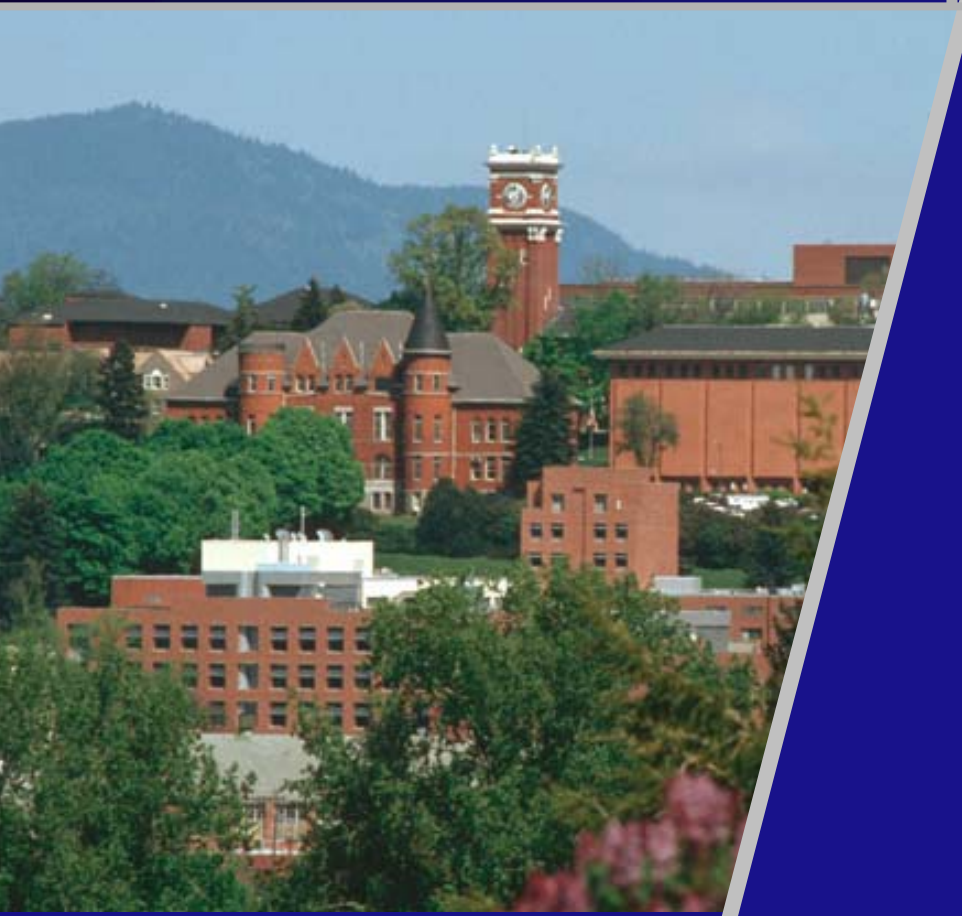


VOC, Aerosol, and Energy Fluxes at the Urban Tower in MILAGRO 2006

Objectives

1) investigate atmosphere/surface exchange of gases, aerosols & energy over the urban landscape

2) evaluate the Mexico City emission inventory through direct measurement of emissions

Direct emissions measurements

- Remote sensing
- Stack measurements
- Emission profiles of different sources
- **Micrometeorological techniques**
  - **Eddy covariance (EC)**
  - **Disjunct Eddy Covariance (DEC)**
  - **Disjunct Eddy Accumulation (DEA)**
  - **Gradient method**
  - Relaxed eddy covariance
- Tracer ratio point sources
- Tunnel studies
- Vehicle chasing

MILAGRO Field Campaign
(March 6 to 30, 2006)

VOCs

EC & FOS → olefins

DEC & PTR-MS → toluene, benzene, other aromatics and oxygenated VOC

DEA & GC-FID → specific hydrocarbons

Other trace gases

Gradient method & non-dispersive infrared photometer → CO

Gradient method & LICOR LI-6262 → CO_2

EC & IRGA → CO_2 & H_2O

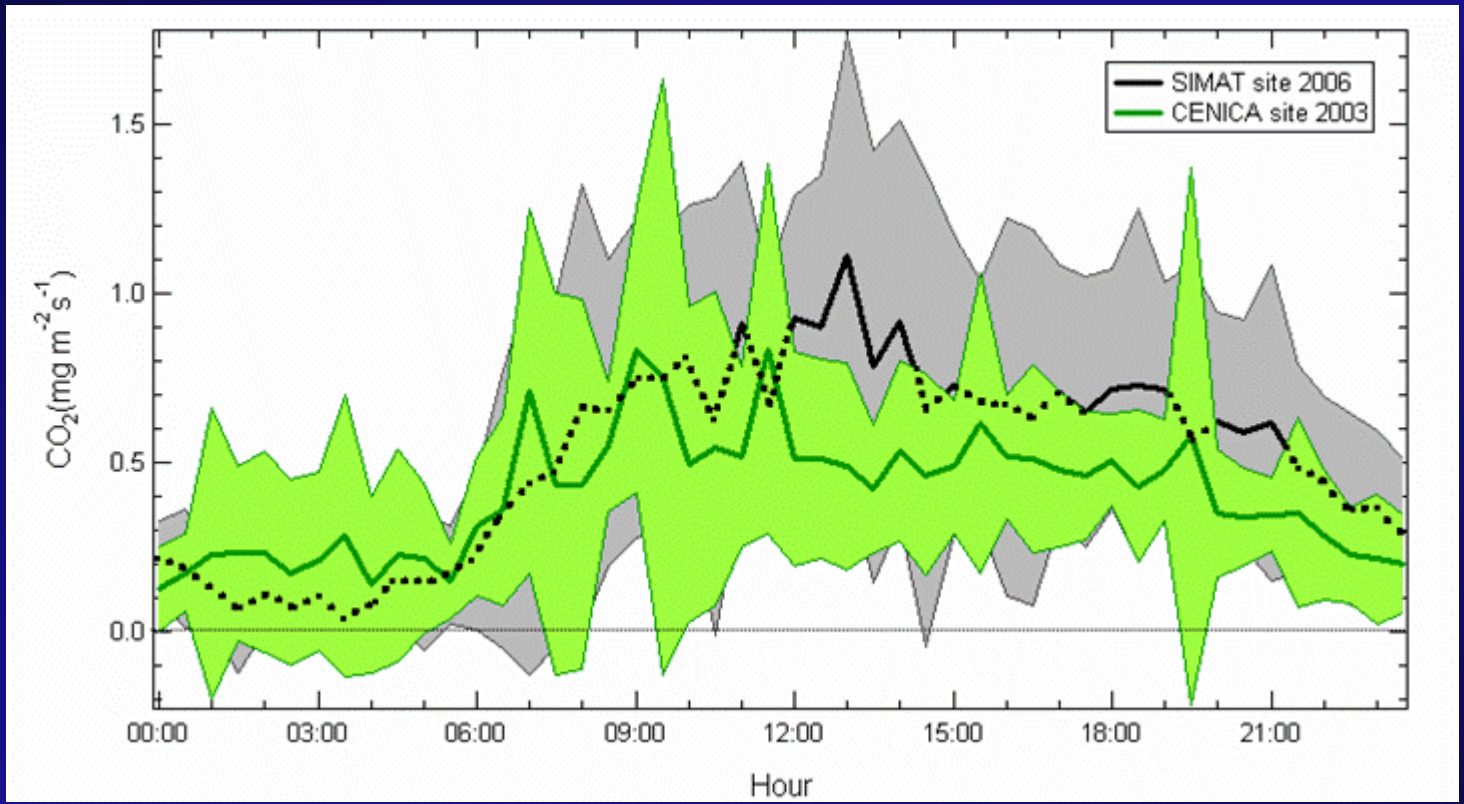
Aerosols

EC & AMS → Sulfates, nitrates, organics, ammonium

Energy and momentum

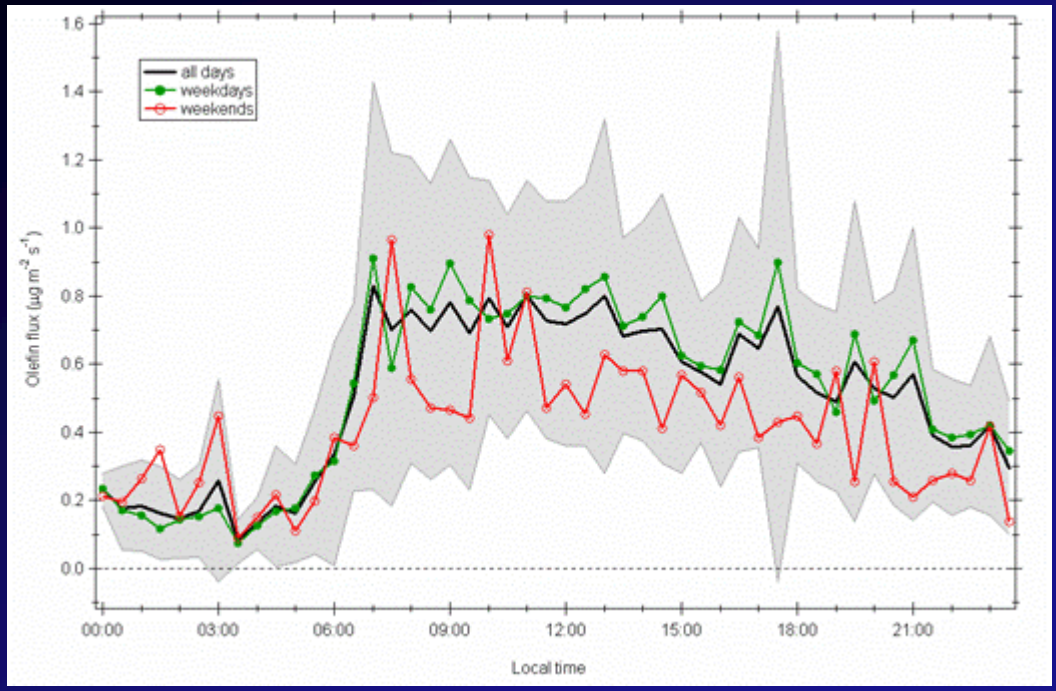
EC & sonic, IRGA, net radiometer → *Q**, *Qh*, *Qe*, *u**

CO_2 fluxes in 2003 and 2006



2006/2003 average daily flux= 1.24

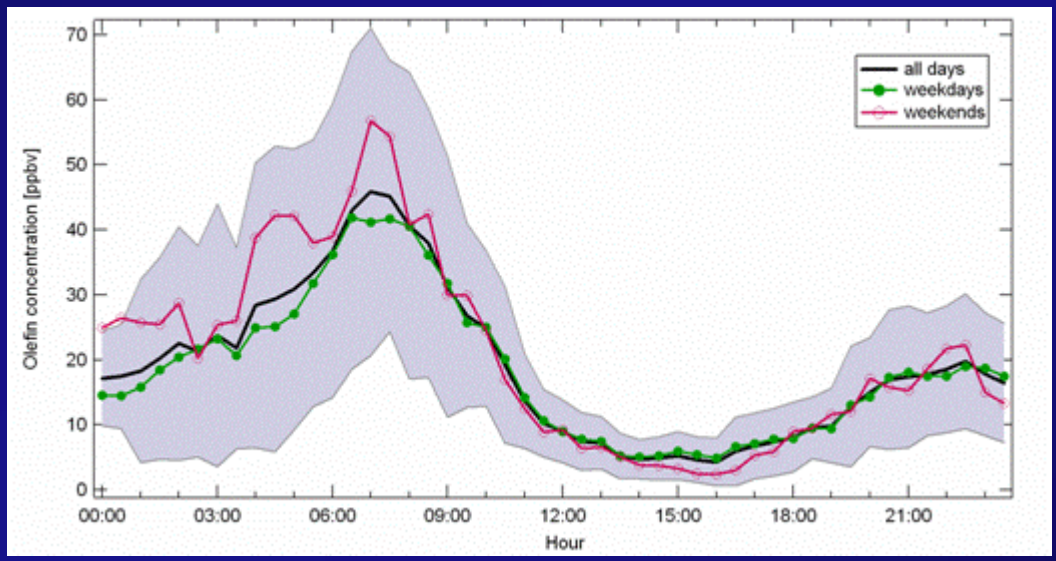
The grey shadow represent ±1 standard deviation from the total averages



