Atmospheric Mercury: Are We Measuring It Correctly?

Robert Talbot

Professor of Atmospheric Chemistry
Director, Institute for Climate and Atmospheric Science
University of Houston

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Pierce et al. (2013)

Table 1. Sensors used for detection of GEM.

Product/type	Detection limit (3σ in ng m^{-3})	Response time	Made in?	Measurement method	Source
Zeeman mercury analyzer RA-915+	2*	1 s	Ambient air	Atomic absorption spectrometer with Zeeman background correction	OhioLumex (2012)
Tekran 2537B	0.1	5 min	Ambient air	Cold vapor atomic fluorescence spectrometry	Tekran (2009)
Lidar	0.5–2*	5–10 s	Lab air, Factory plume	Differential absorption lidar (DIAL)	Edner et al. (1989)
LIF	0.15	10 s	N_2 buffer gas	Sequential two-photon laser-induced fluorescence spectrometry	Bauer et al. (2002, 2003)
CRDS	27	3 s	Lab air	BBO crystal frequency-doubled, pulsed dye laser (line width of 0.1 cm^{-1}) pumped (10 Hz) by a frequency-tripled Nd:YAG laser at 355 nm	Jongma et al. (1995)
CRDS	4.5	75 s	Lab air, Perm source and N_2	Quanta-Ray GCR-16 Nd:YAG laser pumping a PDL-3 dye laser with 10 Hz repetition rate, BBO frequency doubled (0.11 cm^{-1} line width)	Spuler et al. (2000)
CRDS	24	unspecified	Argon	Nd:YAG laser pumping a tunable dye laser frequency doubled (0.1 cm^{-1} line width)	Tao et al. (2000)
CRDS	90*	10 s	Flue gas	Frequency-tripled Alexandrite laser, seeded with a single mode, external-cavity diode laser, UV output line width 0.006 cm^{-1}	Carter (2004)
(Microwave-induced plasmas) MIP-CRDS	400*	5 s	Argon	Alternative plasma sources for CRDS measurement of GEM (tube-shaped MIP source) using Nd:YAG laser with 20 Hz repetition rate pumping a dye laser (line width 0.08 cm^{-1})	Duan et al. (2005)
(Microwave-induced plasmas) MIP-CRDS	~1841	2–5 s	Argon	Alternative plasma sources for CRDS measurements, Nd:YAG laser with 20Hz repetition rate pumping a dye laser frequency doubled (line width 0.08 cm^{-1})	Wang et al. (2005)
CRDS	2.19	0.02 s	Ambient Air	Nd:YAG laser pumping a tunable dye laser (0.00019 nm line width)	Faïn et al. (2010)
CEAS	66	10 s	Injections into static cell	Cavity-enhanced absorption spectroscopy, Hg-Ne pencil lamp	Darby et al. (2012)

* Definition of detection limit not specified (i.e., not necessarily 3σ).

Pierce et al. CRDS 25 Hz

5 min. 0.35 ng m^{-3}

Figure 1. Map showing location of sample sites.

