

# **Physicochemical and oxidative characteristics of semi-volatile components of quasi-ultrafine particles in an urban atmosphere**

Vishal Verma<sup>1</sup>, Payam Pakbin<sup>1</sup>, Ka Lam Cheung<sup>1</sup>, Arthur K. Cho<sup>2</sup>, James J. Schauer<sup>3</sup>, Martin M. Shafer<sup>3</sup>, Michael T. Kleinman<sup>4</sup> and Constantinos Sioutas<sup>1</sup>

<sup>1</sup>Department of Civil and Environmental Engineering, University of Southern California, Los Angeles, CA, USA

<sup>2</sup>Department of Molecular and Medical Pharmacology, School of Medicine, University of California Los Angeles, CA, USA

<sup>3</sup>Environmental Chemistry and Technology Program, University of Wisconsin, Madison, WI, USA

<sup>4</sup>School of Medicine, University of California Irvine, CA, USA

## **Summary**

We assessed the role of semi-volatile compounds in the oxidative potential of ambient quasi-ultrafine particles at an urban site. The investigation follows the study of Biswas et al. (2009), which demonstrated a dominant contribution (up to almost 100 % in few vehicles emissions) of semi-volatile components in the oxidative activity of particulate matter (PM) emitted from heavy-duty diesel vehicles in a dynamometer facility. Concentrated ambient and thermodenuded quasi-ultrafine particles (<180 nm) were collected using the versatile aerosol concentration enrichment system (VACES) at an urban site near downtown Los Angeles. A thermodenuder (TD) was used to selectively remove the semi-volatile components of these aerosols over the temperature range of 50-200 °C. The oxidative potential of PM was measured by means of the DTT (dithiothreitol) assay. Detailed chemical analyses of PM samples, including organic and elemental carbon, water soluble elements, inorganic ions and polycyclic aromatic hydrocarbons (PAHs), were conducted to quantify the volatility profiles of different PM species, and also to investigate their effect on the measured oxidative potential.

Particle size distributions of ambient and denuded particles measured by the Scanning Mobility Particle Sizer (SMPS) indicated a substantial loss (47%) of the nucleation mode

particles (<50 nm) even at 50 °C, while shrinkage of the Aitken mode particles (>50 nm) became important at higher temperature ranges (70 % volume loss at 200 °C). Thus, nucleation mode particles are internally mixed, consisting mostly of volatile materials, while particles in the Aitken mode are externally mixed.

Refractory constituents, such as metals and elemental carbon, were marginally affected by heating, while labile species such as organic carbon and PAHs showed progressive loss in concentration with increase in TD temperature. The DTT-measured oxidative potential of PM was significantly decreased as the aerosols were heated and their semi-volatile components were progressively removed (42 %, 47 % and 66 % decrease at 50, 100 and 200 °C, respectively). The considerable attenuation of DTT activity with aerosol heating demonstrates the significant contribution of semi-volatile compounds to the PM oxidative potential; although it is lower compared to that in DEPs, evaluated in the chassis dynamometer study (Biswas et al. 2009). The difference in oxidative activity profiles between the two studies is attributed to the lower content of semi-volatile species in ambient PM, as a result of the much higher atmospheric dilution, compared to the freshly emitted DEPs in dynamometer studies.

Regression analysis performed between chemical constituents and DTT activity showed that the oxidative potential was strongly correlated with organic carbon and PAHs ( $R \geq 0.80$ ), which further emphasizes the significant role of semi-volatile organic compounds in the PM oxidative potential.

