Determination of Net Flux of Reactive Volatile Organic Compounds (Ozone Precusors) at the Air-Water Interface in the Gulf of Mexico: A Progress Report

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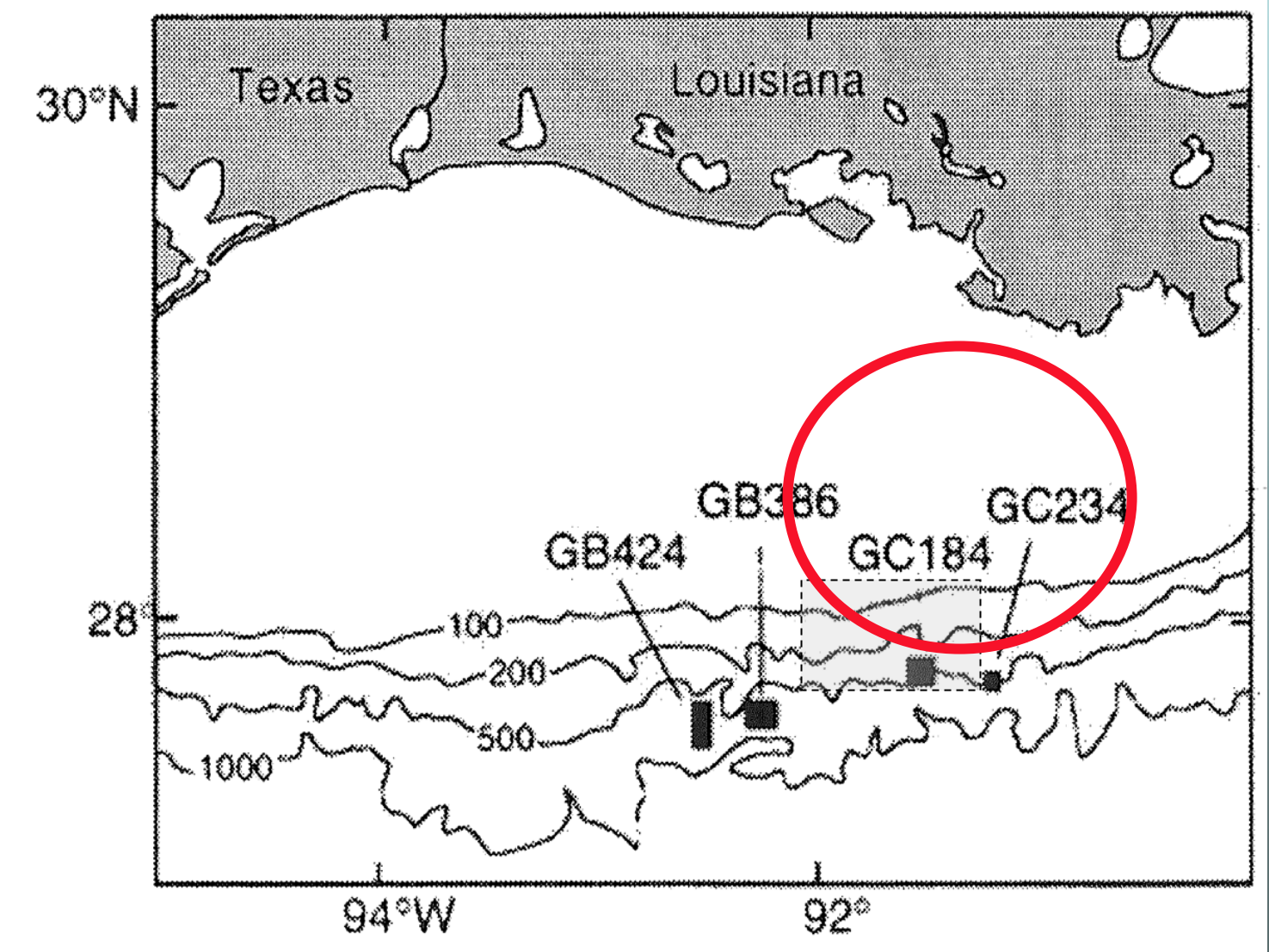
Seepage Estimates

- Estimated global input of 2.5×10^8 L year $^{-1}$ of oil entering the world oceans from natural seepage.
- Remote sensing imagery has provided evidence that seepage in the Gulf of Mexico (GOM) contributes oil at rates of 0.4-1.1 x 10^8 L year $^{-1}$.
- Northern GOM contains over 200 active seeps, as determined by satellite remote sensing surveys.

Seep Background

- Oils in region are predominantly medium-weight crude from an upper Jurassic source rock.
- Some seeps are more or less perennial, producing a visible slick throughout the year. Other seeps display an episodic or intermittent seep process.
- Oil and gas discharges have been observed from seeps associated with mud volcanoes and gas hydrate deposits.
- Most seeps are in deep water well beyond the shelf.
- Crude oils do not contain olefins, but they do emit BTEX.

Green Canyon – Study Area

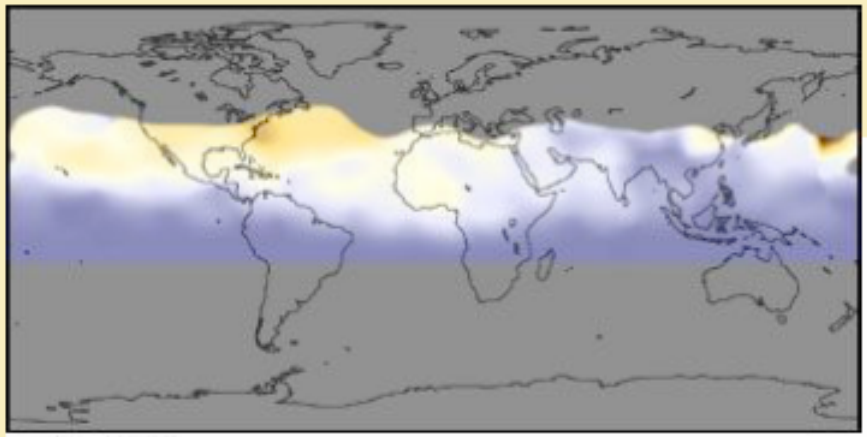


1. Overview of ozone formation chemistry
2. Rationale for analytical capabilities

Key Points:

- Two-year project:
  1st year: methods development and verification
  2nd year: data collection and synthesis
- HRVOC much more important than NMHC
- Sources include: alkane anaerobic reductions(ethene/propene), biogenic emissions, and VOCs from petroleum (BTEX)
- Target HRVOCs in northern GOM
- Perform both on-site and lab analyses for HRVOCs
- Project delayed by Katrina/Rita and LSU funding lag

Good Ozone
or Bad Ozone?

