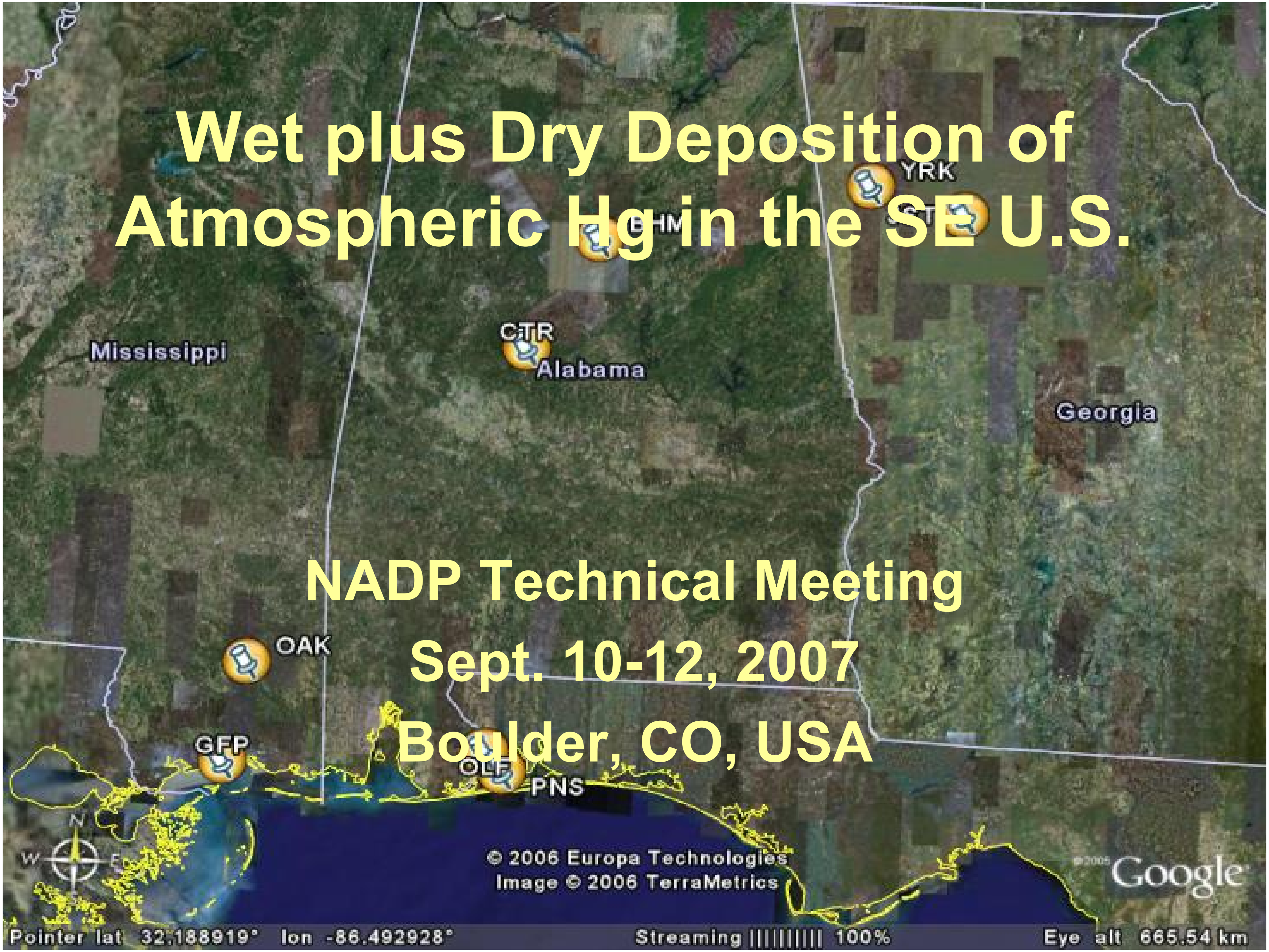
Wet plus Dry Deposition of Atmospheric Hg in the SE U.S.