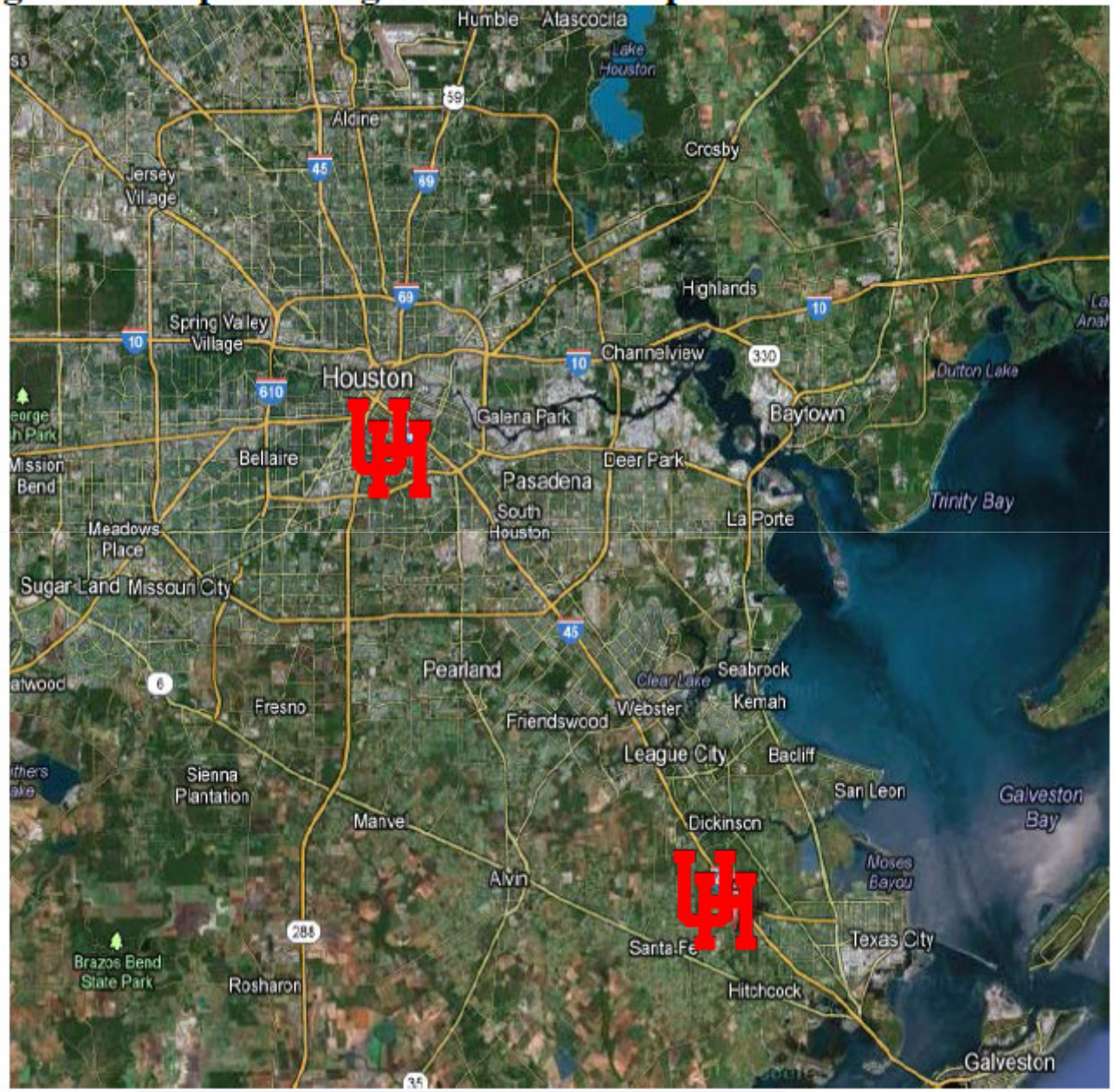
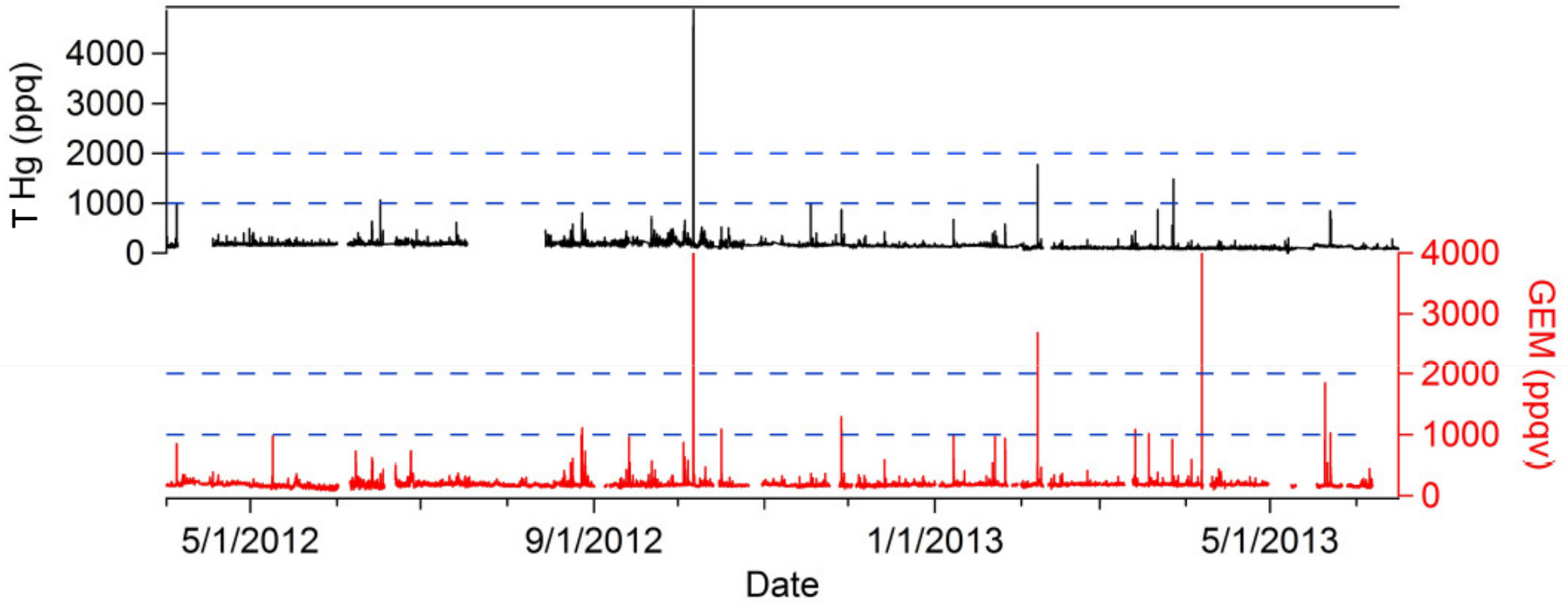
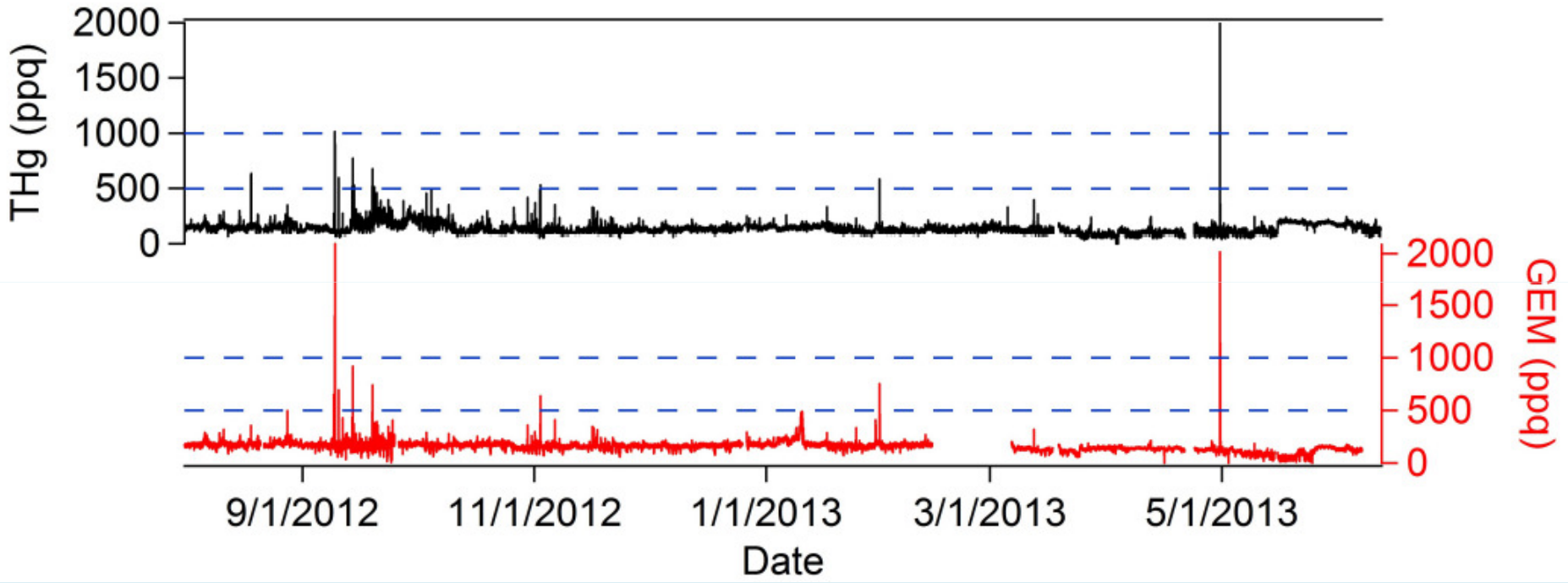


