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Online detection of the oxidative potential of ambient particulate matter by electron paramagnetic resonance spectroscopy

BOHS
The Chartered Society for Worker Health Protection
25 - 27 September 2017
Glasgow Marriott Hotel
IPXII
Inhaled Particles XII

Introduction

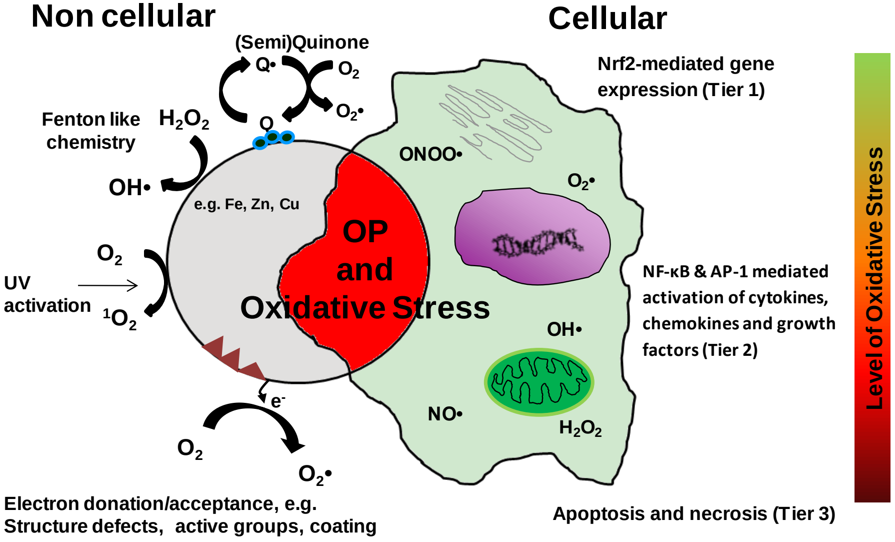
What is Oxidative Potential?

Collective term for compounds containing and/or generating oxygen radicals or oxidative agents. Further often used terms are redox activity and reactive oxygen species (ROS).

Why is it of relevance?

- ➢ OP formed in cells change the redox status of the cells

→ triggering processes leading to pro-inflammation and oxidative stress in biological systems (e. g. *Li et al. 2003, Delfino et al. 2005, Brook et al. 2010*).

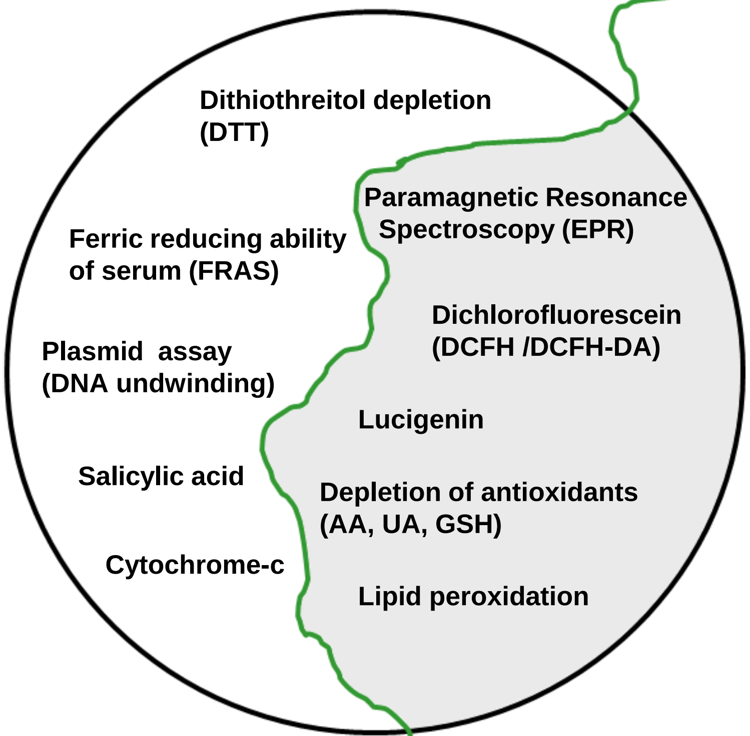


Hellack et al. 2017, Env. Sci. Nano

- ➢ **ROS/OP** is nowadays considered as a relevant indicator of PM induced health effects (Ayres et al. 2008).

Introduction

OP approaches



„Off-line Methodology“ Disadvatages

Sample collected on filter for several hours to days and subsequently analysis in lab

→ Poor time resolution

→ Sampling on filters

→ Labour intensive, requires large resources (equipment/man-power)

→ Exposure → Analysis takes hours (at least 24-48 h)

Hellack et al. 2017, Env. Sci. Nano

Introduction

Online-OP approaches?

Dithiothreitol depletion (DTT)

Paramagnetic Resonance Spectroscopy (EPR)?!

