# Quantifying Mercury Emissions from Large Point Sources in the Southeastern U.S. during NOMADSS

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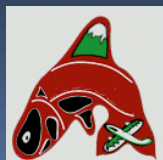[3]University of Colorado, Boulder, CO
[4]National Center for Atmospheric Research, Boulder, CO
[5]National Oceanic and Atmospheric Administration, Boulder, CO
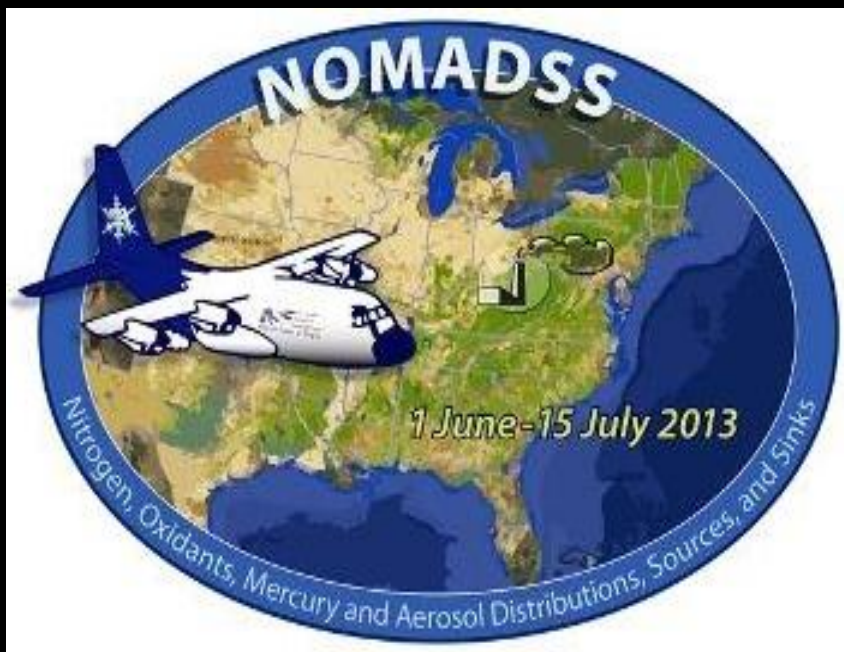
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UNIVERSITY of WASHINGTON
BOTHELL

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# Nitrogen, Oxidants, Mercury and Aerosol Distributions, Sources and Sinks



**NOMADSS Hg science goals**
- Characterize emissions from large U.S. Hg point sources
  - coal-fired power plants generate 50% of U.S. anthropogenic emissions
- Study regional scale Hg distribution and atmospheric chemistry

**Today's focus**
- Overview of source assignments for large Hg-rich pollution plumes

# Aircraft Hg Measurements: Detector for Oxidized Hg Species (DOHGS)



Inlet



- Species measured
  - Total atmospheric Hg (THg)
  - Gaseous Elemental Mercury (GEM)
  - Reactive Mercury (RM) by difference
- Time resolution: 2.5 min
- Mean overall uncertainties
  - THg, GEM: 7–8%
  - RM: ~45 pg/m$^3$
- RM LOD (3$\sigma$): 110 pg/m$^3$

# Supporting Data

C-130 measurements* (technique, investigators)

- $SO_2$ (UV fluorescence, U. Colorado-Boulder)
    - 10 s data averaged to 2.5 min
- $NO, NO_2$ (chemiluminescence, NCAR CARI group)
- $CO_2$ (CRDS, CARI group)
- CO (VUV fluorescence, CARI group)
    - 1 s data averaged to 10 s, 2.5 min
- VOCs (fast GC-MS, CARI group; PTR-MS, NCAR + NOAA)
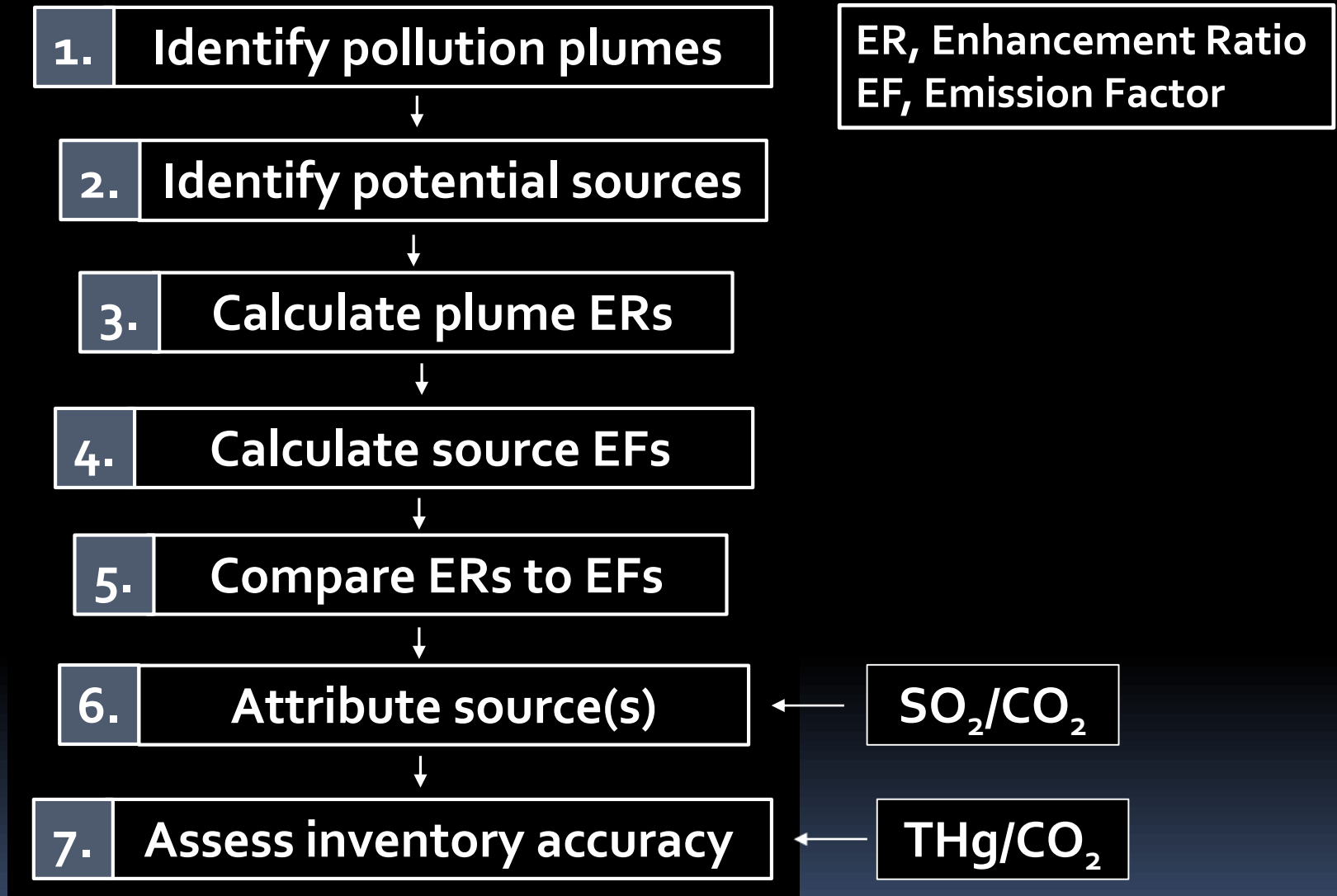    - 15 s every 2 min (GC-MS); 1s disjoint (PTR-MS)

Emissions inventories (EPA)

- EPA National Emissions Inventory (NEI)
- EPA Toxics Release Inventory (TRI)
- EPA Air Markets Program Database (AMPD)

Transport modeling

- NOAA HYSPLIT dispersion model

# Hg Point Source Analysis Protocol

1. **Identify pollution plumes**
   ↓
2. **Identify potential sources**
   ↓
3. **Calculate plume ERs**
   ↓
4. **Calculate source EFs**
   ↓
5. **Compare ERs to EFs**
   ↓
6. **Attribute source(s)** ← **$SO_2/CO_2$**
   ↓
7. **Assess inventory accuracy** ← **$THg/CO_2$**

