VOC emissions and trends in Los Angeles basin

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Outline

- Motivation and data
- Determination of urban emission ratios
- Week-end vs week-day
- Preliminary comparison with inventories
- Summary

Motivation and data

How can we improve the emissions inventory for greenhouse gases, ozone and aerosol precursors (extracted from CalNex White Paper - Jan. 2008)

A first step : evaluation of the emission inventory
Target species : VOC

observations
[VOC]/[tracer]

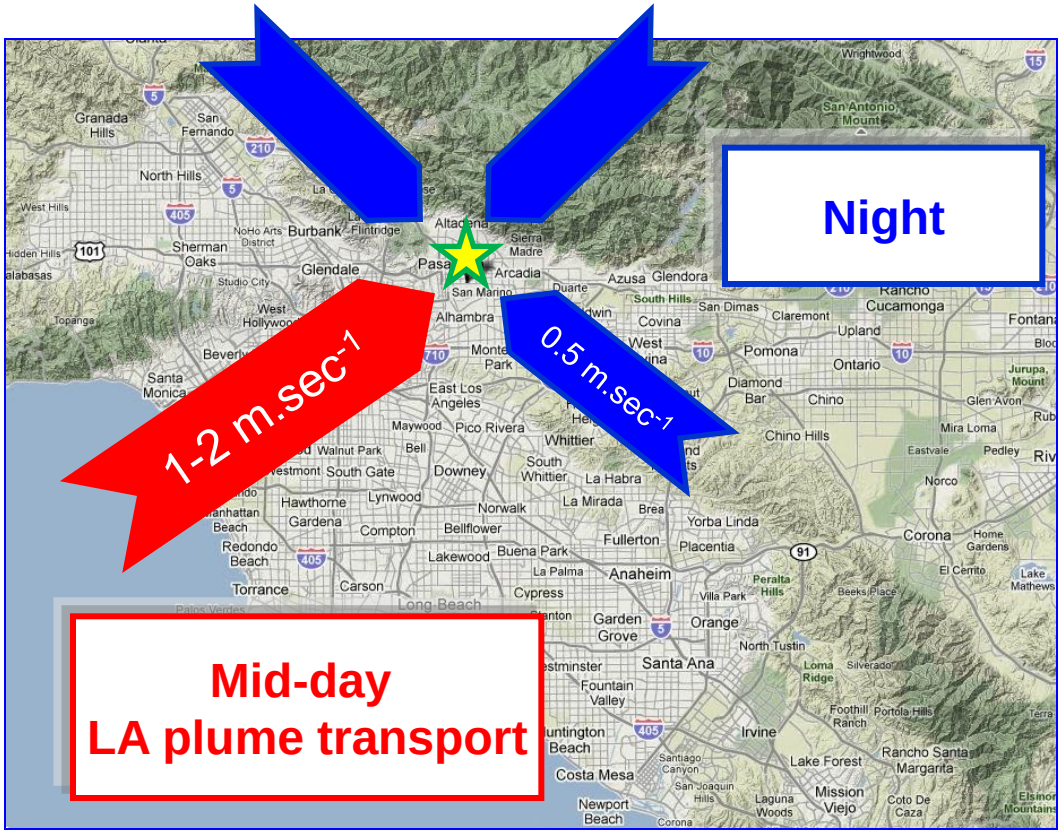
Detailed VOC composition
- CalNex 2010 at Pasadena

emission inventory
Q_{VOC}/Q_{tracer}

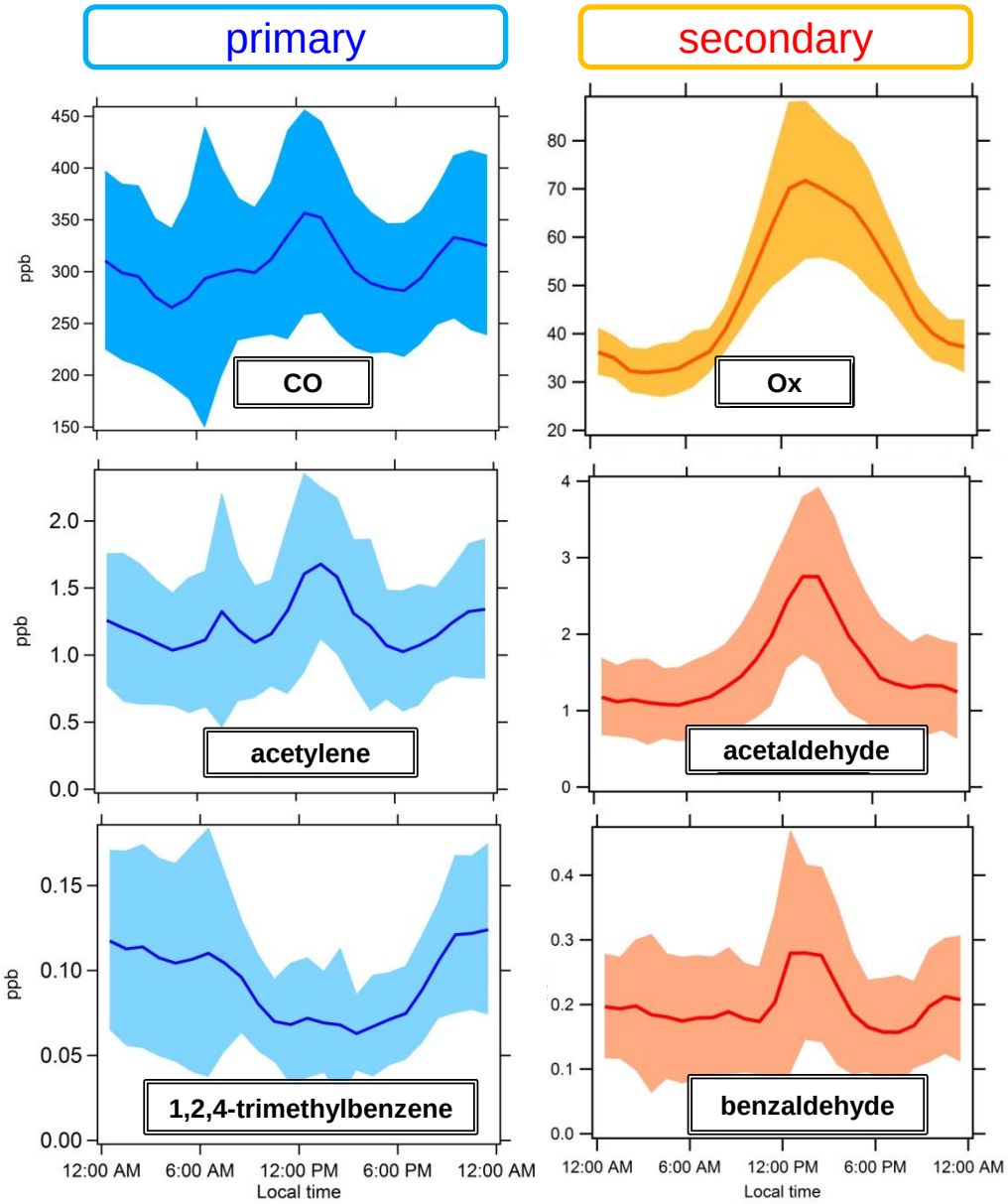
Hourly emissions of major regulated and non regulated pollutants :
- NEI (national) – 2005/dec.2008
- CARB (regional) - 2008

