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Stevanovic, S., Miljevic, B., Surawski, N.C., Vaattovaara, P., Brown, R., & Ristovski, Z. (2012) The influence of oxygenated organic aerosols (OOA) and its volatile organic content on the oxidative potential of diesel particulate mater. In *European Aerosol Conference 2012*, 2-7 September 2012, Parque de las Ciencias, Granada, Spain. (Unpublished)

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## The influence of oxygenated organic aerosols (OOA) and its volatile organic content on the oxidative potential of diesel particulate mater

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Keywords: biofuels, reactive oxygen species, profluorescent nitroxide.

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Airborne particulate matter pollution is of concern for a number of reasons and has been widely recognised as an important risk factor to human A number of toxicological health. and epidemiological studies reported negative health effects on both respiratory and cardiovascular system. Despite the availability of a huge body of research, the underlying toxicological mechanisms by which particles induce adverse health effects are not yet entirely understood. The production of reactive oxygen species (ROS) has been shown to induce oxidative stress, which is proposed as a mechanism for many of the adverse health outcomes associated with exposure to particulate matter (PM). Therefore, it is crucial to introduce a technique that will allow rapid and routine screenings of the oxidative potential of PM.

In our previous studies we applied a new profluorescent nitroxide molecular probe (bis(phenylethynyl) anthracene-nitroxide; BPEAnit) [1], developed in an entirely novel, rapid and noncell based assay, for assessing the oxidative potential of particles derived from various combustion processes (e.g. wood smoke and various diesel engines and fuels) [2,3].

One of the most important outcomes of our research thus far was that the oxidative potential per PM mass significantly varies for different combustion sources as well as different combustion conditions and feedstock used. However, possibly the most important finding from our studies was that there was a strong correlation between the organic fraction of particles and the oxidative potential measured by the PFN assay, which clearly highlights the importance of organic species in particle-induced toxicity [2,4] and reinforces the further investigations to explore this correlation.

To gain an insight into this relationship, additional measurements were conducted on an ethanol fumigated modern common rail diesel engine. In addition to running the engine with various levels of ethanol substitution several biofuels were used. Tests were designed to present emission differences due to changes in fuel and load settings.

A more detailed analysis of the organic content was performed to support the ROS measurements. This involved volatility measurement using a Volatility-Tandem Differential Mobility Analyser (V-TDMA) and particle composition using an Aerodyne Aerosol Mass Spectrometer (cToF-AMS). For detection of organic fraction we also used the ultrafine organic tandem differential mobility analyzer UFO-TDMA.

Volatility measurements indicating the overall organic coating on particles correlated with measured oxidative potential, but not as strong as in previous measurements. This indicated that ROS content is a function of organic particle composition but does not always exhibit a simple linear trend with volatility data. To investigate this relationship in more detail the data from the AMS were used. The fraction at the m/z of 44 (f44) was used as a tracer for the oxygenated organic aerosol (OOA) and 57 (f57) as the tracer for hydrocarbon like organic aerosol (HOA). The highest correlation was observed between the ROS concentration and the OOA.

Therefore the oxidative potential of the PM, measured through the ROS concentration, although proportional to the total volatile organic volume percentage shows a much higher correlation with the oxygenated organic fraction. This highlights the importance of the surface chemistry of particles for assessing the health impacts. It also sheds a light onto new aspects of particulate emissions that should be taken into account when establishing relevant metrics for health implications of various emissions.

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