

The seasonality of mercury in wet deposition at three MDN sites in the northeast U.S.: the role of regional atmospheric transport as determined by trajectory analysis

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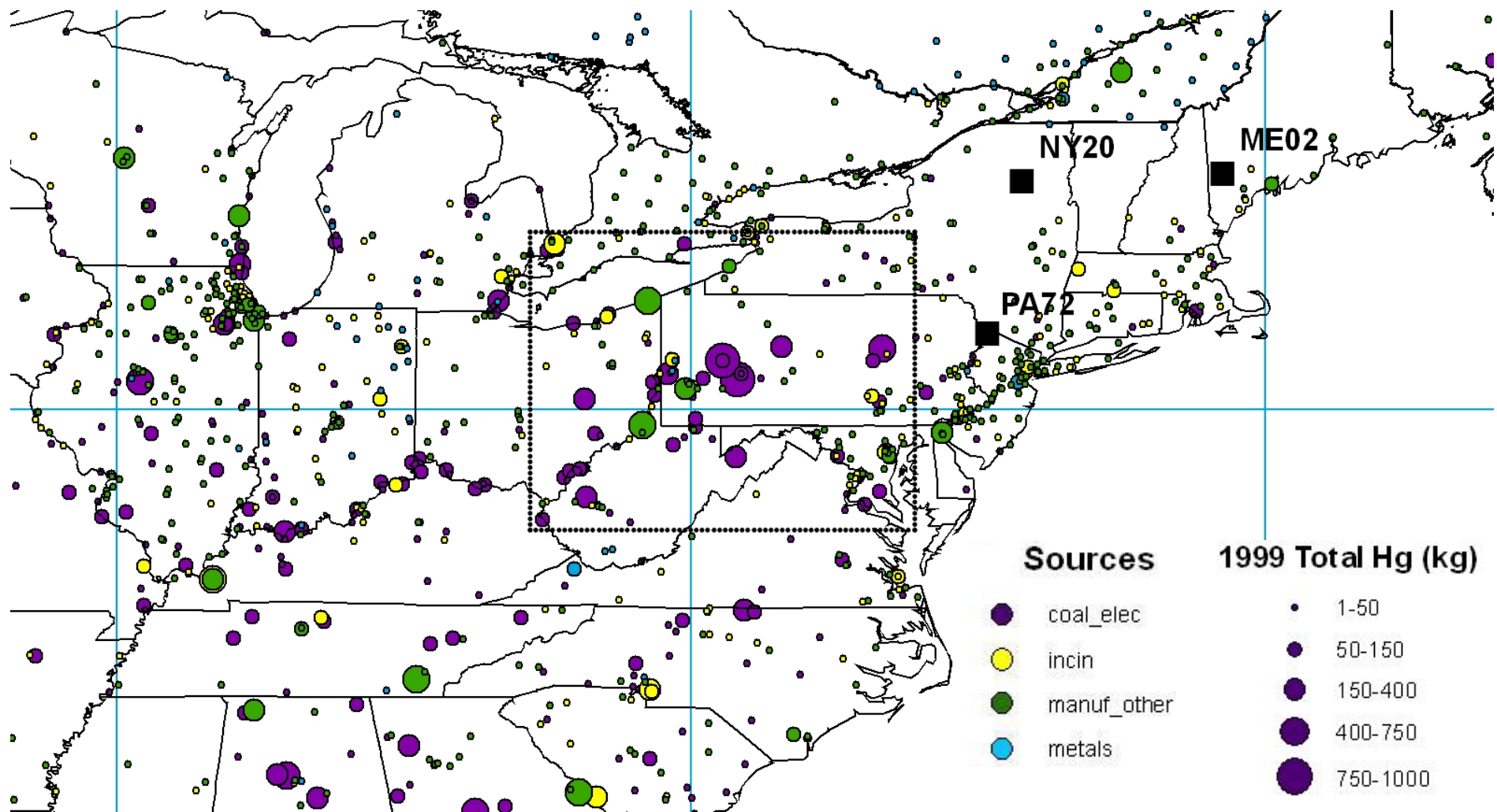
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Objectives of Study

- Investigate the potential impact of Hg emissions from the coal-fired power plant (CFPP) region of the Ohio River Valley on downwind MDN receptor locations.
 - In what seasons is the impact most discernible?
 - Has there been a significant decrease in annual mean Hg concentration at MDN receptor locations?
 - To what extent are Hg and SO_4 concentrations at MDN receptor locations correlated?

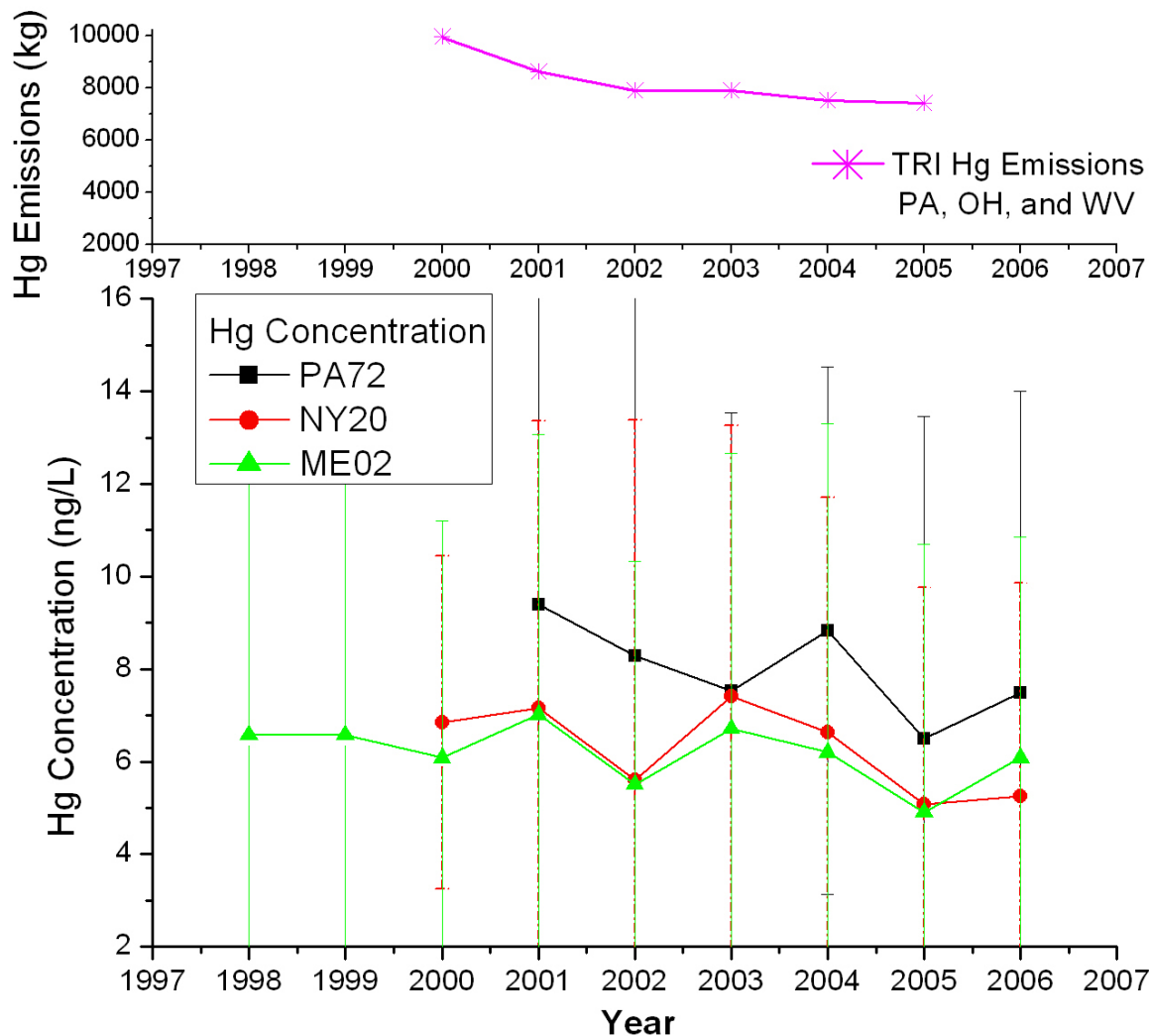
Point sources of Hg, 3 MDN sites, and the CFPP “source box”



