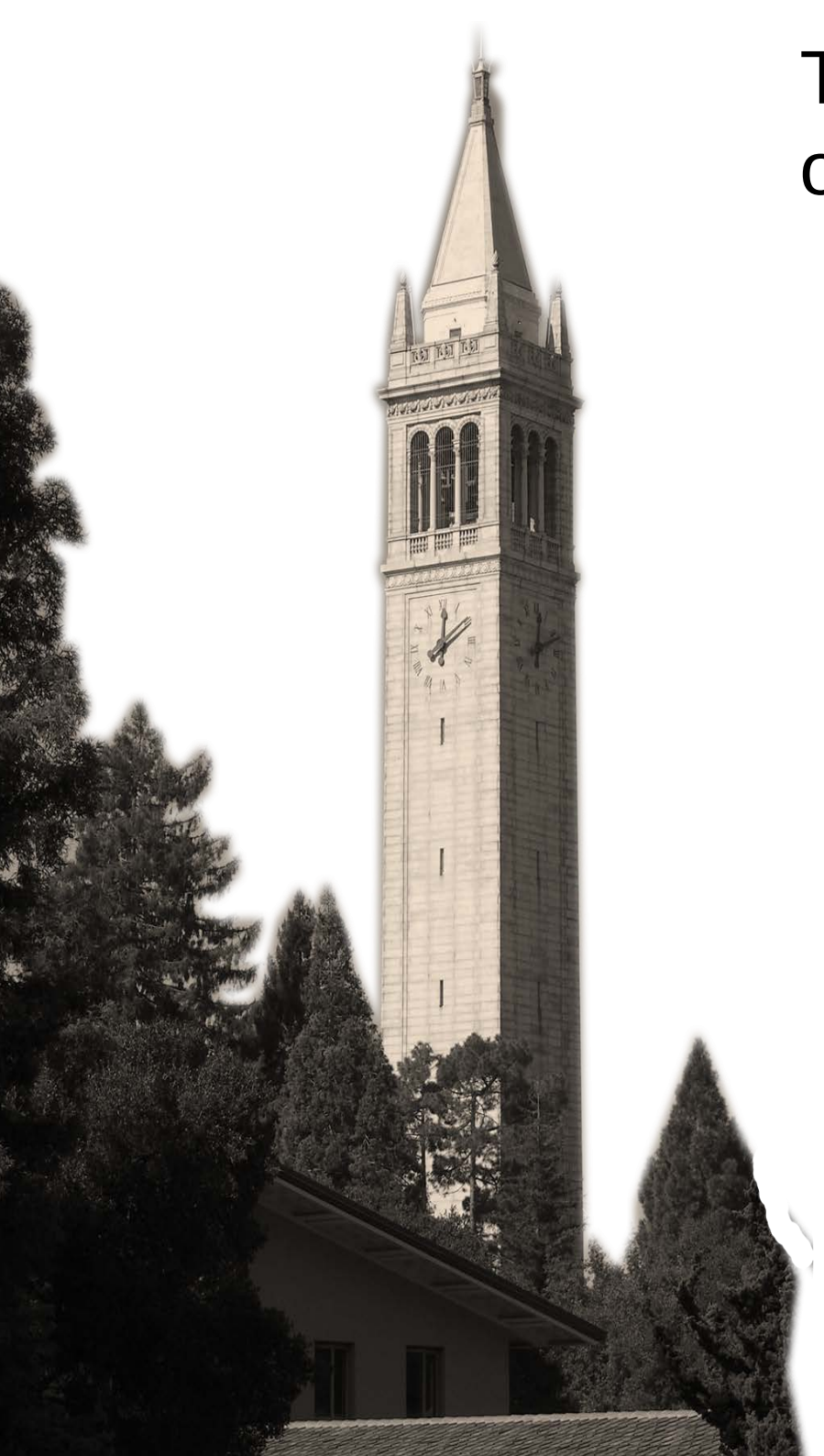

The Changing NOy Budget of the Southeast US

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Prof. UC Berkeley

Paul Romer
Kaitlin Duffey
Paul Wooldridge
SOAS Colleagues

$NSF

Questions/Motivation

What processes govern the natural background NO_x in the Southeast US?

How close were we to that background in 2012?

At that NO_x what chemistry governs O_3 and aerosol?

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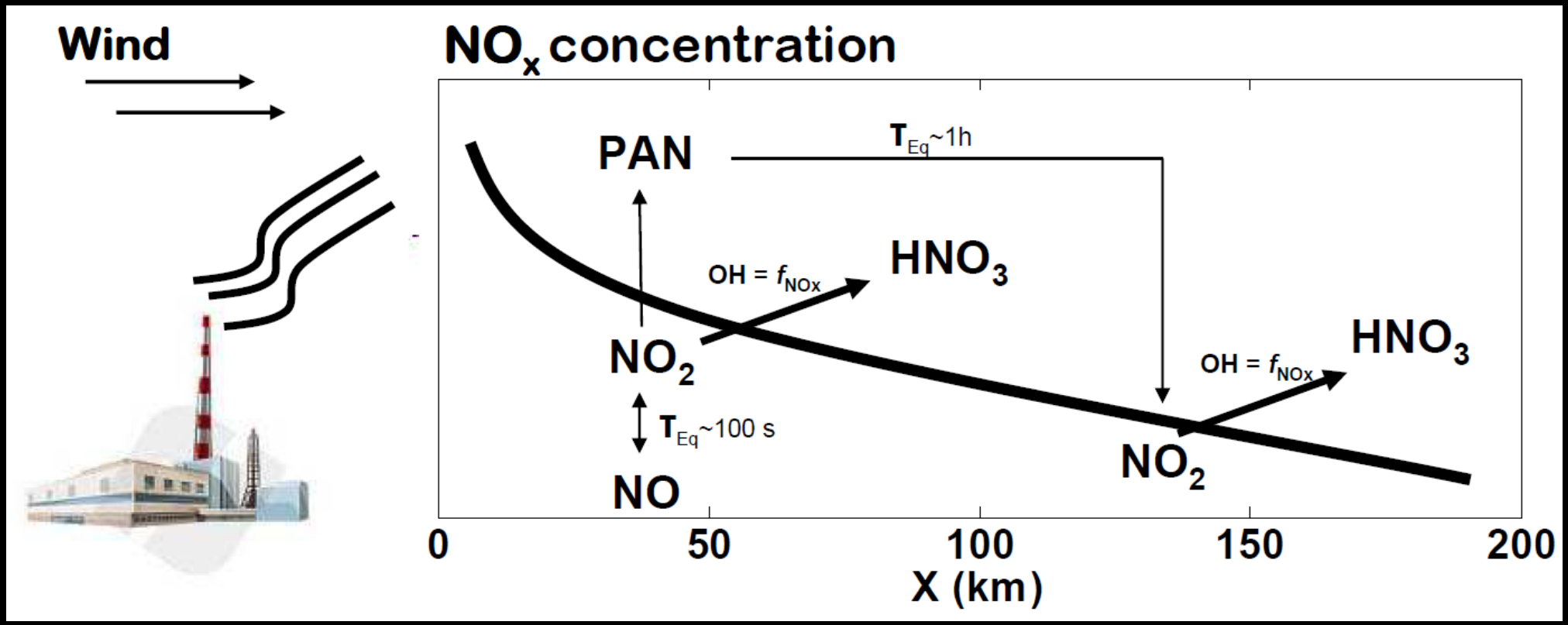
Interactions of Chemistry and meteorology



Background

Browne et al. ACP 2012, 2013, 2014

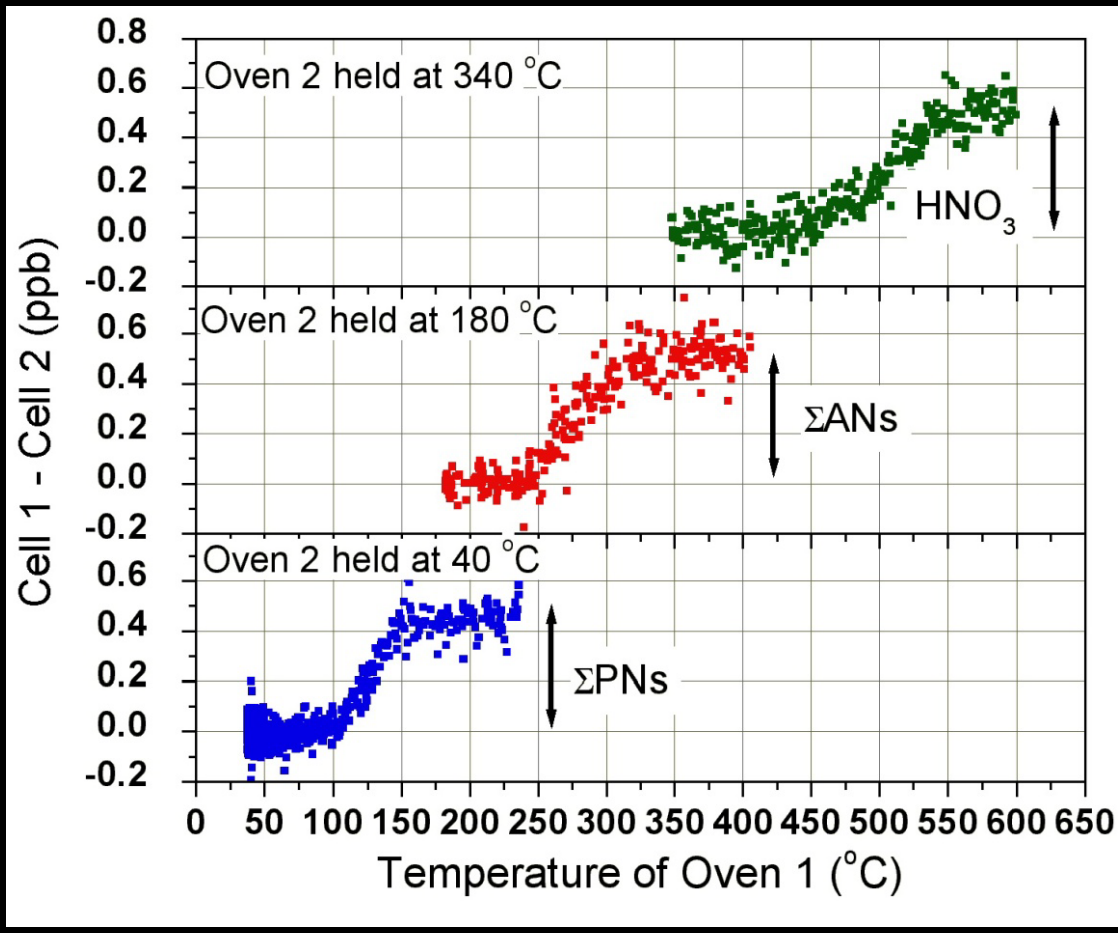
Perring, Pusede and Cohen, Chem Reviews, 2013