Fast olefin sensor (FOS) in EC mode
(Hills Scientific Fast Isoprene Sensor)

Fluxes

2006/2003 = 1.4

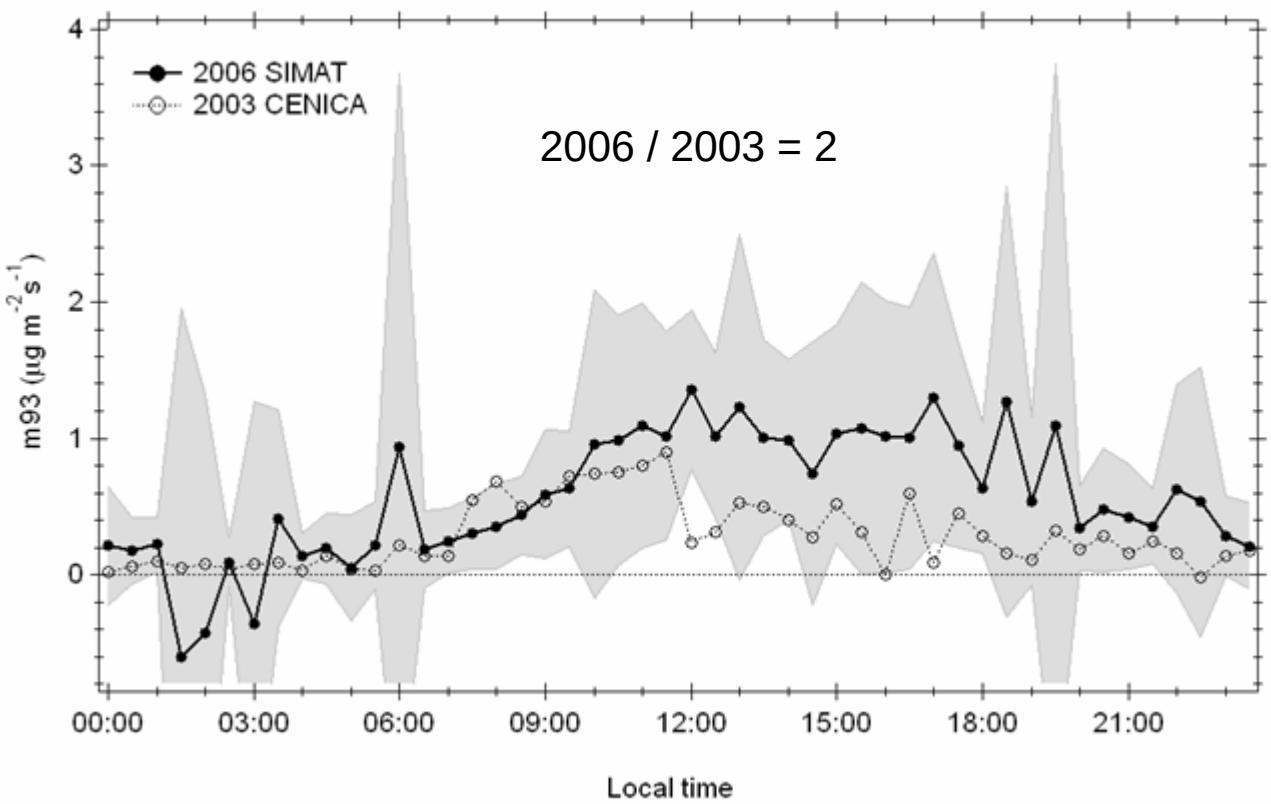


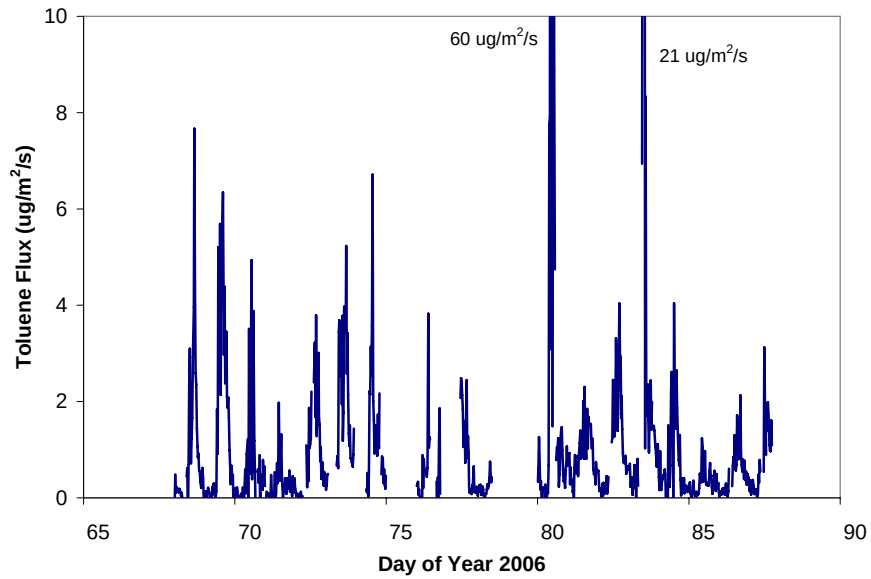
Olefin measurements

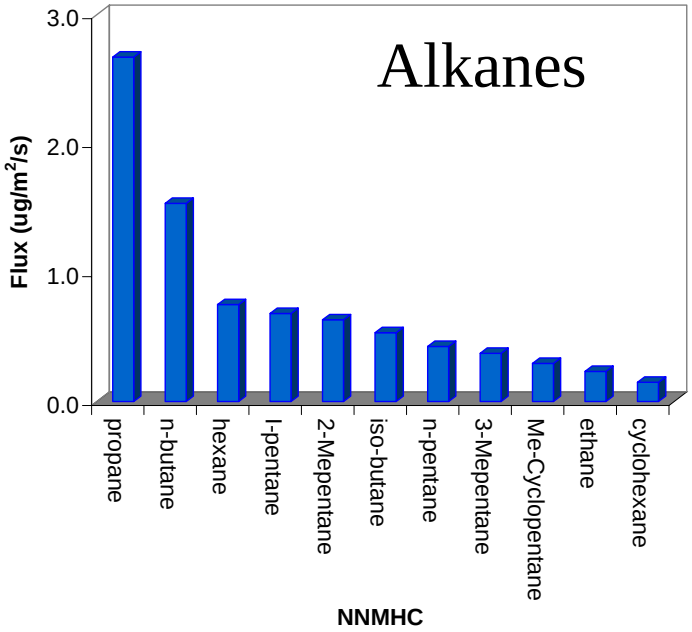
Ambient concentration

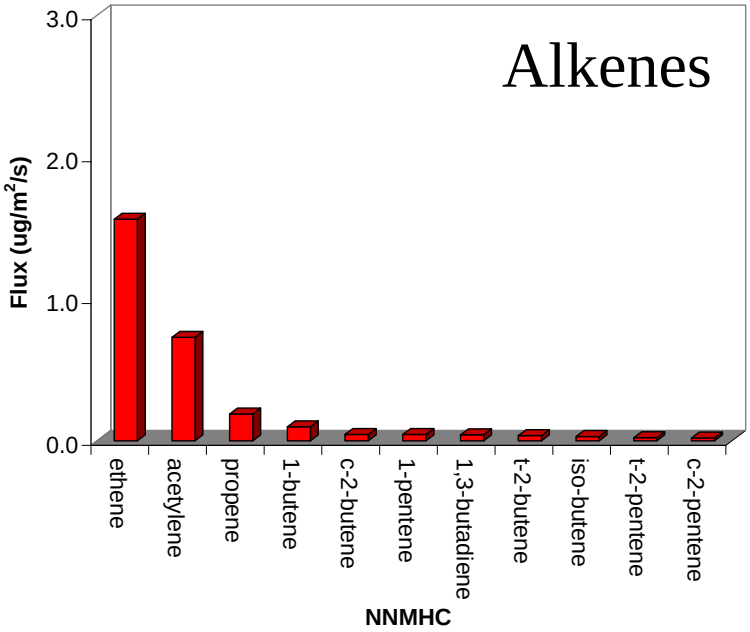
In both figures the grey shadow represent ±1 standard deviation from the total averages

