The influences of National Forests and Wind Circulations on Volatile Organic Compounds (VOCs) in the Lewiston-Clarkston Valley of the U.S.

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NW AIRQUEST Meeting, October 26, 2023

Introduction

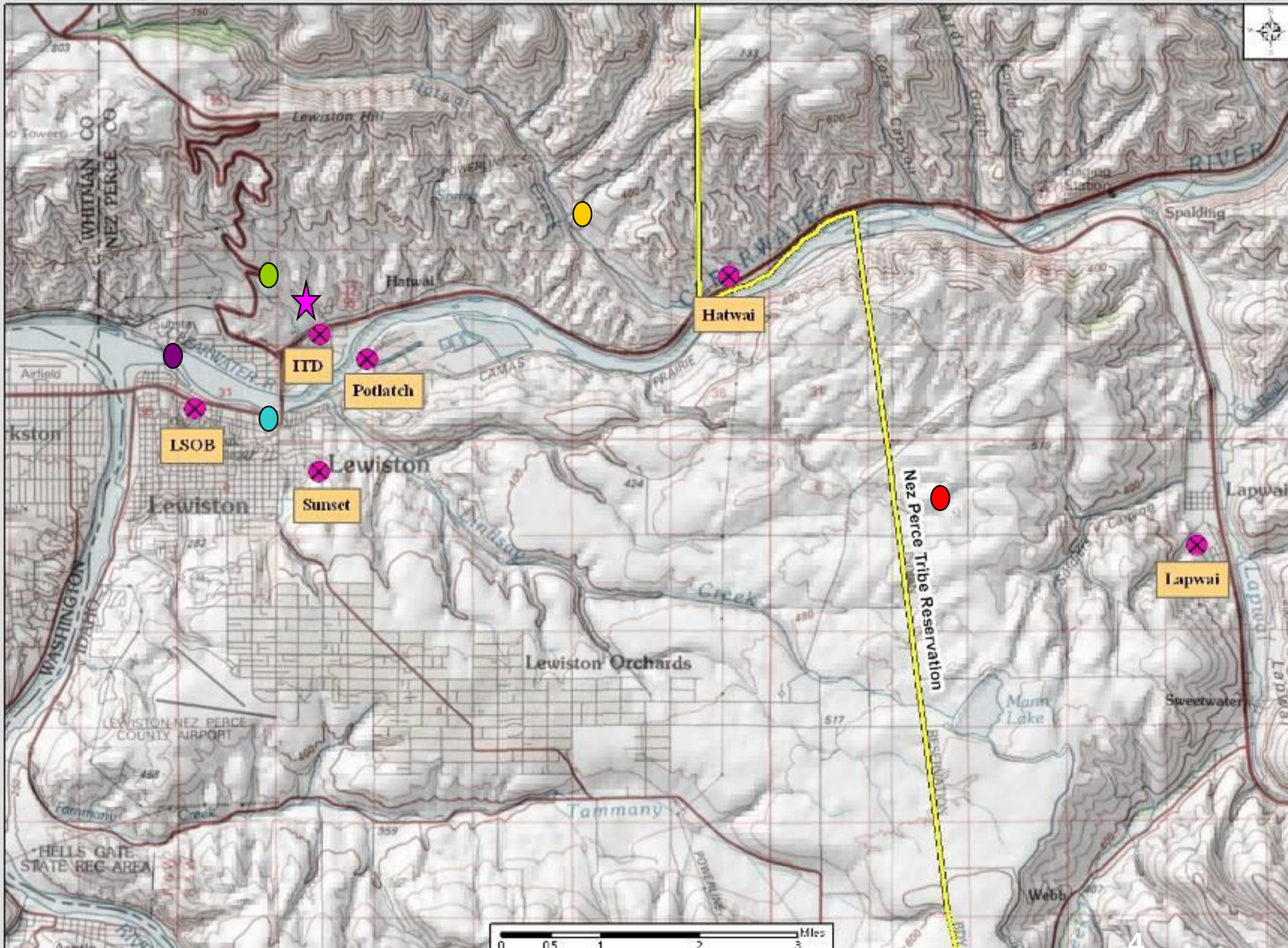
- Formaldehyde (HCHO), SO_2, H_2S, VOCs, ……
- Adverse health effects
- Important role in atmospheric chemistry
- Measurements and PMF modeling
- Important questions
- Brief Review