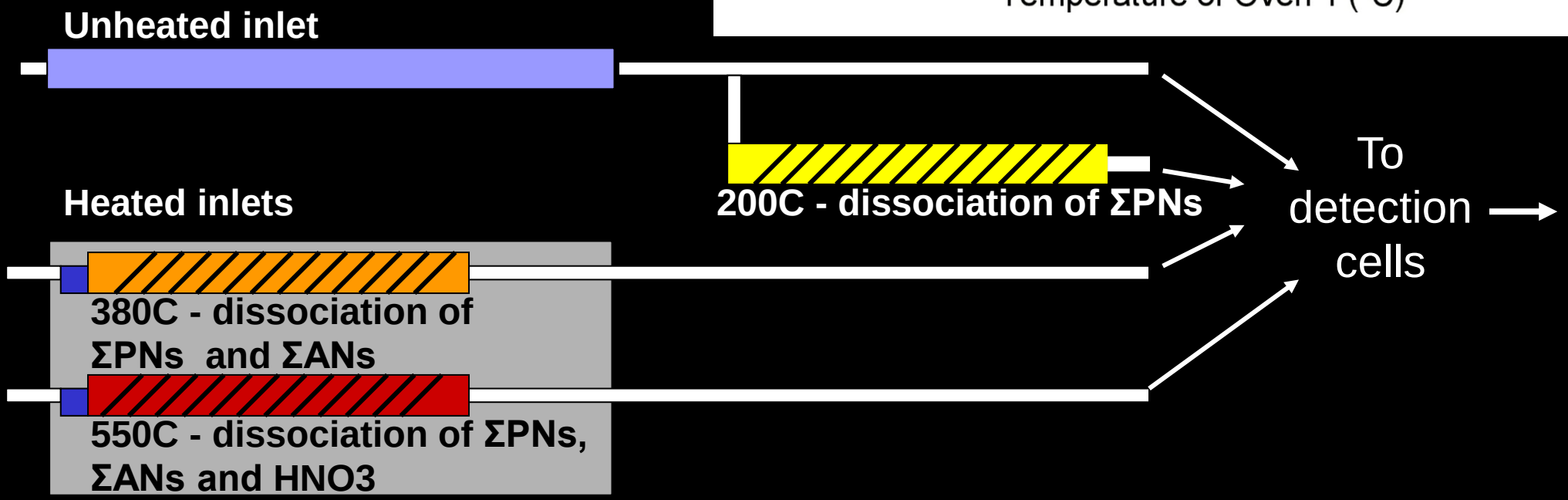
See also BEARPEX special issue of ACP and related papers elsewhere

- In the Boreal forest $RONO_2$ formation is the major NO_x sink
- $RONO_2$ hydrolysis possibly the largest source of HNO_3
- The chemistry of NO_x, O_3, and OH is strongly dependent on the effective yield of $RONO_2$ from the ensemble of RO_2+NO reactions.