**ER, Enhancement Ratio**
**EF, Emission Factor**

•**Approach works well only for power plants**

# Hg Point Source Analysis Protocol – *Continued*

Alternative approaches to source identification:

**Case 1. Power plant source; $SO_2/CO_2$ ER cannot be determined**
- **Approach: Use CO and/or $NO_x$ data instead**
- **Limitations:**
  - **$NO_x$ is not conserved**
  - **Inventory data for CO less certain than for $NO_x$, $SO_2$, $CO_2$**

Case 2. Non-power plant source
- Issues:
  - No real-time emissions data (only annual)
  - $CO_2$ emissions are not inventoried
- Approach: Use VOC tracers to assist source attribution

# Hg Point Source Analysis Protocol – *Continued*

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# Point Source Survey 1: RF-07 (Ohio River Valley)



C-130 flight track during RF-07

- Plume times (2.5 min data)
  - ①: 19:10 UTC
  - ②: 20:45 UTC
  - ③: 21:37:30 UTC
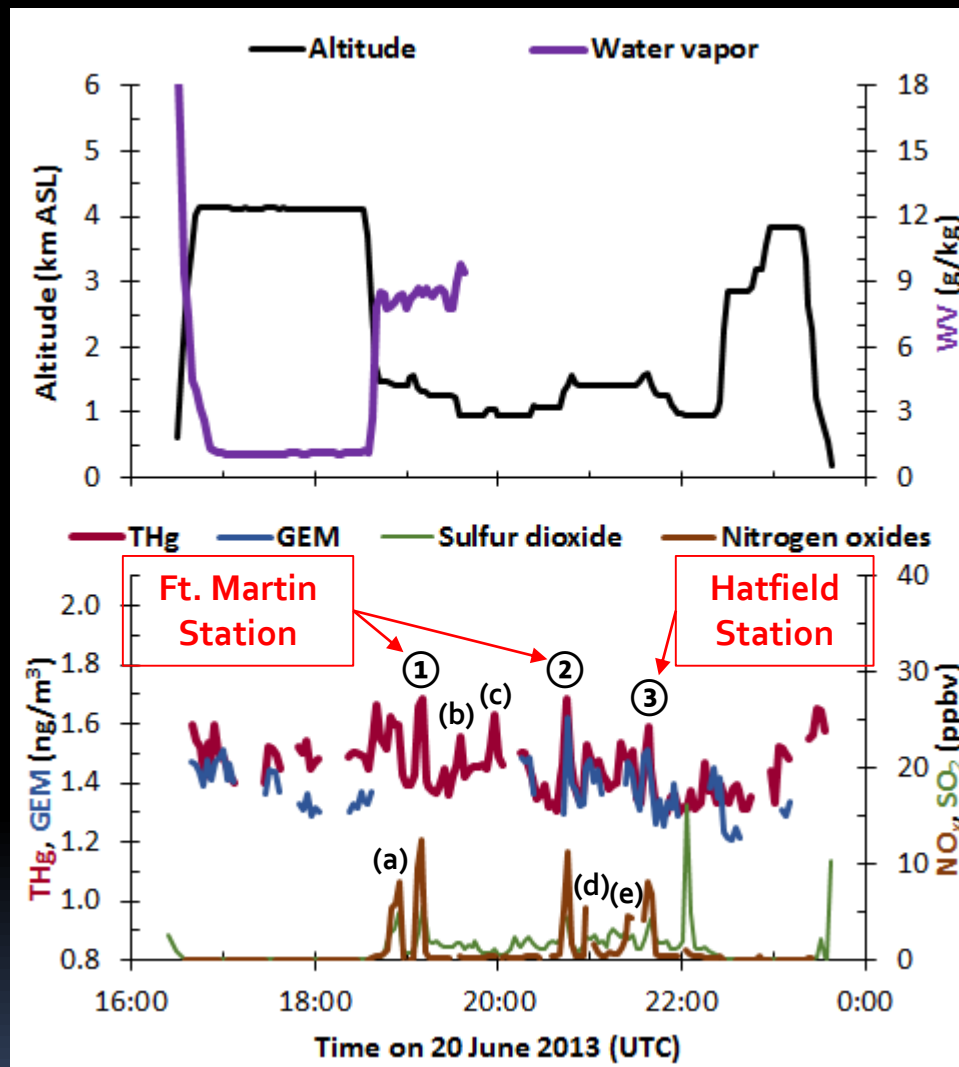


Selected C-130 measurements (2.5 min)

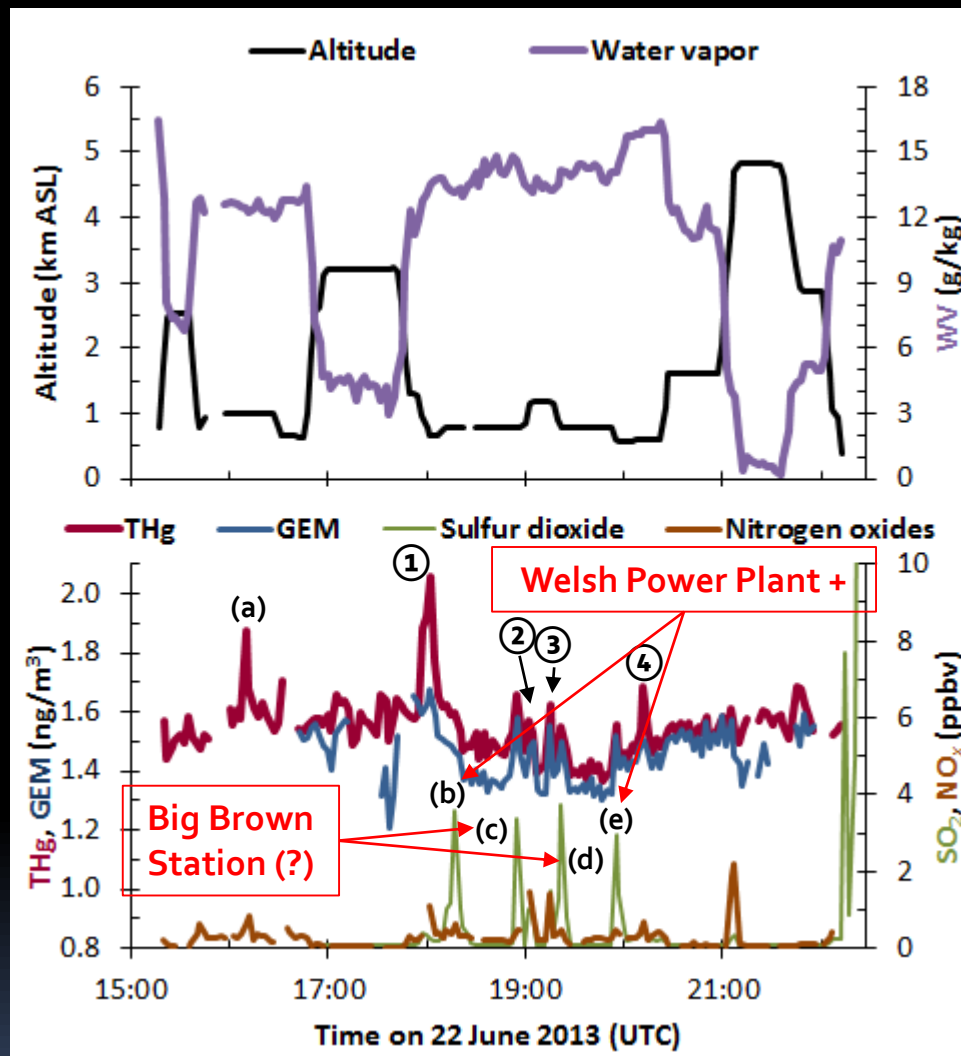# Point Source Survey 2: RF-08 (AL and Northeastern TX)



