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Fine and Ultrafine Particulate Matter in the Los Angeles Basin: Trends in Sources and Composition and Oxidative Potential

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Motivation and Objectives

- Sources of ambient particulate matter (PM) are not equally toxic - exposure to the emissions of different sources triggers different series of acute and chronic health outcomes.

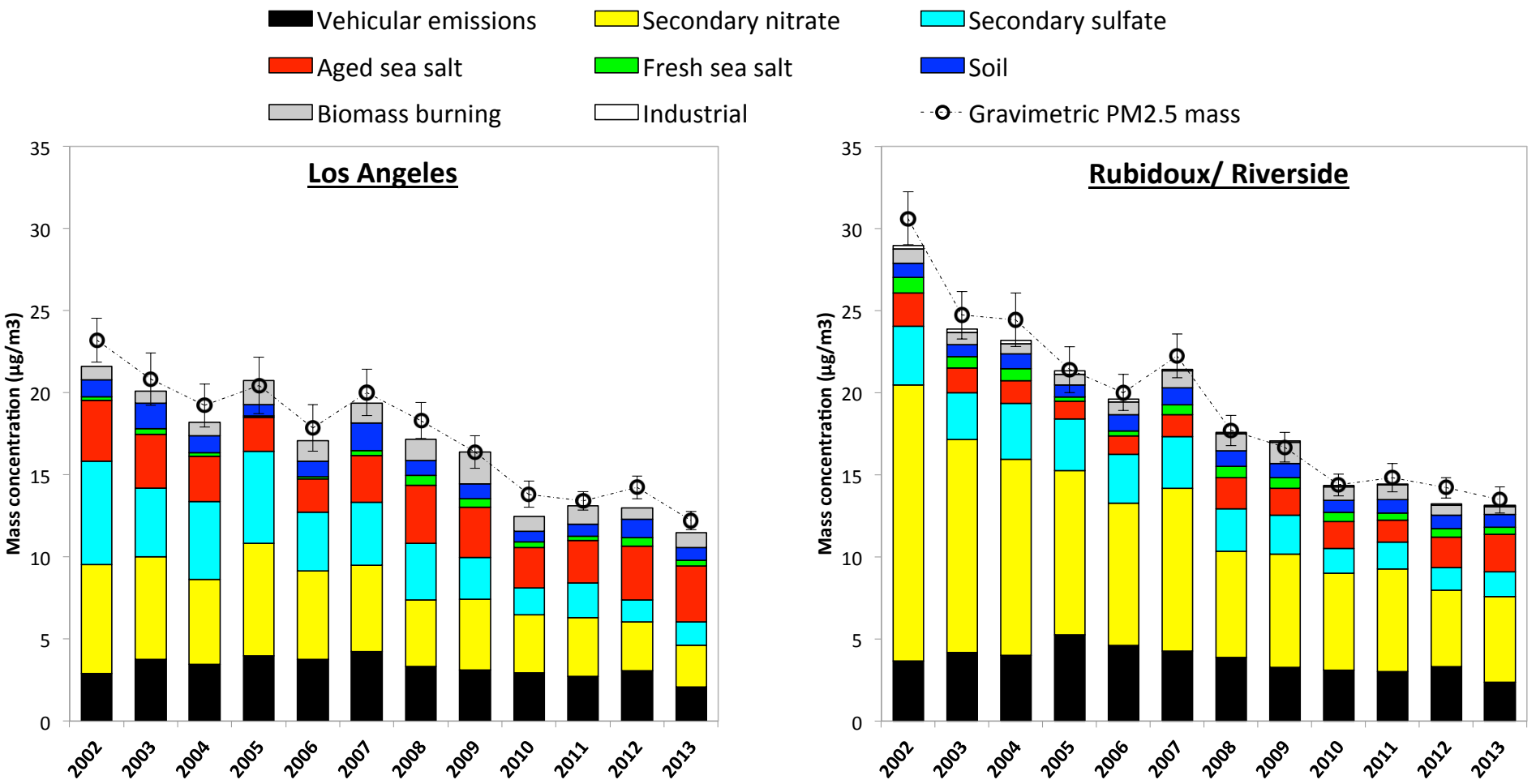
- Previous studies have shown that that stringent regulations on mobile sources, in particular starting in 2007, have resulted in major reductions in tailpipe emissions in Los Angeles (Hasheminassab et al., 2014; Bishop et al., 2013; Lurmann et al., 2015; McDonald et al., 2015).

- A recent comparison with previous studies in Central LA revealed considerable reduction of elemental carbon (EC) and organic carbon (OC), along with tracers of tailpipe emissions (e.g. PAHs, hopanes and steranes) in $PM_{0.18}$ and $PM_{2.5}$ (*Shirmohammadi et al., 2016*).

- In this study , we investigate the oxidative potential (OP) of ambient PM generated from a variety of sources in Los Angeles, with a focus on tailpipe and non-tailpipe traffic emissions.

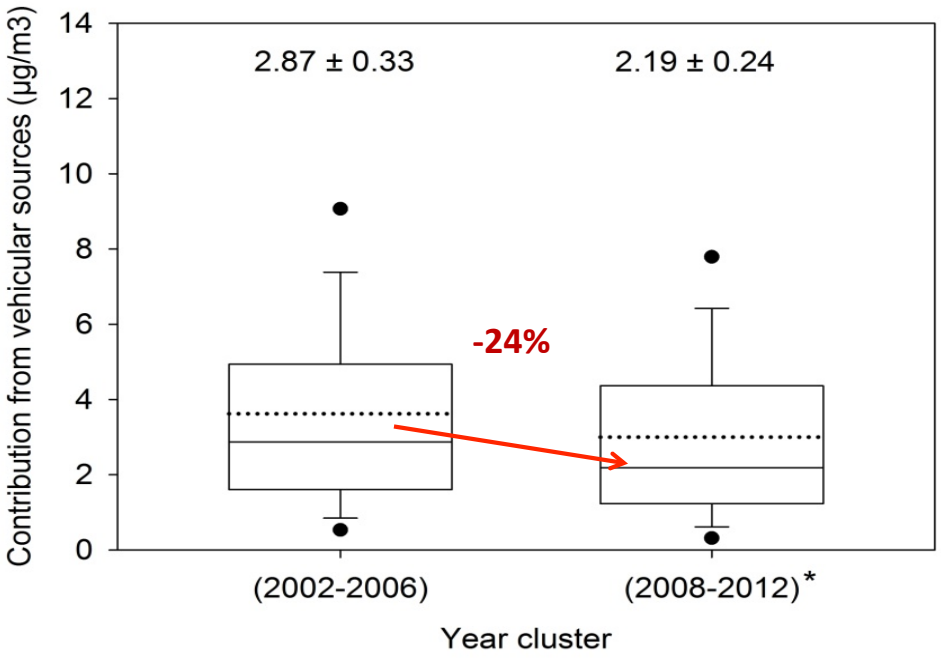
- The oxidative potential of size – fractionated PM is compared to earlier studies in Los Angeles

Annual Average Source Contributions to PM2.5 Mass
(*Hasheminassab et al, Atmos. Chem. & Physics, 2014)*