Figure 2. Data shown from UH Moody Tower site.



Urban Houston: Hg^o measured with just a 2537 unit is much lower than with a speciation system.

Figure 3. Data shown from UH Coastal Center site.



Coastal Center: ~equal with both systems.

Figure 4. Hg Baseline comparison at UH Moody Tower site.

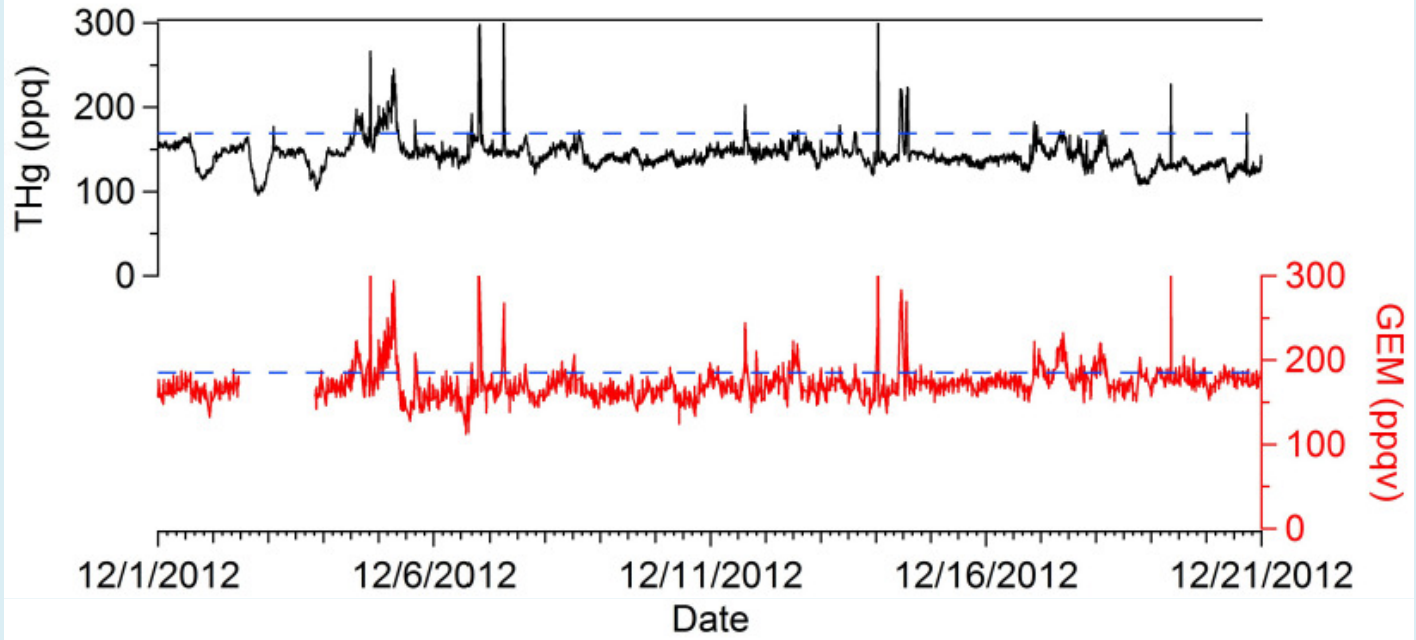
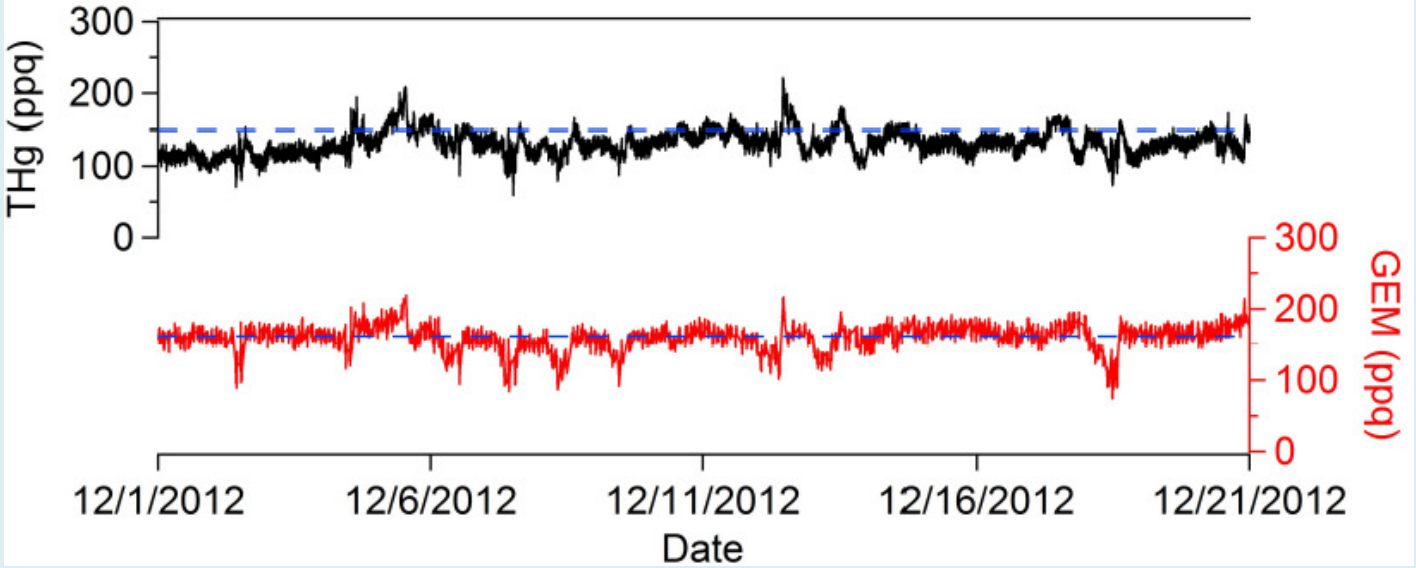