Pasadena groundsite

GC-MS instrument (Gilman, 2010)
C2-C11 NMHC, C6-C9 aromatics, OVOC, DMS
30-min time resolution



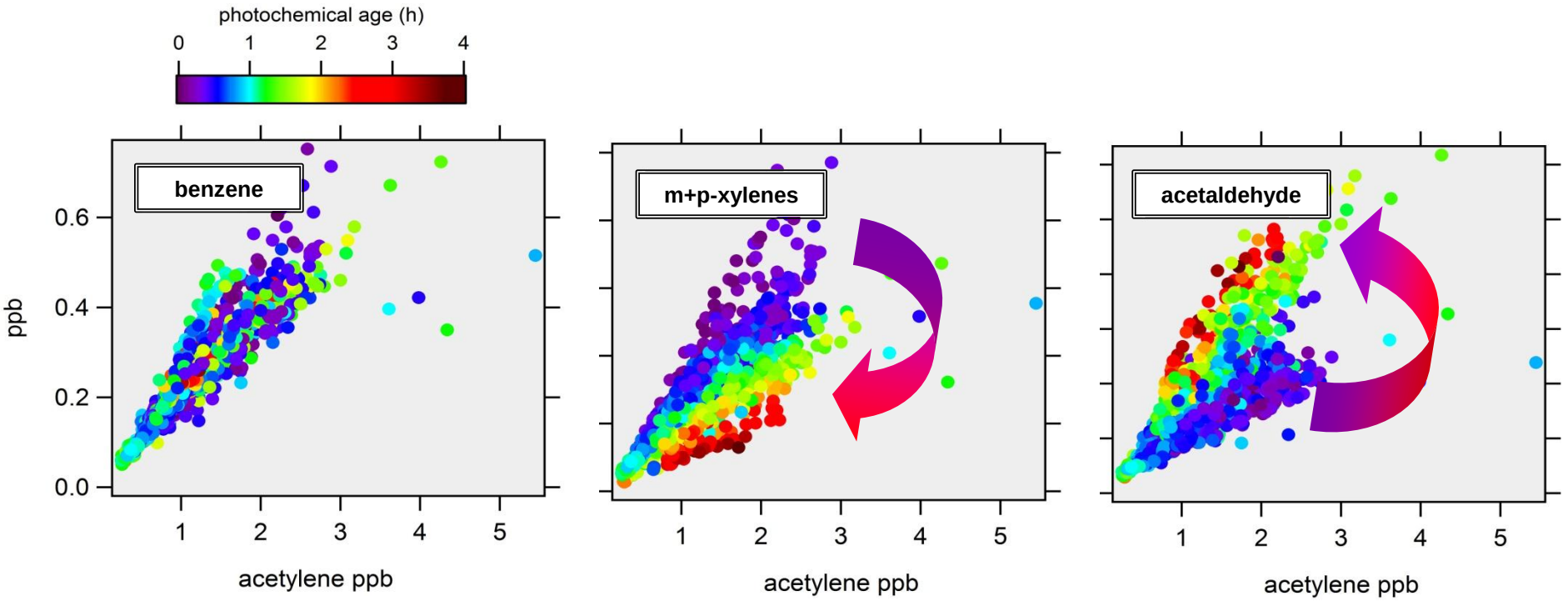
Observations : diurnal profiles



signature of primary emissions, mixing and chemistry

need to define a set of ‘no-chemistry’ conditions to determine urban ER

Enhancement ratios ΔVOC/ΔCO (or C2H2)



