Improving chemical transport model predictions of organic aerosol: Measurement and simulation of semi-volatile organic emissions from mobile and non-mobile sources

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- ARB – Contract #12-318 + Vehicle procurement, testing, and emissions characterization
- CRC A74/E96 – CMU smog chamber experiments
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Science
AAAS

Rethinking Organic Aerosols: Semivolatile Emissions and Photochemical Aging

Allen L. Robinson, *et al.*

Science **315**, 1259 (2007);
DOI: 10.1126/science.1133061

Two hypotheses:

1. Majority of primary organic aerosols are semi-volatile.
2. Important class of secondary organic aerosol precursors (intermediate volatility organic compounds) are missing from models/inventories.

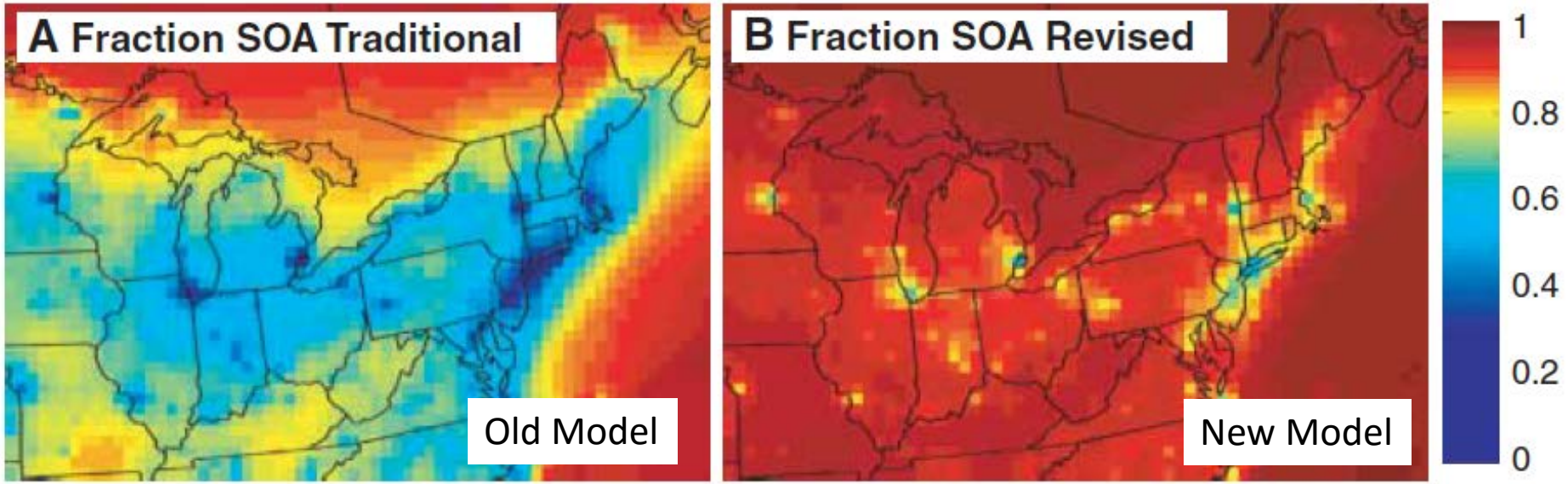
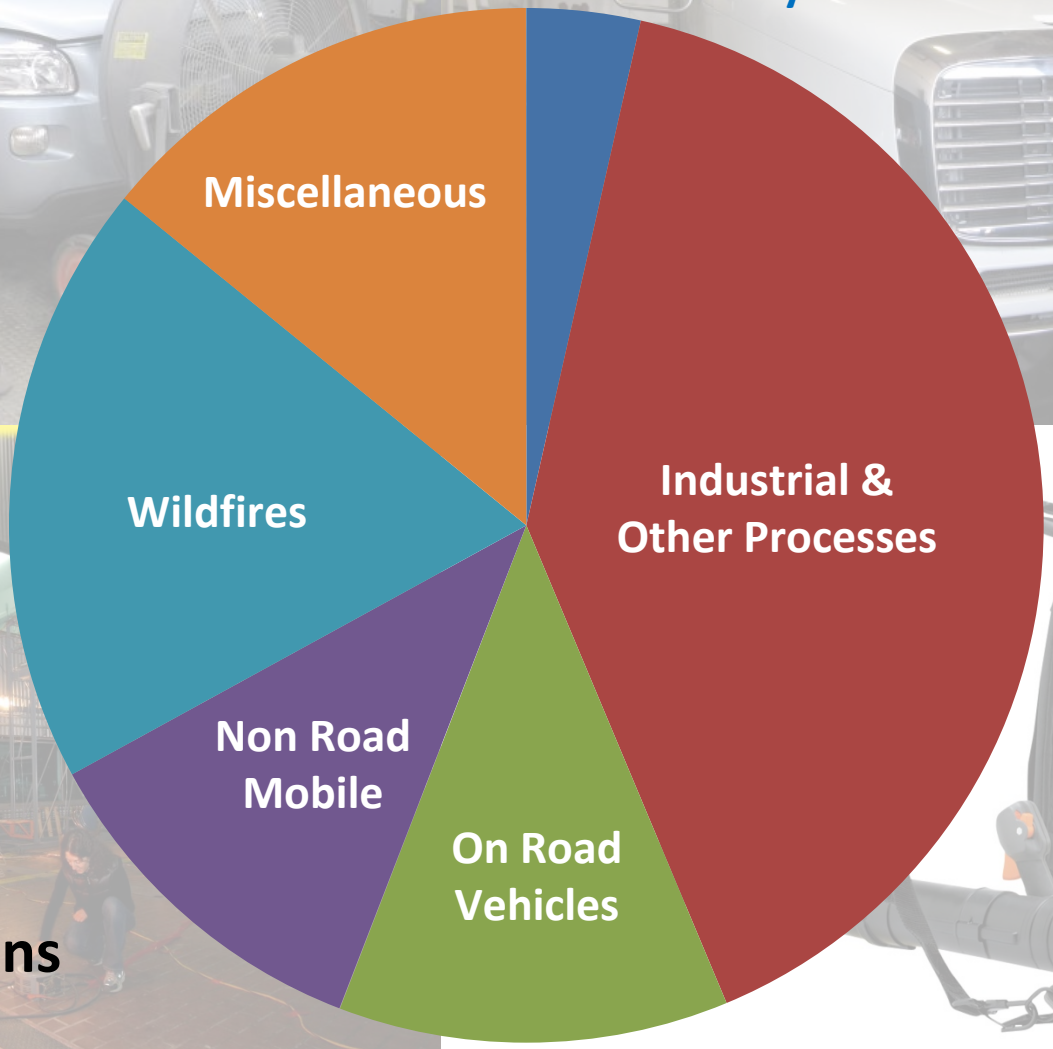


Photo: Daniel Welsh-Bon

US Anthropogenic VOC Emissions



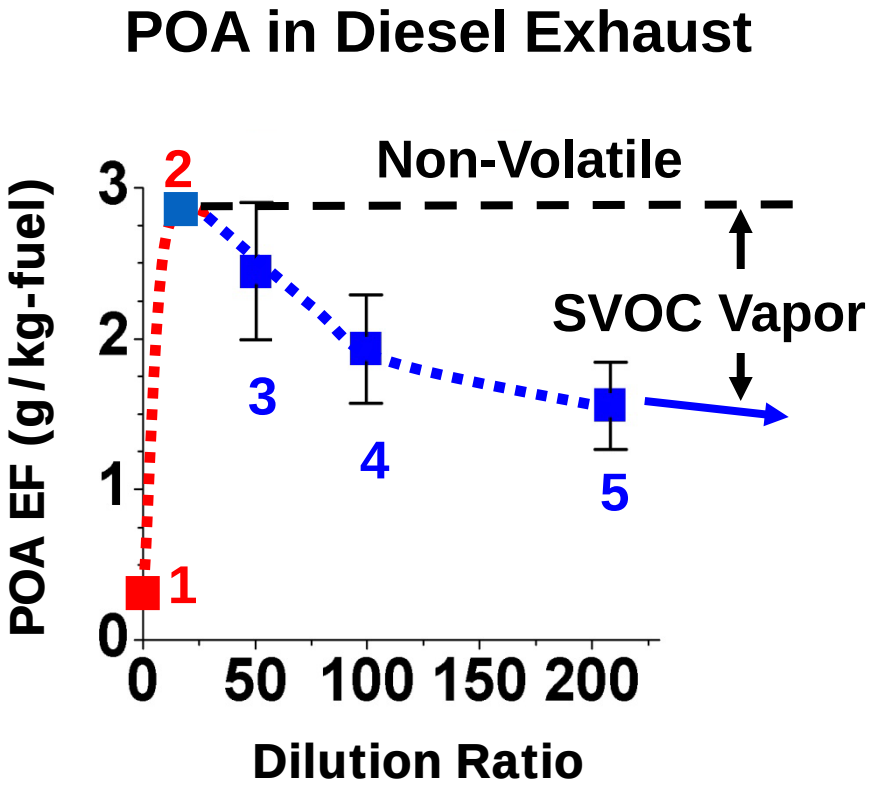
2013
17,624 short tons

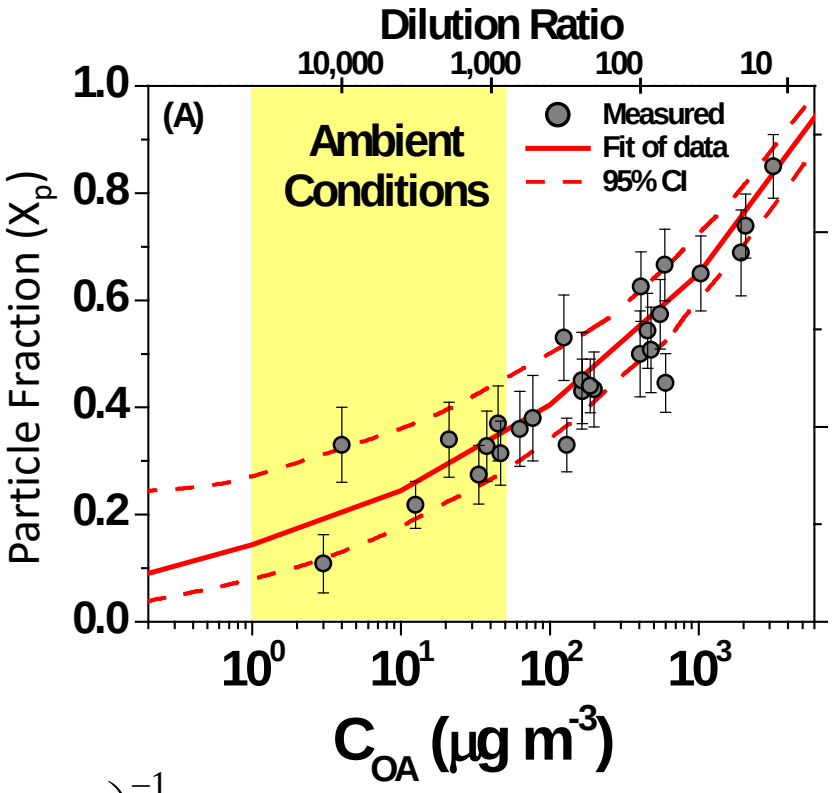
http://www.epa.gov/ttnchie1/trends/

Photo: Daniel Welsh-Bon

Are primary organic aerosol emissions semi-volatile?