C-130 flight track during RF-08
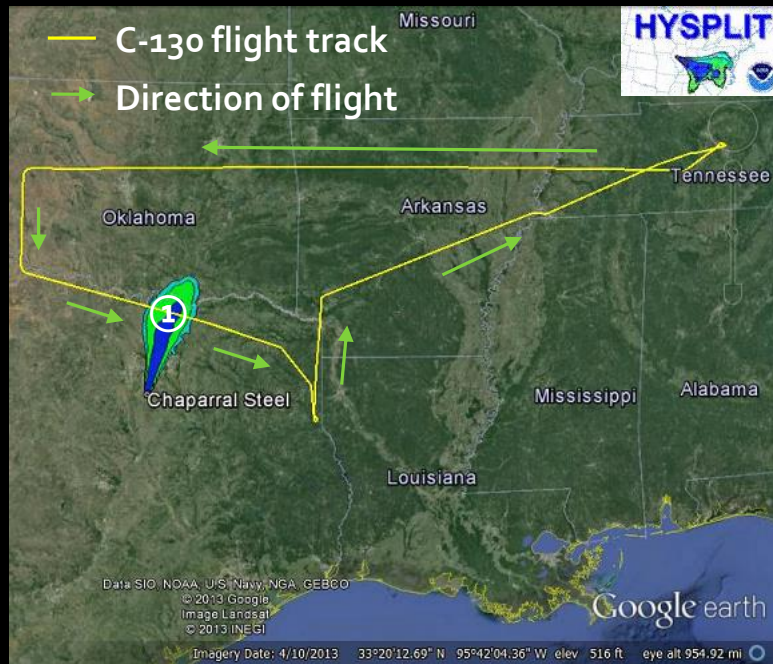
- Plume times (2.5 min data)
  - ①: 18:02:30 UTC
  - ②: 19:02:30 UTC
  - ③: 19:15 UTC
  - ④: 20:12:30 UTC
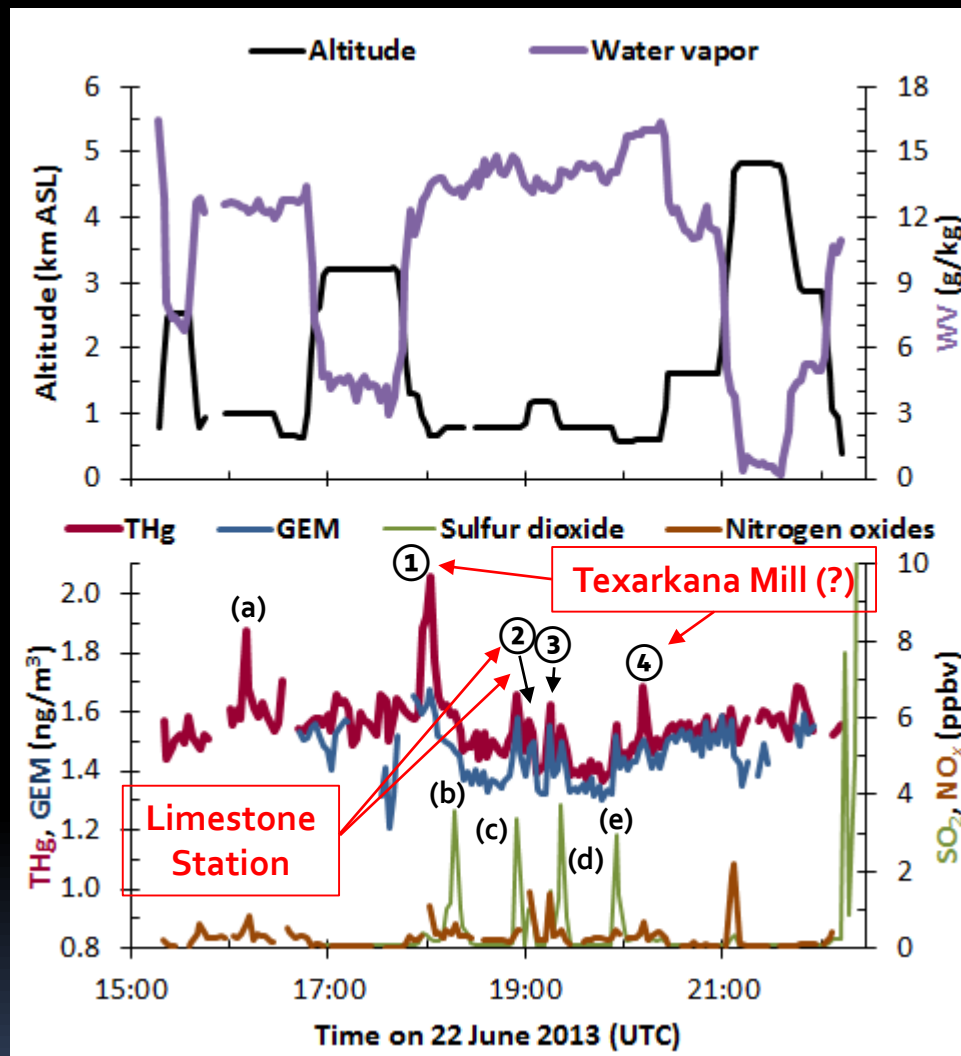
Selected C-130 measurements (2.5 min)

# Texarkana Mill Plume (RF-08, Plume 4)



Selected C-130 measurements (2.5 min)
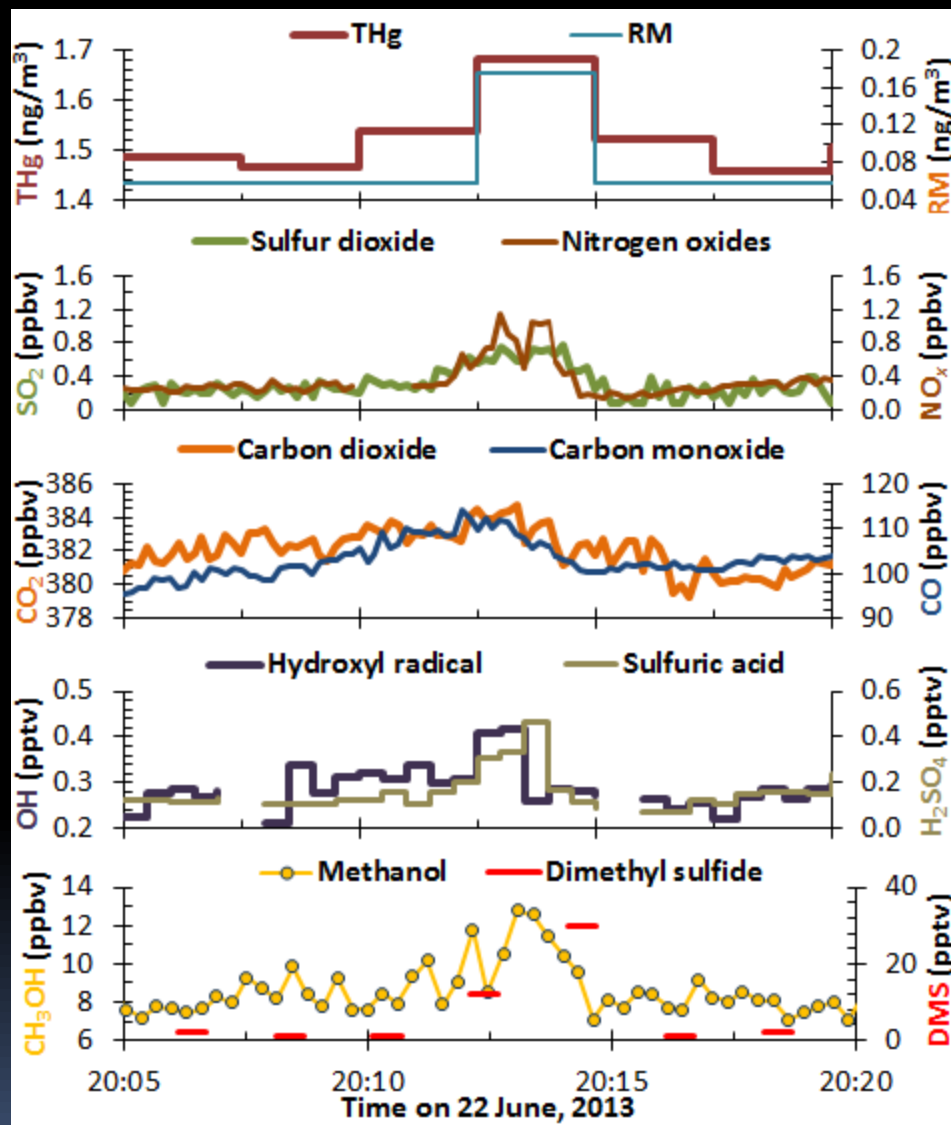
- Plume characteristics
  - Elevated RM
  - Little CO, $CO_2$, $NO_x$ and $SO_2$
  - Elevated OH and $H_2SO_4$
  - Elevated MeOH and DMS

