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Keywords: reactive oxygen species, aerosol, ambient air

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Introduction

Reactive oxygen species (ROS) are referred to as chemically reactive molecules containing oxygen, for example oxygen ions and peroxides including H_2O_2 , $OH\cdot$, $O_2^{\cdot-}$, hydro-organic peroxides, superoxide anion, etc [1, 2]. As one of the main free radical sources, ROS can adversely alter lipids, proteins and DNA and have been implicated in aging and a variety of human diseases [3].

The accurate quantification of ROS is challenging because some components are highly reactive and therefore short-lived. Therefore, off-line techniques usually having a delay of hours, days or weeks may underestimate actual ROS concentrations. This is one reason why on-line techniques (direct sampling into the liquid phase and measuring within a few minutes) are necessary for a reliable ROS quantification [1].

In this study, we use the DCFH assay and the on-line reactive oxygen species (ROS) analyzer to detect and compare ROS in the particle phase of ambient aerosol in different urban areas. Bern (Switzerland) and Beijing (China) were chosen to assess the effects of ambient particles especially ROS on human health.

Methodology

Experiment sites

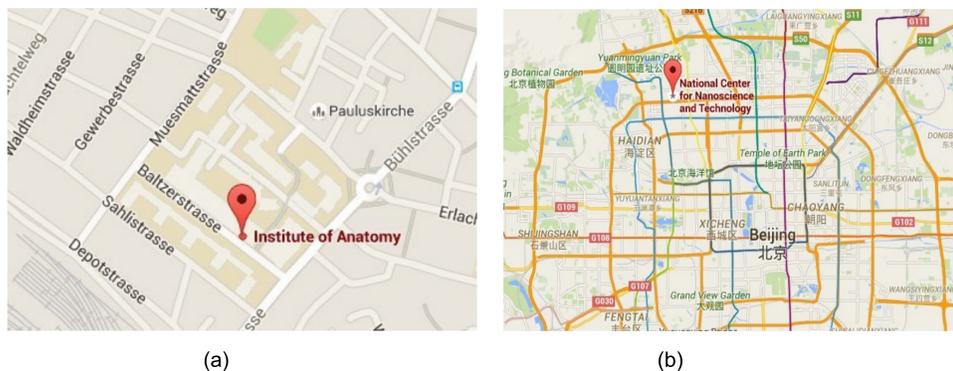


Fig. 1. Experiment sites (a) Institute of Anatomy, Bern, Switzerland; (b) National Center for Nanoscience and Technology, Beijing, China

Measurement periods

1st Campaign in Bern: From 18th to 26th November, 2014

2nd Campaign in Beijing: From 23th January to 27th January, 2015

Instrumentation

1. ROS on-line analyzer (DCFH assay)

In presence of horseradish peroxidase, 2',7'-dichlorofluorescein (DCFH) is oxidized to fluorescent DCF and subsequently detected using a fluorimeter.

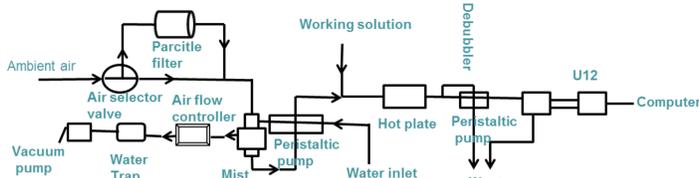


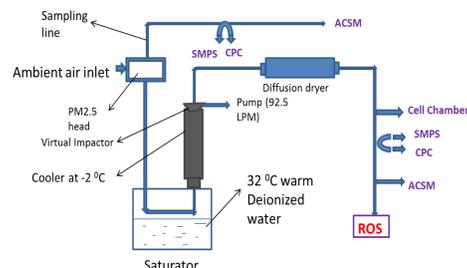
Fig. 2. Flow diagram of on-line ROS analyzer

2. Versatile aerosol concentration enrichment system (VACES) (used only in Bern)

As our ROS analyzer has a detection limit of 1.2 nmol/m^3 without VACES, we used the versatile aerosol concentration enrichment system (VACES, shown in Fig. 3) to enrich the concentration of ambient $PM_{2.5}$ during the Bern campaign.

Fig. 3. Flow diagram of VACES.