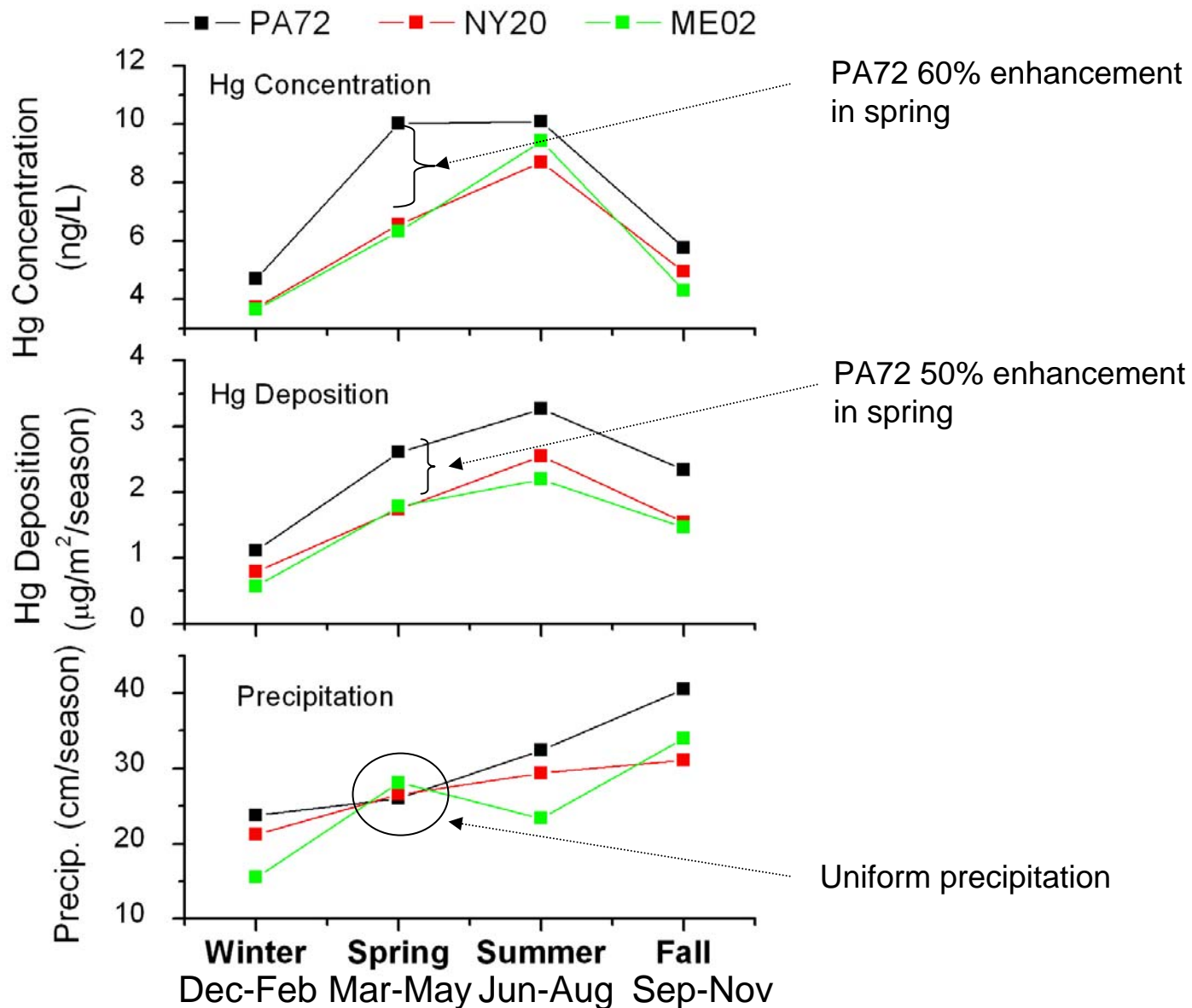
Annual mean precipitation, concentration, and deposition of Hg and SO₄ 2001-2006

| NADP code, Site name | Precip. annual mean (cm) | Hg conc. annual VW mean (ng/L) | Hg dep. annual mean total (μg/m ² /yr) | SO ₄ conc. annual VW mean (μg/L) | SO ₄ dep. annual mean total (mg/m ² /yr) | Hg/SO ₄ Correlation Coefficient (r) (n = 275, p < 0.0001) |
|-------------------------|--------------------------|--------------------------------|---|---|--|--|
| PA72, Millford | 123 ± 16 | 8.0 ± 1.0 | 9.33 ± 1.34 | 1.40 ± 0.28 | 1.66 ± 0.18 | 0.64 |
| NY20, Huntington | 108 ± 16 | 6.2 ± 1.0 | 6.62 ± 1.09 | 1.14 ± 0.17 | 1.17 ± 0.10 | 0.50 |
| ME02, Bridgton | 101 ± 28 | 6.1 ± 0.8 | 6.01 ± 1.23 | 0.88 ± 0.11 | 0.87 ± 0.15 | 0.57 |

