Time-resolved and Online Determination of Reactive Oxygen Species (ROS) in Ambient Air

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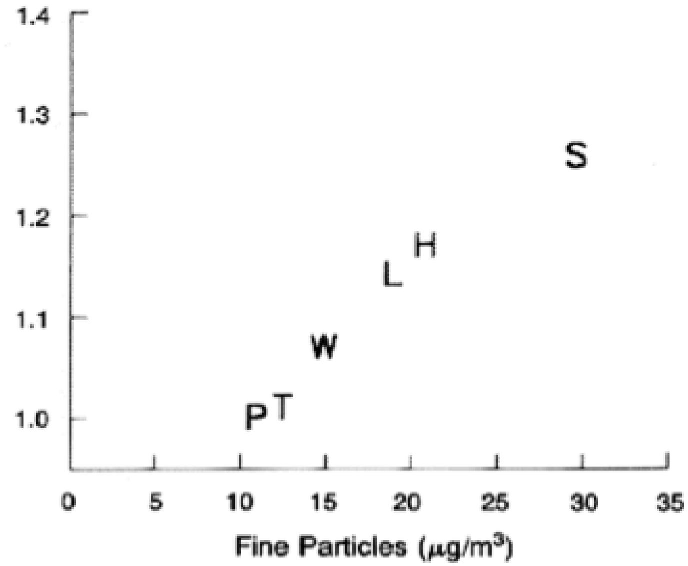
Overview

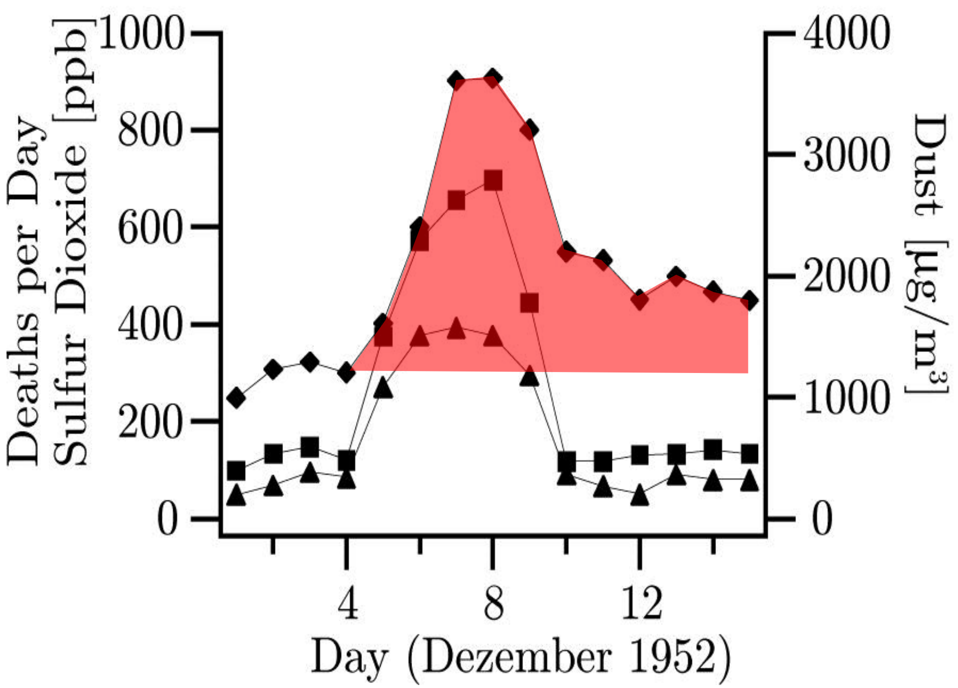
- Oxidative stress - a possible mechanism of particle-induced health effects
- A new instrument measuring reactive oxygen species (ROS) concentration on-line: design and instrument characterization
- First applications of the instrument

Health effects of aerosols

Ambient particle cause negative biological/health effects as observed in epidemiological and laboratory studies



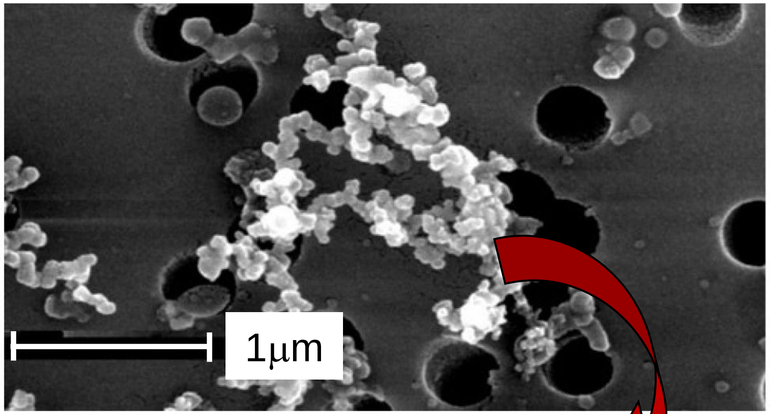
Six cities study, Dockery et al. 1993



◆ ***Deaths*** ■ SO_2 ▲ aerosol particles (dust)

What particle properties are relevant for biological effects?

particles e.g., from combustion sources

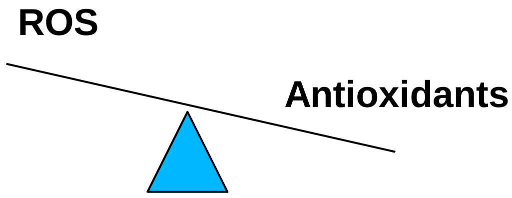


<u>effects in the cell</u>
- ROS?
- *oxidative stress?*
- inflammation

<u>*potential* damaging properties</u>
- organic components
- metals
- mass, size, surface properties

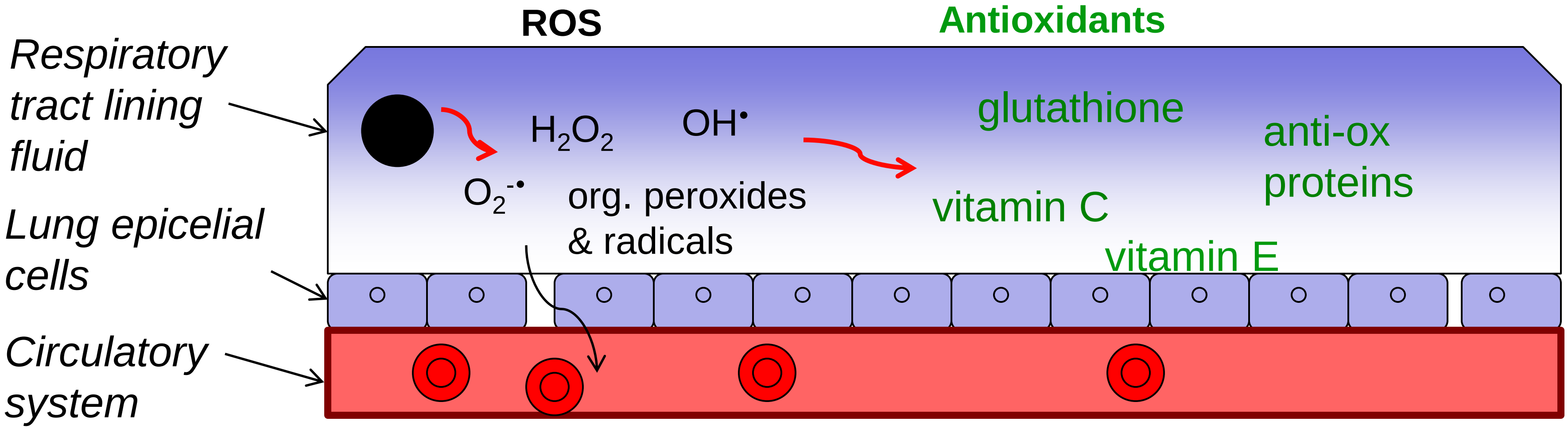
Oxidative stress in the lung

- Oxidative stress = disturbance of prooxidant-antioxidant balance leading to potential biomolecular damage