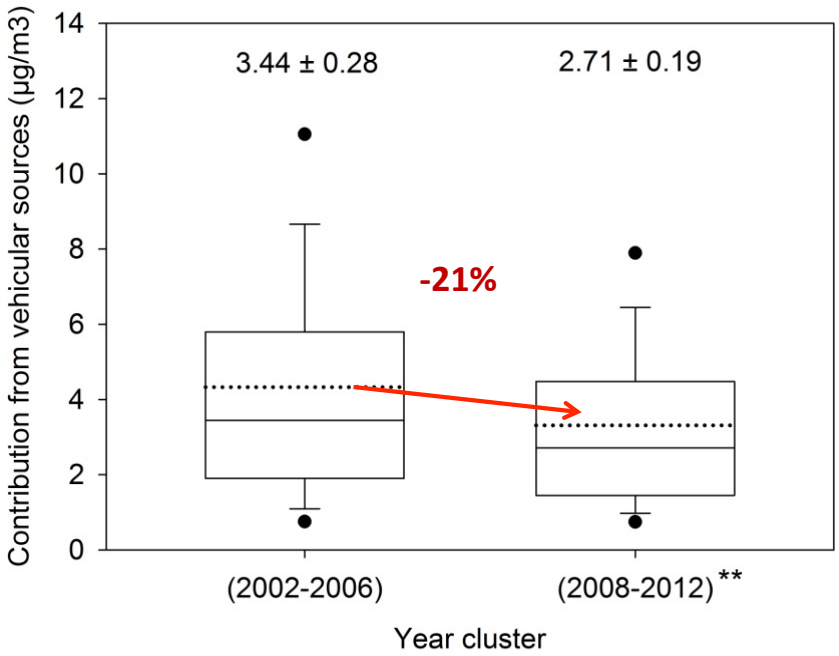


Daily-resolved vehicular emissions source contribution (in µg/m^3) before and after the 2007 emissions standard (*Hasheminassab et al, ACP, 2014*)

Central Los Angeles



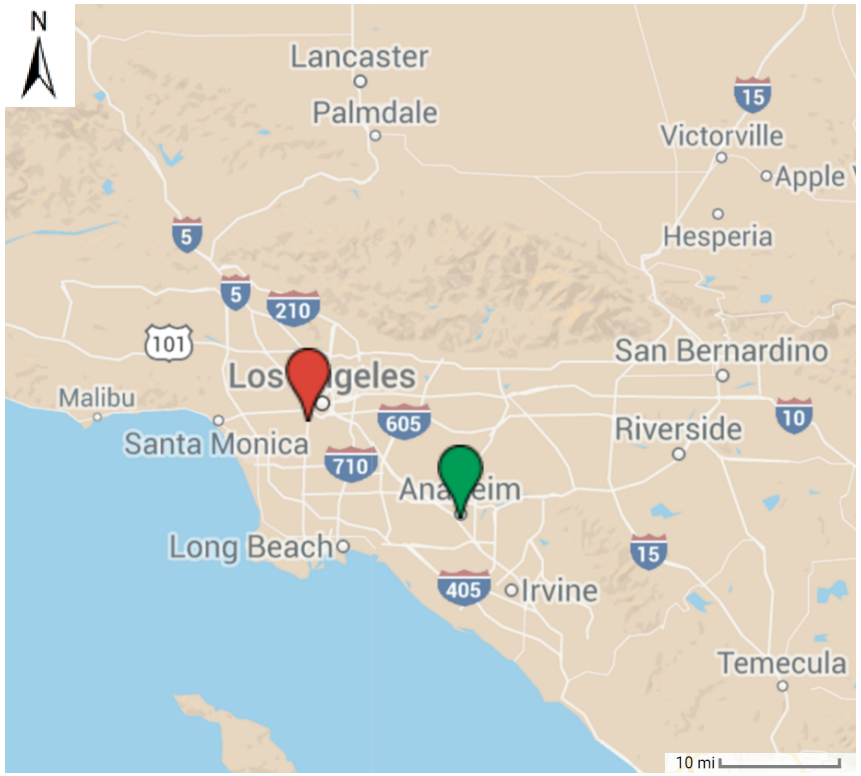
Riverside



Sampling sites

- The Central LA site (**an urban site**) is located ~ 150 m to the east and downwind of a major freeway (I-110) at the Particle Instrumentation Unit (PIU) of the University of Southern California, about 3 km south of downtown Los Angeles.

- **The Anaheim site** (**a suburban site**), Is situated in a residential area and about 500m upwind of freeway I-5



Data Collection and Analysis :

- Time-integrated PM sampling was conducted every week between July 2012 and February 2014
- Ambient PM were collected using Micro-Orifice Uniform Deposit Impactors (MOUDIs), classifying PM in three stages: <0.18 µm (ultrafine), 0.18-2.5 µm (accumulation), and 2.5-10 µm (coarse).

Chemical Analysis:

Samples were chemically analyzed based on the EPA protocol specified for STN field sampling:

- **$PM_{2.5}$ and $PM_{0.18}$ mass concentration:** gravimetrically by pre- and post- weighing the Teflon filters
- **Elemental carbon (EC) and organic carbon (OC):** NIOSH Thermal Optical Transmission (TOT) on quartz filters
- **Organic constituents:** gas chromatography mass spectrometry (GC-MS) on quartz filters
- **Metals and trace elements:** high resolution inductively coupled plasma sector field mass spectrometry (SF-ICPMS)
- **Anions (nitrate, sulfate, phosphate and chloride) and cations (ammonium, sodium, and potassium):** Ion Chromatography (IC)

Toxicological Analysis:

The dithiothreitol (DTT) assay was developed to simulate the in vivo generation of reactive oxygen species (ROS) in which DTT acts as a surrogate of biological reducing agents (NADH and NDPH) (Kumagai et al., 1997;2002).

Source Apportionment:

- Sources of PM2.5 and PM0.18 for Organic Carbon (OC) were quantified in a companion paper by Shirmohammadi et al (STOTEN 2016) using a hybrid Chemical Mass Balance (CMB) model

- The model estimated the relative contributions from: mobile sources (including gasoline, diesel, and smoking vehicles), wood smoke, primary biogenic sources (including emissions from vegetative detritus, food cooking, and re-suspended soil dust), and anthropogenic secondary OC (SOC).