Data from a small diesel generator (and a woodstove) suggested YES.





$$X_p = \sum_{i=1}^{n} f_i \left(1 + \frac{C_i^*}{C_{OA}}\right)^{-1}$$

Hildeman et al. AST 1989
Lipsky and Robinson ES&T 2006

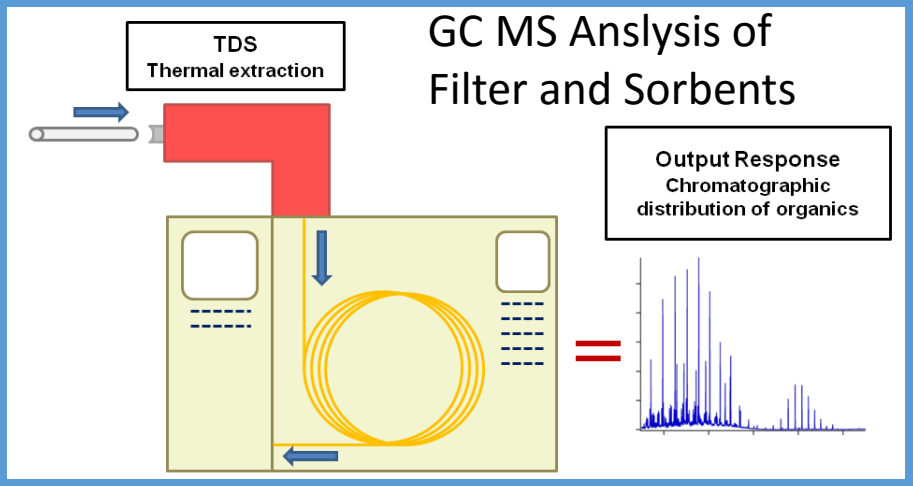
Robinson et al. Science 2007

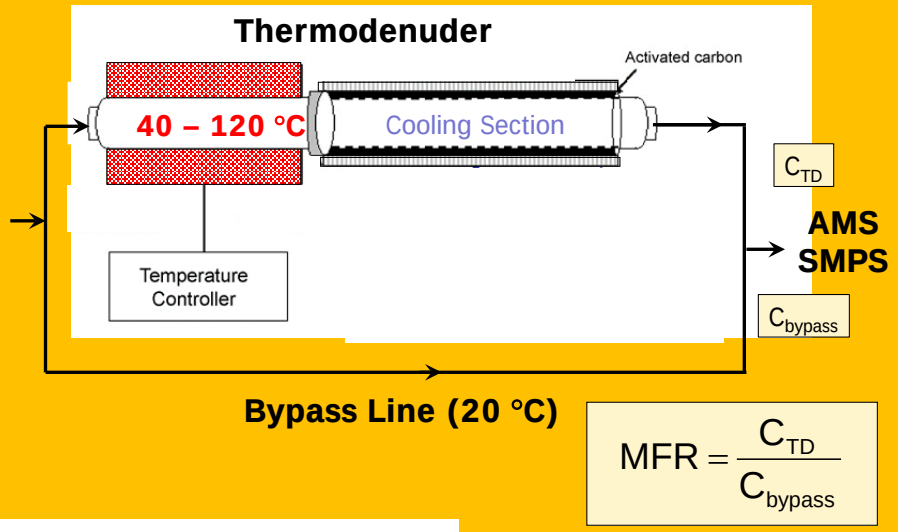
What about “real-world” sources?

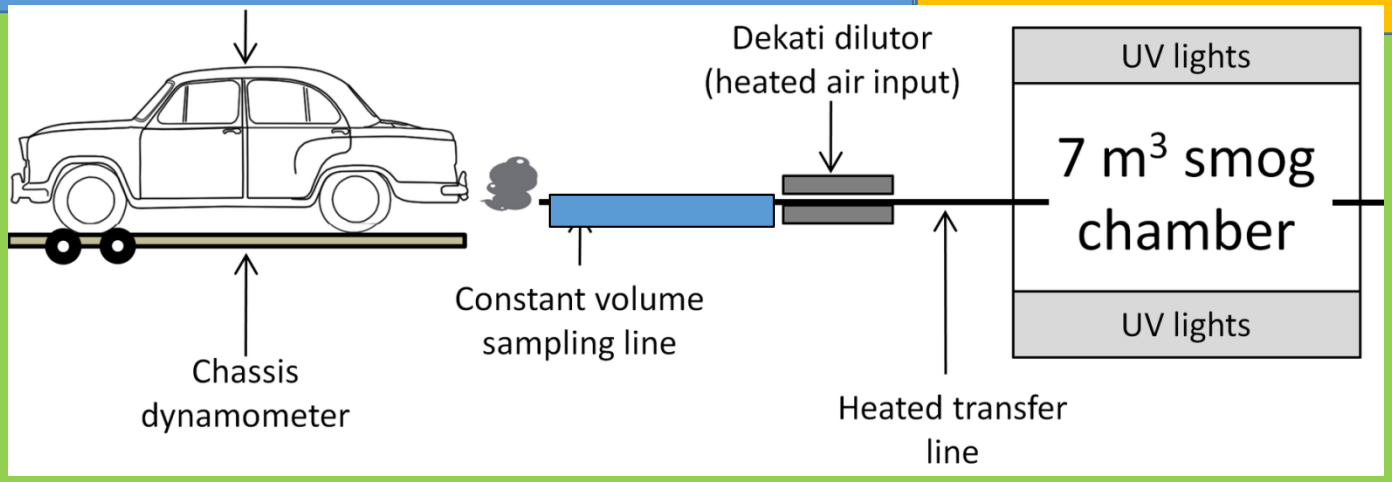
- Mobile sources
  - Dynamometer testing

Source	model years	#	
on-road vehicles			
Pre-lev	1987~1994	11	~50 gasoline vehicles
Lev1	1994~2003	16	
Lev2	2004 and Later	20	
Medium duty diesel truck	2001, 2005	2	5 diesel
Heavy duty diesel truck	2006, 2007 and 2010	3	
off-road engines			
Transport transportation unit	1998	1	7 small off road
2-stroke		3	
4-stroke		3	

  - Highway tunnel: ~2 weeks
- Wildfires – 13 different fuels







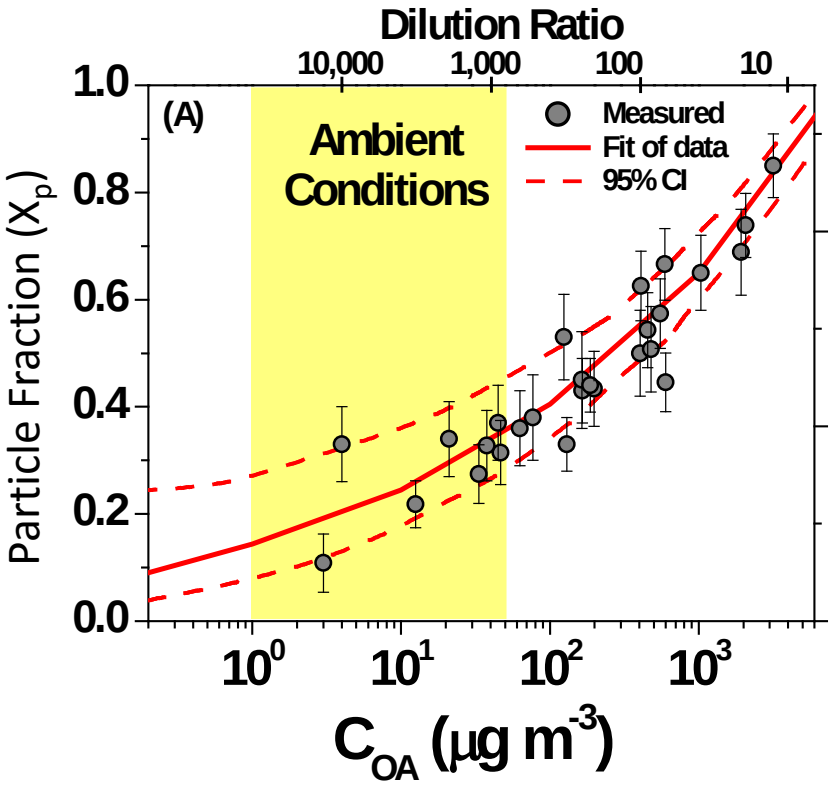
Chamber 25 – 35x more dilute than CVS

QBT ~ adsorbed vapors (artifact)

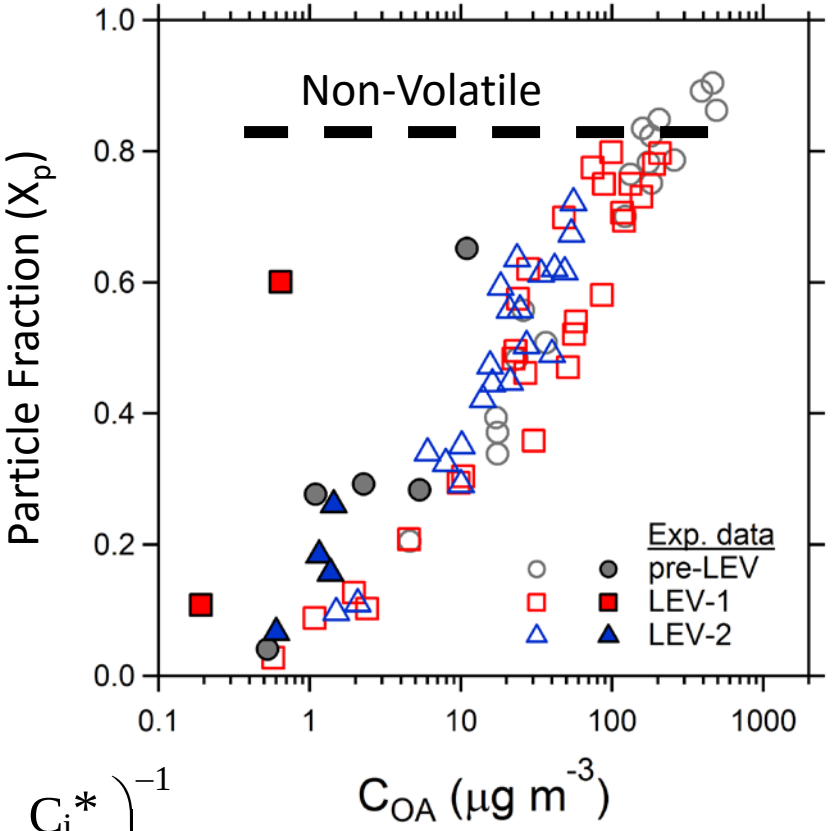
Q - QBT ~ particulate carbon

Primary organic aerosol is semivolatile

Small diesel generator



Gasoline Vehicles (n=66)