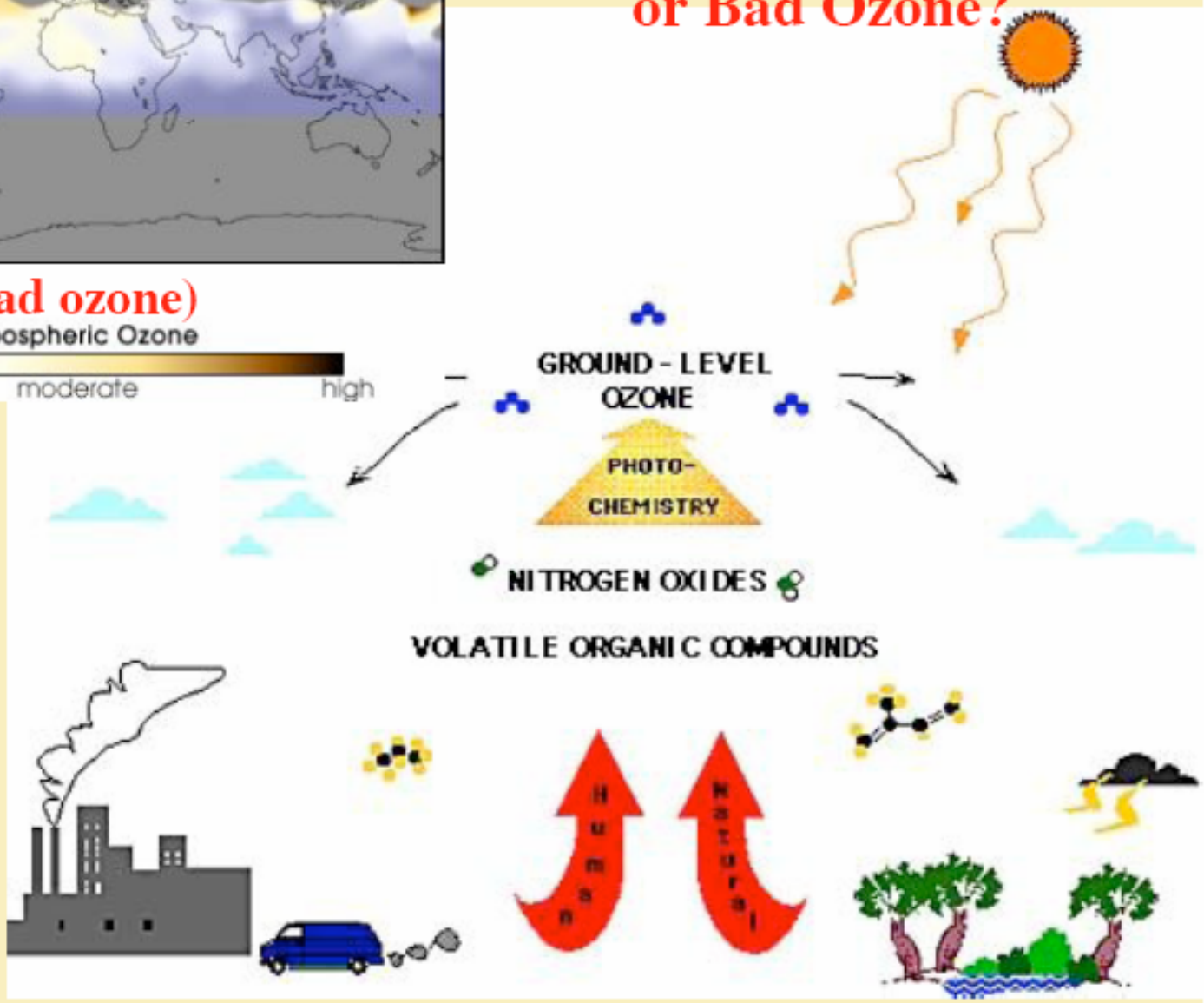


July 1, 1999

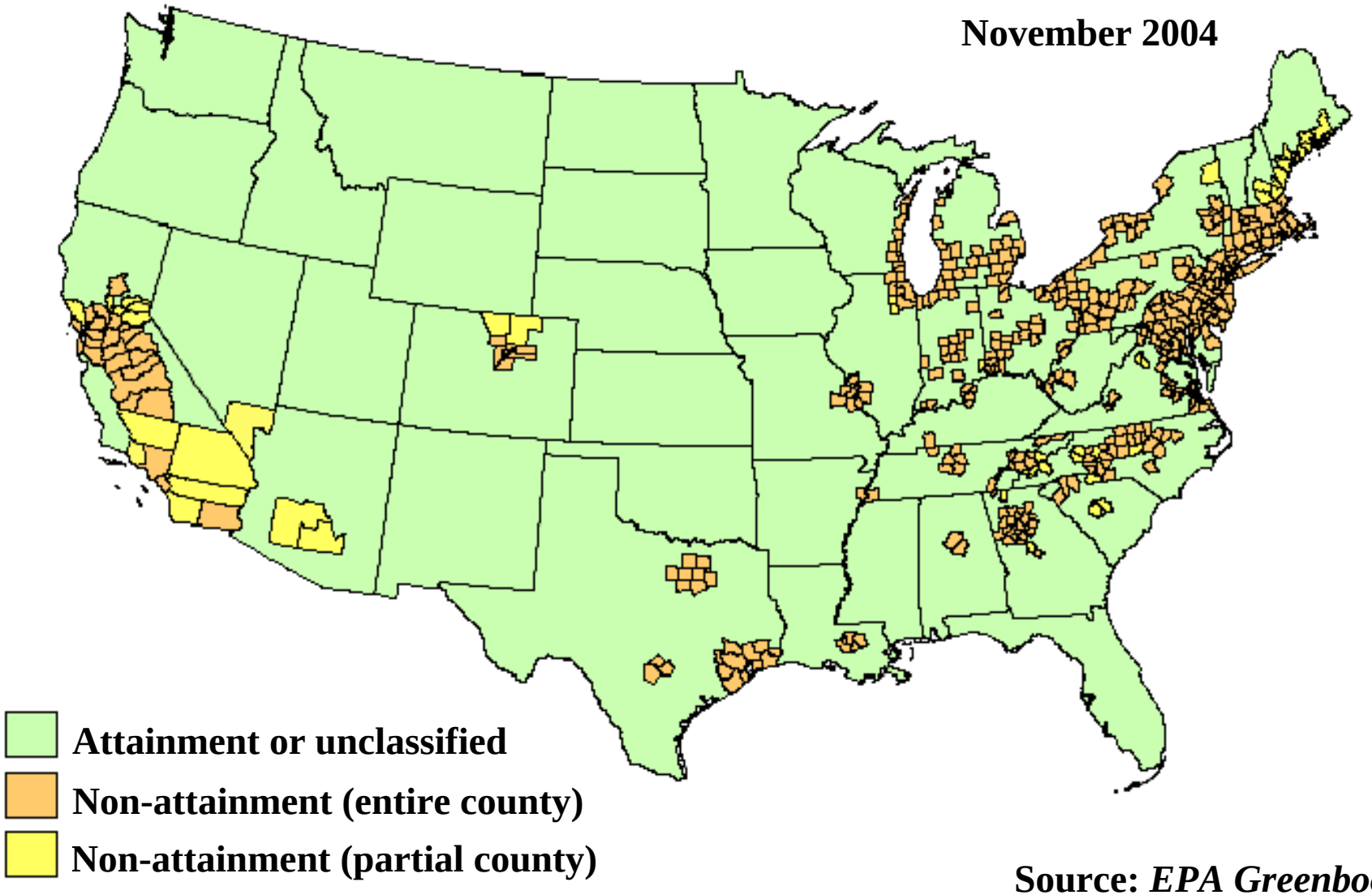
(bad ozone)