### **References**

Biswas, S., Verma, V., Schauer, J. J., Cassee, F. R., Cho, A. K. and Sioutas, C., 2009. Oxidative Potential of Semi-Volatile and Non Volatile Particulate Matter (PM) from Heavy-Duty Vehicles Retrofitted with Emission Control Technologies. *Environmental Science & Technology* 43 (10), 3905-3912

# Physicochemical and oxidative characteristics of semi-volatile components of quasi-ultrafine particles in an urban atmosphere

Vishal Verma<sup>1</sup>, Payam Pakbin<sup>1</sup>, Ka Lam Cheung<sup>1</sup>, Arthur K. Cho<sup>2</sup>, James J. Schauer<sup>3</sup>, Martin M. Shafer<sup>3</sup>, Michael T. Kleinman<sup>4</sup> and Constantinos Sioutas<sup>1</sup>



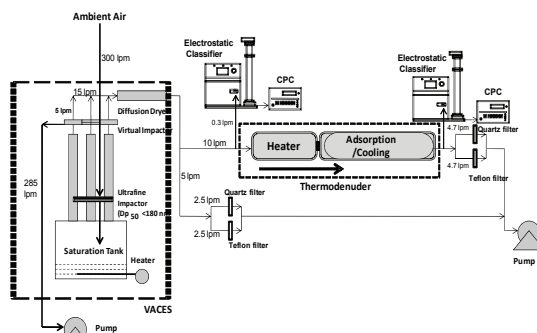
<sup>1</sup>Department of Civil and Environmental Engineering, University of Southern California, Los Angeles, USA  
<sup>2</sup>Department of Molecular and Medical Pharmacology, School of Medicine, University of California Los Angeles, USA  
<sup>3</sup>Environmental Chemistry and Technology Program, University of Wisconsin, Madison, USA  
<sup>4</sup>School of Medicine, University of California Irvine, USA



## Introduction

- Atmospheric particles are a complex mixture of numerous semi-volatile (most organic compounds and the major inorganic ions – ammonium, sulfate and nitrate) and non-volatile (metals, elemental carbon and few organic compounds) species.
- Certain semi-volatile compounds, such as polycyclic aromatic hydrocarbons (PAHs) and their derivatives, are known to be genotoxic and carcinogenic.
- Semi-volatile fraction of diesel exhaust particles (DEPs), evaluated in chassis dynamometer facilities, is found to be highly redox-active and constitutes a dominant percentage (up to almost 100 % in few vehicles emissions) of the PM oxidative potential.
- Various atmospheric processes, including dilution and photo-chemical reactions significantly alter the physicochemical and oxidative characteristics of ambient semi-volatile compounds in an urban environment.
- An improved understanding of these characteristics and the overall contribution of semi-volatile compounds to the atmospheric aerosol toxicity is essential in elucidating the health risks related to PM exposure.

## Experimental Setup



### Sampling Location

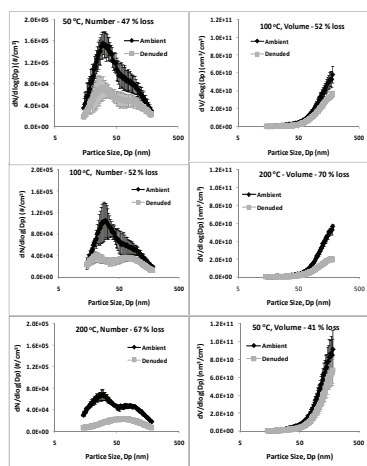
Particle Instrumentation Unit (PIU) on the campus of University of Southern California (USC) - representative of typical urban air quality conditions in downtown Los Angeles.

### Sampling Protocol

- Sampling was conducted in fall, 2009 for a period of 6 consecutive weeks.
- PM volatility was investigated in the 50-200 °C temperature range.

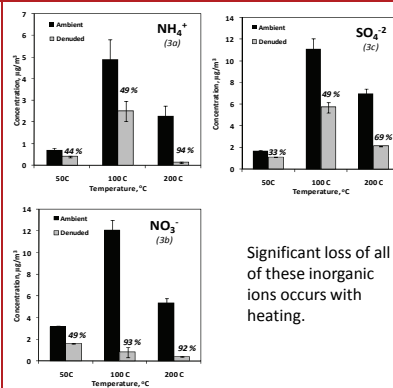
Chemical and Toxicological Analysis	Method
Water soluble ions	Ion Chromatography
Elemental and Organic Carbon	ACE (aerosol characterization experiments)-Asia Method
Polycyclic Aromatic Hydrocarbons (PAHs)	Thermal Desorption- Gas chromatography/mass spectrometry (TD-GCMS)
Oxidative Potential	Dithiothreitol (DTT) Assay

## Number and Volume Size Distributions



- Nucleation mode (<50 nm) is internally mixed (mostly volatile materials), while particles in the Aitken mode (>50 nm) are externally mixed.
- Number loss is mostly governed by the loss of nucleation mode particles, while shrinkage of Aitken mode particles is reflected in the volume reduction.
- At lower temperature (50 °C), the number loss dominates due to Kelvin effect; while particle shrinkage also becomes prominent at higher temperatures (100 and 200 °C).