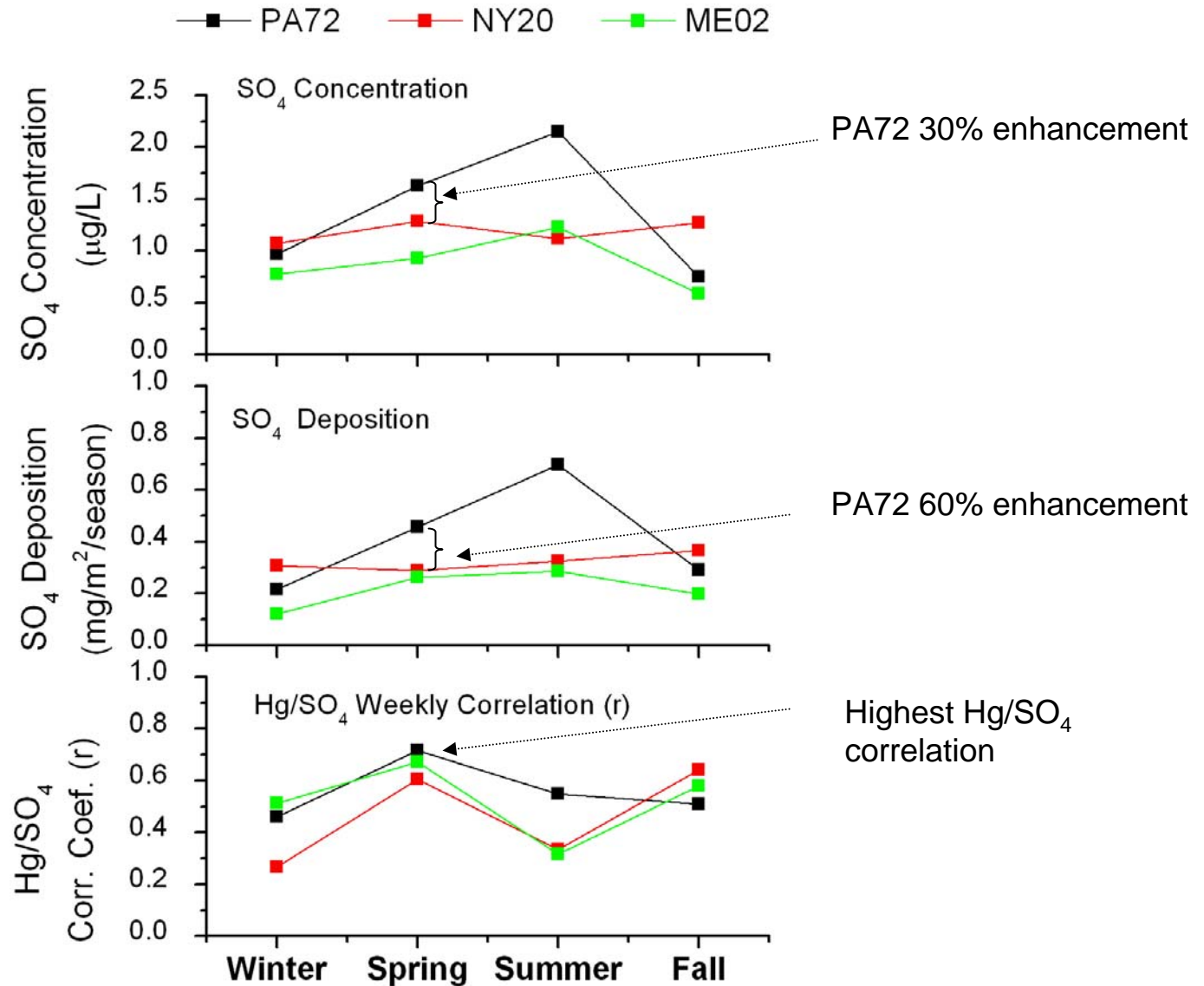
Comparison of annual vw-means of Hg concentration with regional Hg emissions



