Laboratoire des Sciences du Climat et de l'Environnement

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# OH reactivity measurements in Paris during the winter campaign of the MEGAPOLI project (January-February 2010)


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## Abstract:

The hydroxyl radical (OH) is the main oxidant of the troposphere and the main sink of most volatile organic compounds (VOCs). Despite the unique information that OH reactivity measurements can provide about atmospheric photochemistry (oxidant capacity of the atmosphere), few measurements are available due to the complex equipment required. A new more simple method developed by Sinha et al. (ACP, 2008) provides a promising alternative for quantifying the total OH reactivity of ambient air. The method is based on the fast measurements (e.g. using a PTR-MS instrument) of a molecule not normally present in the atmosphere (here pyrrole, C4H5N) which reacts at a known rate with artificially generated OH radicals. Comparing the measured signals of pyrrole with and without ambient air within a constant OH field permits the quantification of the total OH reactivity of ambient air. For the first time, this method was deployed in Paris to measure the total OH reactivity in a large urban center along with simultaneous measurements of individual VOCs performed during the EU-MEGAPOLI (Megacities: Emissions, urban, regional and Global Atmospheric POLlution and climate effects, and Integrated tools for assessment and mitigation) winter campaign (January 15-February 15, 2010). The campaign took place in downtown Paris at a site classified as an urban background site, being therefore representative of the atmospheric composition of Paris. Experimental details of the OH reactivity system and its characterization are shown here. Among the various tests performed, the NO interference study is presented, as NO varied over the day by two orders of magnitude (from 1 to 100 ppb). Finally, preliminary results of the OH reactivity variability during the campaign are discussed.


## 1. Context:

MEGAPOLI* = European project (2008-2011) including 23 partners

Main objectives:

- ***To assess impacts of megacities on local, regional and global air quality;***
- To quantify feedbacks among megacities air quality, local and regional climate, and global change; and
- To develop improved integrated tools for prediction of air pollution in megacities

* http://megapoli.dmi.dk

Megacity Plume Case Study: ***PARIS*** → 2 intensive campaigns : July 2009 and ***January-February 2010***


***OH Reactivity measurements*** in the center of Paris at Laboratoire d'Hygiène de la Ville de Paris (LHVP)

MEGAPOLI framework completes the OH reactivity data set with other compounds data sets (CO, NO, $NO_2$, $O_3$, NMHC, VOC) measured at LHVP

## 2. Methodology

$$X + OH \xrightarrow{k} products$$

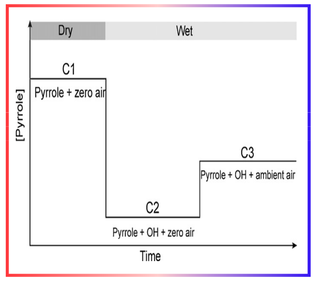
(where X = atmospheric species reacting with OH)

$$reactivity = \sum_i k_{i(X+OH)} \cdot [X_i]$$

**Total OH reactivity method or the "Comparative Reactivity Method" (CRM)**

A molecule not normally present in ambient air is introduced into a glass reactor (here pyrrole, C4H5N) :

- ✓ Pyrrole's concentration is monitored with a PTR-MS** (Proton Transfer Reaction - Mass Spectrometer) (C1)
- ✓ Synthetically generated OH radicals are introduced into the cell to react with the pyrrole. Pyrrole concentration decreases to (C2)
- ✓ Ambient air is introduced into the cell. Competition for the OH between the OH reactive species and pyrrole. Less OH is consumed by pyrrole. Concentration of pyrrole increases to (C3)




***(Sinha et al., 2008***)***

$$R_{air}(s^{-1}) = \frac{C_3 - C_2}{C_1 - C_3} \cdot k_{Py} \cdot C_1$$

where :

- $k_{Py}$ = rate coefficient of the pyrrole with OH ($cm^3 molecule^{-1} s^{-1}$)
- C1, C2 and C3 = volume mixing ratios (molecule $cm^{-3}$)

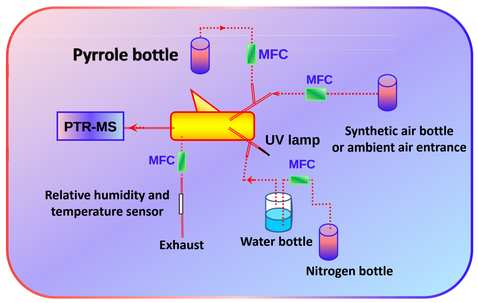
** PTR-MS by IONICON

***Sinha V., Williams J., Crowley J.N., Lelieveld J., *The Comparative Reactivity Method – a new tool to measure total OH reactivity in ambient air*, Atmos. Chem. Phys., vol. 8, 2008

## 3. Experimental setup and conditions:

**Experimental conditions :**

- ✓ Internal volume of the glass reactor : 100 sccm
- ✓ Continuous flows of gases (total flow of around 244 ml/min):
  - Pyrrole : 4 ml/min (standard bottle of 10 ppm)
  - Nitrogen : 90 ml/min
  - Zero air : 150 ml/min
- ✓ Artificial OH production:
  - Humidification of the nitrogen by bubbling it through a water bottle;
  - Photolysis of the water molecules with the UV produced by the mercury lamp;
- ✓ Ambient air brought to the reactor via a Teflon pump;