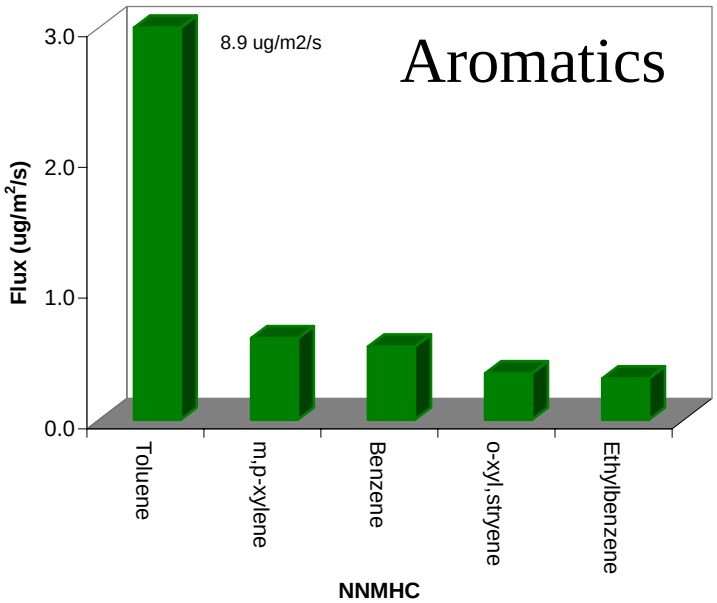
Toluene DEC PTR-MS Fluxes







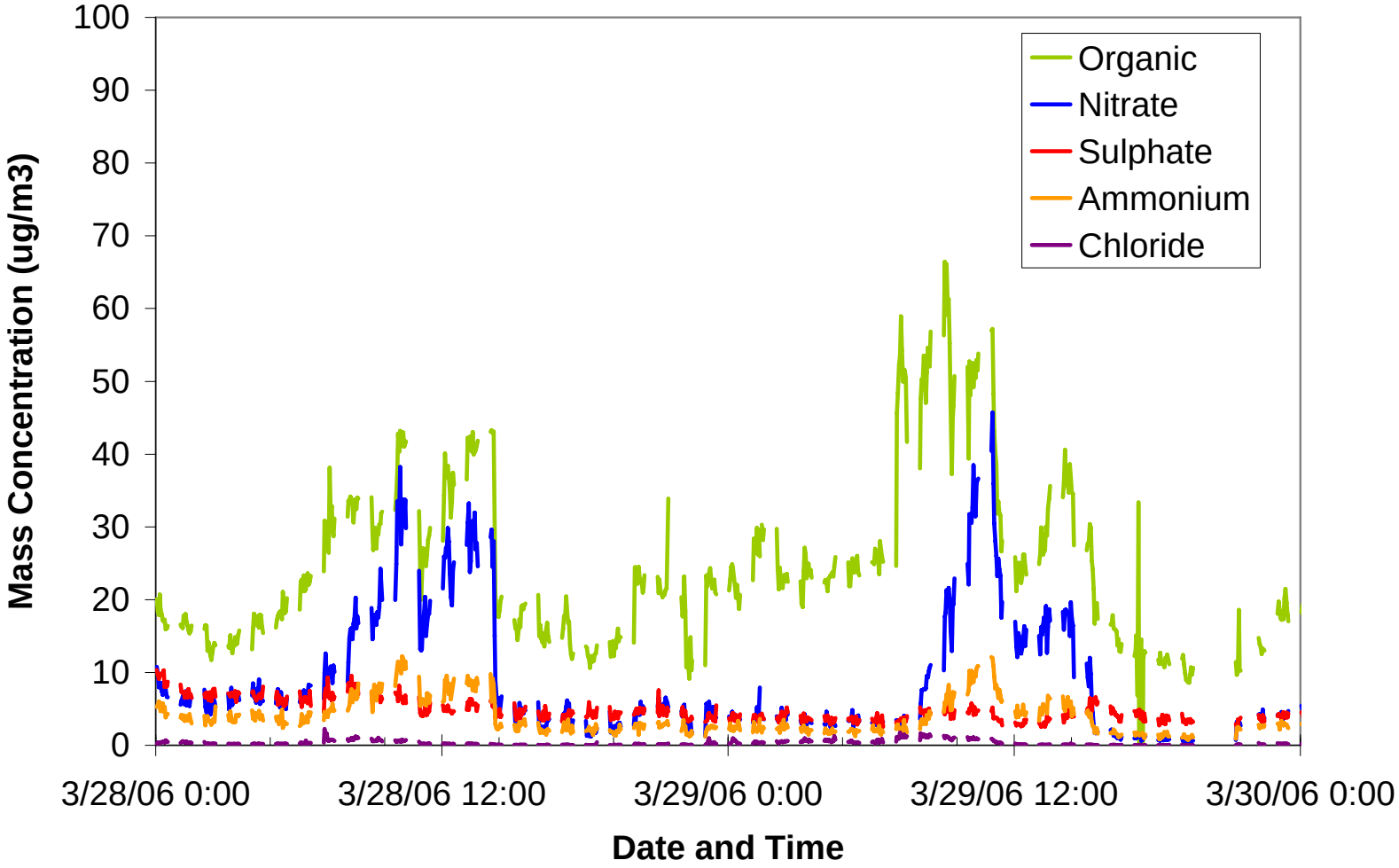




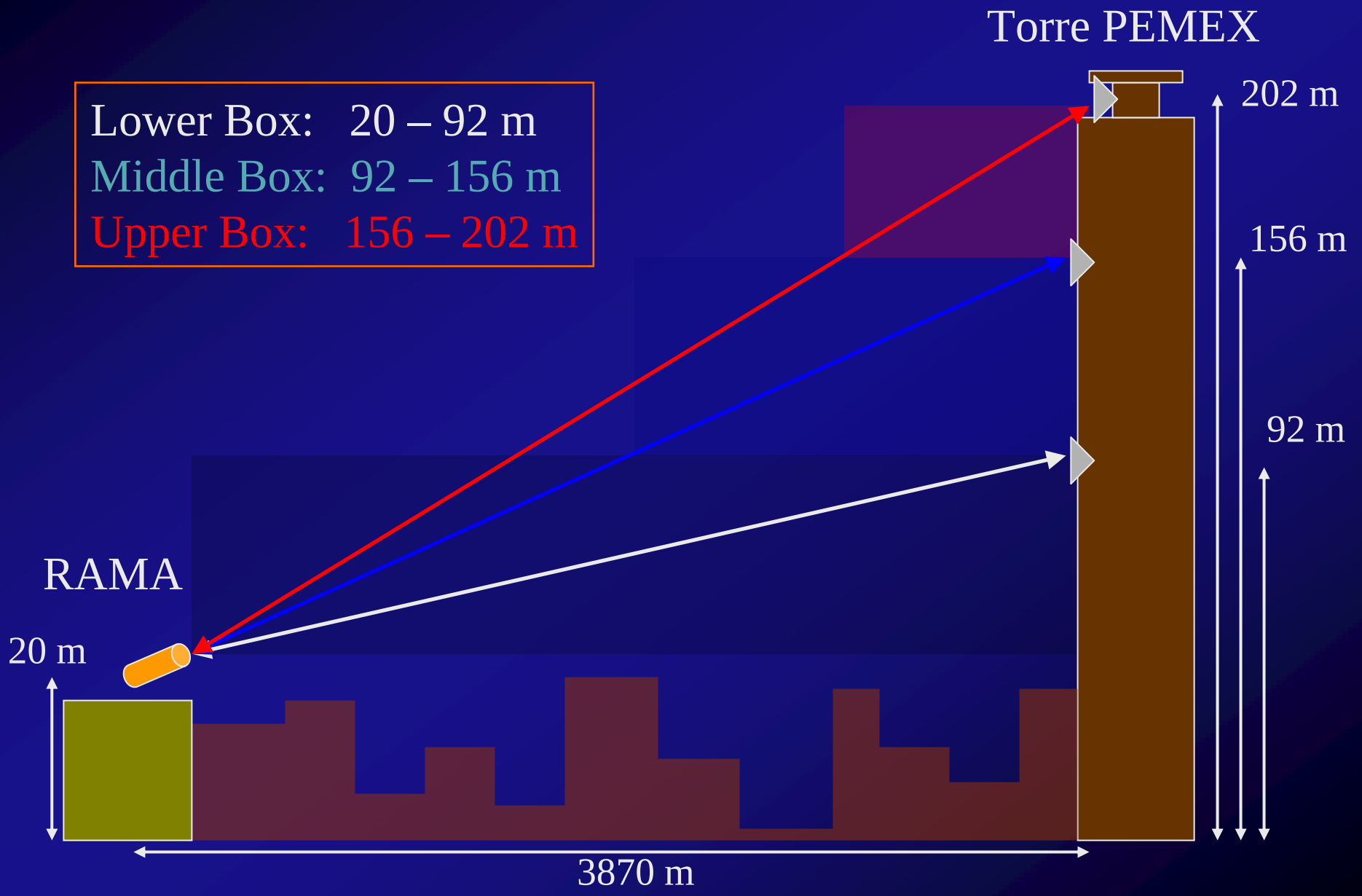
Average individual hydrocarbon fluxes using DEA GC-FID

$$F_\chi = (w'\,c_\chi')_{up} - (w'\,c_\chi')_{down}$$

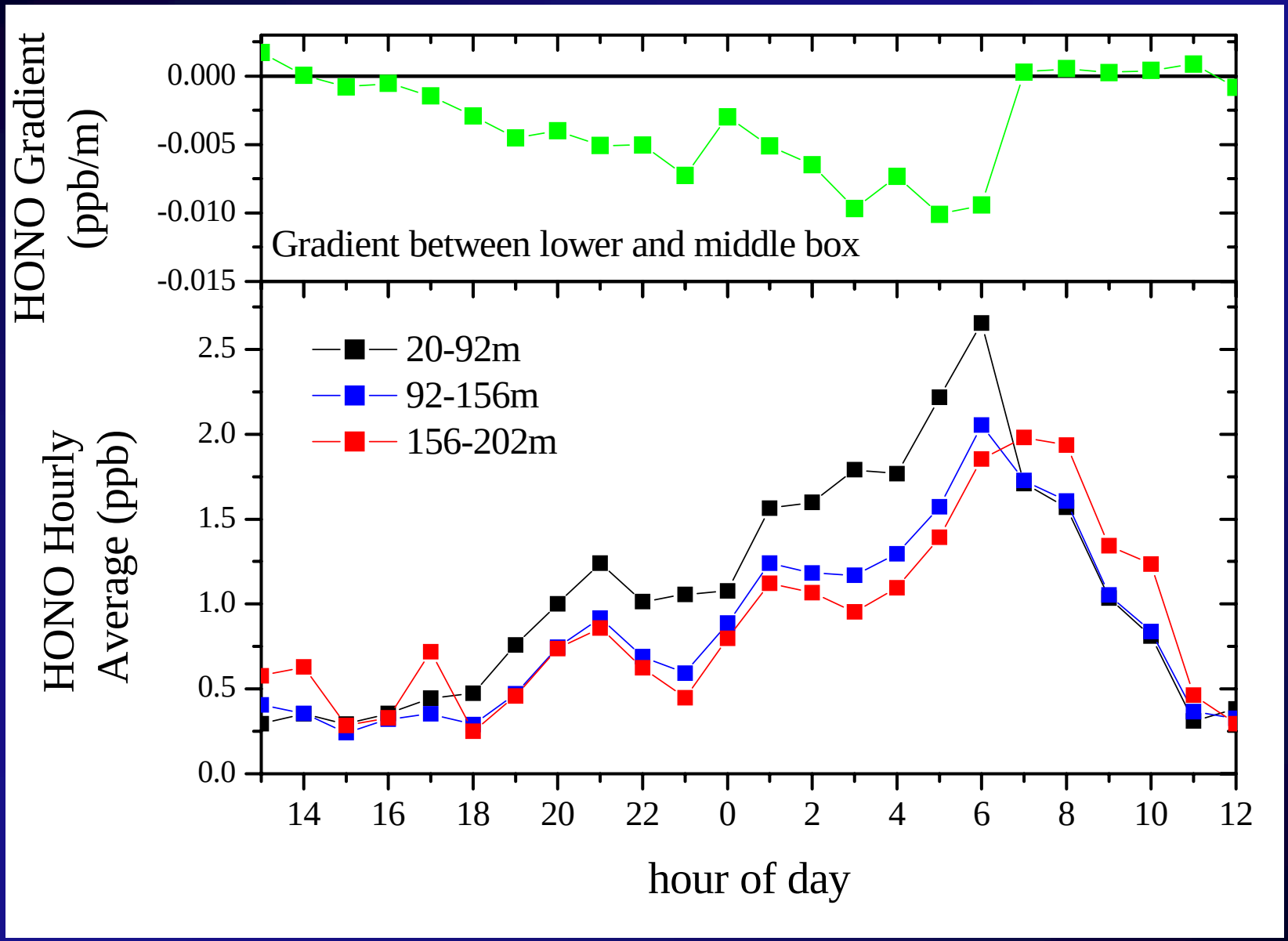
Daily aerosol concentrations above the urban landscape



Setup of the LP-DOAS Instrument in Mexico City



Hourly Averaged HONO Concentrations / Gradients



Summary & Highlights

- Successful direct eddy flux measurements
  - Olefins & individual NMHC
  - PTRMS species—toluene, other aromatics, & selected oxygenated VOC
  - Aerosols (AMS): organic, nitrate, chloride, sulfate
  - CO2 and energy fluxes, CO gradients

- VOC & CO2 fluxes higher than observed in MCMA2003; differences appear to be consistent with higher activity levels near the 2006 site
- In both studies, fluxes of VOCs, CO2 and CO showed clear diurnal profiles and a strong correlation to vehicular traffic.
- Toluene concentrations & fluxes exhibited large, short term variations—related to roadway repairs, painting & other non-mobile sources

- Organic aerosol concentrations (and fluxes) dominate the aerosol component

- CO2 fluxes measured in Mexico City are in agreement with other urban CO2 studies, which have also found that the urban surface is a net source of CO2.
- The energy balance distribution and radiative parameters observed are similar to distributions reported for other urban sites.

- Vertical gradients of O3, NO2, HCHO, and HONO have been observed.
  - During many nights O3 was depleted in the lowest 200m of the NBL.
  - NO3 levels were low (< 10ppt) during the experiment, most likely due to weak stability and high NO emissions.
  - High HONO levels can be explained with a formation on/near the surface and a slow upwards transport during the night.