- VOC data are consistent with a (Kraft) paper mill source

# Point Source Survey 2: RF-08 (AL and Northeastern TX)



C-130 flight track during RF-08

- Plume times (2.5 min data)
  - (b): 18:17:30 UTC
  - (c): 18:55 UTC
  - (d): 19:15 UTC
  - (e): 19:55 UTC



Selected C-130 measurements (2.5 min)

- SO₂/CO₂ not quantifiable for "Big Brown"

# Other Point Source Surveys: RF-10 (Northeastern TX)

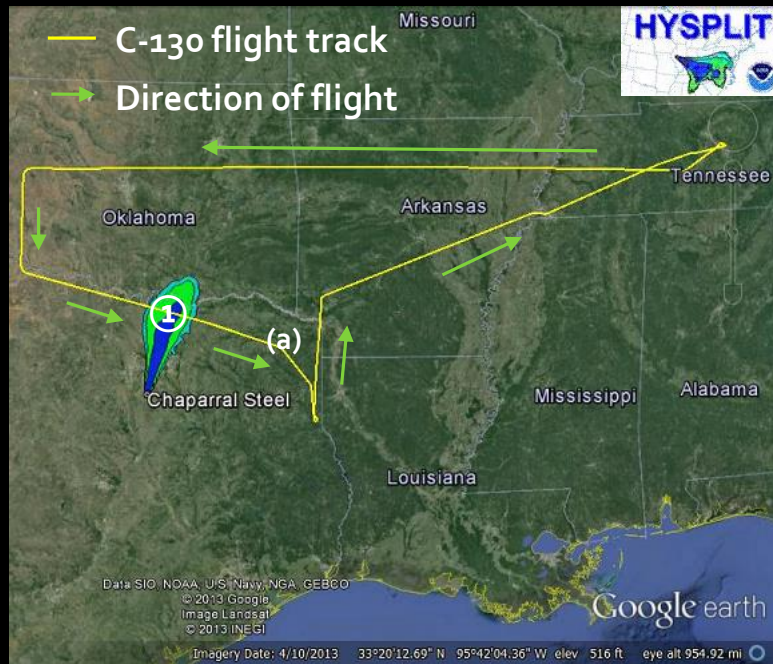

C-130 flight track during RF-10

- Plume times (2.5 min data)
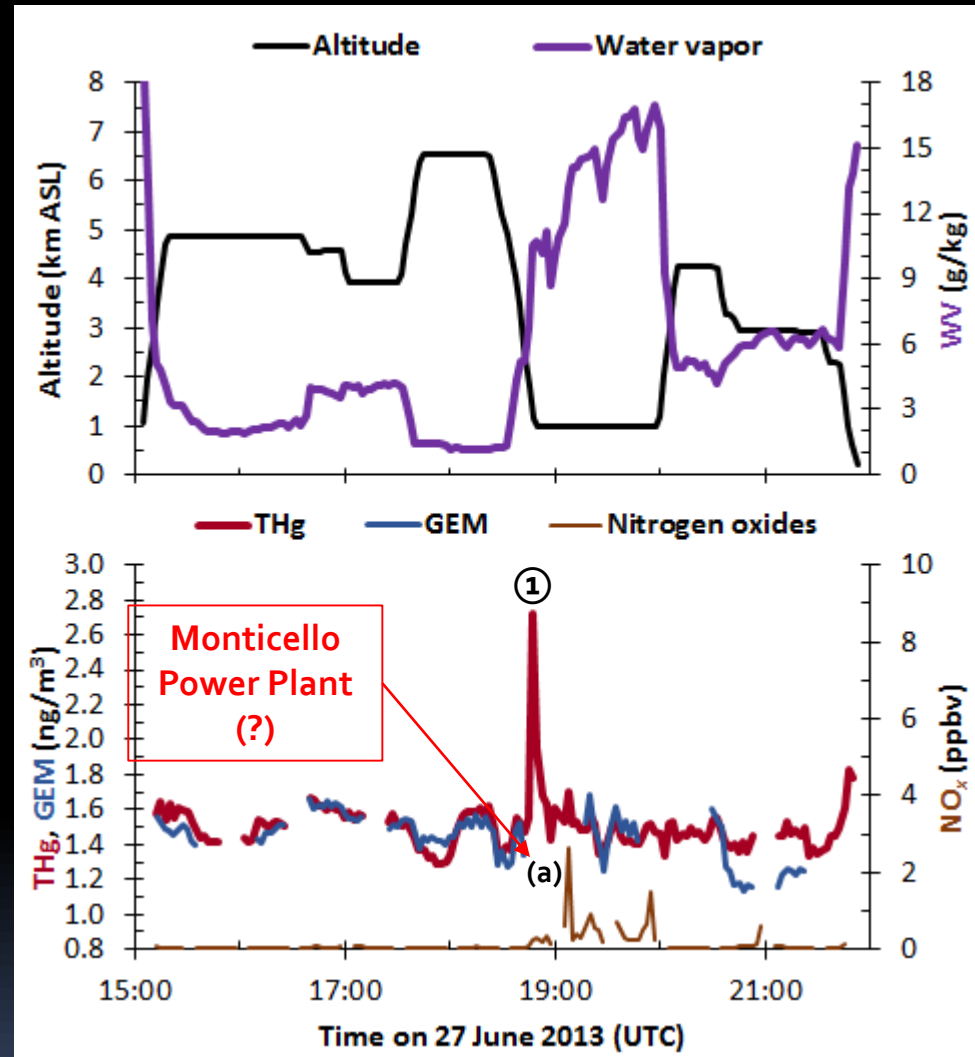  - ①: 18:47:30 UTC
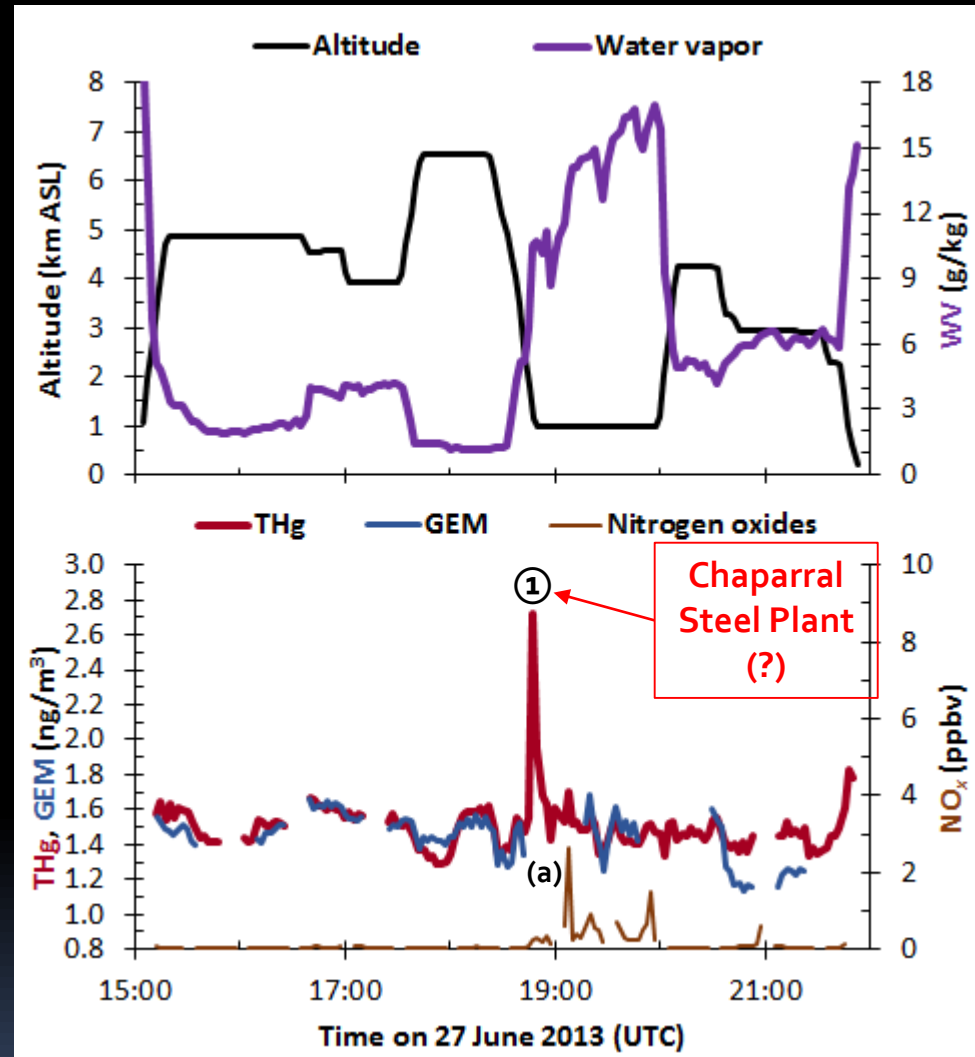
Selected C-130 measurements (2.5 min)