- Oxidative stress can be induced by ROS in the lung lining layer

- Antioxidant depletion may cause damage to cell membranes, proteins & DNA



PM induced ROS in the lung

Formation routes of ROS from aerosol particles:

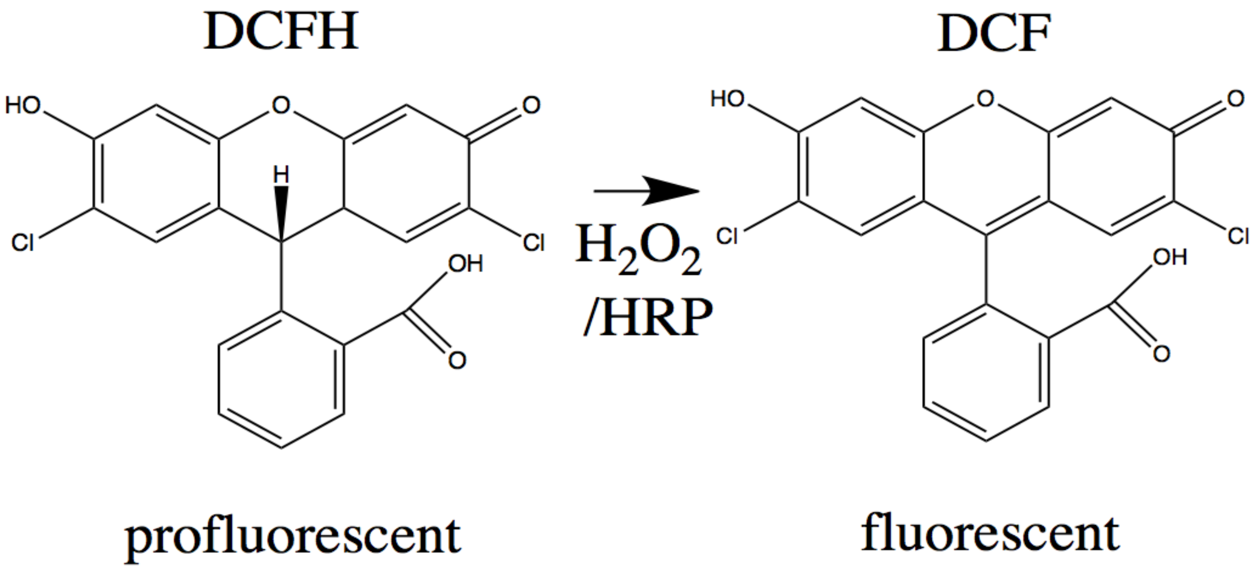
1. Particle bound ROS **–** e.g. H_2O_2, ROOH, radicals
   = reactive and short-lived

2. (Catalytic) ROS production in the lung lining fluid by redox active components; e.g., quinones and metals

3. Metabolism of organics (e.g. PAHs) may lead to ROS formation

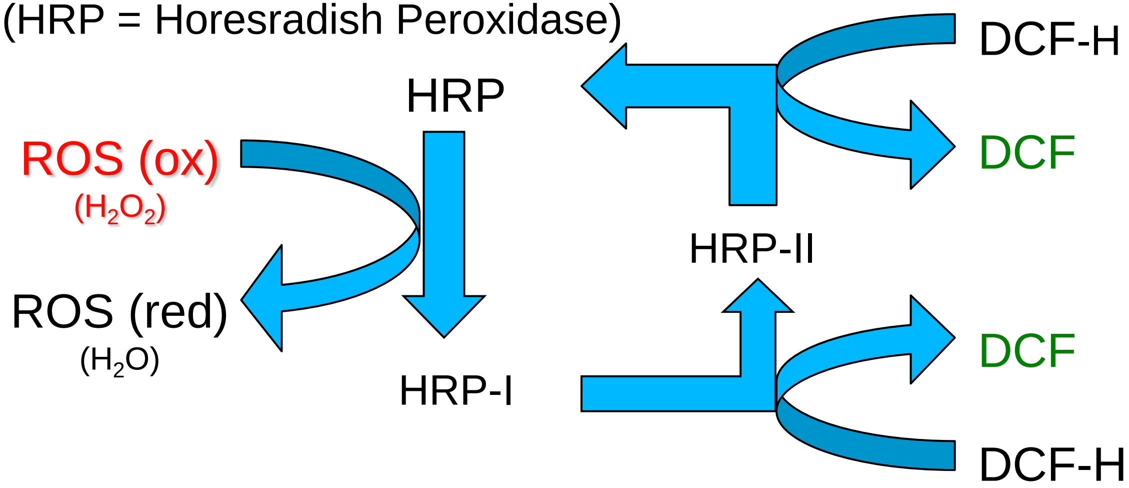
Measuring ROS concentrations in solution
- the reaction system

- DCFH is oxidised by ROS in the presence of **Horseradish Peroxidase** to the fluorescent product DCF; ***excited at 470 nm*** and ***emitting at 520 nm.***
- DCFH reacts with almost all ROS



Measuring ROS concentrations in solution *- the reaction system*

(HRP = Horesradish Peroxidase)



$$I \propto [DCF] \propto [H_2O_2]$$

- The fluorescence is directly proportional to the concentration of DCF
- While the DCFH assay gives a linear relationship with H_2O_2, organic peroxides react much slower with HRP.
- **This assay gives an indication of ROS activity related to an equivalent H_2O_2 concentration. NOT an absolute ROS concentration.**