Tropospheric Ozone

low moderate high

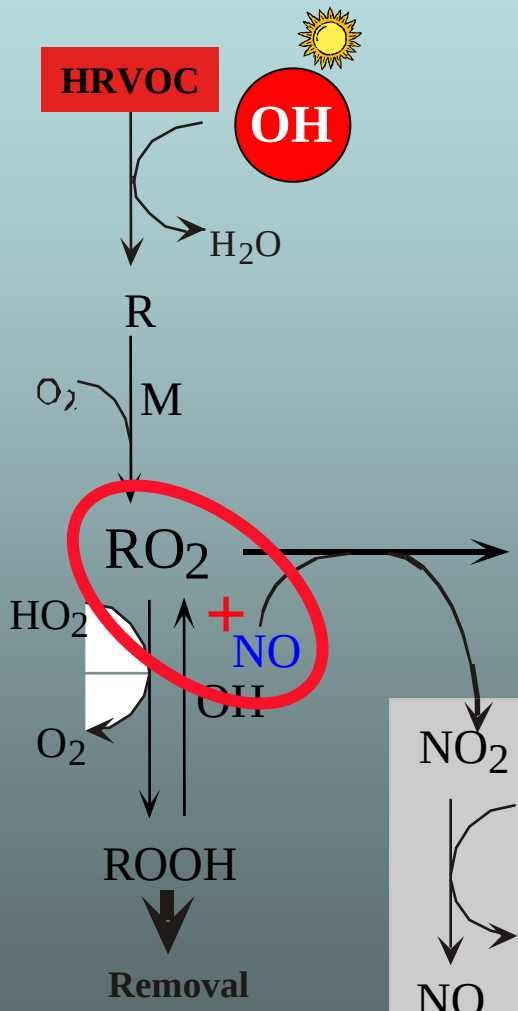


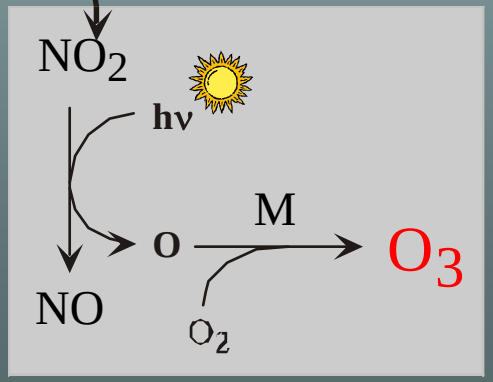
Attainment of 8-Hour Standard

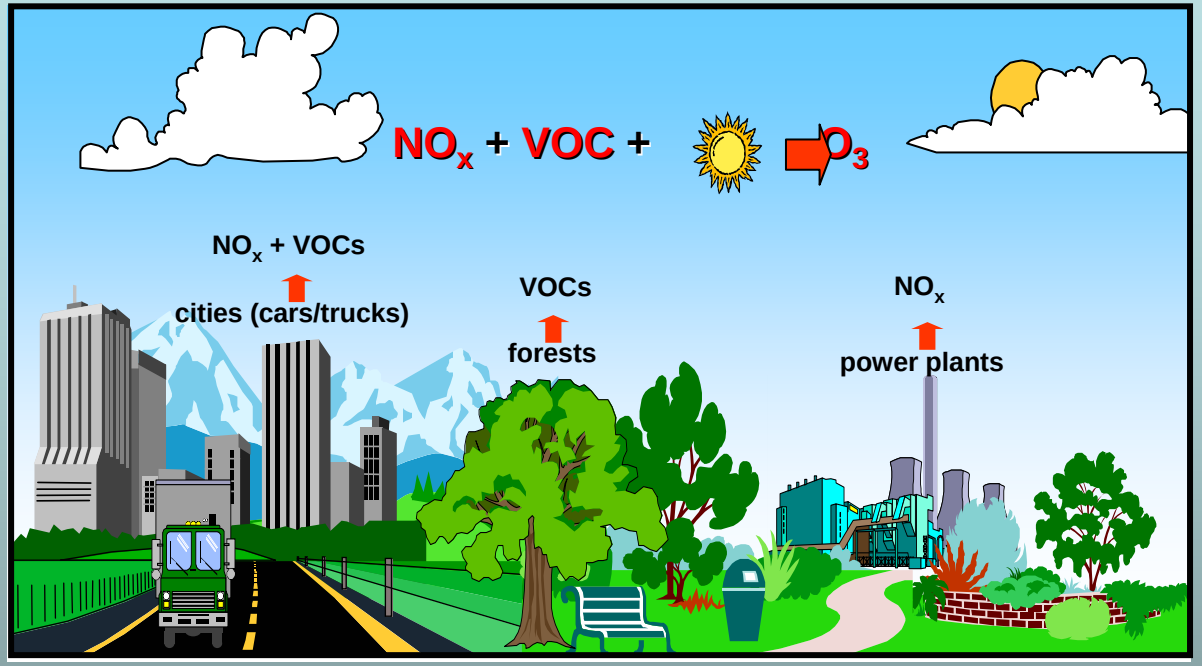


Source: *EPA Greenbook*

Lower Tropospheric Ozone Production







Uses up ozone

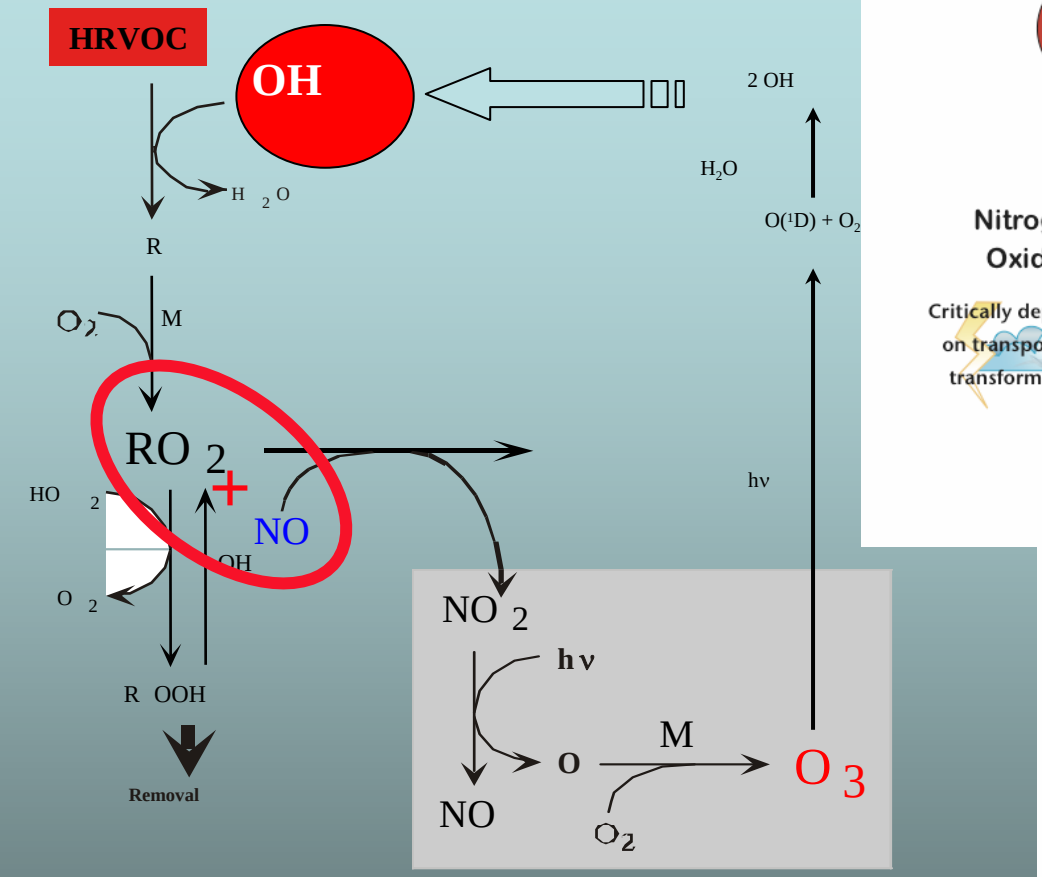
$$NO + O_3 \rightarrow NO_2 + O_2$$

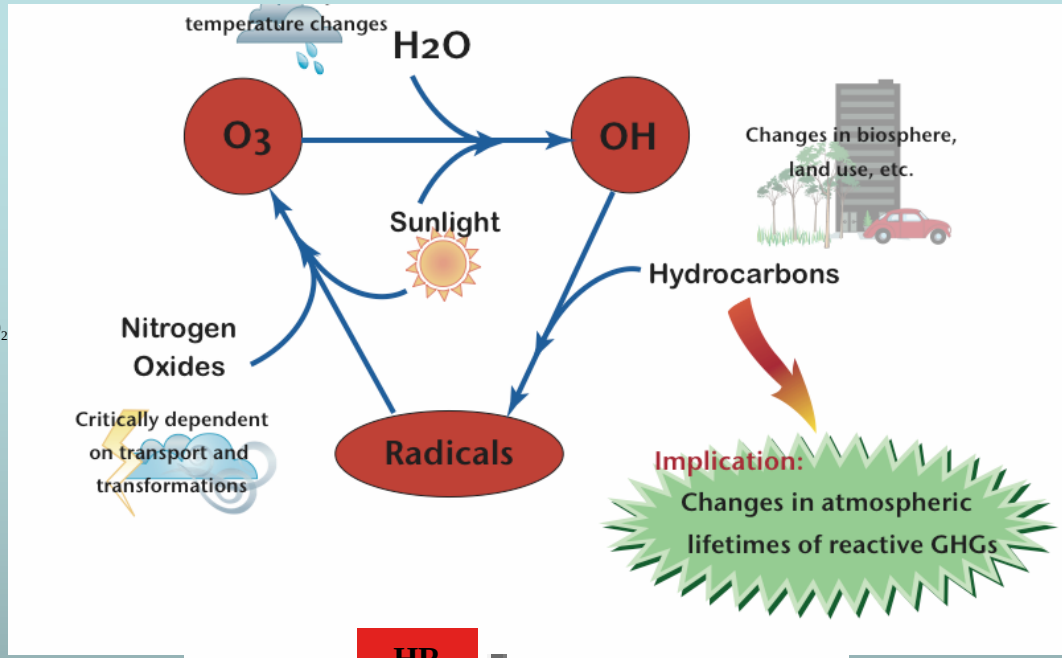
$$NO_2 + h\nu \rightarrow NO + O(^3P)(phot)$$

$$O(^3P) + O_2 + M \rightarrow O^3 + M(fast$$

Produces ozone

Tropospheric O_3 Production





$$OH + \text{HR VOC} \xrightarrow{O_2} RO_2\cdot + H_2O$$

$$RO_2\cdot + NO \rightarrow NO_2 + RO\cdot$$

$$RO\cdot + O_2 \rightarrow \text{carbonyls} + HO_2\cdot$$

$$HO_2\cdot + NO \rightarrow NO_2 + OH$$

$$NO + O_3 \rightarrow NO_2 + O_2$$

}Lowers ozone

$$NO_2 + h\nu \rightarrow NO + O(^3P)(\text{phot})$$

$$O(^3P) + O_2 + M \rightarrow O^3 + M(\text{fast})$$

}Increases ozone

Oxidation of hydrocarbons (RH) proceeds by a similar mechanism involving organic peroxy radicals (RO_2). A generic reaction sequence is

$$\text{(HRVOCs)}\ RH + OH \xrightarrow{O_2} RO_2 + H_2O \qquad \textit{(RG 6)}$$

$$RO_2 + NO \rightarrow RO + NO_2 \qquad \textit{(RG 7)}$$

+ hv -> NO + O_3

$$RO + O_2 \rightarrow R'CHO + HO_2 \qquad \textit{(RG 8)}$$

followed by *(RG 4)-(RG 5)*. Carbonyl compounds (here R'CHO) go on to react with OH, producing additional O_3. They may also photolyze to produce additional HO_x and branch the chain, as in the case of CH_2O:

$$CH_2O + h\nu \xrightarrow{2O_2} CO + 2HO_2 \qquad \textit{(RG 9)}$$

The chain is terminated by loss of HO_x, which takes place mainly by

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad \textit{(RG 10)}$$

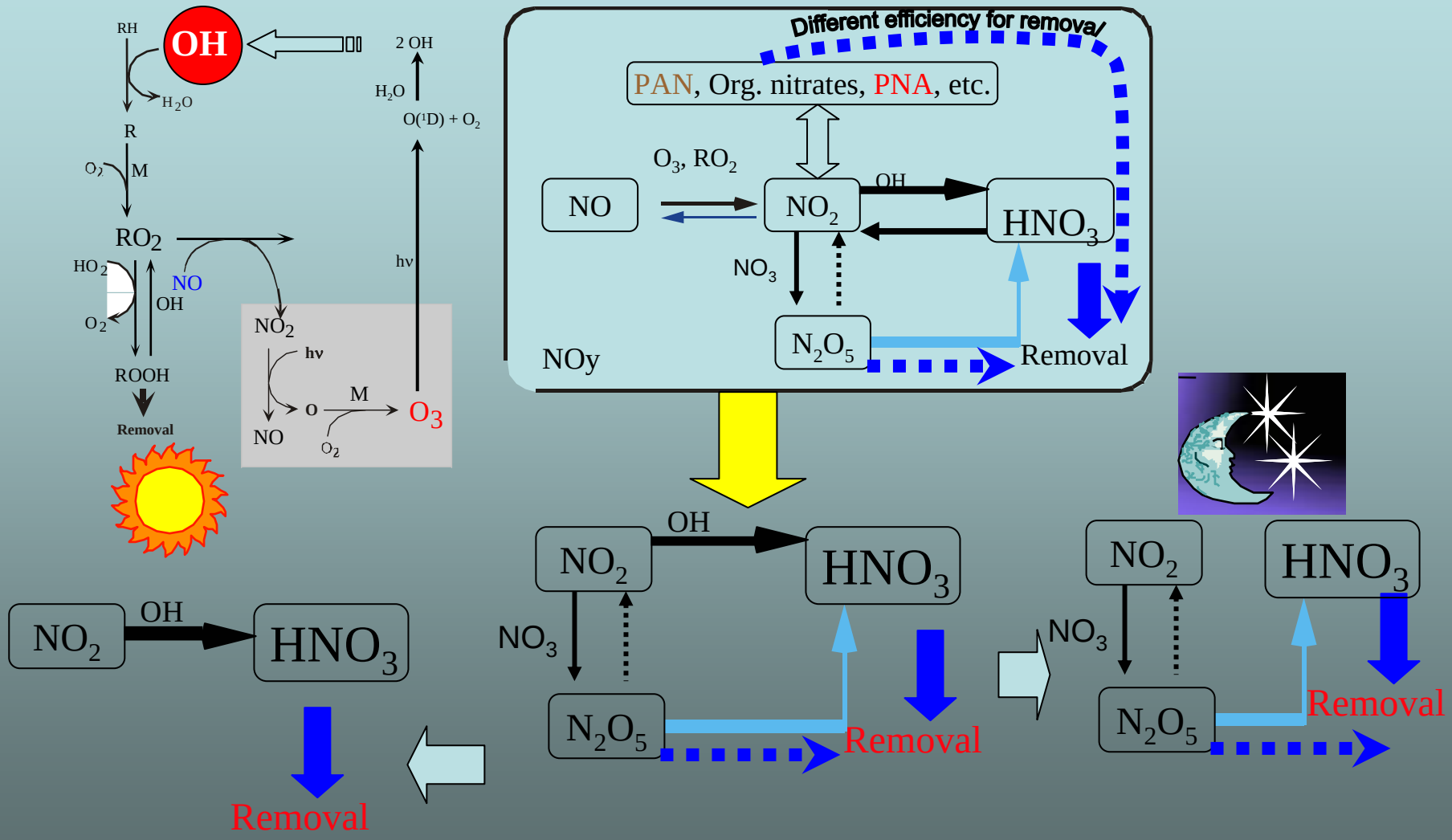
$$RO_2 + HO_2 \rightarrow ROOH + O_2 \qquad \textit{(RG 11)}$$

$$OH + HO_2 \rightarrow H_2O + O_2 \qquad \textit{(RG 12)}$$

$$NO_2 + OH + M \rightarrow HNO_3 + M \qquad \textit{(RG 13)}$$

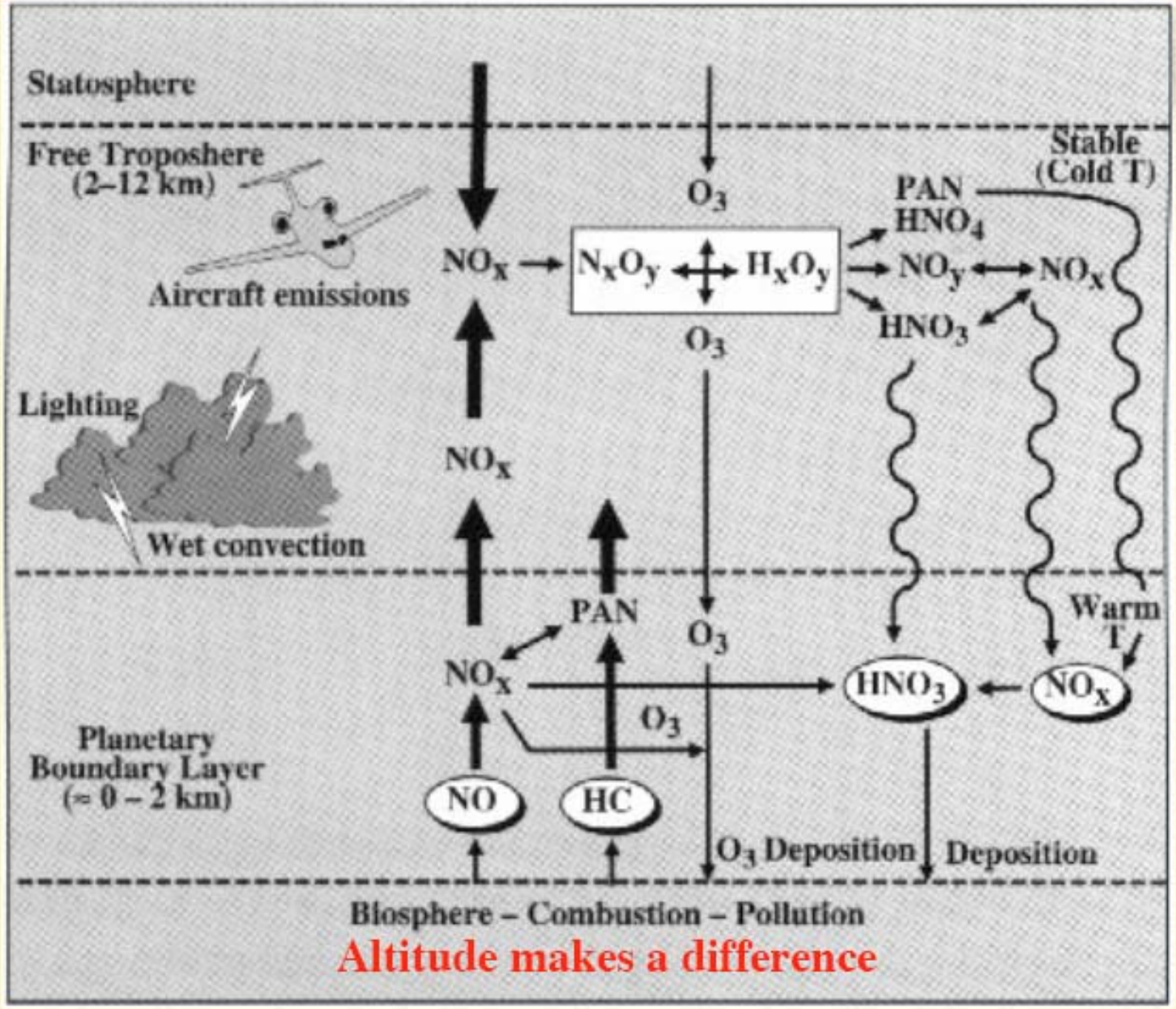
Importance of Nighttime Chemistry

Example: How nitrogen oxides can be removed from the troposphere



Nitrogen oxides removed during day AND nighttime

What are their relative efficiencies?