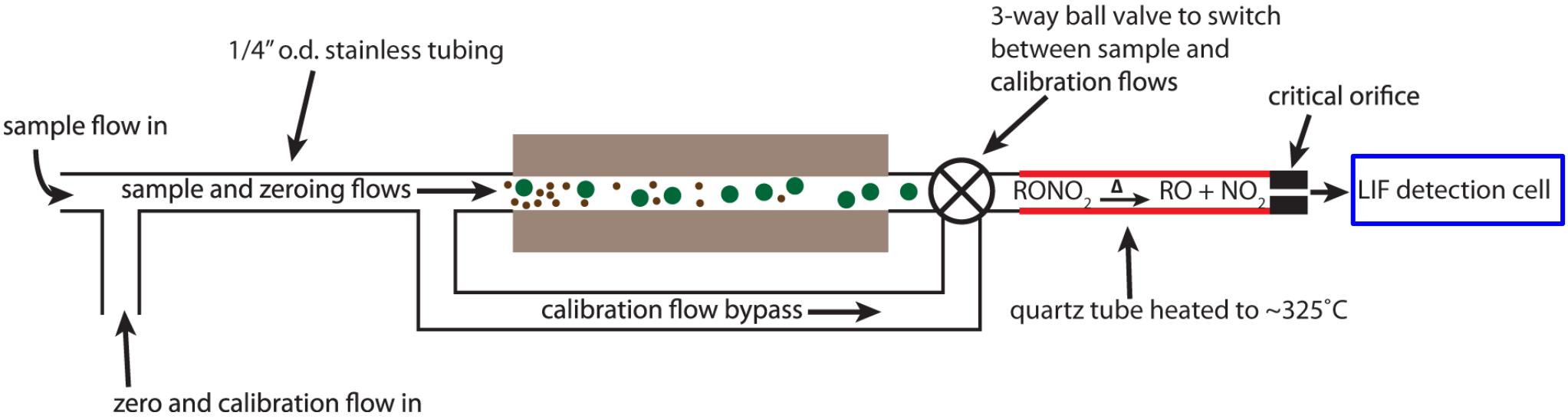
Thermal Dissociation

followed by LIF detection of resulting NO_2 to infer ΣPNs, ΣANs and HNO_3



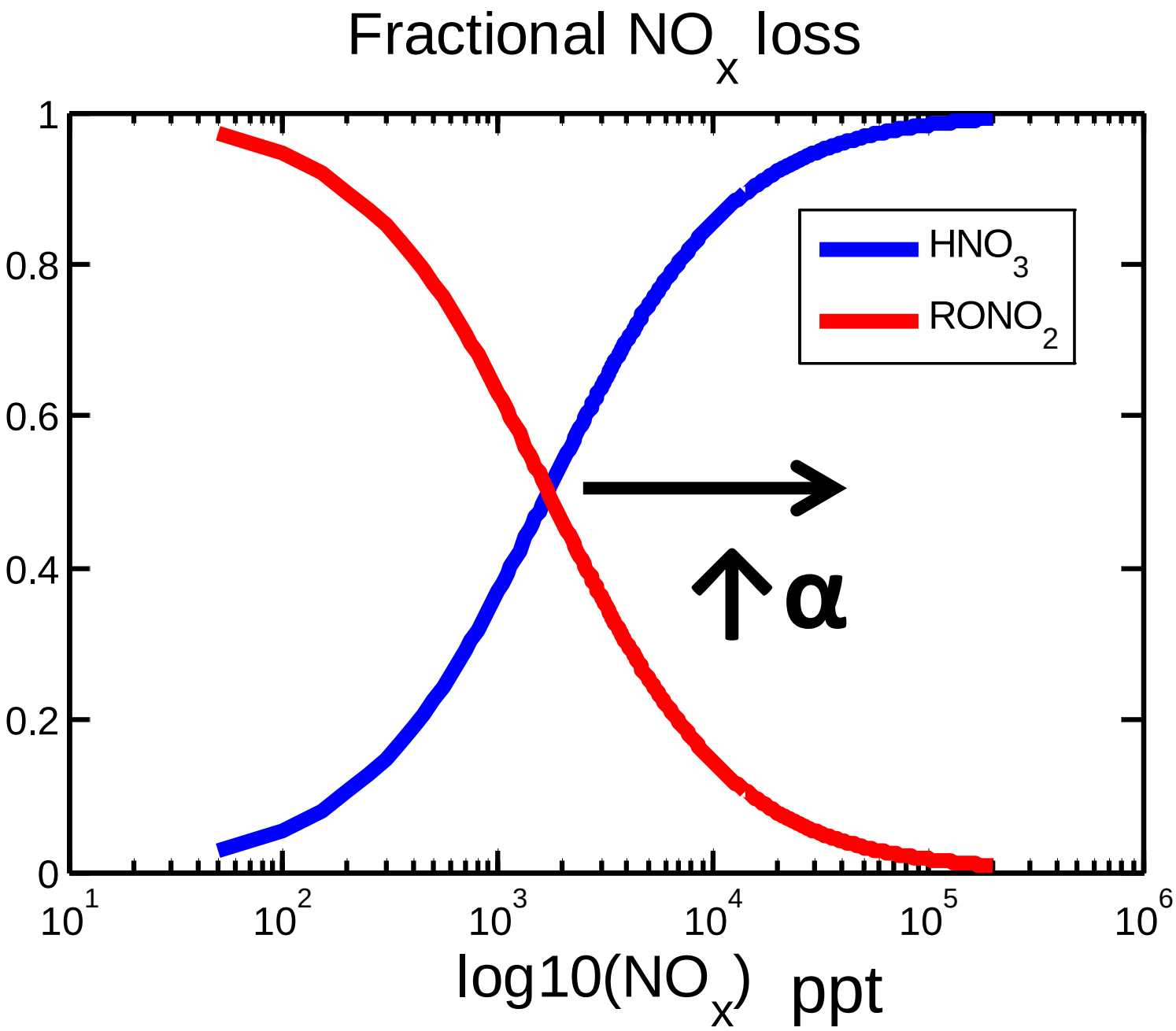


Also aerosol organic nitrate



A. W. Rollins et al. *Environ. Sci. Technol.* 44, 5540-5545, 2010

Under low NO_x conditions $RONO_2$ formation is the primary NO_x loss



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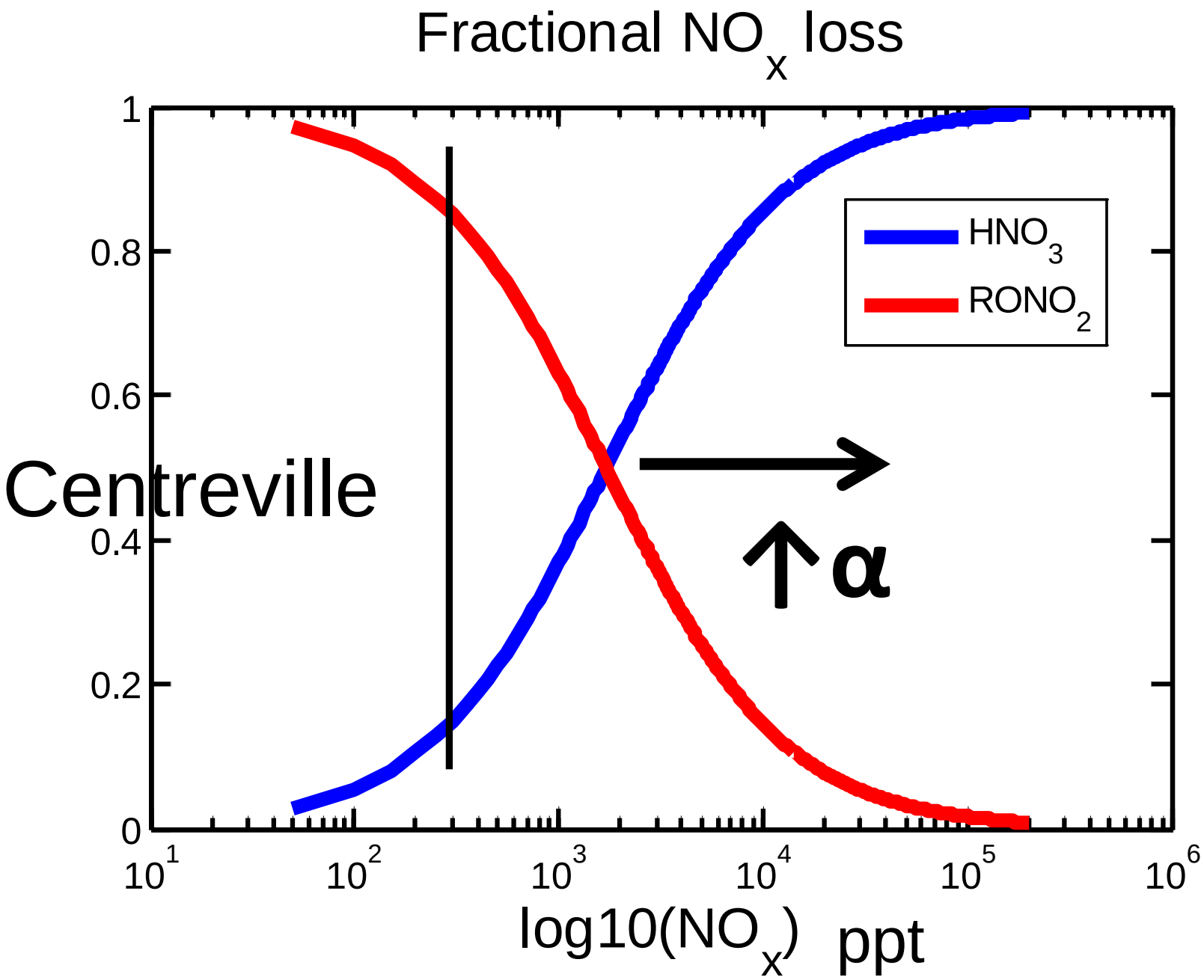
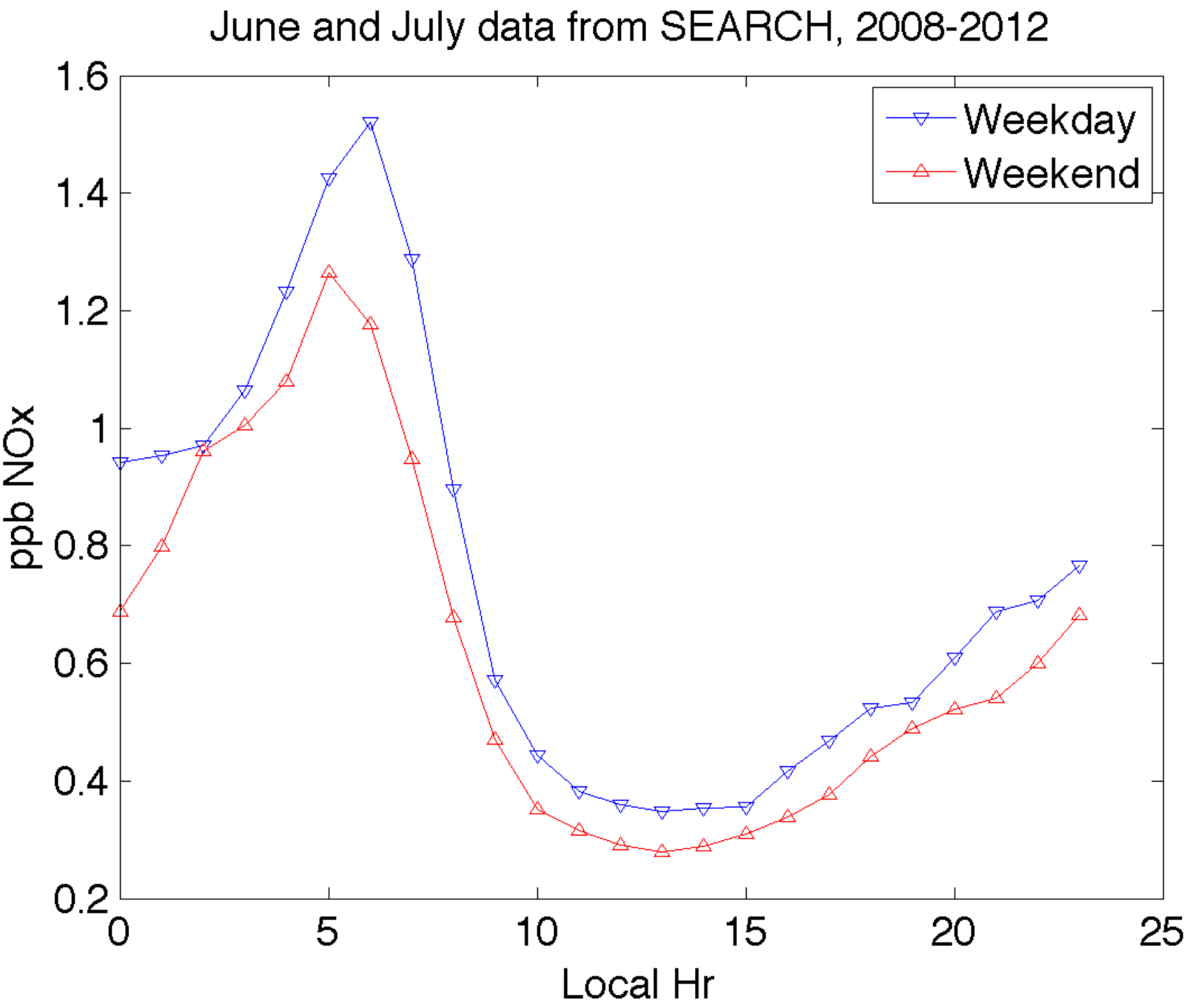
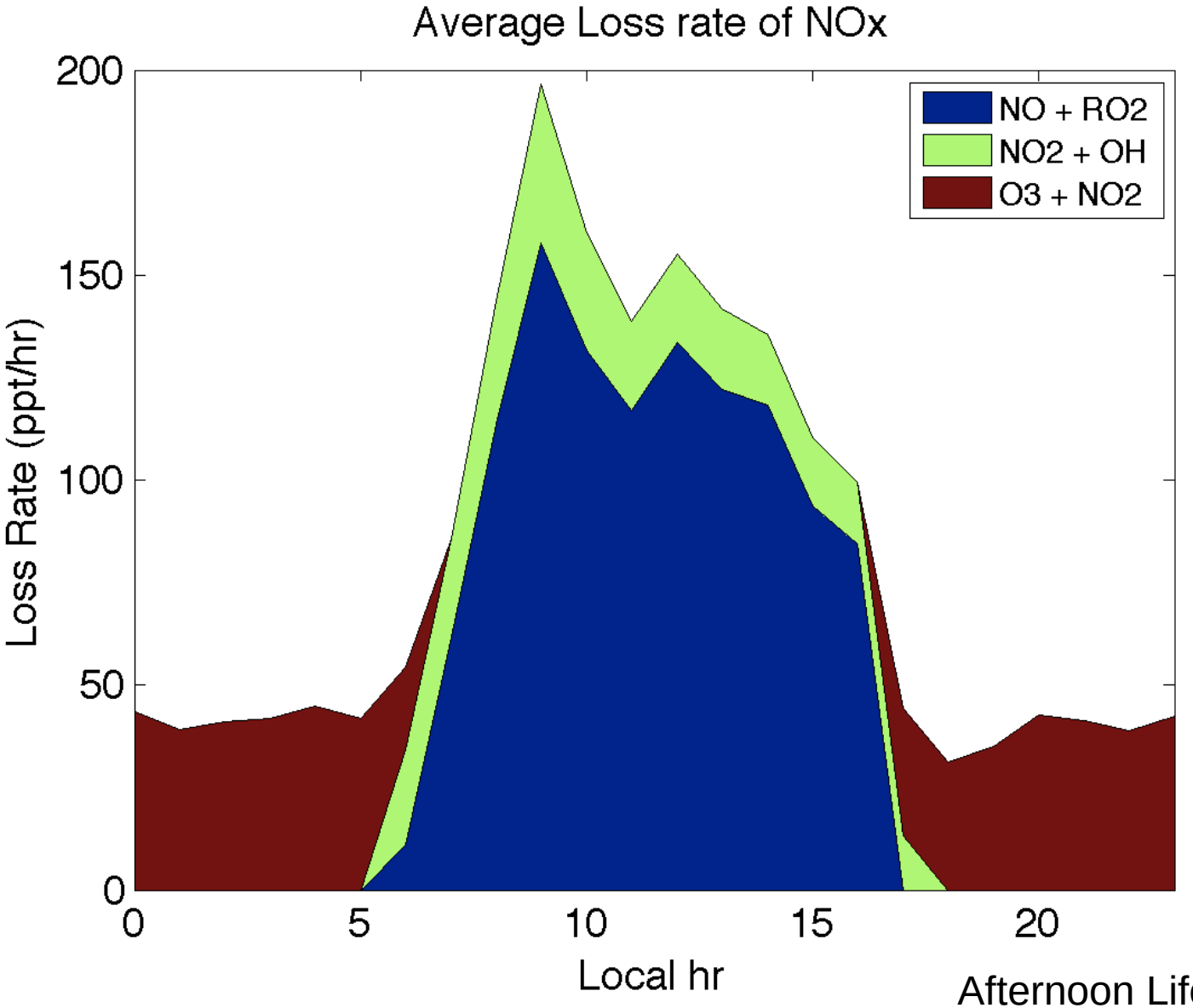



June and July data from SEARCH, 2008-2012
Weekday
Weekend
ppb NOx
Local Hr
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