Figure 5. Hg Baseline comparison at UH Coastal Center site.



Same result.

Table 1

Tekran System employed	Mean Hg (ppqv)	Median Hg (ppqv)	Maximum Hg (ppqv)	# of Large spikes**	90th %	10th %
GEM (MT) Speciation System	185 ± 136	178	27,327	12	213	153
THg (MT) Tekran 2537B	169 ± 65	167	4,877	6	210	106
GEM (CC) Speciation System	161 ± 46	162	2,100	8	194	119
THg (CC) Tekran 2537B	149 ± 64	144	3,100	8	205	96

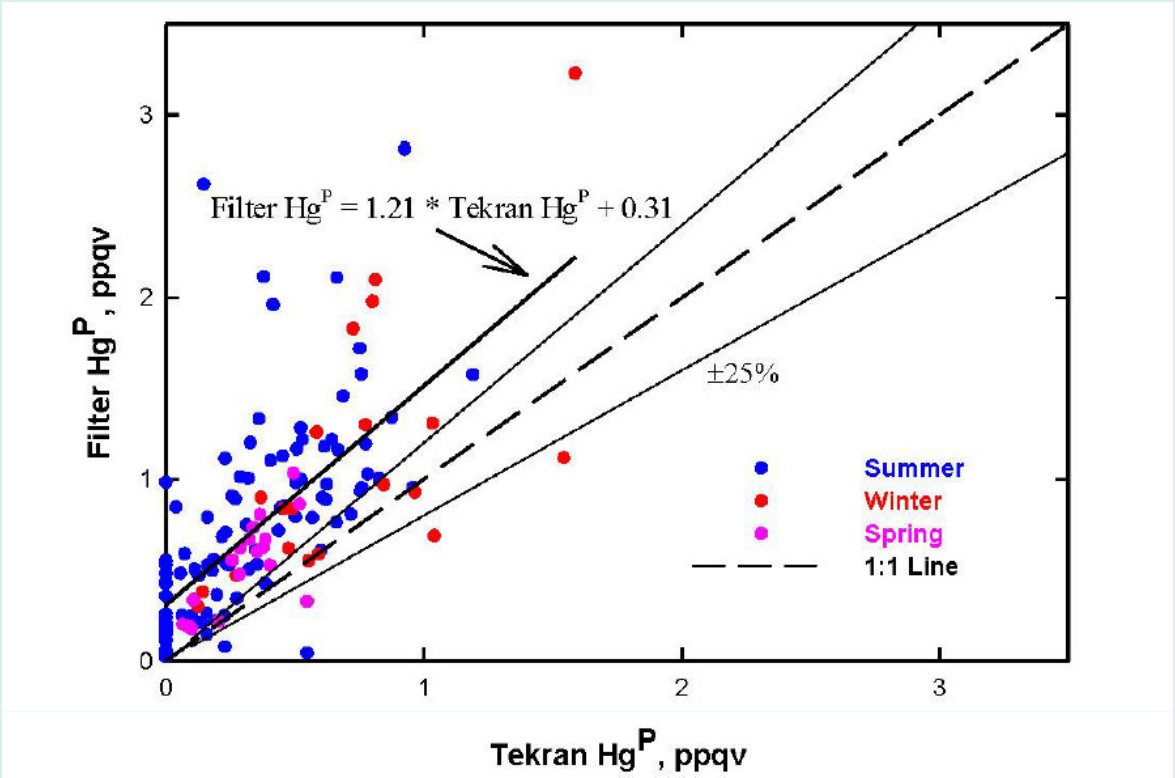
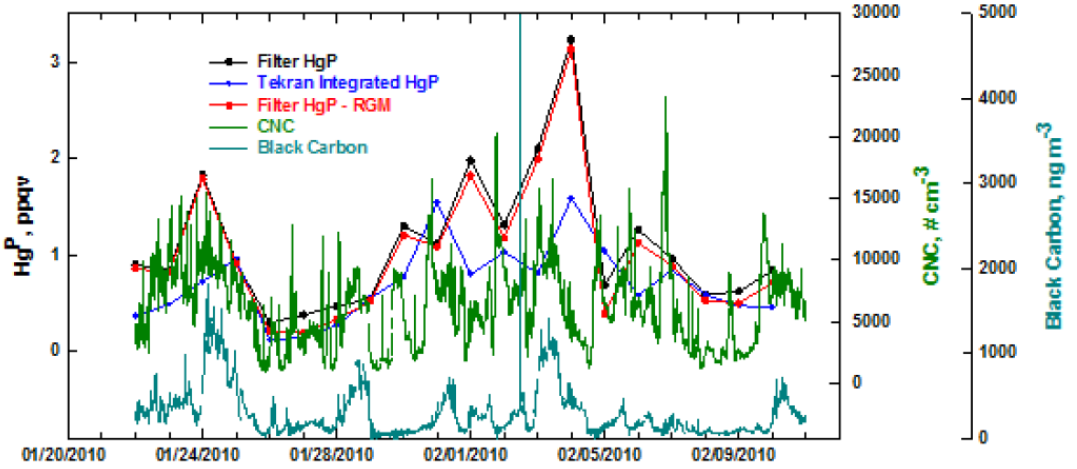