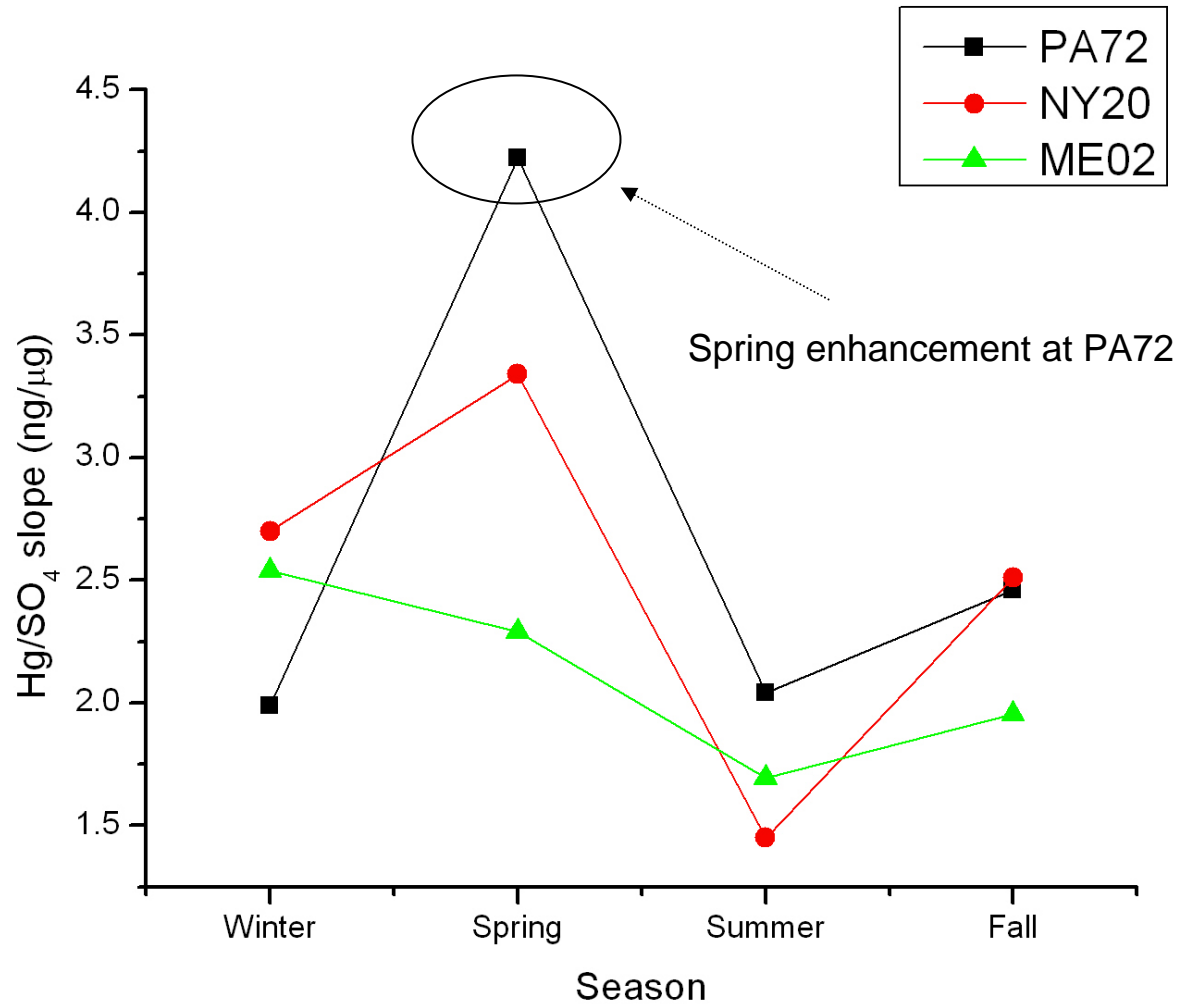
Seasonal Hg means, 2001-2006



Seasonal sulfate means, 2001-2006



Slopes of Hg/SO₄ weekly correlations by season (2001-2006 data)



Approach for trajectory analysis

- Simple, semi-quantitative method that quantifies the number of trajectory locations that are within a specified area encompassing a high density of point source emissions (Weiss-Penzias et al., JGR, 2006).
- Hypothesis to be tested:
 - Given that there is a springtime enhancement in Hg concentration at PA72, is this correlated to greater trajectory residence time in the CFPP source box relative to other seasons and other MDN locations?

Quantifying weekly integrated trajectory residence time (TRT_w)

$$TRT_w = \sum_{i=1 \rightarrow 7} (TRT_{di} * PF_{di})$$

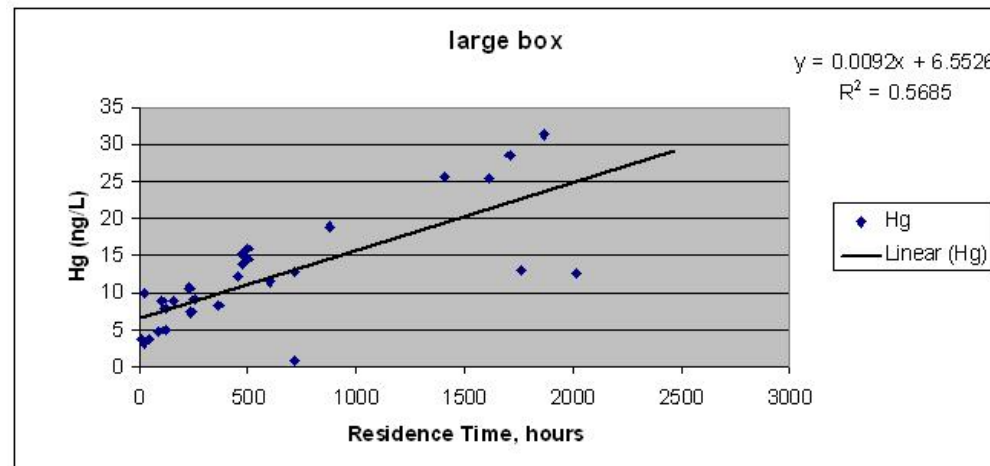
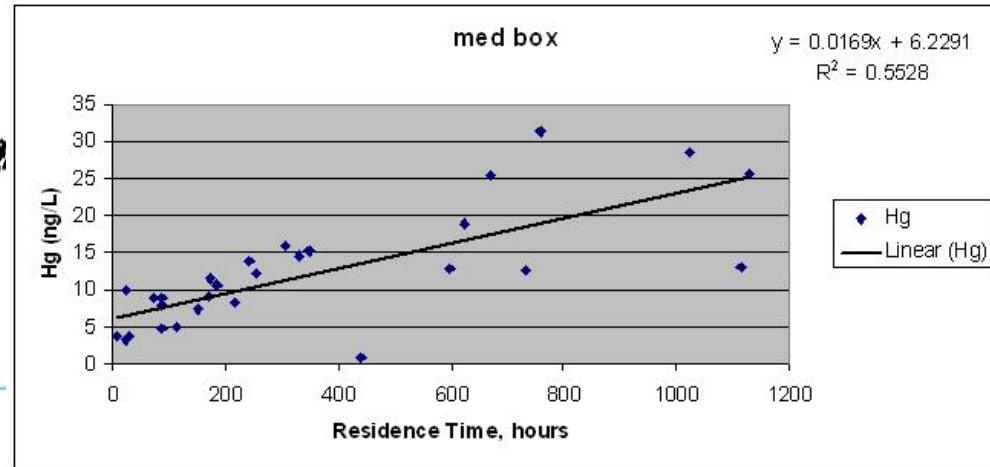
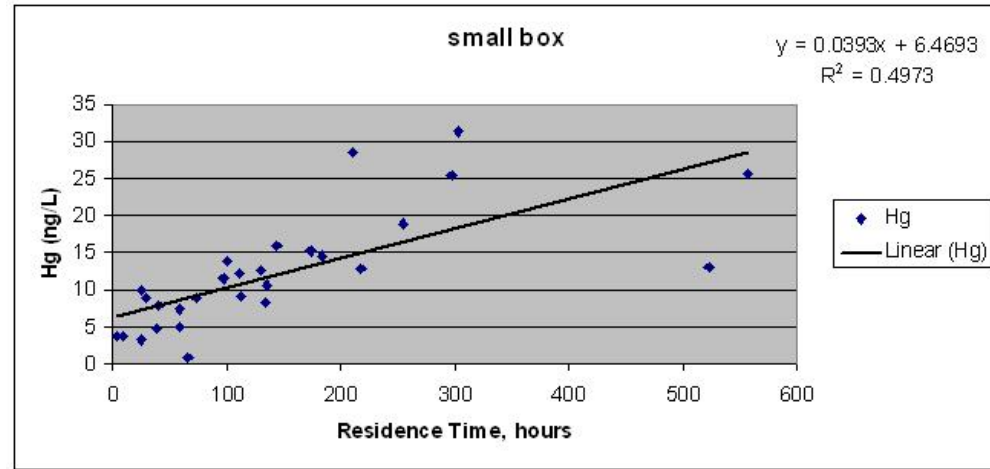
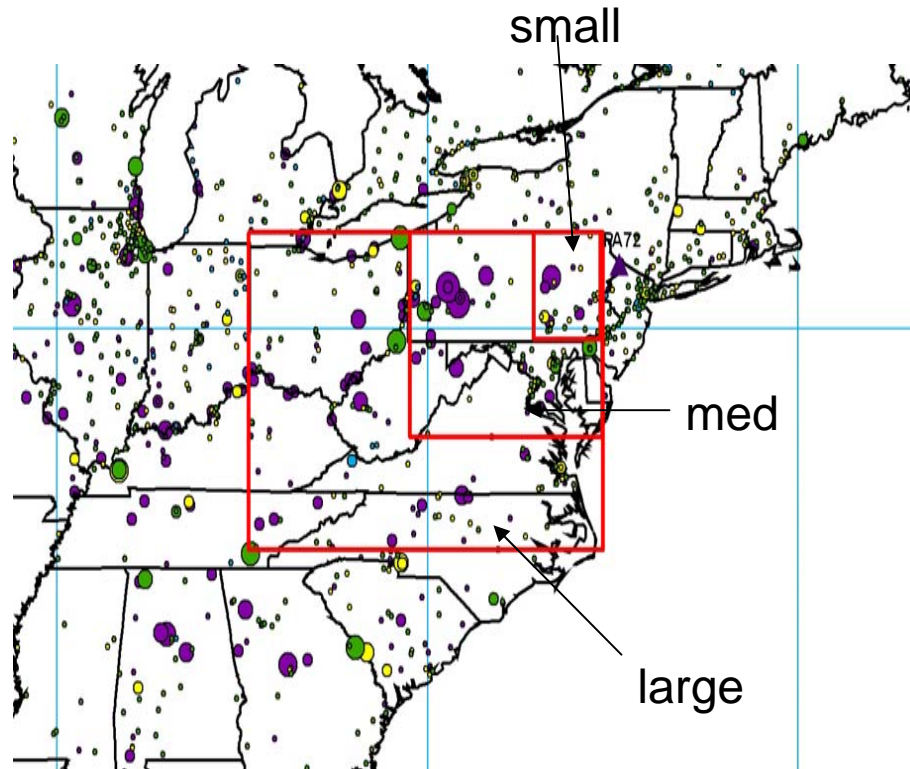
Daily trajectory residence
Time in source box < 1 km
altitude (36 trajectories, -120
hrs each, 4320 total hours).