Contributors

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Jochen Stutz, Laura Lawrence, Olga Pikelnaya, and Stephen C. Hurlock, University of California Los Angeles

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Measured and Modeled Emissions

Species	Measured Average Flux (mol/hr/grid)	Emission Inventory (mol/hr/grid)	EI Stdev (5 grids)	Obs/EI
ALK	8383 (DEA)	7898	1278	1.1
OLE	594 (DEA) 699 (FOS)*	1294	156	0.5
ARO	1483 (PTRMS)	1969	448	0.8
ARO	6540 (DEA)	1969	448	3.3
ARO adj**	3020 (DEA)	1969	448	1.5

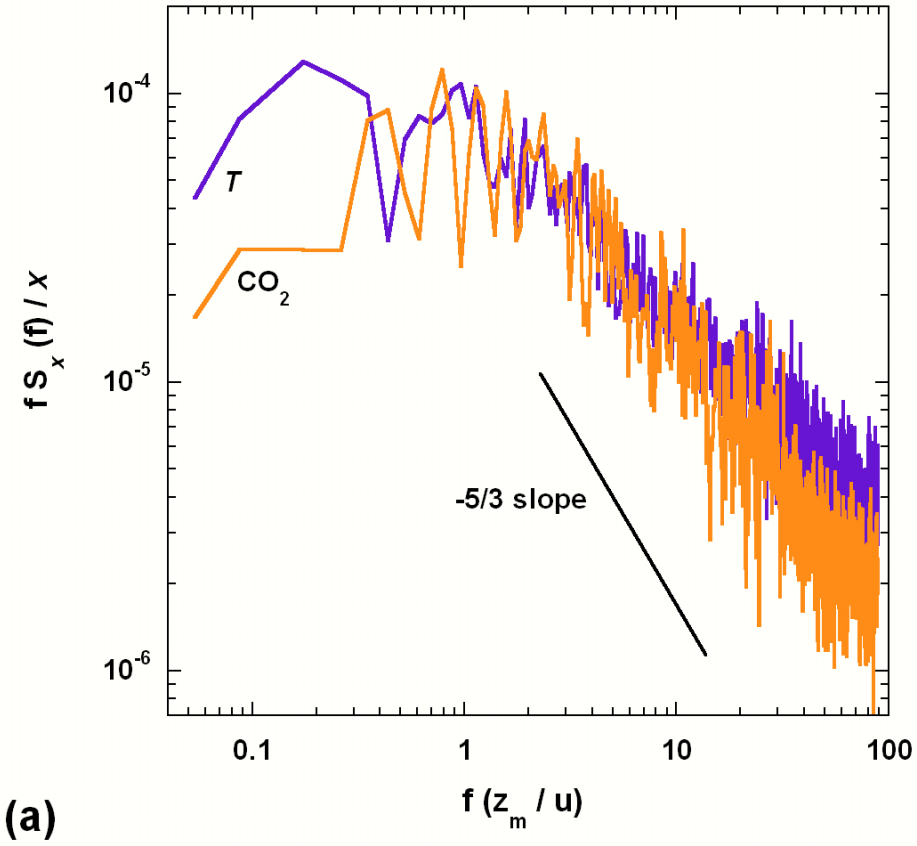
- *Measured with the Fast Olefin Sensor as propene
- **days with sidewalk repair omitted

Validity for the eddy covariance system:

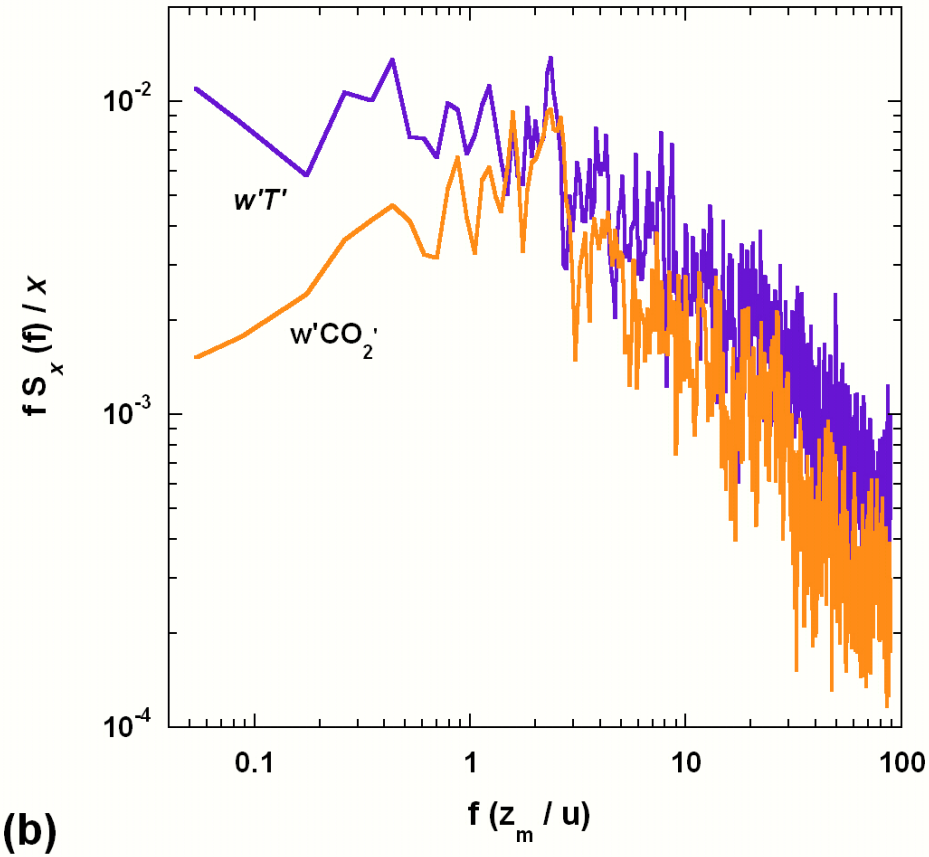
Criterion 1: Statistical characteristics of the raw instantaneous measurements (e.g. wind speed not to exceed 25 m s^{-1})

Criterion 2: **Stationarity test:** the average flux from 6 continuous subperiods of 5 min is within 60% of the flux obtained from a 30 min average.

Criterion 3: **Spectra and cospectra analysis:** the flux system is fully capable of measuring turbulence fluxes if the spectra and cospectra at high frequencies show the expected behavior in the inertial subrange, range where the net energy coming from the energy-containing eddies is in equilibrium with the net energy cascading to smaller scales where it is dissipated.



(a)



(b)

Power density spectra

The -5/3 slope indicates the theoretical slope in the inertial subrange.

Power density cospectra

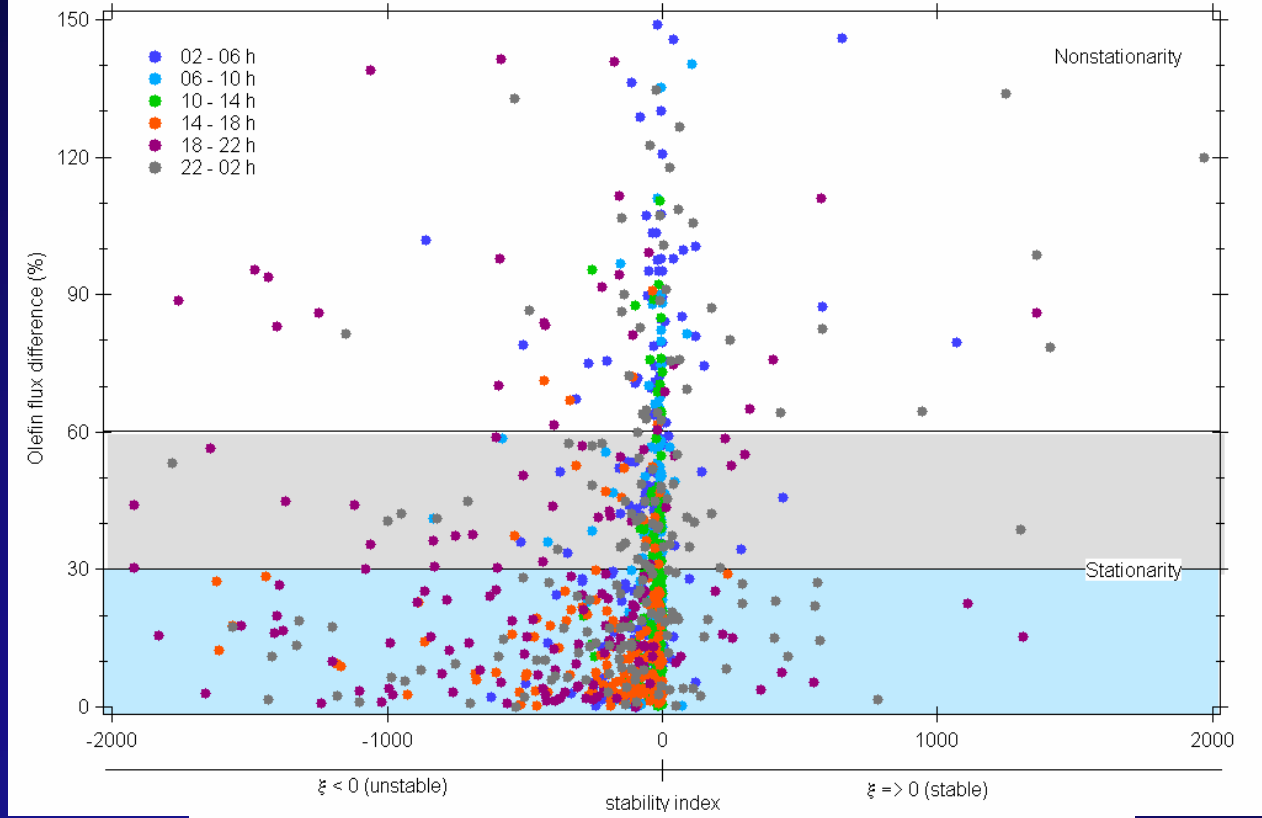
The shape and details of the CO_2 and *T* spectra and cospectra correspond closely over the entire range of frequencies measured.

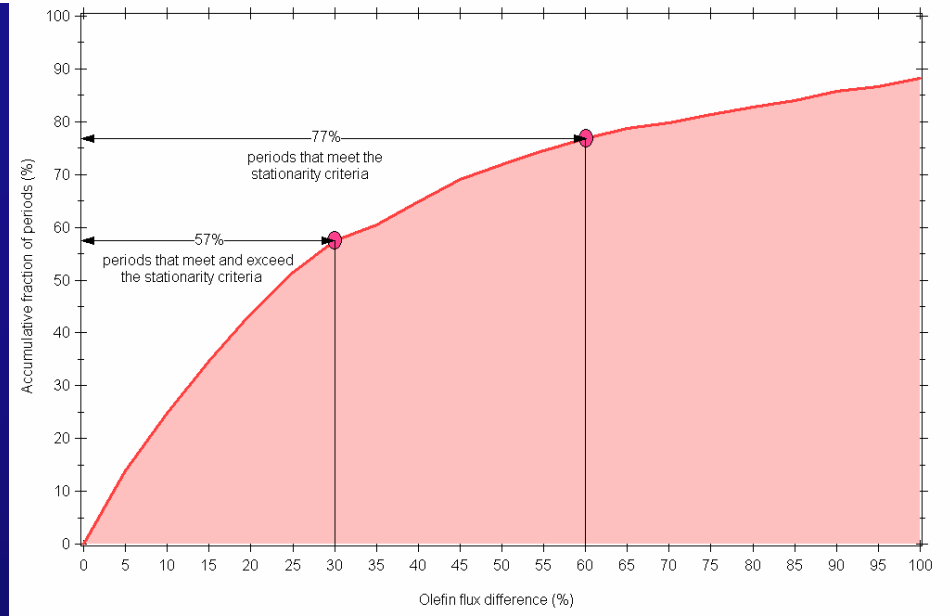
2003

Stationarity test

(olefin fluxes)

In 57% of the periods, the flux difference was less than 30%, which indicates periods that meet and exceed the stationarity criteria. In 20% of the periods, the flux difference was between 30 and 60%, which means that these periods have an acceptable quality.