Measuring ROS concentrations *online*

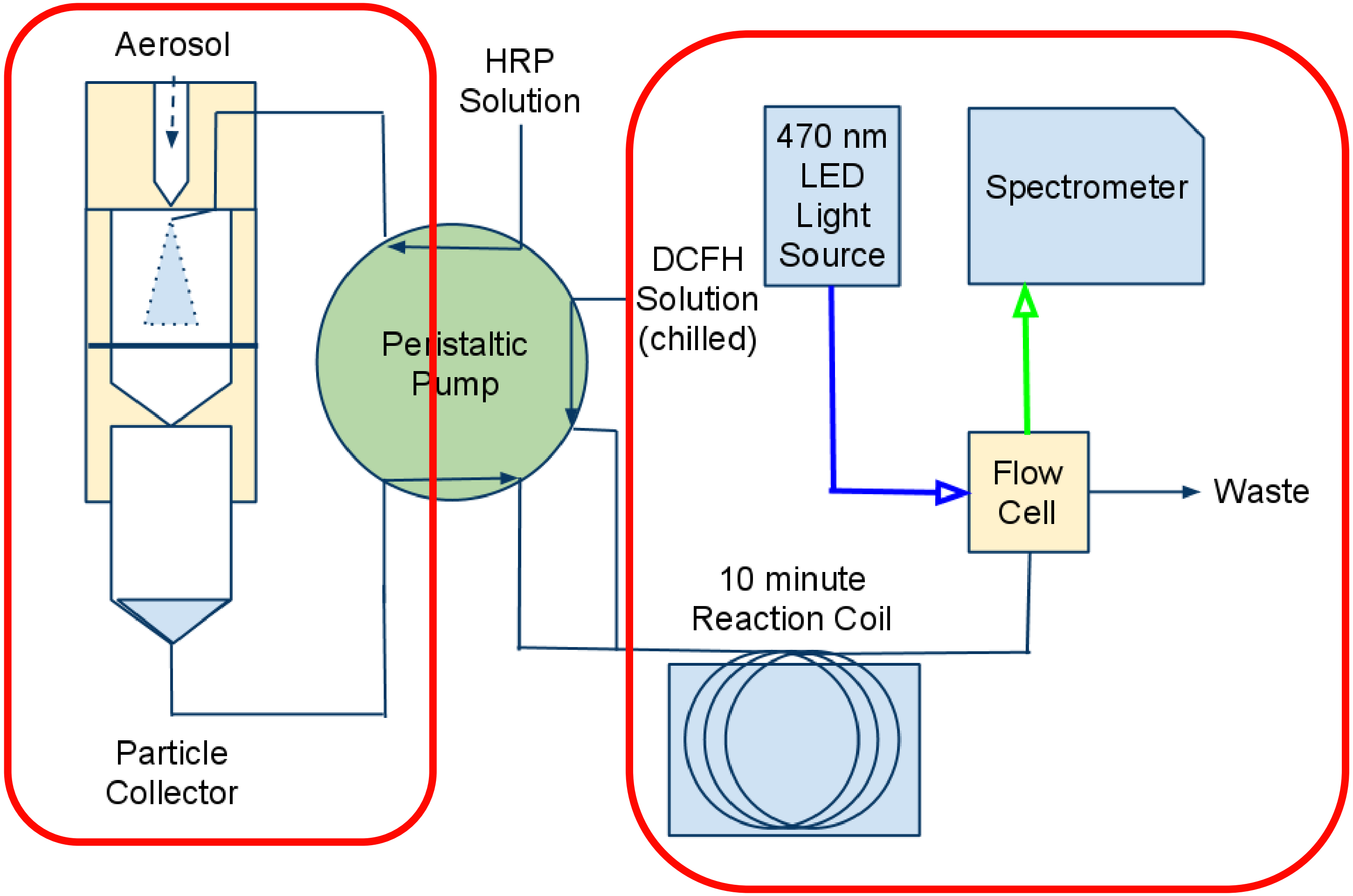
- Many current aerosol studies measuring composition use *off-line filter collection techniques*

- The time delay between collection and analysis possibly allows for ***degradation and loss of reactive components***

- *Online* analysis allows for fast analysis that ***minimizes loss of reactive components*** and allows for higher time resolution

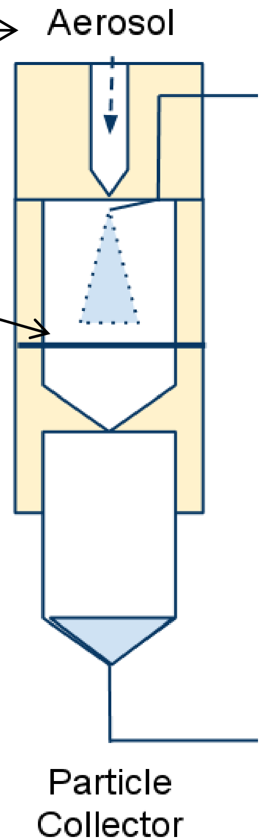
- *Online* analysis allows for ***high time resolution***