5
10
15
20
25

NO_x Chemical Loss Processes



Afternoon Lifetime: ~3hrs

The chemical lifetime of NO_x in 2012 during midday was ~3hrs

- Local sources and sinks in approximate steady state
- $RONO_2$ chemistry plays a major role in setting HO_x and O_3 levels by regulating NO_x
- If there is uptake of NO_x by the biosphere, the lifetime is even shorter.

Questions

What is the source of NO_x?

Needs to be ~150ppt/hr (larger if we don't have all the sinks accounted for—e.g. forests)

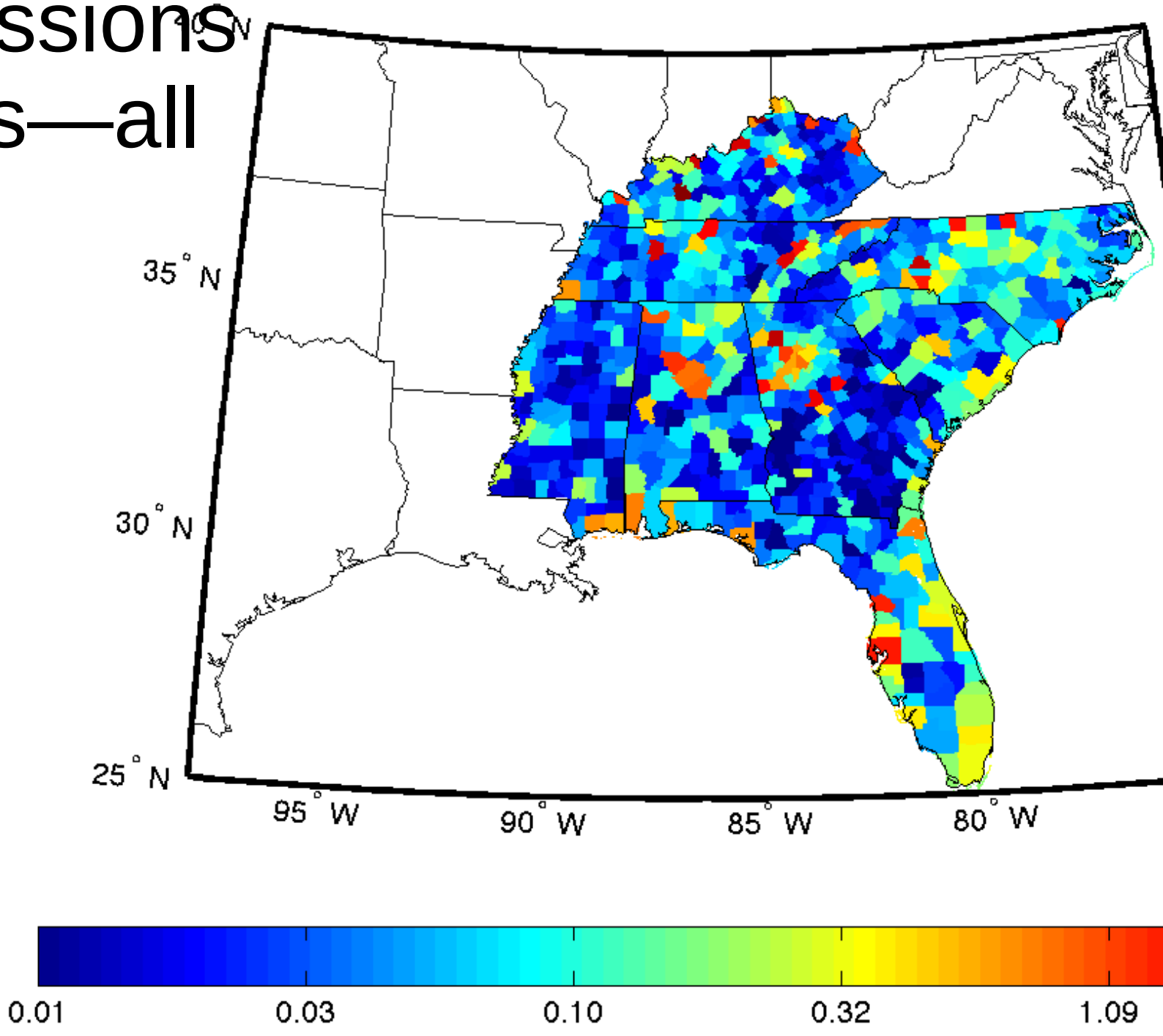
Questions/Motivation

How close were we to the natural background NO_x in 2012?