Microfluidics / Sensors

Dichlorofluorescein (DCFH /DCFH-DA)

A Microfluidic Paper-Based Analytical Device (μPAD) for Aerosol Oxidative Activity
Environ Sci Technol. 2013 January 15; 47(2): 932–940. doi:10.1021/es304662w.
Yupaporn Sameenoi†, Orawon Chailapakul‡,

Microfluidic Electrochemical Sensor for On-line Monitoring of Aerosol Oxidative Activity
J Am Chem Soc. 2012 June 27; 134(25): 10562–10568. doi:10.1021/ja3031104.
Yupaporn Sameenoi†, Kirsten Koehler‡, Jeff Shapiro‡, Kanokporn Boonsong†, Yele Sun§,∥, Jeffrey Collett Jr.§, John Volckens‡, and Charles S. Henry†,*

LABORATORY EVALUATION OF A MICROFLUIDIC ELECTROCHEMICAL SENSOR FOR AEROSOL OXIDATIVE LOAD
Aerosol Sci Technol. 2014 May 1; 48(5): 489–497. doi:10.1080/02786826.2014.891722.
Kirsten Koehler[1], Jeffrey Shapiro[2], Yupaporn Sameenoi[3], Charles Henry[4], and John Volckens[2]

An online monitor of the oxidative capacity of aerosols (o-MOCA)
Arantzazu Eiguren-Fernandez, Nathan Kreisberg, and Susanne Hering
Atmos. Meas. Tech., 10, 633–644, 2017
www.atmos-meas-tech.net/10/633/2017/
doi:10.5194/amt-10-633-2017

Determination of Aerosol Oxidative Activity using Silver Nanoparticle Aggregation on Paper-Based Analytical Devices
Analyst. 2013 November 21; 138(22): 6766–6773. doi:10.1039/c3an01235b.
Wijitar Dungchai[a], Yupaporn Sameenoi[b,d], Orawon Chailapakul[e], John Volckens[c], and Charles S. Henry[b,*]

An automated online instrument to quantify aerosol-bound reactive oxygen species (ROS) for ambient measurement and health-relevant aerosol studies
Atmos. Meas. Tech., 9, 4891–4900, 2016
www.atmos-meas-tech.net/9/4891/2016/
doi:10.5194/amt-9-4891-2016
Francis P. H. Wragg[1], Stephen J. Fuller[1], Ray Freshwater[1], David C. Green[2], Frank J. Kelly[2], and Markus Kalberer[1]

Development and testing of an online method to measure ambient fine particulate reactive oxygen species (ROS) based on the 2′,7′-dichlorofluorescin (DCFH) assay
Atmos. Meas. Tech., 6, 1647–1658, 2013
www.atmos-meas-tech.net/6/1647/2013/
doi:10.5194/amt-6-1647-2013
L. E. King and R. J. Weber

Project

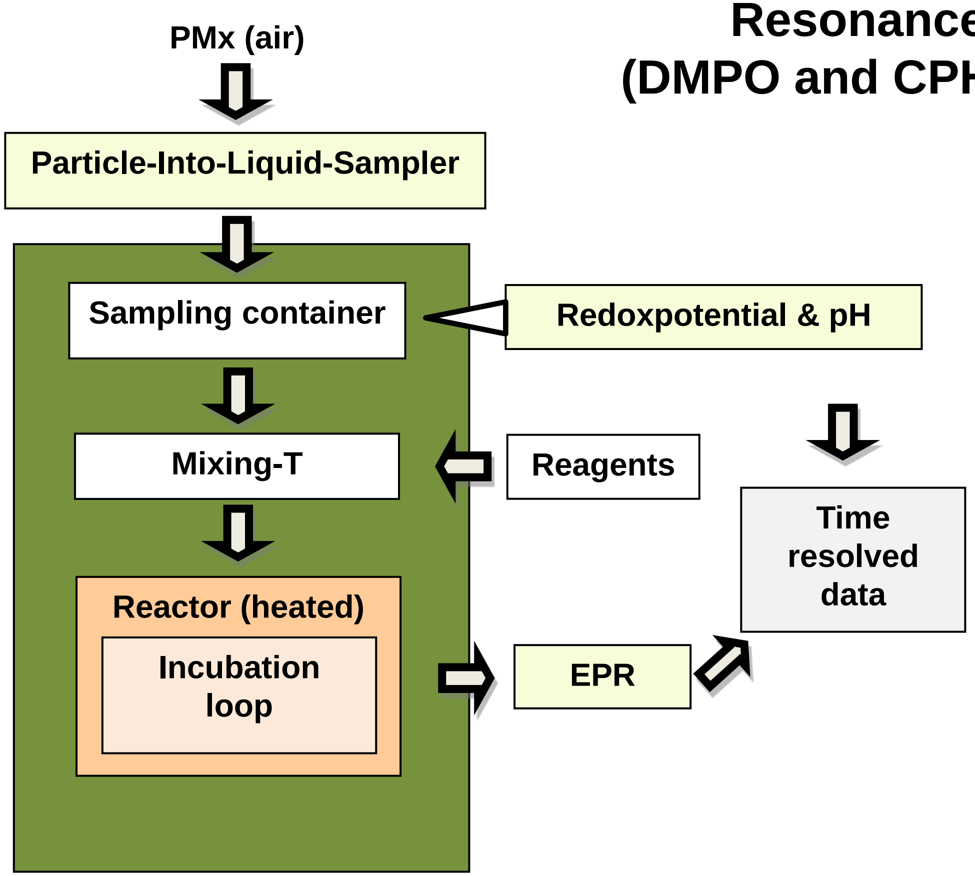
Combining…

Particle-Into-Liquid-Sampler

+

Electron Paramagnetic Resonance (EPR) (DMPO and CPH approach)