Brief Review

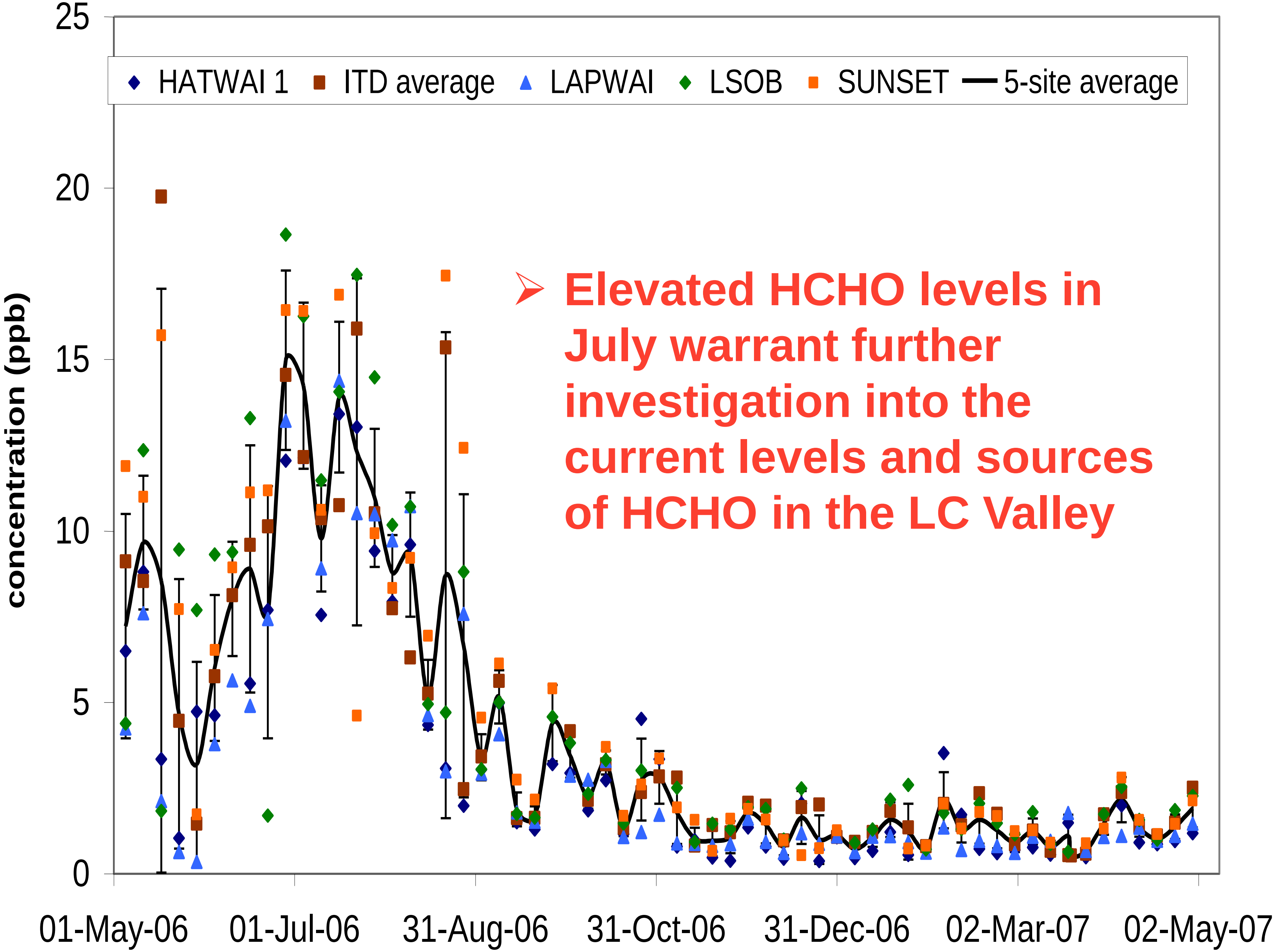
- **HCHO: One of the key pollutants responsible for overall cancer risk nationwide**

Concern: A previous study discovered elevated HCHO levels in the LC Valley

LOCATIONS OF PREVIOUS MONITORING SITES (2006-2007)



24-HR HCHO CONCENTRATIONS (2006-2007)



- **Elevated HCHO levels in July warrant further investigation into the current levels and sources of HCHO in the LC Valley**

RECENT MEASUREMENTS (4 WEEKS EACH SUMMER 2016-2017)

12-hr sampling: 7 AM to 7 PM & 7 PM to 7 AM

MACL at Sunset site (2016-2017)