NADP Technical Meeting

Sept. 10-12, 2007

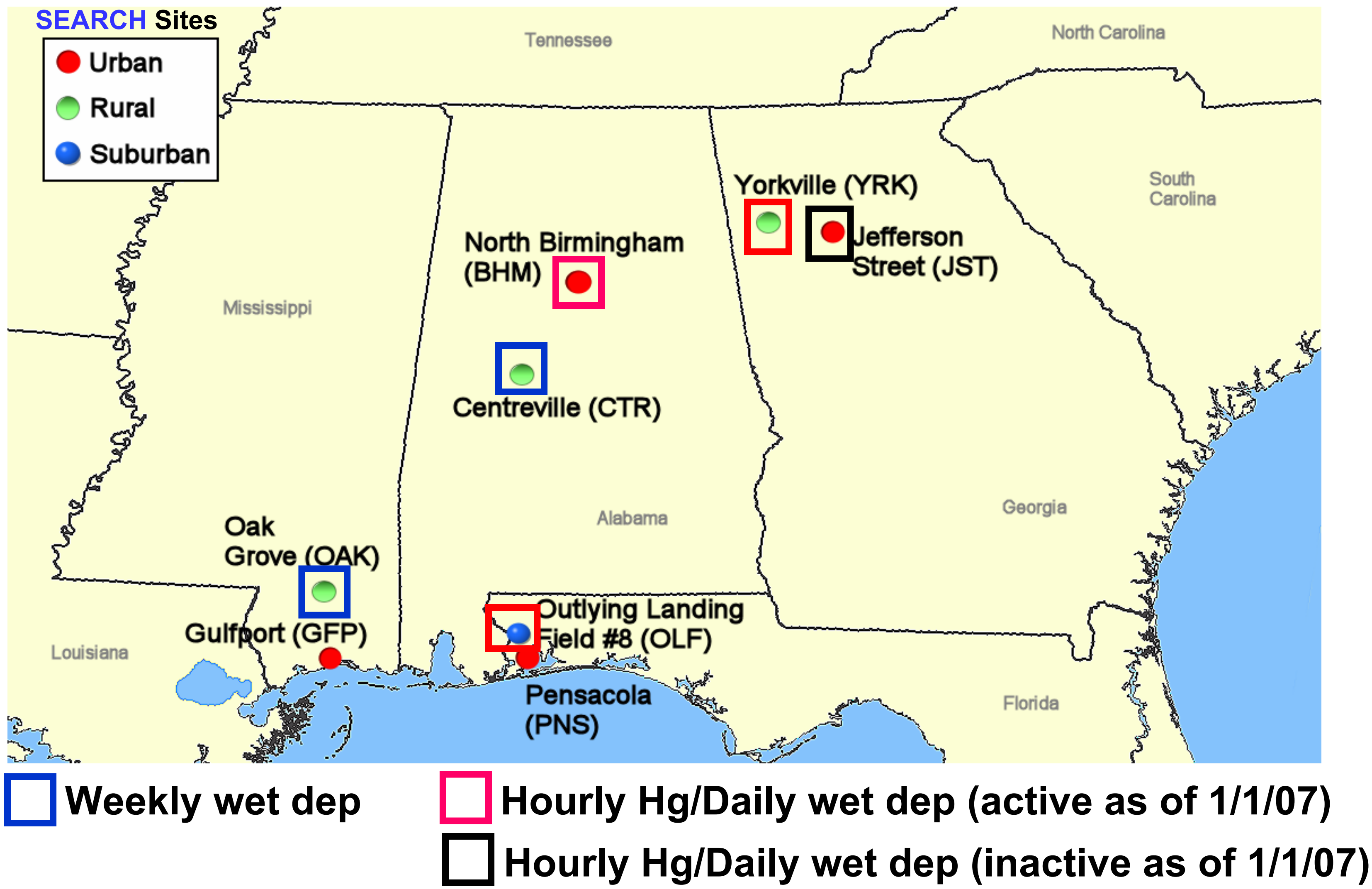
Boulder, CO, USA

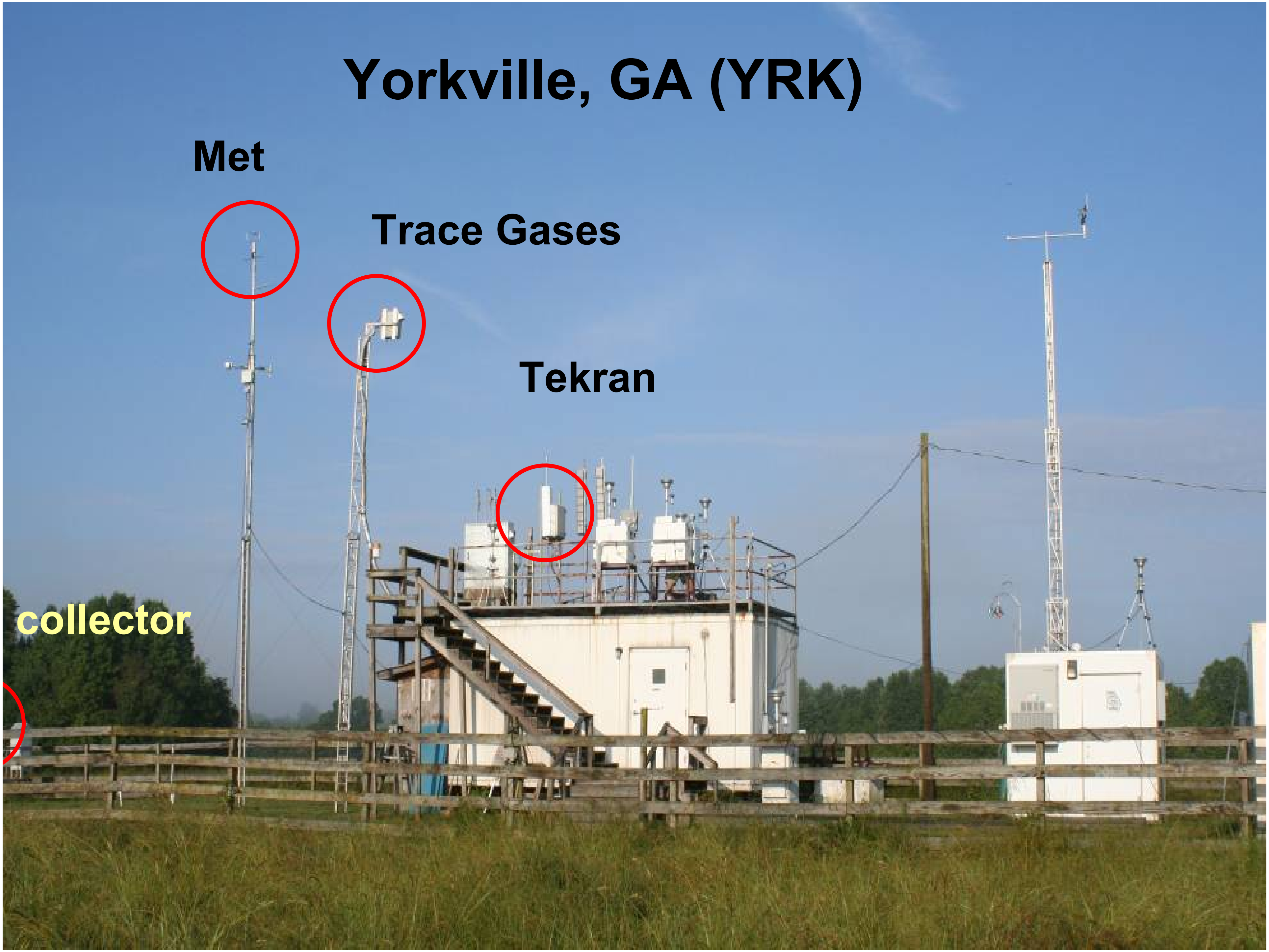


Outline

- Routine Measurements and Deposition Estimates
- Coarse Particle Hg
- Further Thoughts

SEARCH Network
Hg-related measurements




Yorkville, GA (YRK)
Met
Trace Gases
Tekran
collector

SEARCH Atmospheric Hg Measurements

~99%

- **Hg^0 - Tekran 2537A**
  - 5 minute averages (every other hour)
  - Gold trap pre-concentration
  - CVAFS detection

≤1%

- **RGM - Tekran 1130 Module**
  - 60 minute average (every other hour)
  - KCl thermal annular denuder
  - Desorption at 500C

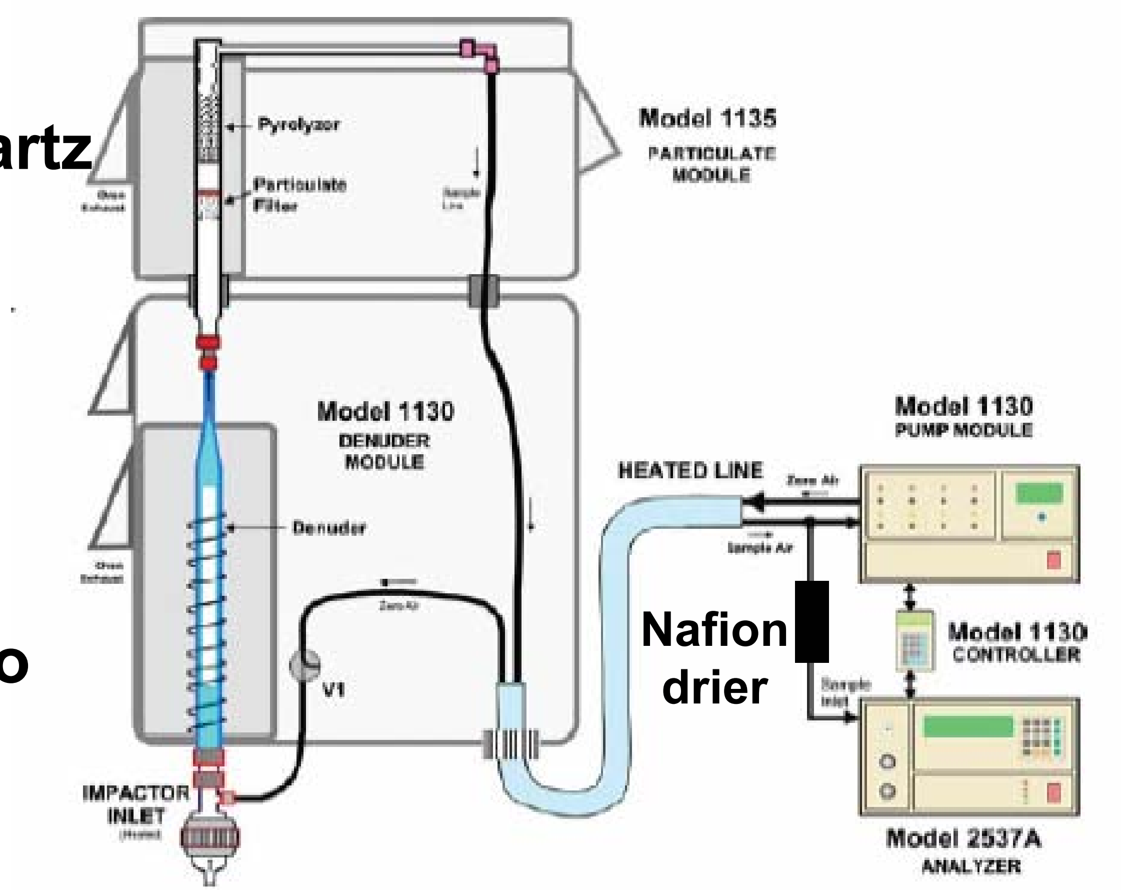
≤1%

- **Hg_P - Tekran 1135 Module**
  - 60 minute average (every other hour)
  - Impactor @ inlet removes particles >2.5 micron
  - Quartz filter (downstream of impactor)
  - Desorption at 800C

Tekran Configuration

$Hg_{PM2.5}$ on quartz filter

RGM on KCl denuder (analogous to HNO_3)



Nafion drier

PM$_{2.5}$

Air in

Hg^0 transmits quantitatively

Tekran Modifications Made in SEARCH

- Nafion drier (keep water out of detector)
- Soda lime trap (keep reactive gases out of detector)
- Log flows (confirm proper operation and calculations)
- Log temperatures (confirm operation)

Data Verification Activities

- Hg^0 injection onto 2537A traps

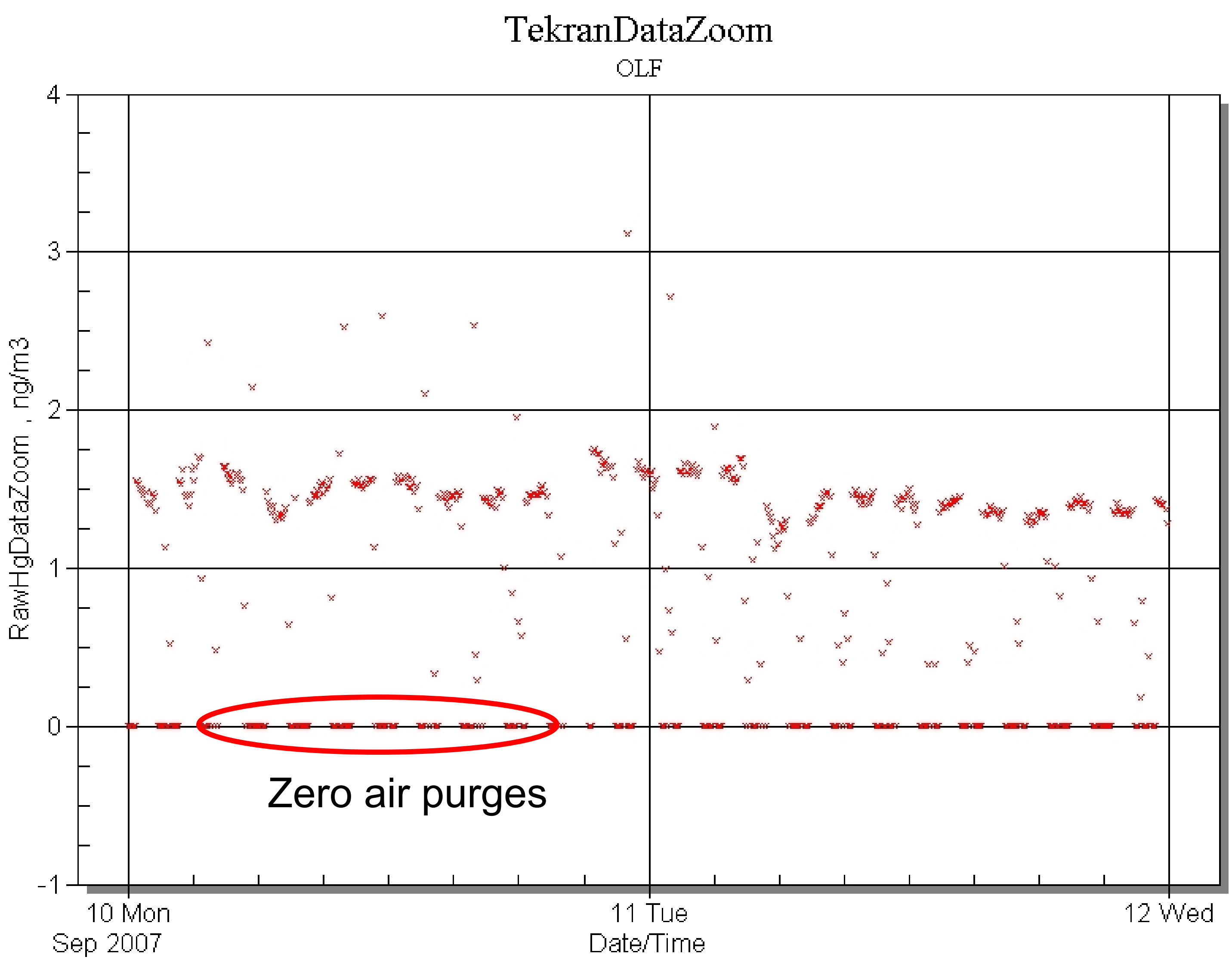
  100 +/- 2% recovery
- Method of Addition Hg^0 injection at inlet