Table 2. Statistical summary as a function of season. All values are stated in ppqv.

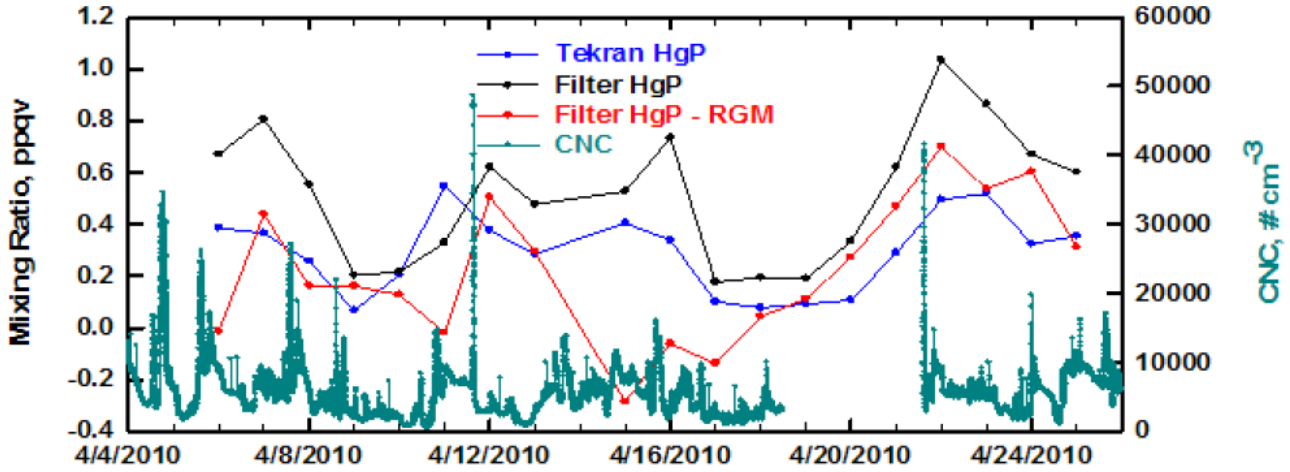
Season	Filter Hg^P Median	Filter Hg^P Range	Tekran Hg^P Median	Tekran Hg^P Range	RGM Median	RGM Range
Summer	0.70	0.05–2.8	0.25	0.0–0.96	0.0	0.0–3.5
Winter	0.92	0.30–3.2	0.62	0.0–2.8	0.07	0.0–0.46
Spring	0.54	0.18–1.0	0.28	0.0–0.95	0.14	0.0–2.3

Figure 2. Time series record of various aerosol measurements at Thompson Farm during winter 2010. The Tekran Hg^P measurements were integrated to correspond to the 24-hour filter samples for Hg^P.



Winter: GOM uptake not apparent on filter, but speciation system saw lower values at times.

Figure 3. Time series of various aerosol measurements at Thompson Farm in spring 2010. The Tekran Hg^P data was integrated to correspond to the 24 hour filter samples for Hg^P.