Ambient particles go into the saturator and achieve saturation, then they are drawn through a condenser and grow to super-micrometer size. The grown particles are then drawn through a virtual impactor. The concentrated particles from the minor flow of the impactor finally pass through a diffusion dryer to remove the excess water on the particles and return them back to their original size.



3. Aerosol chemical speciation monitor (ACSM)

ACSM routinely characterizes and monitors the mass and chemical composition of non-refractory sub-micron particulate matter in real time. Under ambient conditions, mass concentrations of particulate organics, sulfate, nitrate, ammonium, and chloride are obtained with a detection limit $<0.2 \mu\text{g/m}^3$ for 30 min of signal averaging [4].

4. Scanning mobility particle sizer (SMPS)

Used for particle mass and size distribution analysis.

Data analysis

In Bern we measured ROS after the VACES. Therefore we had to correct the measured signal with the concentration enrichment factor CE using the following equation: $CE = (Q_{tot}/Q_{min})(1-WL)\eta_{vi}$, where Q_{tot} and Q_{min} are the intake and minor flows of the impactor, respectively, and η_{vi} and WL are the collection efficiency and fractional losses of the impactor [5]. In Beijing, during haze days, we measured ROS directly without VACES. Using the mass concentration calculated from SMPS, we determined the ROS content in H_2O_2 equivalent per μg particle mass.

Results and discussion

Fig. 4 and Fig. 5 present a preliminary overview of the time variation of PM_{10} mass concentration as well as ROS concentration and content in Bern and Beijing, respectively. In Bern, PM_{10} concentrations are less than $20 \mu\text{g/m}^3$ while in Beijing heavy haze up to $232 \mu\text{g/m}^3$ were observed during the measurement periods. ROS concentrations in Bern were between $0.2\text{--}5 \text{ nmol/m}^3$ and in Beijing up to 13 nmol/m^3 .

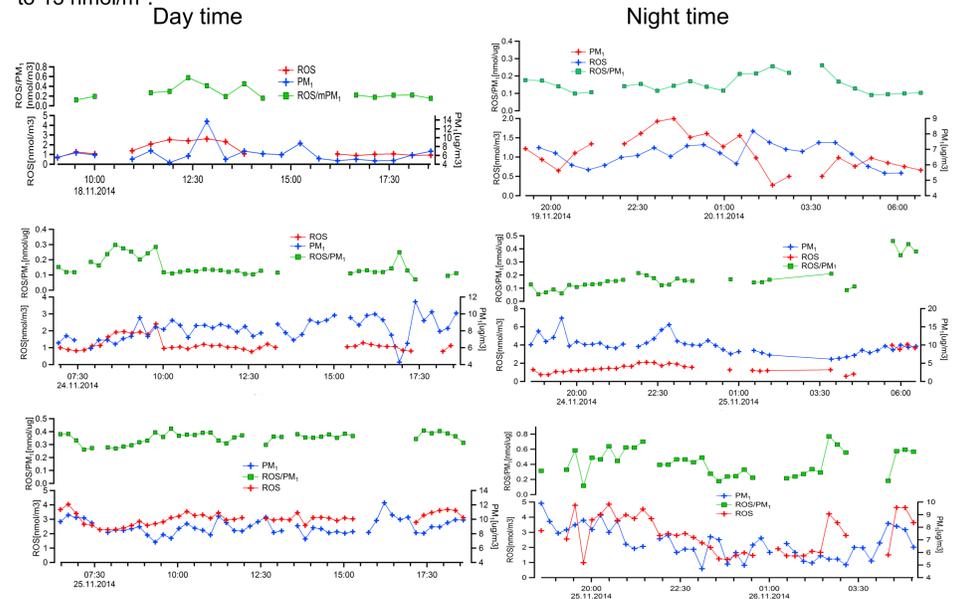


Fig. 4. PM_{10} [$\mu\text{g/m}^3$] and ROS [nmol/m^3] concentration as well as ROS content in the particle phase [$\text{nmol}/\mu\text{g}$] measured in Bern during daytime and nighttime.