  100 +/-5% recovery, no fictive RGM or $Hg_{PM2.5}$
- Parallel denuder/filter sampling

  RGM 100 +/- 10%, $Hg_{PM2.5}$ 88 +/- 20%
- Spiked denuder experiments (RGM)

  $HgCl_2$ recoveries 56-167% (n=20)
- Automated and Manual Data review

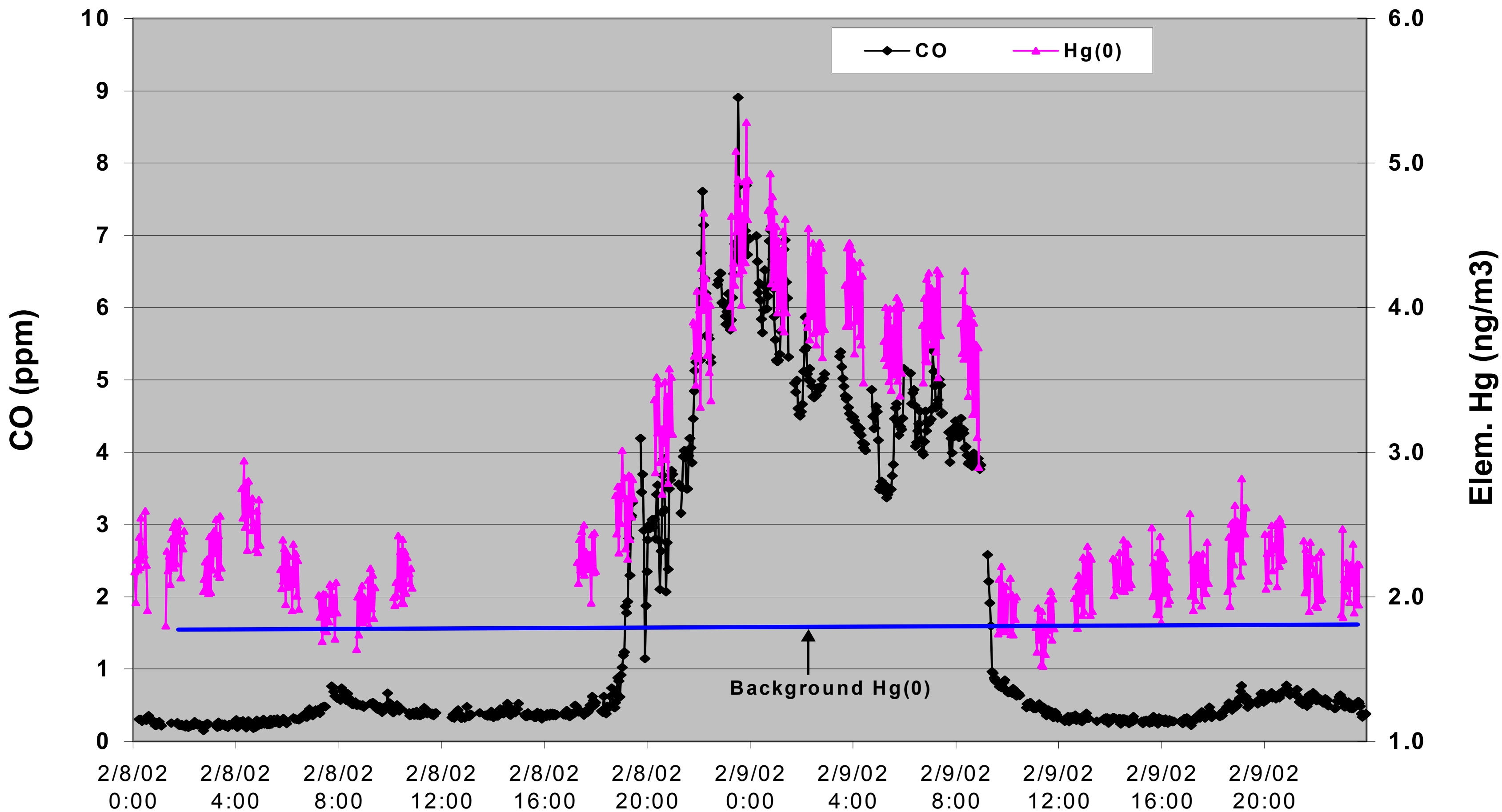
Raw 5-minute Time Series



Supporting SEARCH Measurements

- Discrete Particles and Gases (24-hour)
  - $PM_{2.5}$ and PM_{10} (filter-based mass, speciation)
  - NH_3 (annular denuder)
- Continuous Particles (1-min to 1-hr)
  - PM2.5, TC, BC, NH_4^+, NO_3^-, SO_4^{2-}
- Trace Gases (1-min)
  - O_3, NO, NO_2, NOy, HNO_3, SO_2, CO
- Meteorology and Visibility (1-min)
  - WS, WD, T, RH, BP, SR, rainfall, Bsp (dry)

Urban Mercury Measurements Jefferson Street 2/8-9/02

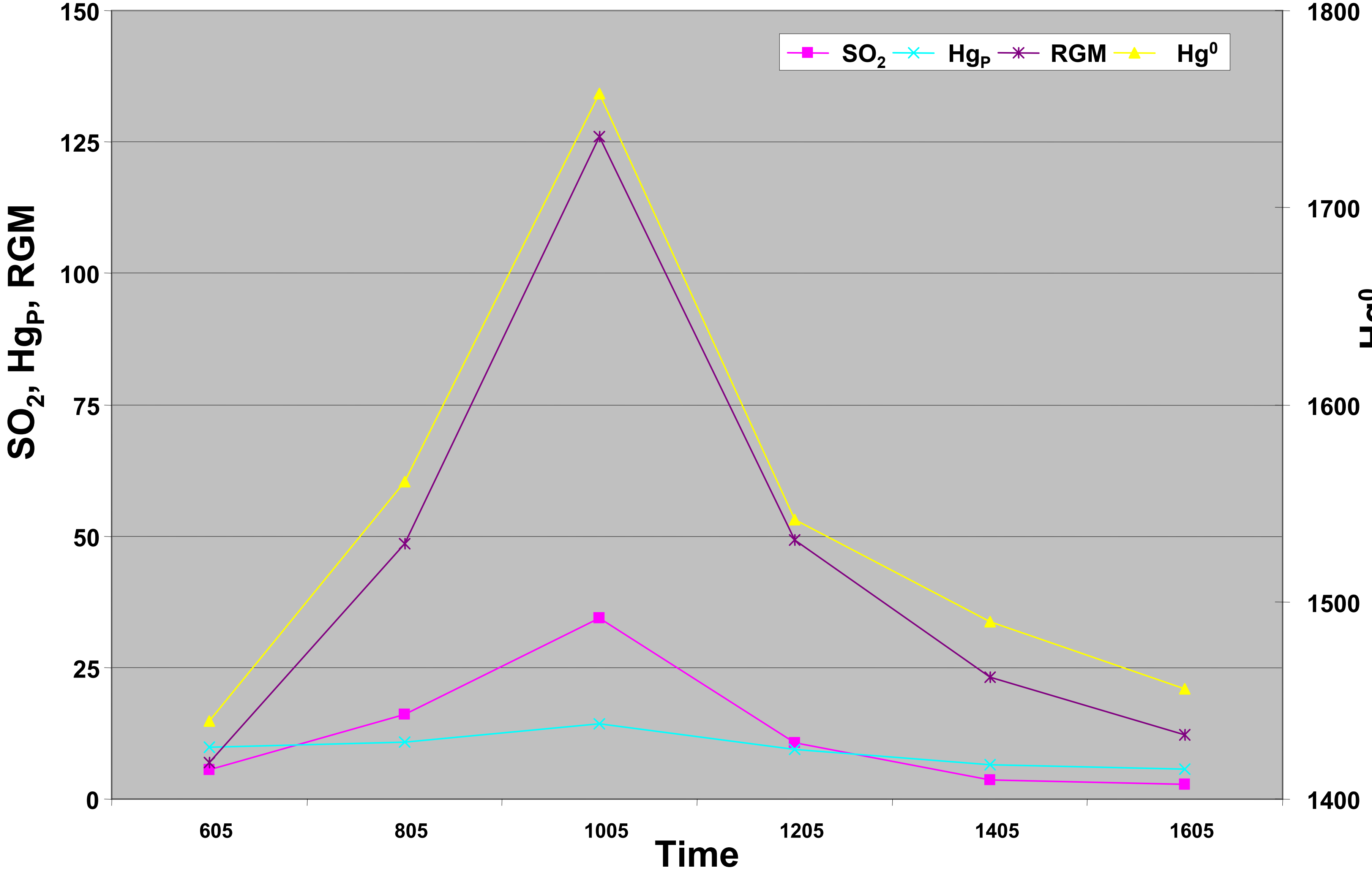


CO and Hg^0 track each other during major excursions

Hg(0) vs. CO regression slopes Nocturnal events @ JST

Month (2002)	Lower 95% CI	Upper 95% CI	r-sq.
January	0.24	0.54	0.51
February	0.47	0.58	0.62
March	0.57	0.67	0.78
April	1.47	1.69	0.68
May	1.63	1.91	0.71
June	2.36	2.71	0.73
October	0.96	1.15	0.68
November	0.37	0.46	0.66
December	0.60	0.68	0.78