Precipitation factor between 0-1
(daily fraction of weekly precip.)

Assumptions and Limitations

- Trajectory model errors are typically 20% of distance traveled over length of trajectory (Stohl, 1998).
- All trajectories over a 24-hr period were considered for each day that there was measureable precipitation. Actual rain may have occurred only during part of day.
- Numerous smaller emission sources exist outside of “source box”, i.e. local to the sites.
- Size and shape of source box are arbitrary, however, correlation statistics are relatively insensitive to box size.

2004-2005 spring Hg concentration vs. TRT_w at PA72 for 3 source box sizes.



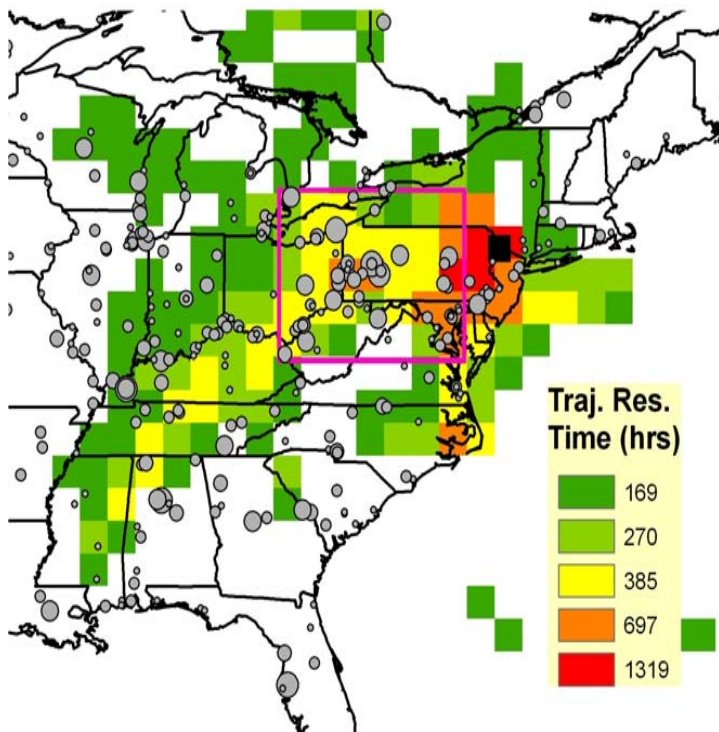
Example daily/weekly precipitation, concentration, and trajectory data for PA72

| Start Date | Precip. (in) | PF _d | Hg (ng/L) | NO ₃ (μg/L) | SO ₄ (μg/L) | TRTd (hrs) | TRTw (hrs) |
|------------------|-----------------|-----------------|--------------|---------------------------|---------------------------|---------------|---------------|
| 7/6/2004 | 0 | 0 | 3.97 | 1.21 | 1.3 | 251 | 3.3 |
| 7/7/2004 | 0.25 | 0.16 | | | | 21 | |
| 7/8/2004 | 0 | 0 | | | | 747 | |
| 7/9/2004 | 0 | 0 | | | | 810 | |
| 7/10/2004 | 0 | 0 | | | | 422 | |
| 7/11/2004 | 0 | 0 | | | | 183 | |
| 7/12/2004 | 1.36 | 0.84 | | | | 0 | |
| 7/13/2004 | 0 | 0 | 13.86 | 2.07 | 2.17 | 0 | 336.5 |
| 7/14/2004 | 0.4 | 0.42 | | | | 27 | |
| 7/15/2004 | 0.03 | 0.03 | | | | 353 | |
| 7/16/2004 | 0 | 0 | | | | 603 | |
| 7/17/2004 | 0 | 0 | | | | 669 | |
| 7/18/2004 | 0.5 | 0.52 | | | | 582 | |
| 7/19/2004 | 0.03 | 0.03 | | | | 354 | |