- Source assignment still tentative for plume 1

# Other Point Source Surveys: RF-10 (Northeastern TX)
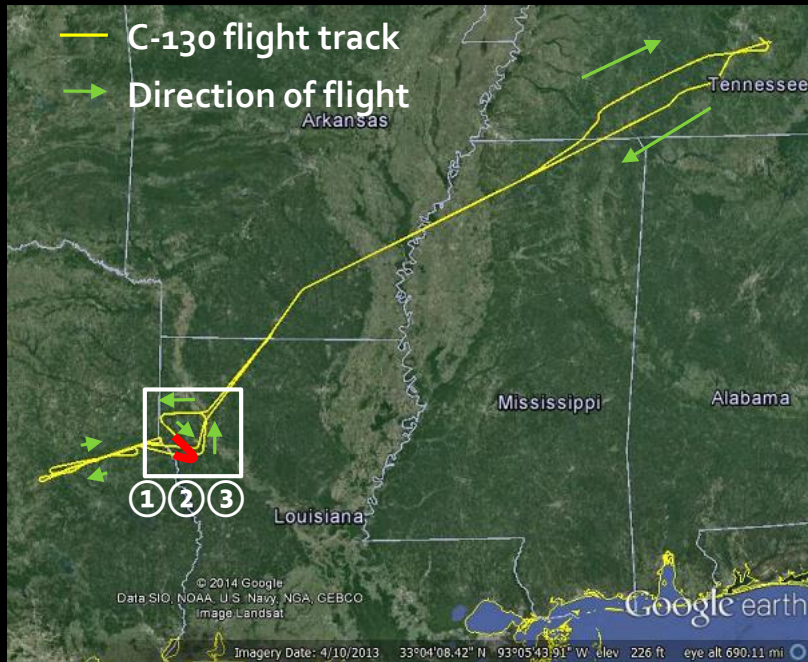


C-130 flight track during RF-10

- Plume times (2.5 min data)
  - (a): 19:07:30 UTC



Selected C-130 measurements (2.5 min)

- Source assignment based on NO$_x$, CO and CO$_2$ data
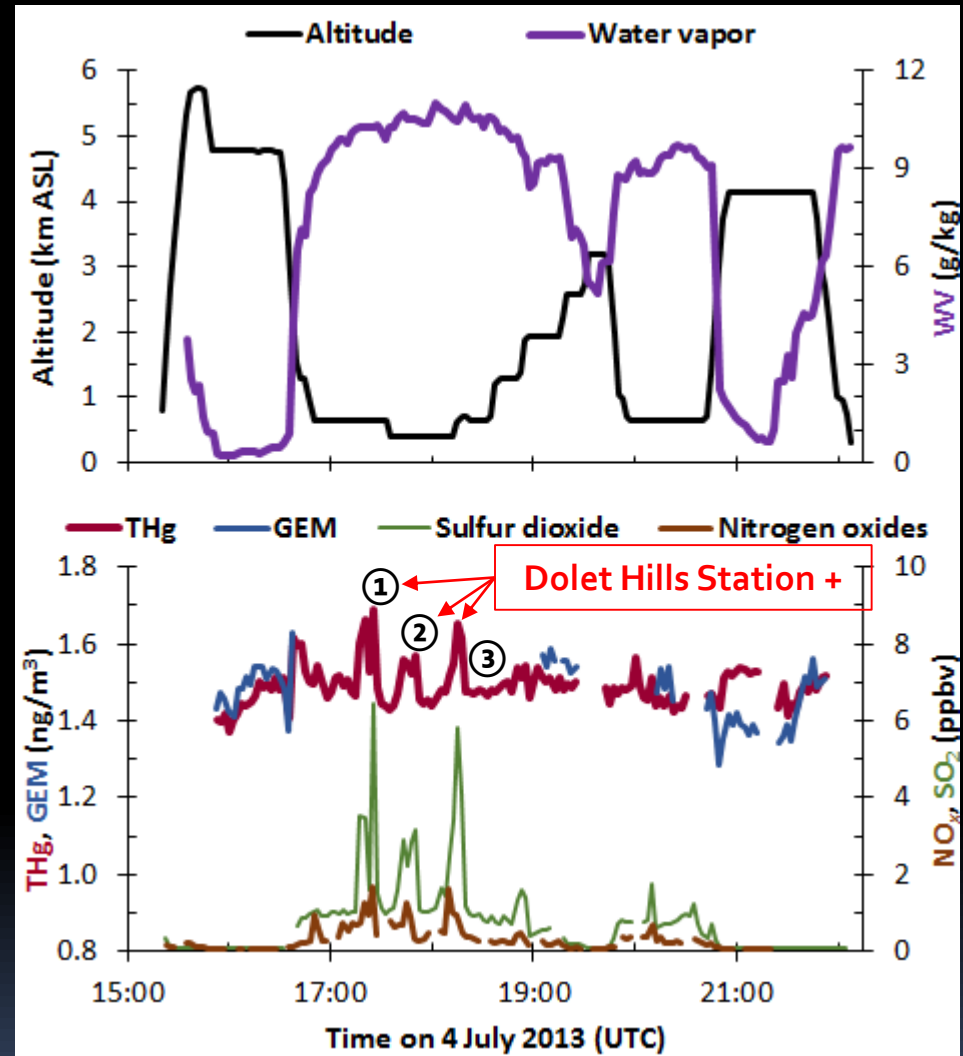
# Other Point Source Surveys: RF-13 (Western LA)



C-130 flight track during RF-10

- Plume times (2.5 min data)
  - ①: 17:25 UTC
  - ②: 17:50 UTC
  - ③ 18:15 UTC



Selected C-130 measurements (2.5 min)

- Dolet Hills plume closely associated with additional source(s)

# Summary

- Preliminary source assignments were made for the most Hg-rich pollution plumes sampled, many of which were also the largest with respect to other species (e.g., $NO_x$, $SO_2$, $CO_2$, OH, $H_2SO_4$).

- Most plumes were attributed to large coal-fired power plants.