Emission + Photochemical depletion + Photochemical production

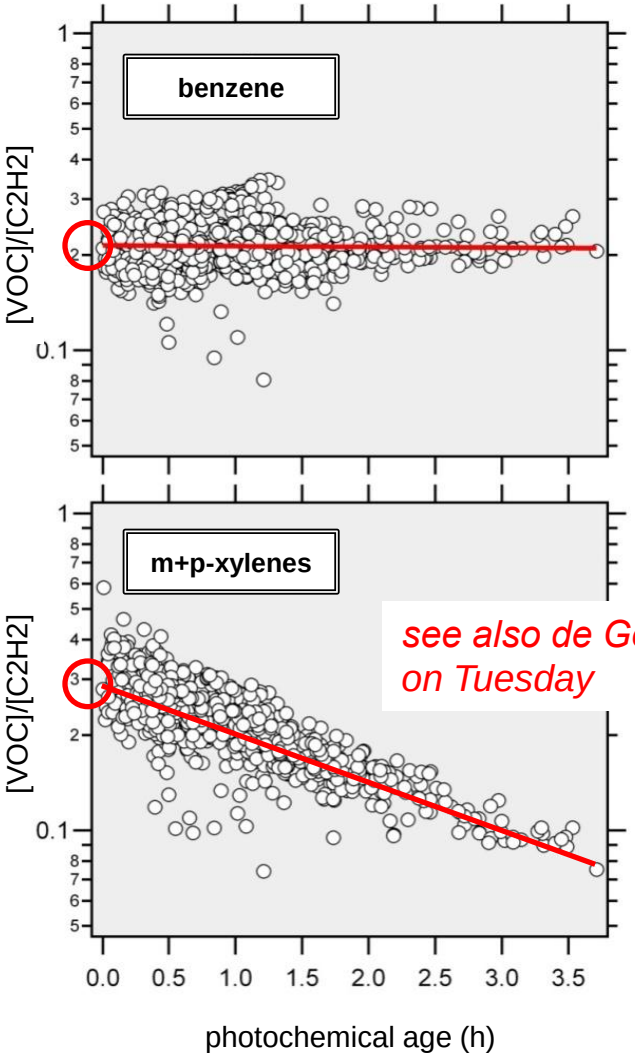
Photochemical age (Calvert, 1976) :

$$\Delta t = \frac{1}{[OH](k_{124TMB} - k_{benzene})} \times \left[\ln\left(\frac{[124TMB]}{[benzene]}\right)_{t=0} - \ln\left(\frac{[124TMB]}{[benzene]}\right) \right]$$

Methods to estimate urban ER

Photochemical age method (OH)

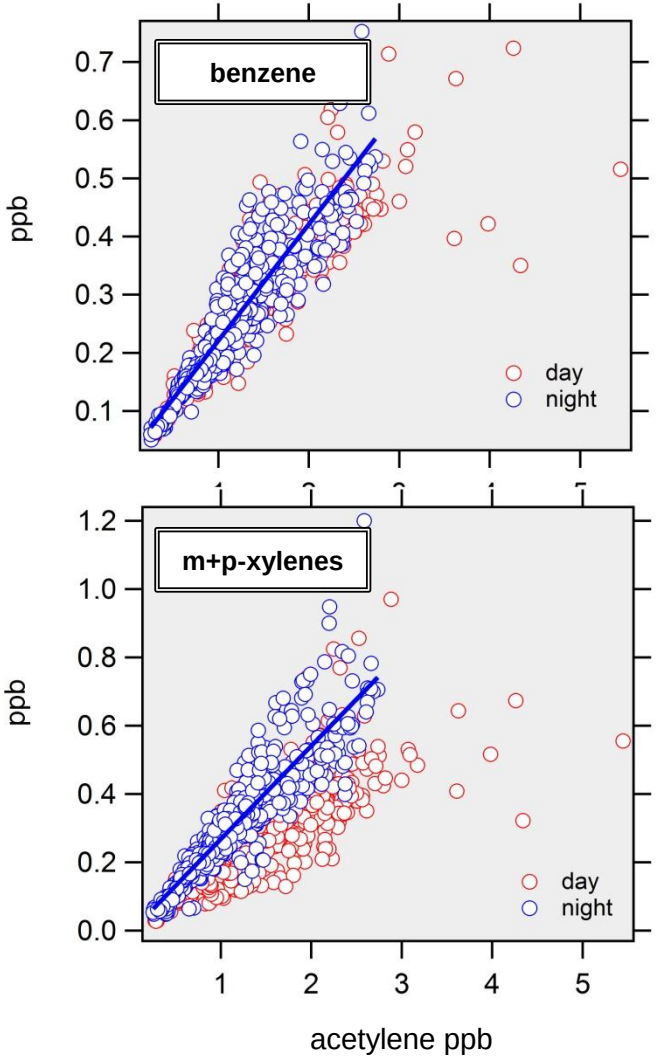
(de Gouw, 2005 ; Warneke, 2007)



