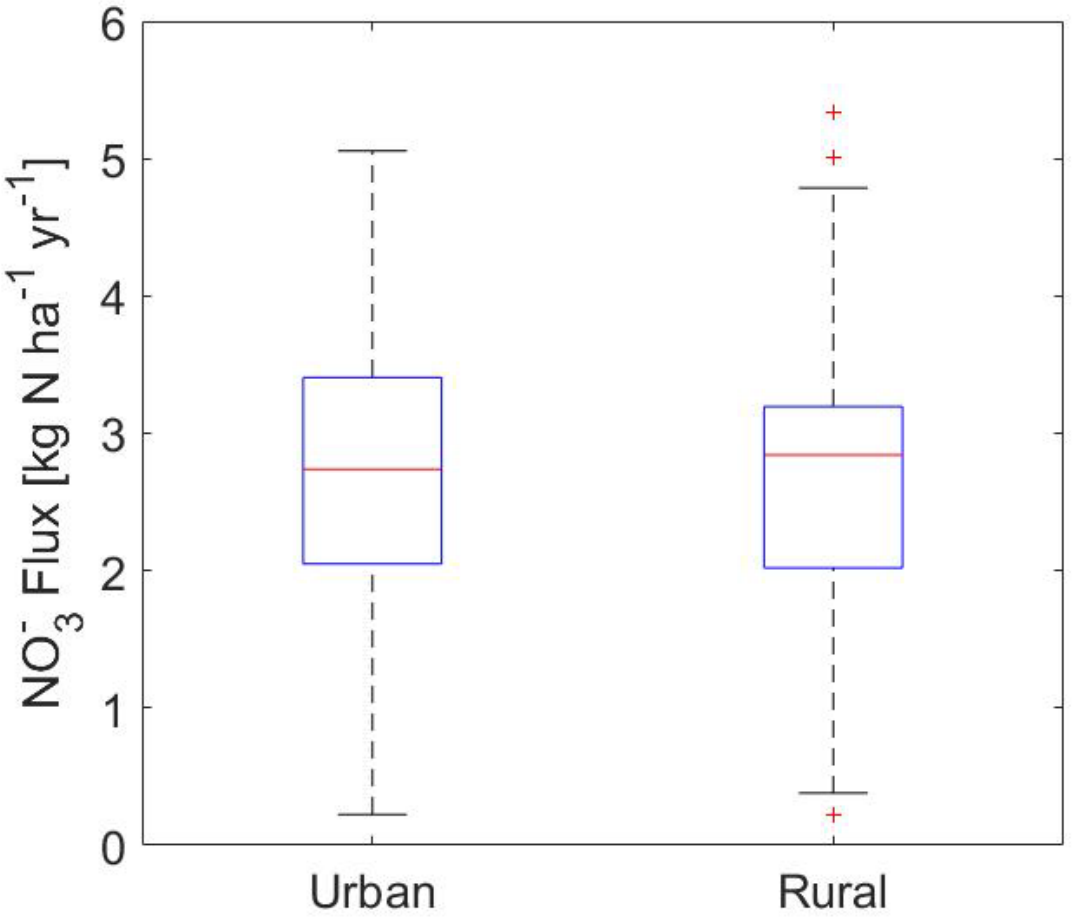
6 urban sites in Pittsburgh, PA
- Variety of land use types
- Sites we has access to

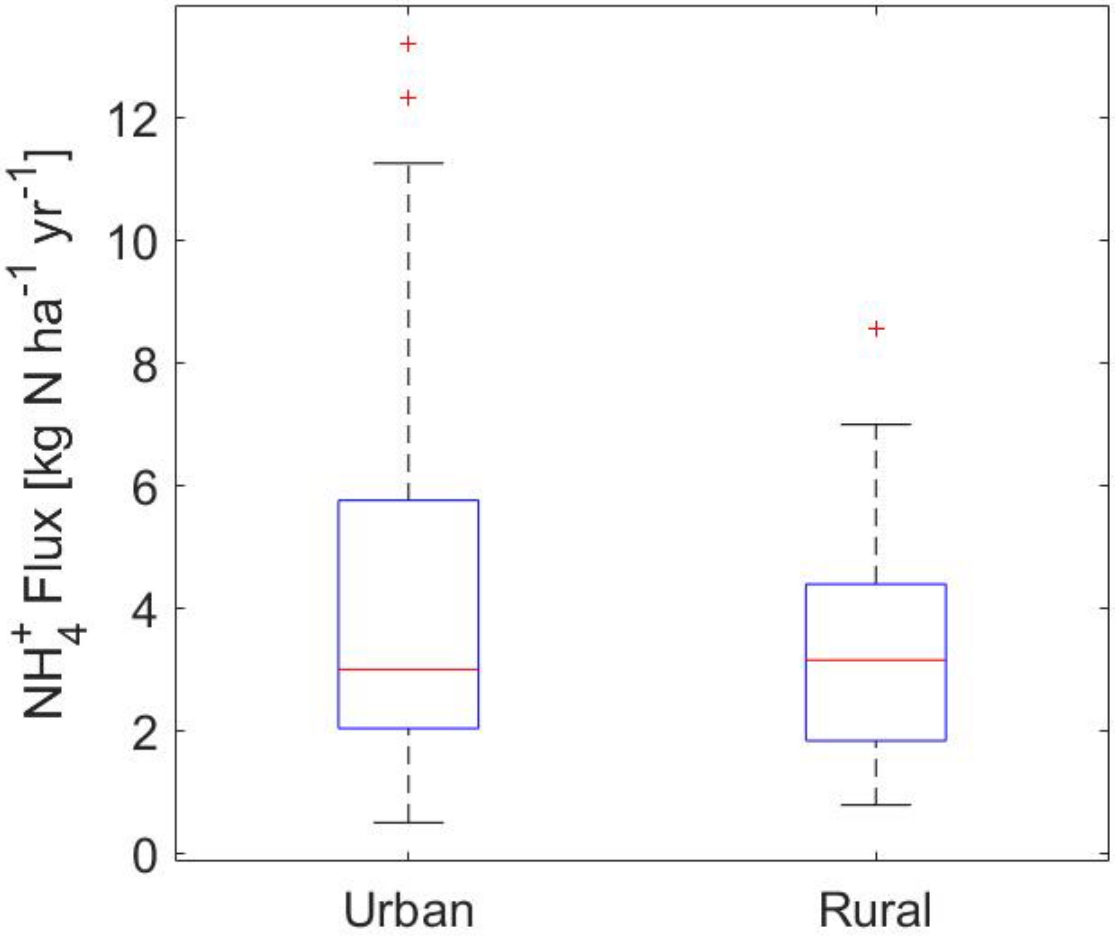
2 rural sites in the Laurel Highlands
- 70 miles away from urban center