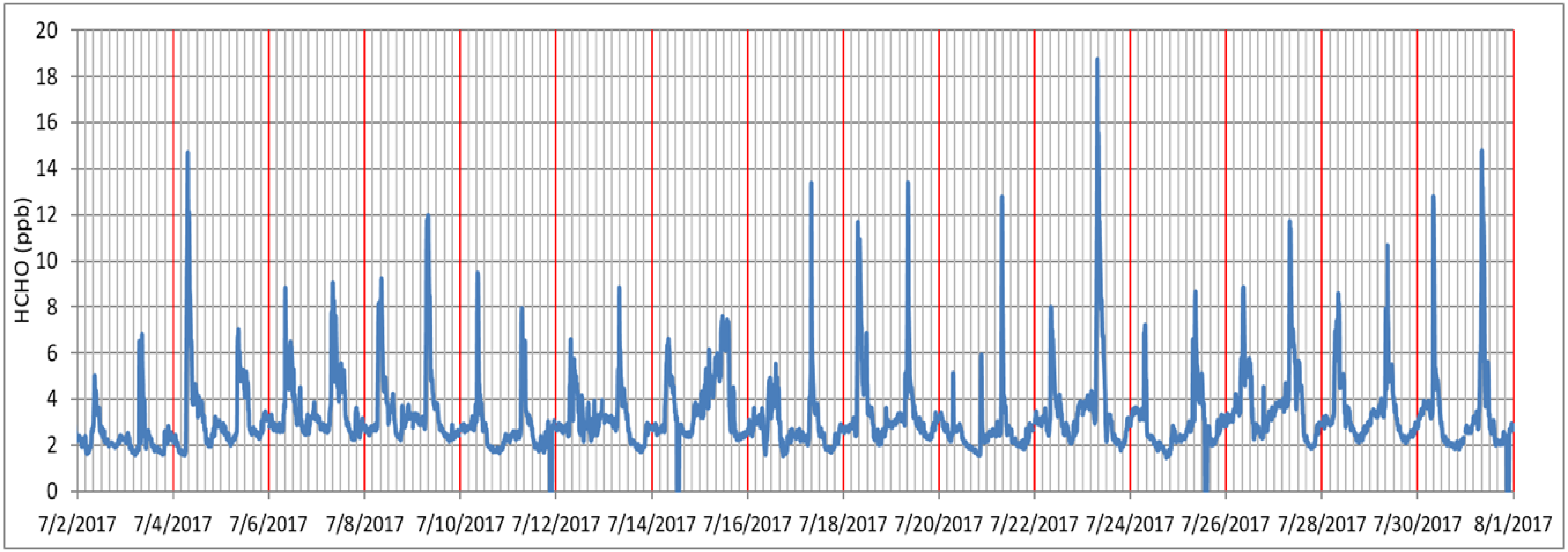
1-min measurements in addition to 12-hr sampling

Positive Matrix Factorization (PMF) Modeling Results

- Four major sources:
  - Emissions from a local paper mill
  - Biogenic sources
  - Secondary formation & background
  - Traffic sources

Important Questions

Which source is causing the early morning spikes?
How is it causing the early morning spikes?