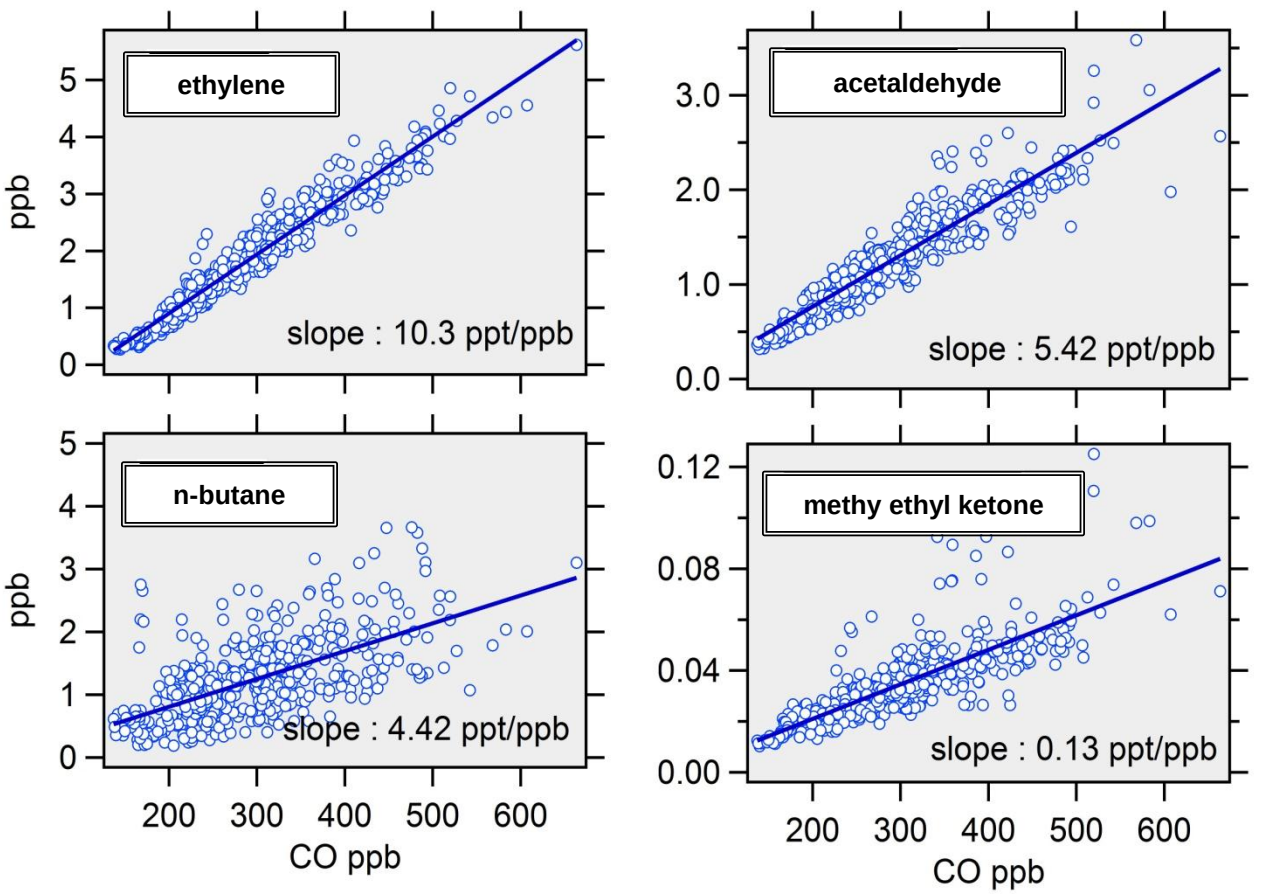
see also de Gouw's poster on Tuesday

Linear regression fit method (LRF)

from nighttime data (22:00 – 06:00) when Δt < 1 h



Linear regression fit method (LRF)



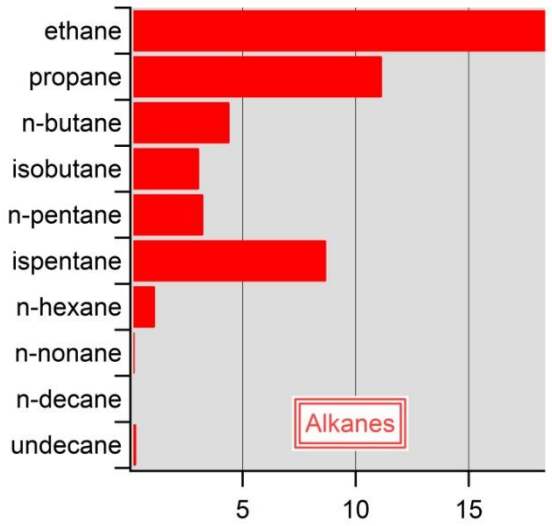
R^2 > 85%
Alkanes >C4
Aromatics
Alkenes
Aldehydes

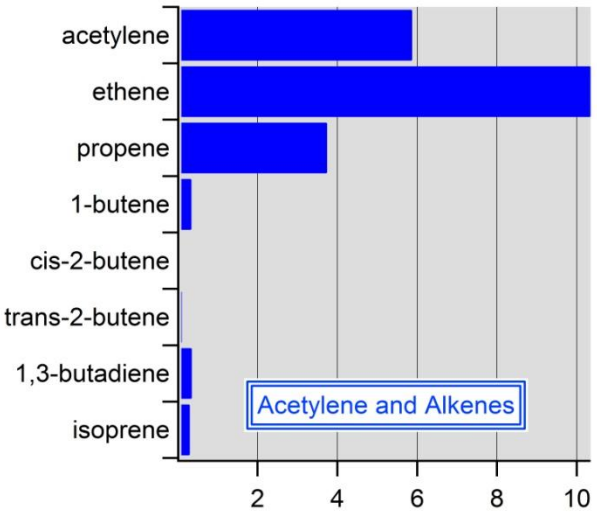
60% < R^2 < 80%
C2-C4 alkanes
Ketones
Alcohols