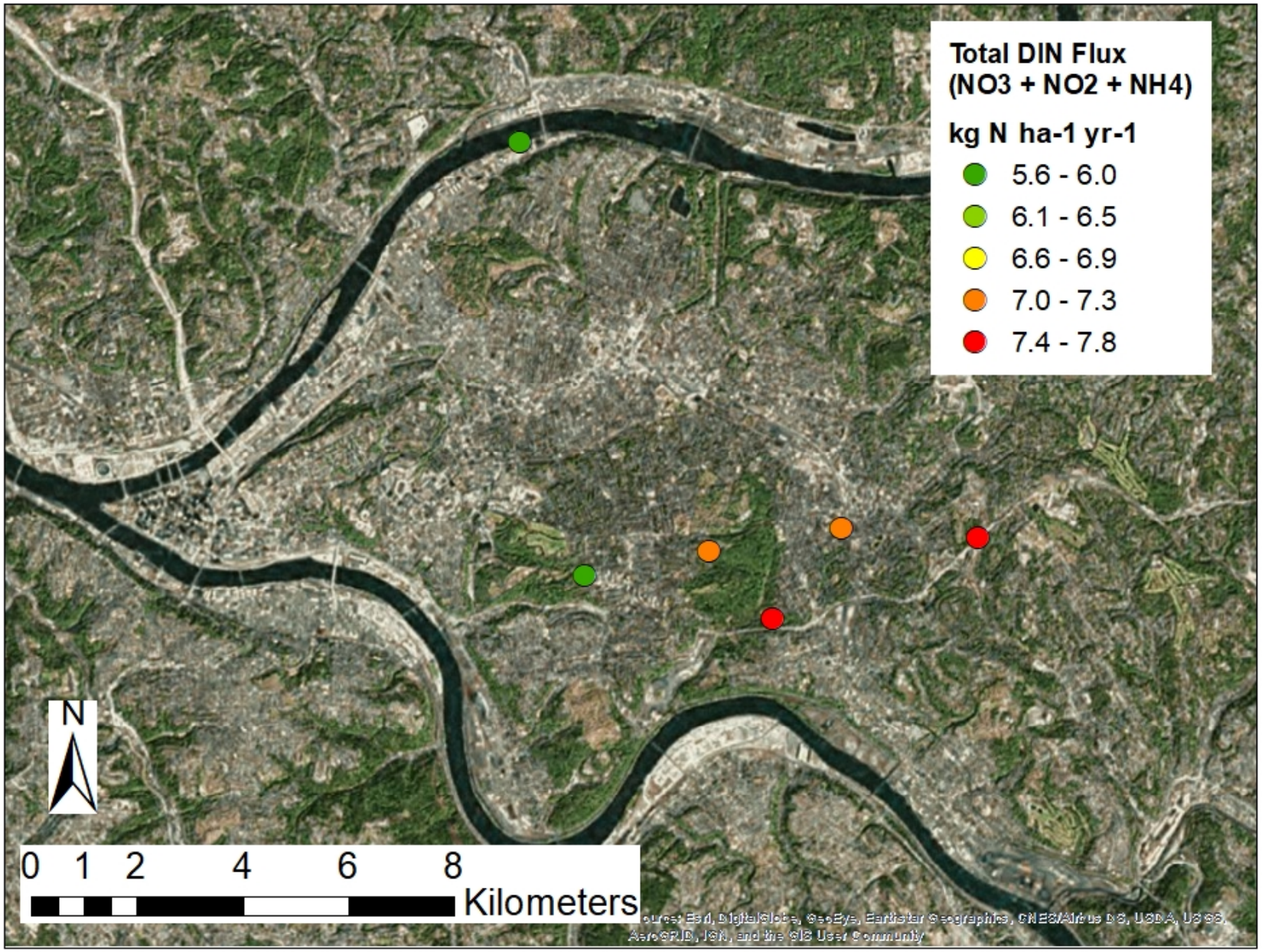
Compared data with the NTN-CASTNET site at Laurel Hill state park