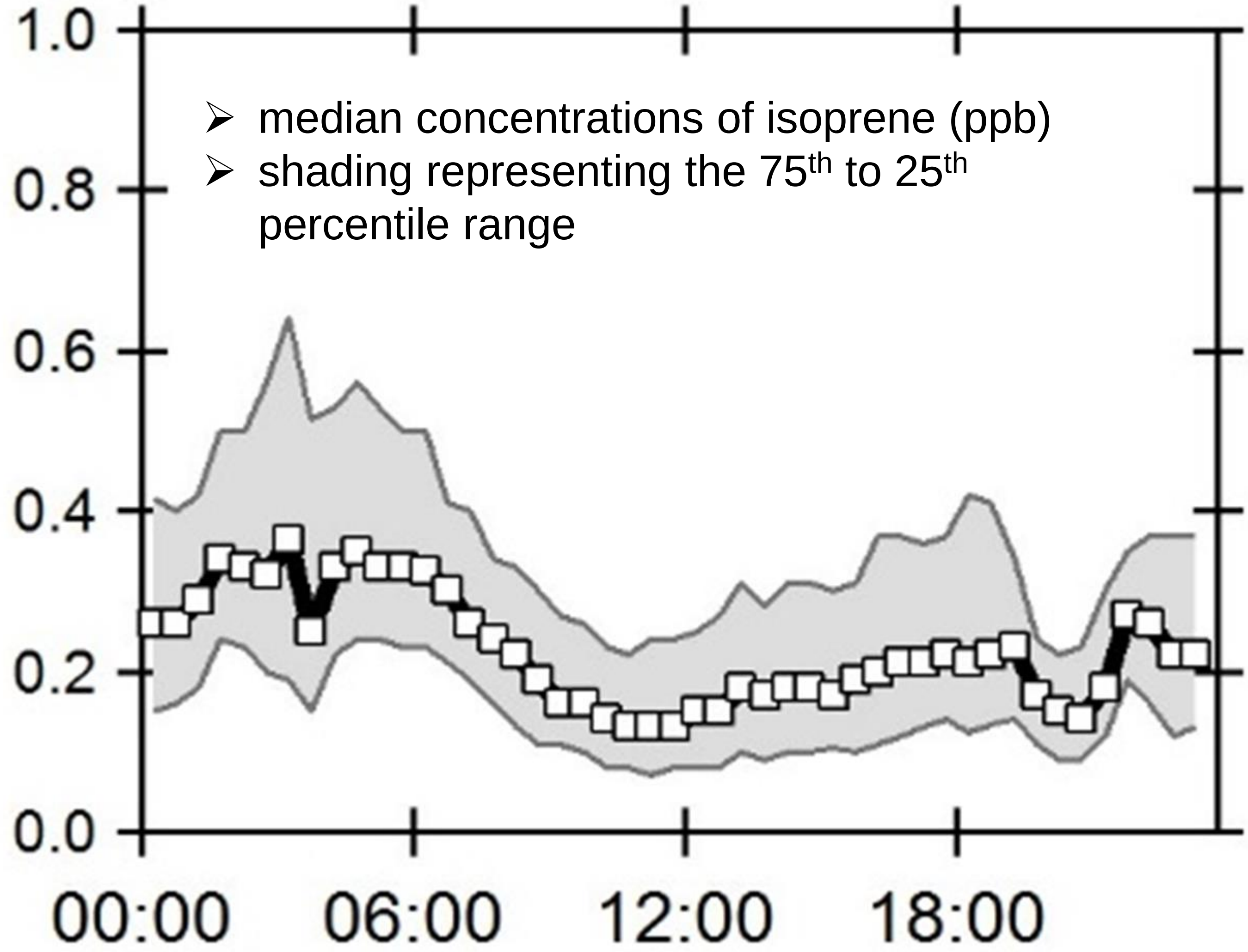


Average concentrations

Year	Species	Site	Average (ppbv)	Standard Deviation	Samples
2016	HCHO	**Sunset**	**2.02**	**0.93**	**86**
		Hatwai	**2.35**	**0.75**	**53**
		Asotin	**2.97**	**1**	**50**
	CH3CHO	Sunset	1	0.64	86
		Hatwai	0.99	0.5	53
		Asotin	1.2	0.77	50
2017	Species	Site	Average (ppbv)	Standard Deviation	Samples
	HCHO	**Sunset**	**4.81**	**0.85**	**56**
		Hatwai	**3.19**	**0.92**	**56**
		Asotin	**4.63**	**1.12**	**56**
	CH3CHO	Sunset	1.98	0.76	56
		Hatwai	1.79	0.52	56
		Asotin	2.02	0.70	56

< HCHO in July 2006:10-20 ppb; What caused the decrease?

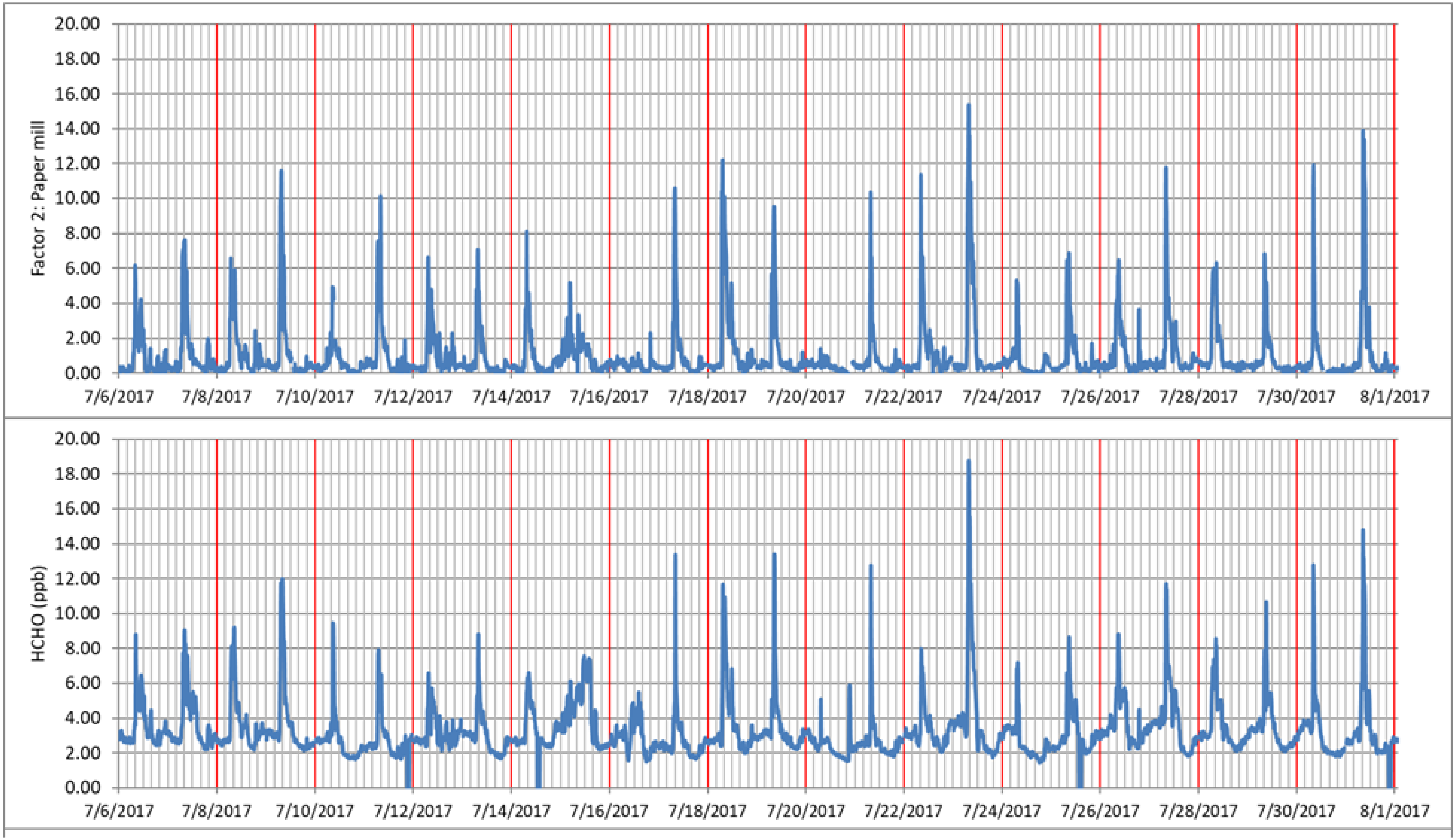
Concentration diurnal pattern is opposite to that of its emissions which are tied to photosynthesis