Other PM sources :

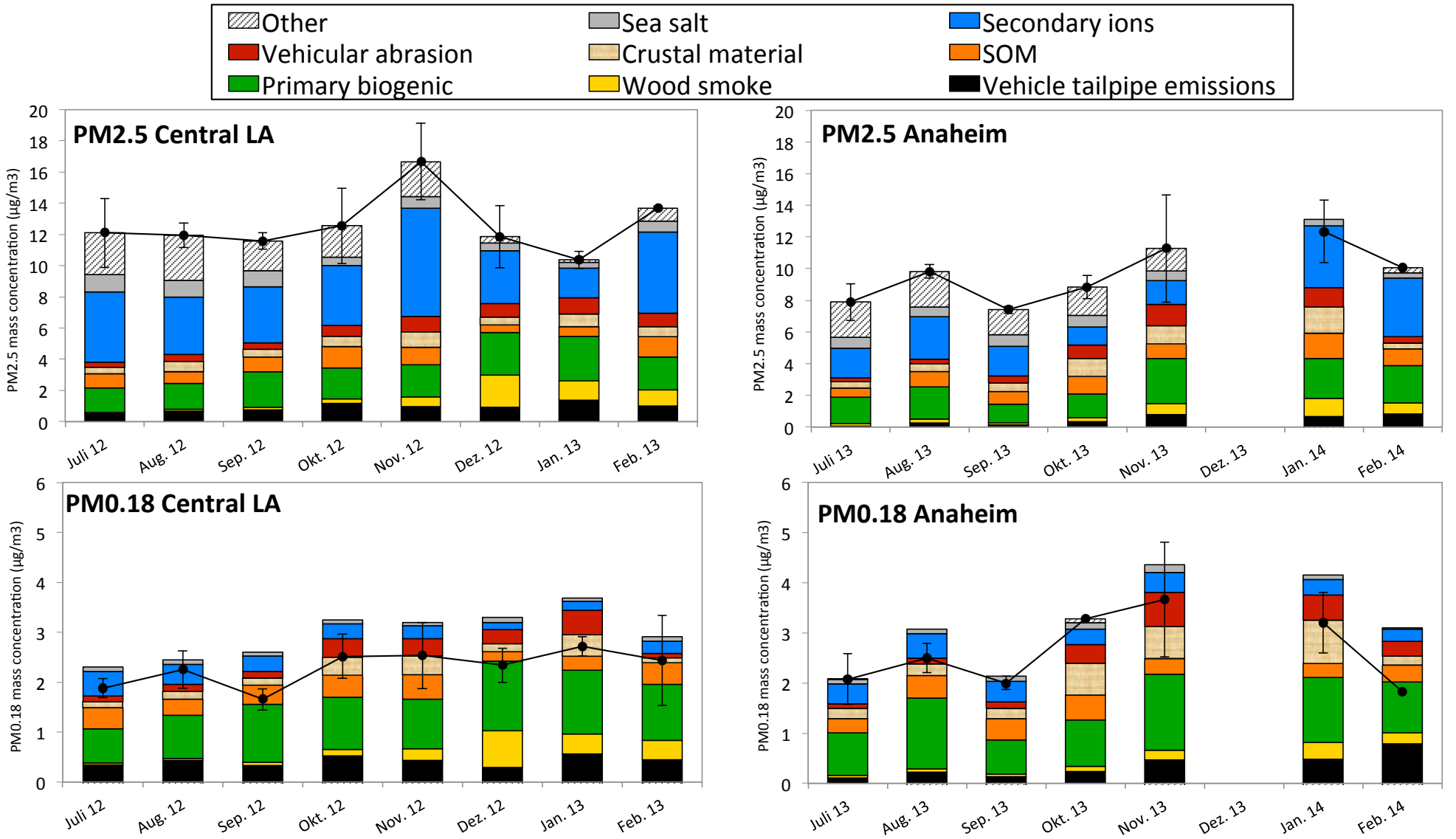
- **Crustal material** = 1.89Al + 1.21K + 1.43Fe + 1.40Ca + 1.66Mg + 1.67Ti + 2.14Si

- **Sea Salt** = $[Na^{+}]$ + ss $[Cl^{-}]$ + ss $[Mg^{+2}]$ + ss $[K^{+}]$ + ss $[Ca^{+2}]$ + ss $[SO_4^{-2}]$

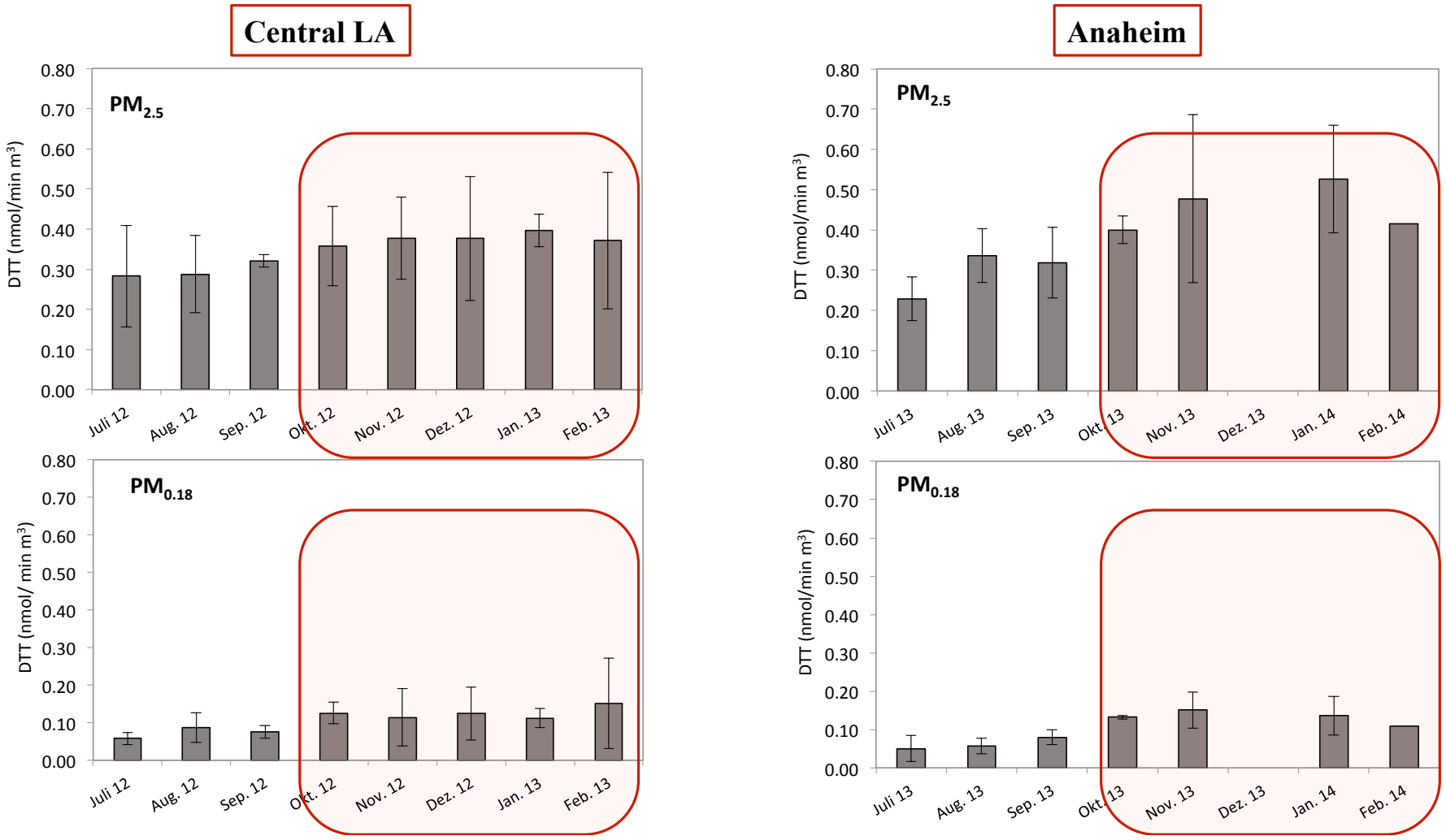
- **Secondary ions**= (sum of NO_3^{-}, NH_4^{+} and SO_4^{-2})

- **Vehicular abrasion=** brake wear contribution from concentrations of Ba .
  - Ba mass fraction of 13.3 ± 0.14 mg/g PM of brake dust in $PM_{2.5}$ was applied for this conversion

  Vehicular abrasion source estimation in this study is mainly associated with contribution from brake ware (so , it doesn't include tire ware).