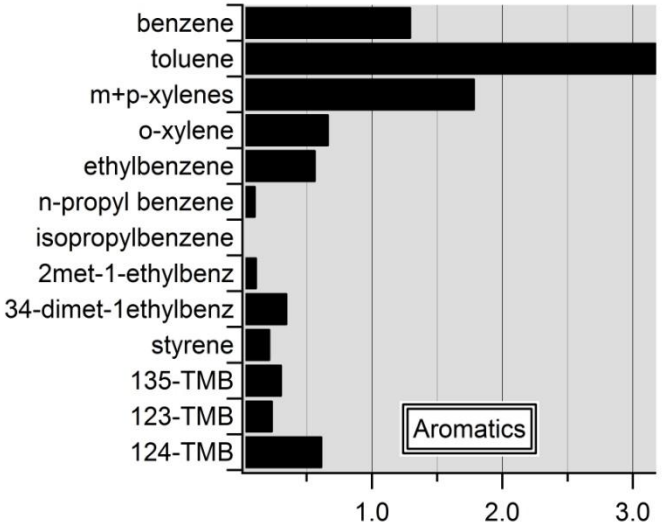
⇒ dominant anthropogenic origin at night

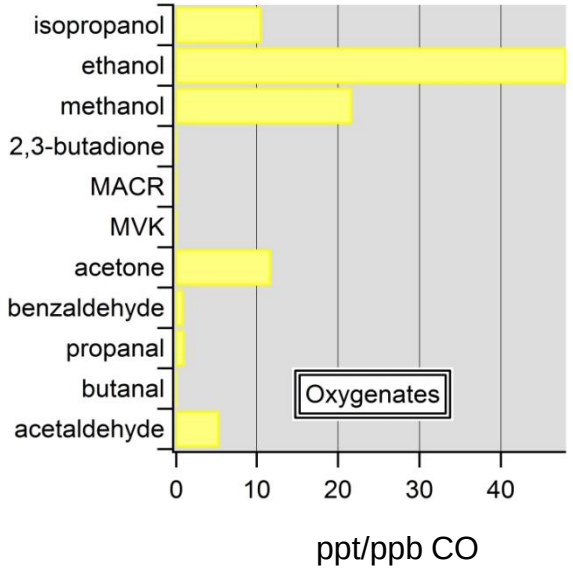
Estimation of urban ER from LRF

ER of 42 VOC





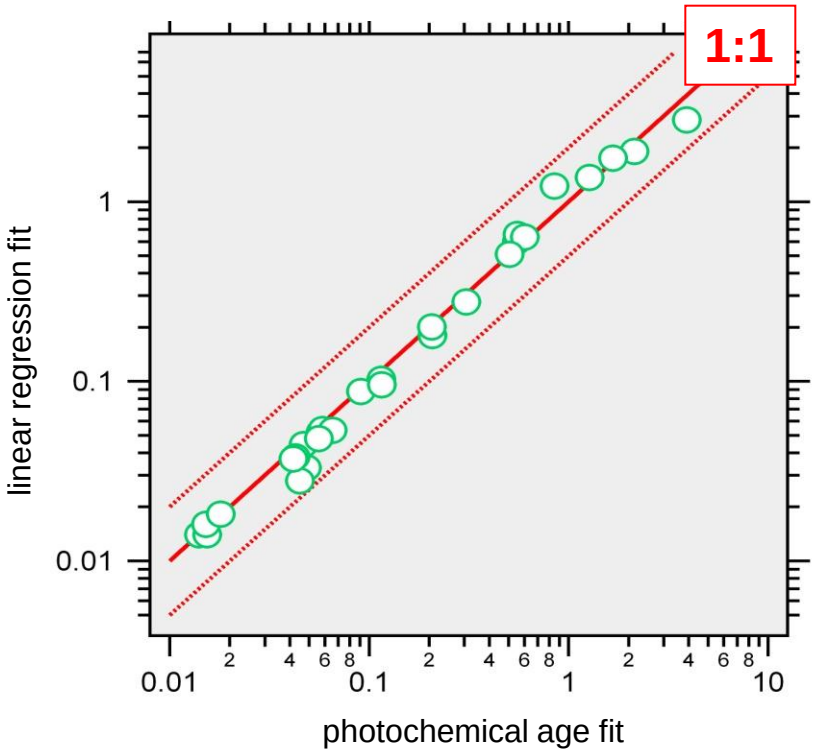




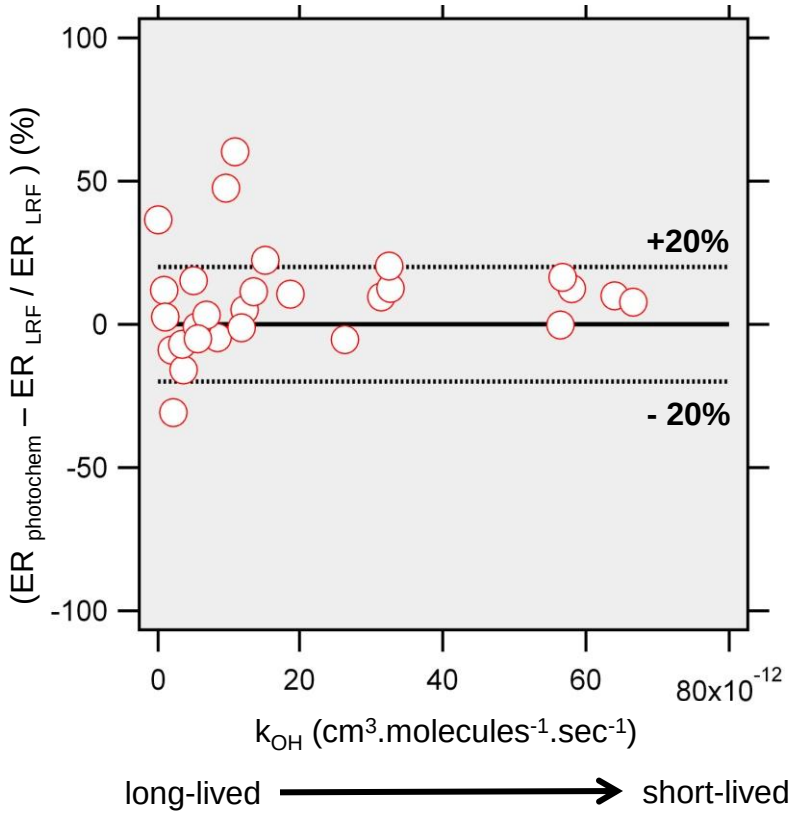
Performance

- for primary anthropogenic VOCs

ER (C2H2) comparison