+



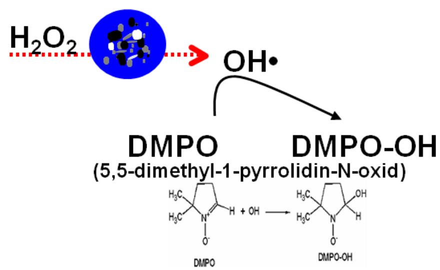
„Reaction section“
(sampling container with conductivity sensor; transport via peristaltic pump controlled by LabView software)

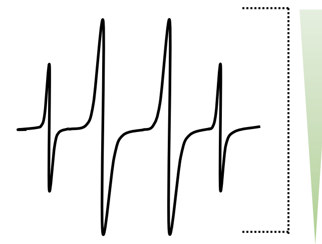
Project

Particle-Into-Liquid-Sampler (PILS) + „Reaction section“ + Electron Paramagnetic Resonance (EPR)

http://www.brechtel.com/products-item/particle-into-liquid-sampler/

1.

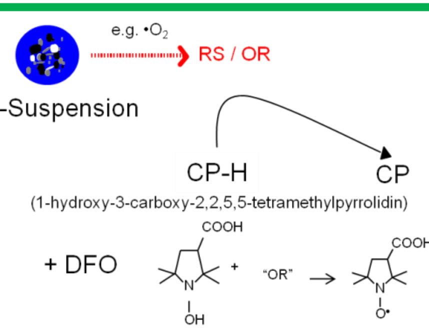


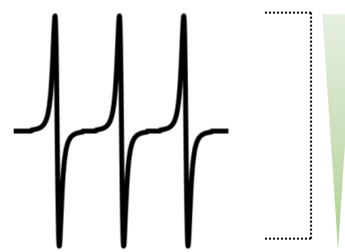


•OH generation

+ redoxpotential (redox cathode), pH value

2.





„Reactivity“

Project

Actual status:
Single components are working solely

a. PILS
b. Software (LabView) for process control (chemical transportation, incubation, liquid transport etc. is/was tested in the lab)
c. EPR method

→ Next step connection of all components; first attempts in the lab using a $CuSO_4$ (EPR-DMPO reactive) demonstrated the function of b. and c. connection.

For proof of concept we perfomed EPR analysis by…

→ PM (TSP) sampling indoor by PILS
→ Manual EPR analysis

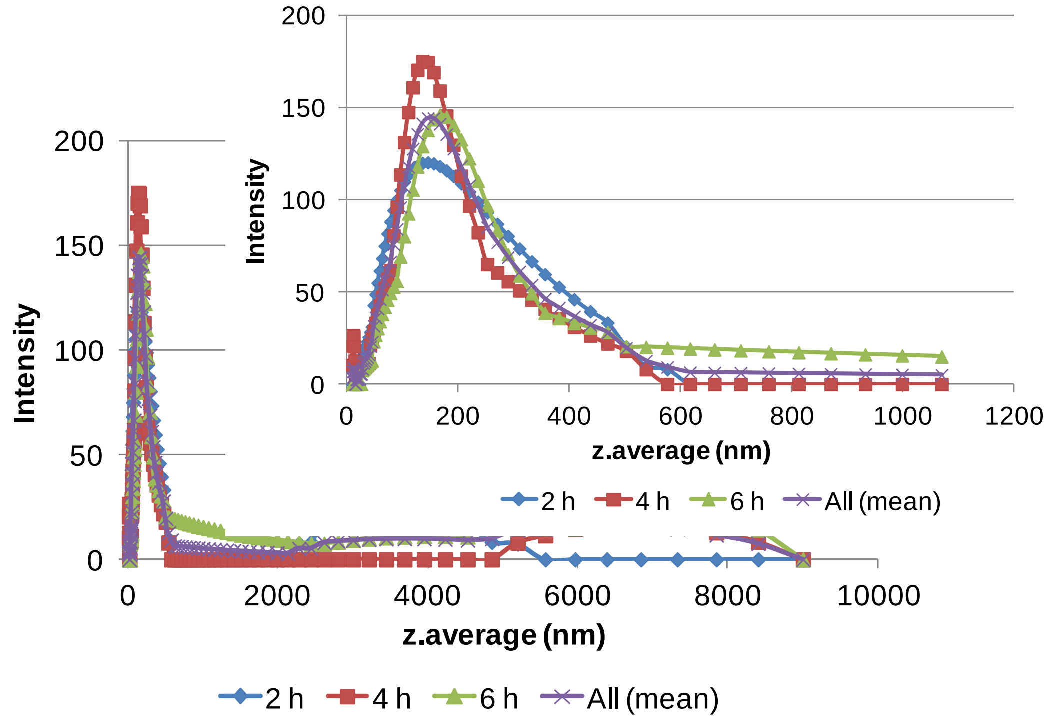
Results – Hall 3 indoor air

2 h, 4 h and 6 h sampling in a construction/experiment hall inclusive a NP-synthesis facility (not working at the analysis day); working processes in the hall are sporadically e.g. metal drilling, sawing