60-minute SO_2 and Hg
4/28/06 Event - OLF



Summary of SEARCH 1-Hr Hg Measurements

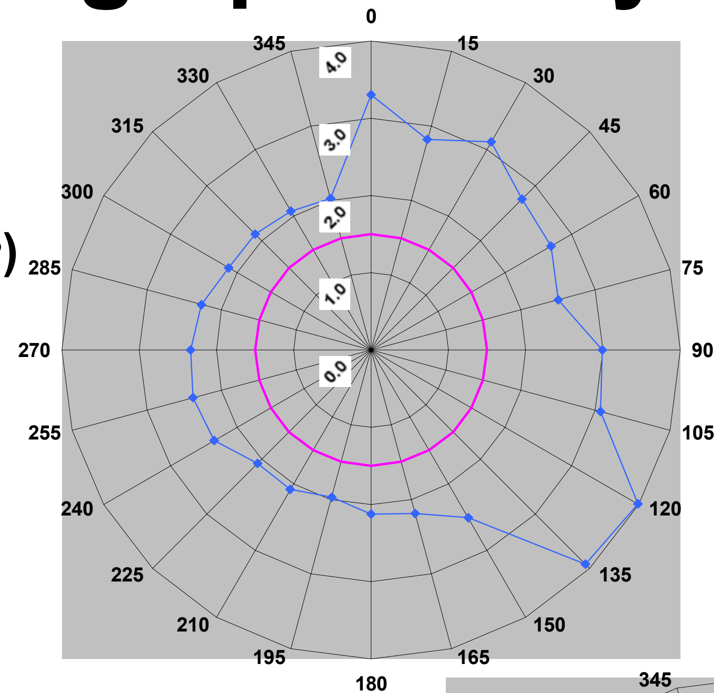
Site	Year	Hg^0 (pg/m^3)		RGM (pg/m^3)		$Hg_{PM2.5}$(pg/m^3)	
		mean	max.	mean	max.	mean	max.
OLF, FL	2004	1490	2440	4.8	182	1.4	48
	2005	1470	2850	2.7	183	1.3	38
	2006	1580	2740	4.0	127	2.5	49
BHM, AL	2004	2490	35,900	56	8560	10.3#	185#
	2005	2420	130,200	77	13,700	24.9	2410
	2006	2570	165,400	82	9210	31.6	2940
YRK, GA	2002/3	1566	9470	4.5	169	nm	nm
JST, GA	2002/3	1917	8400	6.1	288	nm	nm

partial year

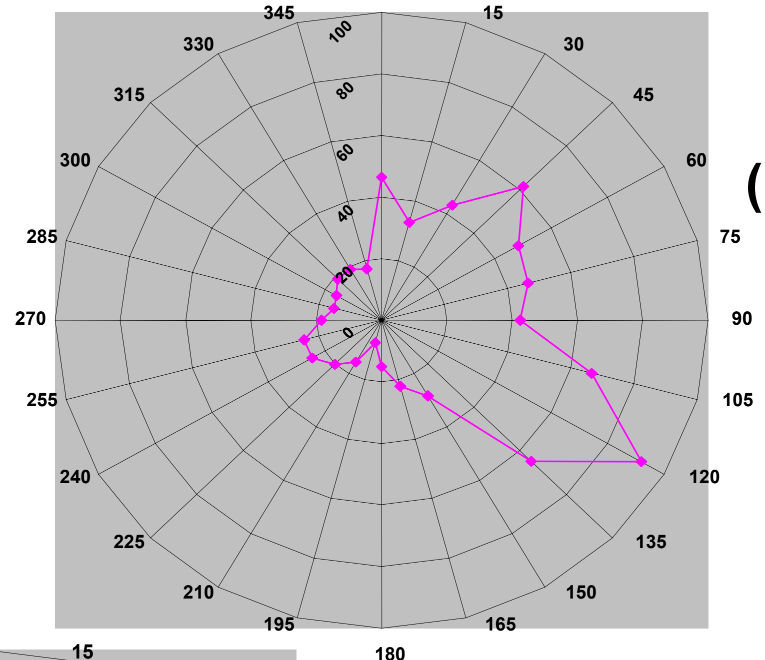
All 3 forms of Hg significantly elevated at BHM; Hg^0 elevated at JST

Hg Species by WD at BHM - 2006

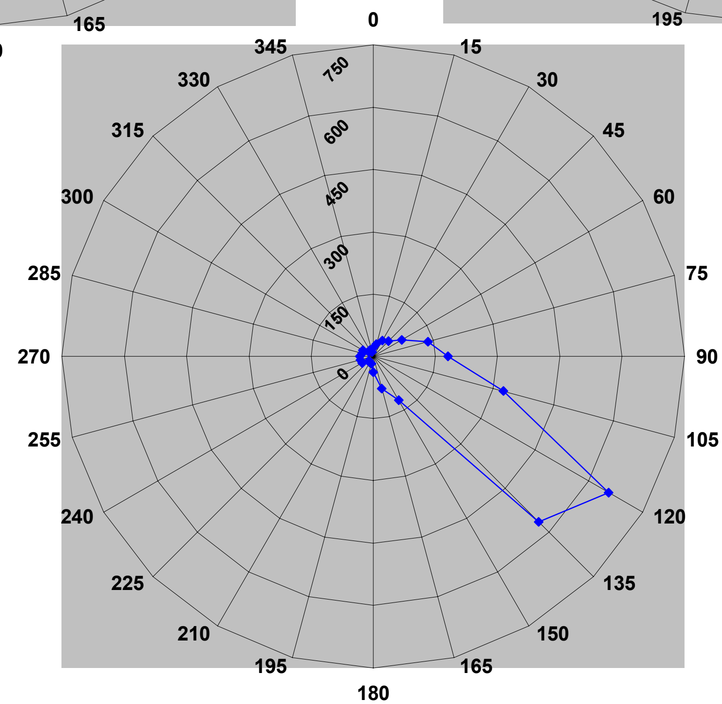
Hg^0 (ng/m^3)



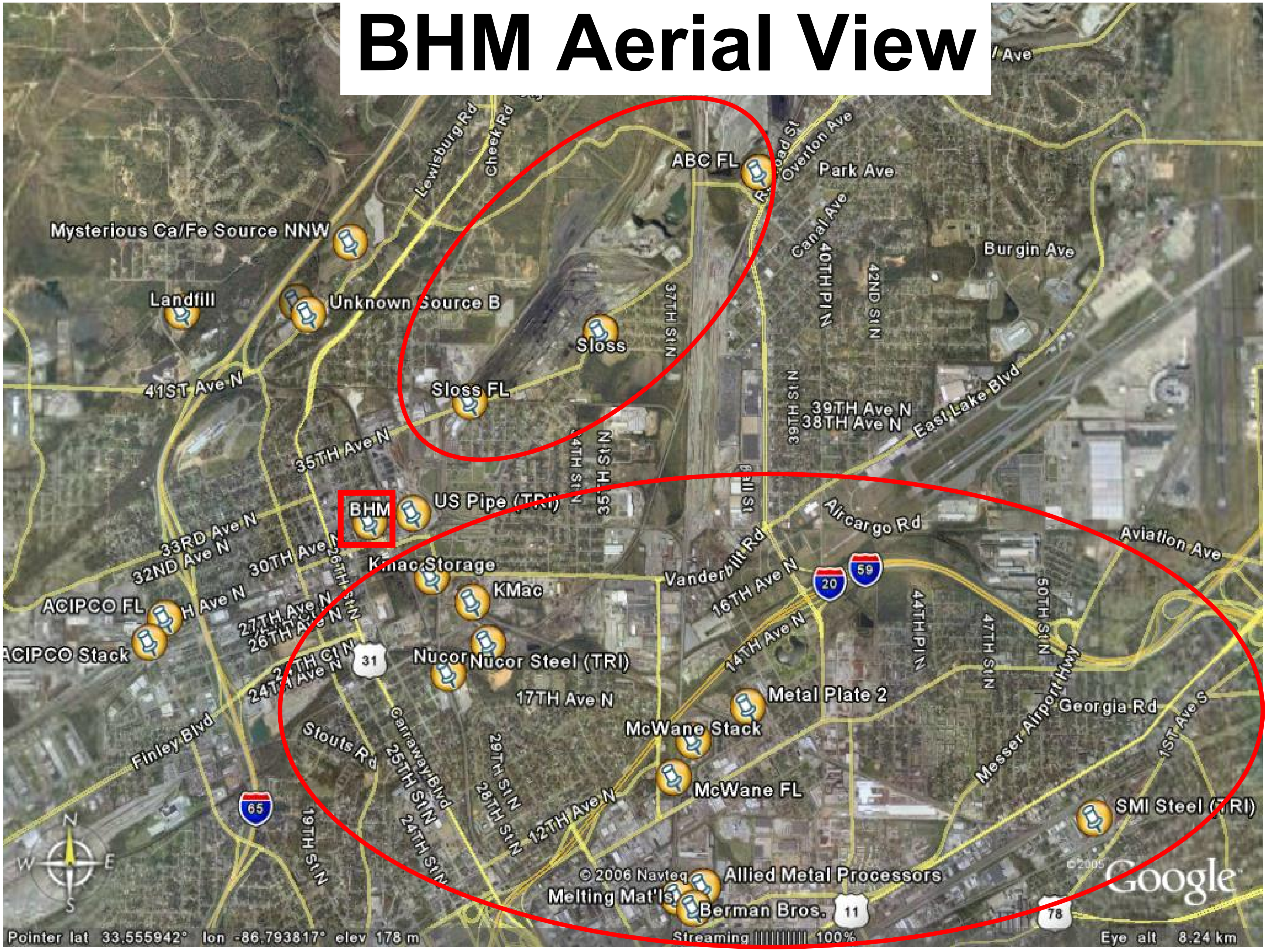
Hg_P (pg/m^3)