Relative difference vs rate coefficient

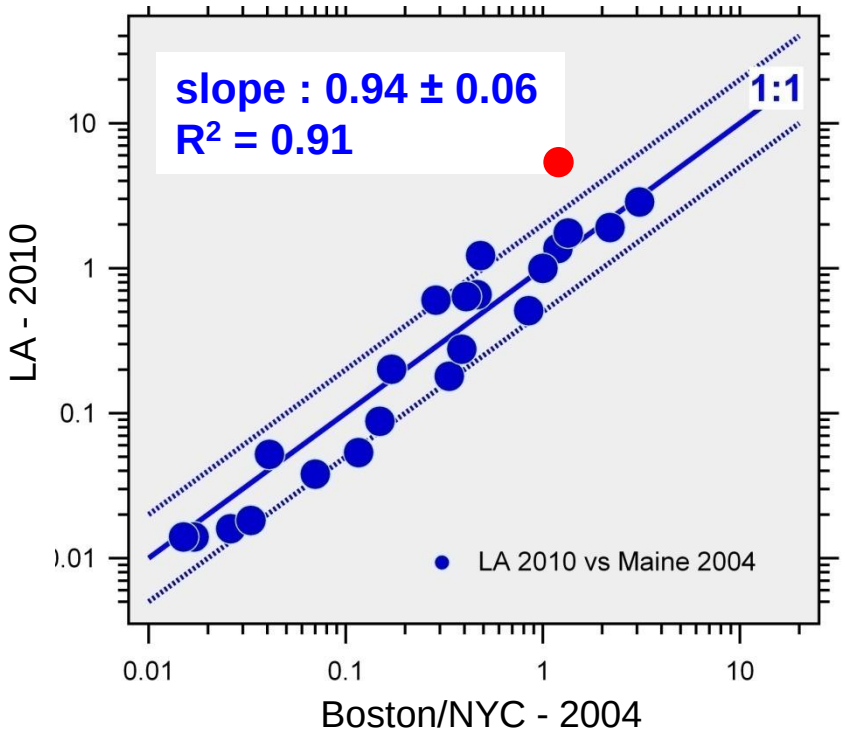


⇒ **very good agreement**

⇒ **relative difference ≤ ± 20%**

Trends : LA vs Boston/NYC-2004

ΔVOC/ΔC2H2

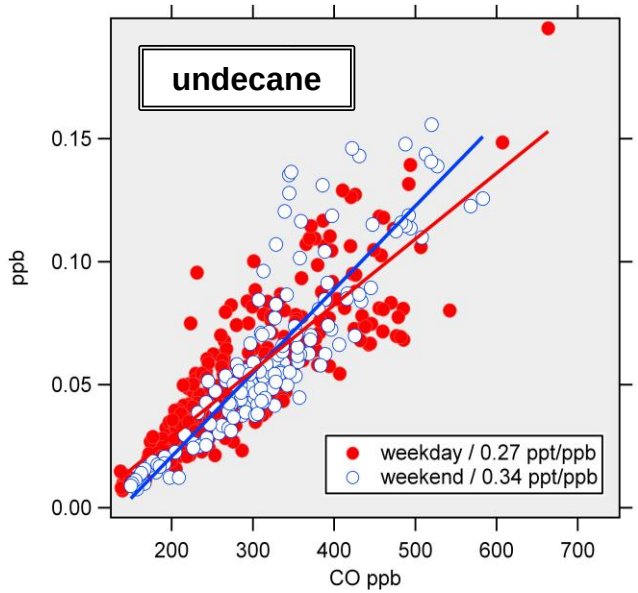


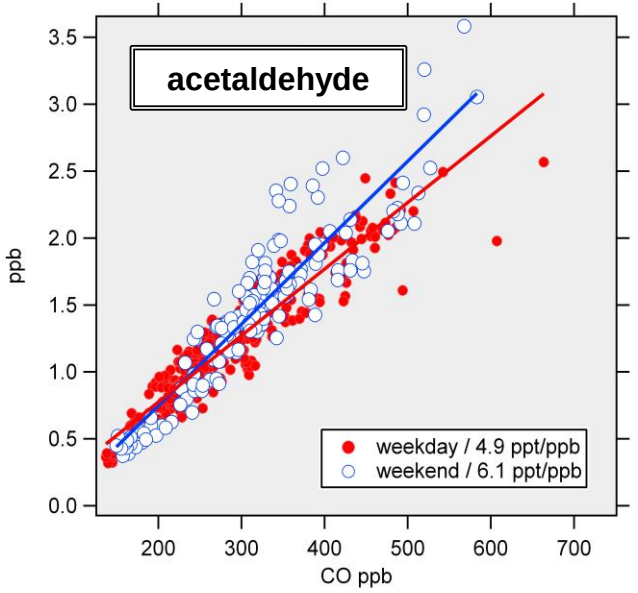
- **ethanol**

very good agreement except for ethanol (biofuel additive to gasoline)