- Power plant source assignments were typically made with a high degree of confidence due to availability of real-time emissions data for this source category; different approaches to plume attribution are required for some power plants and for non-power plant sources.

- Two plumes were attributed to a large paper mill in TX, in part using VOC tracers.

- Will continue to refine source assignments and evaluate Hg emission inventories for all sources that we sampled.
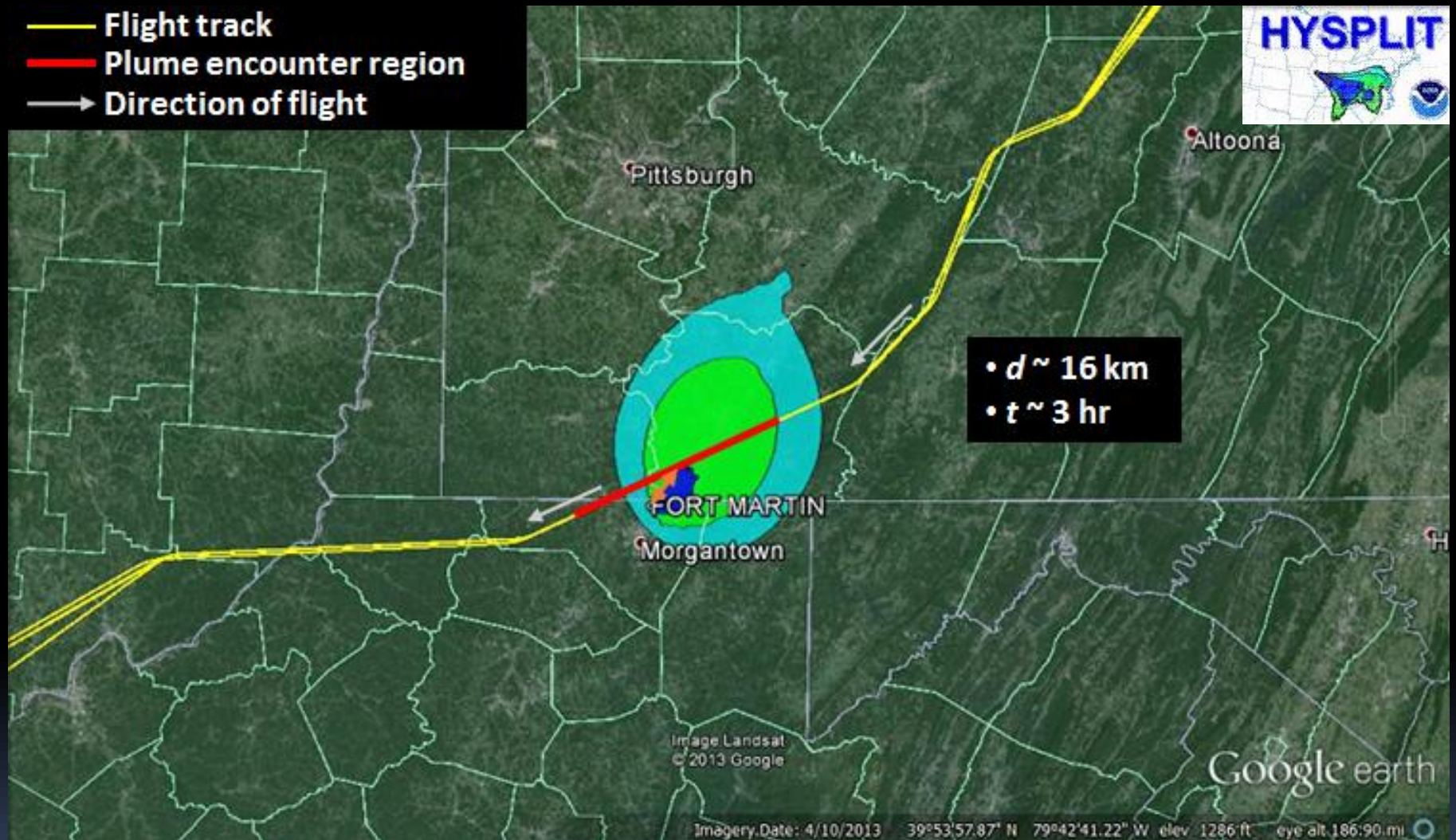
THANK YOU