Summary of Important Questions

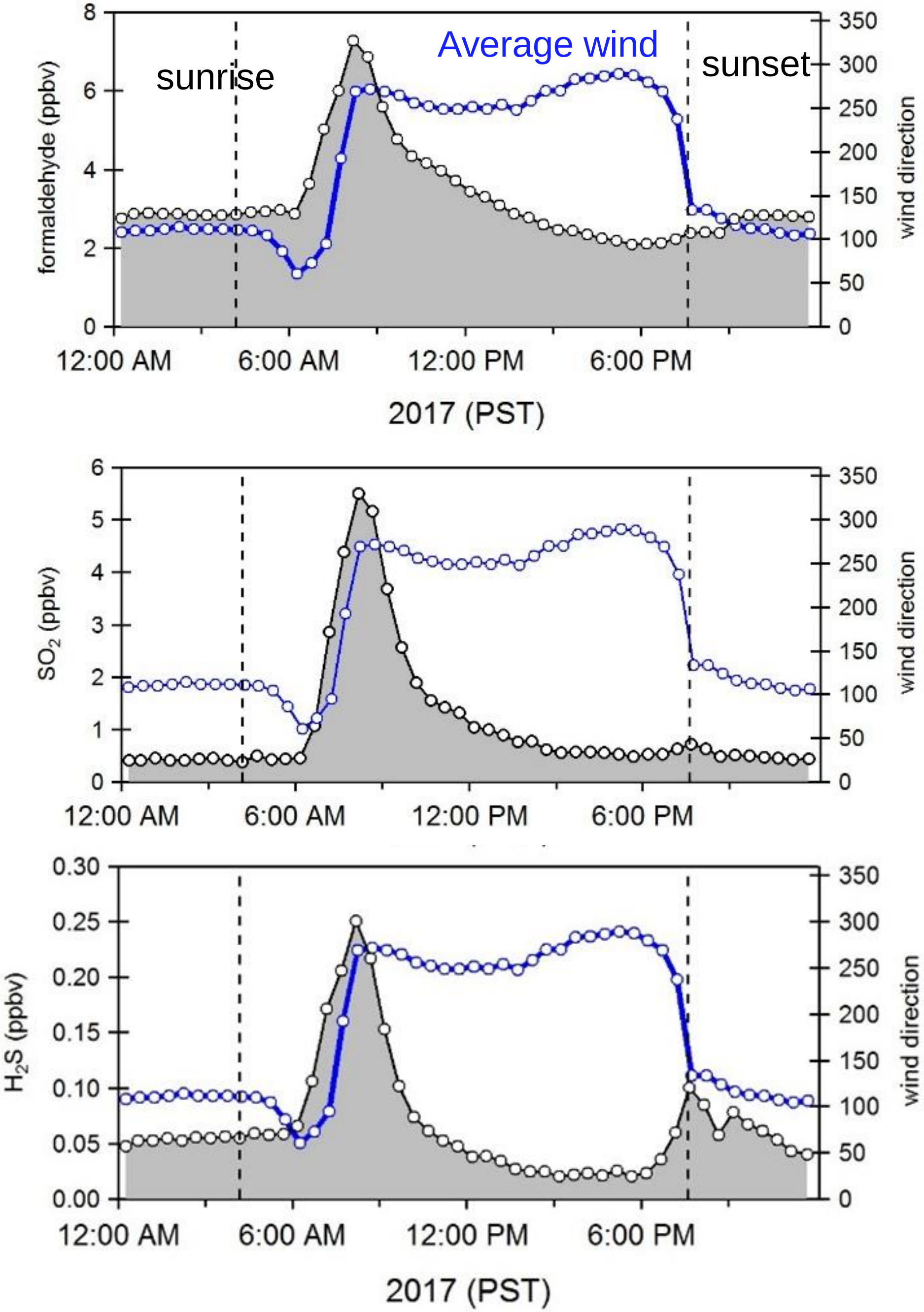
- **Which source is causing the high early morning HCHO spikes?**
- **How is the source causing the early morning HCHO spikes?**
- **What caused significant decadal (2006–2017) decrease in HCHO concentrations?**
- **Biogenic VOCs (e.g., isoprene, methanol, monoterpenes, and acetaldehyde) are higher during nighttime than daytime**
- **How come the diurnal pattern of isoprene concentrations is opposite to that of its emissions that peak in the middle of the day and falling to zero at night because isoprene emission is tied to photosynthesis and is dependent on light and temperature?**