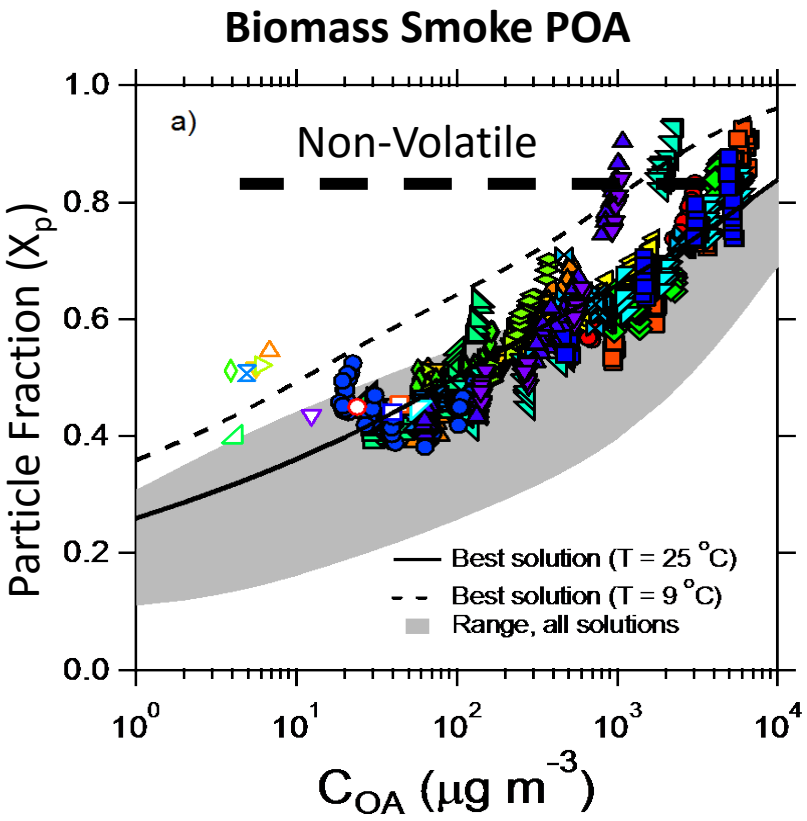


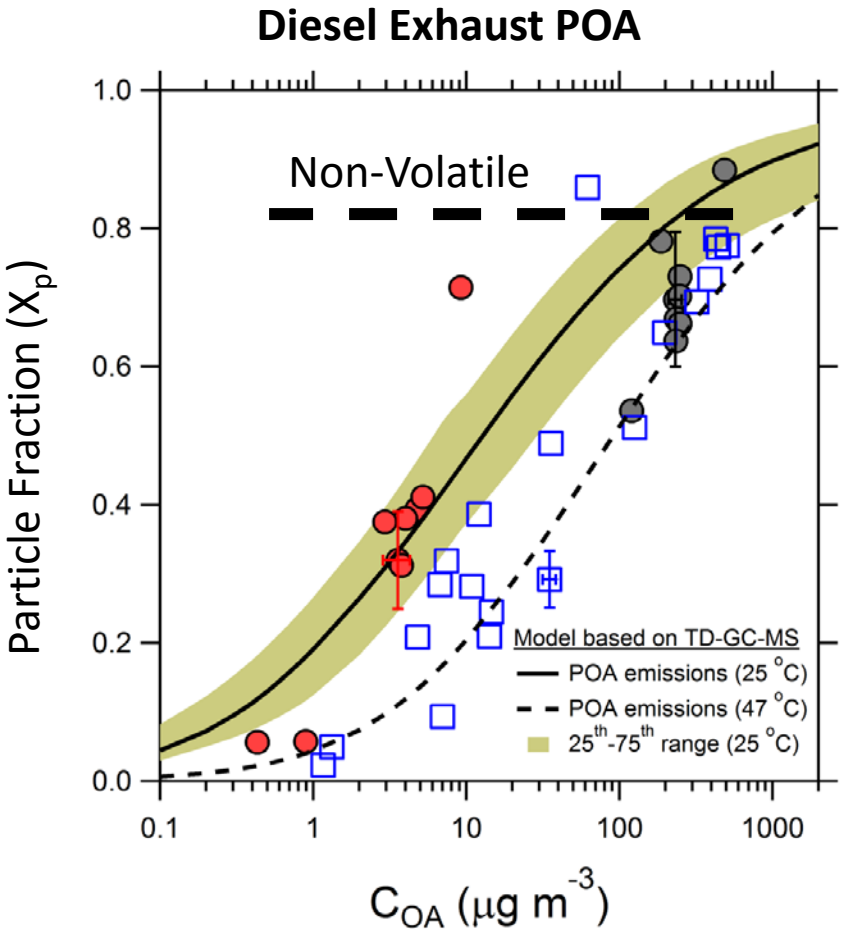
$$X_p = \sum_{i=1}^{n} f_i \left(1 + \frac{C_i^*}{C_{OA}}\right)^{-1}$$

Robinson et al. Science 2007

May et al. AE 2013

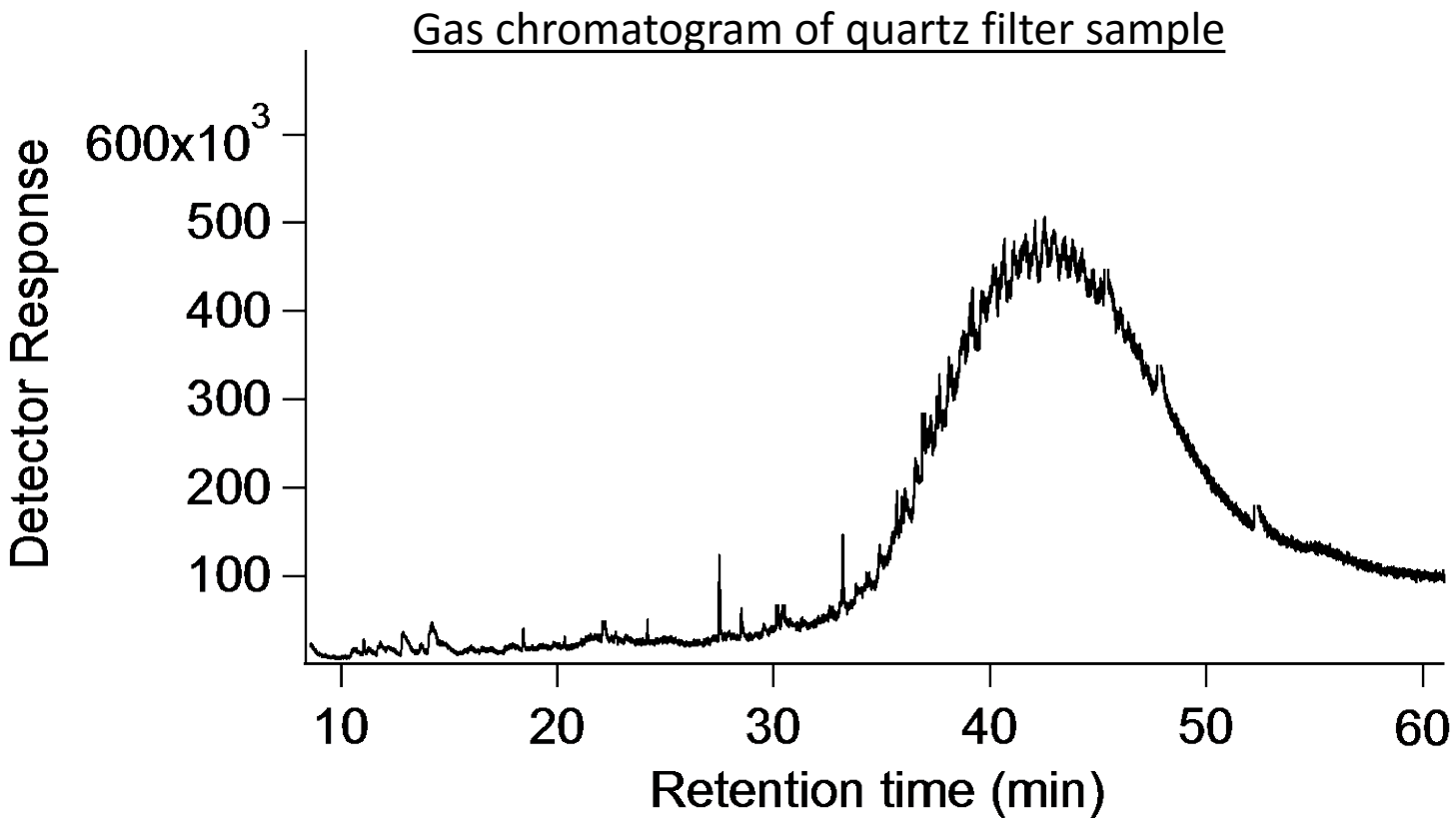
Biomass and diesel POA too!





(May et al. EST 2013; May et al. JGR 2013)