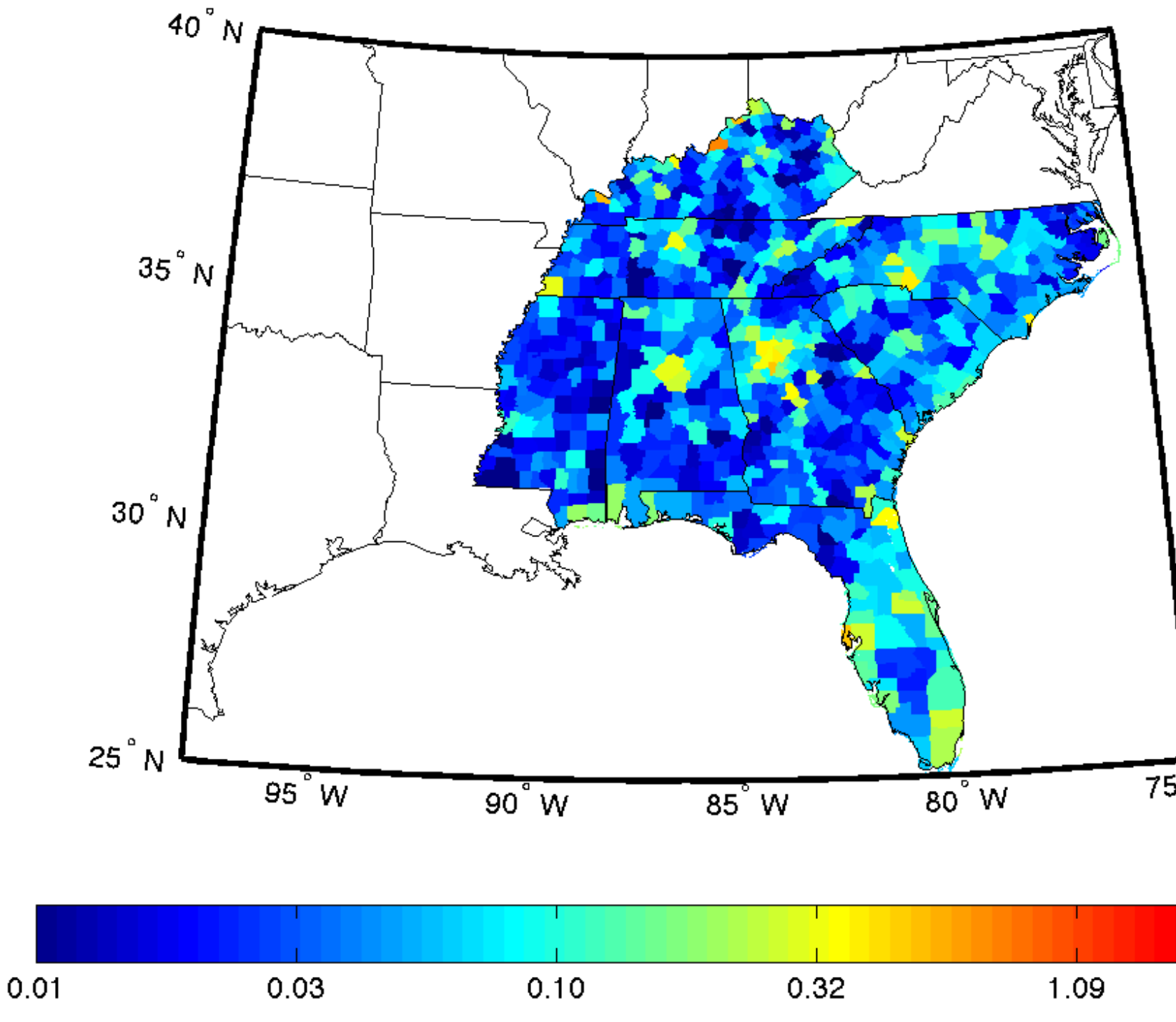
EPA Emissions Estimates—all sources

Moles N/m2/yr

1997

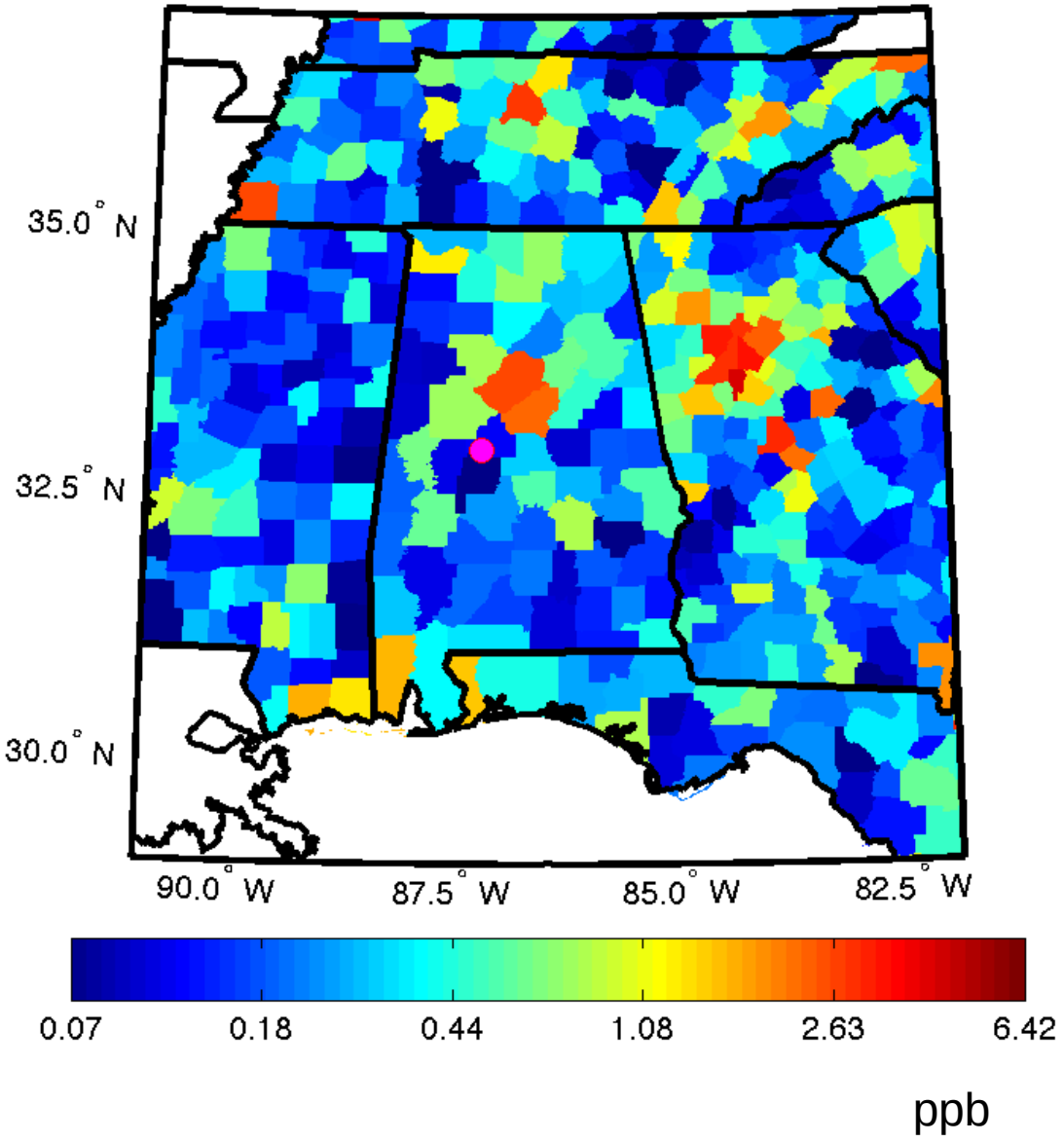


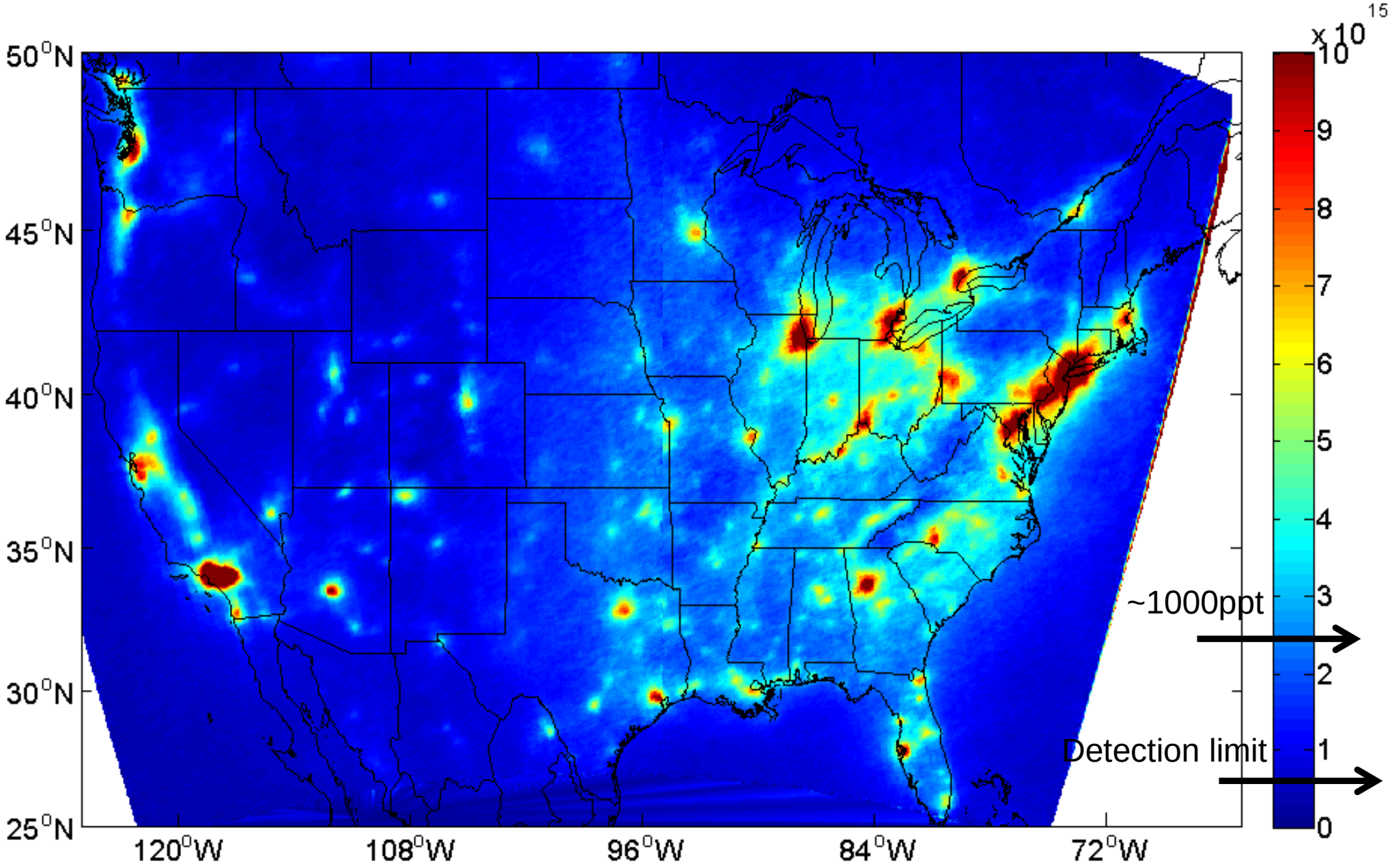
2011



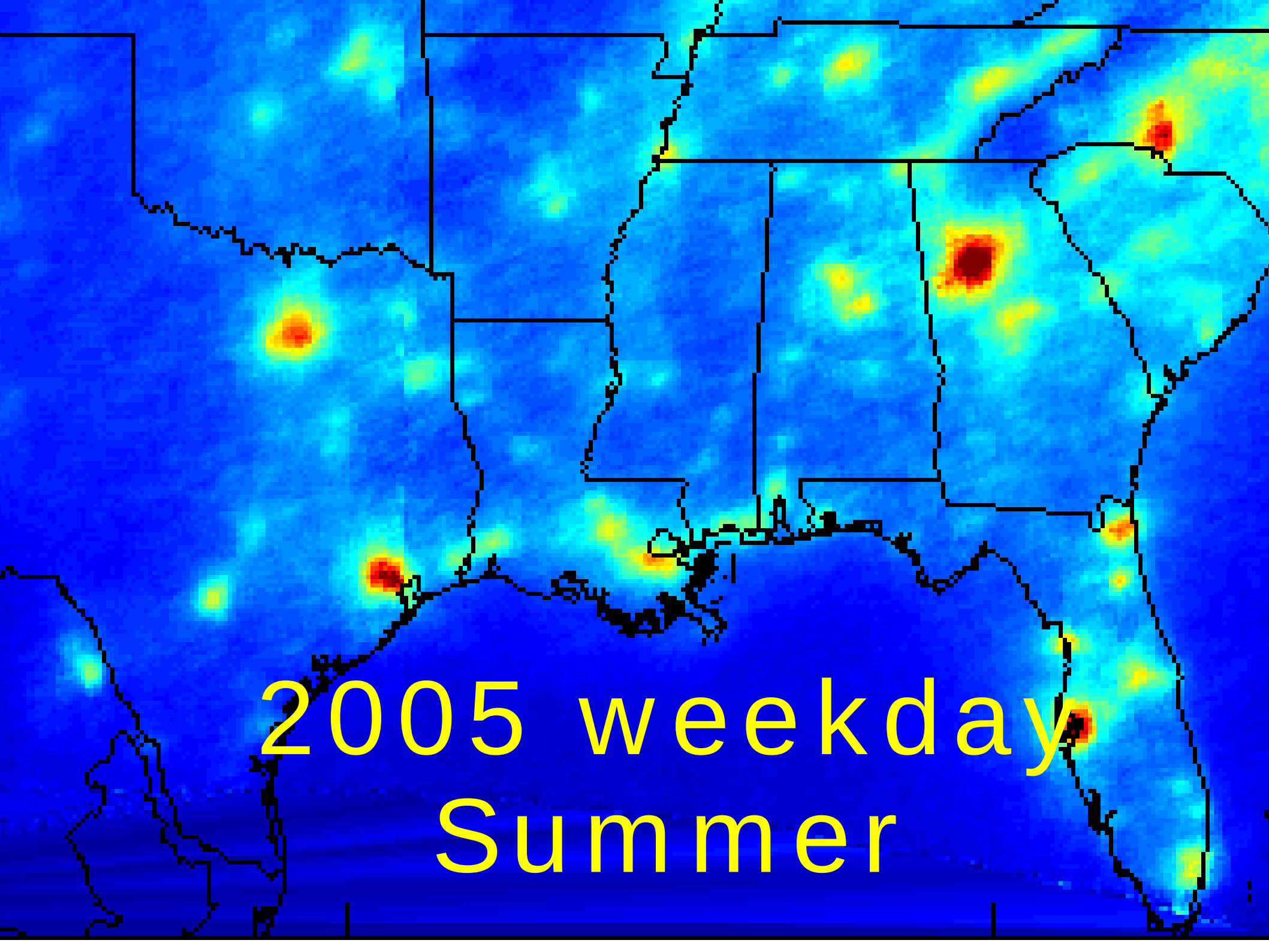
Convert EPA 2011 emissions to ppb

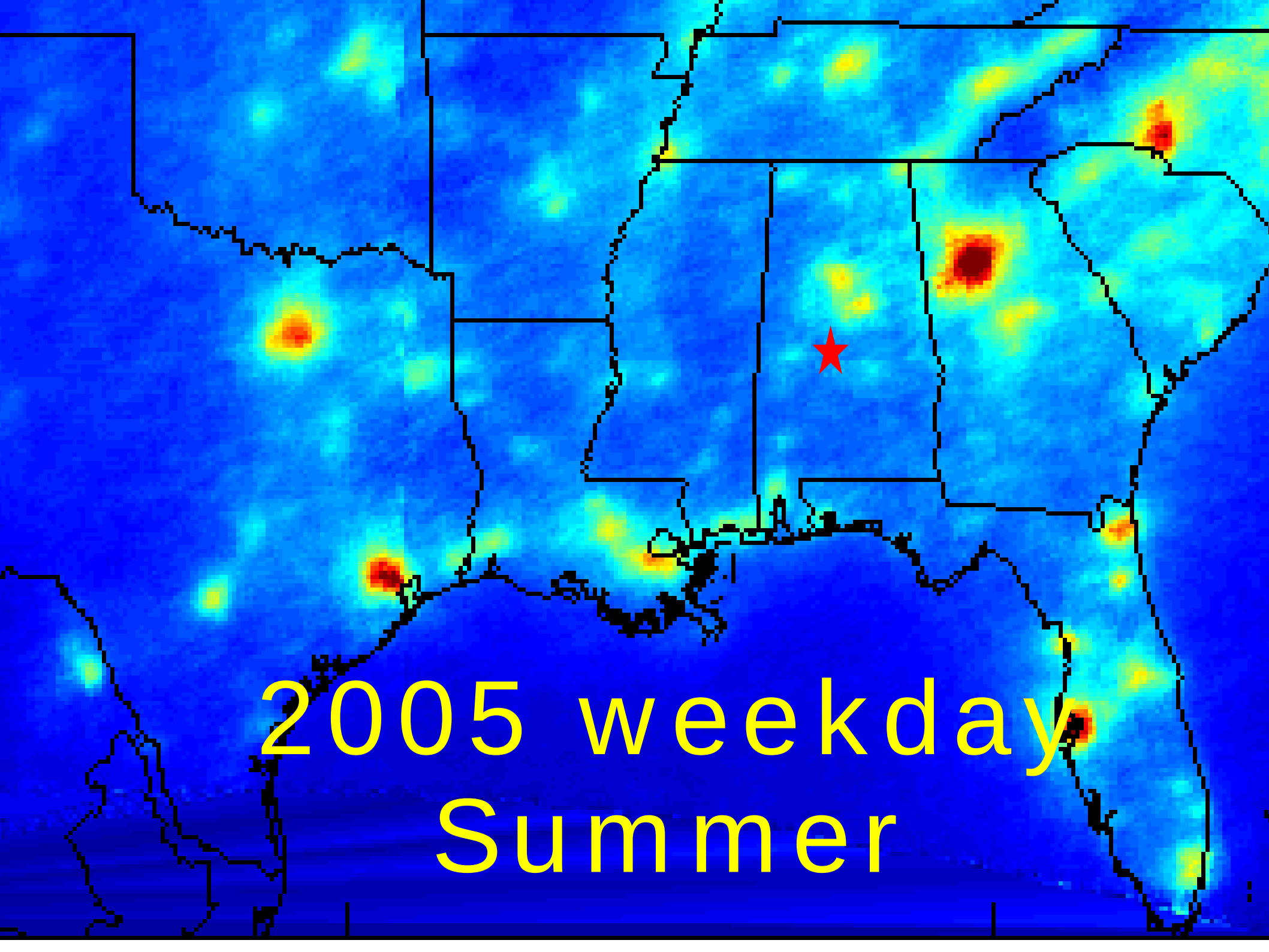
Assuming a 1km boundary layer and a 3 hour lifetime