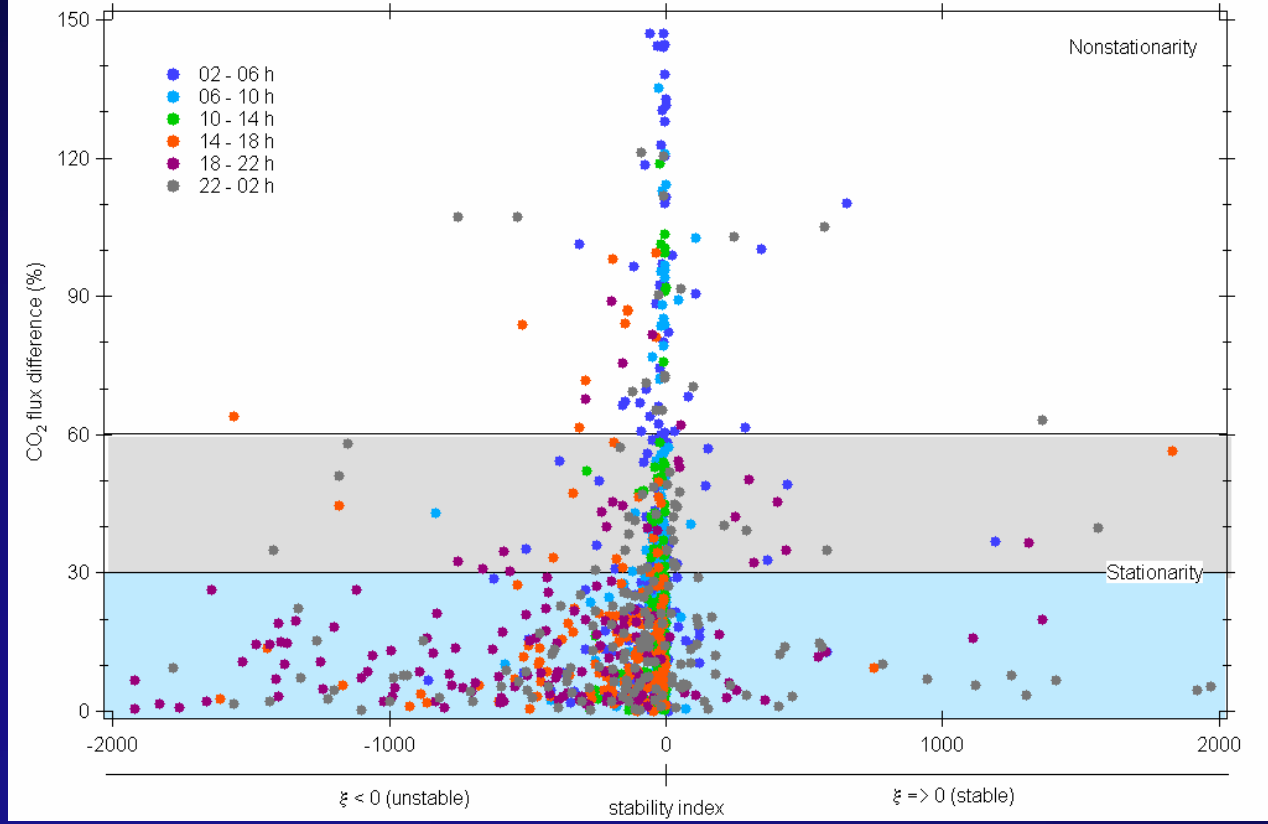


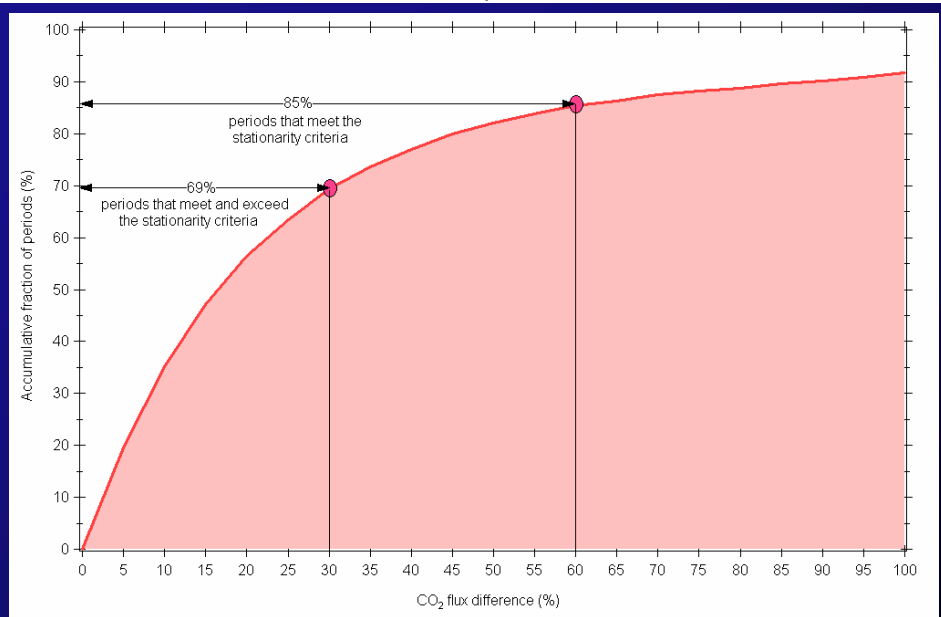
2006

Stationarity test

(CO2 fluxes)

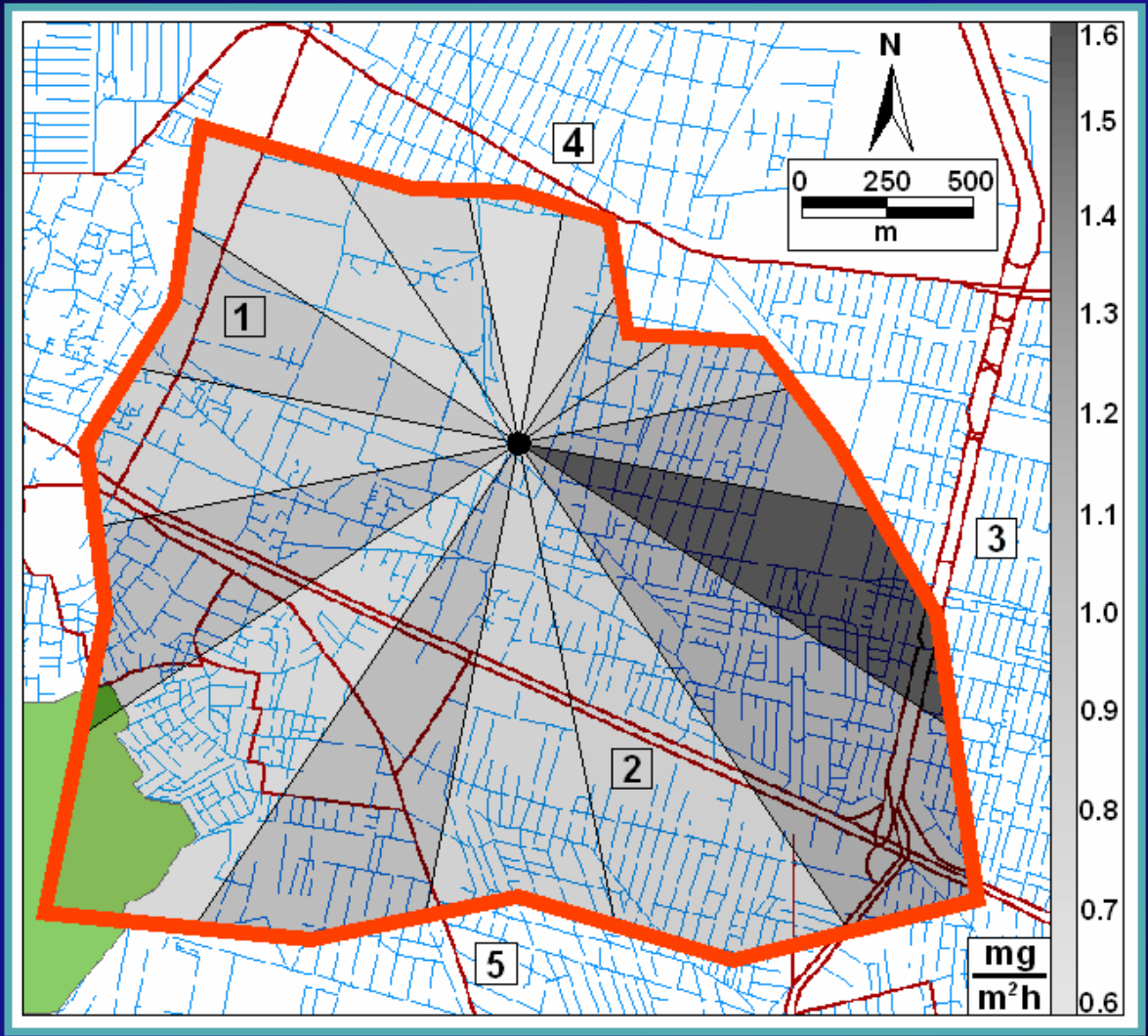
In 69% of the periods, the flux difference was less than 30%, which indicates periods that meet and exceed the stationarity criteria. In 16% of the periods, the flux difference was between 30 and 60%, which means that these periods have an acceptable quality.





2006

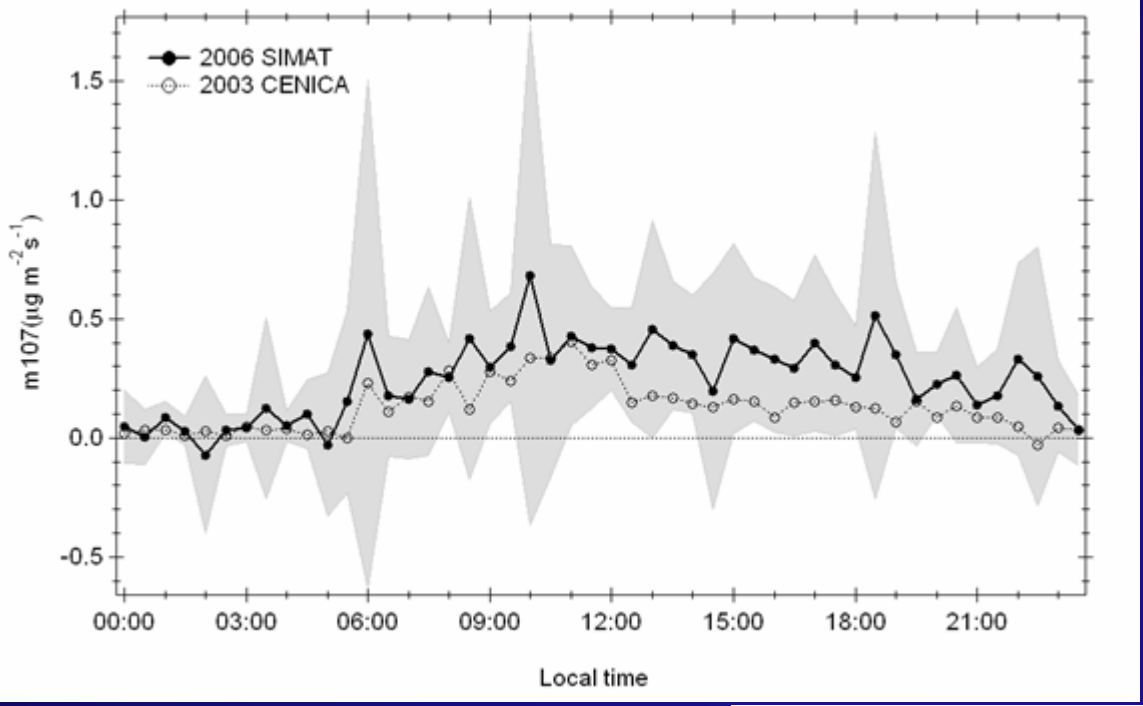
Olefins flux as a function of the upwind direction



2003

The orange contour indicates the fraction of the flux measured equal to 80%.