Altitude makes a difference

Environmental HRVOC Analysis

On-Site

Laboratory

traditional analytical scheme

Temp, wind speed, RH → GC, GC-MS

LSU Analytical Scheme

microFAST GC for HRVOCs
Temp, wind speed, RH

and

TD-GC-TOF-MS

HRVOCs are reactive compounds, can be lost in sample transport

	On Site Speciation	**Lab Speciation**
Pros	Larger number of analyses Real time feed-back No sample loss Less chance for contamination	Traditional approach Good QA/QC Controlled environment (GC-TOF-MS full scanning)
Cons	Difficult to do speciation Slightly less sensitive	Slow analysis Target compounds Possible sample alteration

- **HRVOCs (olefins) have half lives measured in minutes and are important ozone precursors**
- **VOCs (NMHC) are stable and less subjected to sample loss, also less important in ozone formation**

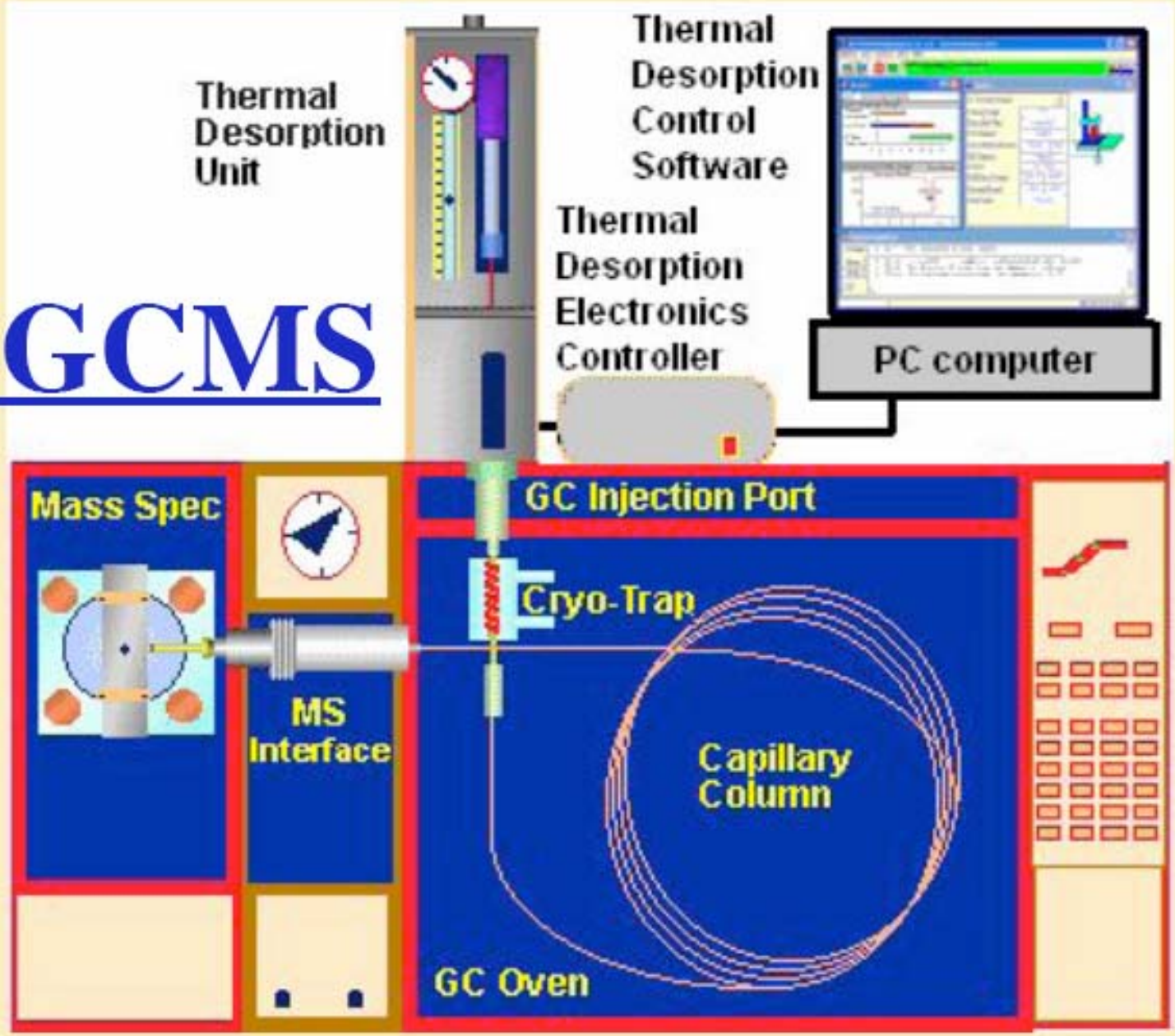
Target Compound GCMS Analysis uses SIM GCMS for sensitive detection of compounds on target list

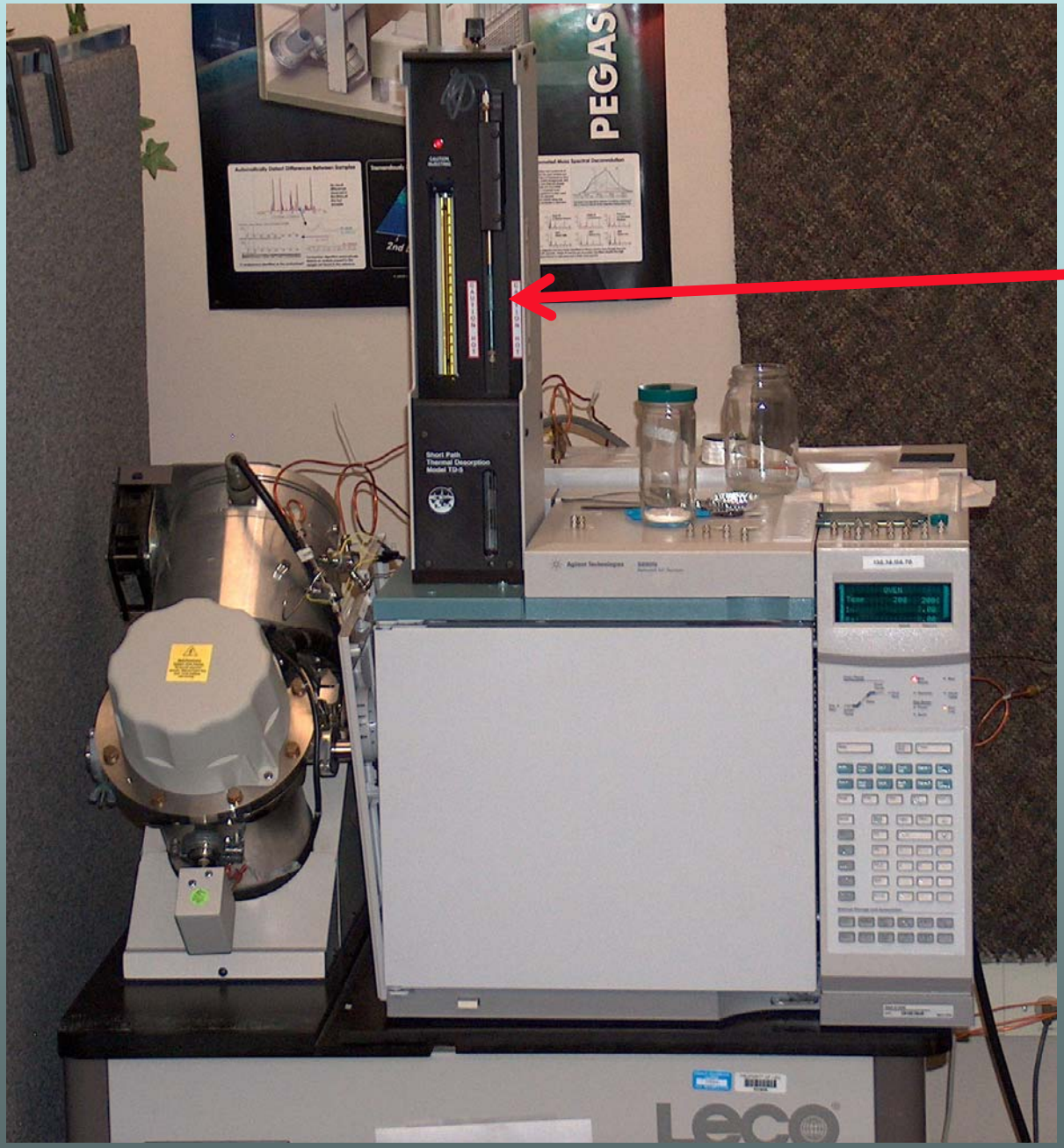
GC TOF-MS Analysis uses fast, full spectrum scanning for sensitive detection of any compound in sample

TD GCMS uses an adsorbent trap to collect compounds in a large volume of sample (typically 500 to 5000ml) over a 30–60 minute time period. Traps are taken to a lab where the compounds are thermally desorbed during the injection function of a GCMS analysis. Detection limits are in the <1 ppb range.

microFAST GC analysis collects a relatively small volume of sample (30–50ml) for on-site thermal desorption onto two capillary GC columns for rapid temperature programmed simultaneous separations using two different stationary phases with FID detection. Cycle time is 5 minutes, with detection limits of 10 ppb or less for C3+ compounds and 50 ppb for ethane/ethylene

