Emissions of SO_2, NO_x, and CO_2 from the Houston Ship Channel Measured by the NOAA WP-3

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1. Background

Importance of SO_2 and NO_x to Houston Air Quality:

- Photochemical oxidation of SO_2 is the key process regulating particle growth in the Houston area [*Brock et al.*, 2003].
- Colocated emissions of NO_x (NO_x = NO + NO_2) and hydrocarbons contribute to ozone formation and reduced air quality [*Ryerson et al.*, 2003].
- Fastest rates of ozone formation and highest yields are predicted when elevated concentrations of NO_x and hydrocarbons are both present.
- Important anthropogenic sources in the Houston urban area include:
  - Fossil-fuel electric power plants
  - Transportation sources
  - Industrial and petrochemical plants
  - Agricultural burning

Importance of the Houston Ship Channel:

- The Port of Houston is a 25-mile long complex that includes more than 150 private industrial companies along the Houston Ship Channel.
- The Houston Ship Channel is a major source of industrial pollution, including SO_2, NO_x, CO_2, CO, and hydrocarbons. It consists of numerous point sources that can be difficult to measure and quantify in inventories.

2. Emission Inventories

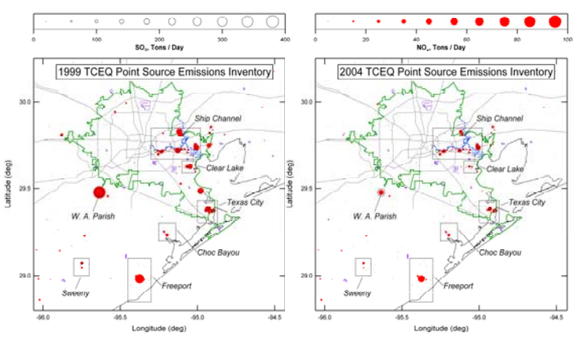
EPA Clean Air Markets Continuous Emissions Monitoring (CEMS) – 2006

- Hourly measurements of SO_2, NO_x, and CO_2 emissions for 130 fossil-fuel power plants and other large fixed-location pollution sources in Texas.

TCEQ Point Source Emissions Inventory – 1999 and 2004

- Annual average of SO_2, NO_x, CO, and hydrocarbon emissions for 1858 fixed-location pollution sources in Texas. Modified to include August 2005 CEMS data for power plants.

Figure 1. The TCEQ Point Source Emissions Inventory shows significant reductions in SO_2, NO_x, and CO for many Houston sources between 1999 and 2004



Reported Emissions in Tons / Day	SO_2	NO_x	CO
Ship Channel			
1999:	96	154	81
2004:	68	99	46
Change:	**-31%**	**-36%**	**-44%**
Clear Lake			
1999:	0.12	22	6
2004:	3.2	8	5
Change:		**-63%**	**-18%**
Texas City			
1999:	29	46	37
2004:	16	23	11
Change:	**-44%**	**-49%**	**-71%**
Chocolate Bayou			
1999:	0.20	11	5
2004:	0.16	10	6
Change:		**-16%**	**+17%**
Freeport			
1999:	7	54	6
2004:	7	32	5
Change:	**+3%**	**-41%**	**-16%**
Sweeny			
1999:	22	17	17
2004:	6	11	4
Change:	**-71%**	**-38%**	**-78%**
W. A. Parish			
1999:	185	90	24
2004:	147	17	20
Change:	**-21%**	**-87%**	**-17%**

Previous work shows that emission inventories may contain large errors. This is true for hydrocarbons [*Ryerson et al., 2003*], and may also be true for SO_2, NO_x, and CO. It is important to evaluate the accuracy of these inventories with independent measurements.

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3. Measurements by the NOAA WP-3 Aircraft

Measurements were acquired during September – October 2006 as part of the TexAQS-GoMACCS field campaign. The instrumented aircraft includes 1-second measurements of SO_2, NO_x, NO_y, CO_2, and CO.

Description of instruments and precision:

SO_2: UV-pulsed fluorescence; ±0.3 ppbv

NO, NO_2, and NO_y: NO/O_3 chemiluminescence, with photolysis to convert NO_2 to NO. NO_y measured by catalytic conversion of all nitrogen oxides to NO on a 300°C gold surface in the presence of CO; ±0.1 – 0.5 ppbv.

CO_2: Non-dispersive infrared absorption using a modified LICOR; ±0.4 ppmv.

CO: Vacuum ultraviolet fluorescence; ±0.3 ppbv.

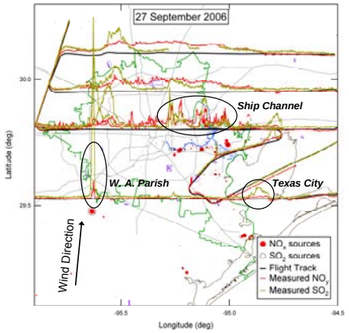


Figure 2. Measurements by the NOAA WP-3 can be used to attribute emissions to sources within the Houston urban region.

4. Urban / Mobile and Industrial Sources of NO_x

Emissions from urban and mobile sources can be distinguished from industrial sources by their characteristic emission ratios of NO_y and CO.