Fast Online Quantification of Oxidizing Particle Components



Fast Online Quantification of Oxidizing Particle Components

5 slpm sampling



hydrophobic filter

Continuous collection and solvent extraction

Aerosol inlet

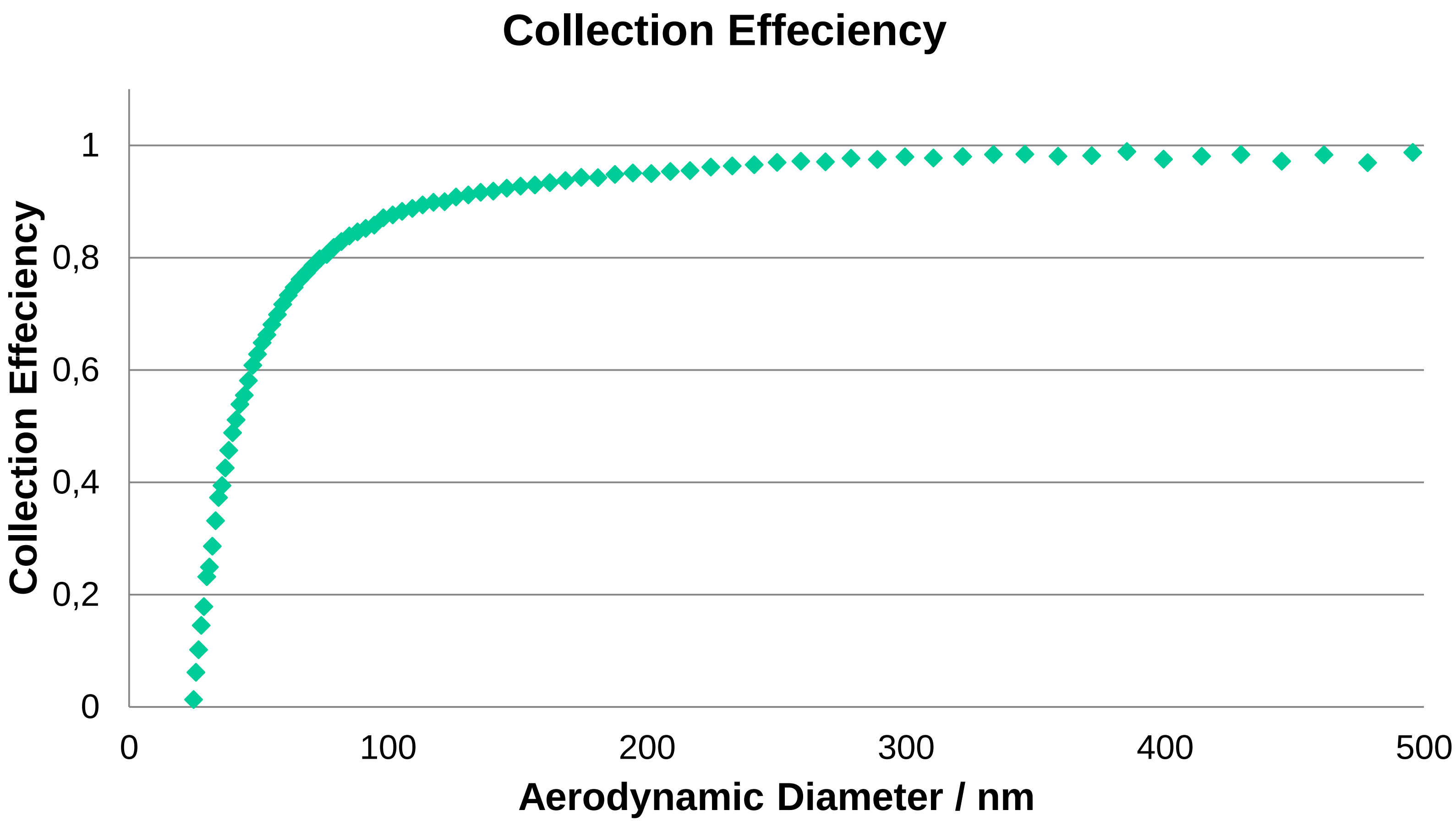
15 cm

HRP solution

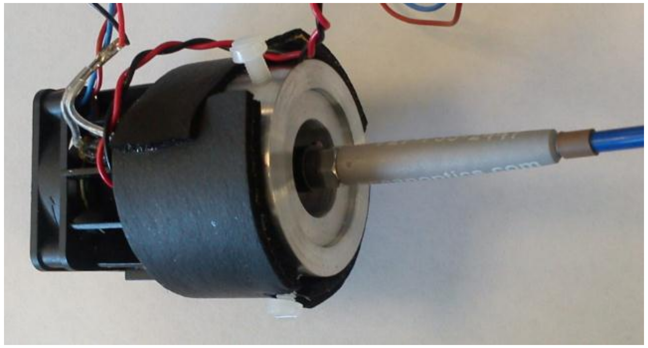
To vacuum pump

To mix with DCFH solution

Particle into liquid sampling