Other
Sea salt
Secondary ions
Vehicular abrasion
Crustal material
SOM
Primary biogenic
Wood smoke
Vehicle tailpipe emissions
PM2.5 Central LA
PM2.5 mass concentration (µg/m3)
PM2.5 Anaheim
PM0.18 Central LA
PM0.18 mass concentration (µg/m3)
PM0.18 Anaheim
Juli 12
Aug. 12
Sep. 12
Okt. 12
Nov. 12
Dez. 12
Jan. 13
Feb. 13
Juli 13
Aug. 13
Sep. 13
Okt. 13
Nov. 13
Dez. 13
Jan. 14
Feb. 14

Monthly-averaged volume-normalized dithiothreitol (DTT) activity (nmol/min m^3) of ambient $PM_{2.5}$ and $PM_{0.18}$ at Central LA and Anaheim



Correlation analysis between the dithiothreitol (DTT) activity (nmol/min m^3) and selected $PM_{2.5}$ and $PM_{0.18}$ species at Central Los Angeles and Anaheim

Numbers in bold indicate statistical significance at the $p<0.05$ level

* Indicates significance at the $p < 0.1$ level

	Central LA		Anaheim	
Species	$PM_{2.5}$ DTT	$PM_{0.18}$ DTT	$PM_{2.5}$ DTT	$PM_{0.18}$ DTT
EC	0.54	**0.67**	**0.72**	**0.86**
OC	**0.79**	**0.89**	**0.81**	**0.87**
PAHs	**0.63**	**0.69**	**0.60**	**0.78**
Hopanes	**0.62**	**0.68**	**0.84**	**0.81**
n-Alkanes	**0.74**	0.57	0.57	**0.85**
Organic acids	**0.66**	**0.69**	0.38	0.13
Levoglucosan	0.56	**0.64**	**0.72**	0.58
Al	0.21	**0.65**	**0.69**	**0.76**
P	0.53	**0.72**	**0.74**	**0.84**
K	0.55	**0.83**	**0.73**	**0.86**
Ca	0.36	**0.70**	**0.62**	**0.83**
Ti	0.48*	0.64	**0.66**	**0.75**
Mn	0.46*	**0.70**	**0.84**	**0.82**
Fe	0.54	**0.75**	**0.81**	**0.83**
Cu	0.51	0.58	**0.81**	**0.88**
Zn	0.54	0.51	**0.83**	**0.88**
Rb	**0.64**	**0.79**	**0.70**	**0.78**
Sr	0.53	**0.72**	0.48*	**0.62**
Pd	0.57	**0.78**	**0.72**	**0.77**
Cd	**0.61**	**0.78**	**0.66**	**0.81**
Sn	0.12	0.22	**0.76**	**0.82**
Sb	**0.60**	**0.75**	**0.66**	**0.84**
Ba	0.58	**0.80**	**0.79**	**0.85**
Pb	0.58	**0.64**	**0.68**	**0.78**

Multiple linear regression (MLR) analysis between the dithiothreitol (DTT) activity (nmol/ min m^3) and chemical species for $PM_{2.5}$ and $PM_{0.18}$ size ranges at Central LA and Anaheim

Central LA $PM_{2.5}$ DTT Activity = 0.01* (**Glutaric + Phtalic + Succinic acids**) + 0.012 * **Ba** R^2= **0.60**

Central LA $PM_{0.18}$ DTT Activity = 0.115* **EC** + 0.014 * **Ba** R^2= **0.64**

Anaheim $PM_{2.5}$ DTT Activity = 0.002* (**Sum of Organic Acids**) + 0.023 * **Cu** R^2= **0.83**

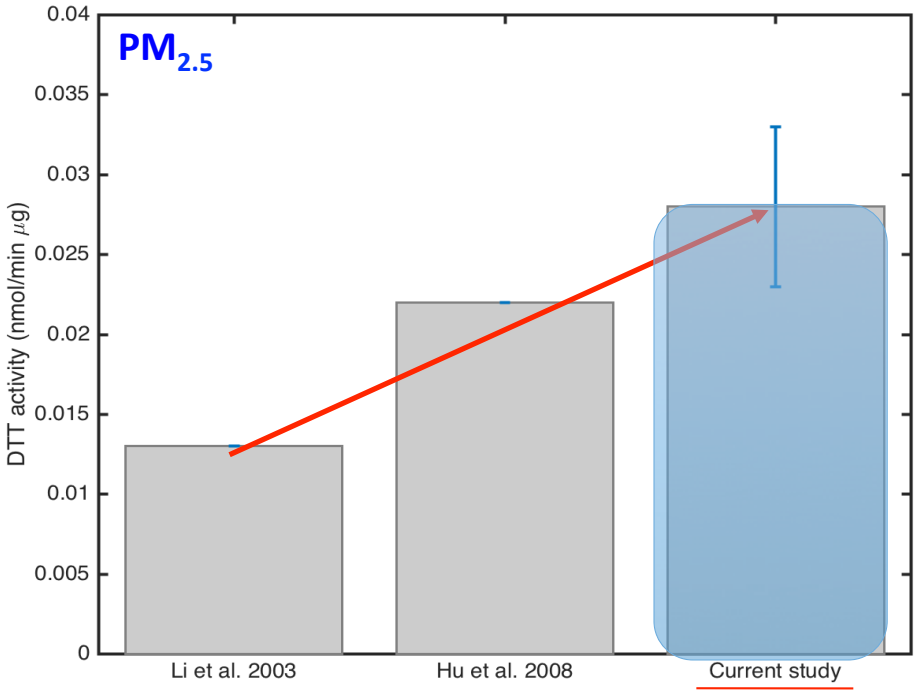
Anaheim $PM_{0.18}$ DTT Activity = 0.136* **EC** + 0.056 * **Pb** R^2= **0.84**

Main sources driving DTT activity ⇨

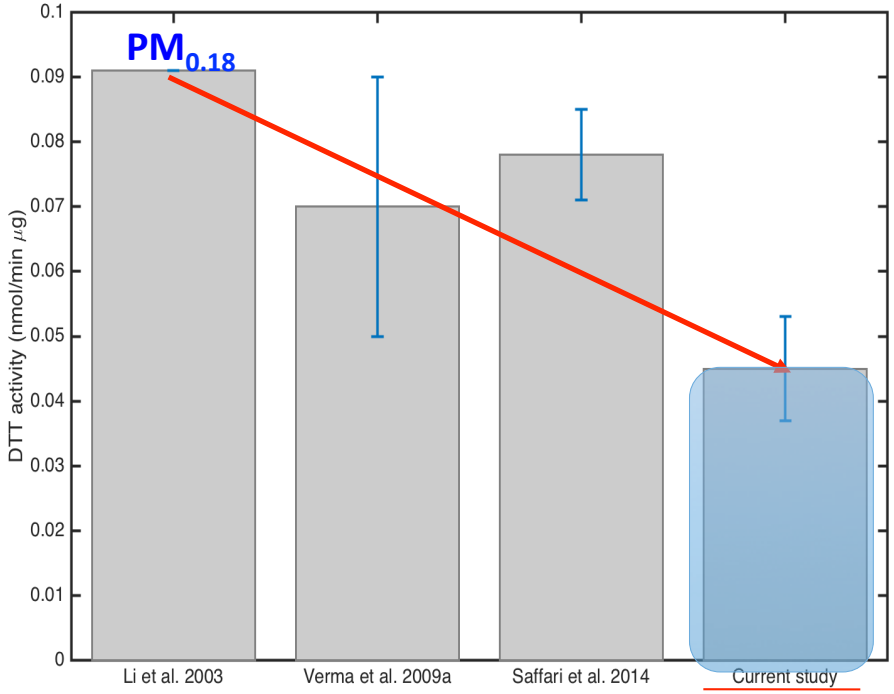
In PM2.5 size range:
Secondary organic aerosols and **vehicular abrasion/ road dust**