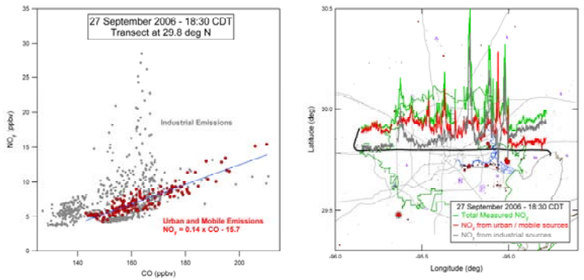


Figure 3. NO_y attributed to urban / mobile and industrial sources in the Houston area.

5. Quantifying Emissions From the Houston Ship Channel

The Houston Ship Channel contains many large point sources that are difficult to distinguish. We quantitatively examine the ship channel emissions in three geographical sections.

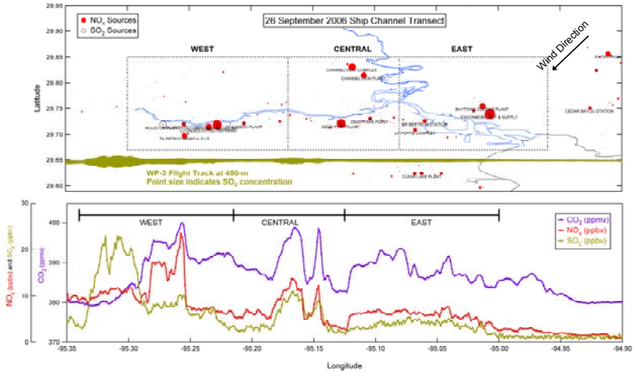


Figure 4. Map of the Houston Ship Channel and aircraft measurements.

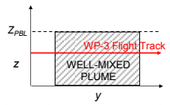
6. Absolute Fluxes From the Houston Ship Channel

We calculate the net flux from each section of the ship channel across a plane defined by the aircraft transect and perpendicular to the wind direction:

$$Net\ Flux = v\cos\alpha \int_0^{Z_{PBL}} n(z)\,dz \int_{-y}^{y} X_m(y)\,dy$$

where *y* and *z* are the cross-wind and vertical coordinates, *v* is a constant, uniform windspeed, *α* is the angle between aircraft track and the direction normal to the wind direction, X_m is the measured mixing ratio enhancement of species *m*, and *n* is the number density of the atmosphere [*White et al.*, 1976].

This can be represent graphically as:



The calculation assumes that the wind speed and emissions are constant between the time of emission and measurement, and that the boundary layer (BL) is well-defined and well-mixed. The close ship channel transects presented here may not be fully mixed, and this is a potential source of error.

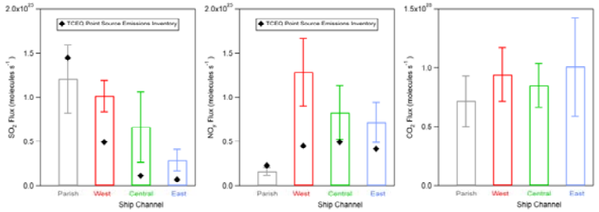
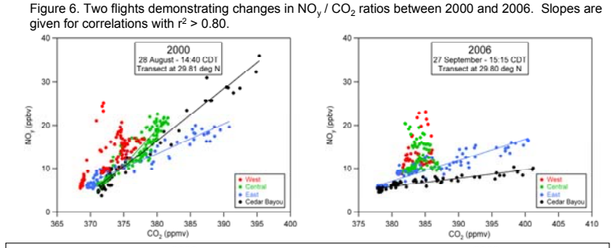


Figure 5. Absolute emission fluxes for the W. A. Parish power plant and sections of the ship channel, calculated for 9/19/2006, 9/25/2006, 9/26/2006, and 9/27/2006.

7. Emission Reductions in the Houston Ship Channel Between 2000 and 2006

The TCEQ Point Source Emissions Inventory and EPA Clean Air Markets CEMS data both report reductions in NO_x emissions from the ship channel between 2000 and 2006. We use emission ratios rather than absolute fluxes to examine changes between 2000 and 2006. The measurements show NO_x reductions for the east section of the ship channel and Cedar Bayou. The measurements also suggest NO_x reductions in the central section of the ship channel, but the high density of sources makes it difficult to quantify this.

Figure 6. Two flights demonstrating changes in NO_y / CO_2 ratios between 2000 and 2006. Slopes are given for correlations with $r^2 > 0.80$.



	2000	2006
● Central Ship	NO_y = **1.62** x CO_2 – 596	
● East Ship	NO_y = **0.68** x CO_2 – 244	NO_y = **0.49** x CO_2 – 178
● Cedar Bayou	NO_y = **1.19** x CO_2 – 437	NO_y = **0.19** x CO_2 – 67

8. Conclusions

- The Houston Ship Channel is an important source of NO_x, SO_2, and CO_2 in the Houston urban area.
- Integrated fluxes suggest that the TCEQ Point Source Emissions Inventory may underestimate SO_2 and NO_x emissions from the ship channel. These results could be better confirmed if CO_2 was included in the emissions inventory.
- Significant reductions in NO_x emissions are observed between 2000 and 2006. These are attributed to improved emission controls for point sources.
- The high density of industrial sources in the Houston Ship Channel makes it difficult to identify emissions from individual sources. Additional analysis is necessary to fully characterize the ship channel emissions.

References

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