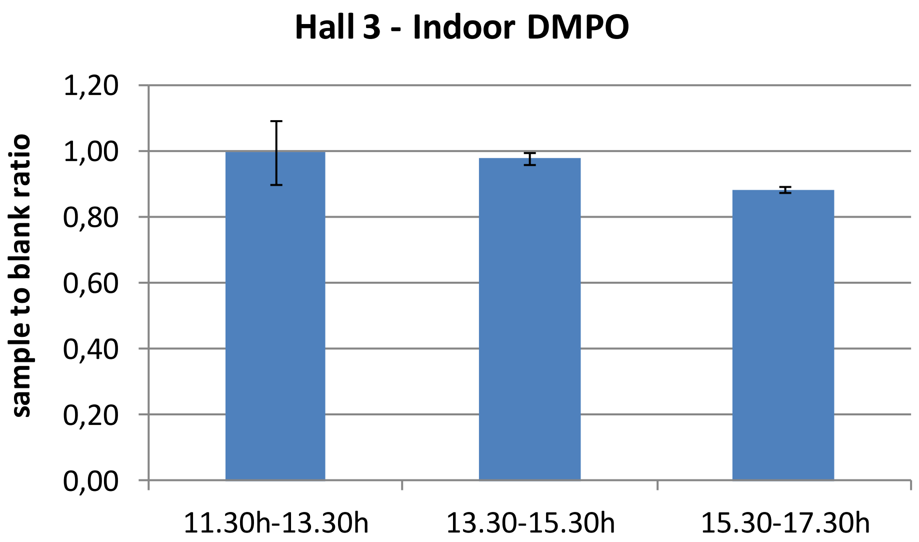
APS (0.5 µm – 20 µm)	**Mean**	**SD**
Median (µm)	3.60	0.46
Mean (µm)	4.67	0.79
Geo. Mean (µm)	3.60	0.49
Mode (µm)	9.24	5.16
Geo. Std. Dev.	2.10	0.11
Total Conc. (mg/m³)	0.009	0.002

DLS		**z.average (nm)**	**PI**
2h	Mean	624	0.28
	SD	46	0.01
4h	Mean	622	0.27
	SD	15	0.01
6h	Mean	715	0.31
	SD	128	0.05

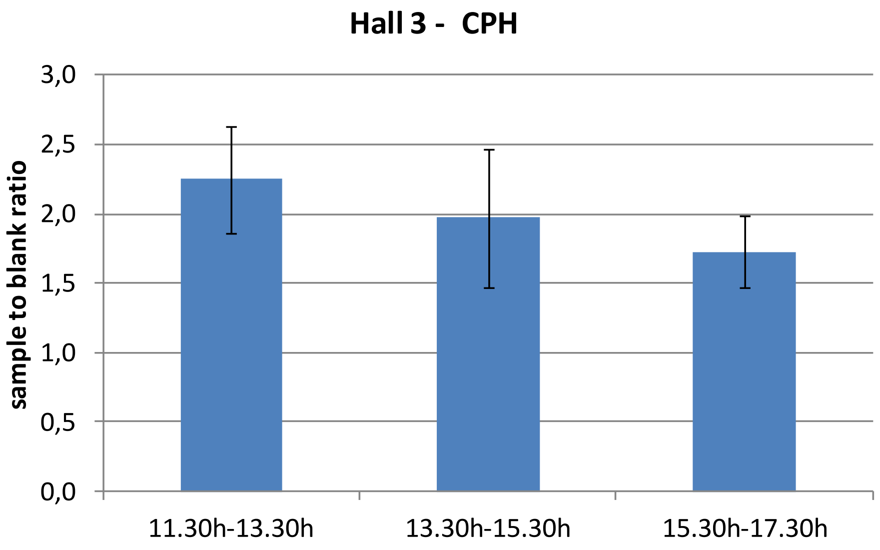
2 h PILS sampling with 1 m³/h
→ 18 µg/m³ (100% sampling efficiency suggested)



Results – Hall 3 indoor air



no reactivity for DMPO



reactivity for CPH!!!