TD-GCMS

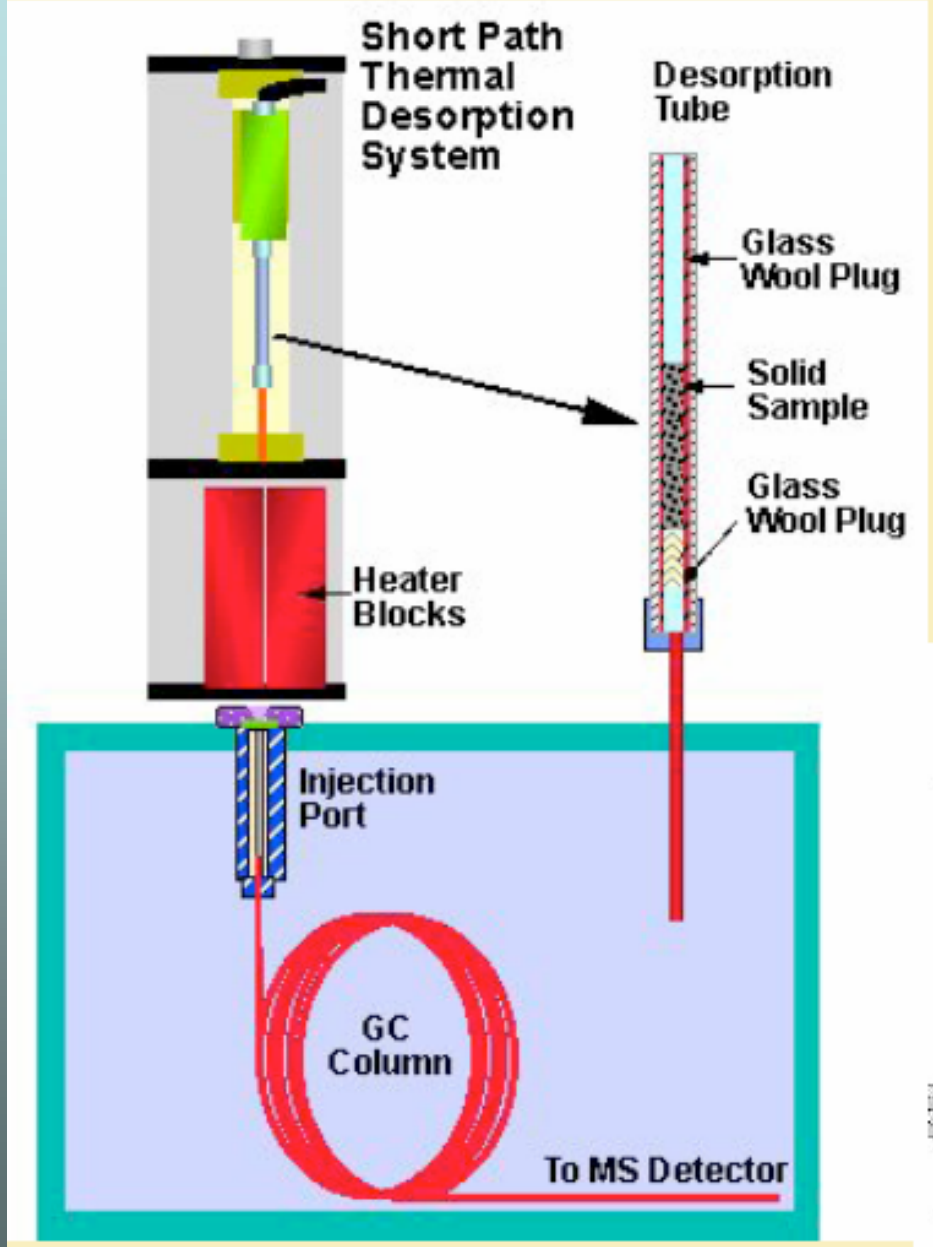

Thermal Desorption Unit
Thermal Desorption Control Software
Thermal Desorption Electronics Controller
PC computer
Mass Spec
GC Injection Port
Cryo-Trap
MS Interface
Capillary Column
GC Oven

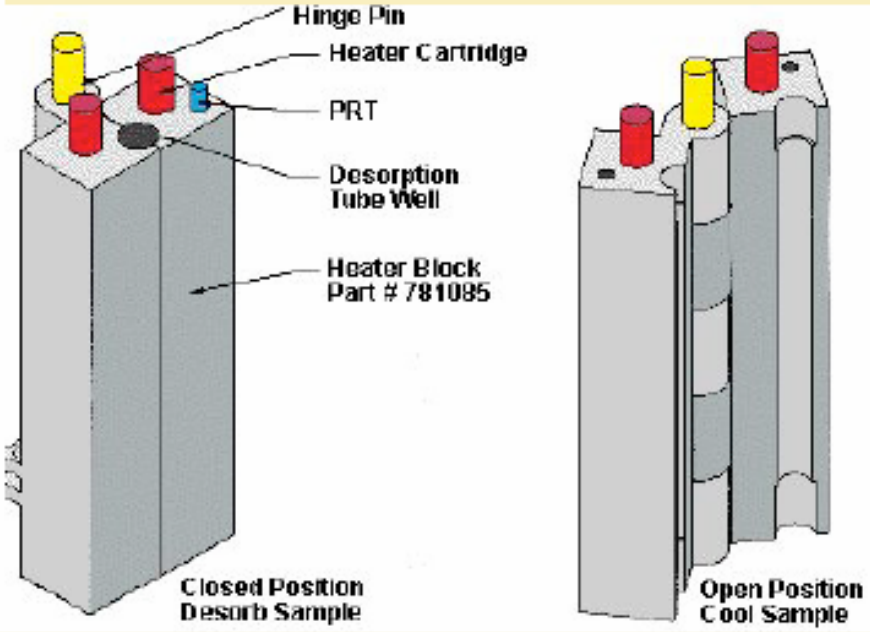


trap

Quad GCMS

TD-GC-TOFMS


Short Path
Thermal
Desorption
System
Desorption
Tube
Glass
Wool Plug
Solid
Sample
Glass
Wool Plug
Heater
Blocks
Injection
Port
GC
Column
To MS Detector


Hinge Pin
Heater Cartridge
PRT
Desorption
Tube Well
Heater Block
Part # 781085
Closed Position
Desorb Sample
Open Position
Cool Sample

Temperature	0	20	40	60	80	100	120	140	160	180	200	22
Methane	0.015	0.006	0.003	0.001								
Ethane	0.060	0.020	0.009	0.004	0.002	0.001						
Propane	0.528	0.147	0.048	0.019	0.008	0.004	0.002	0.001				
n-Butane	3.16	0.794	0.273	0.081	0.030	0.013	0.006	0.003	0.002	0.001		
n-Pentane	25.1	5.00	1.10	0.353	0.110	0.036	0.015	0.007	0.003	0.002	0.001	
n-Hexane	199	31.6	5.60	1.26	0.388	0.106	0.036	0.015	0.007	0.003	0.002	0.0

Adsorbents-Tenax TA

Temperature	0	20	40	60	80	100	120	140	160	180	200	22
1-Butene	2.50	0.550	0.150	0.050	0.019	0.008	0.004	0.002	0.001			
1-Pentene	25.0	4.50	1.00	0.263	0.085	0.031	0.012	0.005	0.002	0.001		
2-Pentene	32.0	6.00	1.30	0.35	0.110	0.038	0.015	0.006	0.003	0.001		
1-Hexene	158	23.0	4.30	1.00	0.285	0.088	0.029	0.011	0.005	0.002	0.001	
3-Hexene	205	28.0	5.10	1.20	0.315	0.096	0.032	0.012	0.005	0.002	0.001	
2-Hexene	240	32.0	6.00	1.30	0.342	0.101	0.034	0.013	0.006	0.002	0.001	