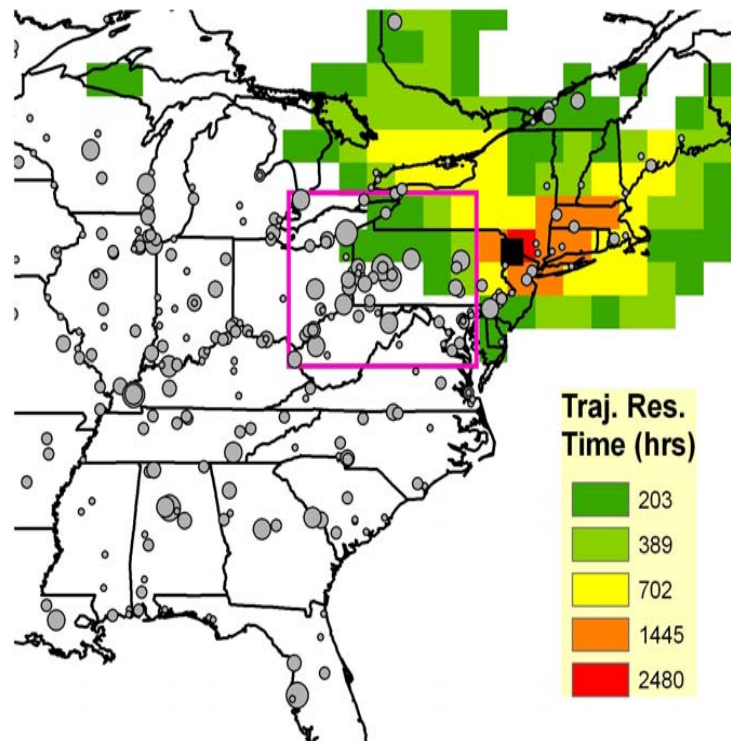
Trajectory density plots – 6 highest and lowest events at PA72 (2004-2005)

| Season | Site | Mean weekly TRT (hrs) | | Mean weekly Hg (ng/L) | | Mean weekly SO ₄ (mg/μL) | |
|---------------|-------------|-----------------------|-----------|-----------------------|------------|-------------------------------------|-------------|
| | | High | Low | High | Low | High | Low |
| Winter | PA72 | 436 | 230 | 7.7 | 2.3 | 1.22 | 0.72 |
| Spring | PA72 | 568 | 77 | 18.6 | 3.7 | 3.49 | 0.64 |
| Summer | PA72 | 529 | 232 | 16.7 | 6.4 | 3.44 | 2.00 |
| Fall | PA72 | 105 | 128 | 10.6 | 4.0 | 0.84 | 0.41 |

Spring - High Hg

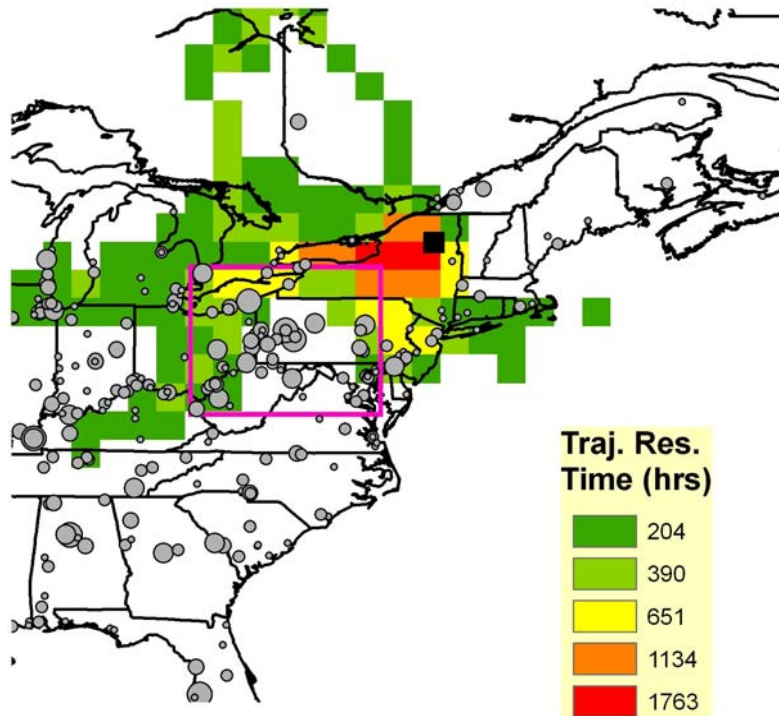


Spring - Low Hg

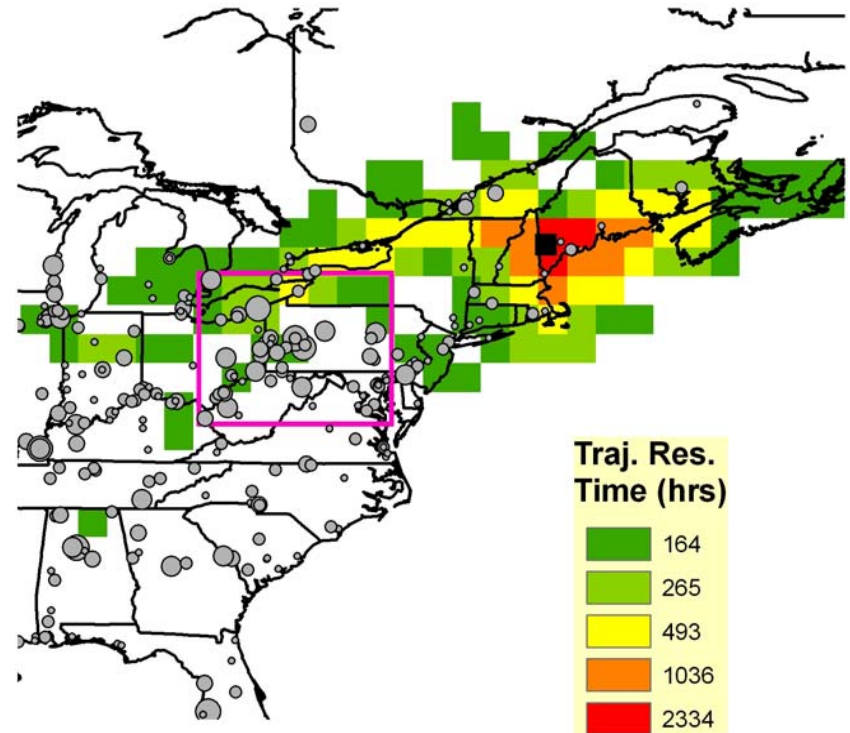


NY20 and ME02 do not show as strong a spring Hg enhancement compared to PA72. This appears to be due to the proximity of PA72 to pollution transport pathway