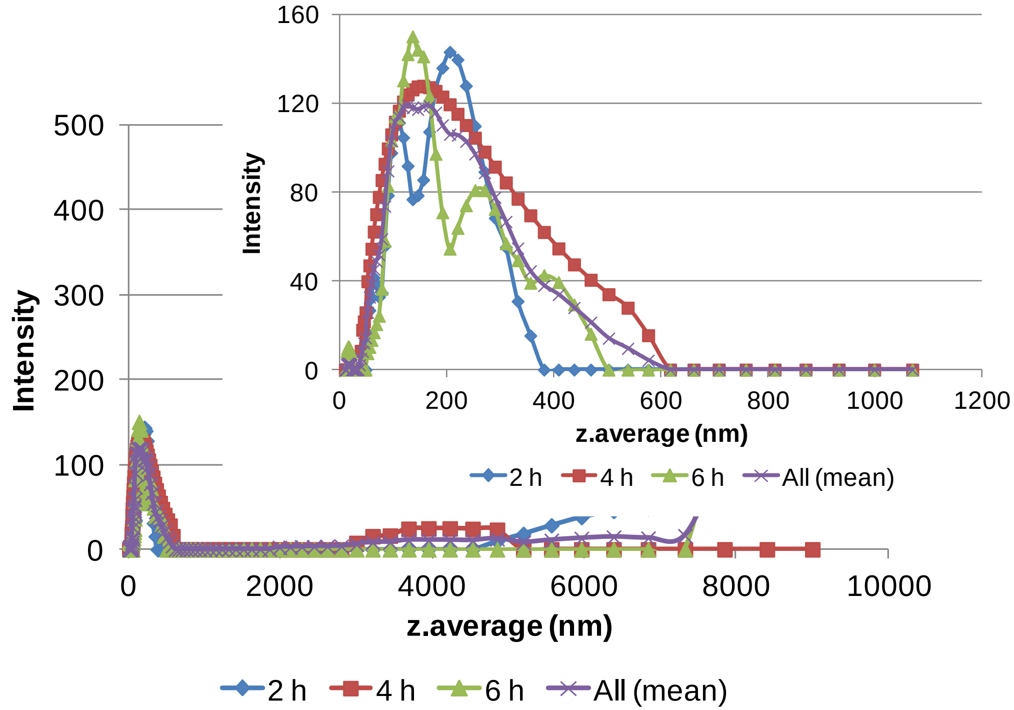
Results – Hall 5 indoor air

2 h, 4 h and 6 h sampling in a construction/experiment hall inclusive filter test facilities (not working at the analysis day)

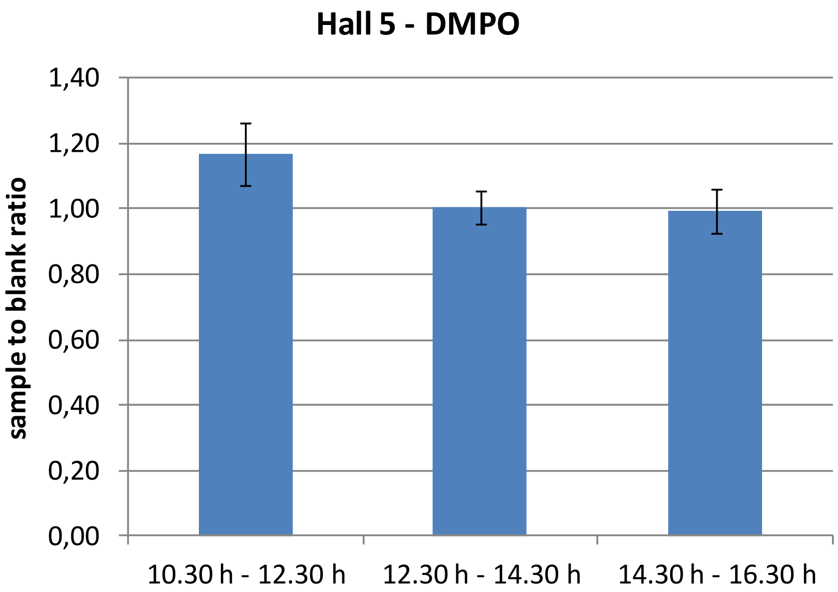
APS (0.5 µm – 20 µm)	**Mean**	**SD**
Median (µm)	3.40	0.31
Mean (µm)	4.82	0.80
Geo. Mean (µm)	3.69	0.44
Mode (µm)	9.40	6.71
Geo. Std. Dev.	2.04	0.15
Total Conc. (mg/m³)	0.014	0.002

DLS		**z.average (nm)**	**PI**
2h	Mean	1388	0.57
	SD	132	0.04
4h	Mean	768	0.34
	SD	66	0.03
6h	Mean	1753	0.70
	SD	773	0.28

2 h PILS sampling with 1 m³/h
→ 28 µg/m³ (100% sampling efficiency suggested)