RGM (pg/m^3)

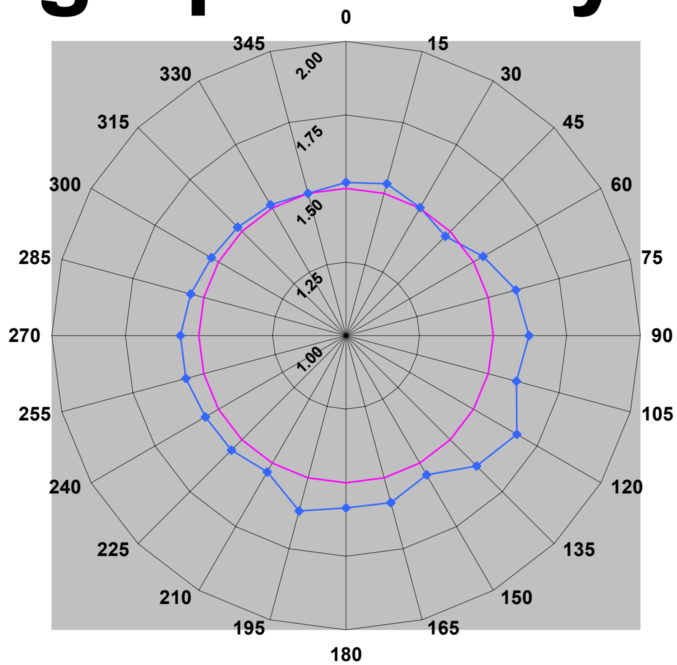


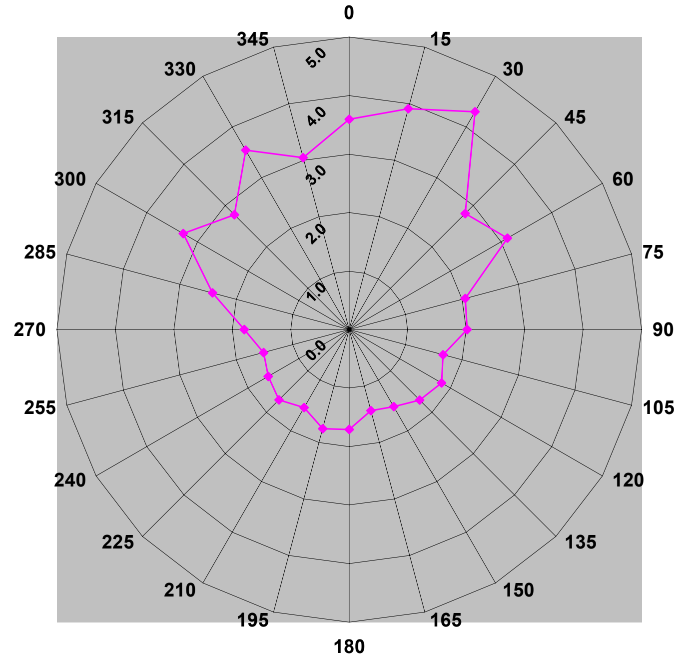
BHM Aerial View



Hg Species by WD at OLF - 2006

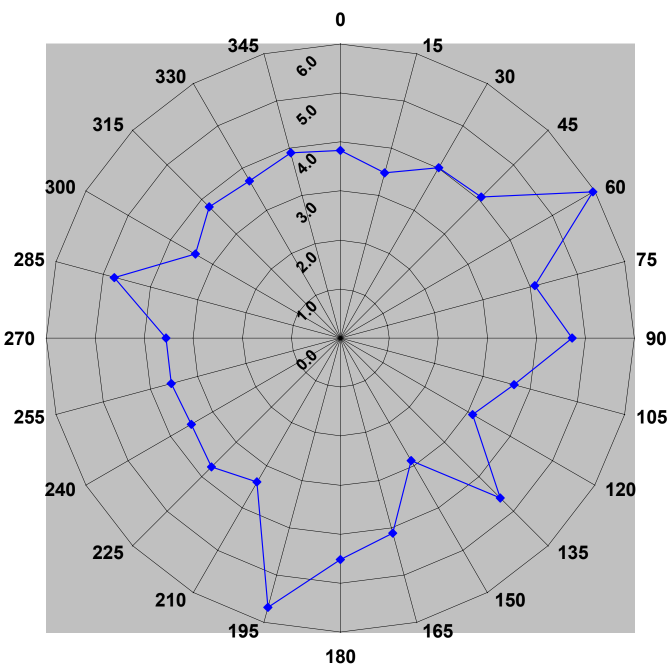
Hg^0
ng/m^3



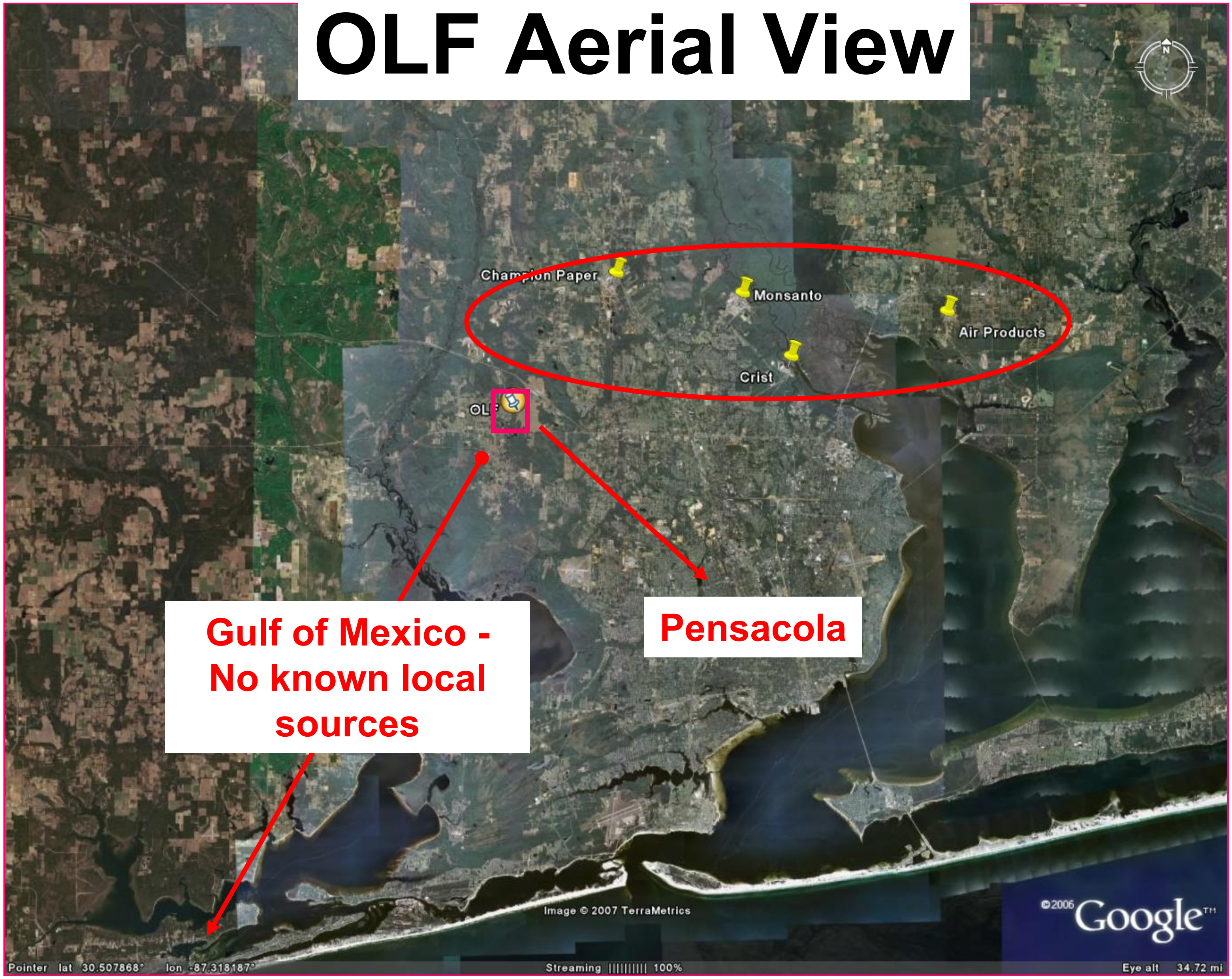


Hg_P
(pg/m^3)