# Extra Slides

# Texarkana Mill VOC HAP Emissions
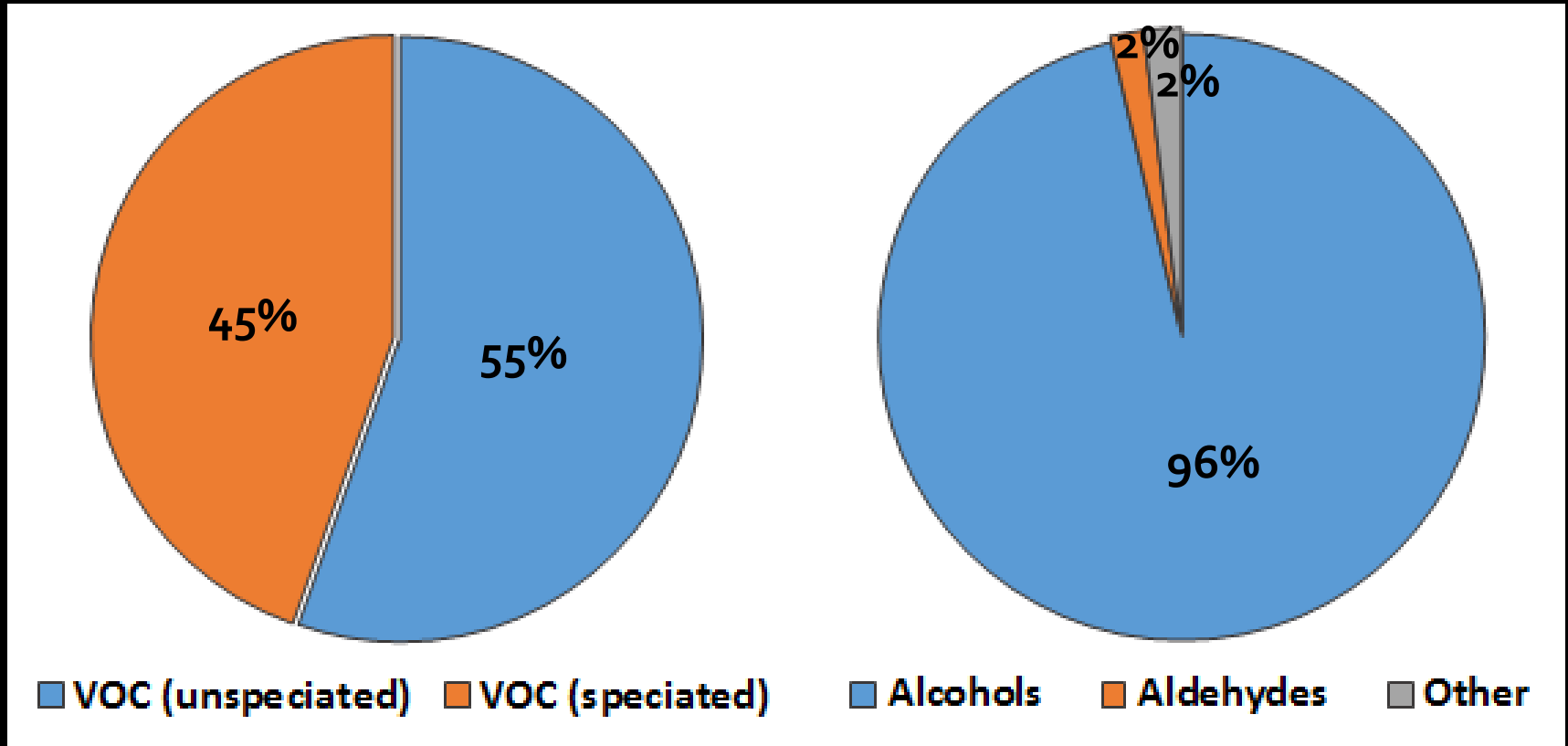


Mass distribution of annual (2011) VOC HAPs emitted from Texarkana Mill
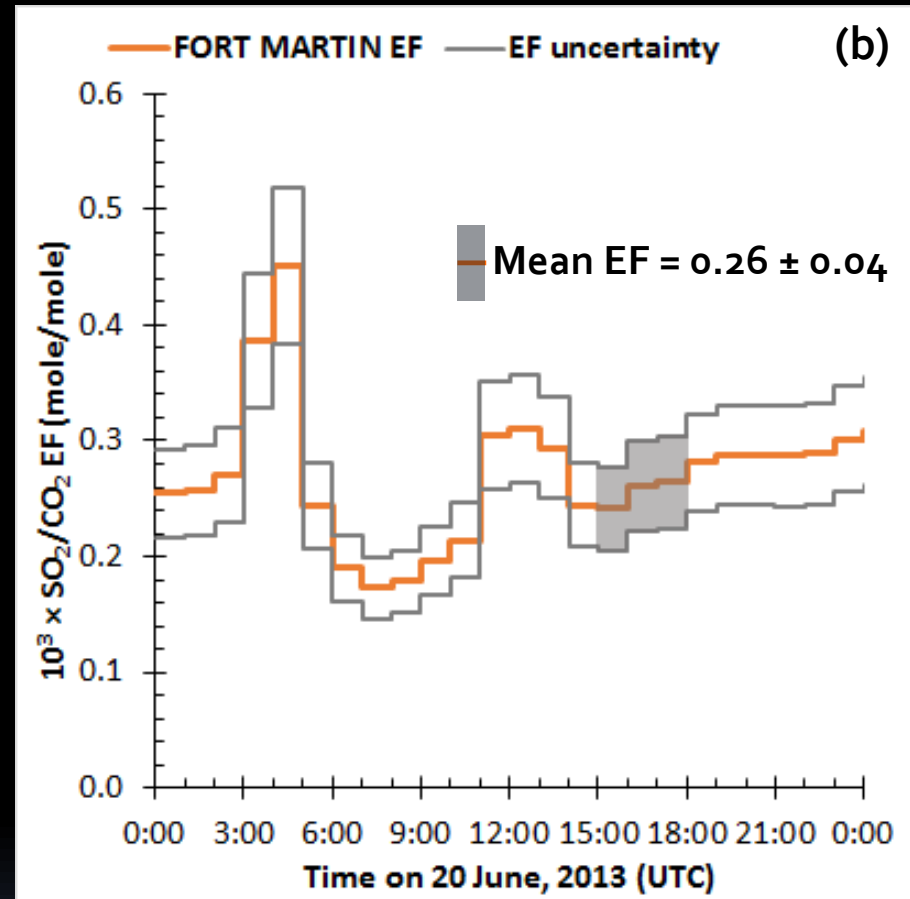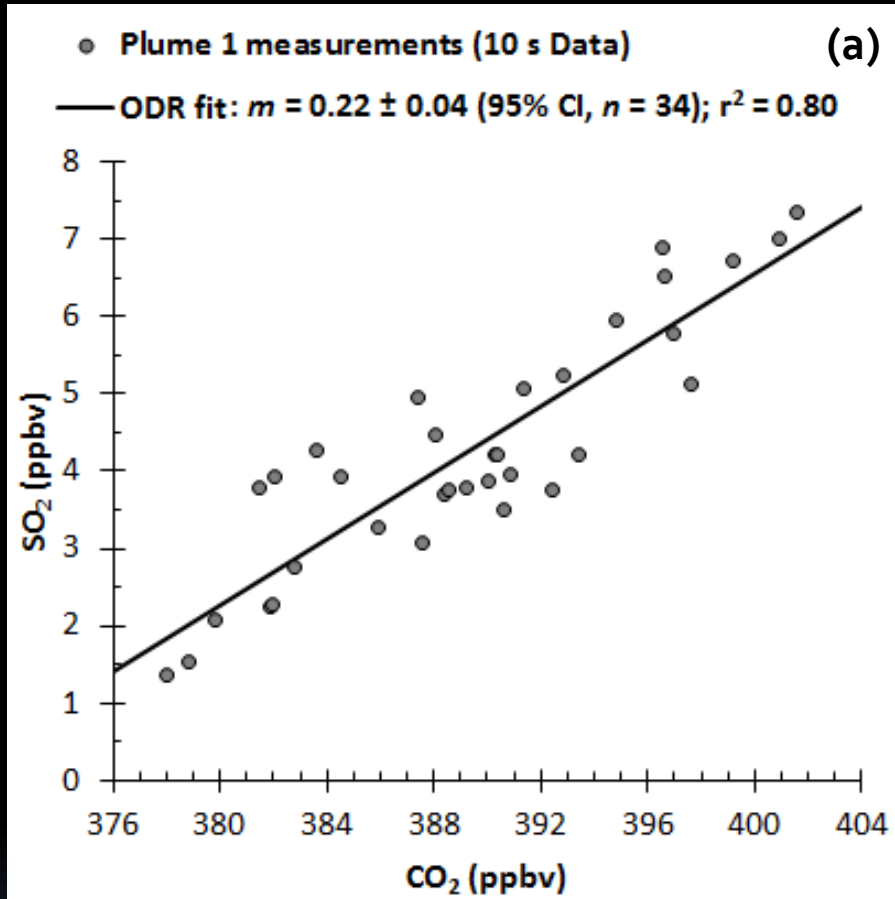
- Methanol accounted for >99% of speciated alcohols
- DMS is not a HAP, but is known to be emitted during Kraft pulping