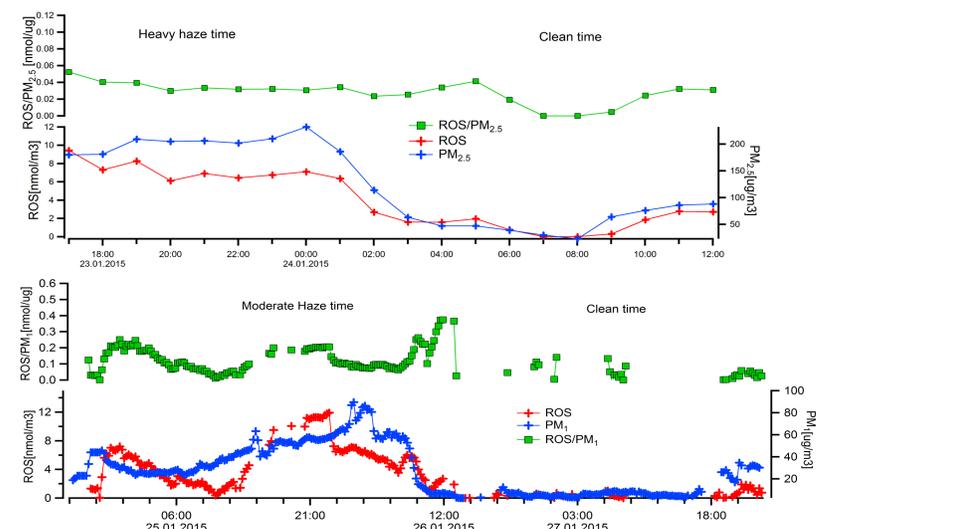


Fig. 5. $PM_{2.5}$ [$\mu\text{g/m}^3$] and ROS [nmol/m^3] concentration as well as ROS content in the particle phase [$\text{nmol}/\mu\text{g}$] measured in Beijing during heavy and moderate haze days as well as clean days.

However, the ROS content per particle mass was on average $0.26 \text{ nmol}/\mu\text{g}$ in Bern and $0.15 \text{ nmol}/\mu\text{g}$ in Beijing (only moderate and haze days). PM has been shown to possess the ability to reduce oxygen to form ROS, but there is also evidence suggesting that the chemical composition and size of PM from different sources have different potency to induce oxidative stress [6,7,8,9]. In order to retrieve further conclusions, more detailed chemical analysis is needed from our data.

Table 1. Comparison of PM_{10} and ROS concentration ranges and range of ROS content in Beijing and Bern ambient air.

Experiment sites	ROS concentration [nmol/m^3]	PM_{10} concentration [$\mu\text{g/m}^3$]	Average ROS content in PM_{10} [$\text{nmol}/\mu\text{g}$]
Institute of Anatomy, Bern, Switzerland	0.01-4.6	4.3-15.6	0.26 ± 0.17
National Center for Nanoscience and Technology, Beijing, China	0.6-15.4	2.5-232.0	$0.15 \pm 0.08^{(1)}$

1) Only average of moderate and heavy haze days

Conclusions

- The developed on-line ROS analyzer can be applied to ambient air measurement.
- ROS concentration in ambient air in Beijing during haze days is somewhat higher than in Bern but it seems that the ROS content per particle mass is lower than in Bern.

References

- [1] Fuller, S.J., et al., Atmos. Environ., 92(2014), 97-103.
- [2] Sagai, M., et al., Free Radical Bio. Med., 14(1993), 37.
- [3] Devasagayam, T.P.A., et al., J. Assoc. Phys. India, 52(2004), 794-804.
- [4] Ng, N.L., et al., Aerosol Sci. Tech., 45(2011), 780-794.
- [5] Sioutas, C., et al., J. Aerosol Sci., 30(1999), 1001-1017.
- [6] Ntziachristos, L., et al., Part Fibre Toxicol., 4(2007), 1-12.
- [7] Cho, A.K., et al., Environ Res., 99(2005), 7-40.
- [8] Liu, Q.Y., et al., Environ Sci. Tech., 48(2012), 12920-12929.
- [9] Sarnat, J.D., et al., Environ. Health Perspect. 116(2008), 459-466.

Acknowledgments

This work was supported by the Swiss National Science Foundation (407040_153970/1) and the China Scholarship Council (201307040040).