For annual averages, no difference between urban and rural sites

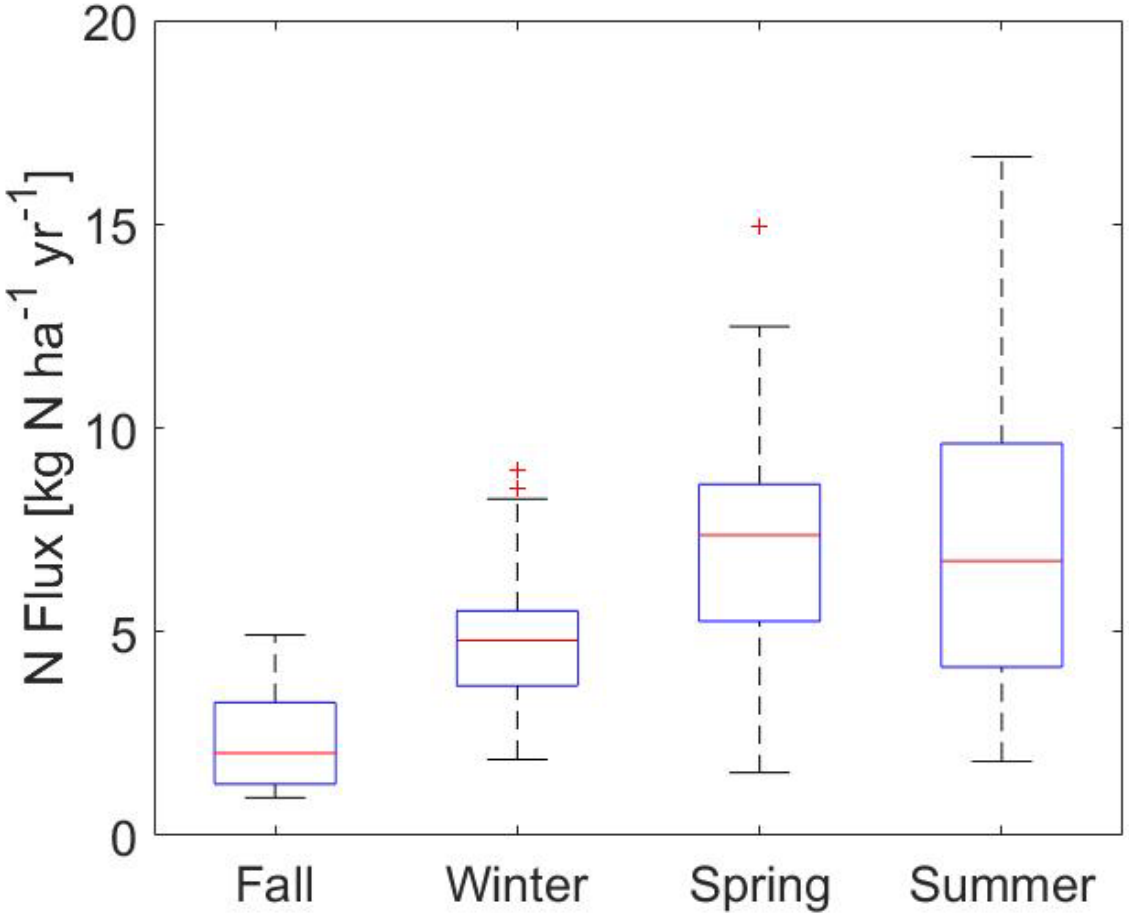




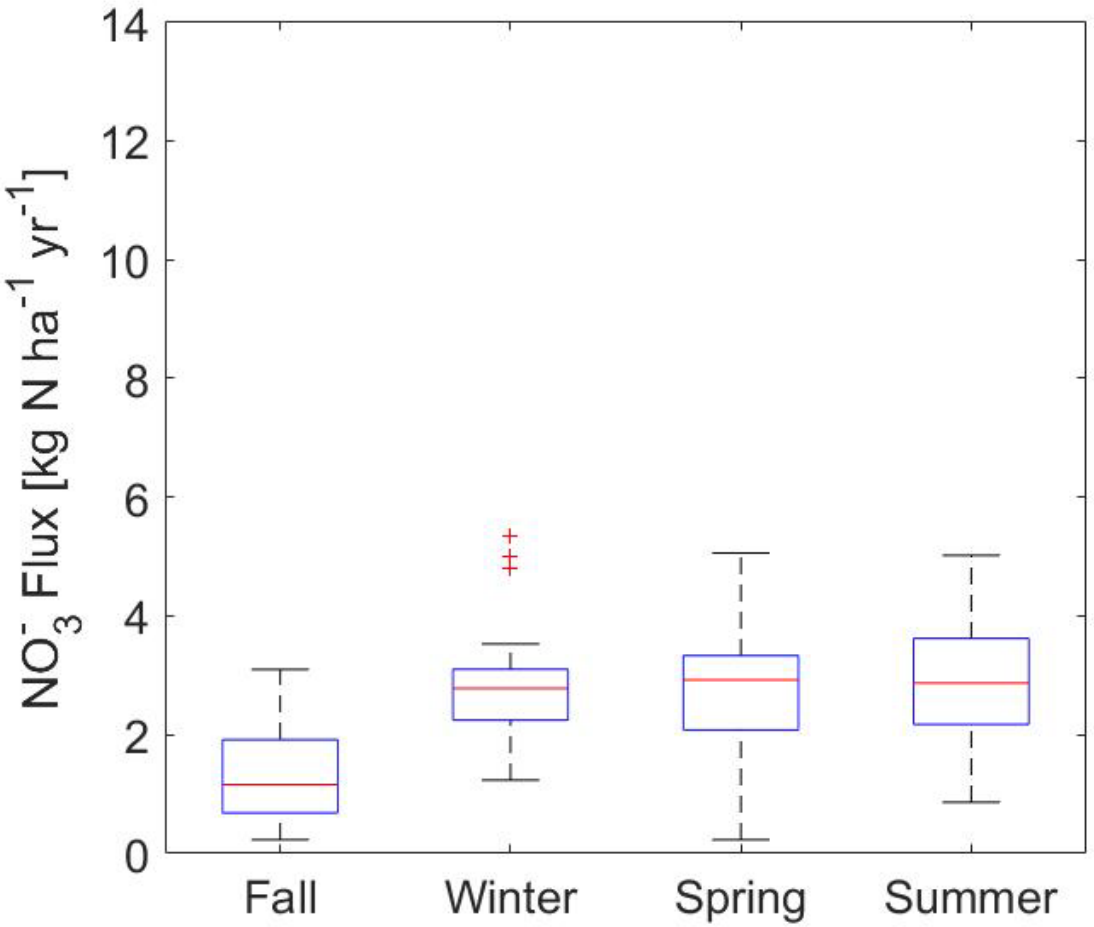


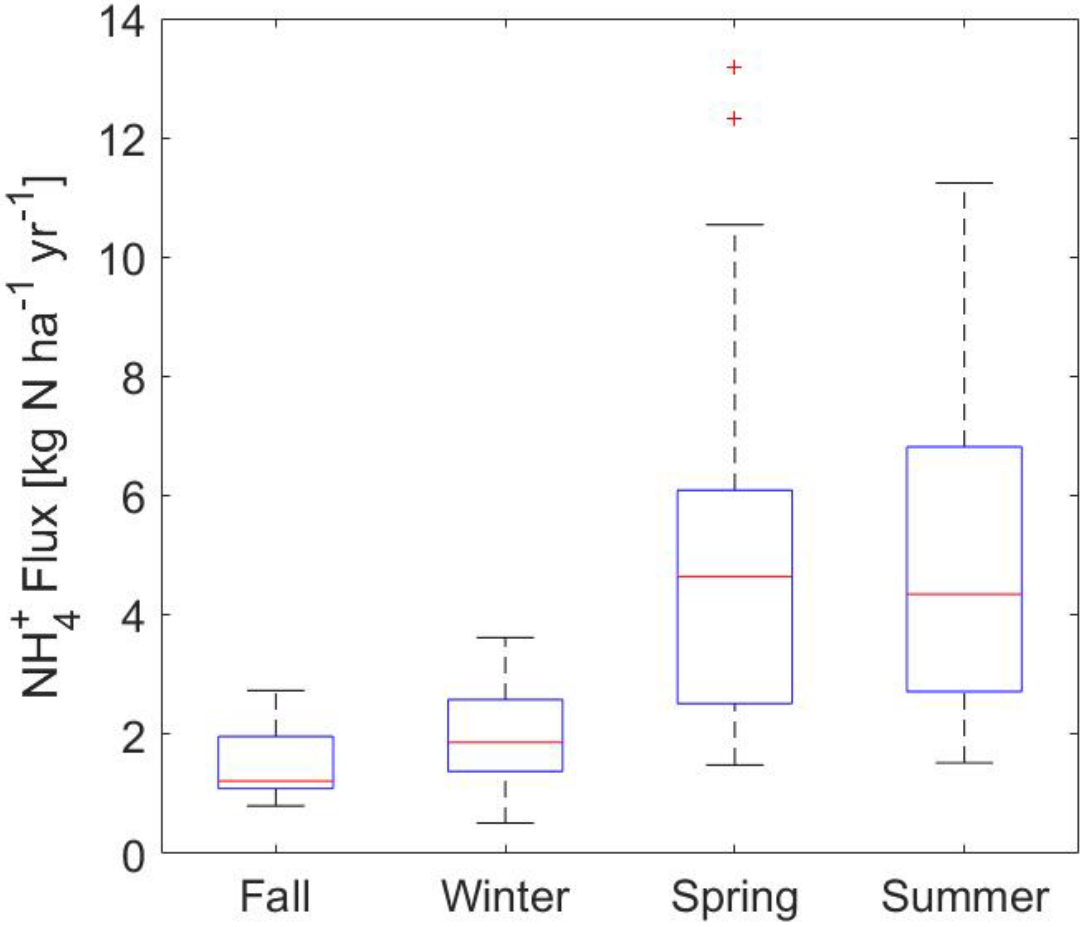
Urban N deposition fluxes are spatially variable

Temporal variation - higher and more variable N deposition fluxes in the spring and summer