2006 / 2003 = 1.7



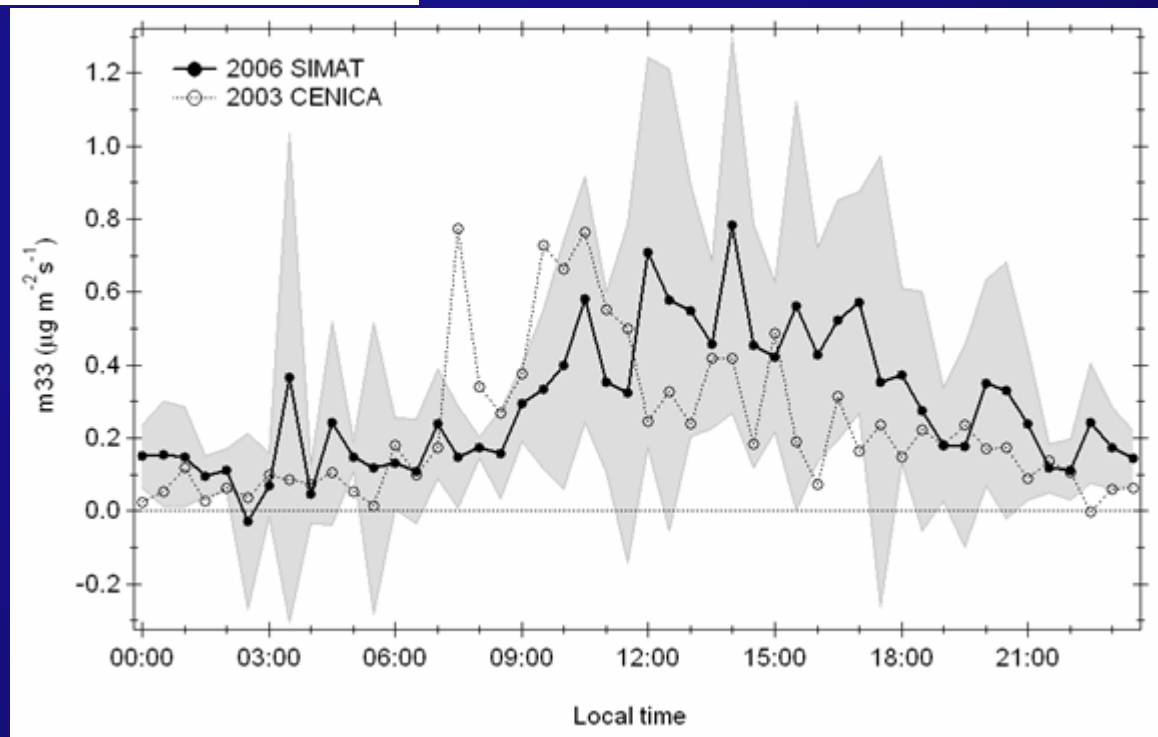
C_2-benzenes

DEC Fluxes

Methanol

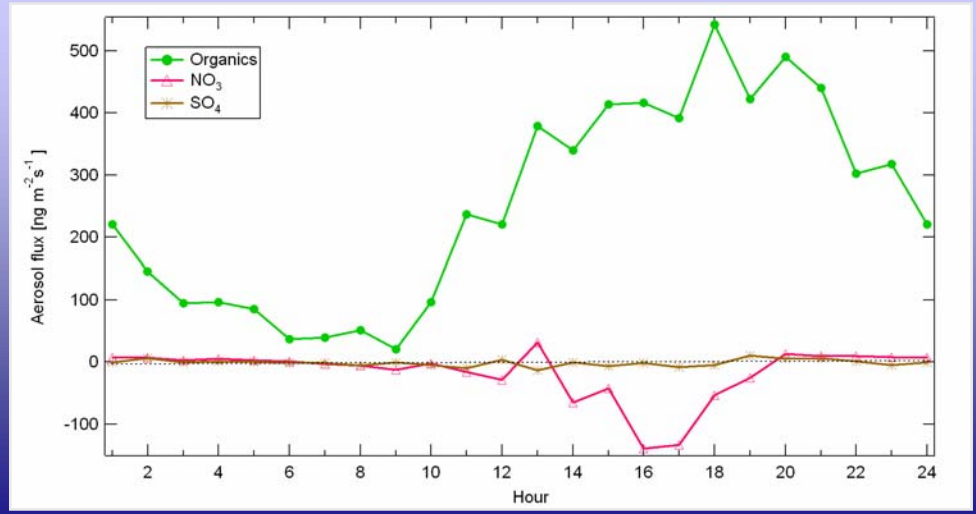
DEC Fluxes

2006 / 2003 = 1.3

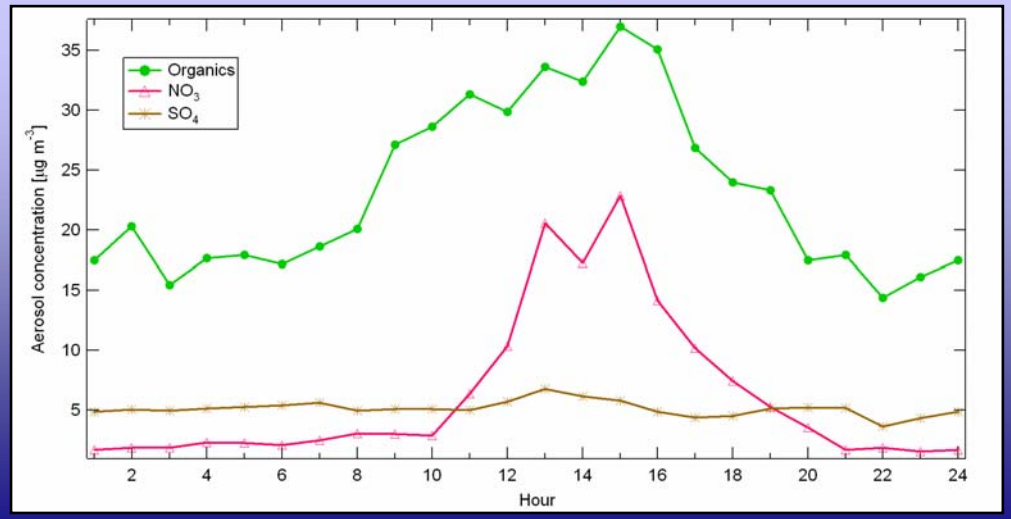


Aerosol flux measurements by AMS in an urban district of Mexico City

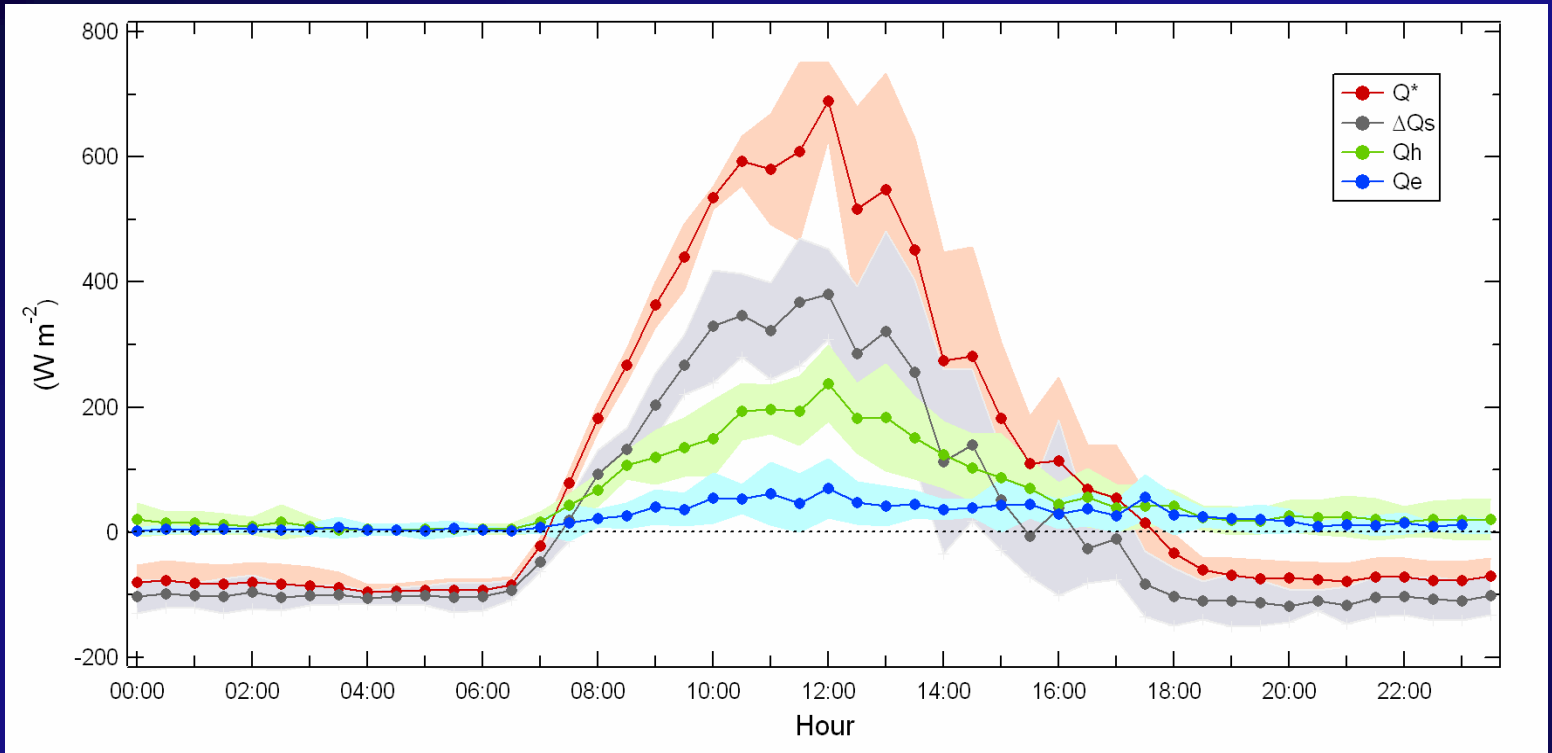
Fluxes



Ambient concentrations



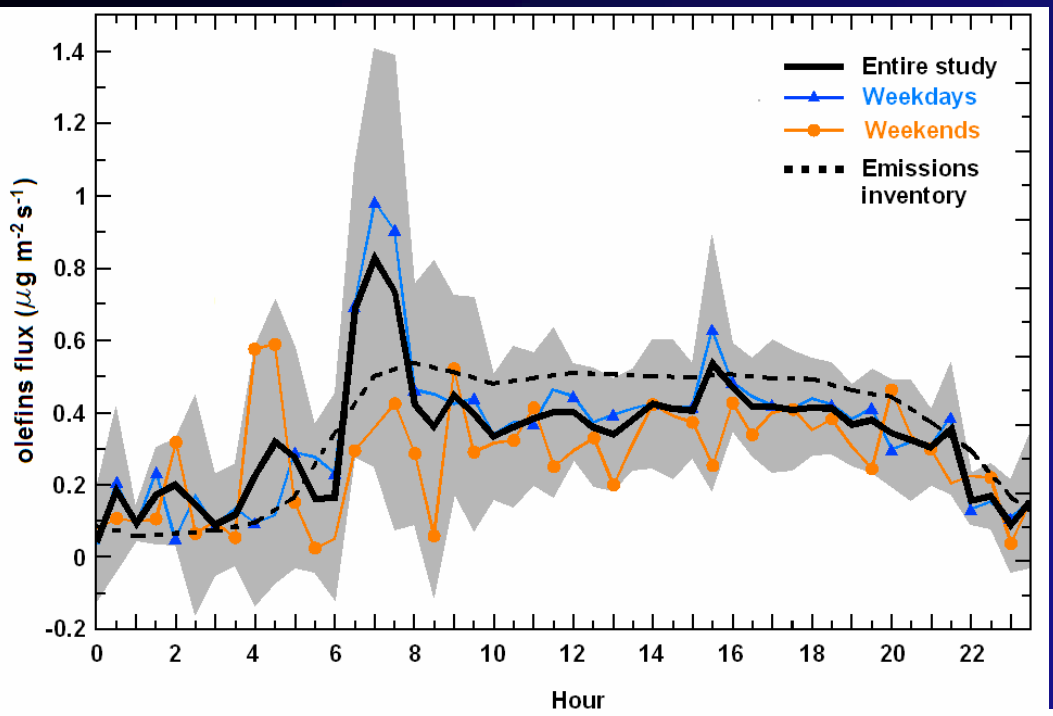
Energy balance



Q* = net all-wave radiation
Qh = sensible heat
Qe = latent heat
Qs = storage heat
Qs = Q* - (Qh + Qe)

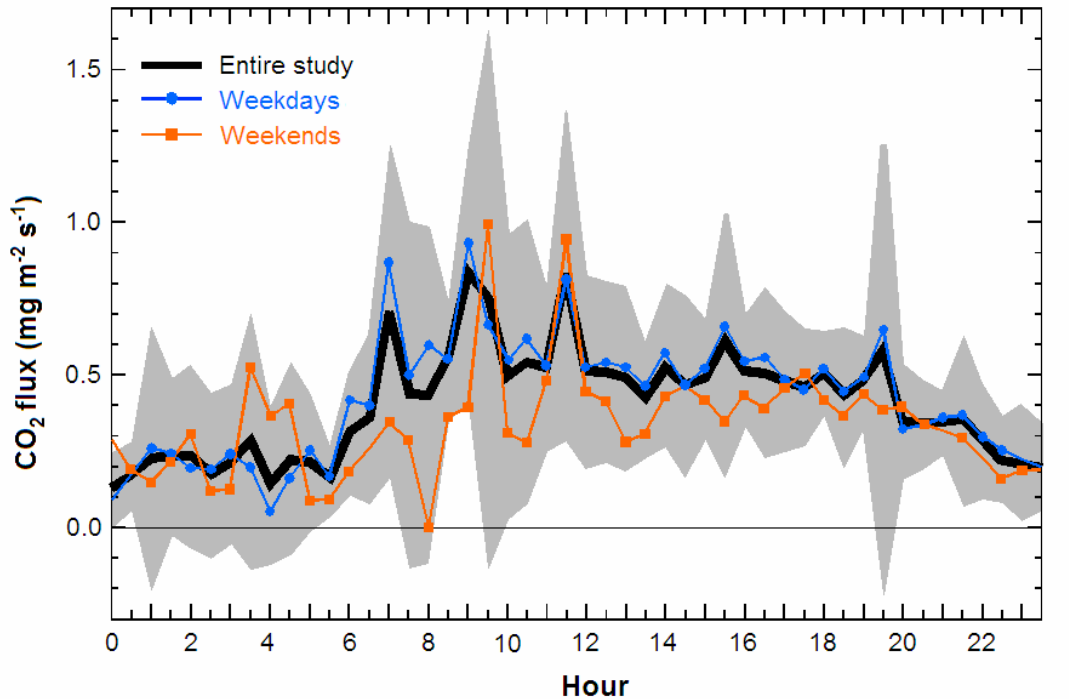
During daytime (Q*>0):