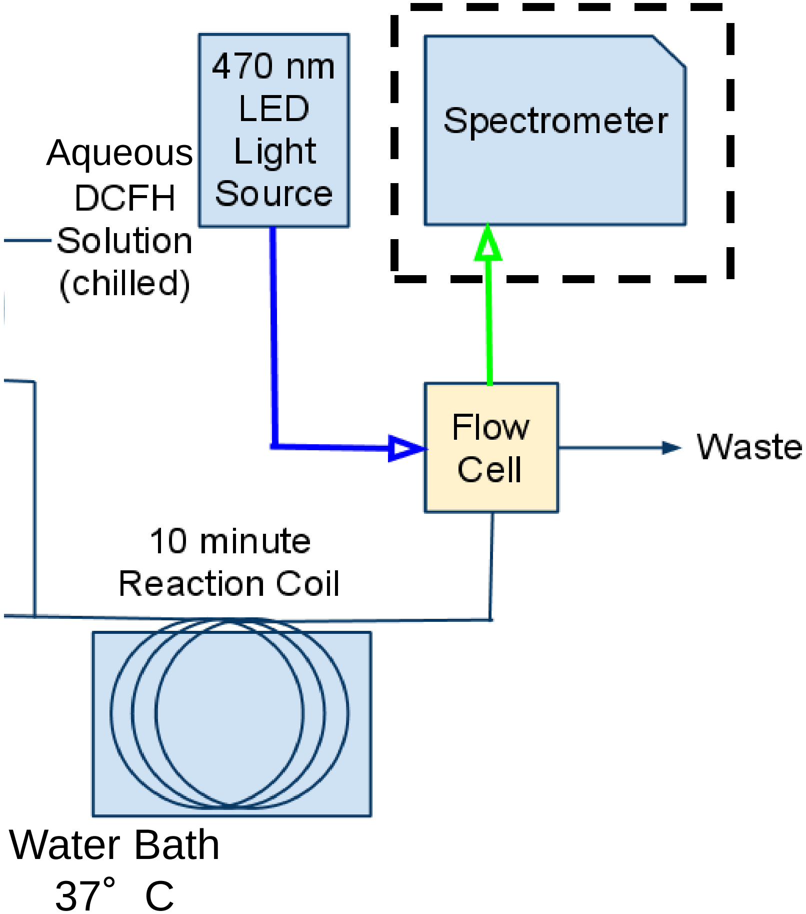
ROS quantification



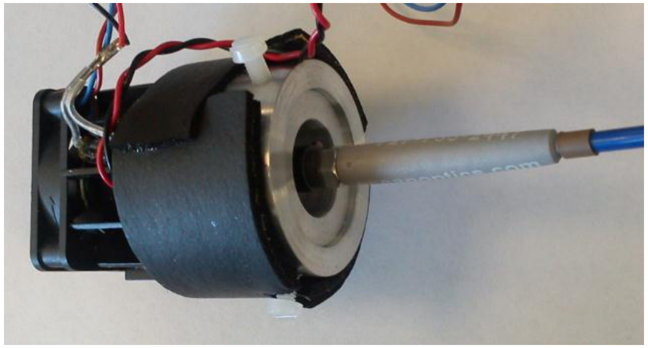
Fan cooled 5 W 470 nm LED

Spectrometer

Connected to LabView program



Experimental set up



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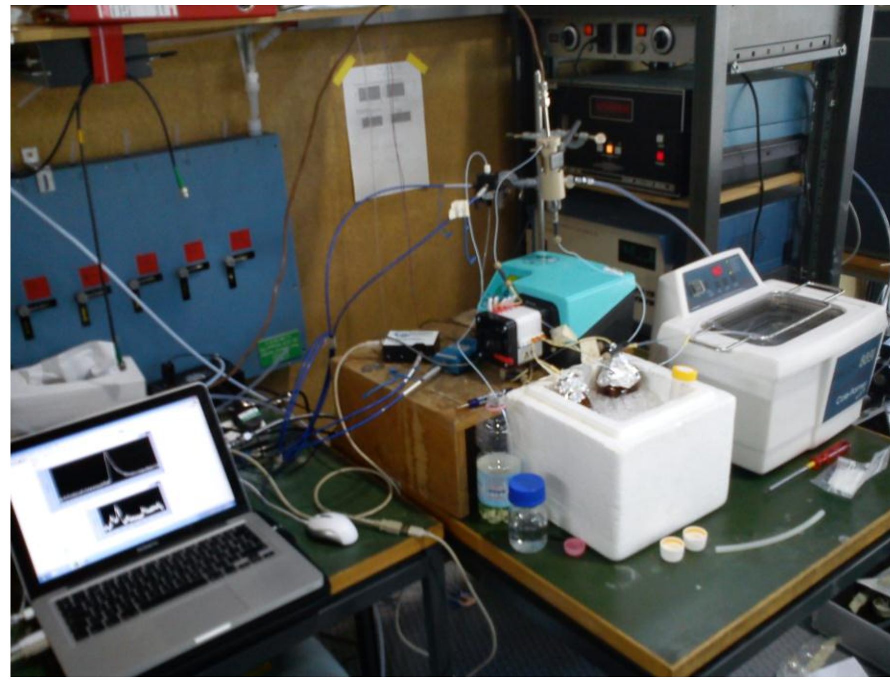
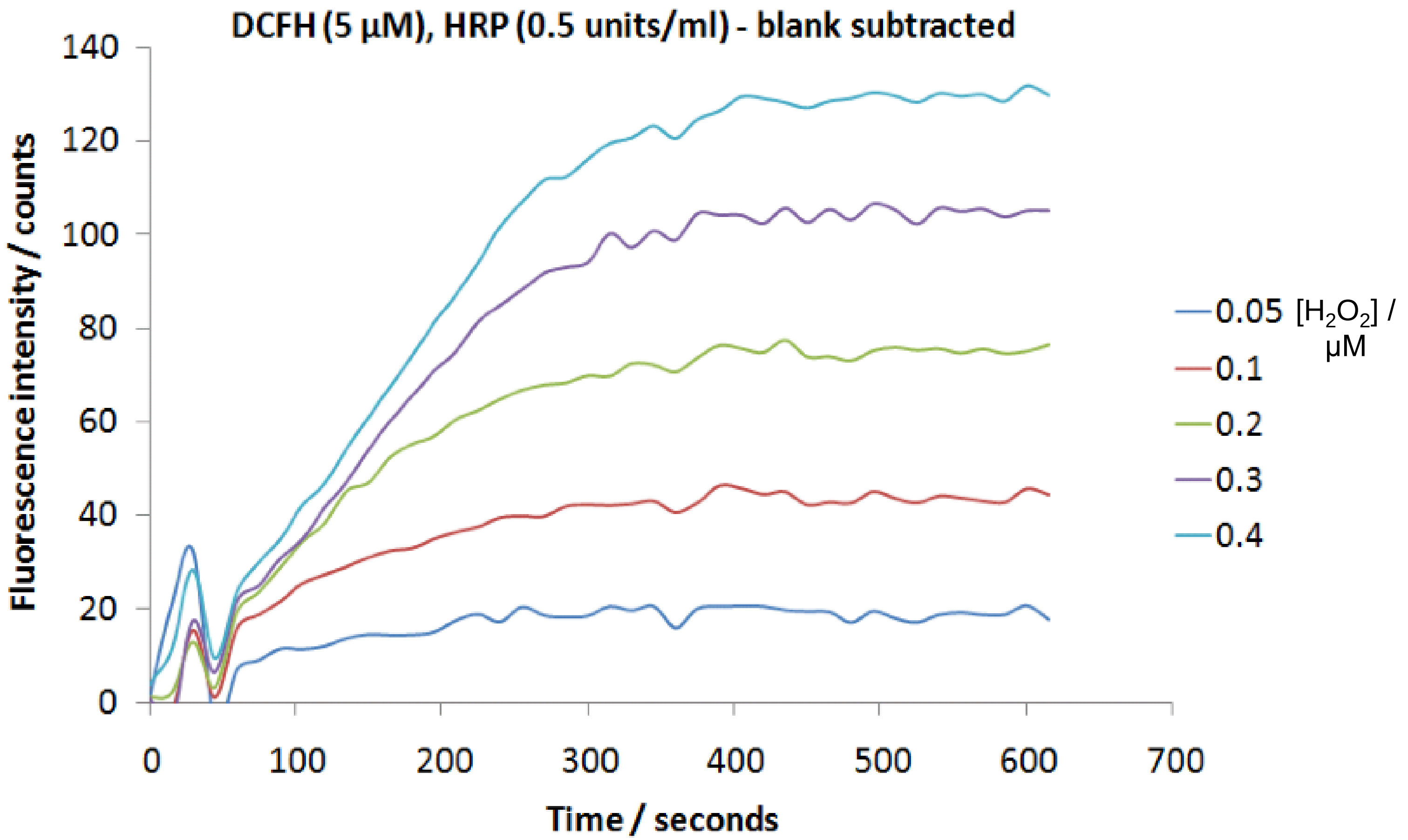
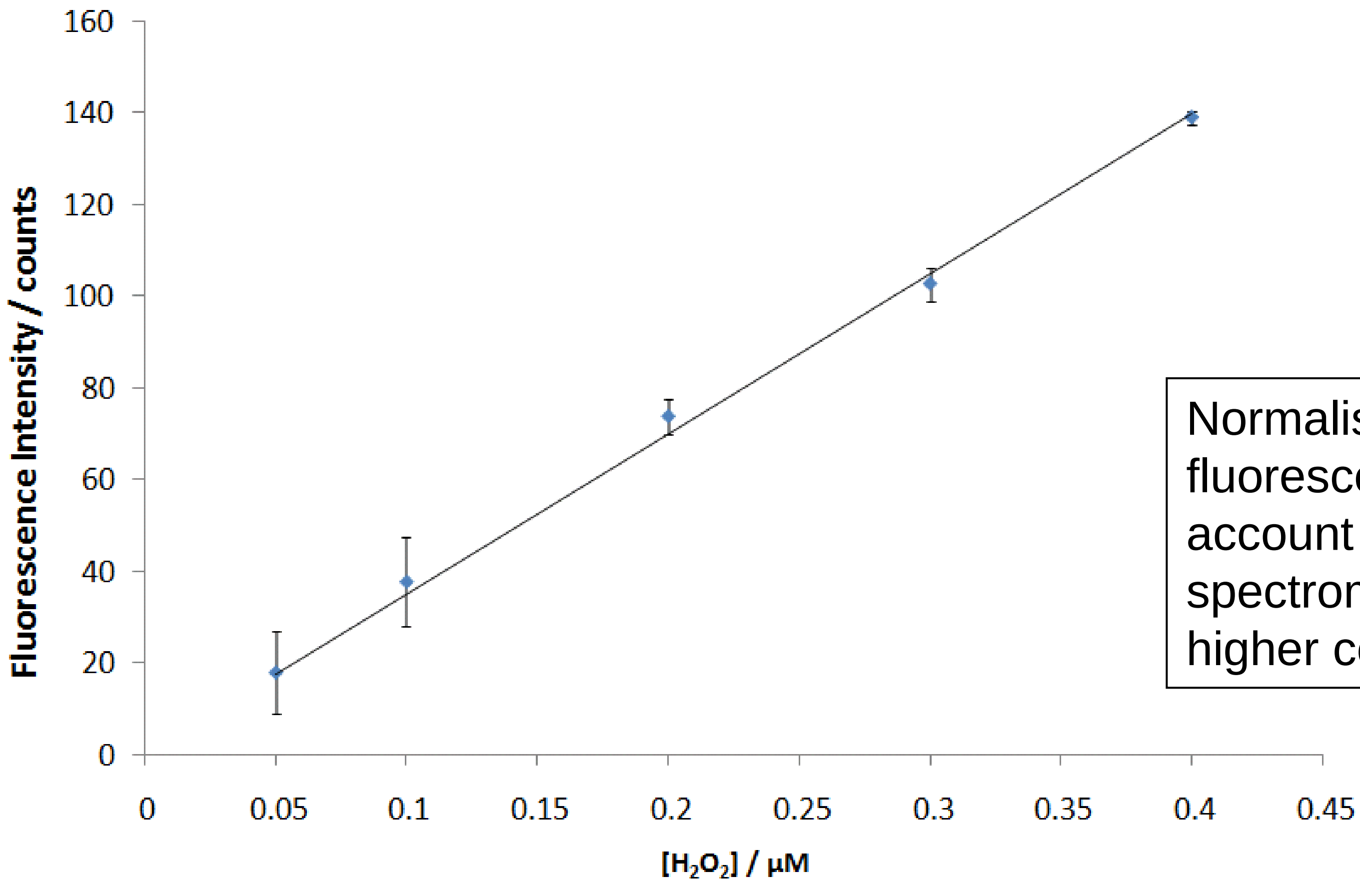