In PM0.18 size range:
Vehicle tailpipe emissions and **vehicular abrasion/ road dust**

Comparison of PM mass-normalized DTT activity (nmol/min µg PM) levels with previous studies in Central LA

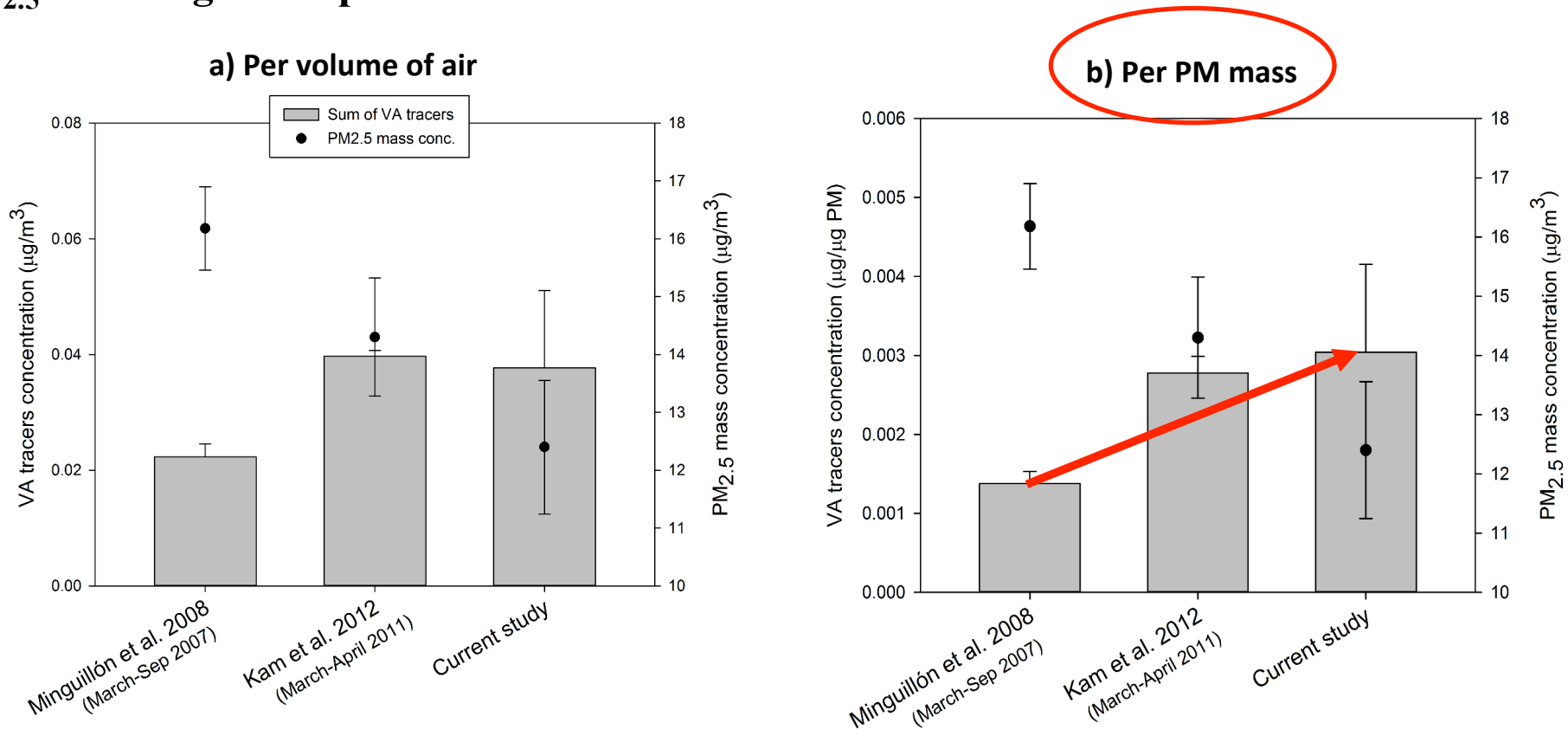


Study	Size fraction	Sampling period
Li et al. 2003	$PM_{2.5}$	Mar-Oct 2002
Hu et al. 2008	$PM_{2.5}$	Mar- Nov 2007
Current study	$PM_{2.5}$	2012-2013



Study	Size fraction	Sampling period
Li et al. 2003	$PM_{0.15}$	Mar 2002
Verma et al. 2009a	$PM_{0.18}$	Aug 2009
Saffari et al. 2014	$PM_{0.25}$	2008-2009
Current study	$PM_{0.18}$	2012-2013

Comparison of the sum of vehicular abrasion (VA) tracers concentrations (i.e. sum of Ba, Cu, Mn, Pb and Sb): a) per volume of air (µg/m^3) and b) per mass collected (µg/µg PM) in $PM_{2.5}$ size range with previous studies conducted at Central LA.



Conclusions

- Despite rapid reduction of tailpipe emissions, the lack of similar reductions (and possibly an increase) in non-tailpipe emissions makes them an important source of traffic-related PM emissions in Los Angeles and a concern for public health.

- A comparison with previous studies conducted in Central LA revealed significant trends in DTT activity of ambient $PM_{2.5}$ and $PM_{0.18}$ in the past decade.

- Ambient $PM_{0.18}$, the toxicity of which was found to be mainly dominated by tailpipe emissions, showed a consistent decrease in DTT activity levels in the past decade, reflecting the major reductions in tailpipe emissions in the LA Basin, as a result of stringent regulations on mobile sources.

- In contrast , in the $PM_{2.5}$ size range, DTT activity levels showed overall a slight increase over the years, which is probably driven by the increase in the contribution of non-tailpipe emissions to ambient $PM_{2.5,}$ counteracting the reductions in the tailpipe emissions in this size fraction.