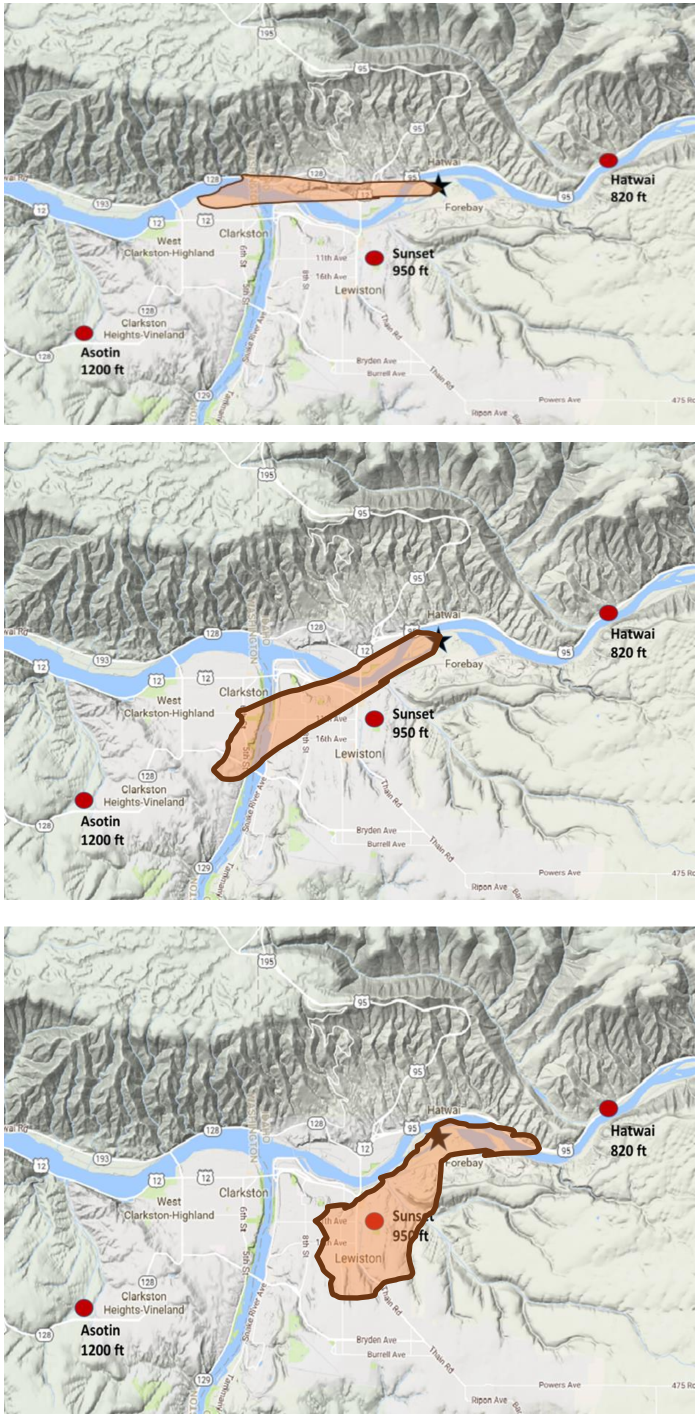
Which source is causing the high early morning HCHO spikes?



The early morning peaks in the observed HCHO concentrations are caused by the emissions of the paper mill

How HCHO spikes?