Week-end vs week-days

diesel-fueled vehicle exhaust related





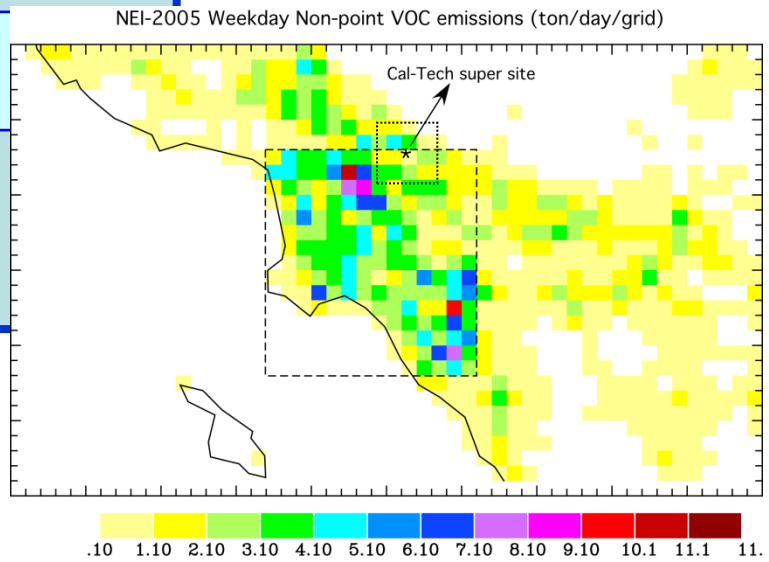
abundances constant
no statistical differences between slopes (t-test ; α = 5%)

$\Rightarrow$ observed VOC and CO emissions are driven by gasoline-fueled LD vehicles
$\Rightarrow$ no weekend-weekday effect from the inventory either

Evaluation of emission inventories

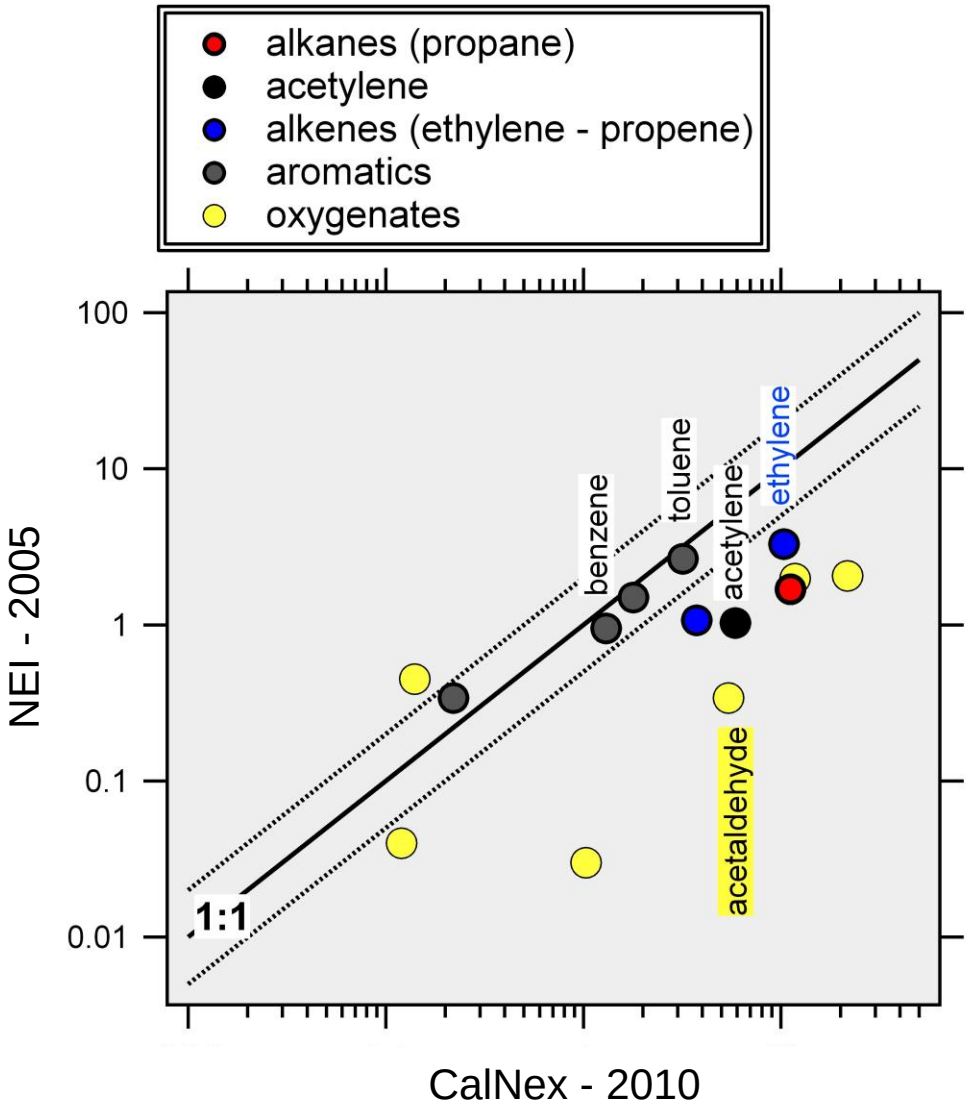
- preliminary
- 2 grids : great LA and Pasadena area

Trace gases	NEI-2005 / dec.2008	CARB-2008
tracer	CO	CO
tracer	acetylene	
alkanes	propane	propane
alkenes	ethylene propene	ethylene
aromatics	BTEX styrene	xylenes
oxygenated	acetaldehyde, butanal, propanal, benzaldehyde, acetone, MACR, MEK, methanol, ethanol, isopropanol	methanol