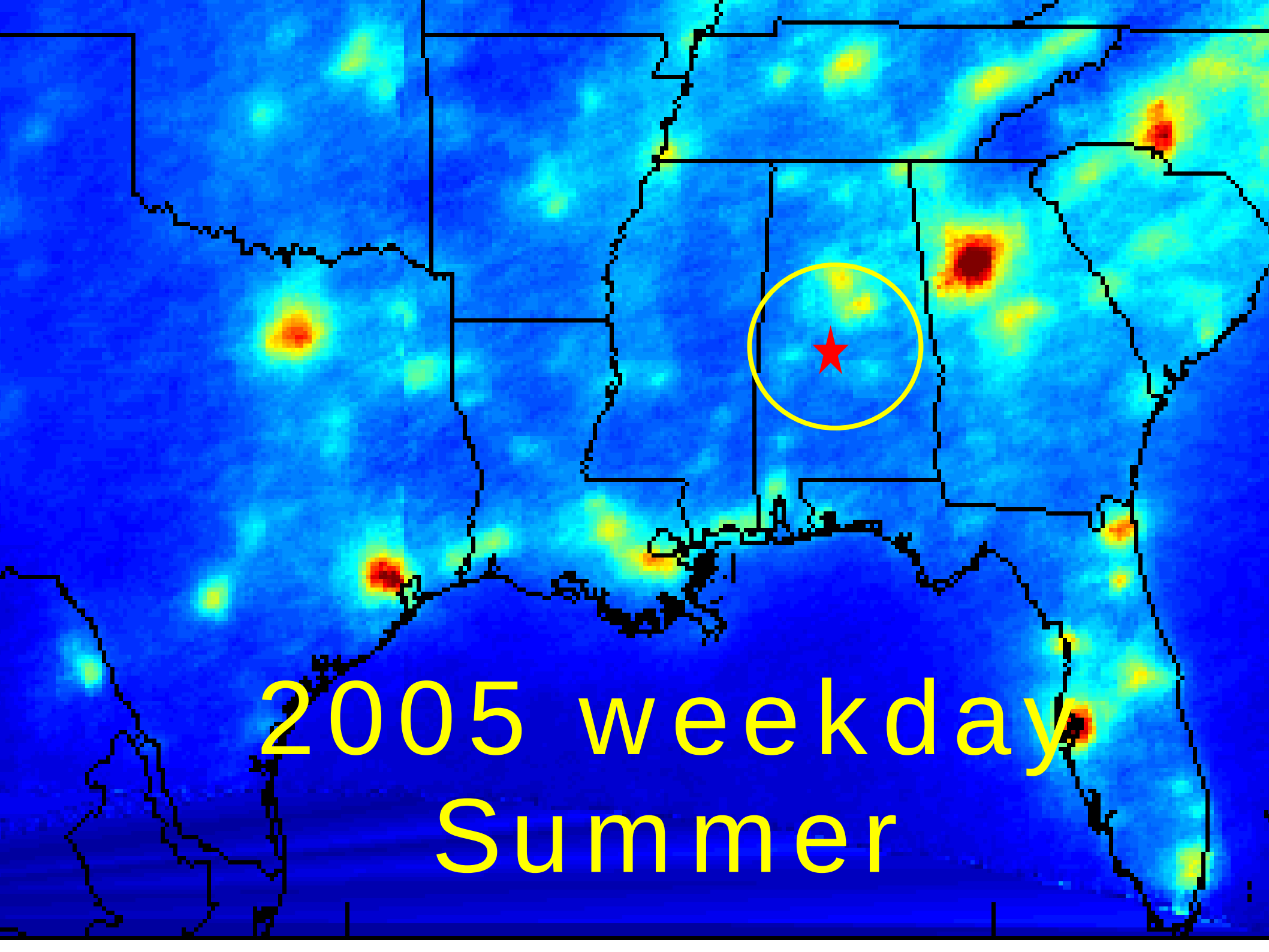


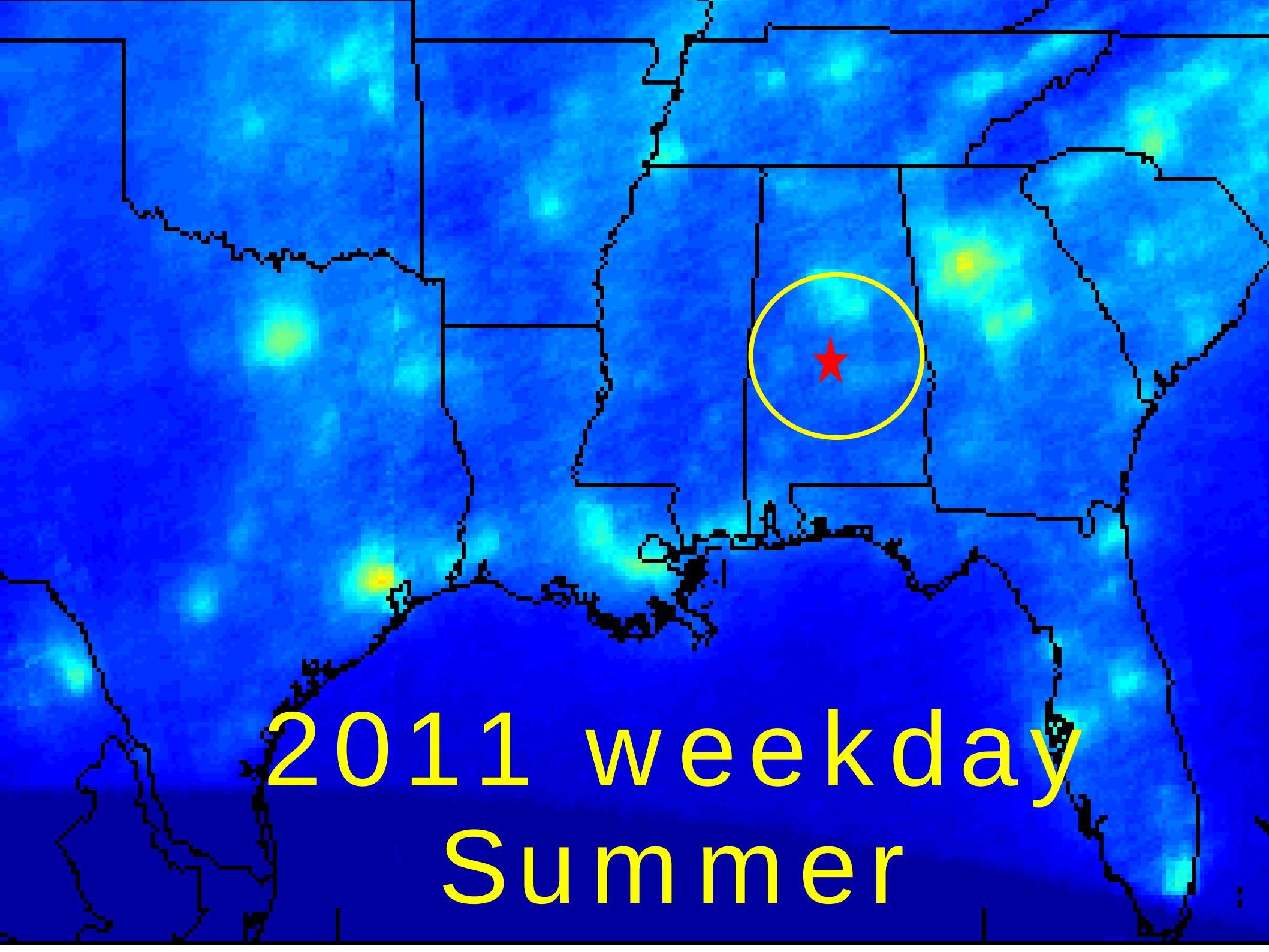


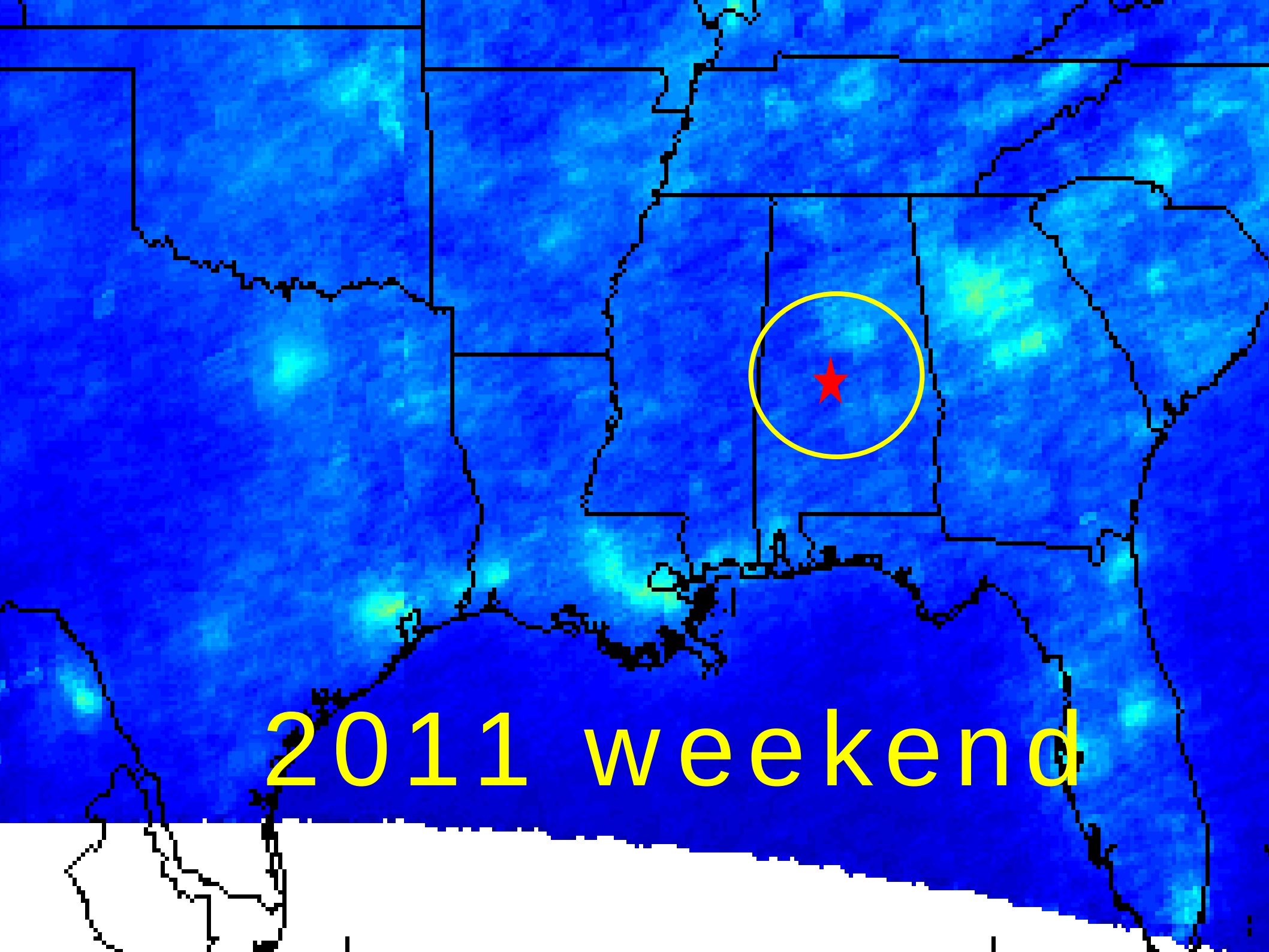
Weekday 2005


2005 weekday
Summer

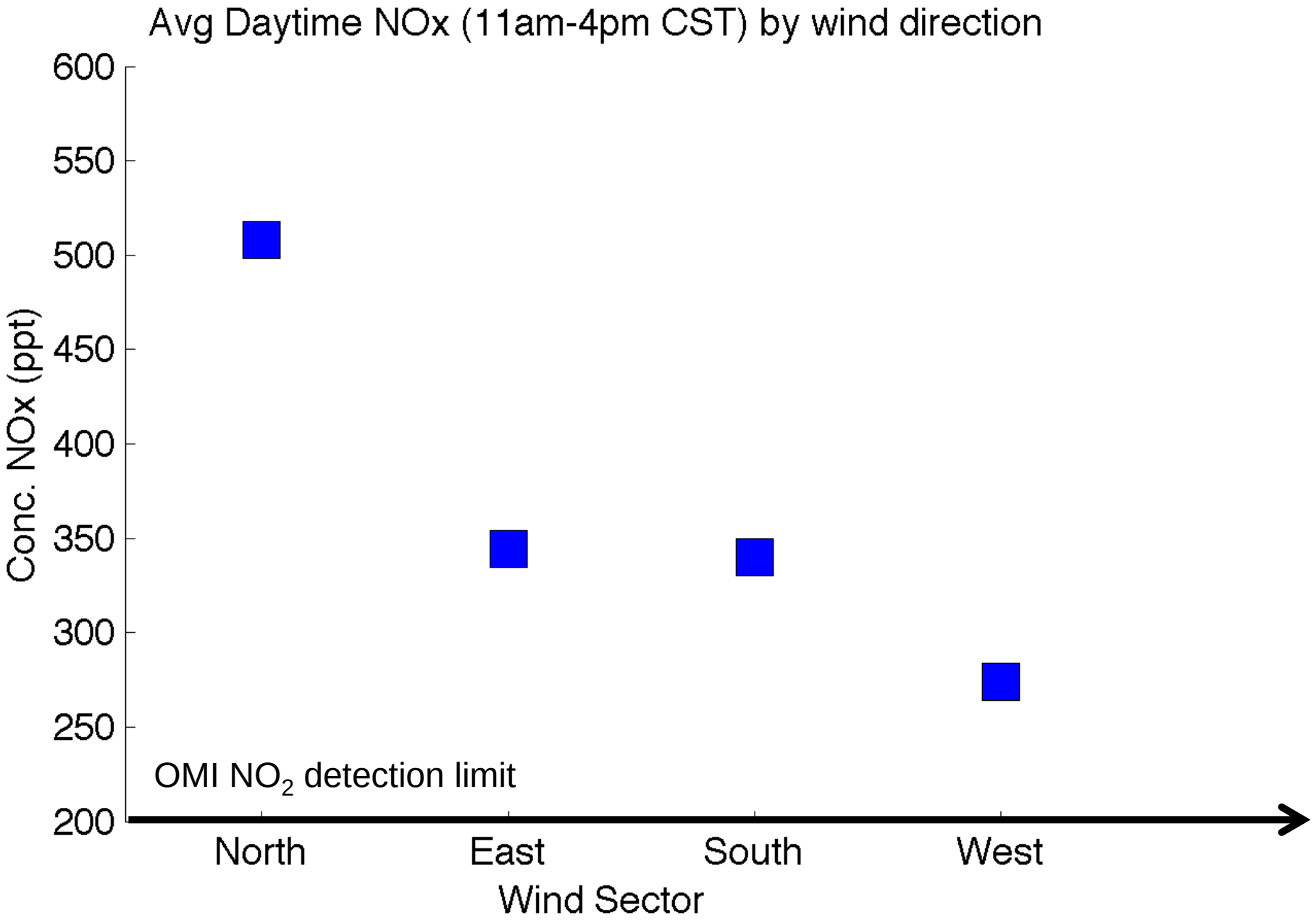

2005 weekday
Summer

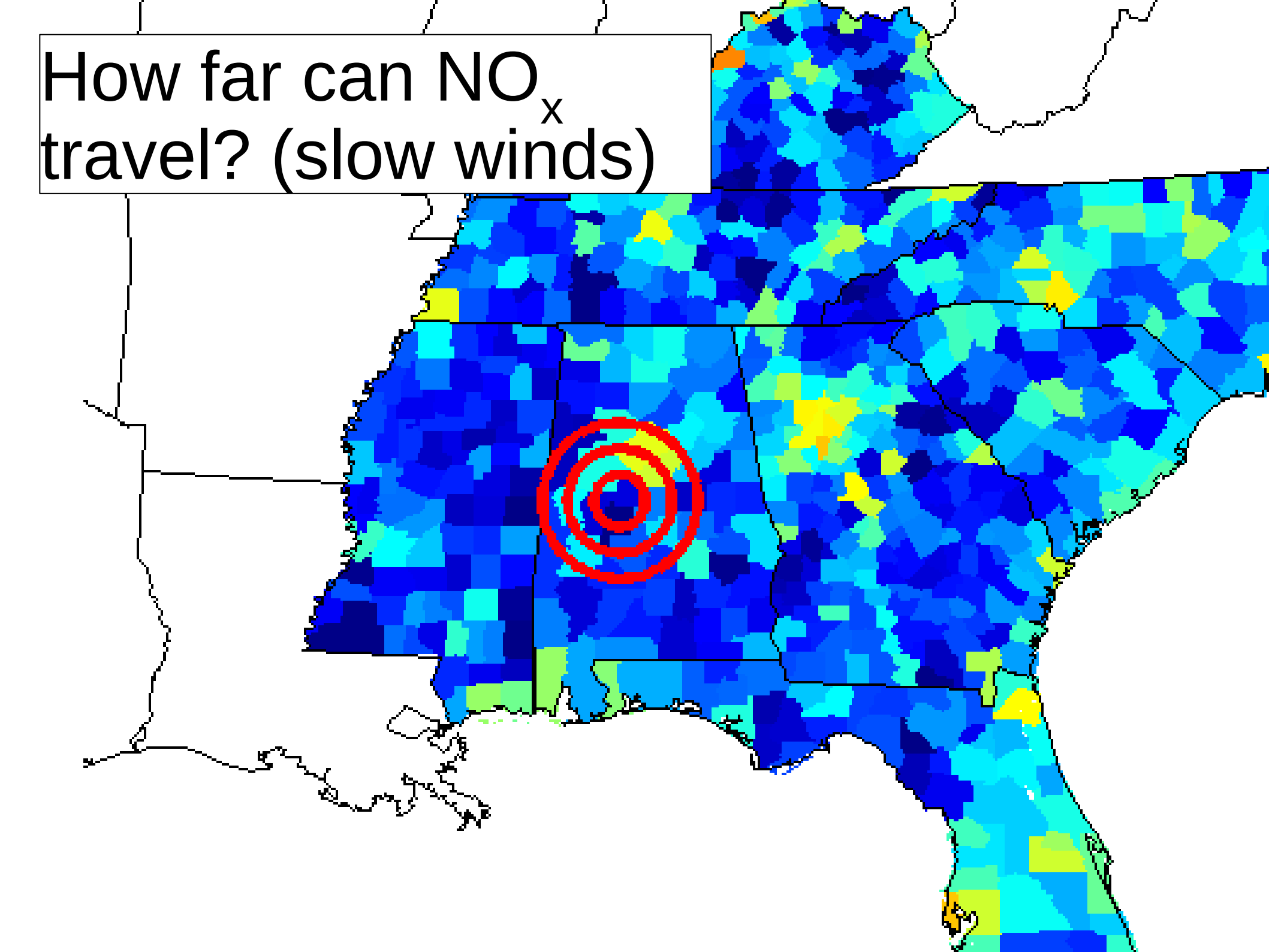

2005 weekday
Summer


2011 weekday
Summer


2011 weekend

NO_x vs Wind Direction




How far can NO_x travel? (slow winds)

3hr lifetime; 275 ppt NO_x

~90 ppt/hr

Daytime emission ~14 ngN-m^{-2}-s^{-1} into a 1km PBL.

Estimates based on NEI for all emissions within 40km of the site 8.3 ngN-m^{-2}-s^{-1}

Most NOx must arise from internal cycling? PAN and ANs?—Effective lifetime longer?