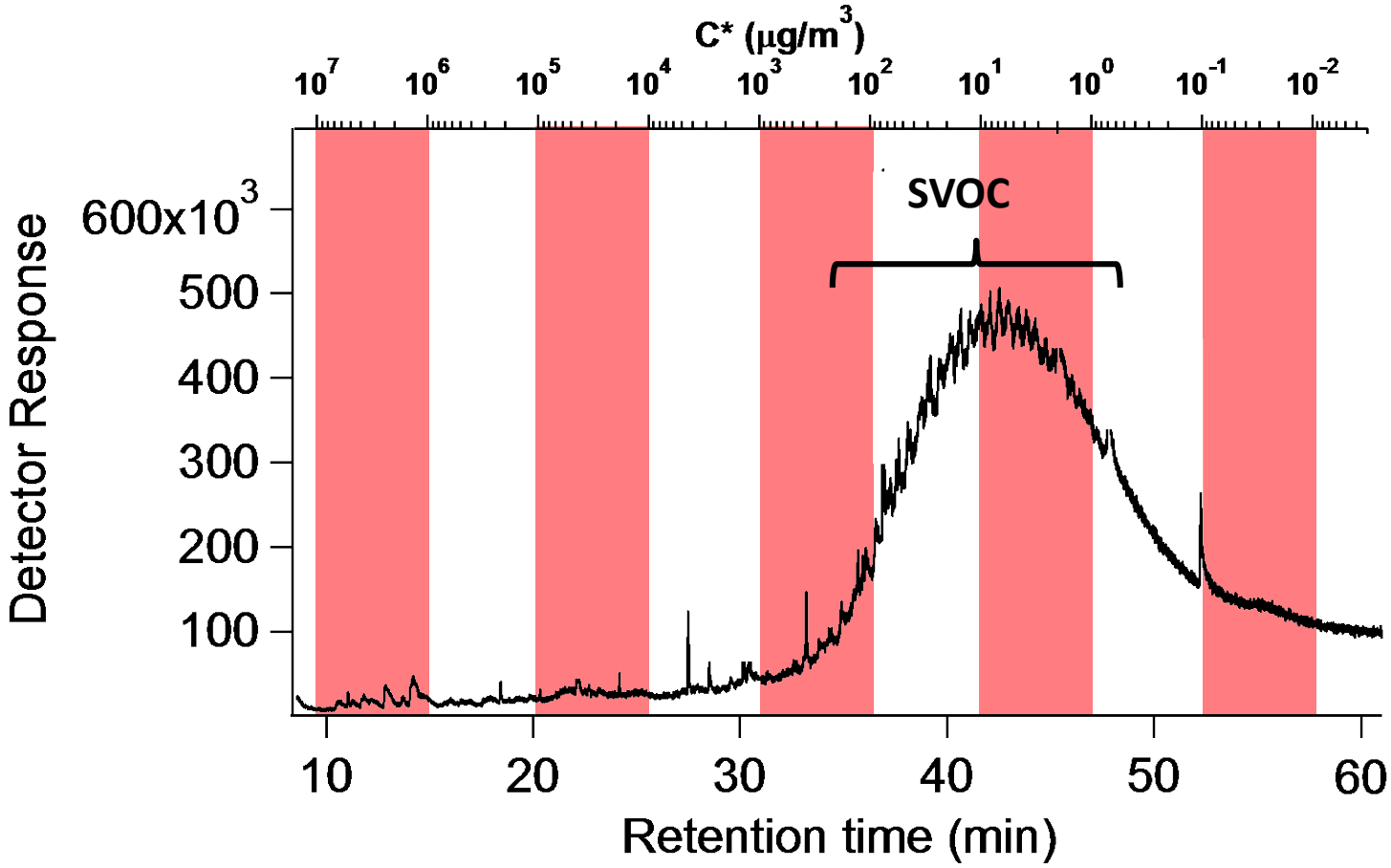
Primary Organic Aerosol Composition



(Presto et al. AST 2012)