Acknowledgments

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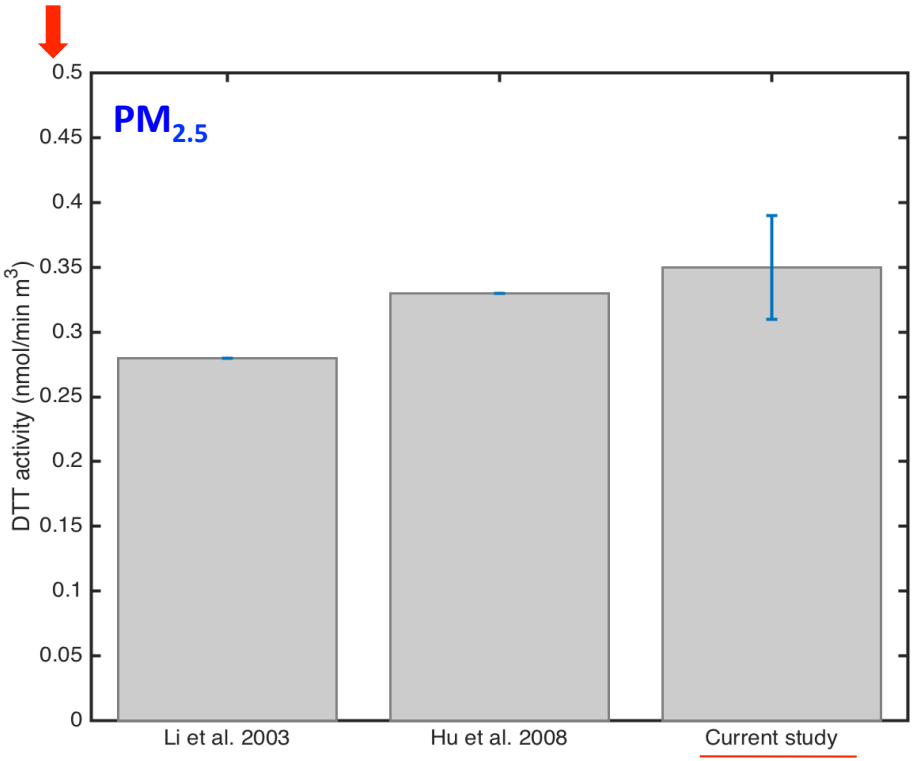
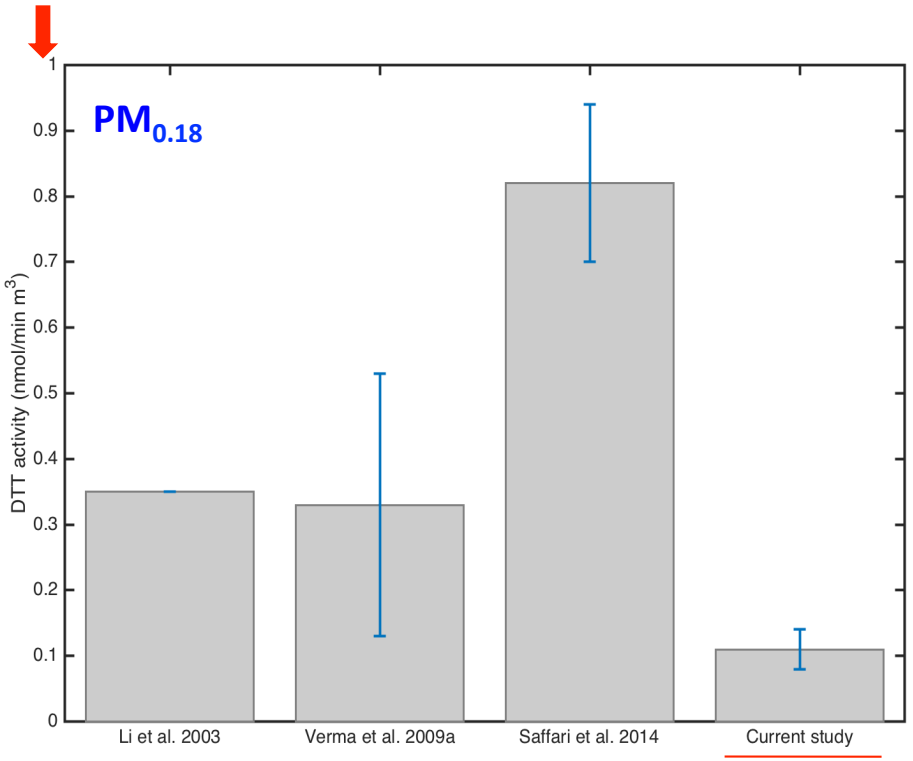
Thank you!

Appendix

Comparison of volume-normalized DTT activity (nmol/min m3) levels with previous studies in Central LA



Study	Size fraction	Sampling period
Li et al. 2003	$PM_{2.5}$	Mar 2002
Hu et al. 2008	$PM_{2.5}$	Mar- May 2007
Current study	$PM_{2.5}$	2012-2013