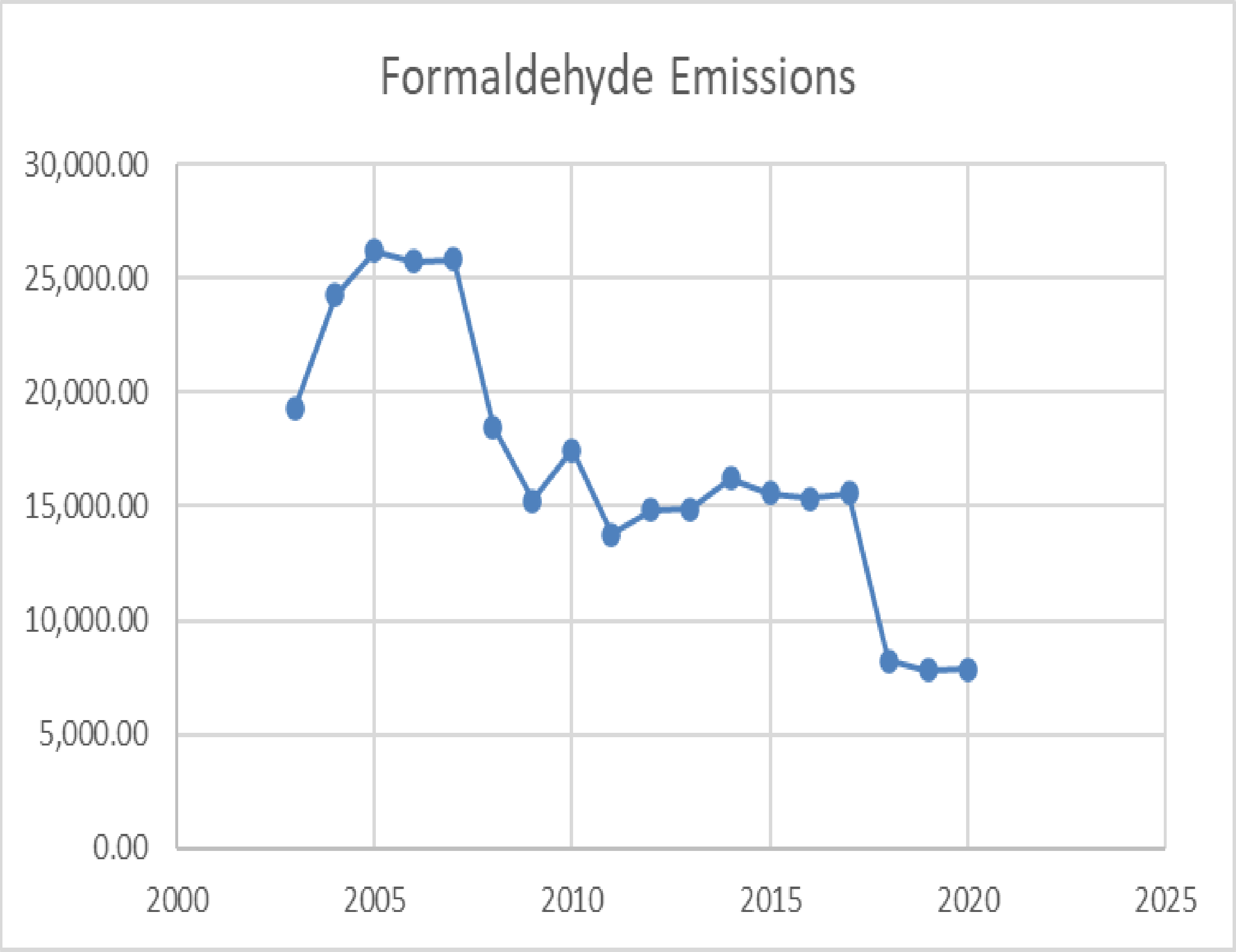




What caused significant decadal (2006–2017) decrease in HCHO concentrations?

- HCHO emissions from the EPA's Toxics Release Inventory (TRI)
- The TRI tracks the management of certain toxic chemicals that may pose a threat to human health and the environment, and U.S. facilities must report to the EPA's TRI annually the significant amount of each chemical that is released to the environment and/or managed through recycling, energy recovery and treatment
- The paper mill of Clearwater Paper Corporation is the only facility in the LC valley that reports HCHO emissions to the TRI
- A part of the Clearwater Paper Corporation became a separate entity in 2012, which was named Idaho Forest Group in Lewiston (IFG – Lewiston). The emissions of IFG – Lewiston were neither reported to the TRI nor included in the emissions from the Clearwater Paper Corporation after the 2012 separation

Clearwater Paper TRI Emissions (Pounds/Year) Over Time (Brown, 2022)