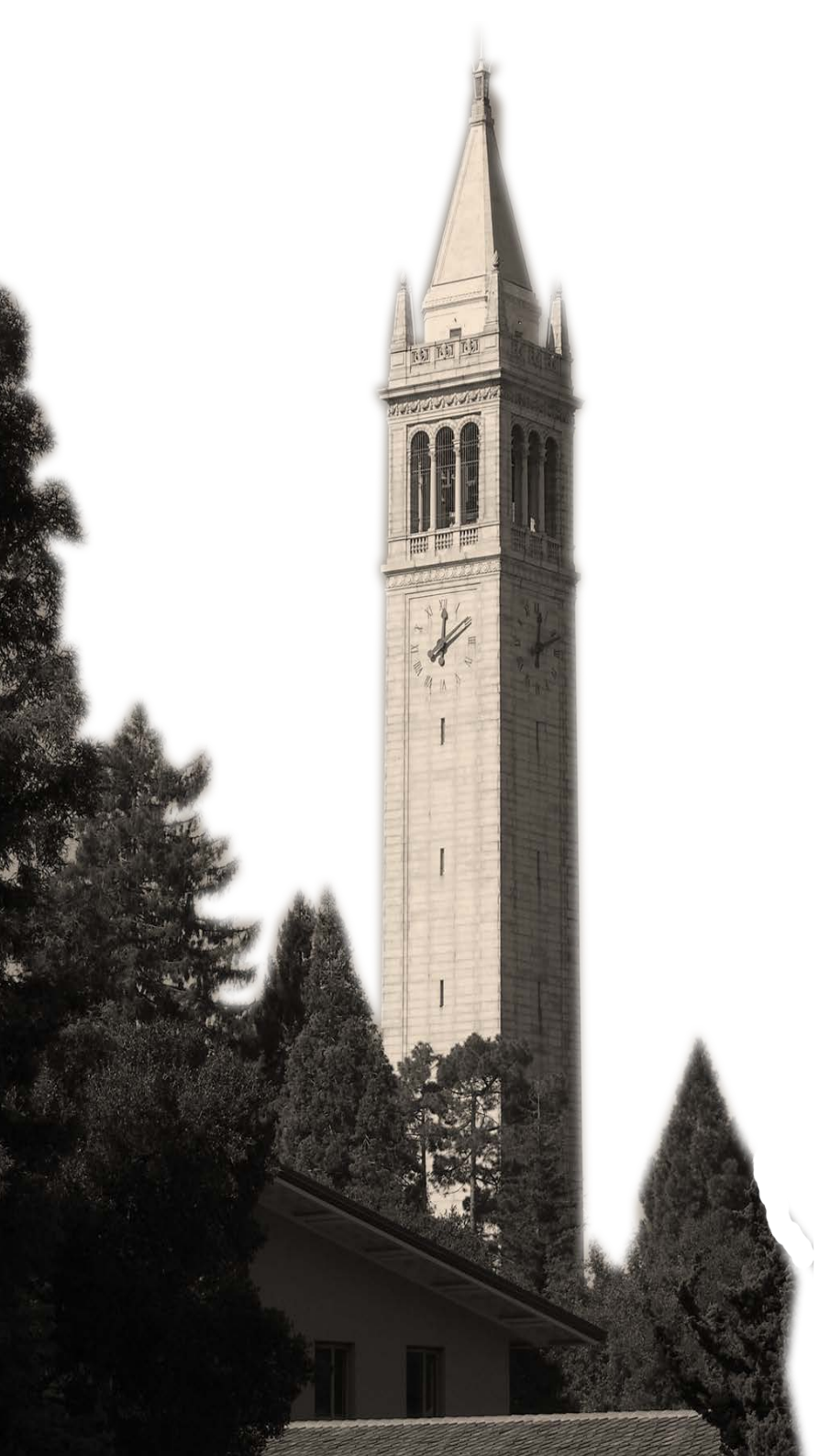
Questions/Motivation

How close were we to that background in 2012?

At Centreville, we are quite close to a background that is not influenced by urban or powerplant sources. Especially on weekends, when winds are slow and when winds are not from the N.

Evidence for local biospheric emissions—tentative (quantifying in progress).

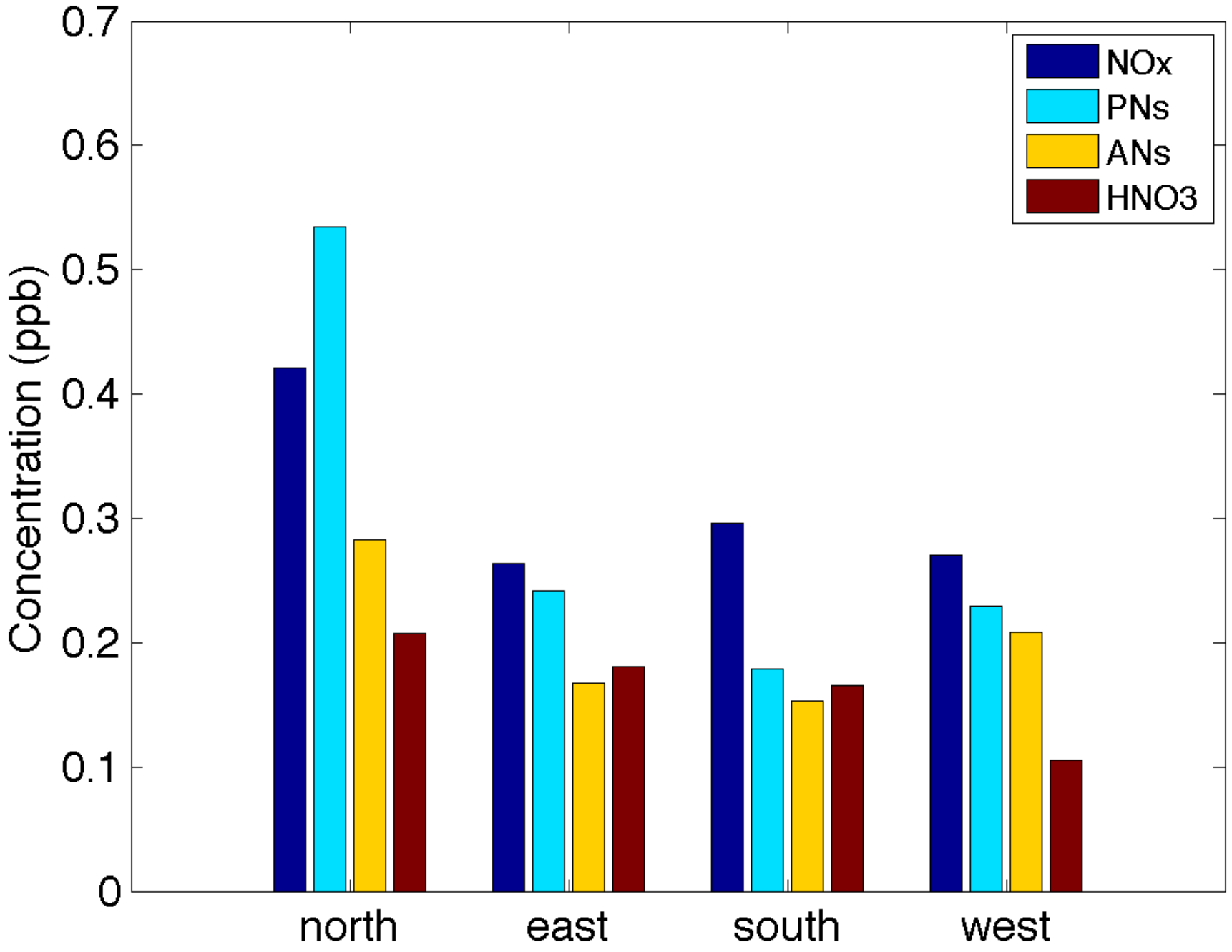
Thank you!



Conclusion

The combination of satellite based instruments, new in situ approaches and laboratory measurements are bringing exciting changes to how we approach describing mechanisms of N exchange and then test our understanding.