Sensitivity calibration with H_2O_2



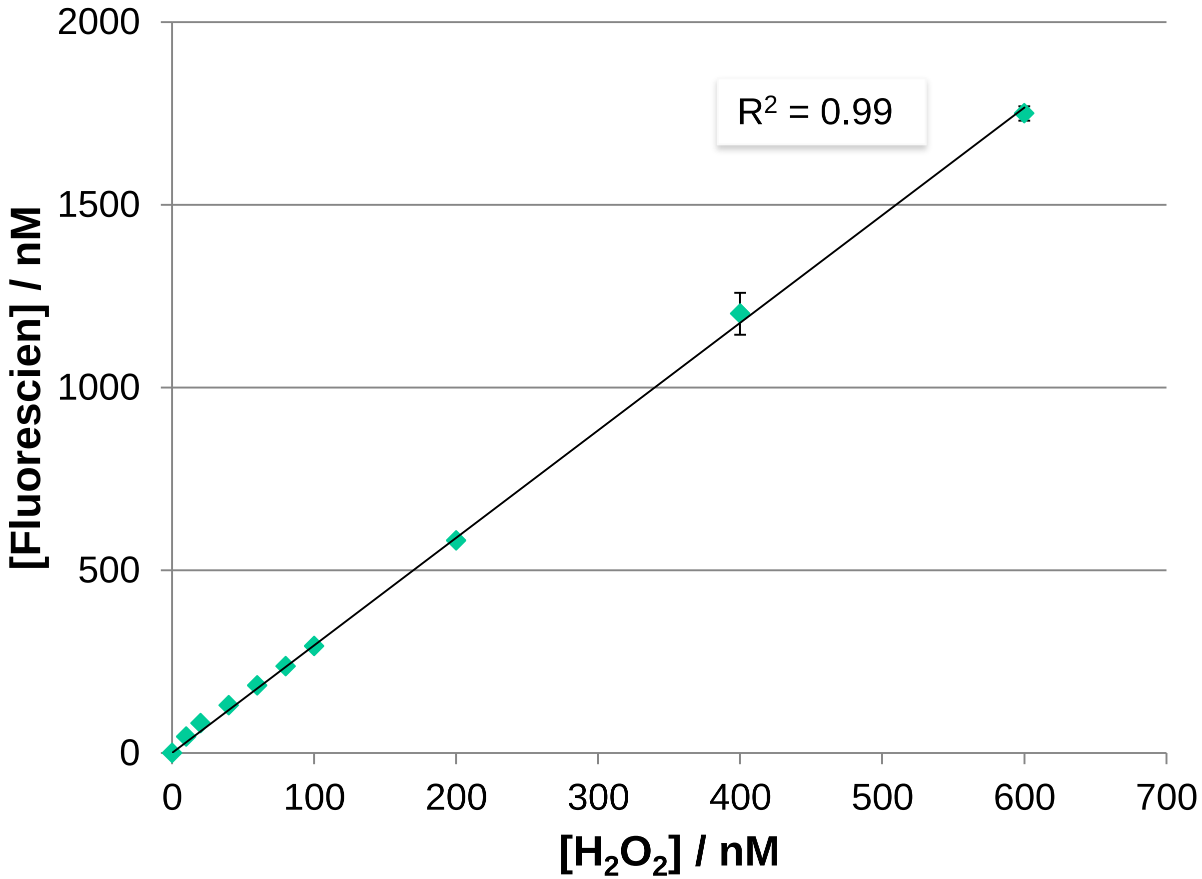
Fluorescence intensity after reaction has gone to completion after <10min

Sensitivity calibration with H_2O_2



Normalised to equivalent fluorescein fluorescence to account for non linear spectrometer behaviour at higher concentrations

Sensitivity calibration with H_2O_2



Dynamic range:

ca. 2 orders of magnitude

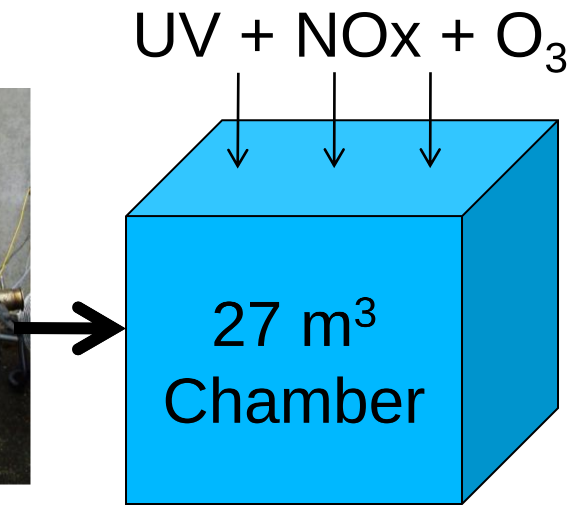
Detection limit:

in liquid H_2O_2: ~ 10 nM

ambient air (5lpm):
4 nmol / m^3

Smog Chamber Experiments

- Experiments at Paul Scherrer Institut (PSI), Switzerland
- Primary moped emissions photochemically aged in smog chamber
- Mopeds conforming to both Euro 1 and Euro 2 emissions regulations



Smog Chamber Experiments

Secondary Organic Aerosol Formation

Primary	Processing	Secondary
Primary organic aerosol (POA) Soot Gaseous volatile organic compounds (VOCs)	→ Oxidation by ozone and OH in the presence of UV light and NOx	Oxidised VOCs condense to form secondary organic aerosol (SOA)