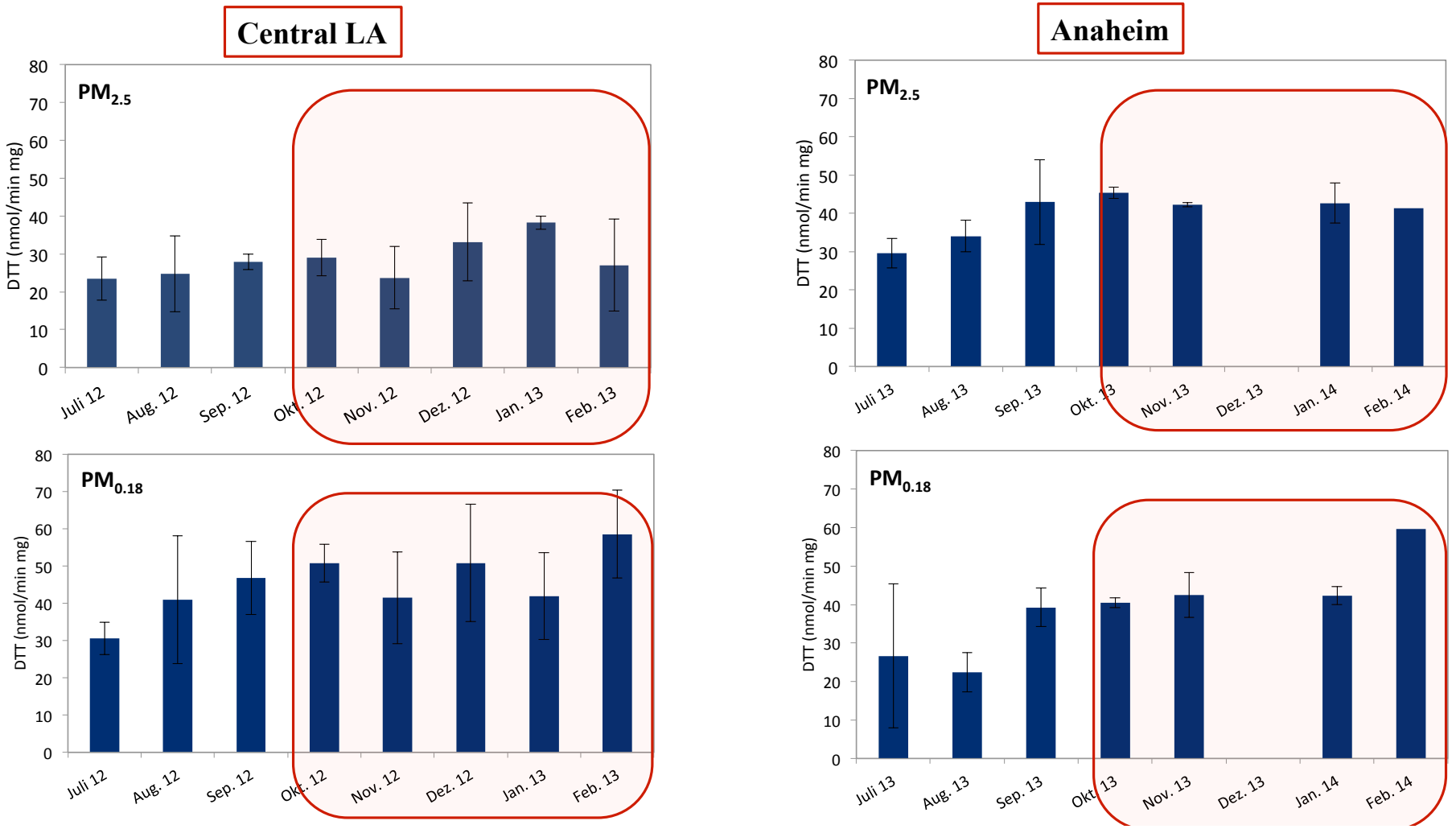


Study	Size fraction	Sampling period
Li et al. 2003	$PM_{0.15}$	Mar 2002
Verma et al. 2009a	$PM_{0.18}$	Aug 2009
Saffari et al. 2014	$PM_{0.25}$	2008-2009
Current study	$PM_{0.18}$	2012-2013

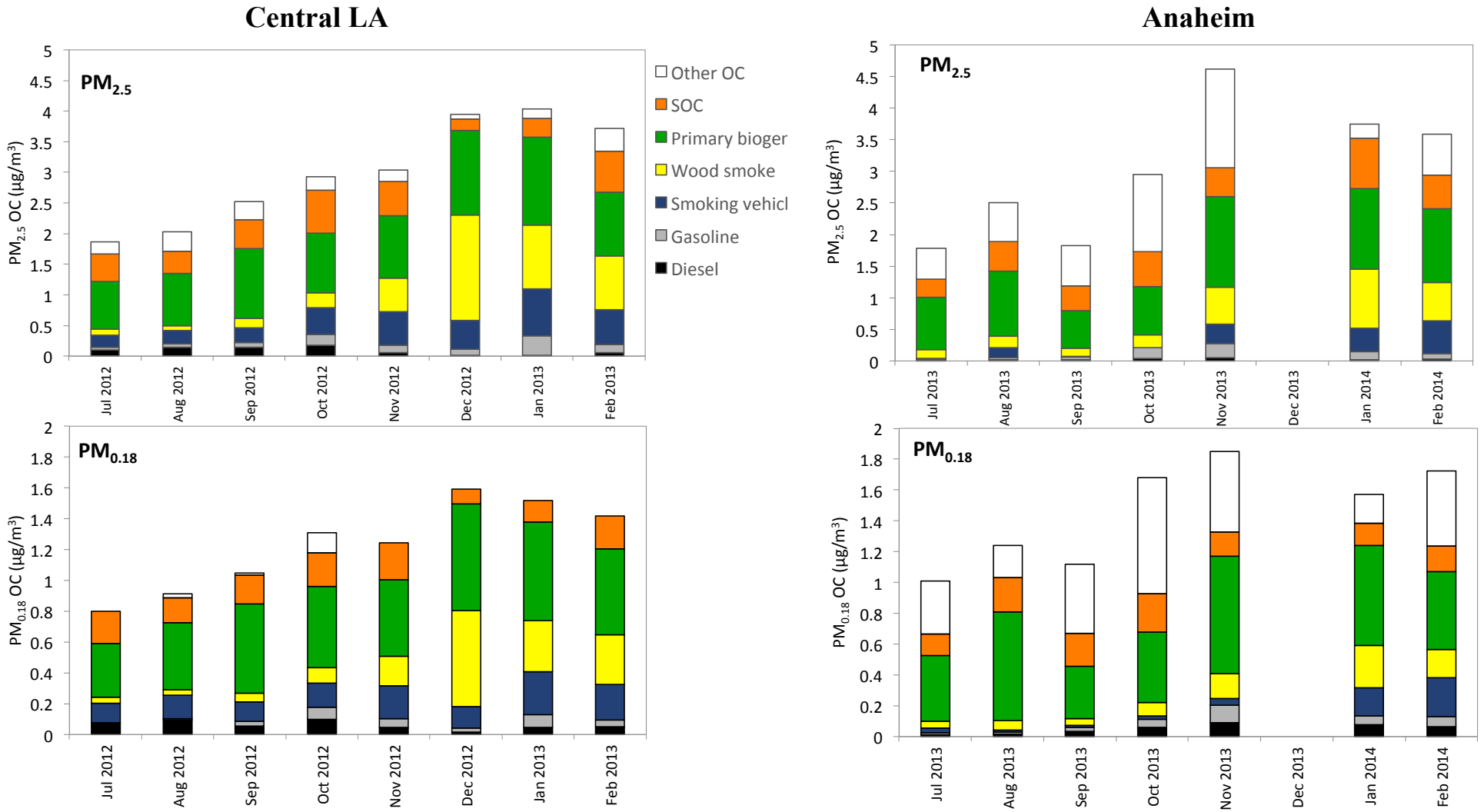
Correlation analysis between the dithiothreitol (DTT) activity (nmol/min m^3) and sources of $PM_{2.5}$ and $PM_{0.18}$ at Central Los Angeles and Anaheim

	Central LA		Anaheim	
Sources	**$PM_{2.5}$ DTT**	**$PM_{0.18}$ DTT**	**$PM_{2.5}$ DTT**	**$PM_{0.18}$ DTT**
Wood smoke	**0.56***	**0.61***	**0.55***	**0.57***
Primary biogenic	**0.68***	**0.76***	0.32	0.21
SOC	**0.62***	-0.14	**0.58***	-0.08
Secondary Ions	-0.07	-0.05	0.49*	0.02
Crustal material	0.33	**0.72***	**0.73***	**0.81***
Vehicular abrasion	**0.58***	**0.80***	**0.79***	**0.85***
Sea salt	-0.46	-0.00	-0.32	0.42
Vehicle tailpipe emissions	**0.69***	**0.77***	**0.72***	**0.88***

Monthly-averaged mass-normalized dithiothreitol (DTT) activity (nmol/min mg PM) of ambient $PM_{2.5}$ and $PM_{0.18}$ at Central LA and Anaheim



Monthly average source contributions (μg/m³) to ambient OC for $PM_{2.5}$ and $PM_{0.18}$ in Central Los Angeles and Anaheim.