# Source Attribution Example: RF-07, Plume 1



Modeled emissions dispersion from nearby Fort Martin coal-fired power plant
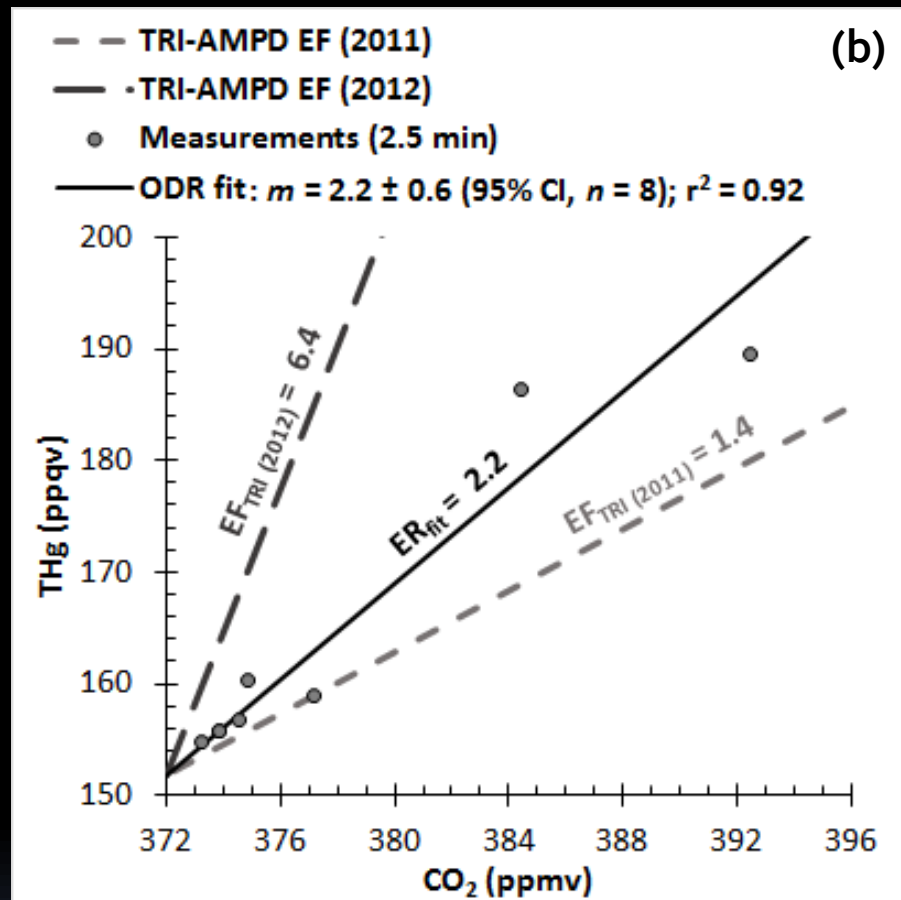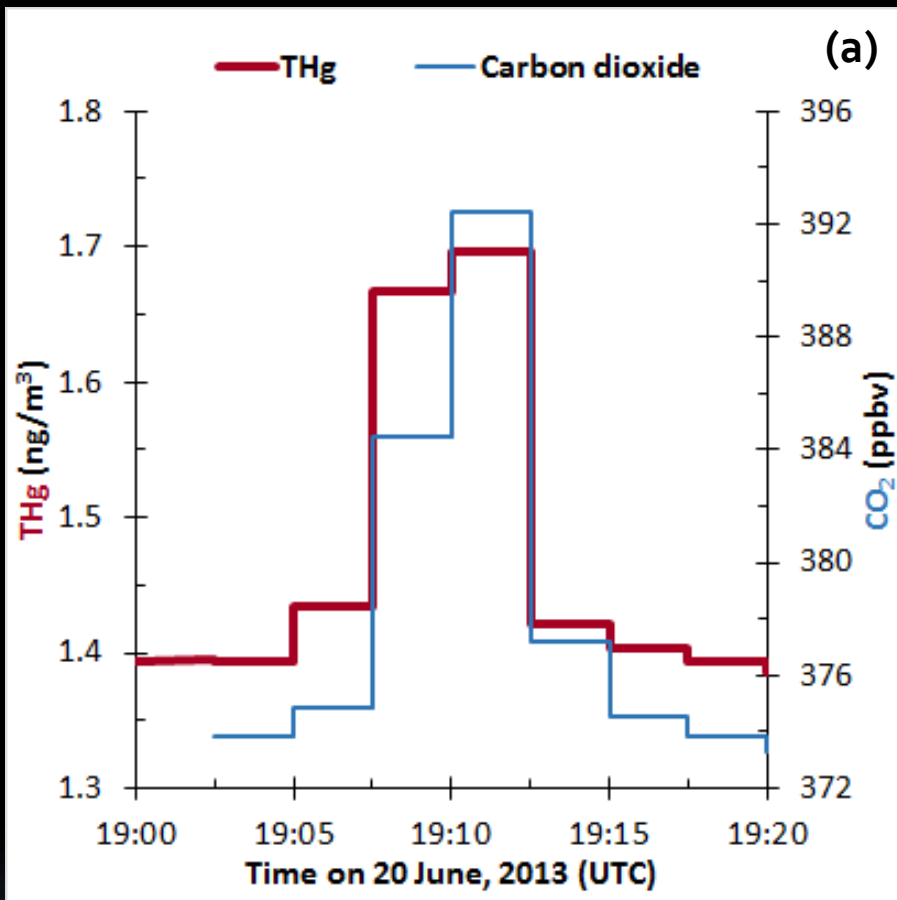(Data sources: EPA TRI, NEI; http://www.ready.noaa.gov)

# Source Attribution Example: RF-07, Plume 1 – *continued*



(a) Observed $SO_2/CO_2$ ER (plume 1) vs. (b) inventory EFs (Ft. Martin Plant)

• Plume 1 $SO_2/CO_2$ ER matches real-time EF for Fort Martin Power Plant
• Ft. Martin was 2nd largest Hg point source in WV in 2012 (326 lbs)

# Inventory Evaluation: Fort Martin Power Plant



(a) Cross-plume Hg and $CO_2$ obs. (2.5 min); (b) Fort Martin ER-EF comparison

- Hg/$CO_2$ ER is ~1/3rd of most recent inventory-based EF
  - But, ER is ~60% higher than previous year's EF
- 2013 Hg data are needed to better evaluate inventories

# Instrument Overview – Detector for Oxidized Hg Species
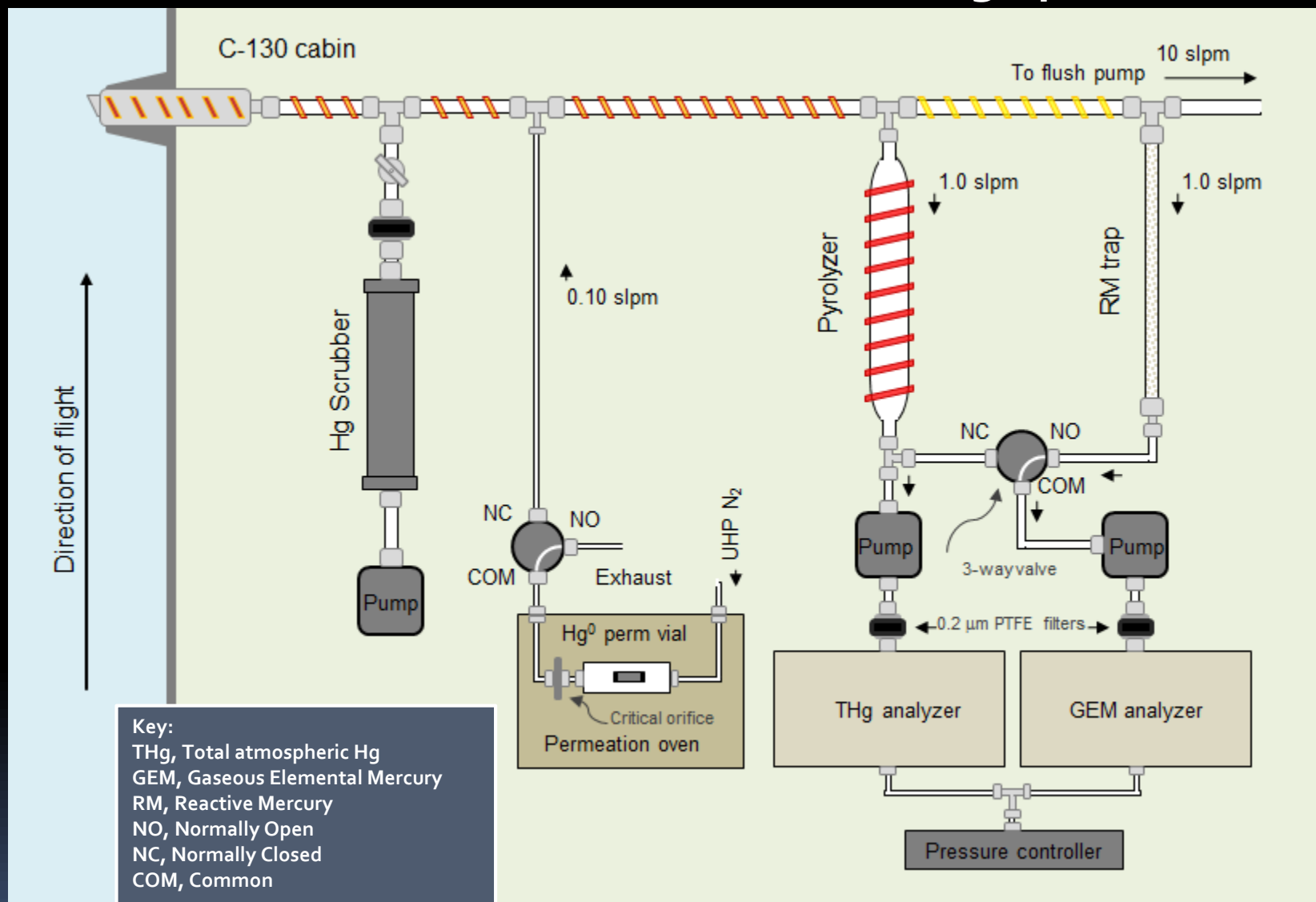


Schematic of the 'UW-DOHGS' as configured on board the C-130