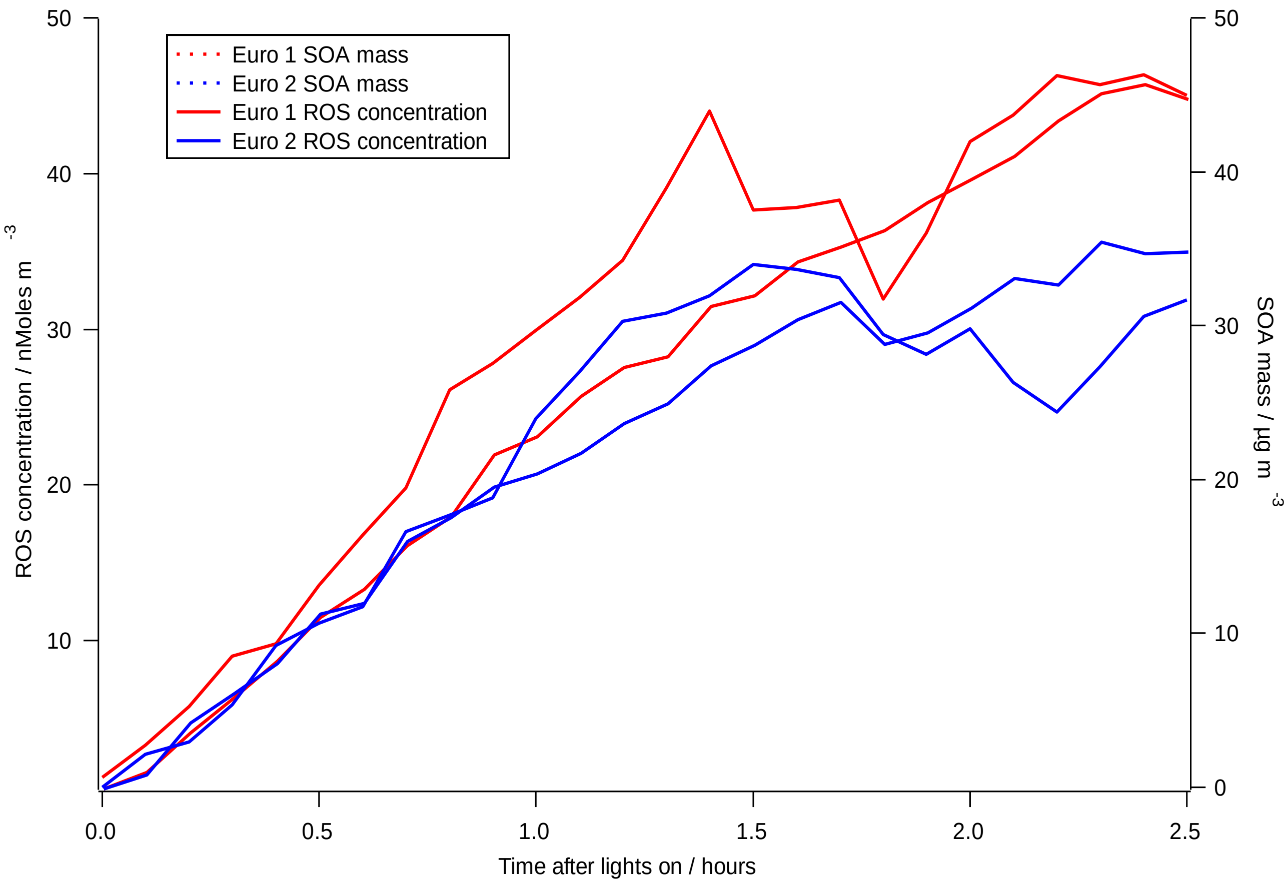
Smog Chamber Experiments

Remove gaseous oxidants

Charcoal Denuder

Online ROS Instrument

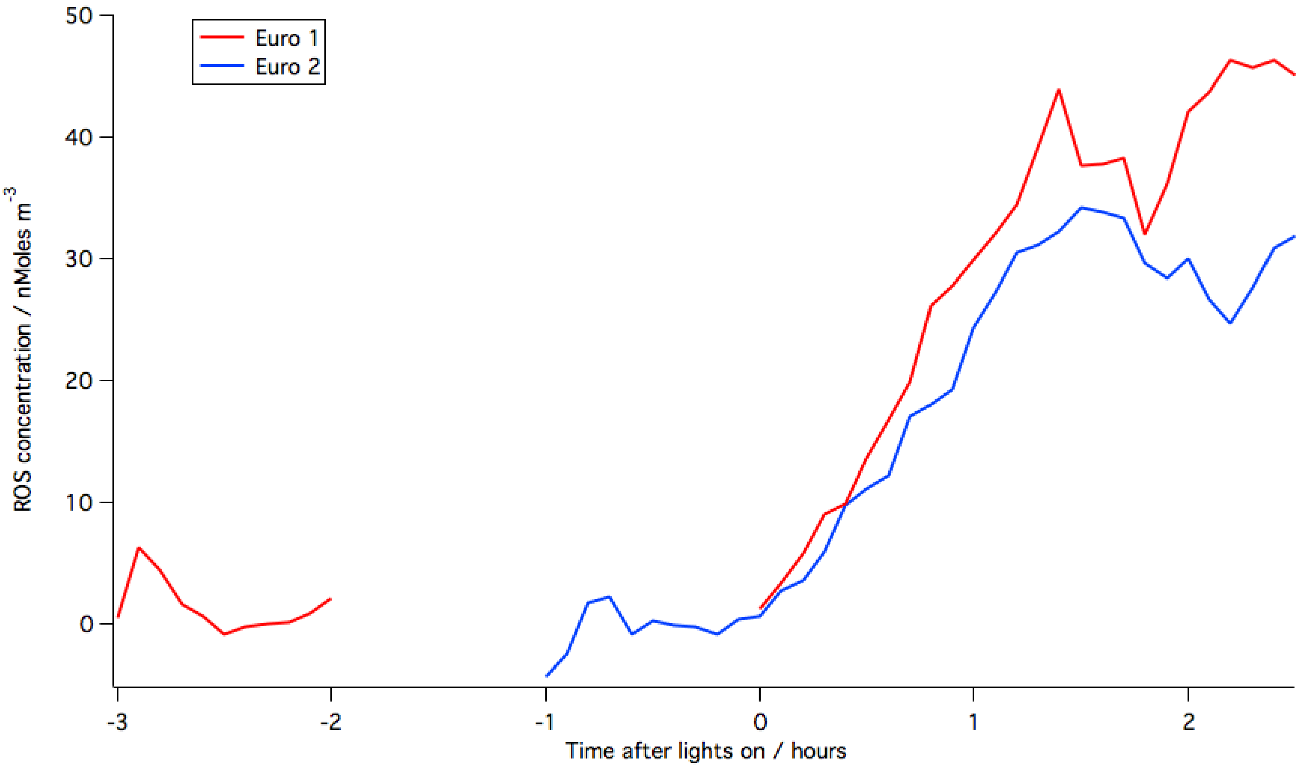
Smog Chamber Experiments



With photochemical SOA formation: increase of ROS

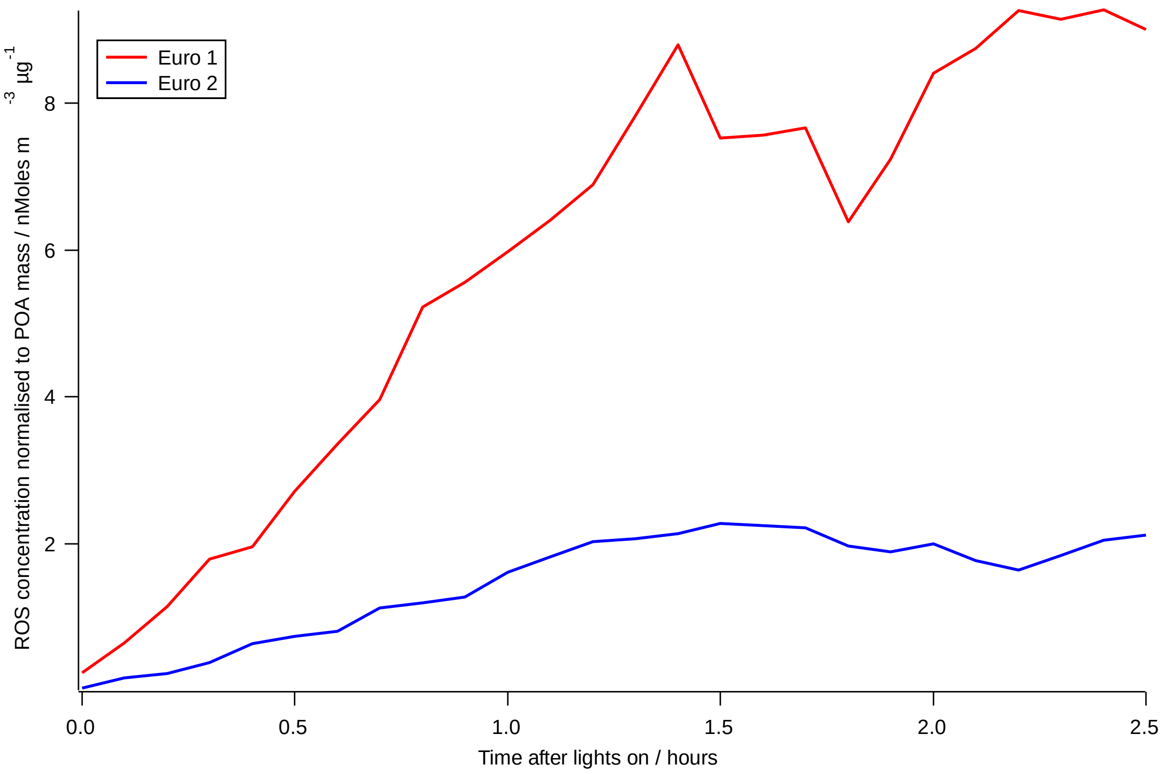
ROS =
ca. 1 nmol μg^{-1} SOA

Smog Chamber Experiments: POA vs. SOA



ROS concentration in POA (before photochemical aging): negligible

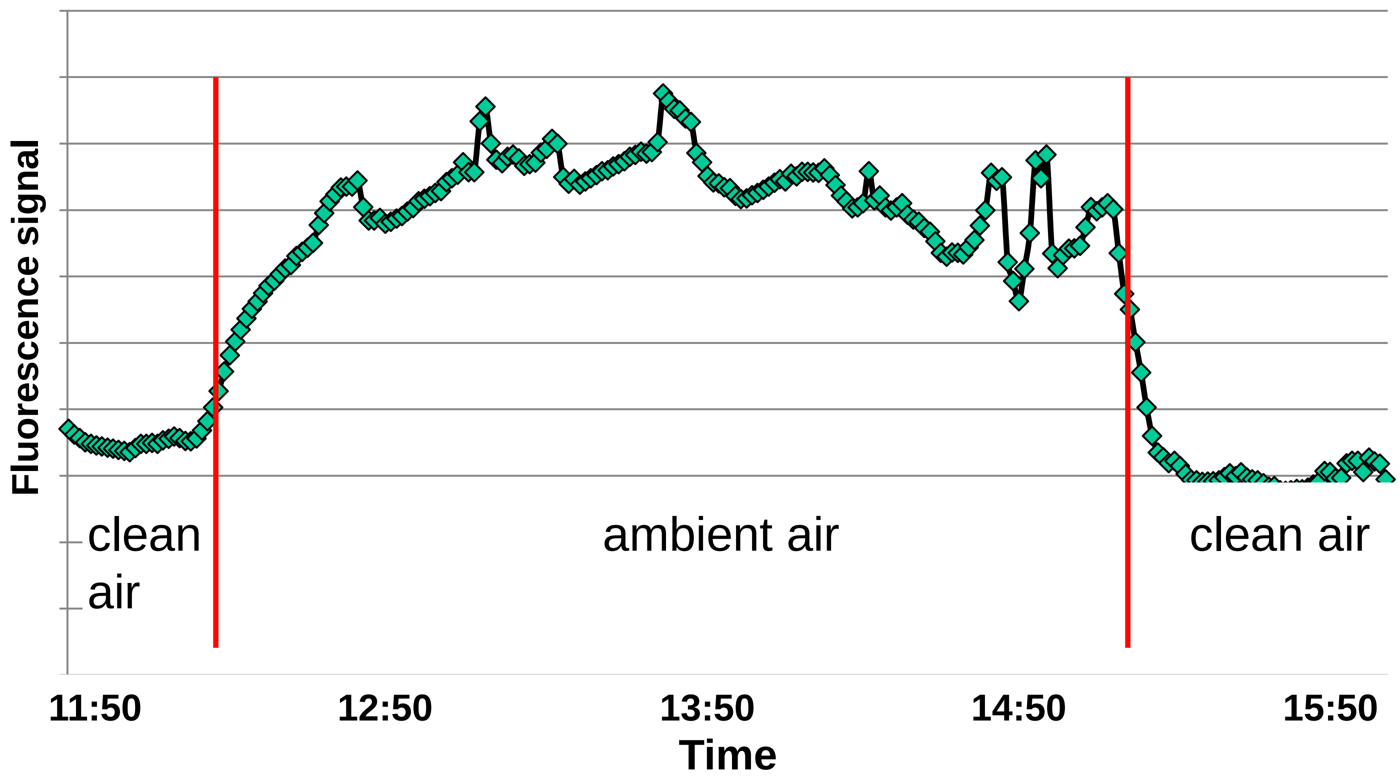
Smog Chamber Experiments: Euro1 vs. Euro2



ROS / µg POA large differences between Euro 1 and Euro 2

Ambient measurements

ROS in ambient urban air (Cambridge)



Conclusions

- Design of online instrument to quantify ROS
- ROS “scavenged” within seconds: reactive ROS are *not lost*
- Time resolution: ca. 10min
- Detection limit: 10nmol (H_2O_2), 4 nmol / m^3
- ROS only observed in SOA from moped emissions
  ROS concentrations of ca. 1 nmol μg^{-1} SOA
- No ROS in primary moped emissions

Acknowledgements

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Thanks for your attention