Output of multiple linear regression (MLR) analysis between the dithiothreitol (DTT) activity (nmol/ min m^3) and chemical species for $PM_{2.5}$ and $PM_{0.18}$ size ranges at Central LA and Anaheim

DTT activity	Species	Unstandardized Coefficient	Units	Standard error	Partial R	P value	R^2
Central LA $PM_{2.5}$	(Constant)	0.12	nmol min^{-1} m^{-3}	0.057	-		0.50
	SOC tracers*	0.01	nmol min^{-1} ng^{-1}	0.004	0.432	0.022	
	Ba	0.012	nmol min^{-1} ng^{-1}	0.003	0.685	0.000	
Central LA $PM_{0.18}$	(Constant)	0.011	nmol min^{-1} m^{-3}	0.021	-		0.60
	EC	0.155	nmol min^{-1} ng^{-1}	0.076	0.37	0.053	
	Ba	0.014	nmol min^{-1} ng^{-1}	0.003	0.658	0.000	
Anaheim $PM_{2.5}$	(Constant)	0.121	nmol min^{-1} m^{-3}	0.051	-		0.83
	Organic acids	0.002	nmol min^{-1} ng^{-1}	0.001	0.490	0.033	
	Cu	0.023	nmol min^{-1} ng^{-1}	0.003	0.891	0.000	
Anaheim $PM_{0.18}$	(Constant)	0.032	nmol min^{-1} m^{-3}	0.009	-		0.84
	EC	0.136	nmol min^{-1} ng^{-1}	0.065	0.453	0.051	
	Pb	0.056	nmol min^{-1} ng^{-1}	0.022	0.533	0.019	

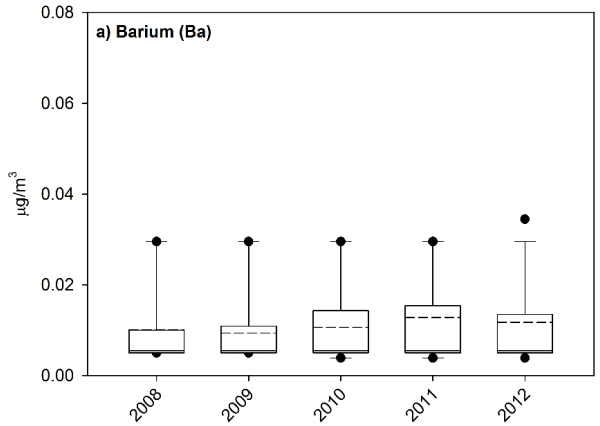
*SOC tracers: ***Glutaric acid+Phtalic acid+Succinic acid***

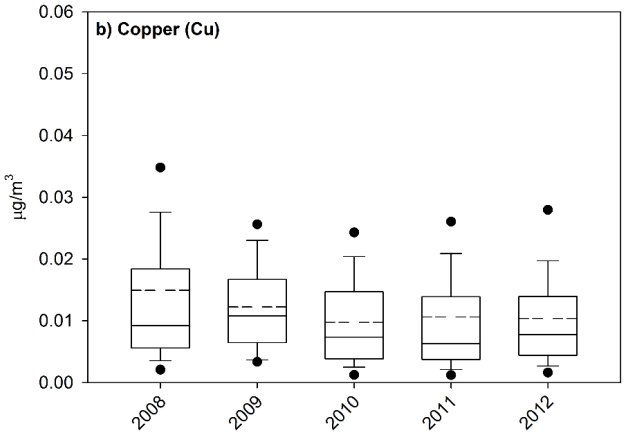
Comparison of volume-normalized DTT activity levels with previous studies in Central LA

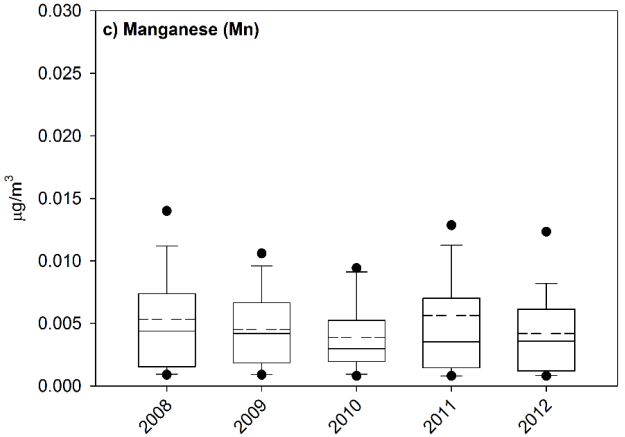
Study	Size fraction	Sampling period	DTT activity (nmol/min µg)	DTT activity (nmol/min m^3)
Li et al. 2003	$PM_{2.5}$	Mar 2002	0.013	0.28
Hu et al. 2008	$PM_{2.5}$	Mar- May 2007	0.022	0.33
Verma et al. 2009b	$PM_{2.5}$	Nov 2007	0.007 ± 0.003	0.35 ± 0.30
Current study	$PM_{2.5}$	2012-2013	0.028 ± 0.005	0.35 ± 0.04

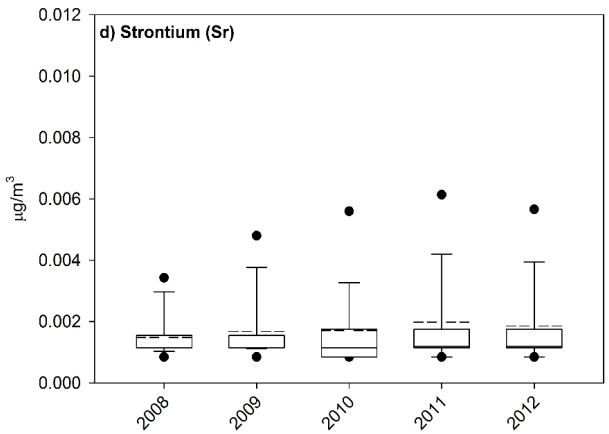
Study	Size fraction	Sampling period	DTT activity (nmol/min µg)	DTT activity (nmol/min m^3)
Li et al. 2003	$PM_{0.15}$	Mar 2002	0.091	0.35
Verma et al. 2009a	$PM_{0.18}$	Aug 2009	0.07 ± 0.03	0.33 ± 0.25
Saffari et al. 2014	$PM_{0.25}$	2008-2009	0.078 ± 0.007	0.82 ± 0.12
Current study	$PM_{0.18}$	2012-2013	0.045 ± 0.008	0.11 ± 0.03

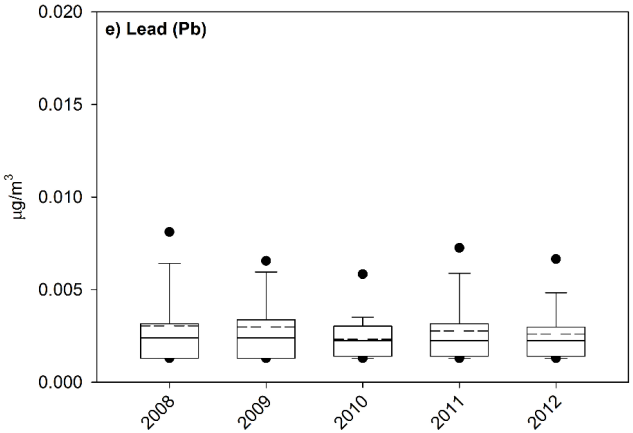
Yearly trends of per volume concentrations (µg/m^3) of individual vehicular abrasion's tracers(i.e. Ba, Cu, Mn, Pb and Sr) in $PM_{2.5}$ size range, obtained from Speciation Trends Network (STN) data at the North Main street, Los Angeles











Yearly trends of per mass concentrations (µg/µg PM) of individual vehicular abrasion's tracers (i.e. Ba, Cu, Mn, Pb and Sr) in $PM_{2.5}$ size range, obtained from Speciation Trends Network (STN) data at the North Main street, Los Angeles