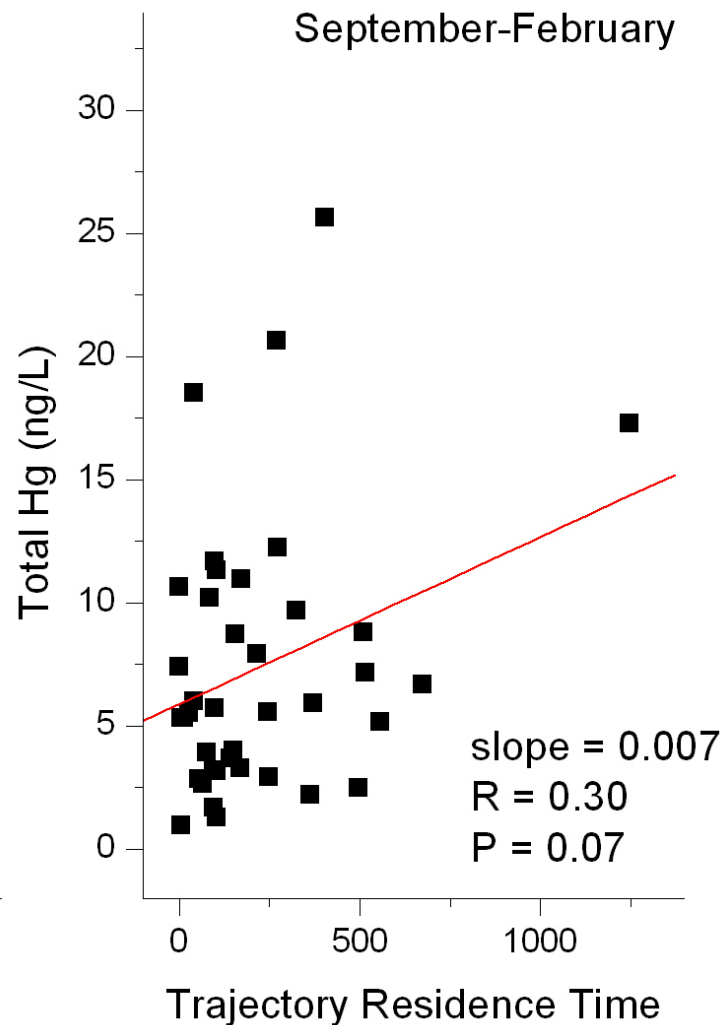
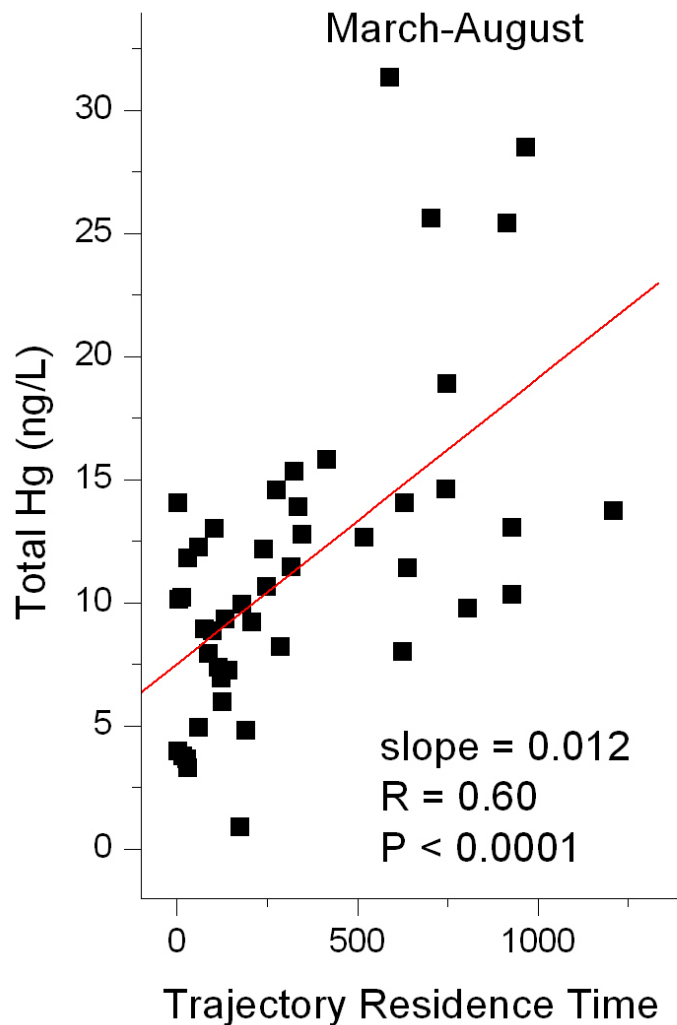
NY20, Spring - High Hg