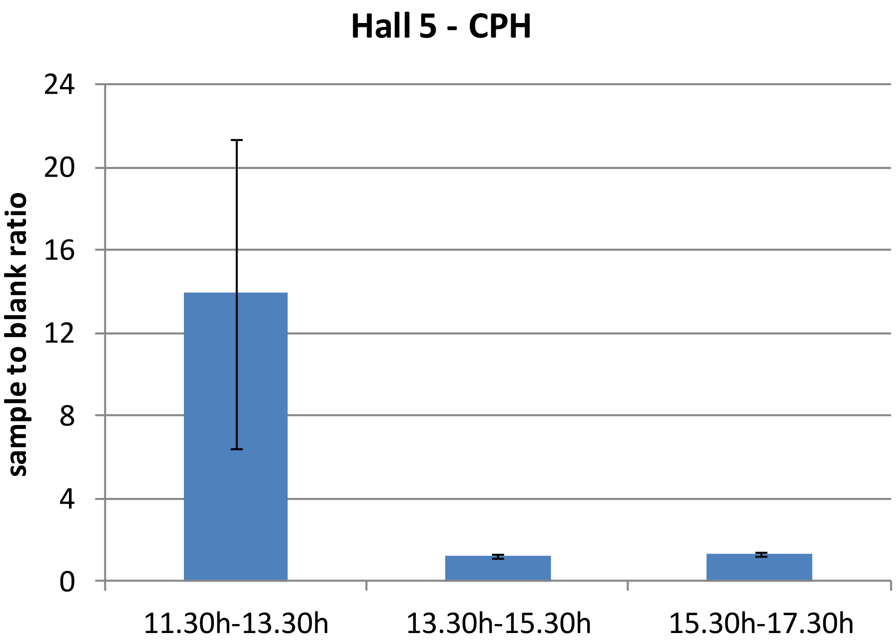


Results – Hall 5 indoor air

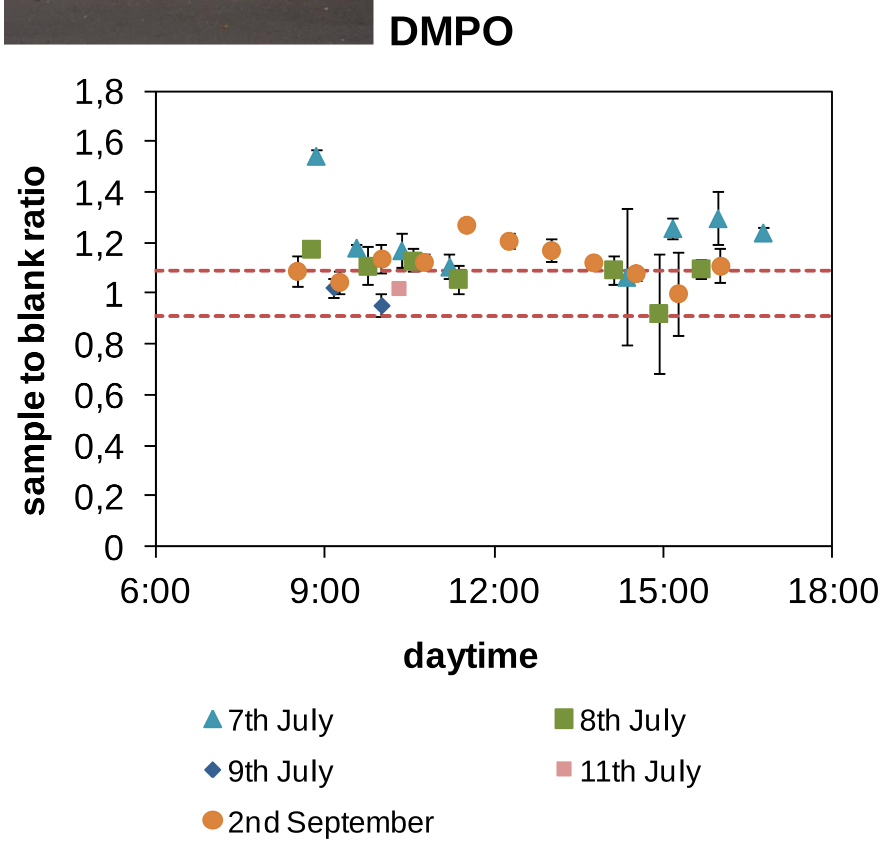


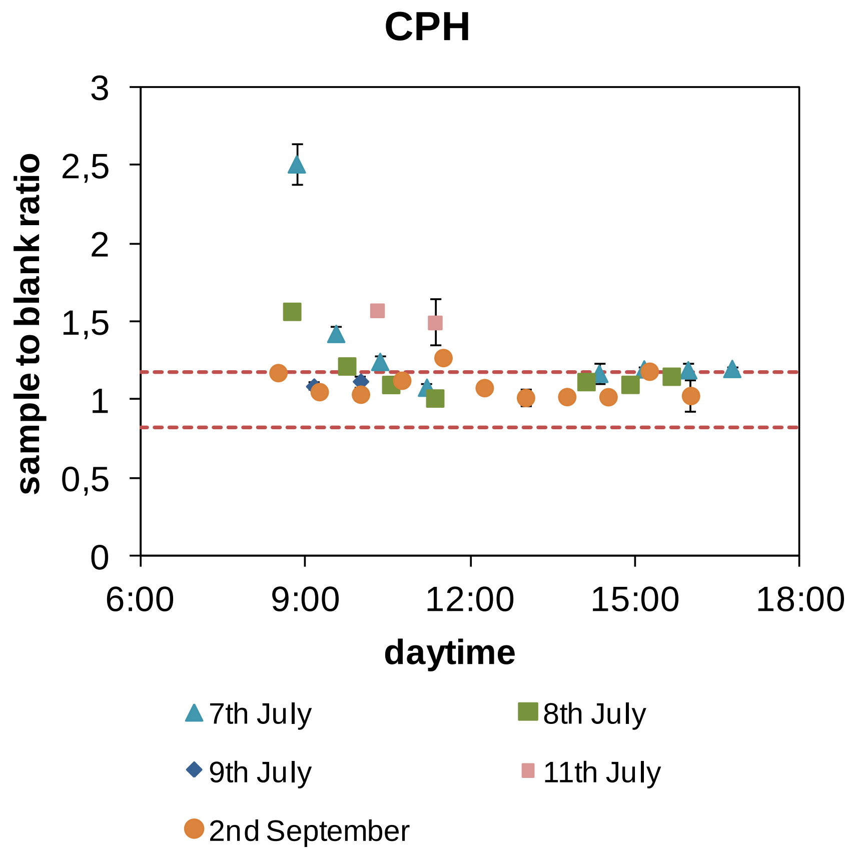
no reactivity for DMPO

reactivity for CPH!!!