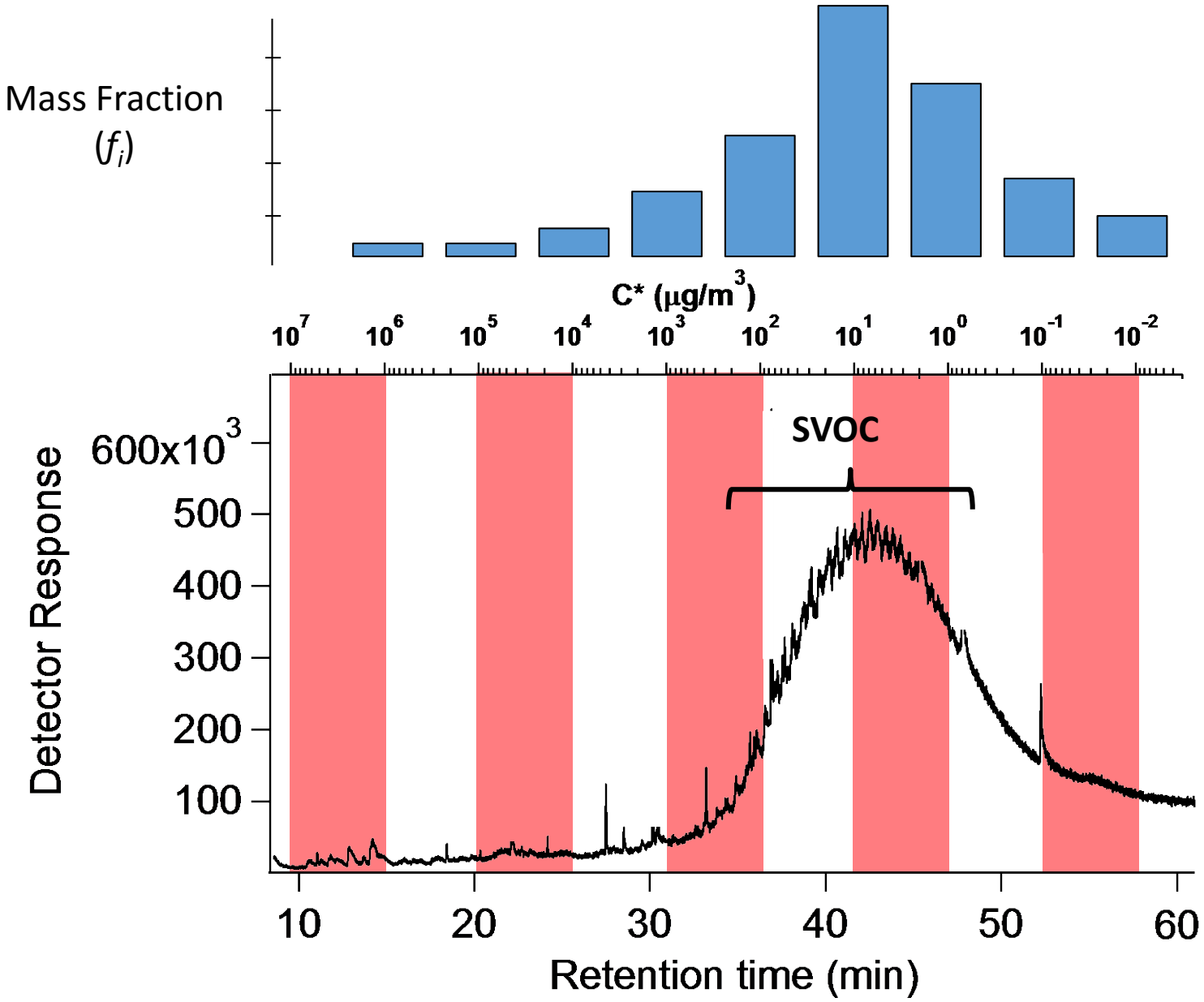
Decreasing volatility

Lots of semivolatile emissions



Presto et al. AST 2012

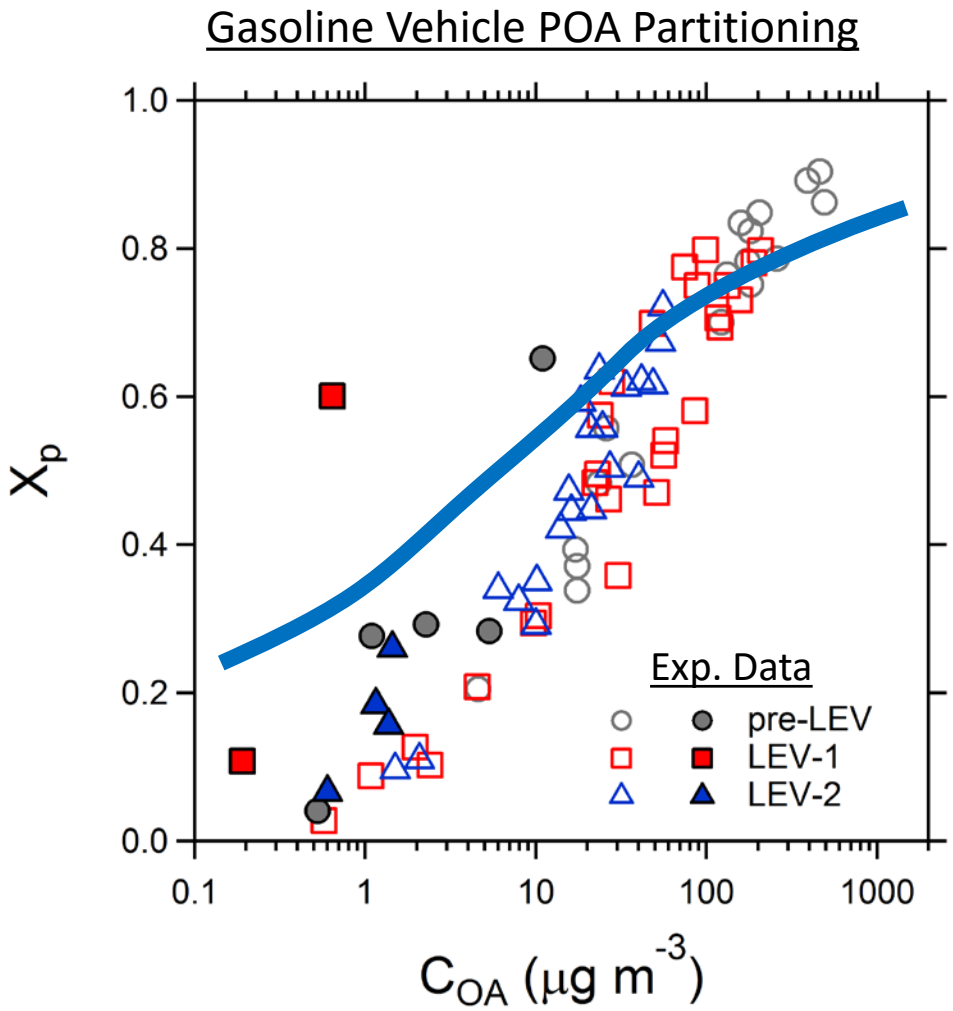
Decreasing volatility

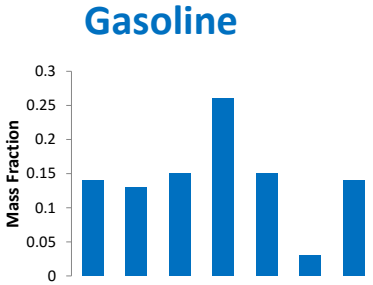


Presto et al. AST 2012

Decreasing volatility

Predictions "match" observations

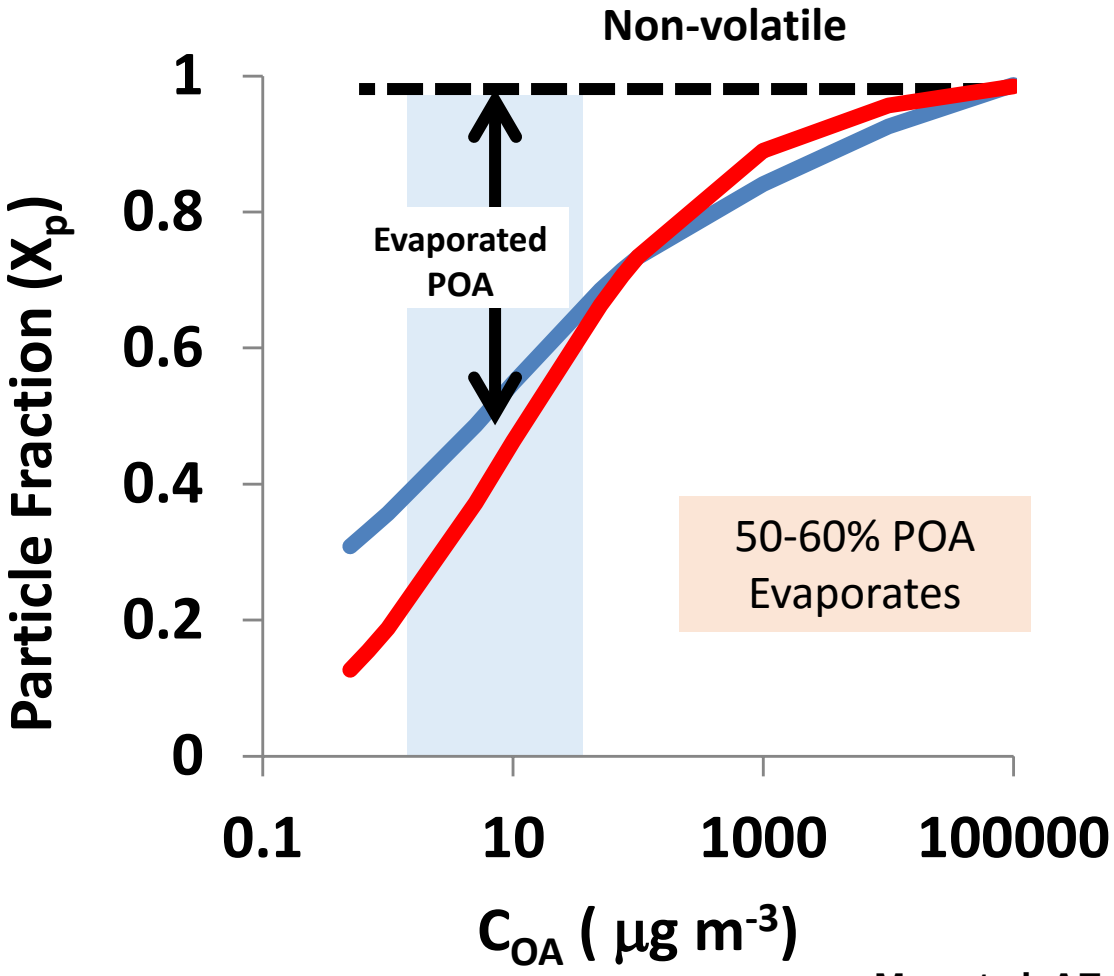


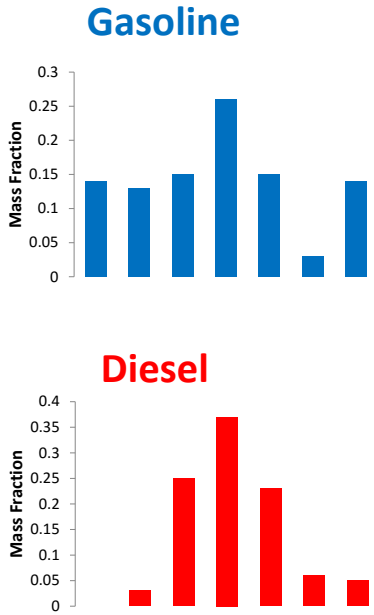


$$X_p = \sum_{i=1}^{n} f_i \left(1 + \frac{C_i^*}{C_{OA}}\right)^{-1}$$

May et al. AE 2013

Predicted POA Evaporation





May et al. AE 2013; May et al. EST 2013

POA Partitioning Conclusions

- **Majority of POA emissions from gasoline, diesel and biomass sources is semivolatile**
- **POA emission inventories biased on traditional source testing biased high (by roughly 50%)**
- **Gas-particle partitioning of POA emissions can be represented using one volatility distribution per source class**
- **Chemical transport model continue to assume POA is non-volatile biasing predictions**

Gas-particle partitioning of primary organic aerosol

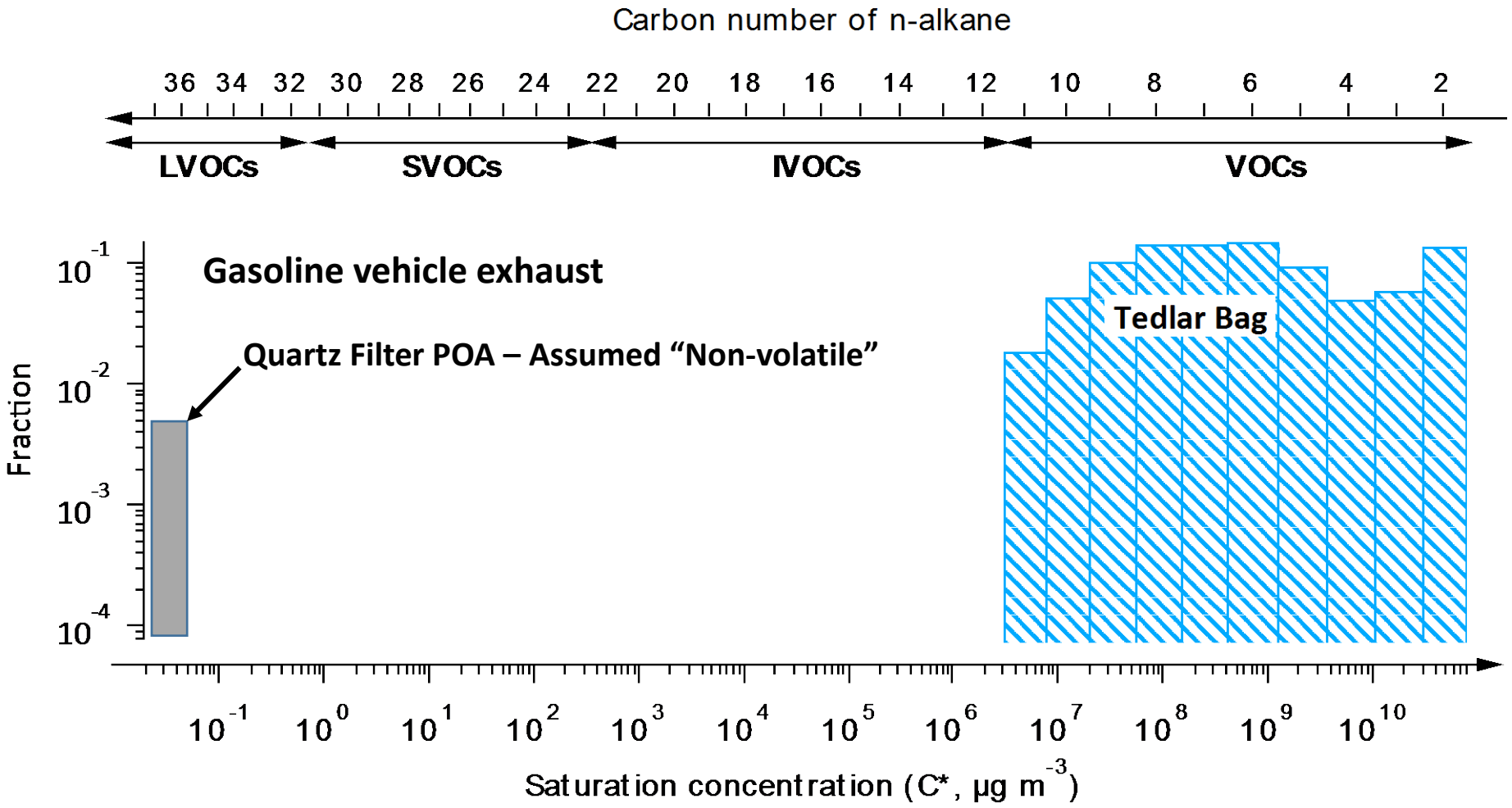
"Gas-particle partitioning of primary organic aerosol emissions: (2) diesel vehicles" (A. A. May et al.) Environmental Science & Technology, 47 (15), 8288–8296, 2013.

"Gas-particle partitioning of primary organic aerosol emissions: (1) gasoline vehicle exhaust" (A. A. May et al.) Atmospheric Environment, 77, 128-139, 2013.

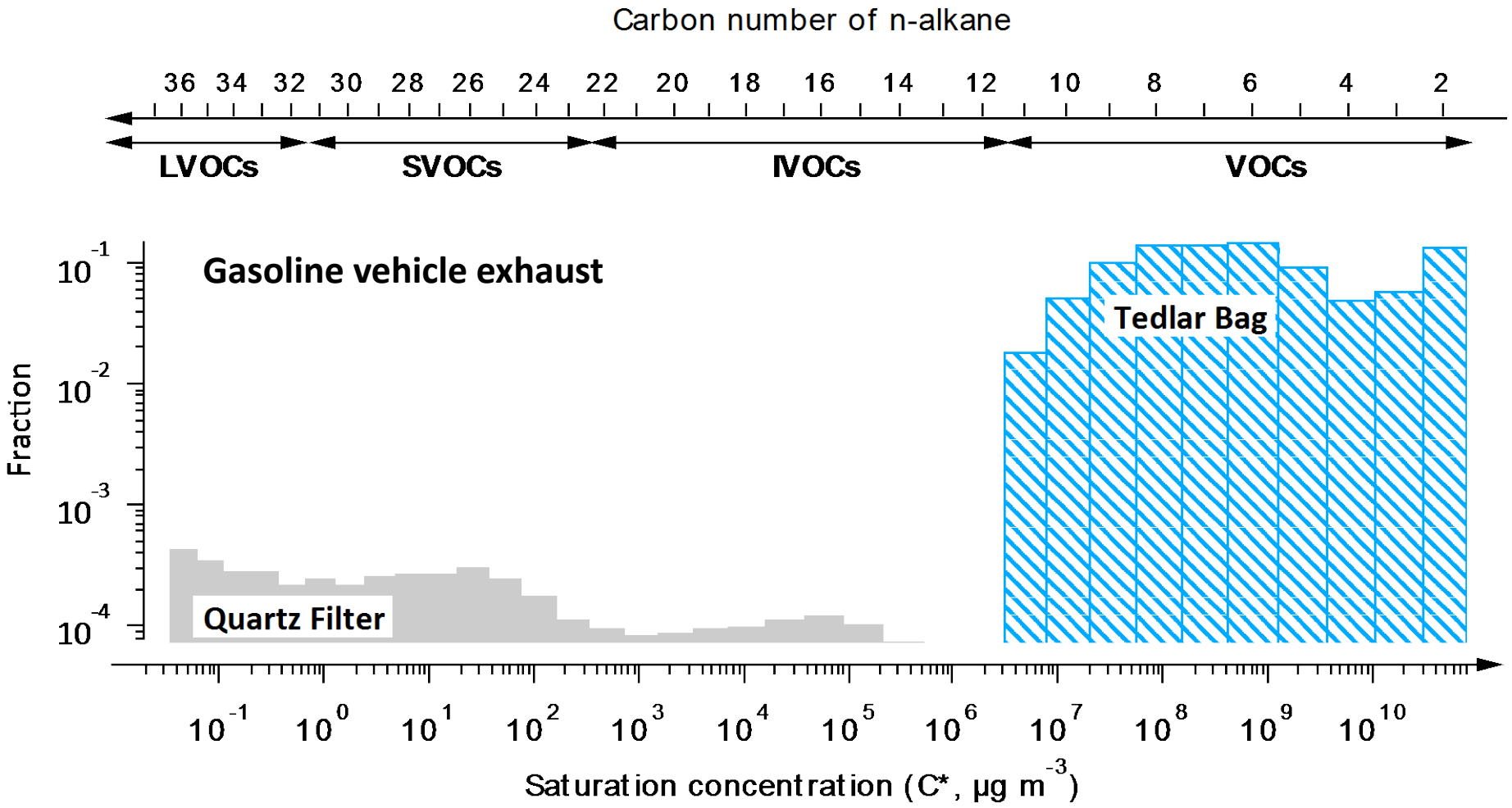
"Gas-particle partitioning of primary organic aerosol emissions 3. Biomass burning" (A.A. May et al.) Journal of Geophysical Research, 118(19), 2013JD020286, 2013.