**MEGAPOLI campaign :**

***From 8th to 23rd of January Reactivity tests :***
- Pyrrole calibrations (dry and humid conditions);
- Method tests (e.g. humidity effect tests; NO effect quantification; flows regulation …)

**From 23rd of January to 15th of February:**
- ***Reactivity measurements***
- Regular check of C1, C2 levels …

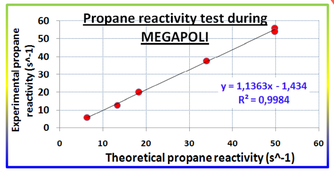
## 4. Tests and results:

### 4.1. Reactivity tests:

**Method validation:**

Injection into the reactor of a propane standard (propane concentration and reaction rate of propane are known) and evaluation of the measured reactivity with the theoretical value.

***The slope of the curve is close to 1.***



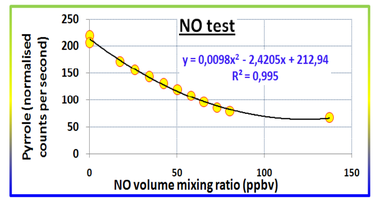

**Potential artifact due to OH recycling in presence of atmospheric NO:**

**OH production:**

- Primary reaction: $H_2O \xrightarrow{184\,nm} OH + H$
- Secondary reaction (in presence of NO):

$$H + O_2 + M \rightarrow HO_2 + M$$

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




***Paris NO values during MEGAPOLI up to 100 ppb.***

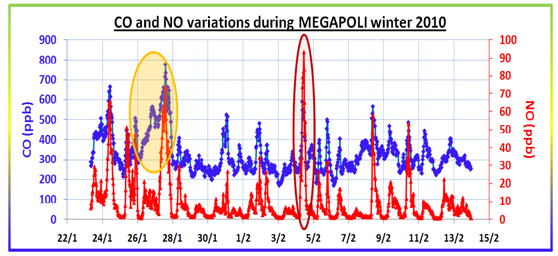
***Decrease of 65% of the pyrrole signal for 80 ppb of NO!***

### 4.2. Pollution plumes during MEGAPOLI:

***Measurements of various (particulate and gaseous) compounds during the MEGAPOLI campaign showed that traffic and wood burning were the most important polluting sources.***

***2 pollutants presented:***

- ➢ CO = long life time compound – signature of a long distance pollution plume
- ➢ NO = short life time compound – signature of local pollution

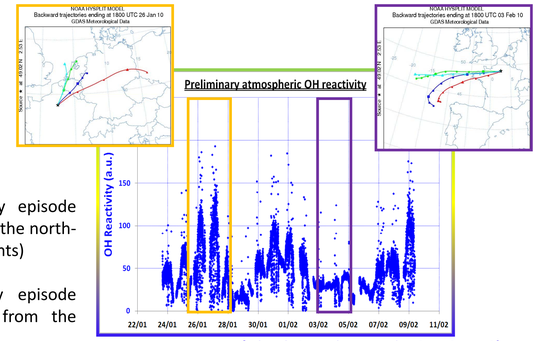



### 4.3. First results on reactivity:

***Influence of the origin of the air masses on the Paris OH reactivity:***

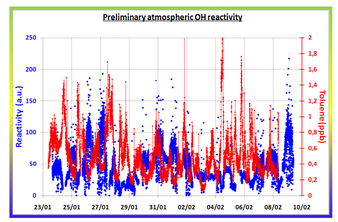
***Two contrasted periods were identified:***

- ➢ 26th-27th of January a high OH reactivity episode corresponding to air masses originating from the north-eastern part of Europe (air charged in pollutants)
- ➢ 3rd-5th of February a low OH reactivity episode corresponding to air masses originating from the Atlantic Ocean (clean air)



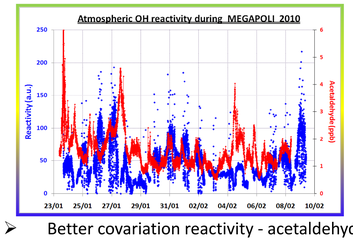

***(Absolute values under treatment)***

***a) Comparison OH reactivity – primary VOC:***




➢ No covariation reactivity - toluene

***b) Comparison OH reactivity – secondary VOC:***




➢ Better covariation reactivity - acetaldehyde

***The reactivity in Paris seems to be influenced more by episodes characterizing the regional-continental scale than local one.***

## Conclusion:

1) **The preliminary OH reactivity results show that the Paris OH reactivity is mainly impacted by regional scale pollution episode rather than direct local emissions.**
2) **First OH reactivity quantification suggests values up to 100 $s^{-1}$. Corrections for the high NO values measured in Paris will result in OH reactivity > 100 $s^{-1}$. Therefore additional tests will be performed for final quantifications.**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