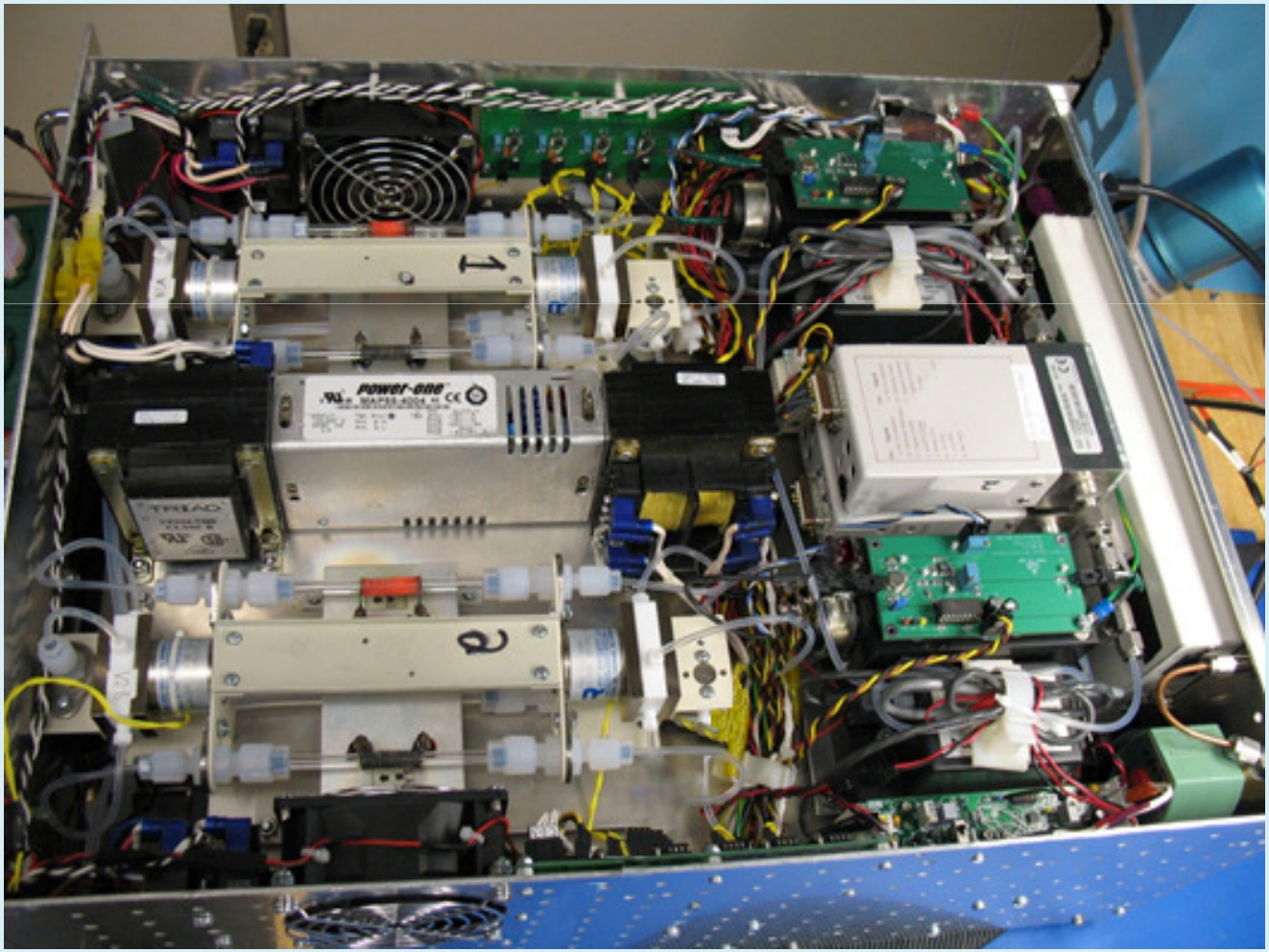


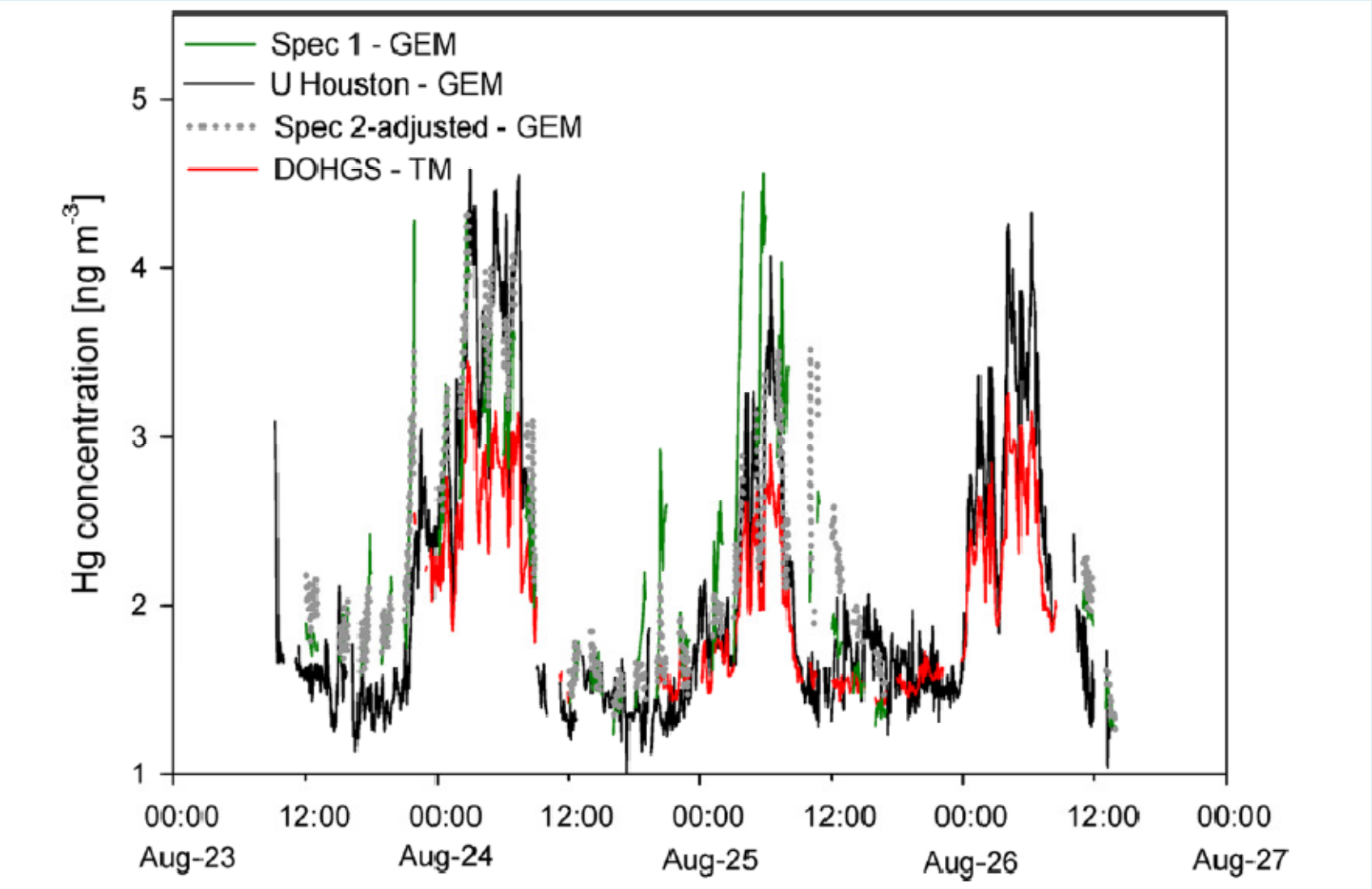
Spring: Filter Hg^P generally higher. could be some GOM uptake on filter.