How important are intermediate volatility organic compound (IVOCs) emissions?

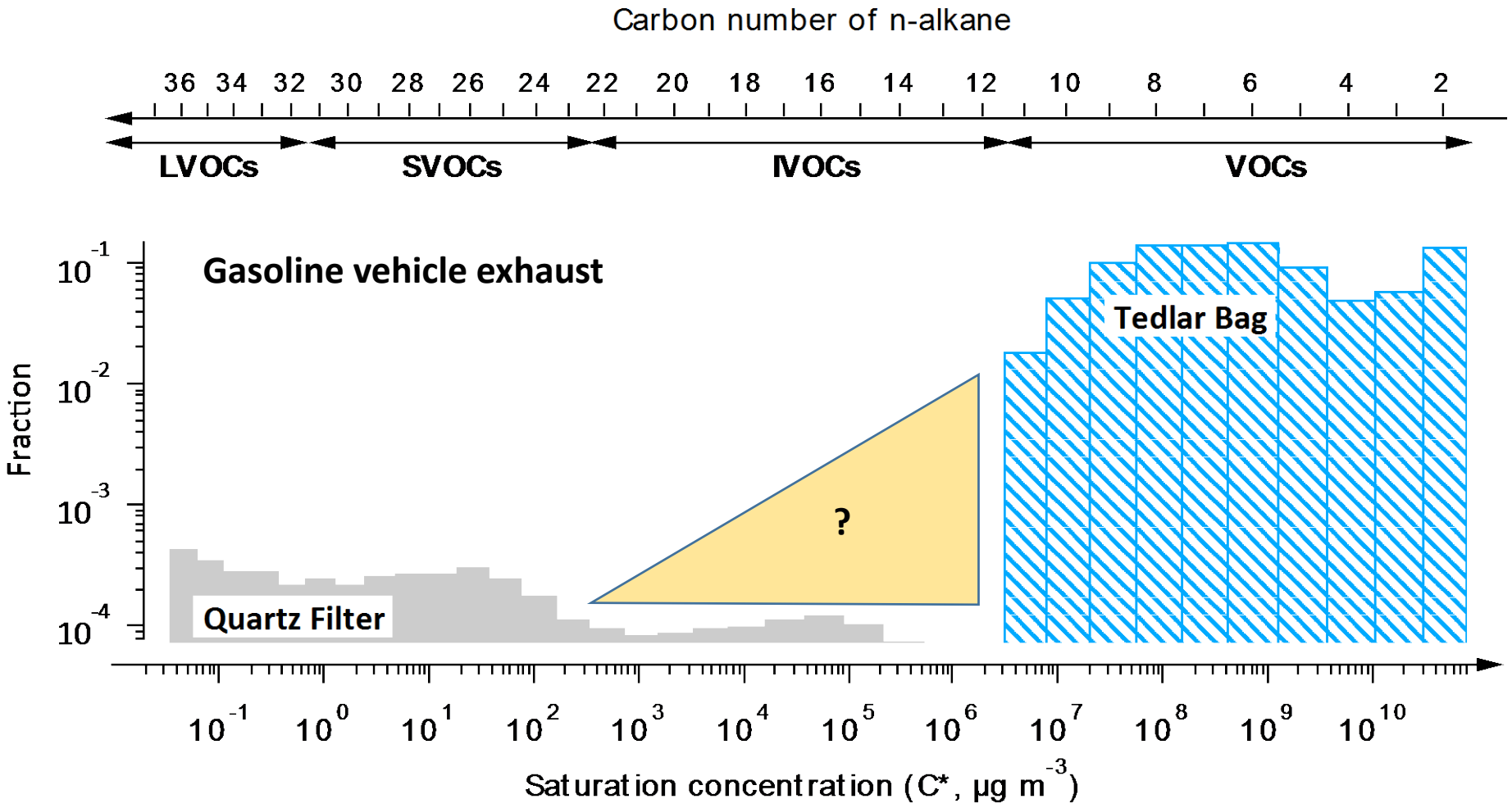
Traditional Emissions Testing



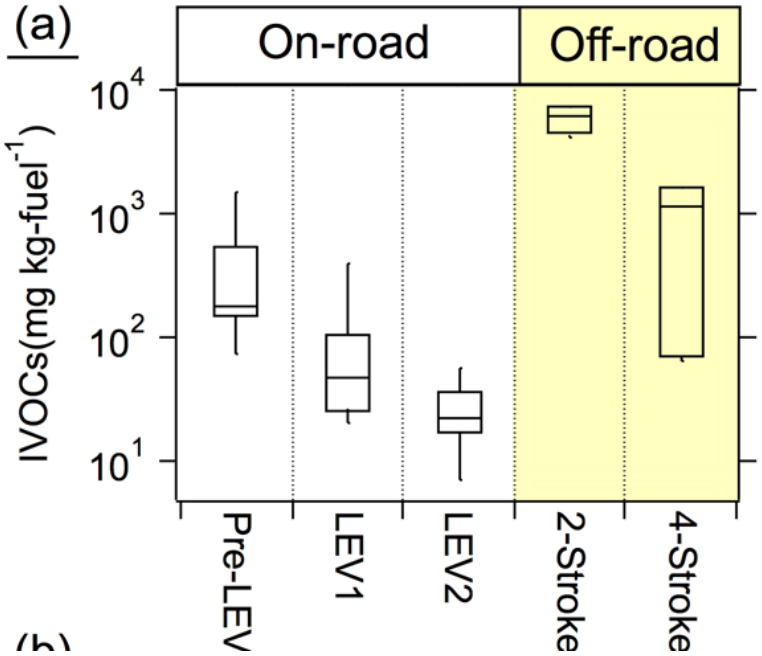
Distributing quartz filter organics in volatility space



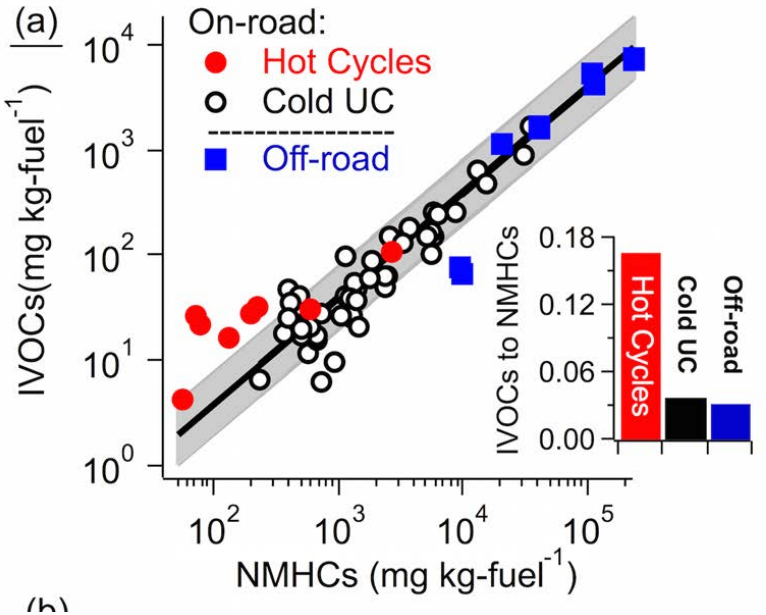
What about IVOCs?