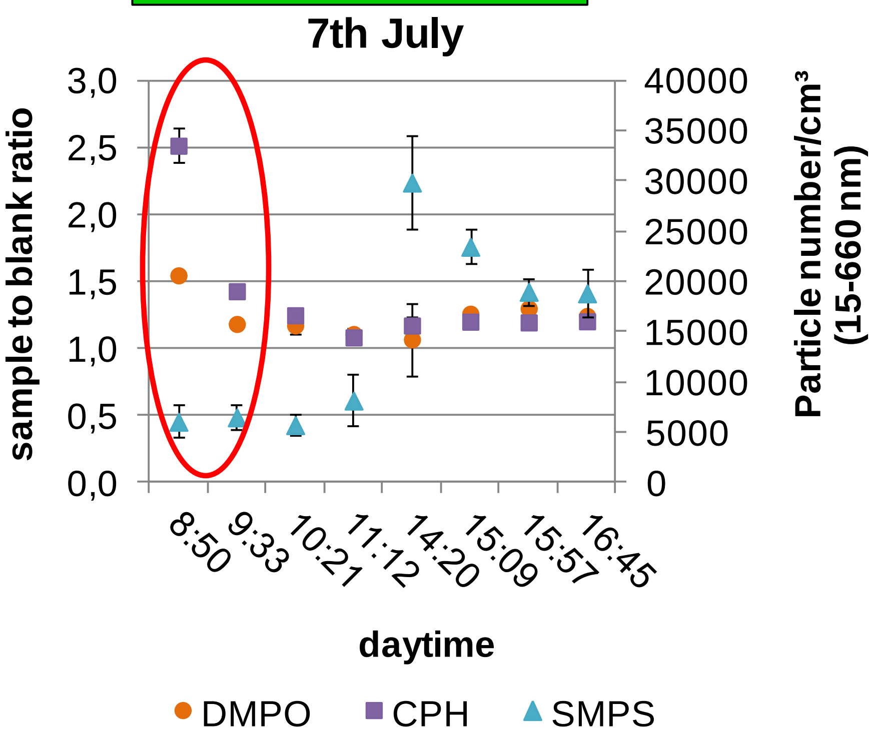
Results – Outdoor



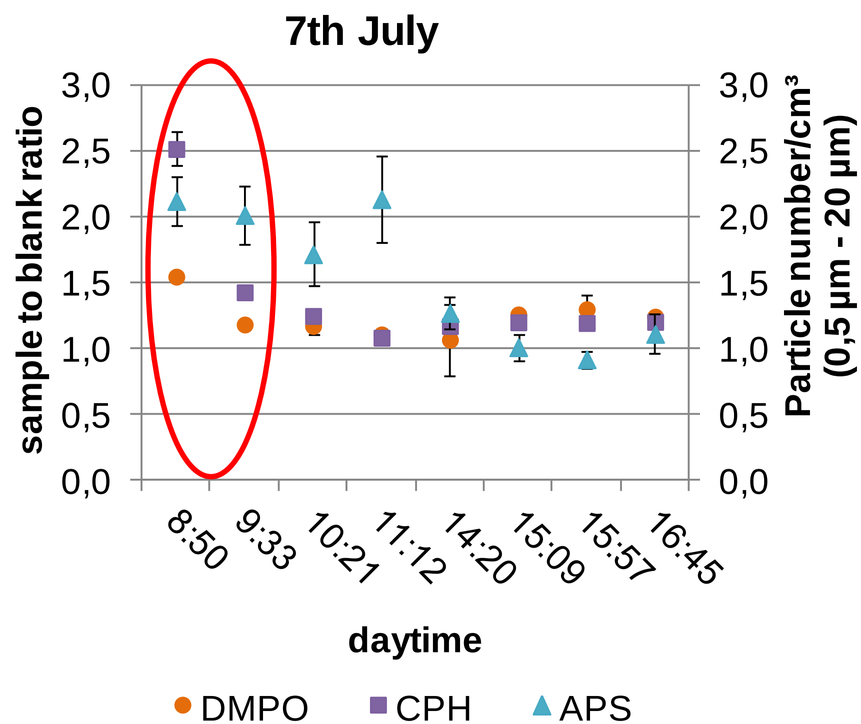


Results – Outdoor

small PM < 660 nm



large PM > 560 nm



Summary and Outlook

- Single components are working solely
- **Proof of concept**

→ **DMPO** for indoor and outdoor low to no signals maybe caused by too low PM concentrations

→ **CPH** for indoor and outdoor PM reactivities were detected

Next steps (~1 year):

- combining all components and testing in lab and outside (PM10 and PM2.5 at outdoor station with higher PM concentration)
- testing Denuder (O_3, NO_2)
- testing particle sampling efficiency
- enrichment of PM for DMPO approach?

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IUF-Leibniz Research Institute for
Environmental Medicine

Thank you!