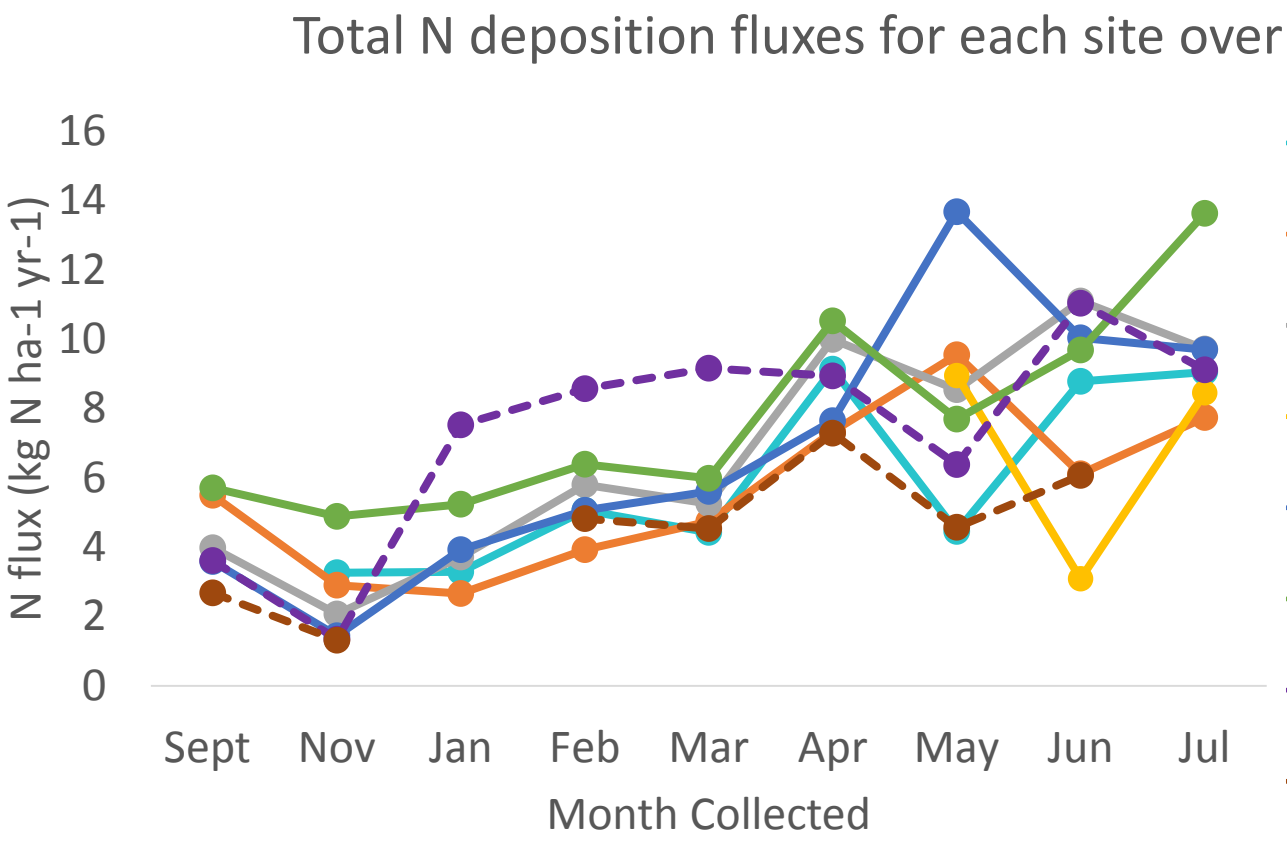


Seasonal variation driven by ammonium



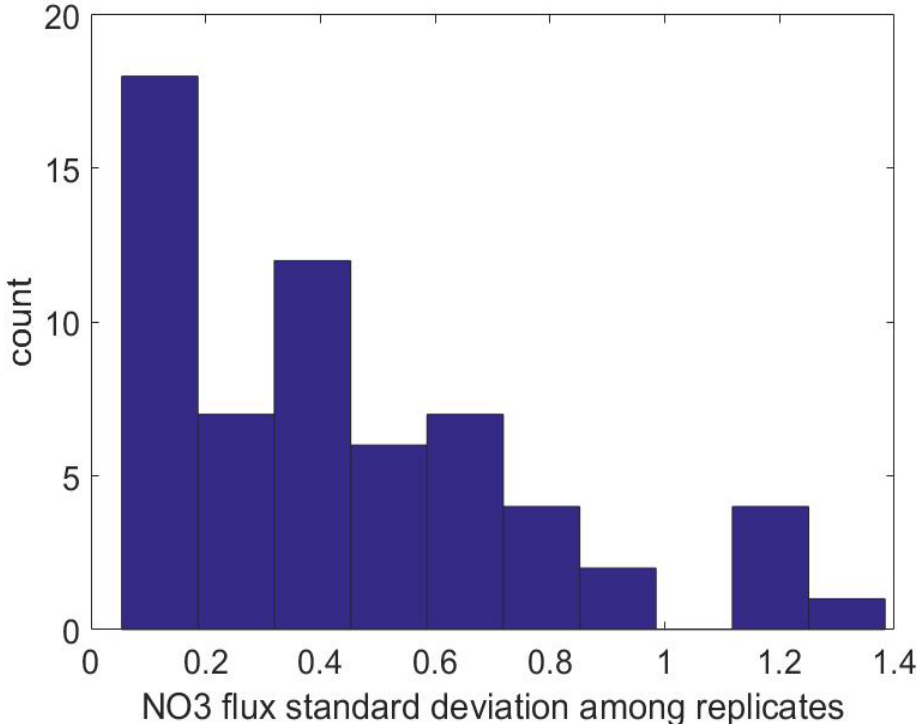


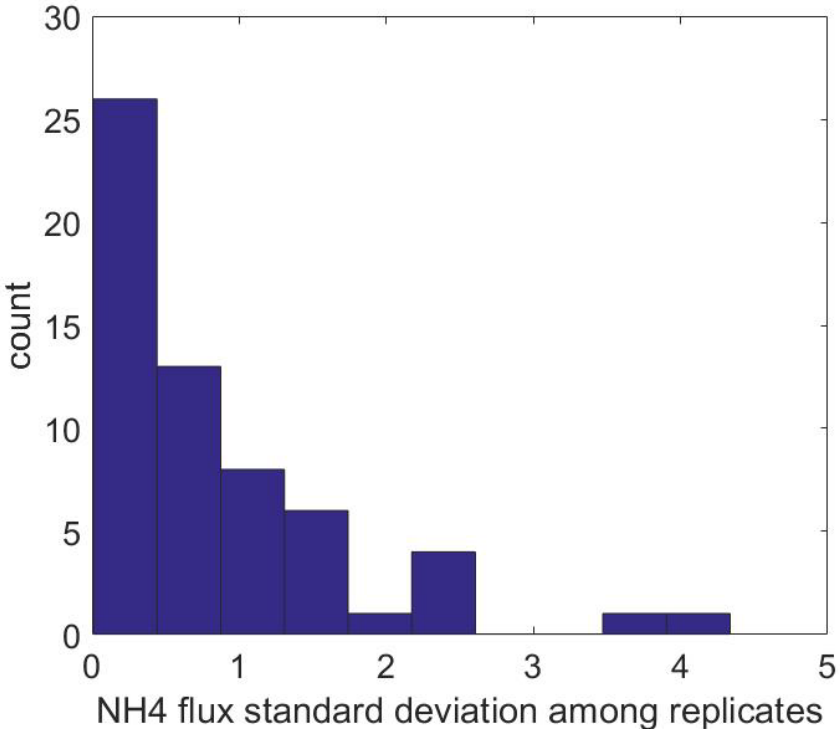
Yearly or seasonal averaging hides much of the variation in fluxes



	Yearly Averages	Highest	Lowest
Tree PGH	**5.93**	9.13	3.26
Hobart Street	**5.61**	9.54	2.66
Frick	**6.69**	11.09	2.08
Riparian	**6.83**	8.95	3.09
NMRWA Office	**6.74**	13.67	1.44
I-376 Roadside	**7.75**	13.63	4.89
Laurel Hills	**7.30**	11.03	1.34
Airglow	**4.87**	7.62	1.32