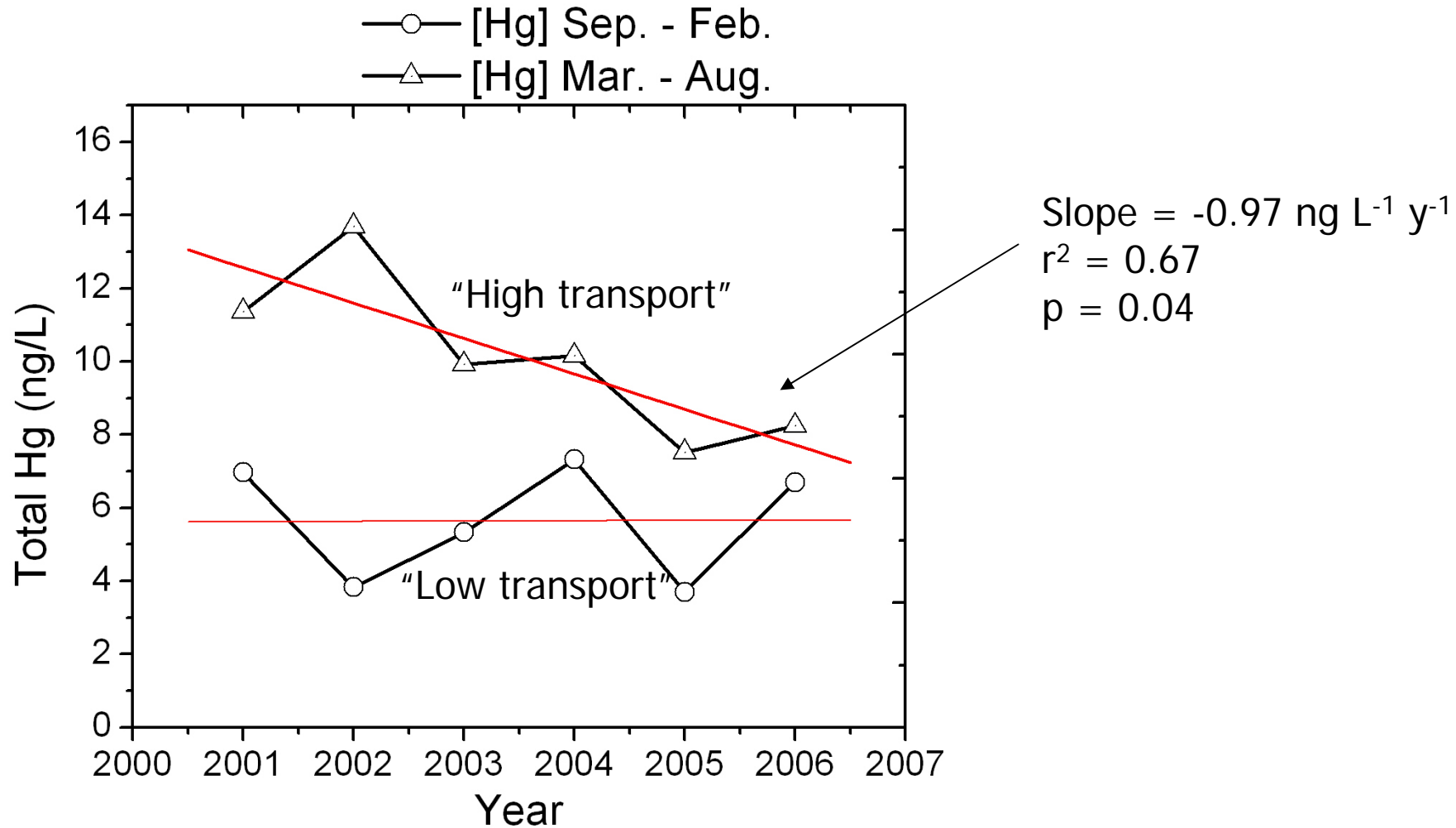
ME02, Spring - High Hg



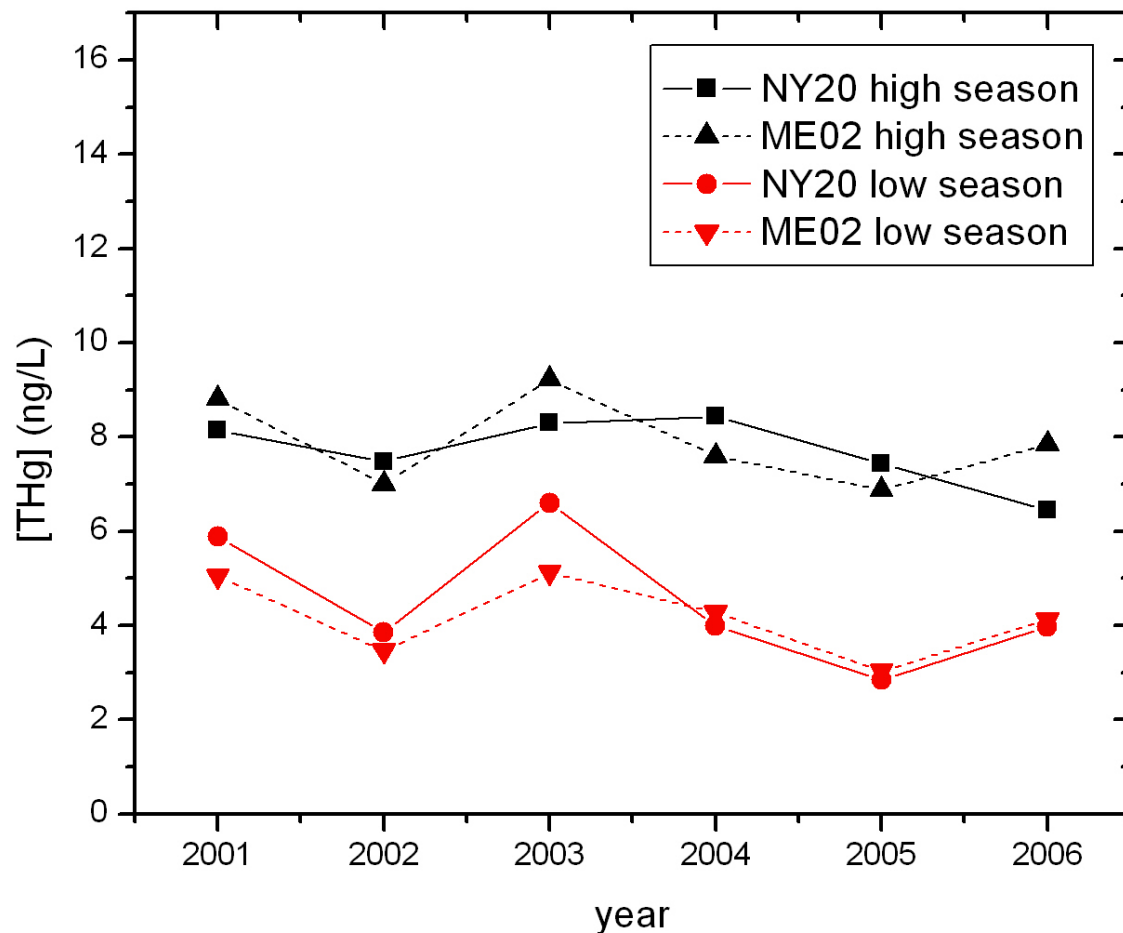
Hg weekly concentration vs. TRT_w at PA72 (2004-2005)



Annual mean Hg concentration at PA72 as a function of season



Annual mean Hg concentration at NY20 and ME02 as a function of season



Conclusions

- PA72 [Hg] displays a 20-30% enhancement in winter, summer and fall, and a 60% enhancement in spring, relative to NY20 and ME02.
- [Hg]/[SO₄] weekly correlation is strongest for PA72 in the spring, suggesting that pollutants are co-located.
- Trajectory density plots show that for PA72 in spring, air mass residence time in “source box” is 8x greater for highest Hg events compared to lowest Hg events (2004-2005).
- Trajectories arriving at NY20 and ME02 largely miss the “source box” during the highest spring events.
- A significant downward trend in [Hg²⁺] at PA72 is observed (2001-2006) during “high transport” seasons (spring-summer), whereas no trend is observed during fall-winter.
- Further work includes incorporating potential source contribution function (PSCF) analysis in order to investigate a multitude of source regions.