IVOCs contribution to gasoline vehicle exhaust

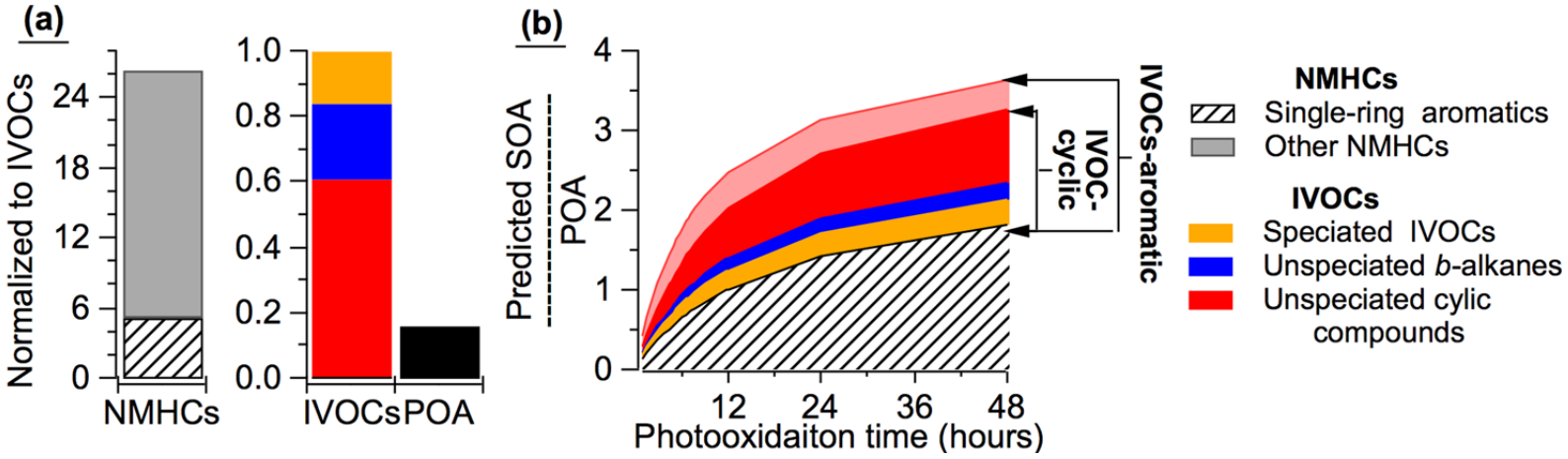


~ 4% NMHC



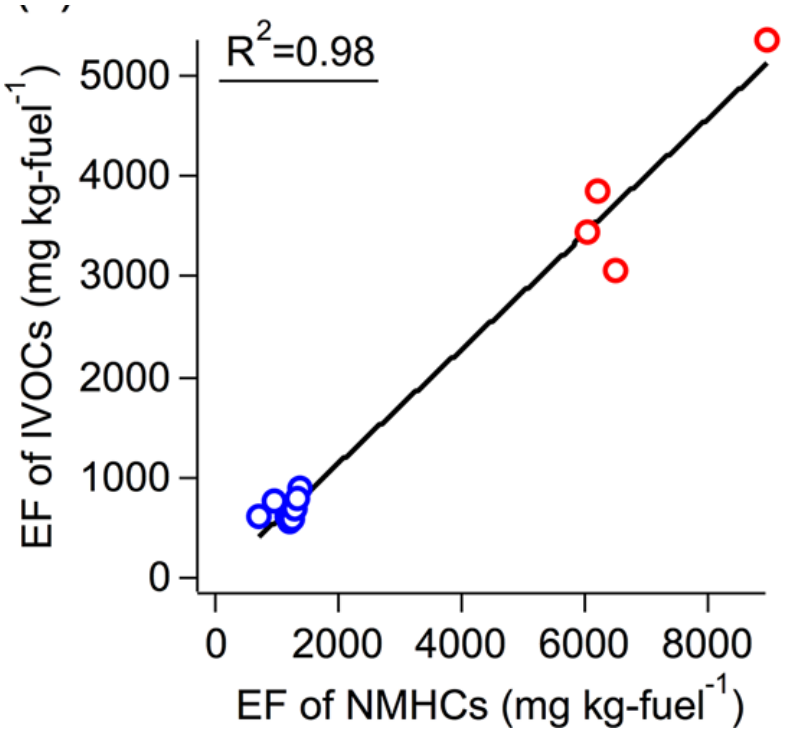
Zhao et al. EST 2016

IVOCs contribute 30-60% of predicted SOA from gasoline exhaust



Zhao et al. EST 2016

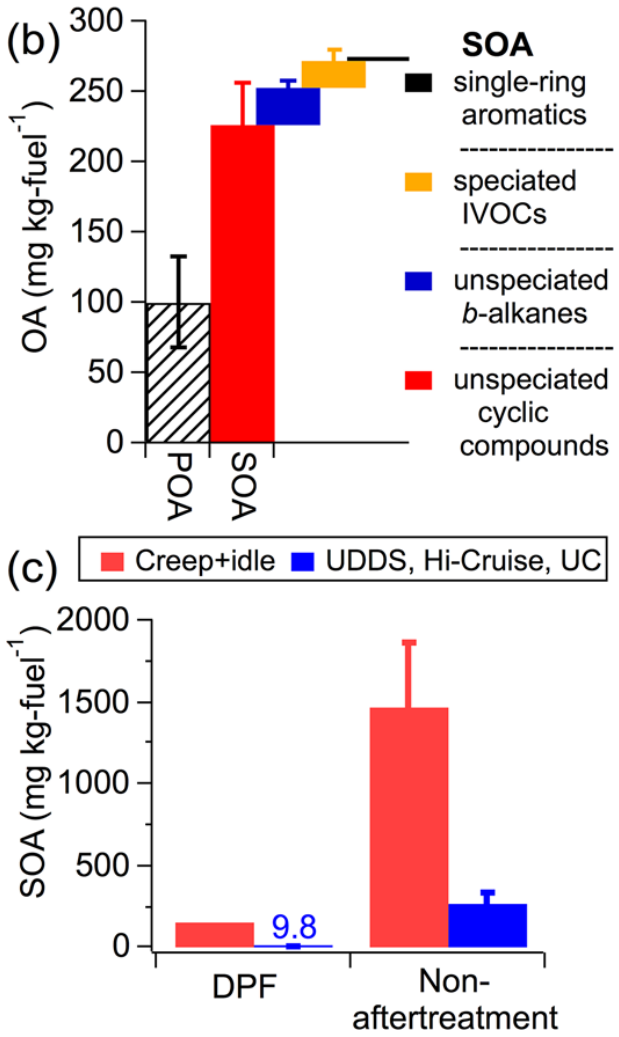
Diesel IVOC emissions scale with NMHC



~ 60% NMHC

Zhao et al. EST 2015

SOA formation from diesel exhaust

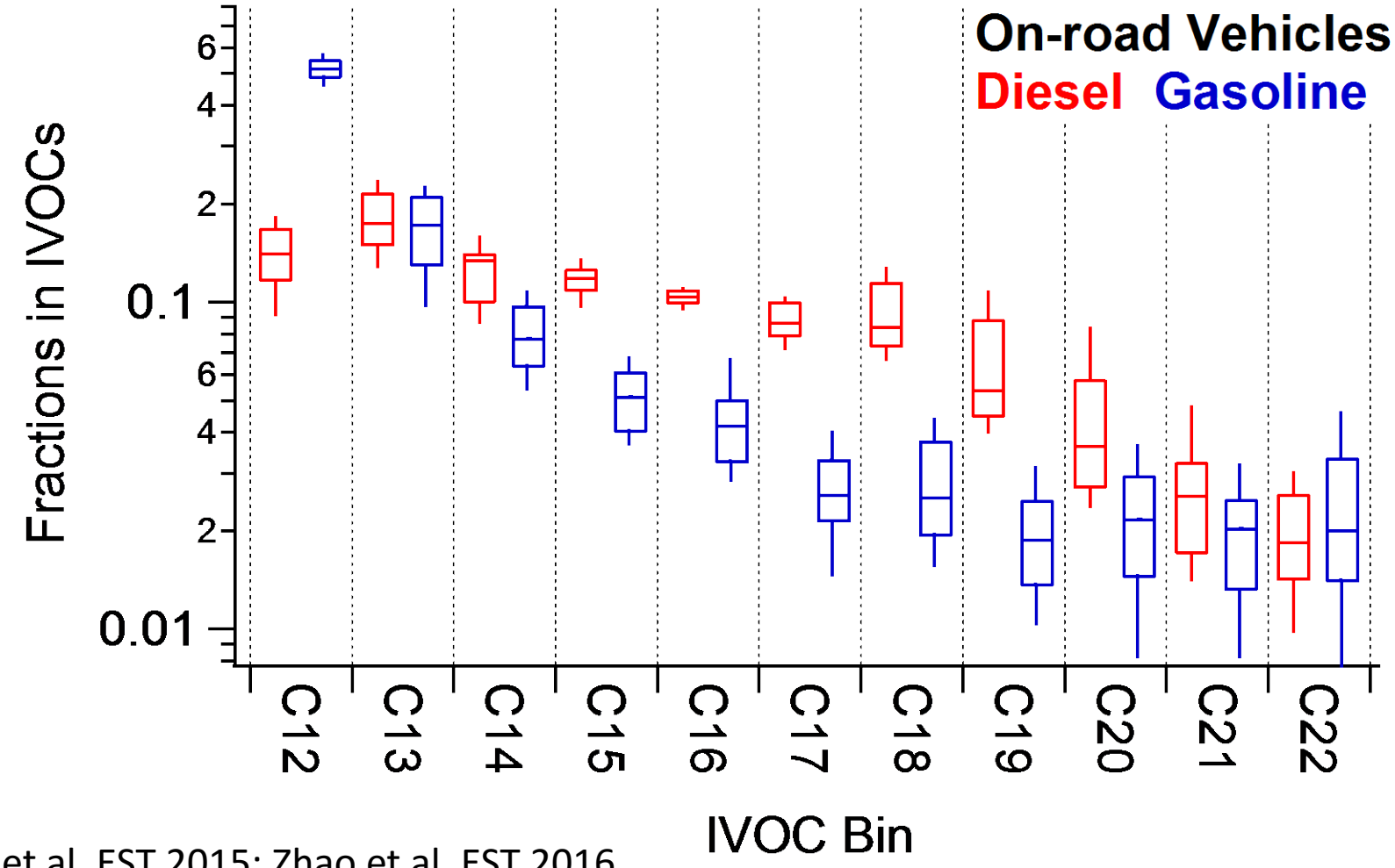


80%+ of SOA from IVOCs

DPF dramatically reduces IVOC emissions and SOA formation

Zhao et al. EST 2015

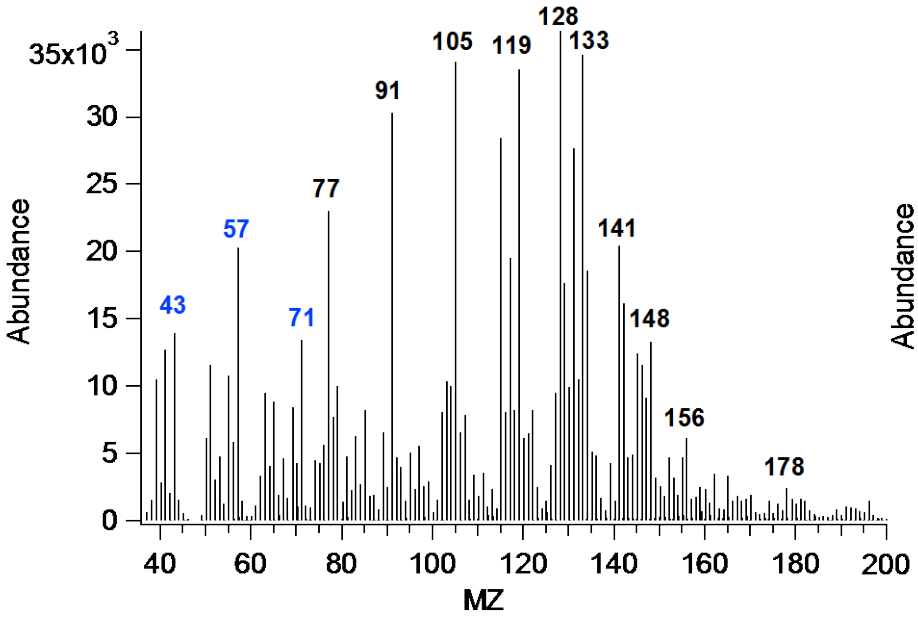
Gas vs. Diesel IVOC Volatility Distribution