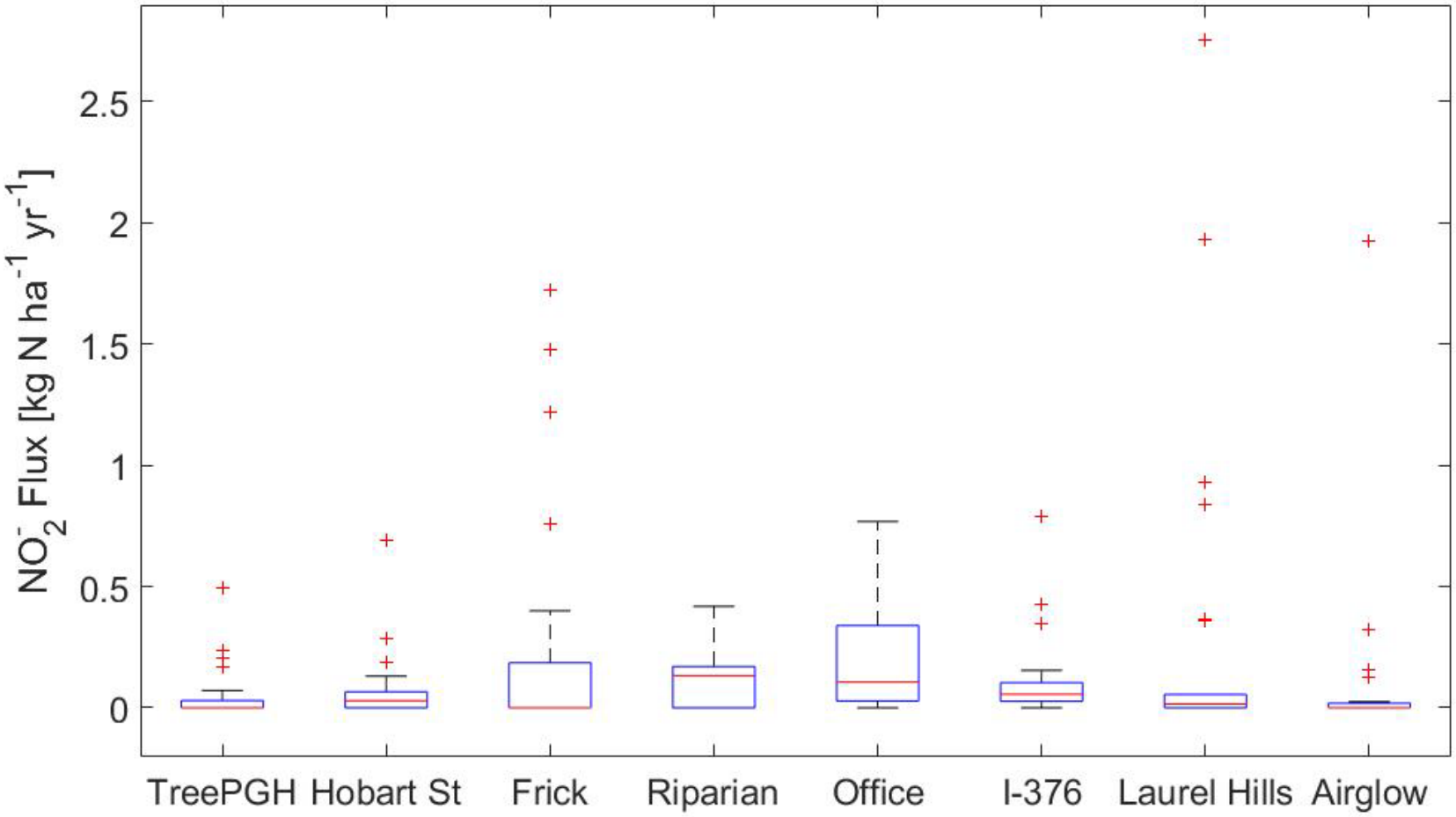
Variation among replicates at the same site over the same time period





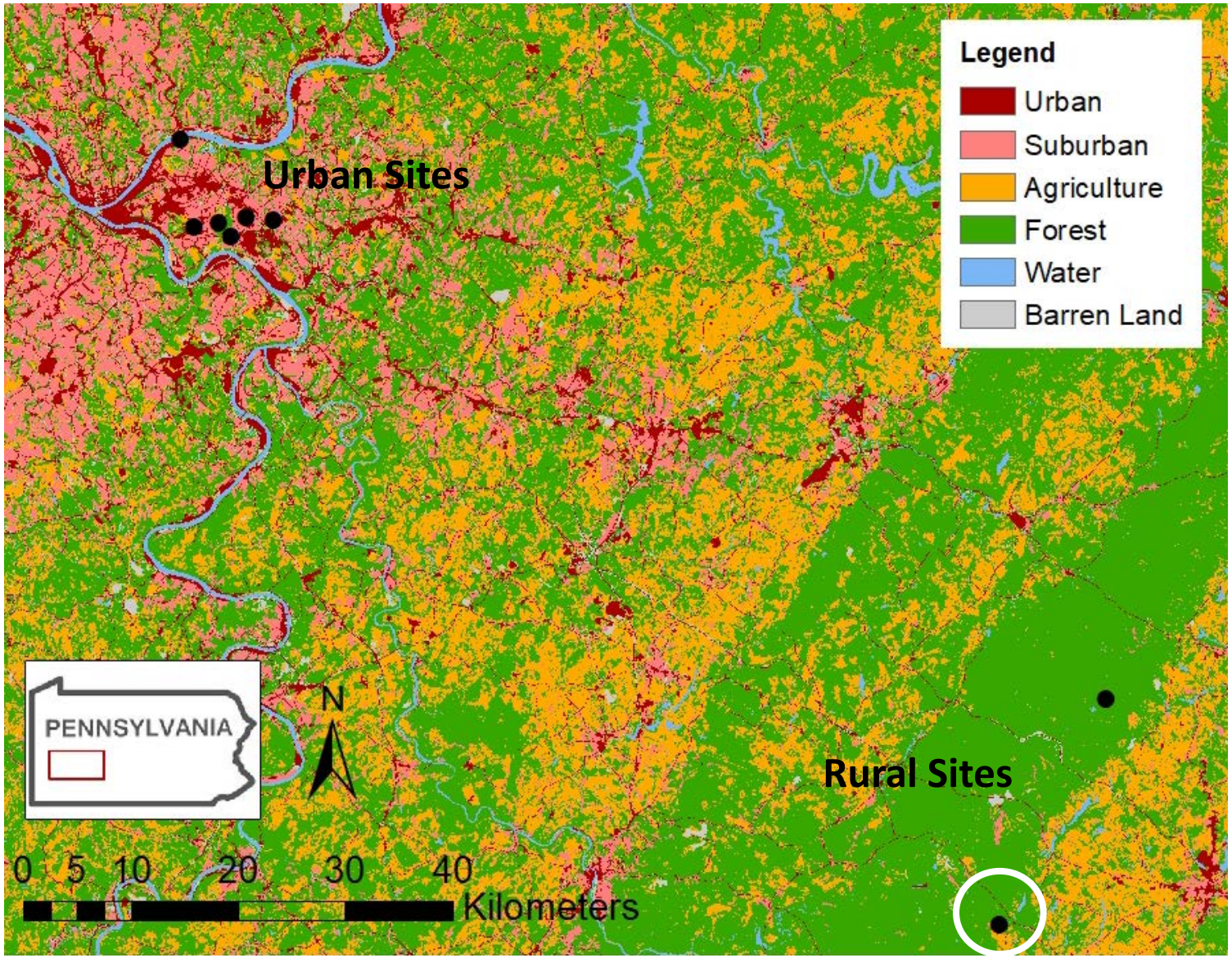
Standard deviation between replicates can be as high as 1.3 kg N ha^{-1} yr^{-1} (NO_3) and 4.3 kg N ha^{-1} yr^{-1} (NH_4) for columns deployed right next to each other