funded by AiF

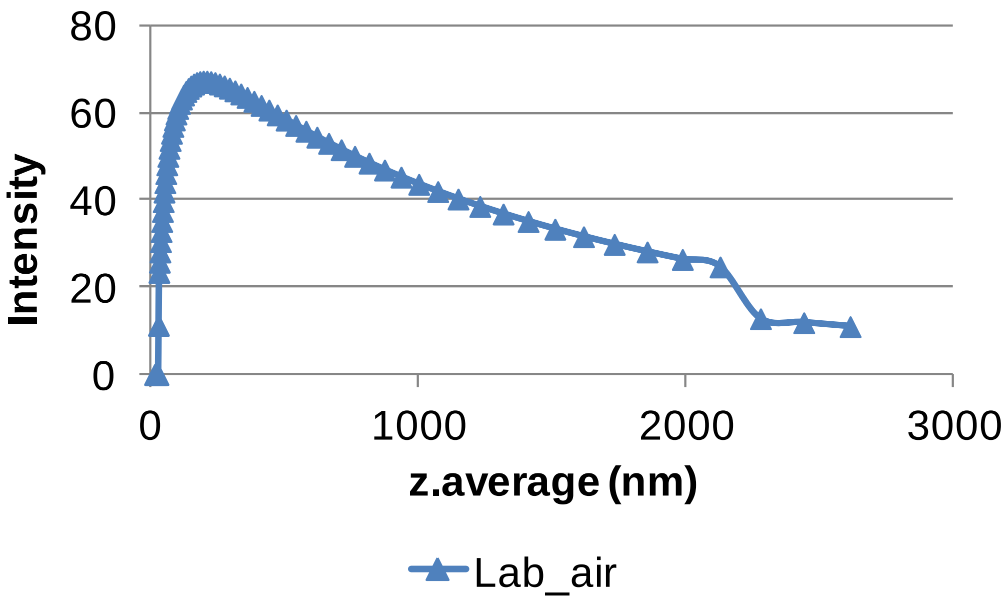
Results – Laboratory air

2 h sampling in a „standard“ laboratory with strong air extraction (> 30 m³/m² and h)

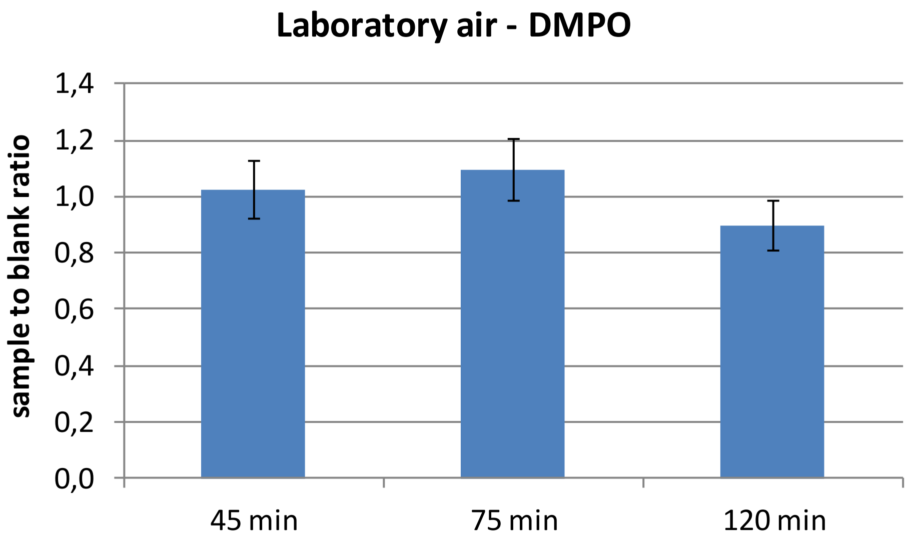
APS (0,5 µm – 20 µm)	**Mean**	**SD**
Median (µm)	1.98	1.51
Mean (µm)	1.86	1.58
Geo. Mean (µm)	1.78	1.53
Mode (µm)	2.12	1.65
Geo. Std. Dev.	1.35	0.12
Total Conc. (mg/m³)	0.0018	0.0105

2 h PILS sampling with 1 m³/h
→ 3.6 µg/m³ (100% sampling efficiency suggested)

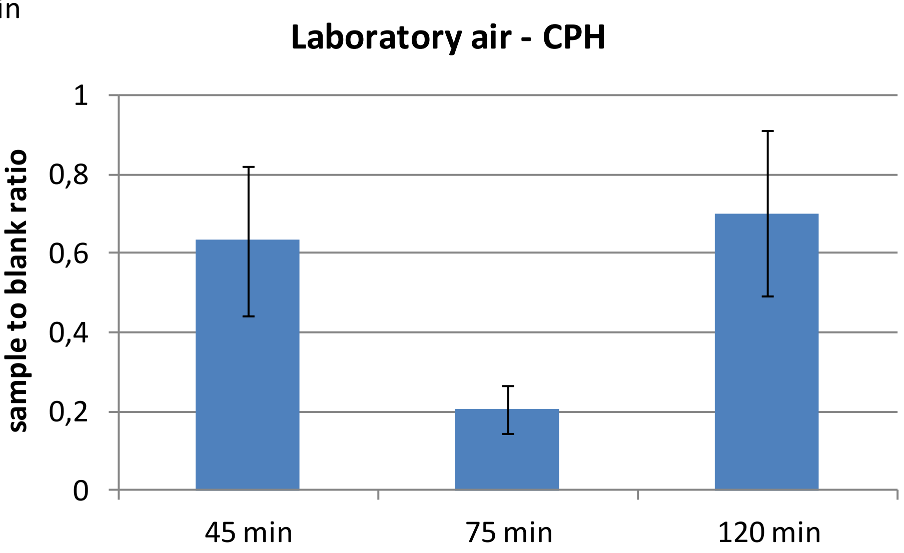
DLS	**z.average (nm)**
Ø (nm)	166.5
Ø (nm)	1255
average	710.8



Results – Laboratory air



no reactivity for DMPO



no reactivity for CPH