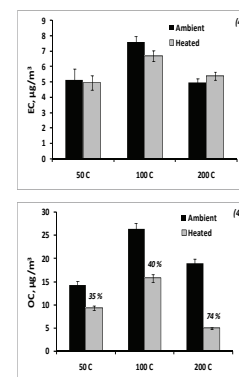
## Water-soluble Ions



The general trends in the loss of ions are consistent with their predominant molecular speciation [ $\text{NH}_4\text{NO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ , and  $\text{H}_2\text{SO}_4$ ] in an urban atmosphere

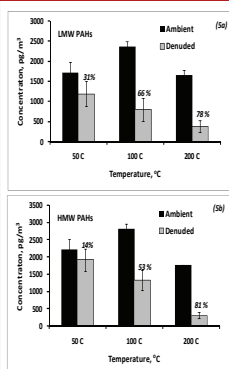
Significant loss of all of these inorganic ions occurs with heating.

## Elemental and Organic Carbon (EC-OC)



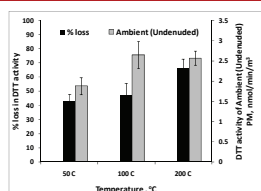
- EC is marginally affected (within the measurement uncertainty) by heating.
- OC is progressively decreased with an increase in TD temperature - loss of semi-volatile organic compounds.

## Polycyclic Aromatic Hydrocarbons (PAHs)



- A substantial evaporative loss of PAHs (up to 80 %) upon heating is evident.
- Higher loss of lower molecular weight (LMW) PAHs than higher molecular weight (HMW) PAHs - decreasing volatility with an increase in number of carbon atoms.

## Oxidative Potential



Species	DTT Activity	
	R	p
$\text{NO}_3^-$	0.85	0.03
$\text{SO}_4^{2-}$	0.79	0.06
$\text{NH}_4^+$	0.77	0.08
OC	0.92	0.01
EC	0.35	0.49
LMW PAHs	0.88	0.02
HMW PAHs	0.80	0.05

- The oxidative potential is decreased by 42%, 47 % and 66 % as the particles are heated at 50, 100 and 200 °C, respectively.
- Highlights the significant contribution of semi-volatile compounds to the oxidative load of ambient quasi-ultrafine particles in an urban atmosphere.
- Excellent correlation between DTT activity and OC concentration - emphasizes the major role of semi-volatile organic compounds in the PM oxidative potential.
- Strong correlation of DTT activity with PAHs - precursors of redox active organic species that augments the PM oxidative potential.

## Conclusions

- A significant fraction (42-66 %) of the oxidative potential of ambient PM is contributed by its semi-volatile compounds. Although it is lower compared to that in DEPs (evaluated in chassis dynamometer setup), which is attributed to the lower content of semi-volatile species in ambient PM, as a result of the much higher atmospheric dilution, compared to the freshly emitted DEPs in dynamometer facilities.
- Species that are volatile at ~ 50 °C and between 100 and 200 °C (e.g. OC) are strongly associated with the DTT activity.
- For a comprehensive assessment of the relative toxicity profiles of semi-volatile and non-volatile components, further mechanistic research is needed, including cellular assays and in-vivo exposure studies focusing on these two categories of PM.

## Acknowledgments

- EPA (STAR program through grant RD-8324-1301-0), and CARB (award no. 2008-2021 to the University of Southern California and award no. 07-307 to the University of California, Irvine).
- Debra A Schmitz at UCLA for the DTT analysis.
- Nancy Daher and Winnie Kam for aerosols sampling.
- Jeff DeMinter and Mike Olson at UWM for the chemical analyses.