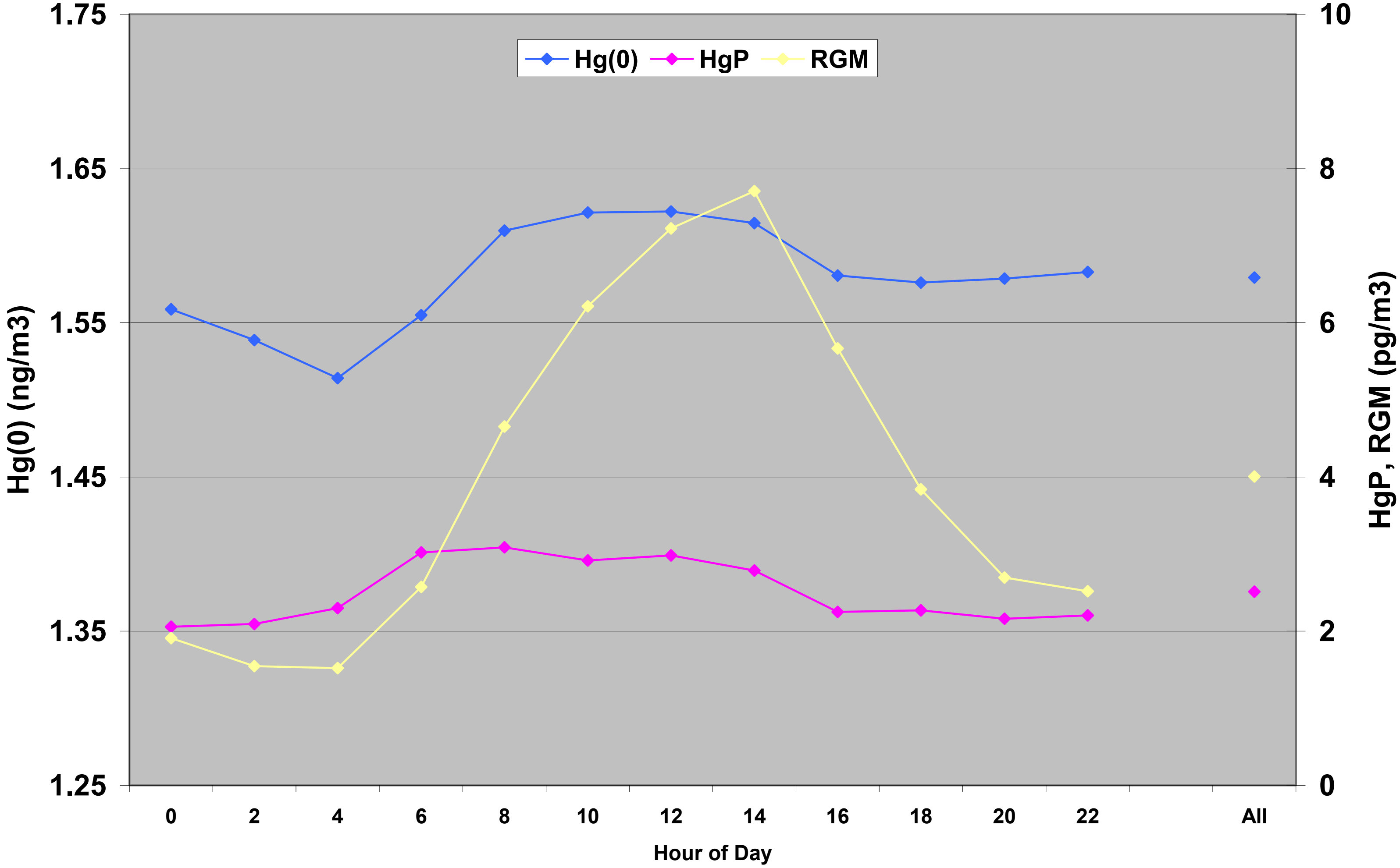
RGM
(pg/m^3)



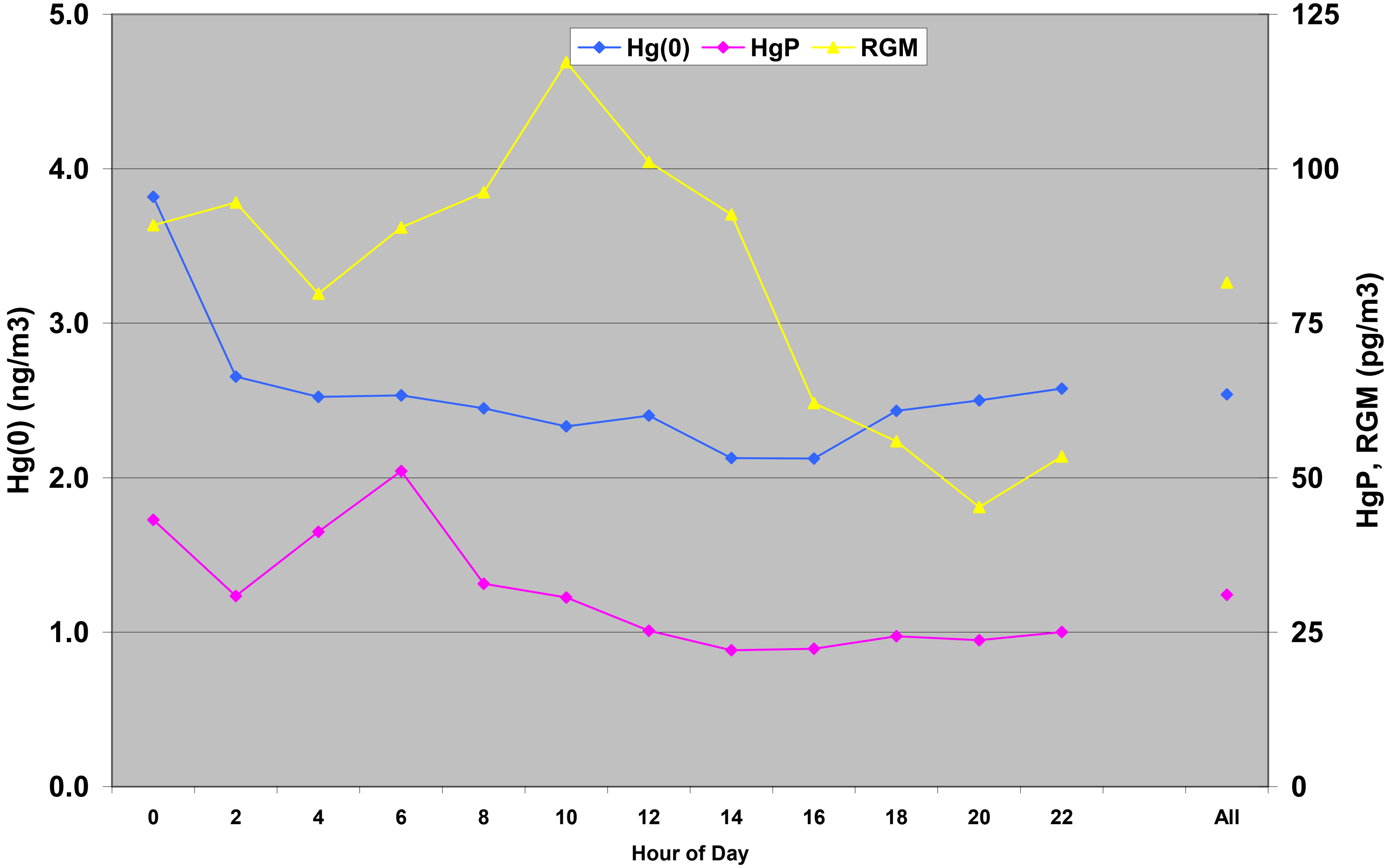
OLF Aerial View



Diurnal Pattern of Hg Species at OLF 2006



Diurnal Pattern of Hg Species at BHM 2006



Dry Deposition Estimates

Unlike wet deposition, dry deposition is difficult to measure. However, dry deposition can be estimated based on analogy with HNO_3 (for RGM) and $PM_{2.5}$ (for $Hg_{PM2.5}$).

No simple analogy for Hg^0

Dry deposition (DD) calculation:

$$DD = \Sigma C_i x V_{di} ,$$

where C_i = hourly concentration and

V_{di} = hourly deposition velocity

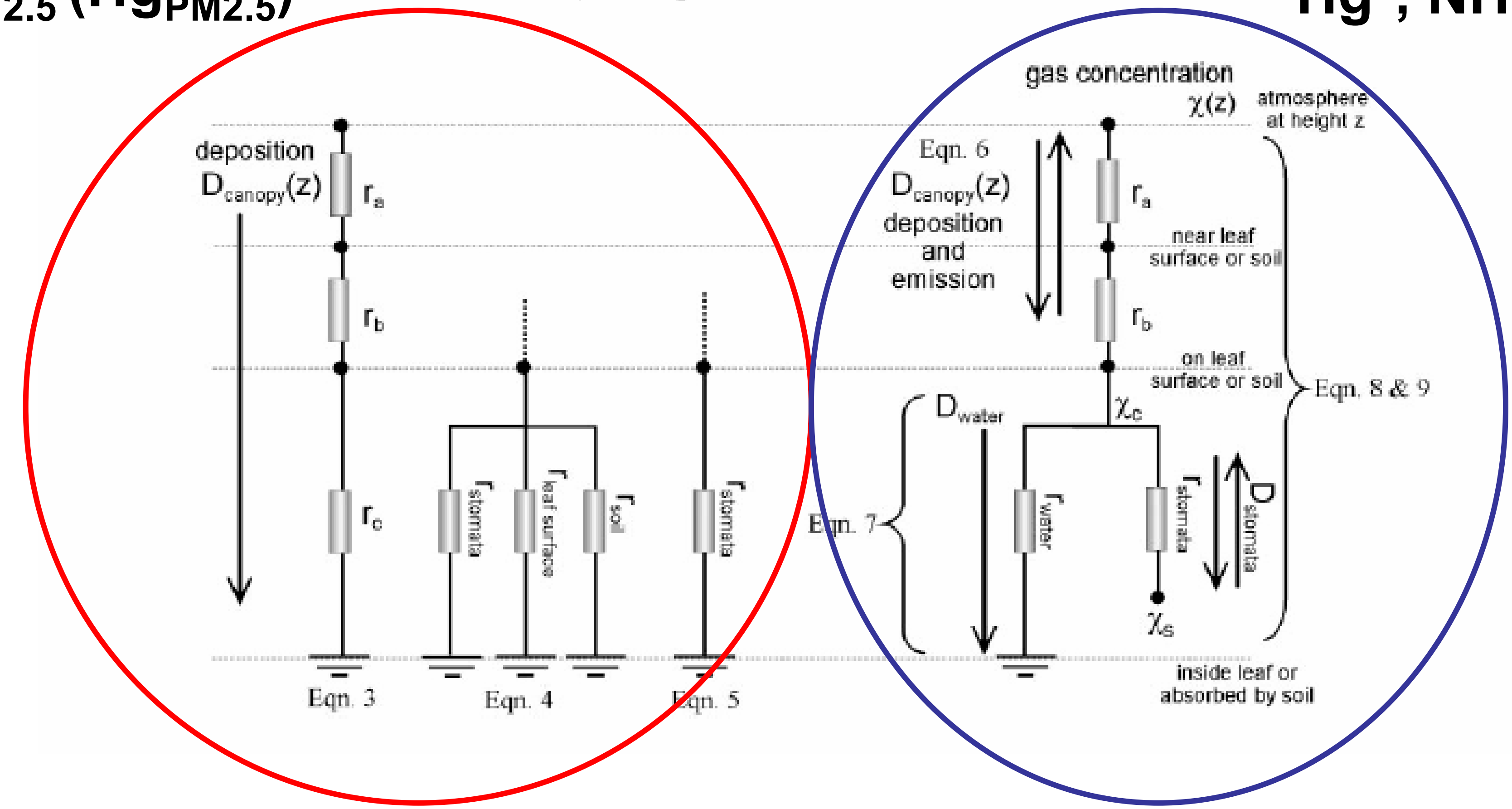
Dry Deposition Resistance Models

$$\text{Flux} = C_i/\Sigma r_{i,} = C_i \times V_{di}$$

HNO_3 (RGM)
$PM_{2.5}$ ($Hg_{PM2.5}$)

R.I. Smith et al. / Atmospheric Environment 34 (2000) 3757–3777

Hg^0, NH_3



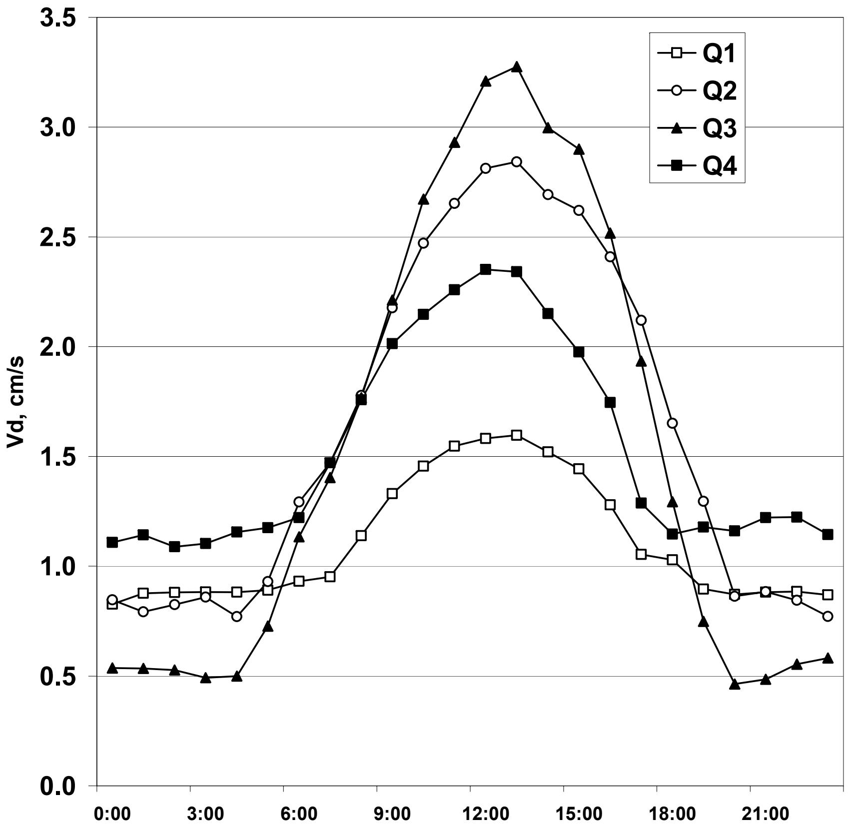
Simple: unidirectional

Complicated: bi-directional

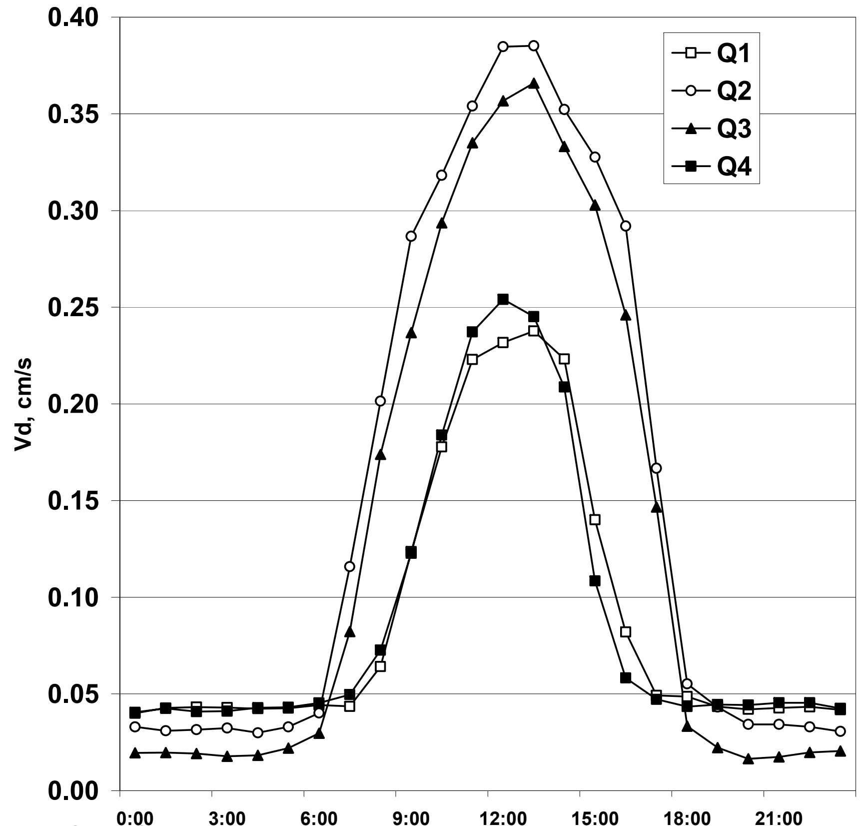
Hourly Deposition Velocity (V_d)

cm/s

HNO_3 (RGM)



$PM_{2.5}$ (Hg_P)



Meyers, T. P., P. Finkelstein, and J. Clarke, 1998: A multilayer model for inferring dry deposition using standard meteorological measurements. Journal of Geophysical Research 103 (D17):22,645-22,661.

Vd exhibits strong diurnal patterns; therefore, ΣC'xVd' NE 0 and it is necessary to measure RGM and Hg_P with high time resolution.

Measured Wet and Estimated Dry Deposition (2005)