Evaluation of emission inventory : NEI

ER (VOC/CO)



Consistency for aromatics

⇒ vehicle exhaust origin

Large discrepancies for other VOC

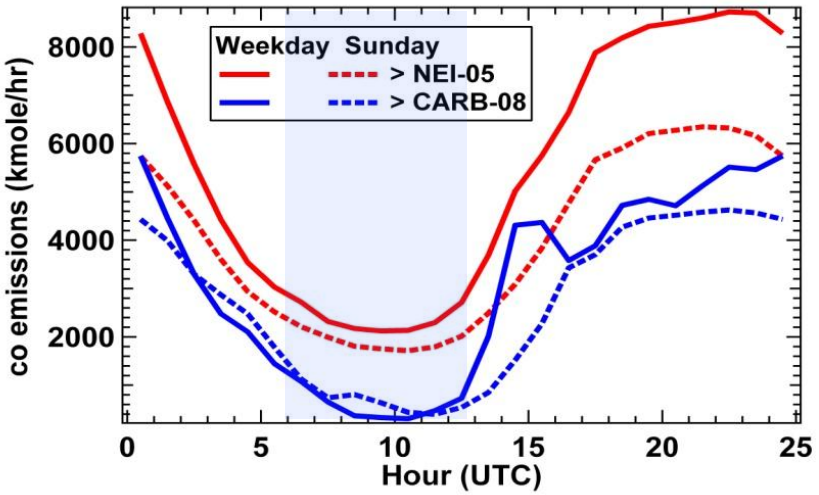
tracer : acetylene

alkenes < propane < oxygenates

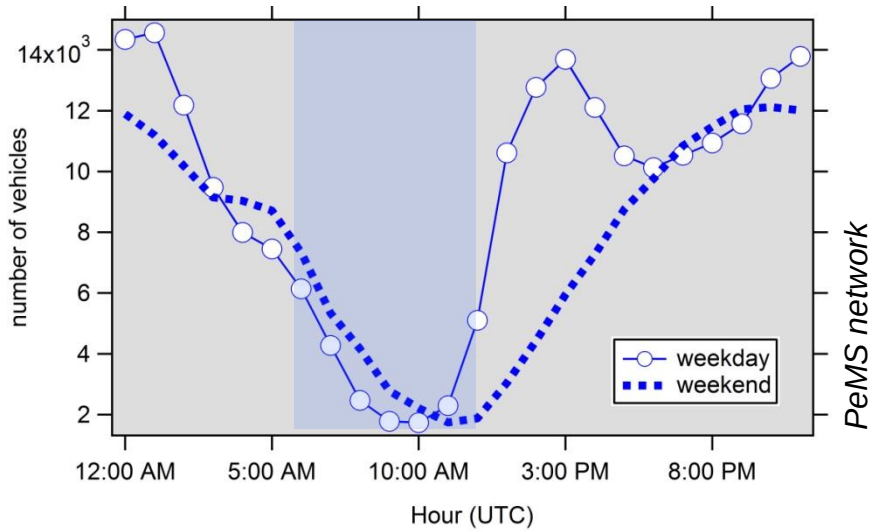
⇒ area source contribution for alkanes and oxygenates

CARB-2008 vs NEI-2005

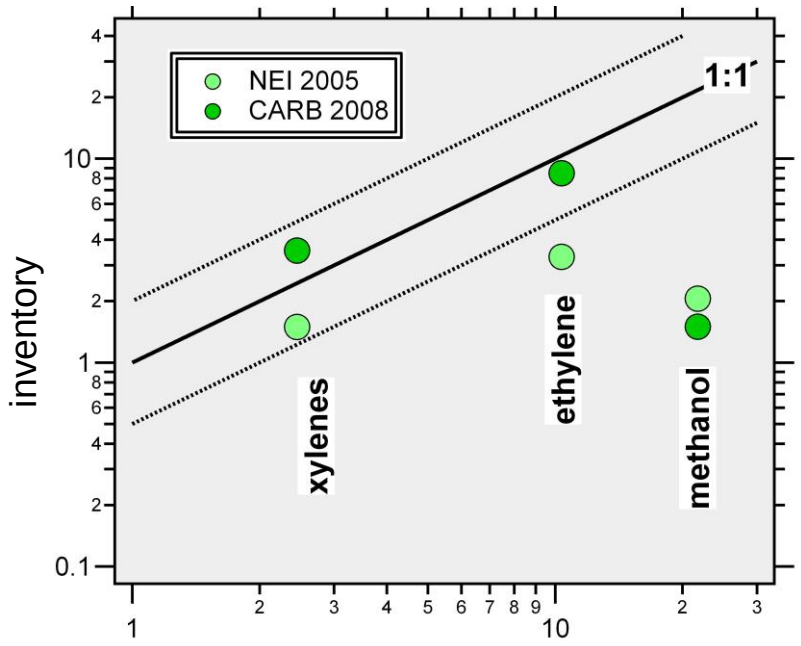
Hourly emissions of CO



Hourly trafic counts



3 non-lumped species : ethylene, xylenes, methanol



CalNex - 2010

Summary

Determination of urban emission ratios :

- ER derived for 42 VOCs at ± 20% ⇒ efficiency of both independent approaches.
- ER consistent with previous datasets.

Weekend vs weekday :

- No weekend effect at the groundsite ⇒ gasoline vehicle exhaust emissions dominate VOC composition (at least observed ones).

Preliminary evaluation of emission inventory :

- Large discrepancies with NEI (overestimation of CO emissions). Consistent previous studies.
- Emission ratios with CARB-2008 seem to agree better

Thank you !