Trap Adsorbents

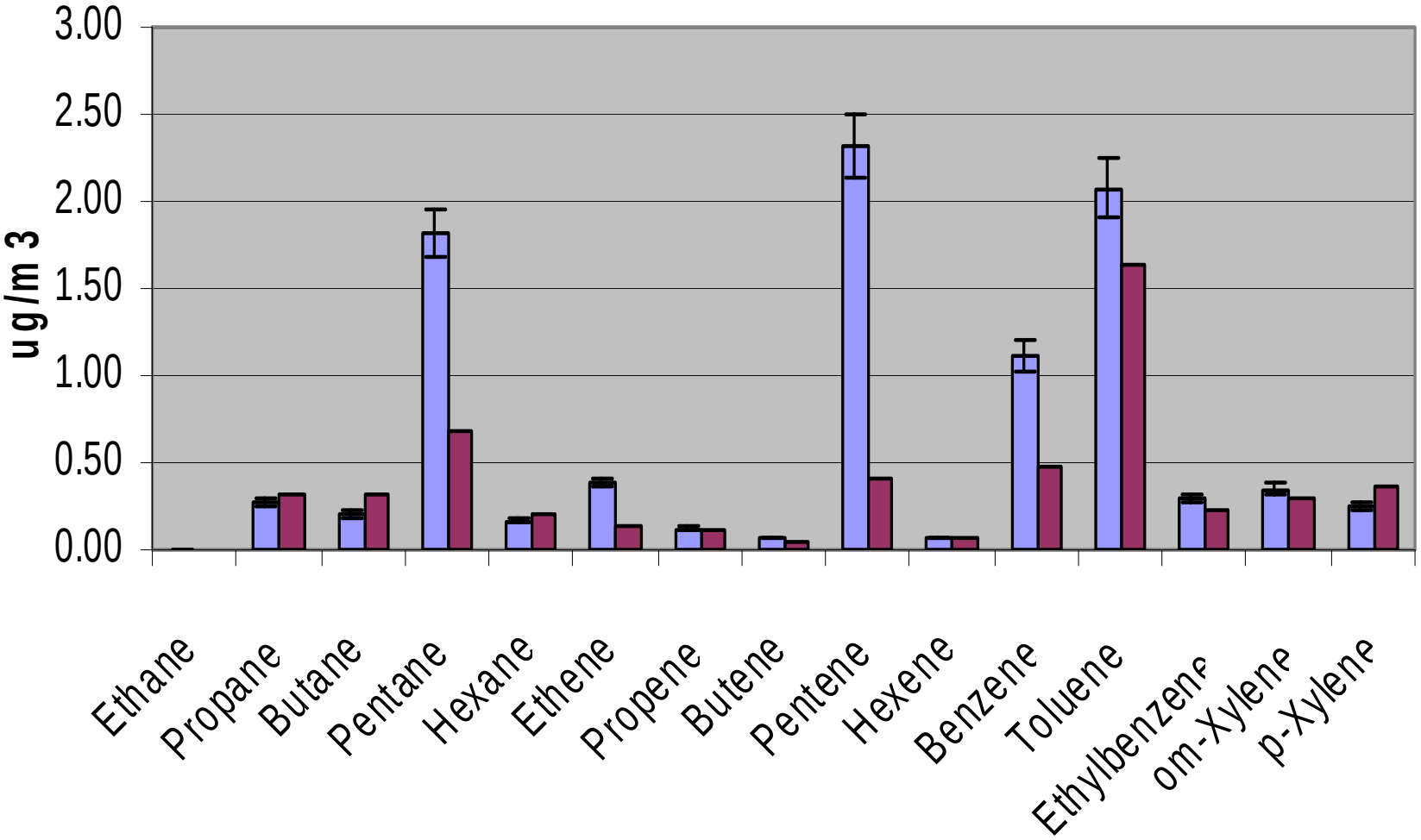
Carboxen 659

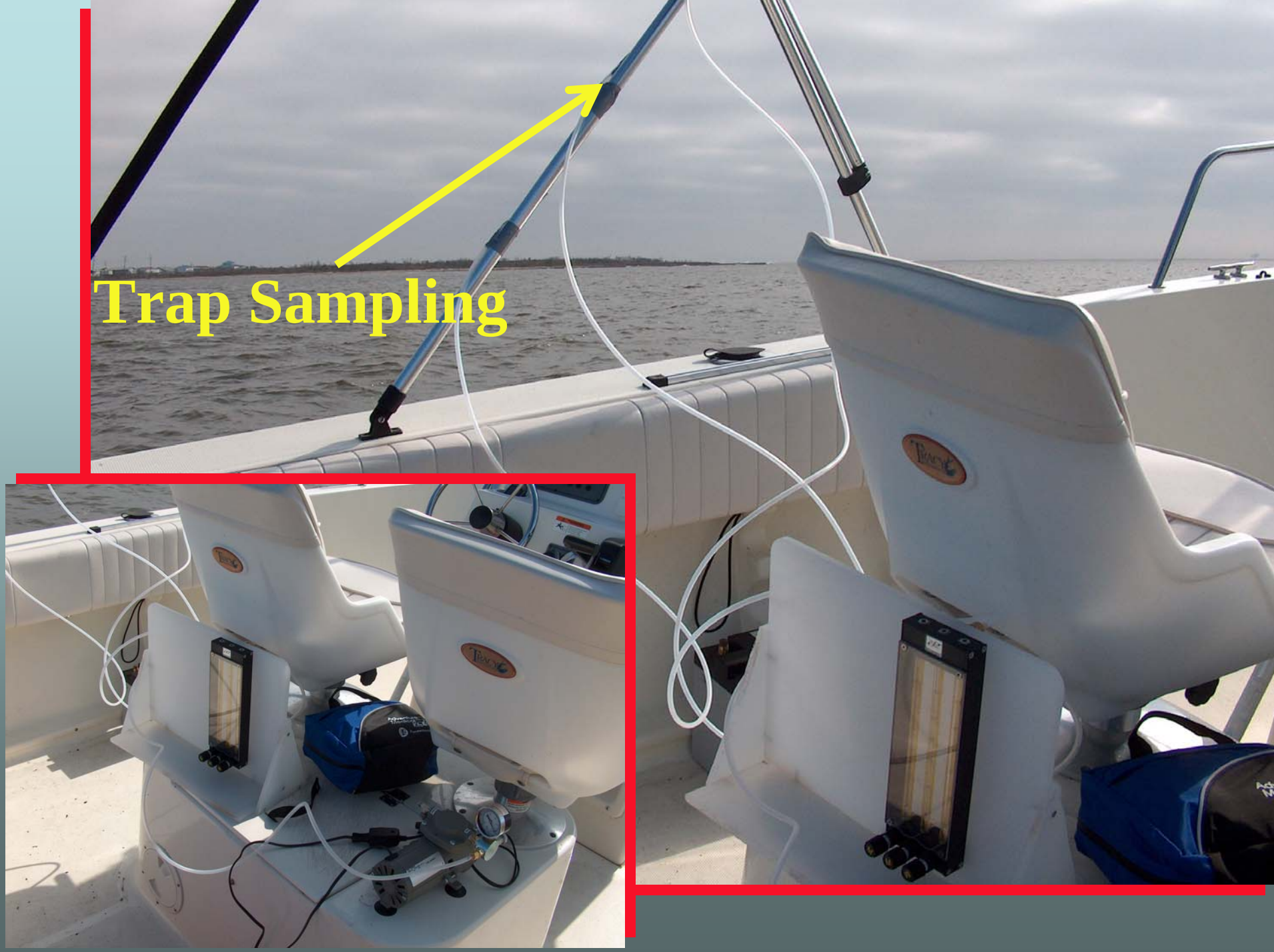
Temperature	0	20	40	60	80	100	120	140	160	180	200	220	240	260	280	300	320
Methane	0.050	0.035	0.025	0.018	0.013	0.010	0.008	0.006	0.005	0.004	0.003	0.002	0.002	0.001	0.001	0.001	
Ethane	0.800	0.500	0.300	0.200	0.119	0.080	0.050	0.320	0.021	0.021	0.011	0.008	0.006	0.005	0.004	0.003	0.00
Propane	6.00	3.00	1.60	0.900	0.510	0.300	0.180	0.100	0.060	0.060	0.024	0.014	0.009	0.006	0.005	0.004	0.00
Butane	50.0	25.0	10.0	5.00	2.50	1.30	0.700	0.350	0.180	0.180	0.048	0.025	0.014	0.009	0.007	0.005	0.00
Pentane	400	200	100	50.0	27.0	13.0	7.50	4.00	2.00	2.00	0.550	0.300	0.160	0.090	0.050	0.023	0.01
Hexane	6,000	2,600	1,200	650	320	160	80.0	40.0	20.0	10.0	5.10	2.80	1.40	0.750	0.379	0.205	0.11
Heptane	22,000	11,000	6,000	3,000	1,500	750	360	200	90.0	90.0	22.0	12.0	6.00	3.10	1.60	0.823	0.49

Carbosieve SIII

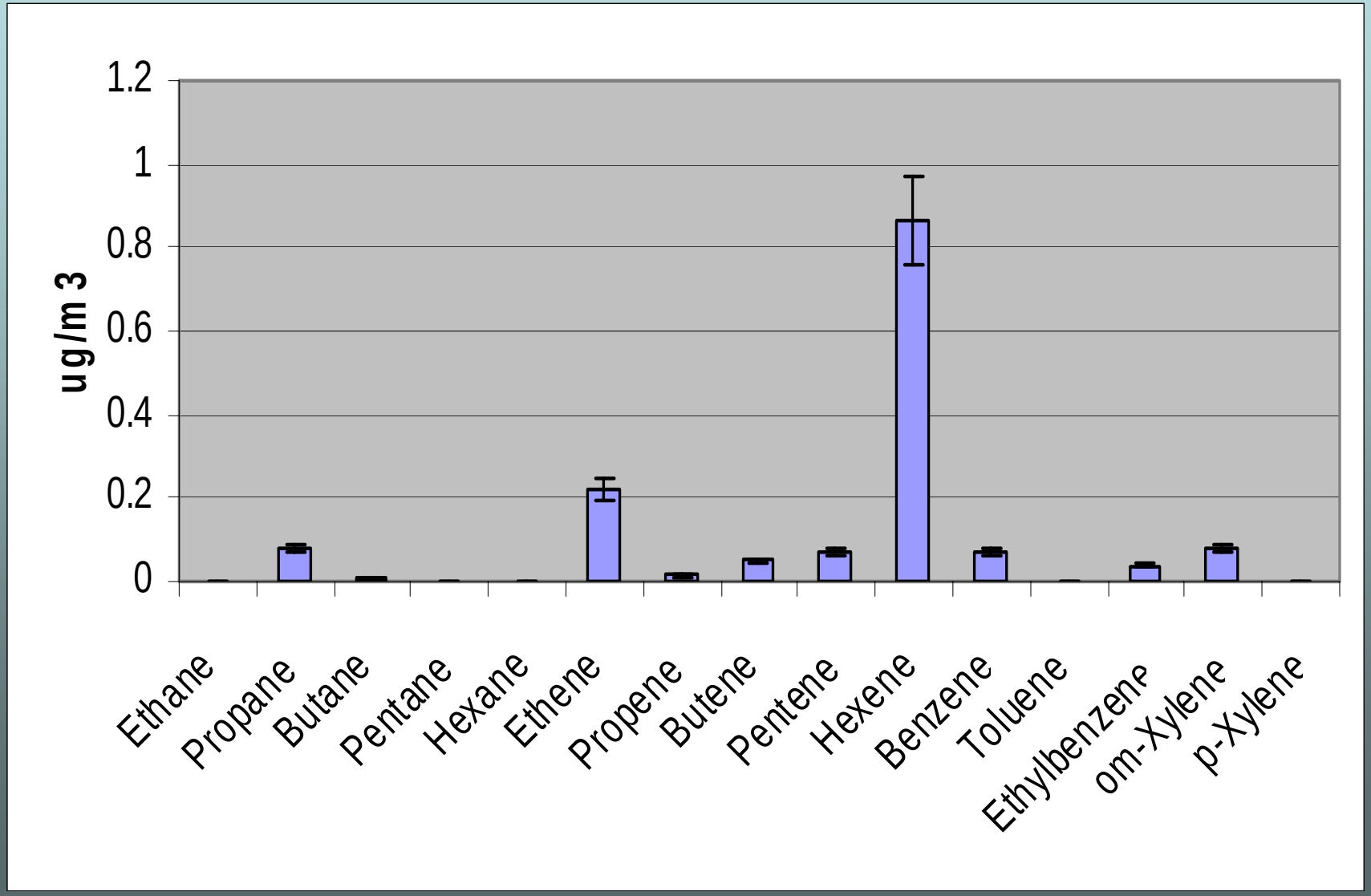
Temperature	0	20	40	60	80	100	120	140	160	180	200	220	240	260	280	300	320
Methane	0.140	0.090	0.059	0.032	0.018	0.011	0.008	0.005	0.003	0.002	0.001						
Ethane	2.00	1.20	0.800	0.510	0.330	0.210	0.140	0.091	0.055	0.035	0.023	0.014	0.010	0.007	0.005	0.003	0.002
Propane	14.0	8.50	5.30	3.40	2.20	1.40	0.900	0.600	0.400	0.230	0.150	0.100	0.060	0.042	0.023	0.016	0.01
Butane	100	63.0	40.0	23.0	15.0	10.0	6.00	3.80	2.30	1.30	0.580	0.560	0.340	0.210	0.137	0.083	0.052
Pentane	1,200	600	350	200	100	65.0	40.0	23.0	15.0	8.00	5.00	3.00	1.80	1.00	0.600	0.350	0.180
Hexane	10,000	5,000	2,500	1,200	600	350	180	90.0	50.0	30.0	20.0	10.0	6.00	3.80	2.10	1.20	0.600
Heptane	20,000	10,000	5,000	2,500	1,200	600	350	200	100	65.0	40.0	23.0	15.0	8.00	5.00	3.00	1.80