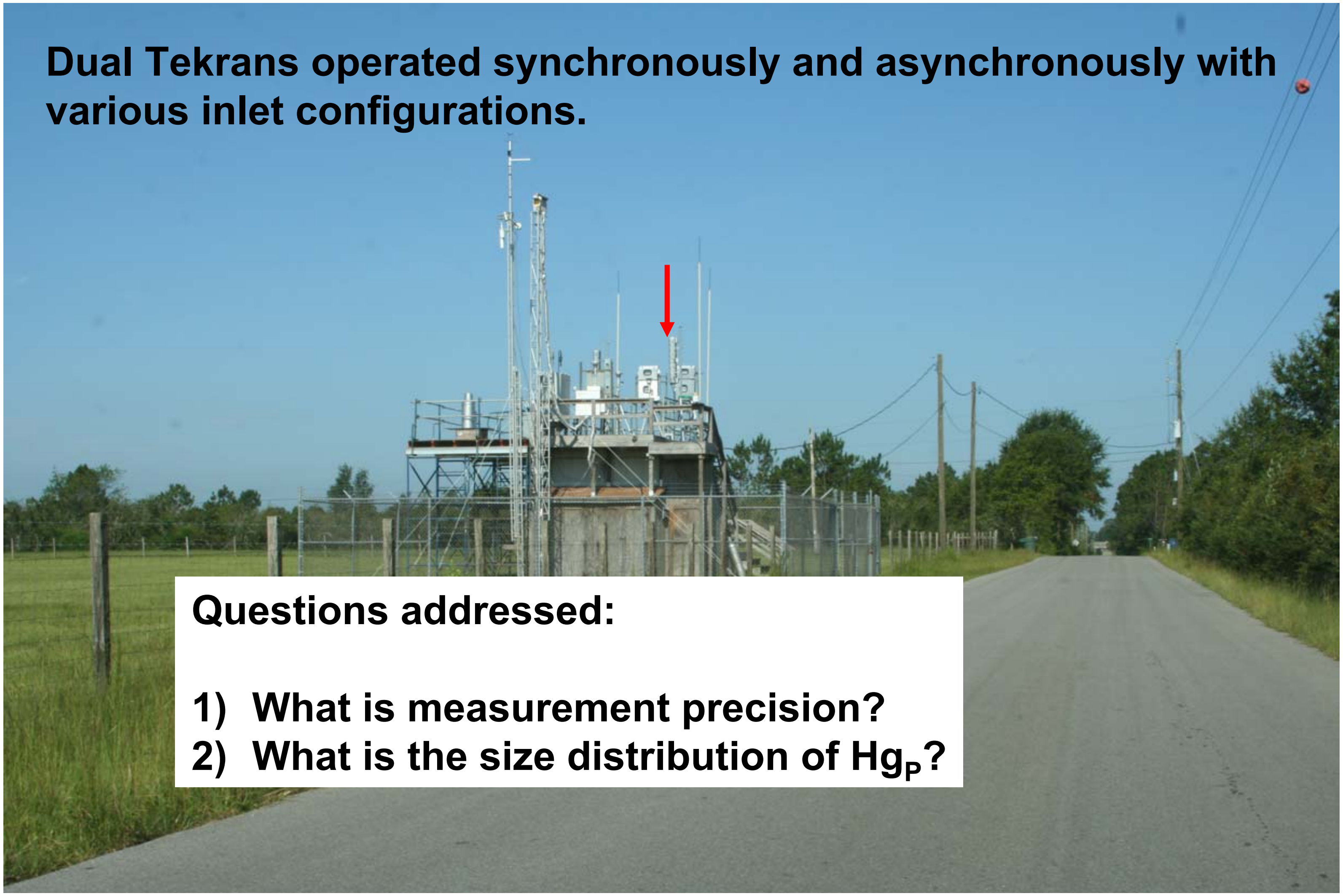
	Wet ($\mu g/m^2$)	Dry ($\mu g/m^2$)	
Site	Total-Hg	Hg_P	RGM
OLF	18.5	0.1-0.2	1.1-2.2
BHM	24.7	0.8-1.6	24-48

Wet Deposition >> Dry deposition at OLF (non-industrial) but comparable at BHM (industrial)

Caveats: 1) Dry Deposition estimate does not include Hg^0
2) Dry deposition estimate for Hg_P includes $PM_{2.5}$

OLF Experiments

Dual Tekrans operated synchronously and asynchronously with various inlet configurations.



Questions addressed:

1) **What is measurement precision?**
2) **What is the size distribution of Hg_P?**

Collocation Experiments at OLF

P = primary Tekran, C = colo Tekran

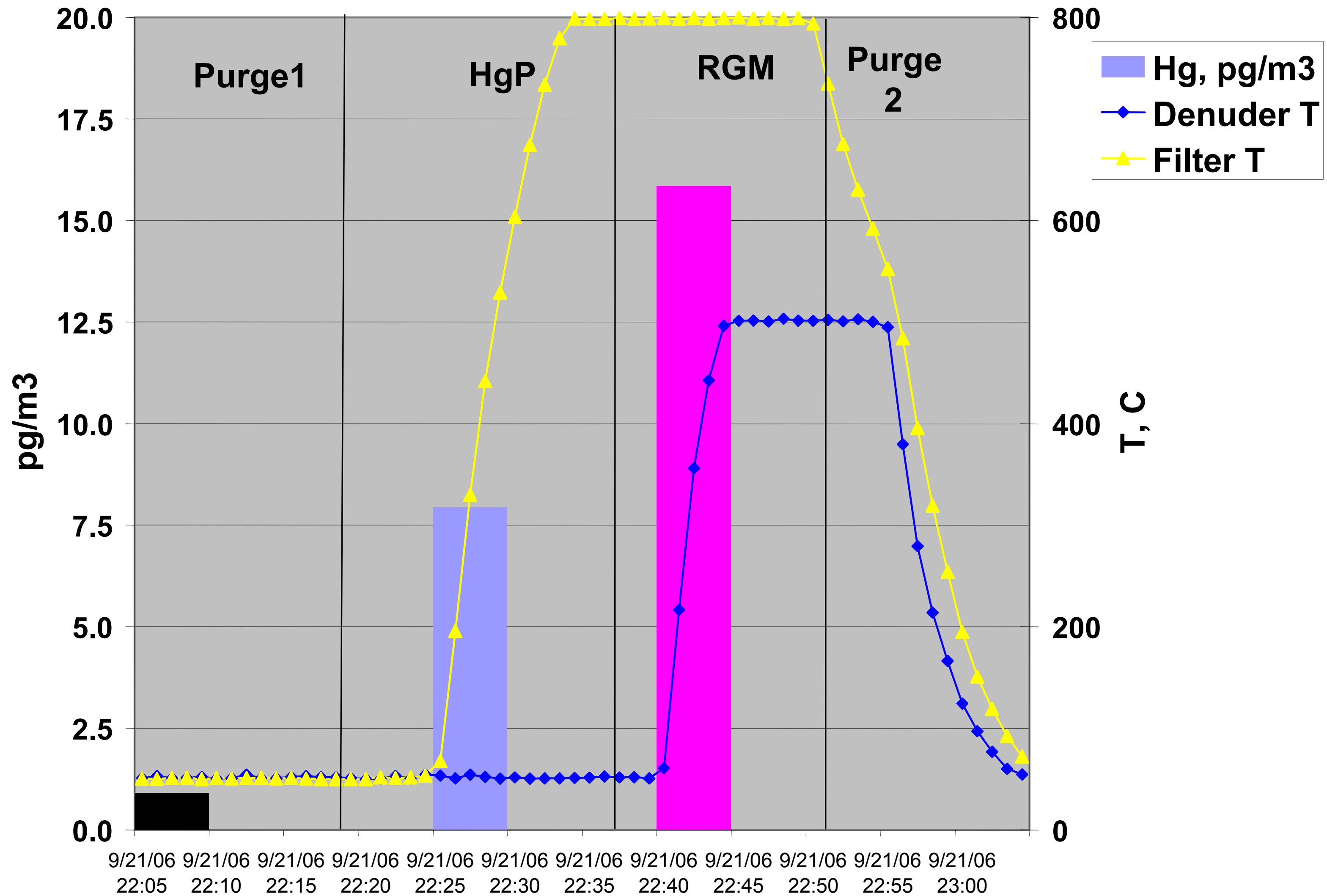
	HgP pg/m^3		RGM pg/m^3	
Inlets	P	C	P	C
$PM_{2.5}/PM_{2.5}$	1.4	1.8	5.4	4.9
$PM_{2.5}$/TSP	2.3	6.9	4.4	5.0
$PM_{2.5}/PM_{2.5}$	1.9	1.8	5.4	4.9
$PM_{2.5}/PM_{10}$	1.6	4.5	3.0	3.4

1) Measurement precision +/- 10% for RGM, +/- 25% for Hg_P
2) Roughly 2-3 times as much Hg_P in PM_{10} and TSP as $PM_{2.5}$
3) RGM may be contaminated by Hg_P if $PM_{2.5}$ inlet removed

Further Thoughts

- Measurement technology is approaching maturity and we are rapidly moving toward a national network for measuring atmospheric Hg (and estimating dry fluxes). We should pause to:
  - Recognize that, except for Hg^0, we are measuring "forms" not "species" (if not, we underestimate uncertainties).
    - For example, if we believe $Hg_{PM2.5}$ is important, then we should investigate size distributions (pilot studies)
  - Think about reporting units (ng/m^3 at 0°C and 1 atm. potentially unrepresentative). Some options are:
    - Use current units, but always report ambient T and BP
    - Use mixing ratios
  - Consider more conventional calibration using bottled $Hg^{0.}$ Some advantages/disadvantages:
    - Automated calibrations (displacement and method of additions)
    - Remote actuation and adjustment
    - Cost and development effort/time
  - Consider whether thermography can (or should) be used to learn more about RGM and $Hg_{PM2.5}$?

Thermography of $Hg_{PM2.5}$ and RGM



Summary and Conclusions

- SEARCH joined MDN and initiated atmospheric Hg measurements in 2000/2001. Plans are to continue through 2010.
- Routine, continuous measurements of atmospheric Hg^0, RGM and $Hg_{PM2.5}$ are obtainable with current technology, but require significant oversight.
- Hg data for 4 southeastern sites shows highly elevated concentrations (all 3 forms) at an industrial site and moderately elevated concentrations (Hg^0 only) at an urban site, relative to rural/suburban sites.
- Based on 2005 data, estimated DD of RGM and $Hg_{PM2.5}$ < WD at rural/suburban sites, but may be comparable at industrial sites (Hg^0 deposition unknown, but likely highly variable in space and time).
- Inlet experiments show roughly 3 times higher Hg_P in PM_{10} and TSP than $PM_{2.5}$. Coarse Hg_P will contribute to dry deposition and may provide clues to atmospheric Hg processing.
- The prospect of a nationwide Hg network is exciting, but we need to continue to think through details of the measurement and reporting process.

Acknowledgements

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Further information about SEARCH can be obtained at:

www.atmospheric-research.com