ΔQs = 50%, Qh =37%, Qe = 13%
β = Qh/Qe = 2.9
α = 0.12
ε = 0.76



2003

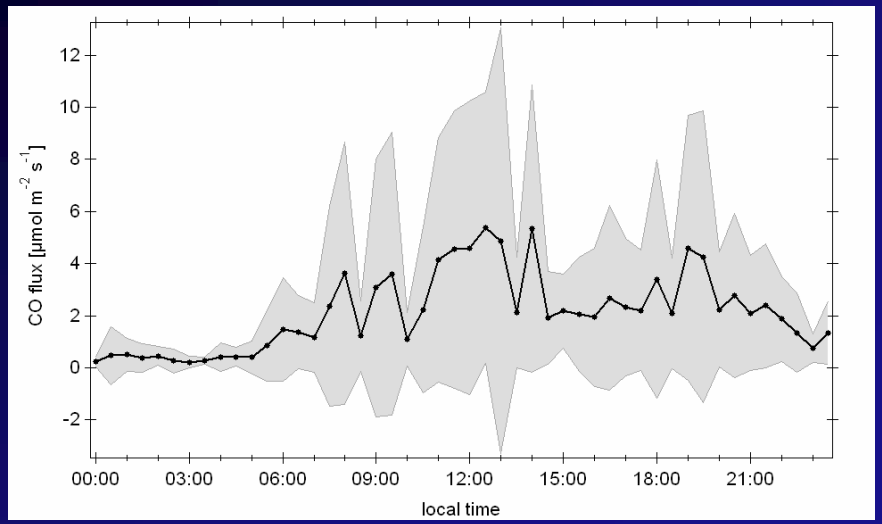
Diurnal profile of olefins flux

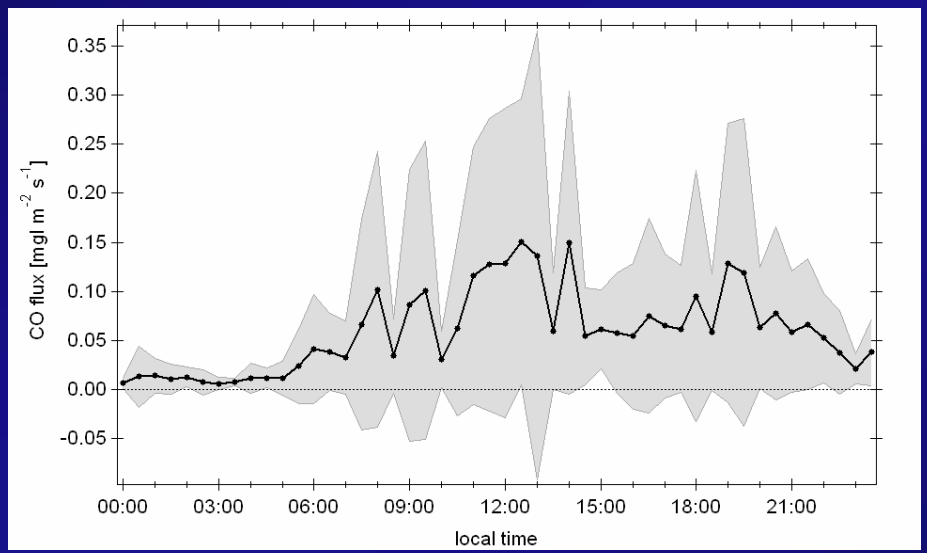


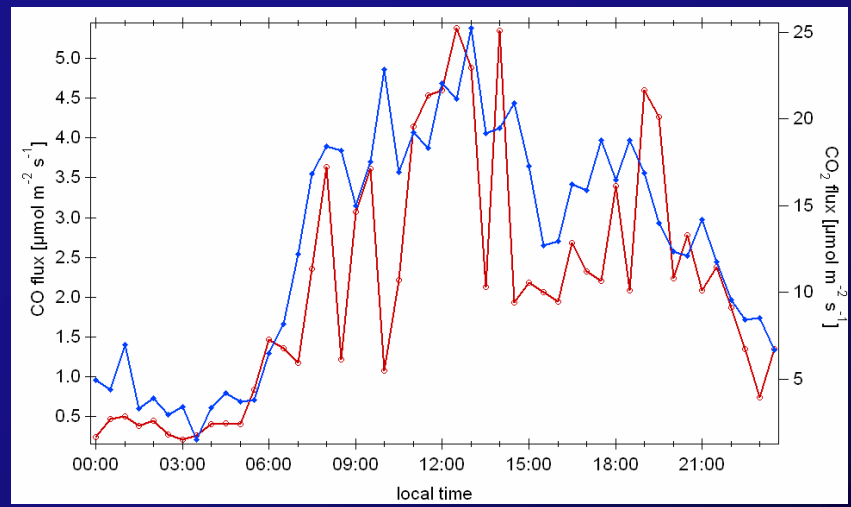
Diurnal profile of CO_2 flux

In both figures the grey shadow represent ±1 standard deviation from the total averages