Baton Rouge Sites
TD-GC-TOFMS




Trap Sampling

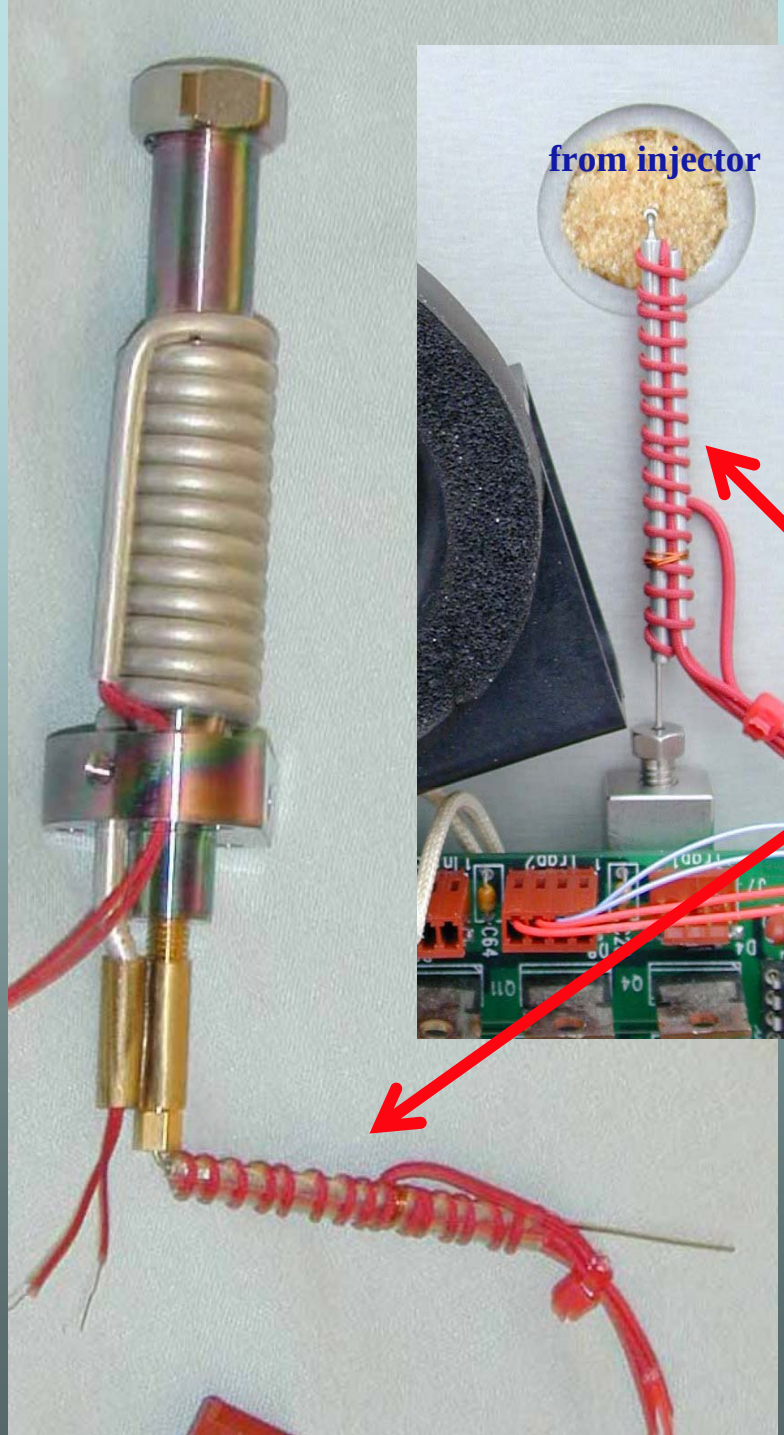
Grand Isle Site
TD-GC-TOFMS

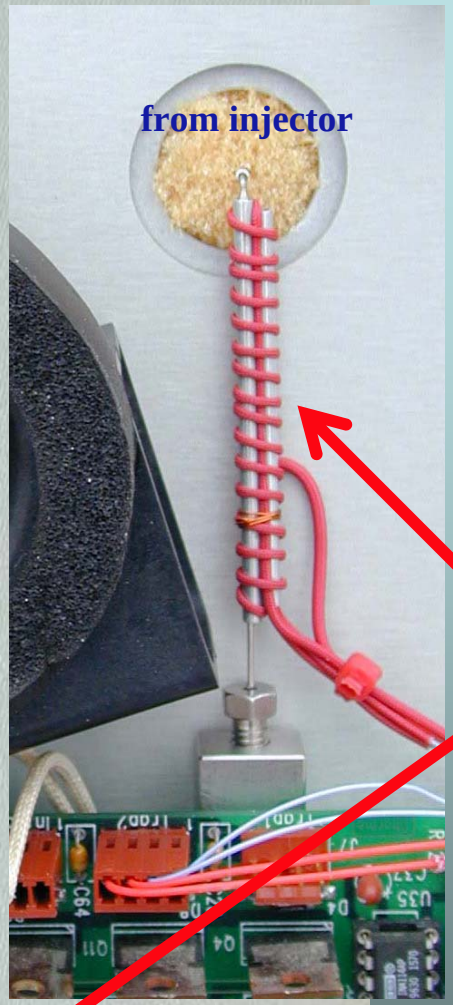


GC Utilities
microFAST GC
Analysis

microFAST GC & Portapack

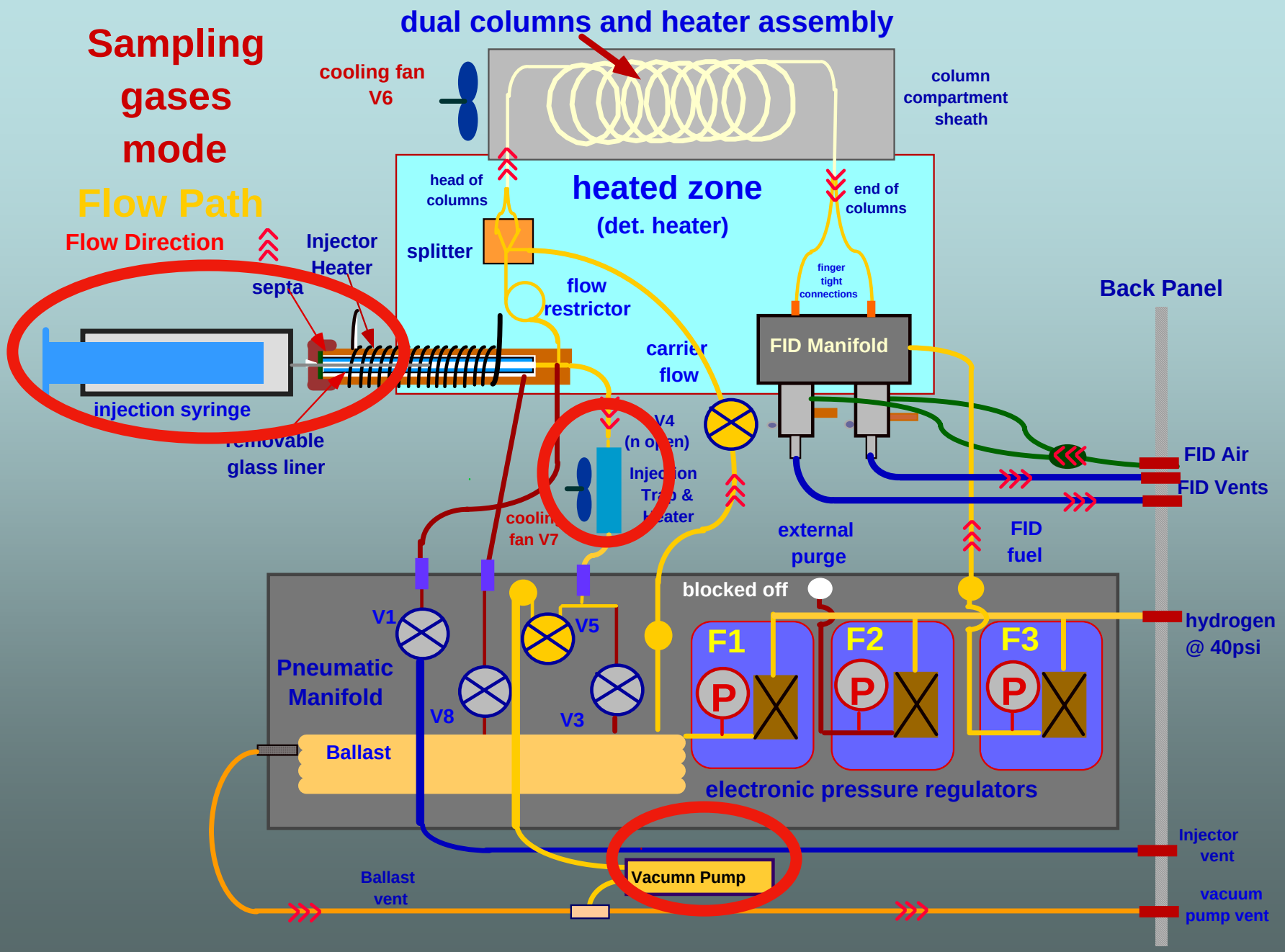
microFAST GC Trap/Injector

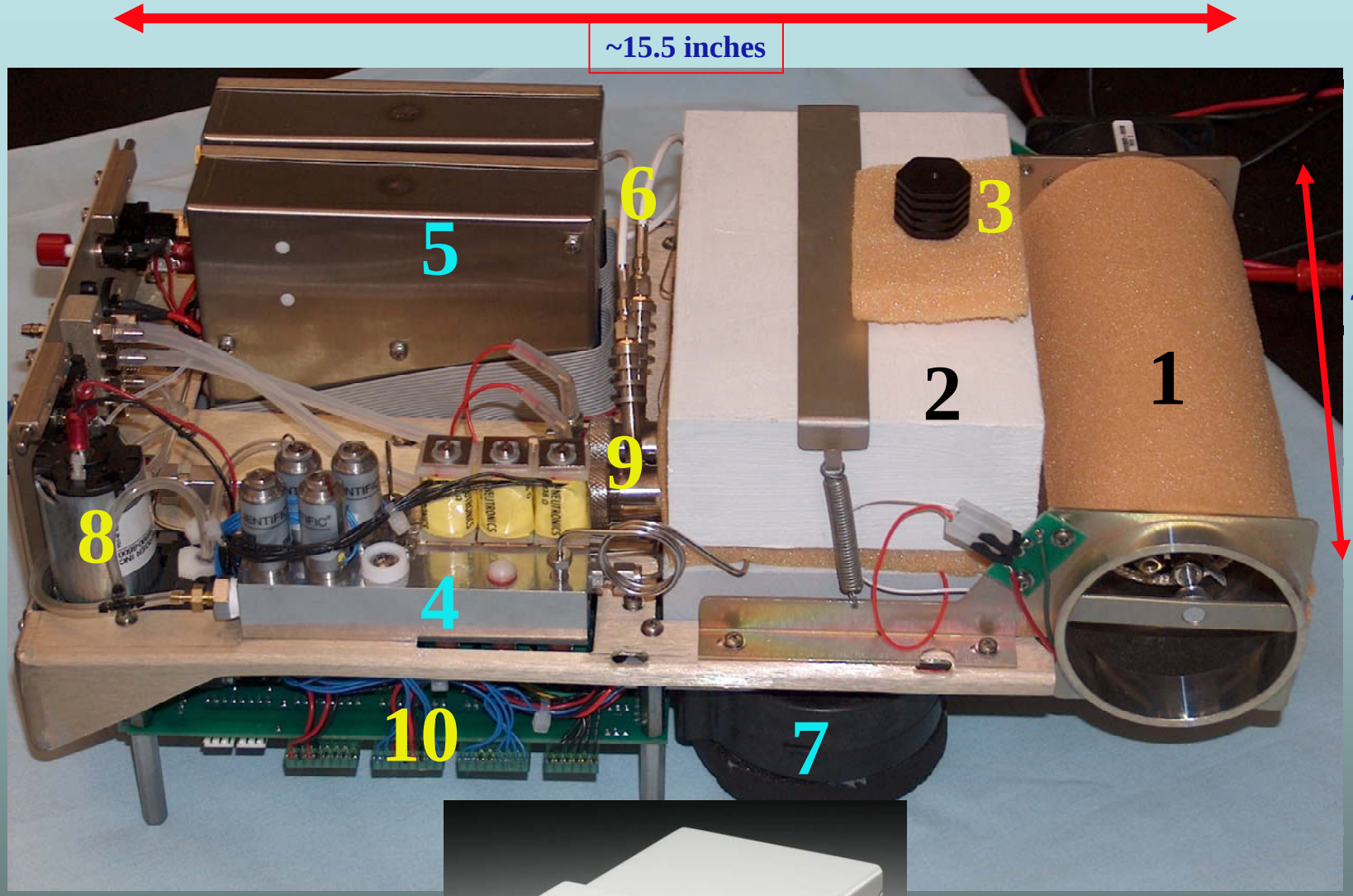




Trap &
heater

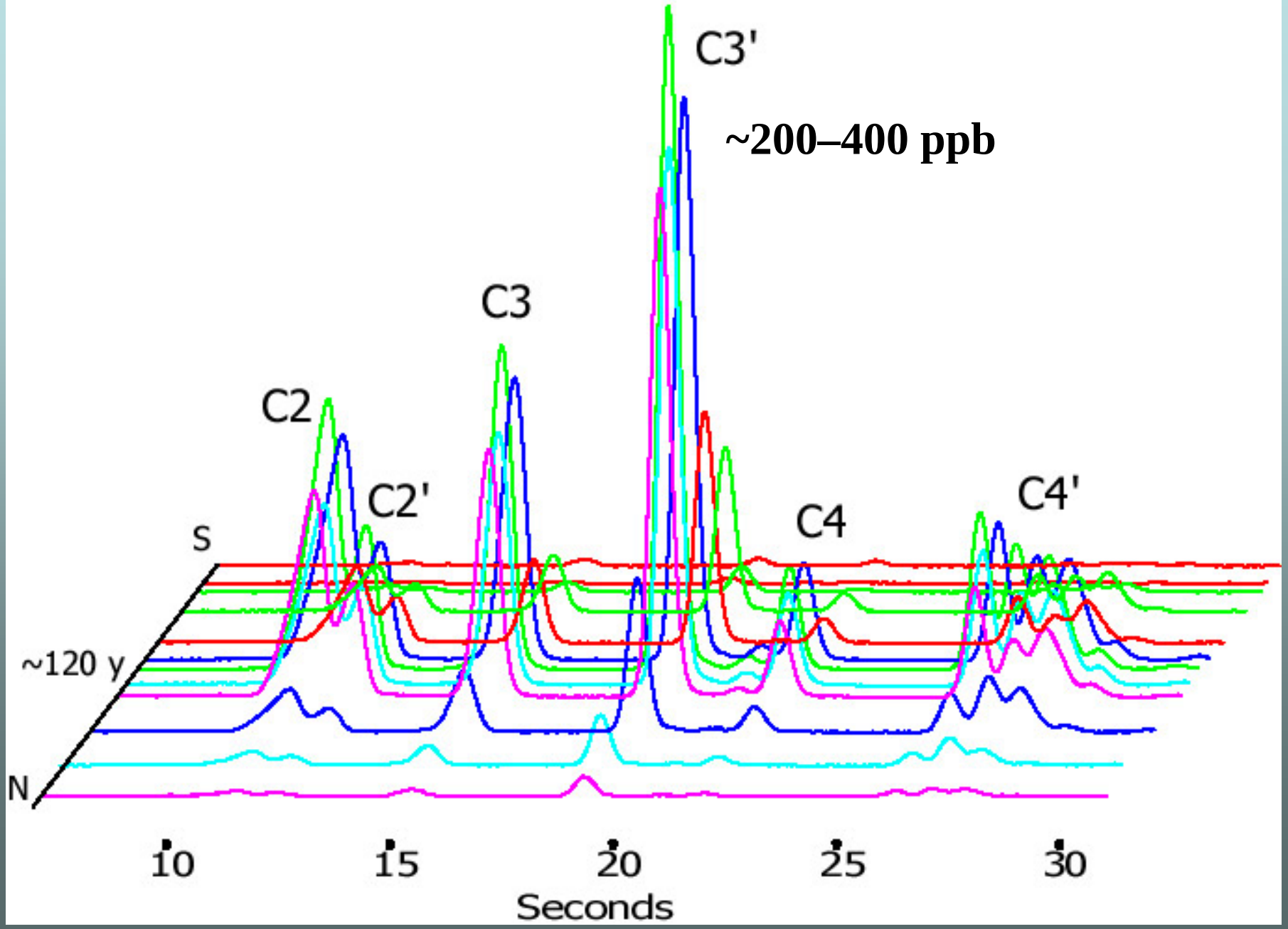
Sample Valve
for Continuous Sampling
of VOCs/HRVOCs


Sampling gases mode
Flow Path
Flow Direction
dual columns and heater assembly
cooling fan V6
column compartment sheath
heated zone
(det. heater)
head of columns
end of columns
splitter
Injector Heater
septa
flow restrictor
finger tight connections
Back Panel
carrier flow
FID Manifold
injection syringe
removable glass liner
V4 (n open)
Injection Trap & Heater
cooling fan V7
FID Air
FID Vents
external purge
FID fuel
blocked off
V1
V5
V8
V3
Pneumatic Manifold