Designed and built a new instrument for Hg^o.

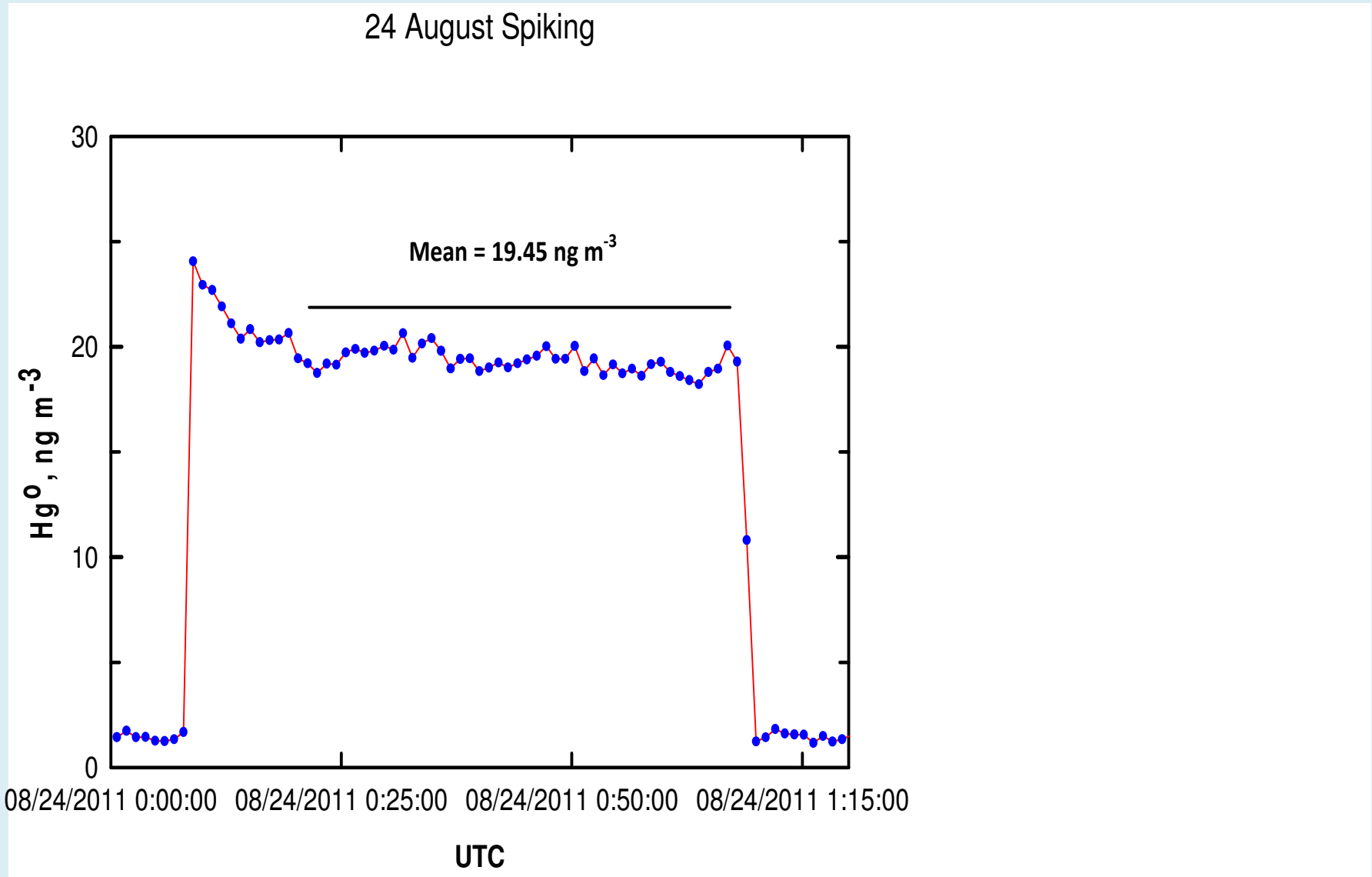
Capable of one minute time resolution.