Nitrite is occasionally a non-negligible proportion of the total DIN flux

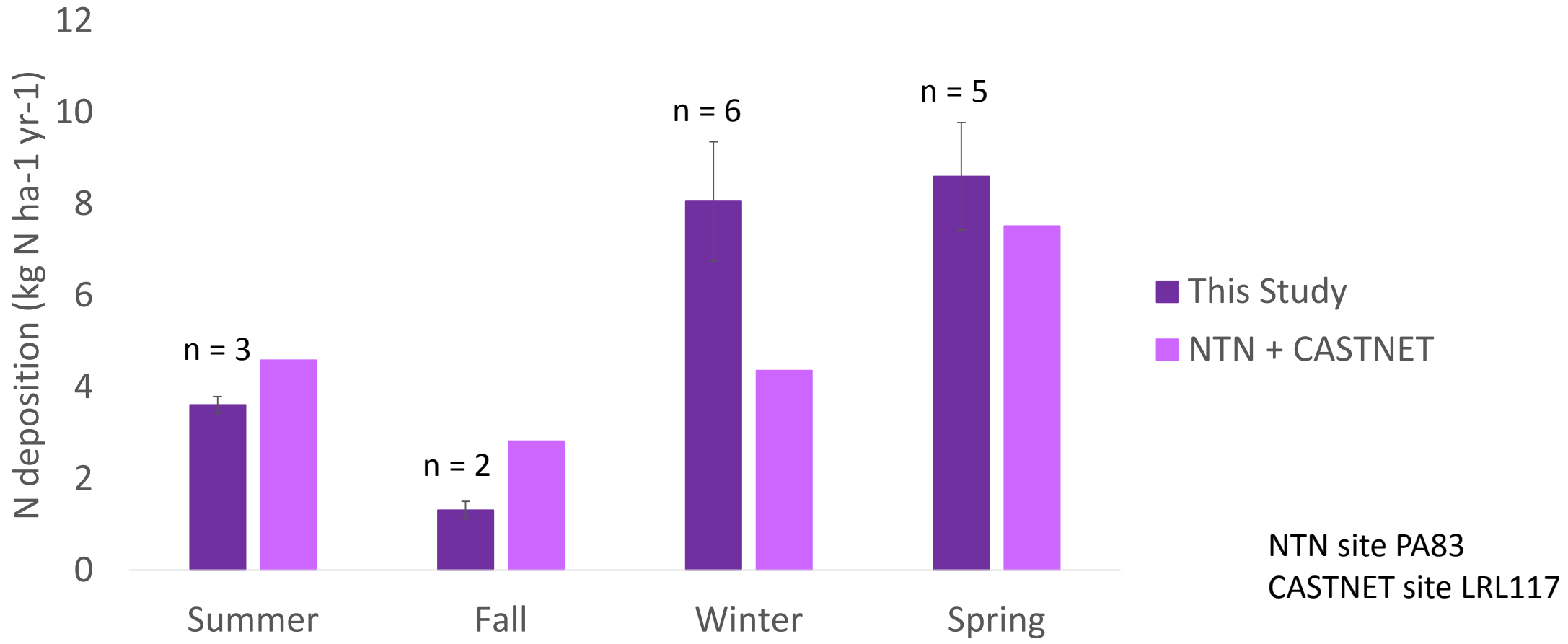


Laurel Hill site in same location as NTN and CASTNET site

NTN site PA83
CASTNET site LRL117

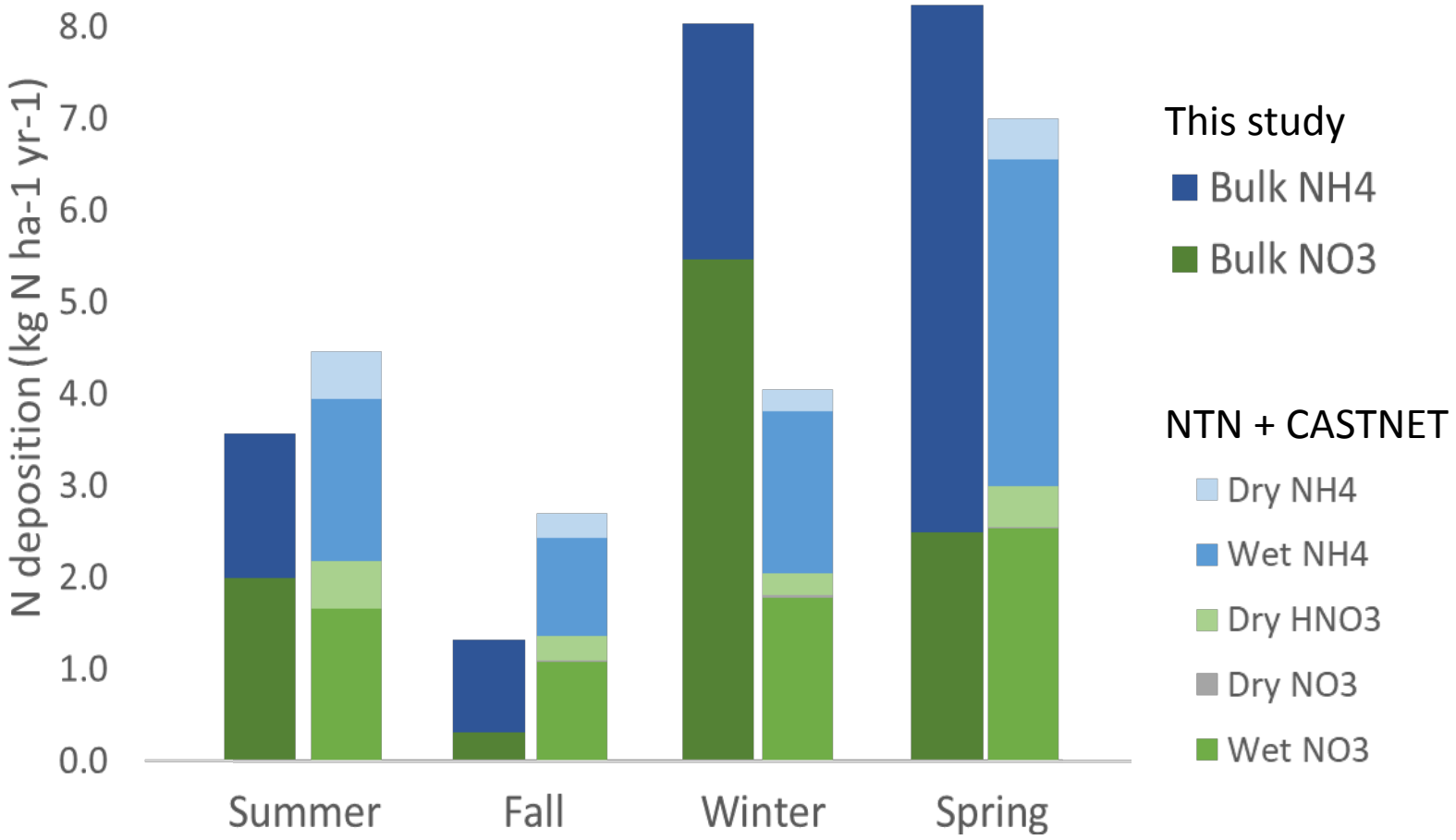


Resin data from Laurel Hills comparable to co-located NTN-CASTNET sites



NTN site PA83
CASTNET site LRL117

Resins and NTN-CASTNET data separated by nitrogen species



Introduction to nitrate stable isotopes