F1
F2
F3
P
hydrogen @ 40psi
Ballast
electronic pressure regulators
Injector vent
Vacumn Pump
Ballast vent
vacuum pump vent

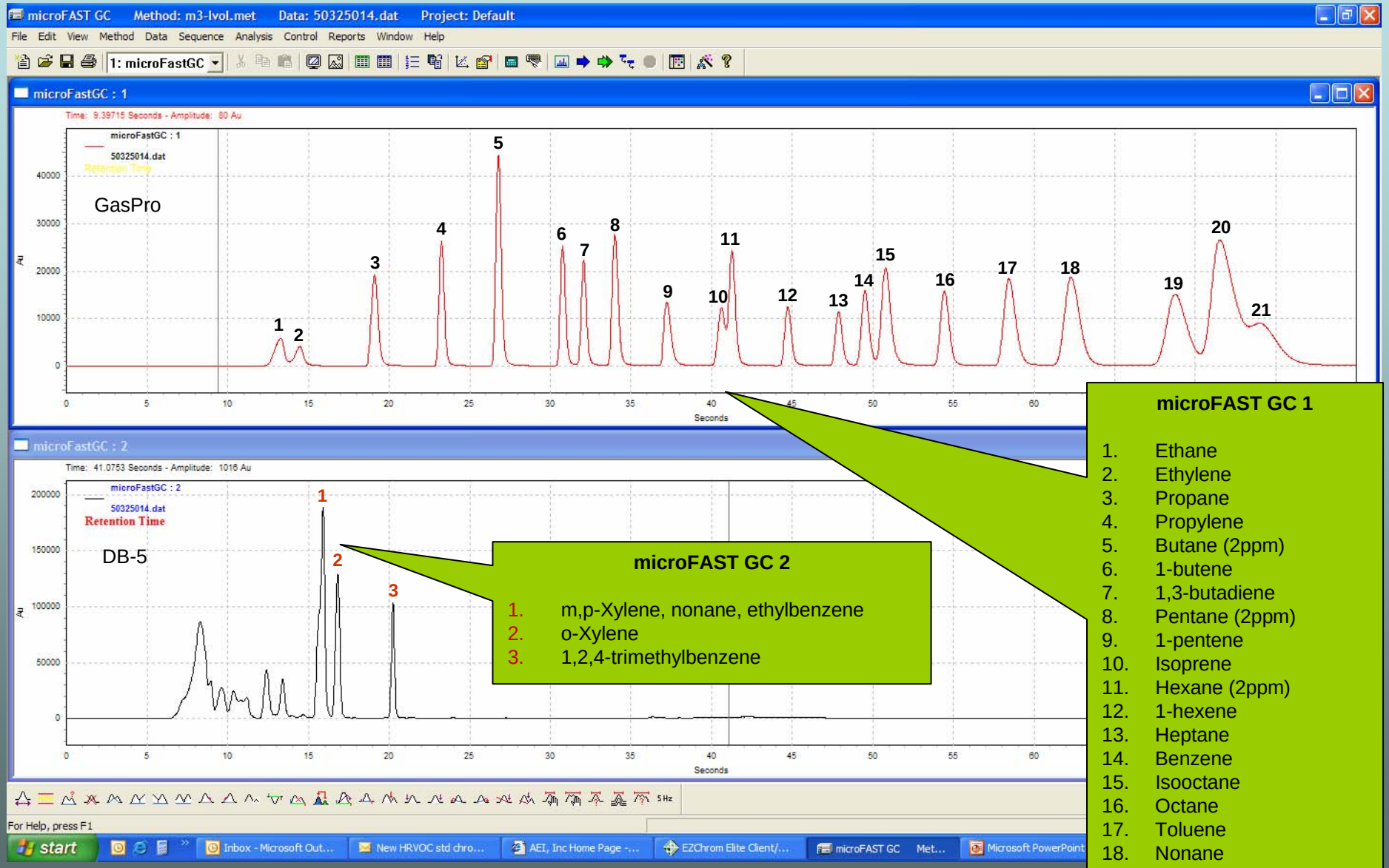


1 Column compartment
2 Isothermal heated zone
3 Injector cap
4 Pneumatic manifold
5 Electrometers
6 Electrometer cables
7 Trap fan
8 Sample pump
9 FIDs
10 Electronic board

microFAST GC Analysis of Soil Gas Across Baton Rouge Fault



HRVOC Component Identification



microFAST GC 2

1. m,p-Xylene, nonane, ethylbenzene
2. o-Xylene
3. 1,2,4-trimethylbenzene

microFAST GC 1

1. Ethane
2. Ethylene
3. Propane
4. Propylene
5. Butane (2ppm)
6. 1-butene
7. 1,3-butadiene
8. Pentane (2ppm)
9. 1-pentene
10. Isoprene
11. Hexane (2ppm)
12. 1-hexene
13. Heptane
14. Benzene
15. Isooctane
16. Octane
17. Toluene
18. Nonane
19. Ethylbenzene
20. m,p-Xylene
21. o-Xylene

Next Step: Collection and Analysis of Samples in the Summer of 2007