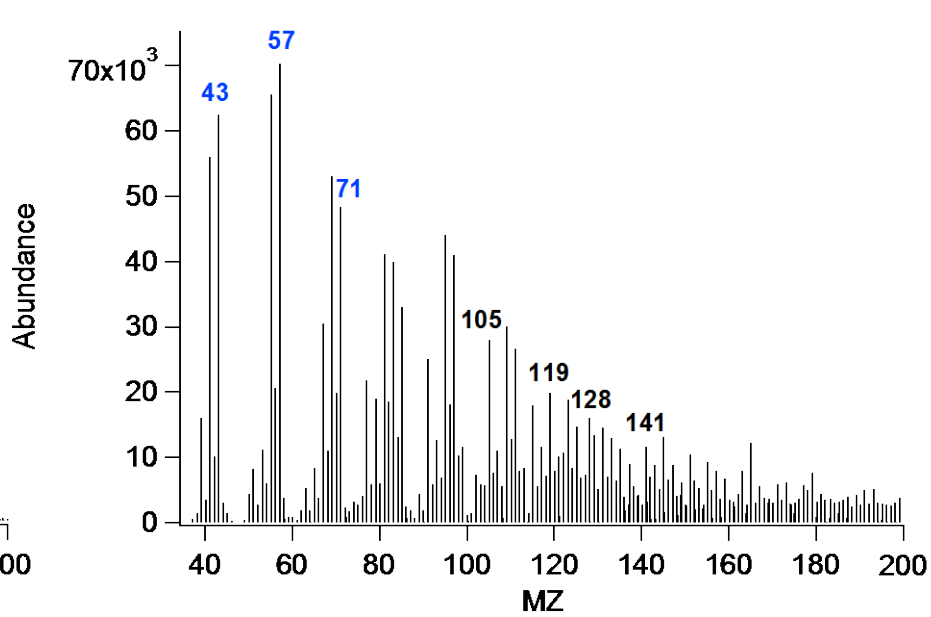
Zhao et al. EST 2015; Zhao et al. EST 2016

Gasoline vs. diesel IVOCs: aromatics vs. aliphatics

On-road Gasoline vehicles



On-road Diesel Vehicles



MZ	*Compounds*	*MZ*	*Compounds*
43, 57, 71	n- & b-alkanes	**147,148,119,105**	C5-Benzaldehyde
119, 134	C4-Benzene	**128**	Naphthalene
134, 148	C5-Benzene	**142**	C1-Naphthalene
133, 134, 105	C2-Benzaldehyde	**141, 156**	C2-Naphthalene

Zhao et al. EST 2015; Zhao et al. EST 2016

IVOC Emissions Conclusions

- **IVOCs are an important class of SOA precursors in vehicle exhaust**
- **IVOC scale with NMHC emissions**
- **Most chemical transport models/inventories do not account for IVOC emissions which contributes to under prediction of SOA in urban areas.**

IVOC emissions papers

"Intermediate-Volatility Organic Compounds: A Large Source of Secondary Organic Aerosol" (Y. Zhao, C.J. Hennigan, A.A. May, D.S. Tkacik, J.A. de Gouw, J. B. Gilman, W.C. Kuster, A. Borbon, A.L. Robinson) *Environmental Science & Technology*, 48(23), 13743–13750, 2014.

"Intermediate Volatility Organic Compound Emissions from On-Road Gasoline Vehicles and Small Off-Road Gasoline Engines" (Zhao, Y.; Nguyen, N. T.; Presto, A. A.; Hennigan, C. J.; May, A. A.; Robinson, A. L.) *Environmental Science & Technology* 50(8), 4554-4563, 2016.

"Intermediate Volatility Organic Compound Emissions from On-Road Diesel Vehicles: Chemical Composition, Emission Factors, and Estimated Secondary Organic Aerosol Production" (Zhao, Y.; Nguyen, N. T.; Presto, A. A.; Hennigan, C. J.; May, A. A.; Robinson, A. L.) *Environmental Science & Technology*, 49(19) 11516-11526, 2015.

Papers published by EPA STAR RD834554

1. "Chemical Transport Model Simulations of Organic Aerosol in Southern California: Model Evaluation and Gasoline and Diesel Source Contributions" (Jathar, S.H.; Woody, M.; Pye, H.O.T.; Baker, K.R.; Robinson A.L.) *Atmospheric Chemistry & Physics*, 17, 4305-4318, doi:10.5194/acp-17-4305-2017, 2017.
2. "Intermediate Volatility Organic Compound Emissions from On-Road Gasoline Vehicles and Small Off-Road Gasoline Engines" (Zhao, Y.; Nguyen, N. T.; Presto, A. A.; Hennigan, C. J.; May, A. A.; Robinson, A. L.) *Environmental Science & Technology* 50(8), 4554-4563, 2016.
3. "Intermediate Volatility Organic Compound Emissions from On-Road Diesel Vehicles: Chemical Composition, Emission Factors, and Estimated Secondary Organic Aerosol Production" (Zhao, Y.; Nguyen, N. T.; Presto, A. A.; Hennigan, C. J.; May, A. A.; Robinson, A. L.) *Environmental Science & Technology*, 49(19) 11516-11526, 2015.
4. "Intermediate-Volatility Organic Compounds: A Large Source of Secondary Organic Aerosol" (Y. Zhao, C.J. Hennigan, A.A. May, D.S. Tkacik, J.A. de Gouw, J. B. Gilman, W.C. Kuster, A. Borbon, A.L. Robinson) *Environmental Science & Technology*, 48(23), 13743–13750, 2014.
5. "Secondary organic aerosol formation from in-use motor vehicle emissions using a Potential Aerosol Mass reactor" (D. S. Tkacik, A. T. Lambe, S. H. Jathar, X. Li, A. A. Presto, Y. Zhao, D. Blake, S. Meinardi, J. J. Jayne, P. L. Croteau, and A. L. Robinson) *Environmental Science & Technology*, 48(19), 11235–11242, 2014.
6. "Primary to secondary organic aerosol: evolution of organic emissions from mobile combustion sources" (A. A. Presto, T. D. Gordon, and A. L. Robinson) *Atmospheric Chemistry and Physics*, 14, 5015-5036, 2014.
7. "Unspeciated organic emissions from combustion sources and their influence on the secondary organic aerosol budget in the United States" (S. H. Jathar, T. D. Gordon, C. J. Hennigan, H. O. T. Pye, G. Pouliot, P. J. Adams, N. M. Donahue, A. L. Robinson) *Proceedings of the National Academy of Sciences*, 111(29), 10473-10478, 2014.
8. "Primary Gas- and Particle-Phase Emissions and Secondary Organic Aerosol Production from Gasoline and Diesel Off-Road Engines" (T.D. Gordon, D.S. Tkacik, A.A. Presto, M. Zhang, S.H. Jathar, N.T. Nguyen, J. Massetti, T. Truong, P. Cicero-Fernandez, C. Maddox, P. Rieger, S. Chattopadhyay, H. Maldonado, M.M. Maricq, A.L. Robinson), *Environmental Science & Technology*, 47(24), 14137–14146, 2013.
9. "Secondary Organic Aerosol Production from Diesel Vehicle Exhaust: Impact of Aftertreatment, Fuel Chemistry and Driving Cycle" (T.D. Gordon, A.A. Presto, N.T. Nguyen, W.H. Robertson, K. Na, K. N. Sahay, M. Zhang, C. Maddox, P. Rieger, S. Chattopadhyay, H. Maldonado, M.M. Maricq, A. L. Robinson), *Atmospheric Chemistry and Physics*, 14, 4643-4659, 2014.

Papers published by EPA STAR RD834554 (cont.)

9. "Secondary Organic Aerosol Formation Exceeds Primary Particulate Matter Emissions for Light-Duty Gasoline Vehicles" (T.D. Gordon, N.T. Nguyen, A.A. Presto, N.M. Donahue, A. Gutierrez, M. Zhang, C. Maddox, P. Rieger, S. Chattopadhyay, H. Maldonado, M. M. Maricq, A. L. Robinson), *Atmospheric Chemistry and Physics*, 14, 4661-4678, 2014.

10. "Gas- and particle-phase primary emissions from in-use, on-road gasoline and diesel vehicles" (May, A. A.; Nguyen, N. T.; Presto, A. A.; Gordon, T. D.; Lipsky, E. M.; Karve, M.; Gutierrez, A.; Robertson, W. H.; Zhang, M.; Brandow, C.; Chang, O.; Chen, S.; Cicero-Fernandez, P.; Dinkins, L.; Fuentes, M.; Huang, S.-M.; Ling, R.; Long, J.; Maddox, C.; Massetti, J.; McCauley, E.; Miguel, A.; Na, K.; Ong, R.; Pang, Y.; Rieger, P.; Sax, T.; Truong, T.; Vo, T.; Chattopadhyay, S.; Maldonado, H.; Maricq, M. M.; Robinson, A. L.) *Atmospheric Environment*, 88, 247-260, 2014.

11. "Gas-particle partitioning of primary organic aerosol emissions 3. Biomass burning" (A.A. May, E.J.T. Levin, C.J. Hennigan, I. Riipinen, T. Lee, J.L. Collett, Jr., J.L. Jimenez, S.M. Kreidenweis, A.L. Robinson) *Journal of Geophysical Research*, 118(19), 2013JD020286, 2013.

12. "Gas-particle partitioning of primary organic aerosol emissions: (2) diesel vehicles" (A. A. May, A. A. Presto, C. J. Hennigan, N. T. Nguyen, T. D. Gordon, A. L. Robinson) *Environmental Science & Technology*, 47 (15), 8288–8296, 2013.

13. "Gas-particle partitioning of primary organic aerosol emissions: (1) gasoline vehicle exhaust" (A. A. May, A. A. Presto, C. J. Hennigan, N. T. Nguyen, T. D. Gordon, A. L. Robinson) Atmospheric Environment, 77, 128-139, 2013.

14. "Time scales for gas-particle partitioning equilibration of secondary organic aerosol formed from alpha-pinene ozonolysis" (R. Saleh, N. M. Donahue, A. L. Robinson) Environmental Science & Technology, 47(11), 5588–5594, 2013.

15. "Analyses of turbulent flow fields and aerosol dynamics of diesel engine exhaust inside two dilution sampling tunnels using the CTAG model" (Y. Wang, B. Yang, E. M. Lipsky, A. L. Robinson, M. Zhang) Environmental Science & Technology, 47(2), 889–898, 2013.

16. "Volatility of organic molecular markers used for source apportionment analysis: measurements and implications for atmospheric lifetime," (A. A. May, R. Saleh, C. J. Hennigan, N. M. Donahue, and A. L. Robinson) Environmental Science & Technology, 46(22), 12435–12444, 2012.

17. "Determination of volatility distributions of primary organic aerosol emissions from internal combustion engines using thermal desorption gas chromatography mass spectrometry," (A. A. Presto, C. J. Hennigan, N. T. Nguyen, and A. L. Robinson) Aerosol Science & Technology, 46(10), 1129-1139, 2012.

18. "A volatility basis set model for summertime secondary organic aerosols over the eastern U.S. in 2006," (R. Ahmadov, S.A. McKeen, A.L. Robinson, R. Bahreini, A. Middlebrook, J. de Gouw, J. Meagher, E.-Y. Hsie, E. Edgerton, S. Shaw, M. Trainer) Journal of Geophysical Research-Atmospheres, 117, D06301, doi:10.1029/2011JD016831, 2012.