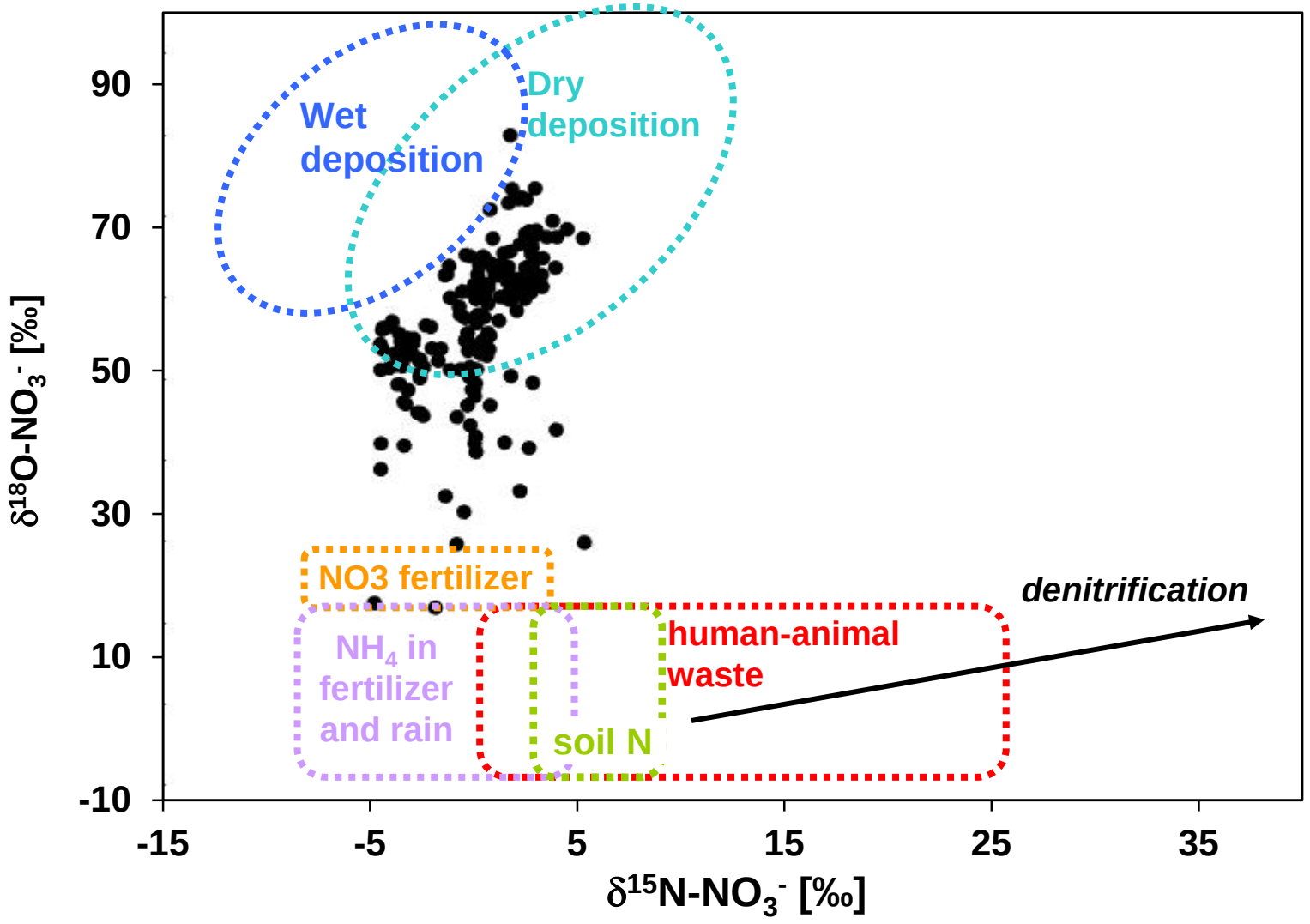
Elements naturally have different abundances of their various isotopes

- same element but slightly different mass

Chemical and biological reactions selectively choose certain isotopes

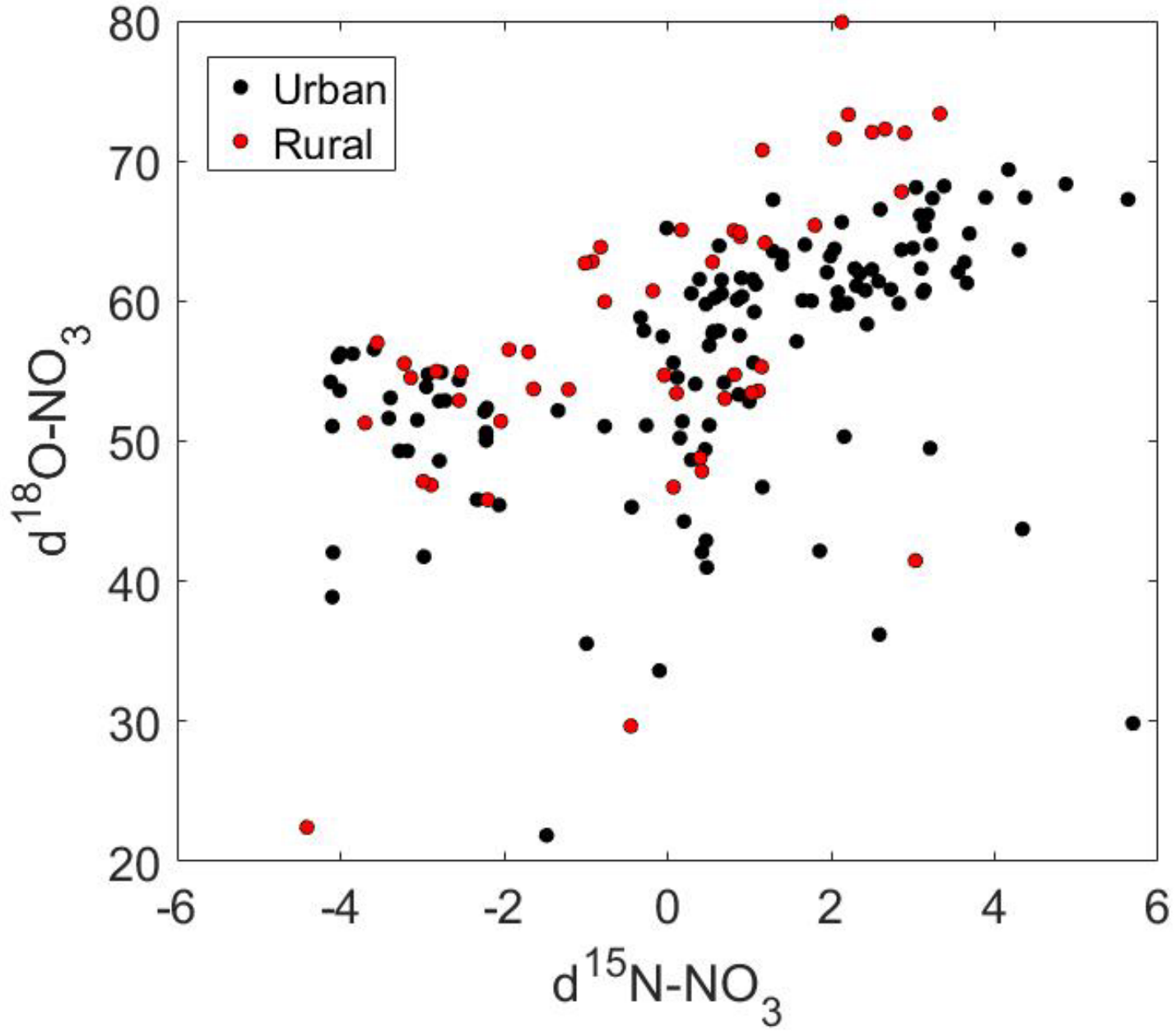
The difference between the amount of the heavier isotope (^{15}N or ^{18}O) compared the natural abundance gives information about the reactions that molecule went through

- Measured as per mille (‰)