NOy and Wind Direction



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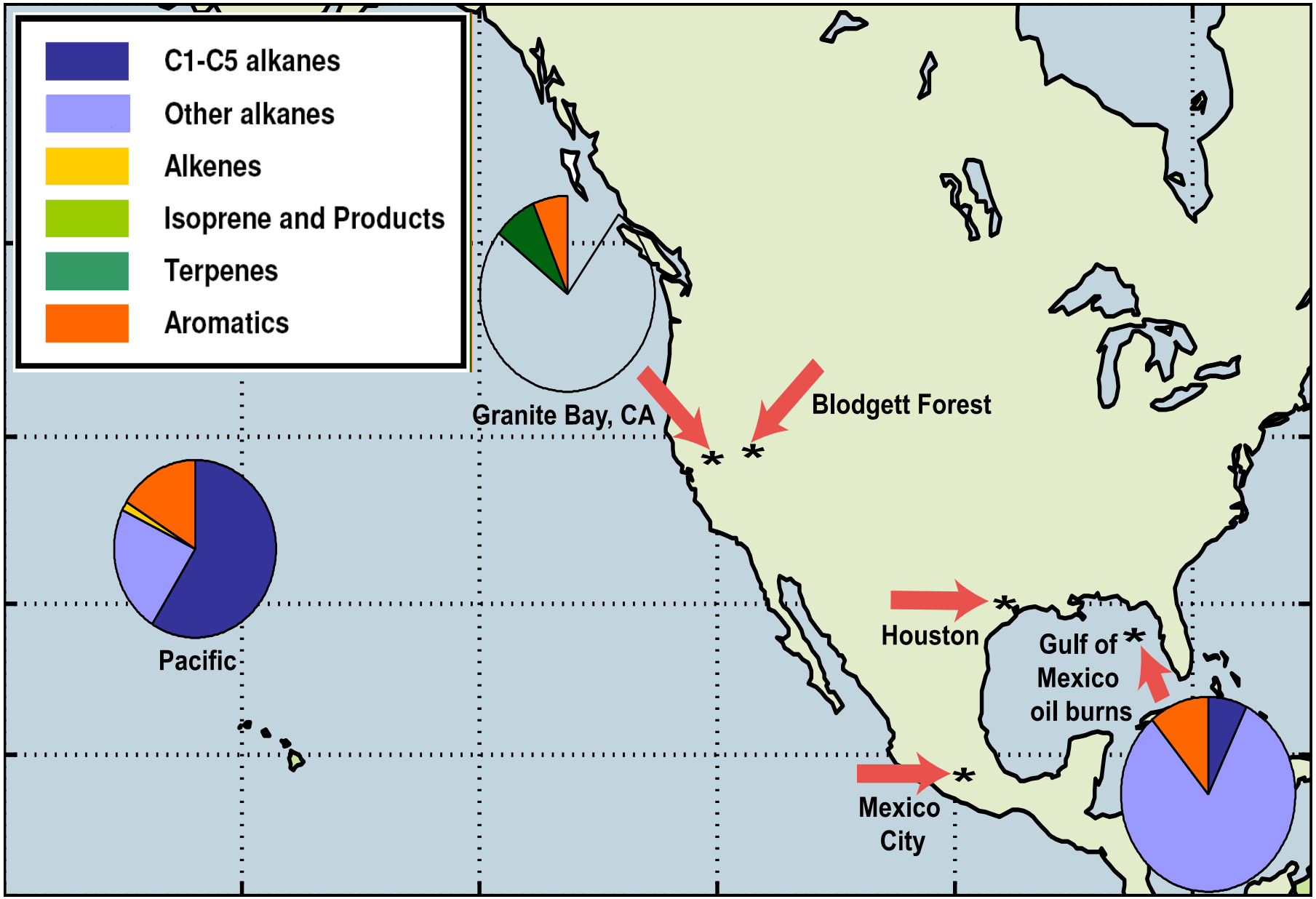
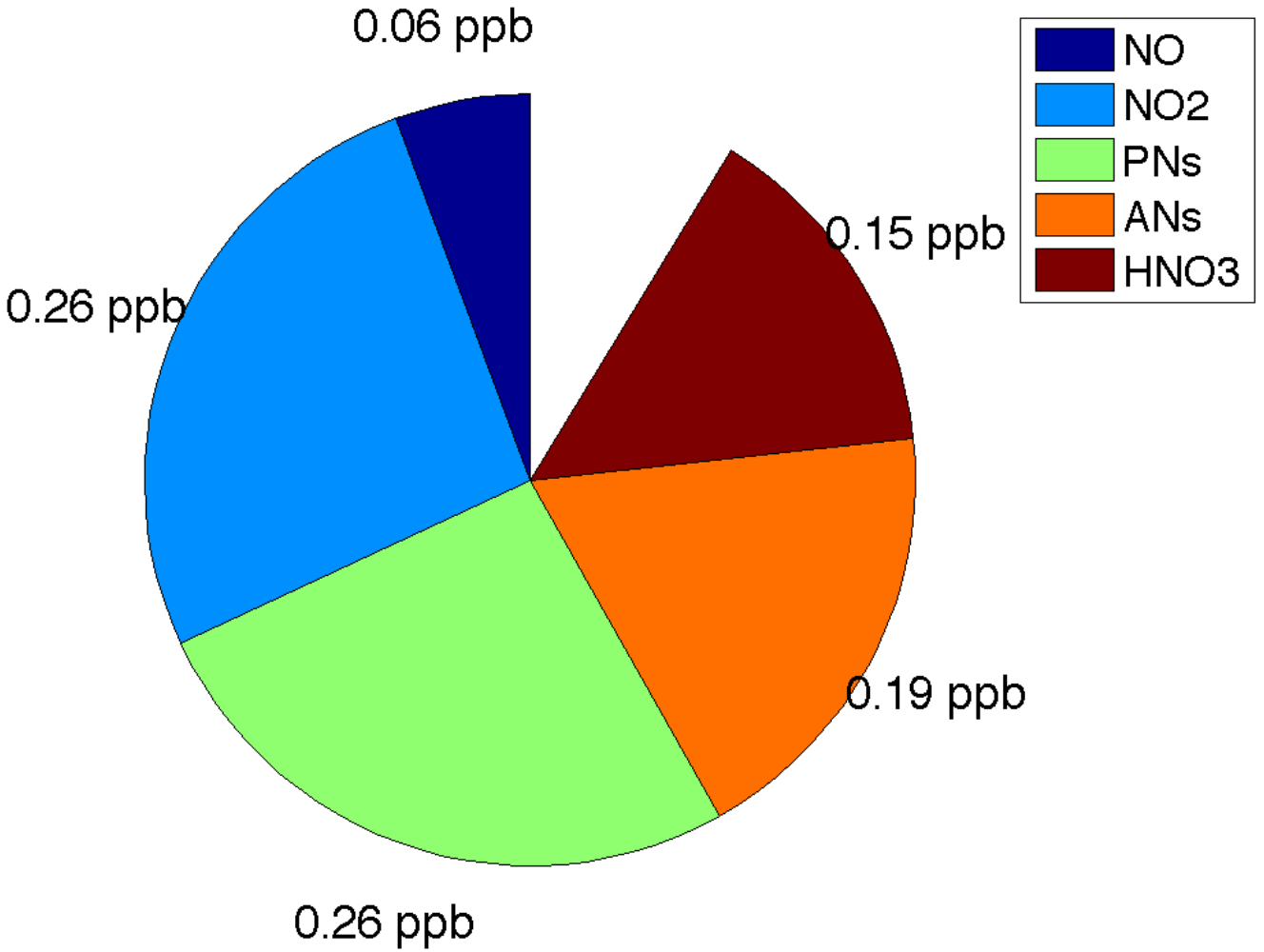

C1-C5 alkanes
Other alkanes
Alkenes
Isoprene and Products
Terpenes
Aromatics
Granite Bay, CA
Blodgett Forest
Pacific
Houston
Gulf of Mexico oil burns
Mexico City

Breakdown of NO_y



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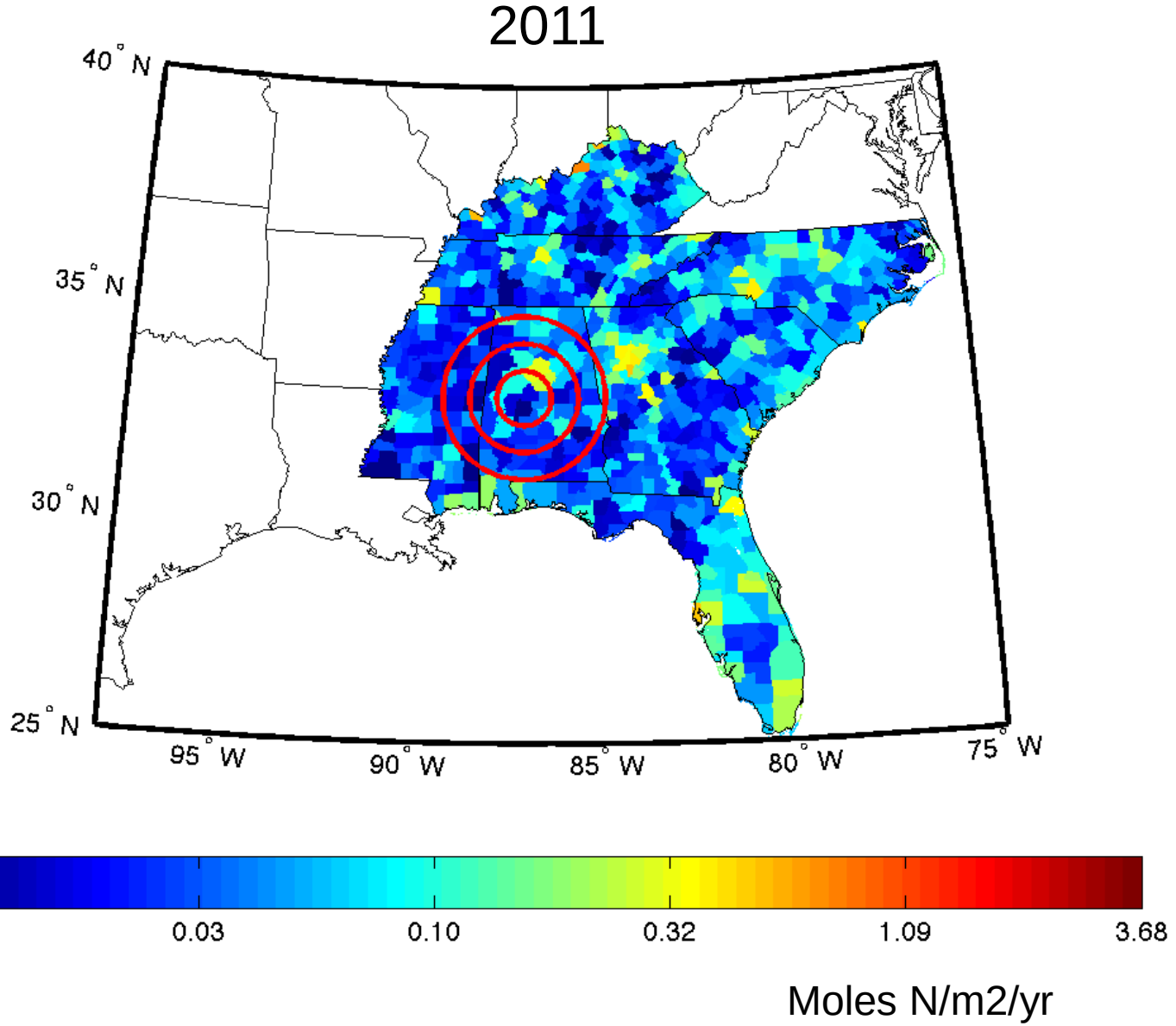
Sources: Soils; Direct emissions from vegetation; ...

Sinks: $RONO_2$ production; uptake by ecosystems

How far can NO_y travel? (fast)



Declining Concentrations (24hr avg)