RGM removal allows us to get Hg^o and TGM, and GOM by difference.





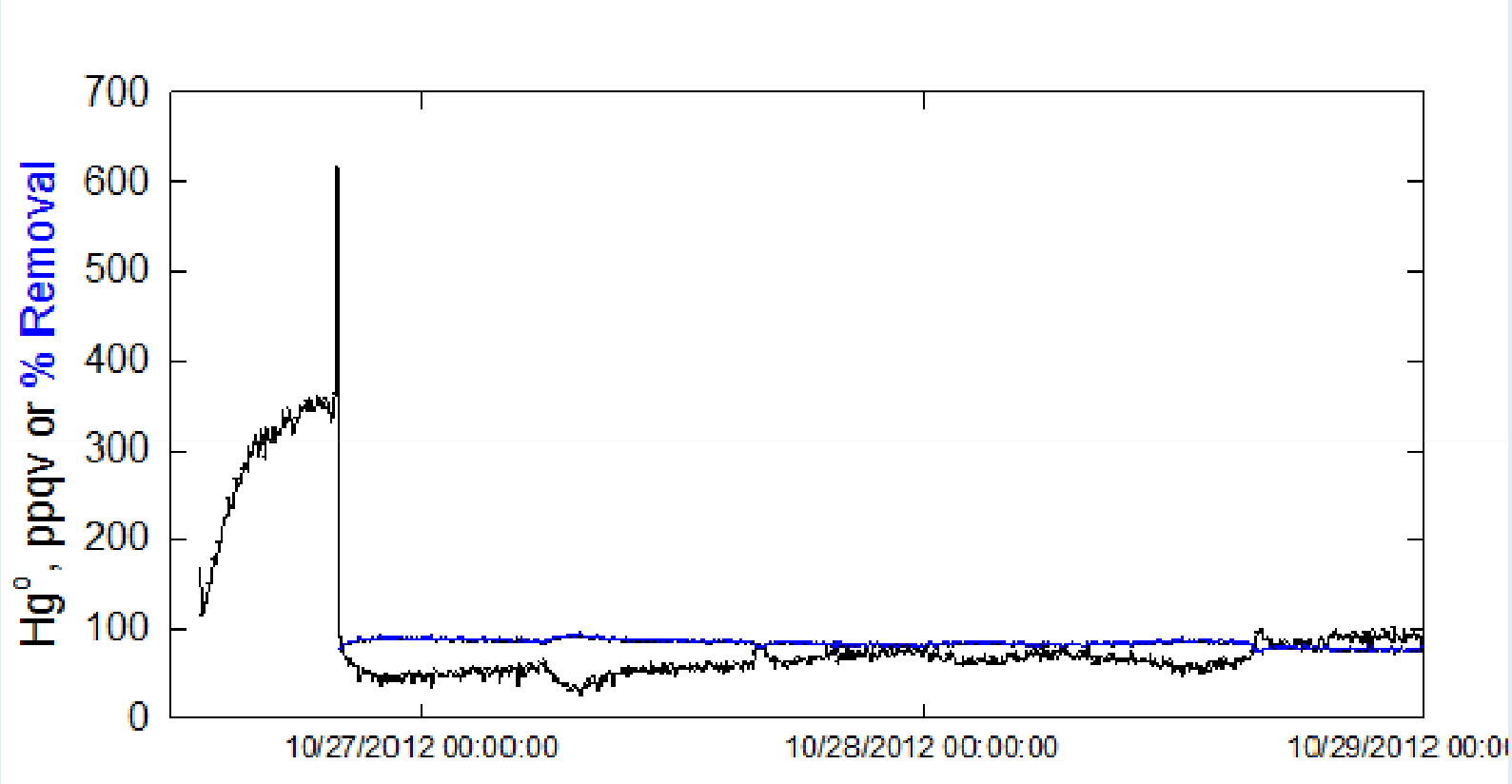
Gustin et al., 2013


24 August Spiking
Mean = 19.45 ng m-3
Hg0, ng m-3
30
20
10
0
08/24/2011 0:00:00
08/24/2011 0:25:00
08/24/2011 0:50:00
08/24/2011 1:15:00
UTC

Results of Tests to Remove GOM from a Zero Air Stream.

MATERIAL	PERCENT $HgCl_2/HgBr_2$ REMOVED
Molecular Sieve $Na_{12}(AlO_2)_{12}(SiO_2)_{12}$ xH_2O (Aldrich)	90
KCl Coated Tekran GOM Denuder	70
PUF/XAD-2 Resin/PUF (Restek)	70
Sodium Nitrate (Rutter and Schauer, 2007b)	70
Diatomaceous Earth	40
KCl Coated Glass Beads	10
Acid Washed Glass Beads	5
KCl Coated Quartz Wool	10
KCl Coated Annual Denuder 4-Channel (URG)	5
Polysulfone Cation-Exchange Membrane (Pall)	5
Soda Lime (Tekran)	0
Bubble Through Deionized H_2O	0
Bubble Through CH_3OH (Aldrich)	0

Removal of GOM by molecular sieve.



Now, lets get to work and figure this out!