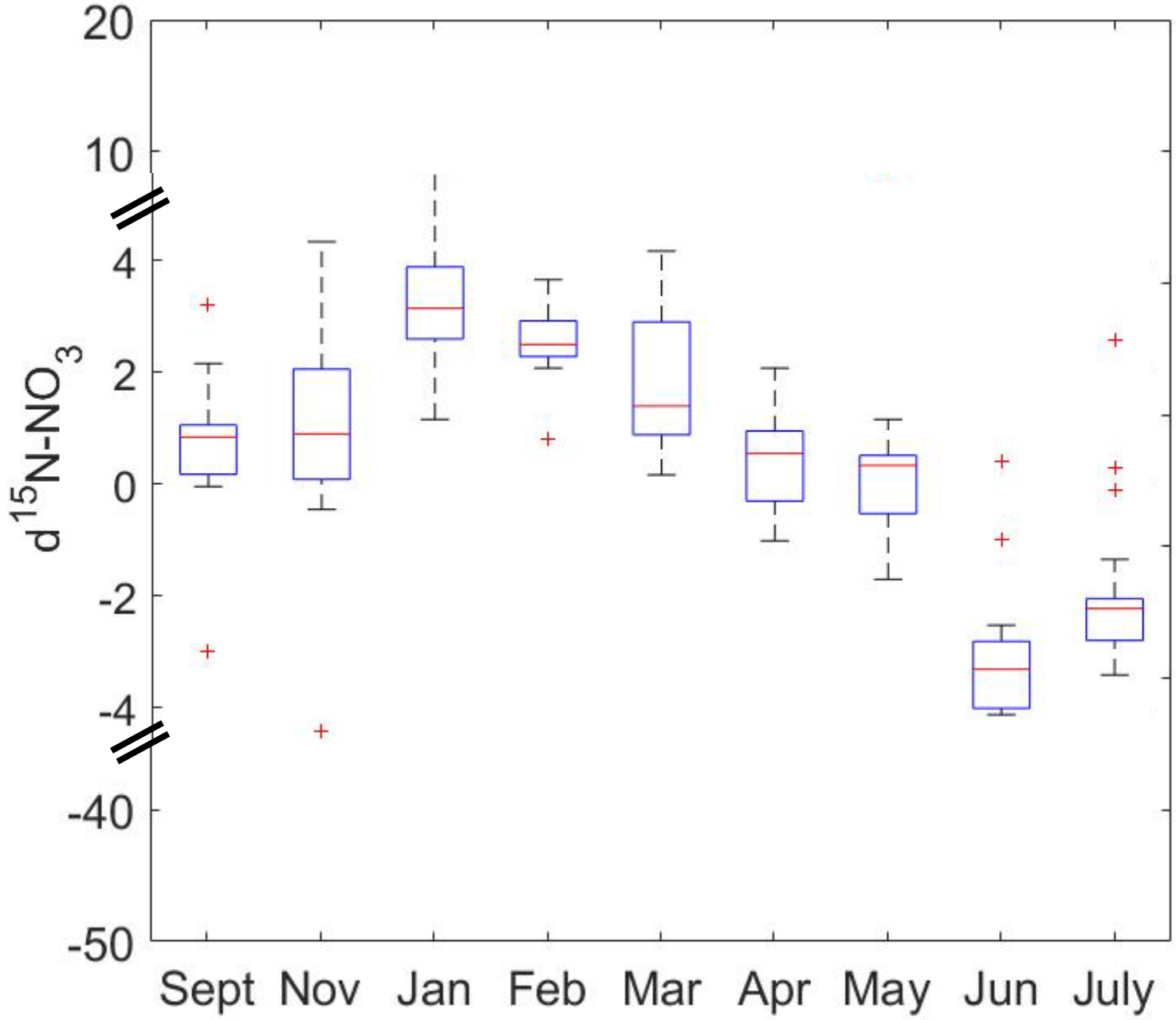
$\delta^{15}N$ and high $\delta^{18}O$ values indicate that IER data is in the range of other atmospheric deposition studies

(Elliott et al. 2009, Elliott et al. 2007, Kendall et al. 2007)



Urban and rural sites do not have distinct isotope ranges

Seasonal variation in $\delta^{15}N$ due, in part, to changing source contribution



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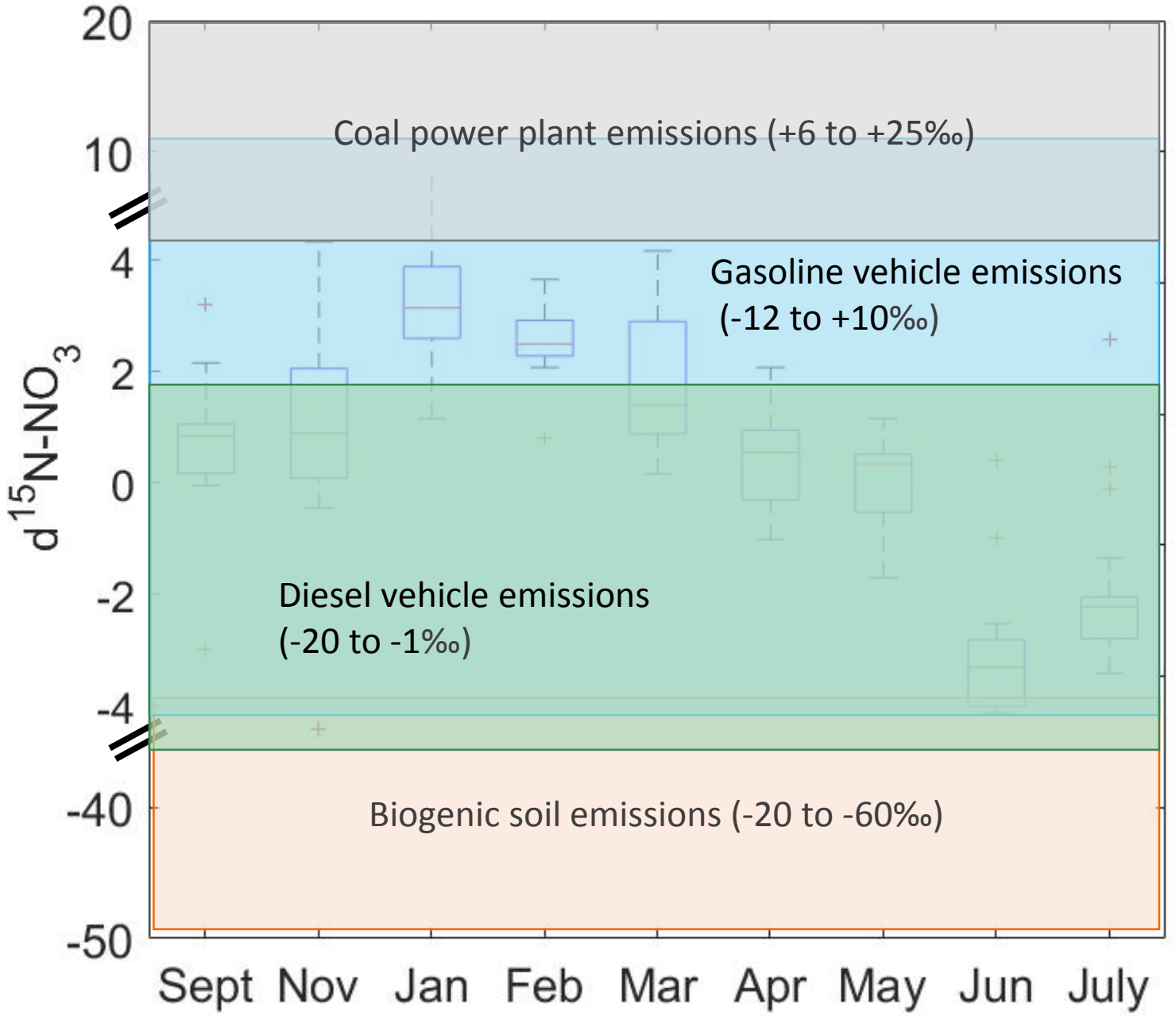

(Miller et al. 2017)

Comparison to other urban deposition studies

Source	Location	Type of collection	Total N dep flux (kg N ha^{-1} yr^{-1})
This study	**Pittsburgh, PA**	**Bulk**	**5.9 – 7.6**
Bettez & Groffman 2013	Baltimore, MD	Bulk	6.3 - 7.0
Lohse et al 2008	Phoenix, AZ	Bulk	<6
Bettez & Groffman 2013	Baltimore, MD	Throughfall	11.1 - 13.3
Decina et al. 2017	Boston, MA	Throughfall	3.8 - 13.8

Conclusions

No significant difference in yearly **average** deposition fluxes between rural and urban sites

However, certain sites/months receive drastically different fluxes

- There is even variation in reps deployed in the same place at the same time
- If not from different sources, what could be the cause of this?

Need finer spatial scale sampling to understand drivers of flux variability

- Ion exchange resins are a good tool for this type of analysis

Implications for future atmospheric research

Searching for the one true flux of urban atmospheric deposition for nutrient budgets

- Is this possible?
- Is it even representative of true conditions?

Selecting a representative urban site

- Challenges of landscape heterogeneity
- Variation among individual replicates

Acknowledgements

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