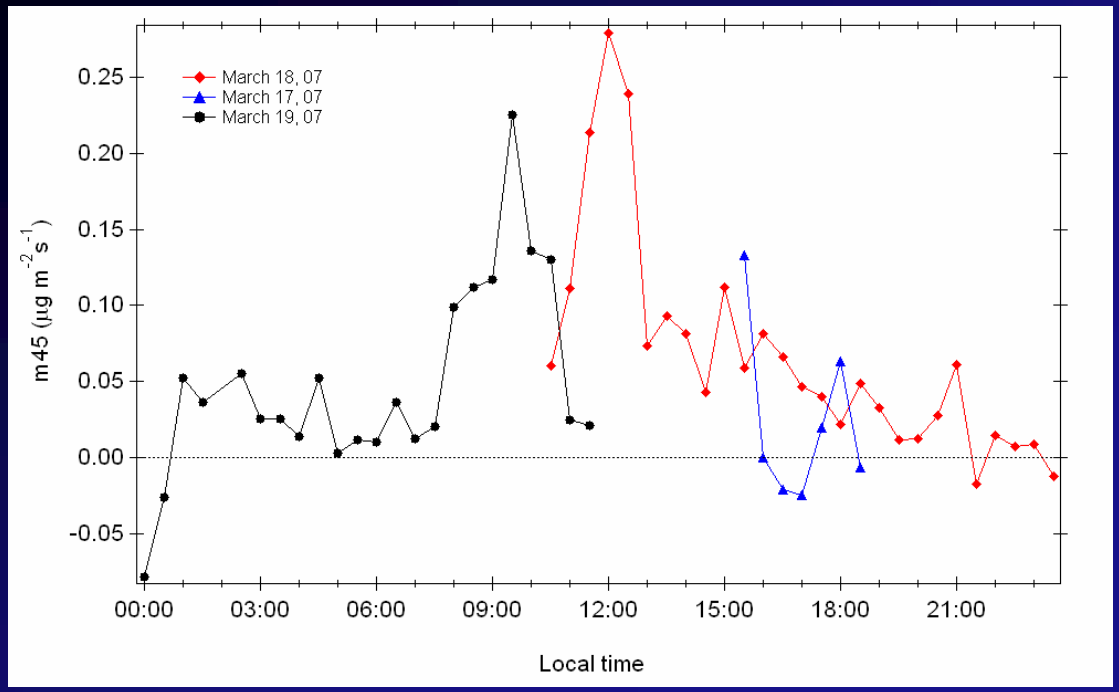
Additional figures for CO fluxes



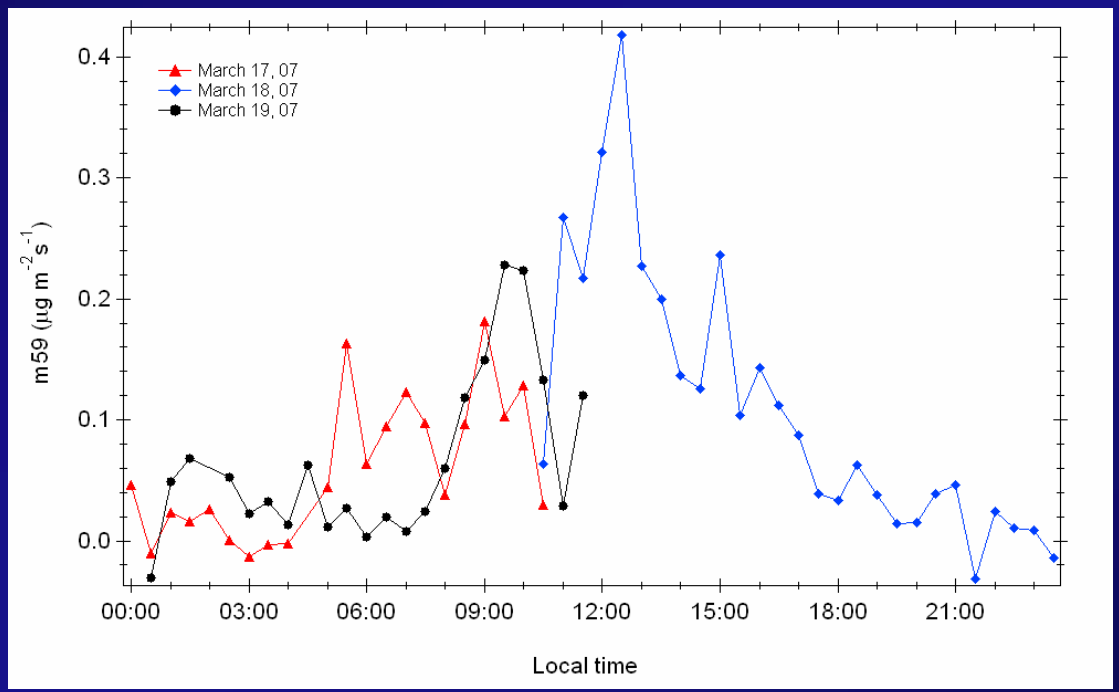




2006



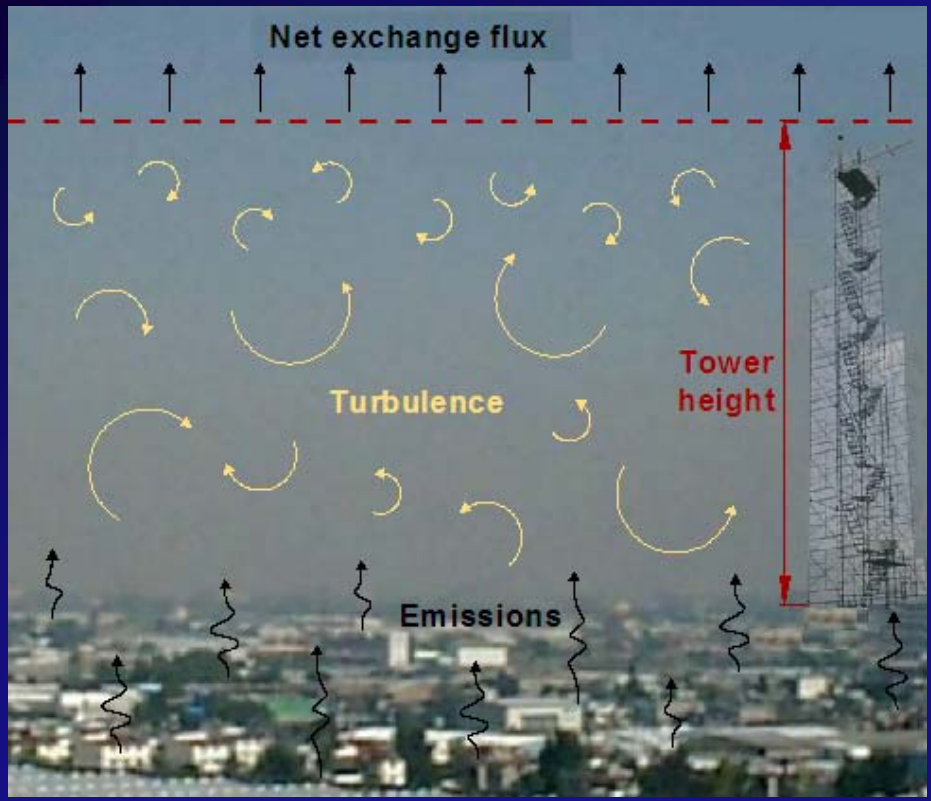
Acetaldehyde flux



Methanol flux

2006

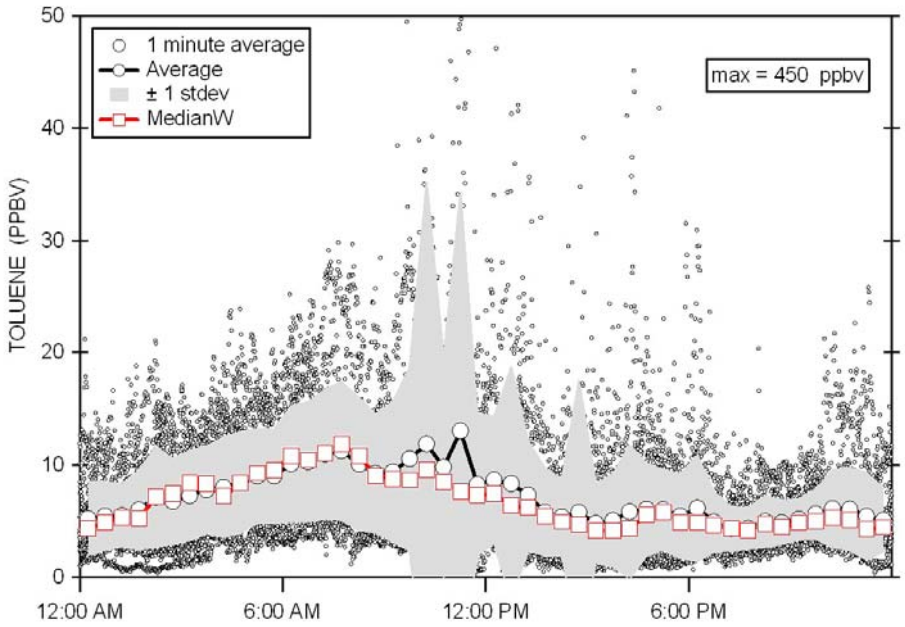
Eddy Covariance (EC) Flux Method

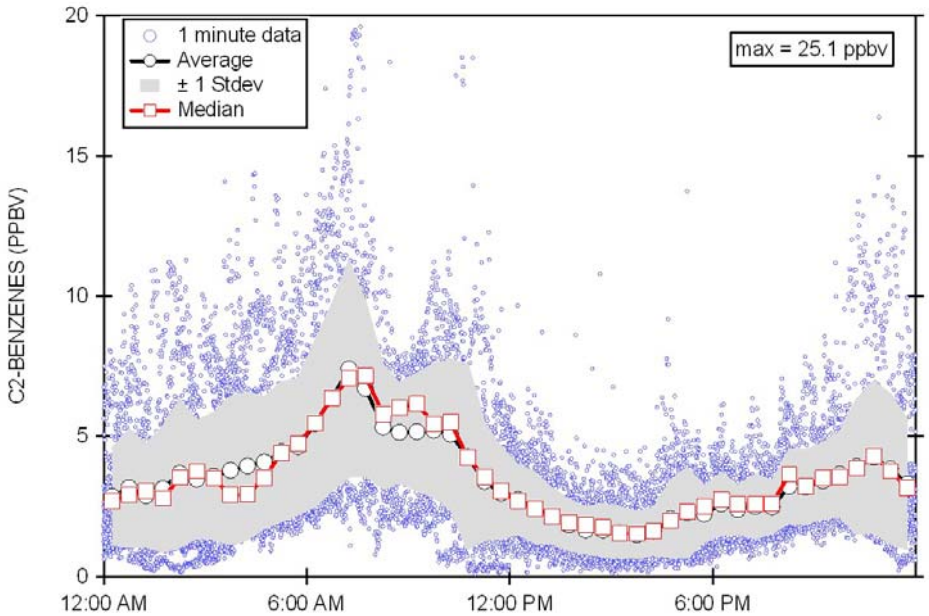


$$F_\chi = \overline{w' c_\chi'} = \frac{1}{N}\sum_{i=1}^{N} w'(t_i)c'(t_i)$$

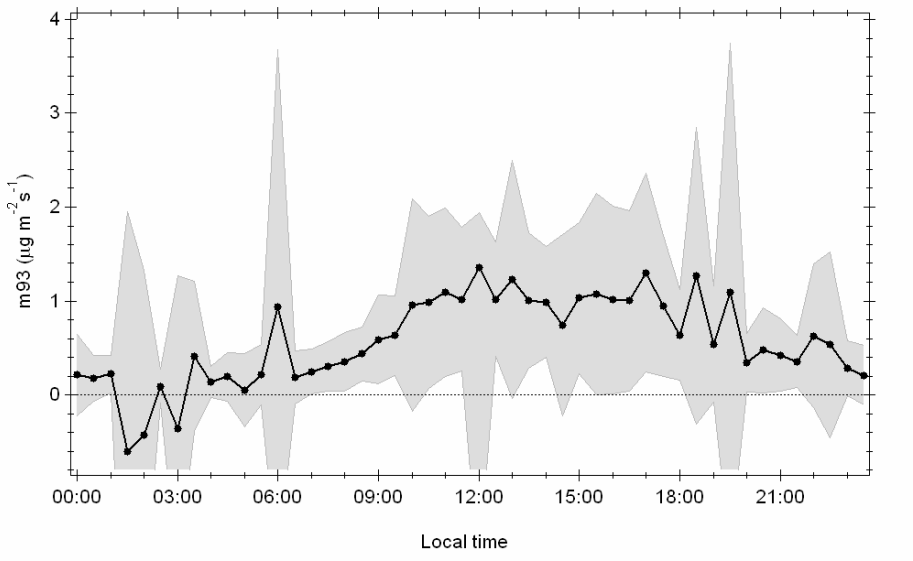
- **Fast response sensors**
- **Fast response data acquisition systems**

The flux of a trace gas (F_χ) is calculated as the covariance between the instantaneous deviation of the vertical wind velocity (w') and the instantaneous deviation of the trace gas concentration (c_χ') for time periods between 30 min. and an hour.

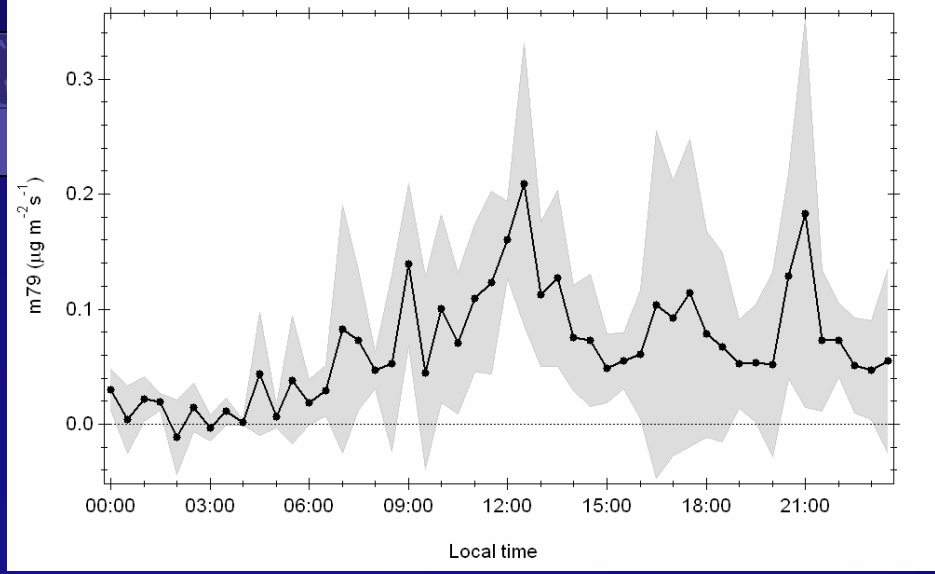




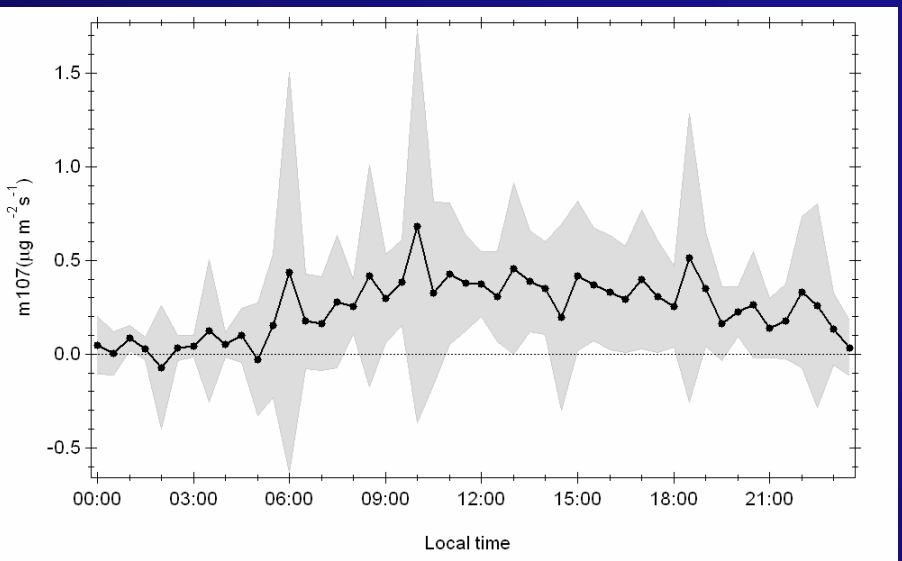
Toluene and benzene diurnal averages



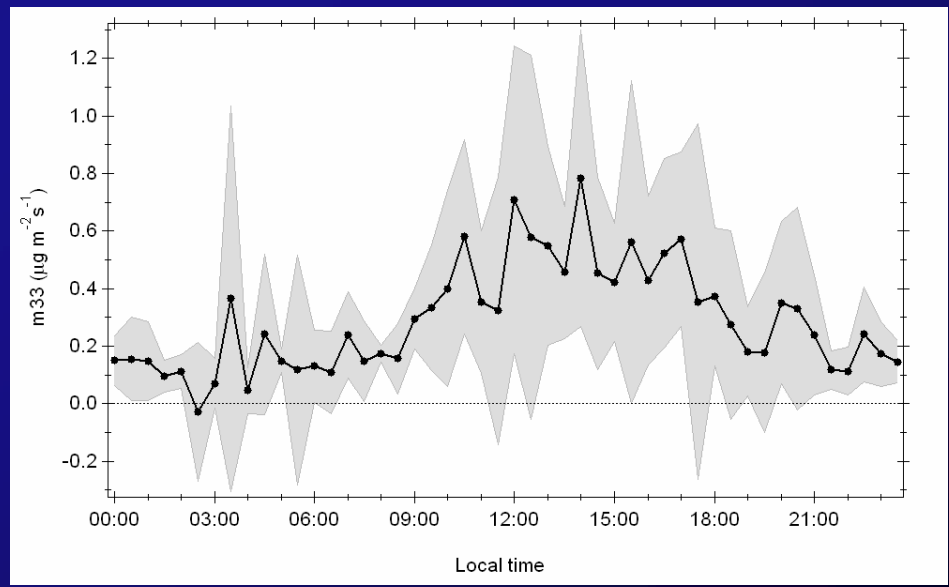
toluene



benzene



C_2-benzenes



methanol

2006