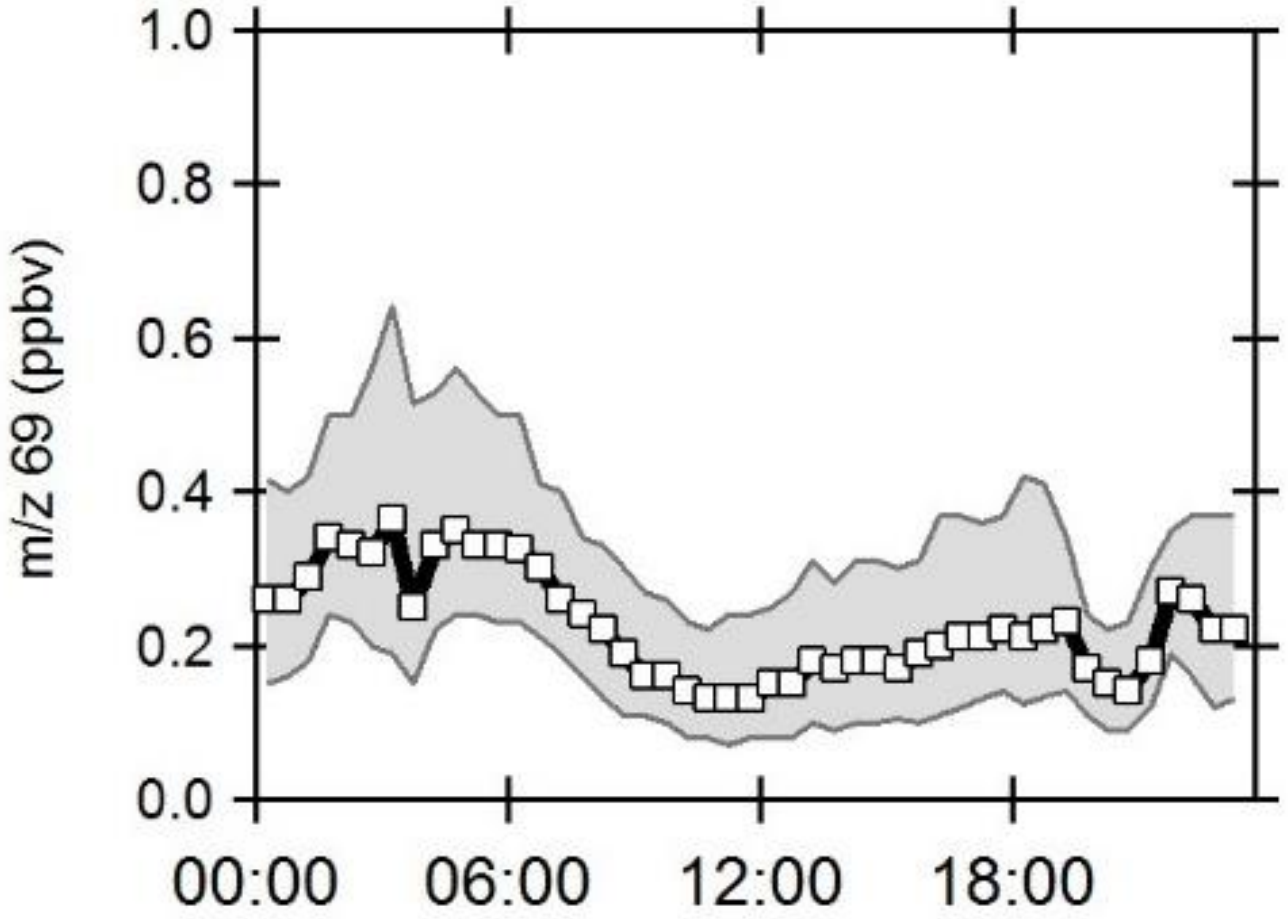


- Significant decrease in emissions from 2007 to 2009, which was before the separation in 2012
- The decrease in TRI emissions after 2017 could be attributed to the use of updated emission factors as well as a small process change from a batch digester to a continuous digester

What caused significant decadal (2006–2017) decrease in HCHO concentrations?

- The paper mill may have contributed to the HCHO decline by reducing emissions
- VOC emissions from mobile sources have significantly decreased due to increasingly stricter regulations and more effective technologies
- This may have led to a decrease in direct HCHO emissions from traffic sources as well as a reduction in photochemical production of HCHO by chemical reactions of VOCs emitted from mobile sources

The diurnal pattern of isoprene



Atmos. Chem. Phys., 9, 3027–3042, 2009
www.atmos-chem-phys.net/9/3027/2009/

Atmospheric Chemistry and Physics

Nocturnal isoprene oxidation over the Northeast United States in summer and its impact on reactive nitrogen partitioning and secondary organic aerosol

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[5]National Center for Atmospheric Research, 1850 Table Mesa Dr., Boulder, CO 80305, USA

Substantial amounts of isoprene were observed after dark

Isoprene peaked at night in places downwind of forests; the high nighttime isoprene concentrations are caused by emissions of isoprene in forest during daytime (late afternoon/early evening), followed by advective transport to the sites

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 103, NO. D17, PAGES 22,437–22,447, SEPTEMBER 20, 1998

Nighttime isoprene chemistry at an urban-impacted forest site

T. K. Starn,[1,2] P. B. Shepson,[1] S. B. Bertman,[3] D. D. Riemer,[4] R. G. Zika,[4] and K. Olszyna[5]

Environmental Science & Technology

Article

pubs.acs.org/est

Nighttime Chemistry and Morning Isoprene Can Drive Urban Ozone Downwind of a Major Deciduous Forest

Dylan B. Millet,[*,†] Munkhbayar Baasandorj,[†,‡] Lu Hu,[†,§] Dhruv Mitroo,[||] Jay Turner,[||] and Brent J. Williams[||]

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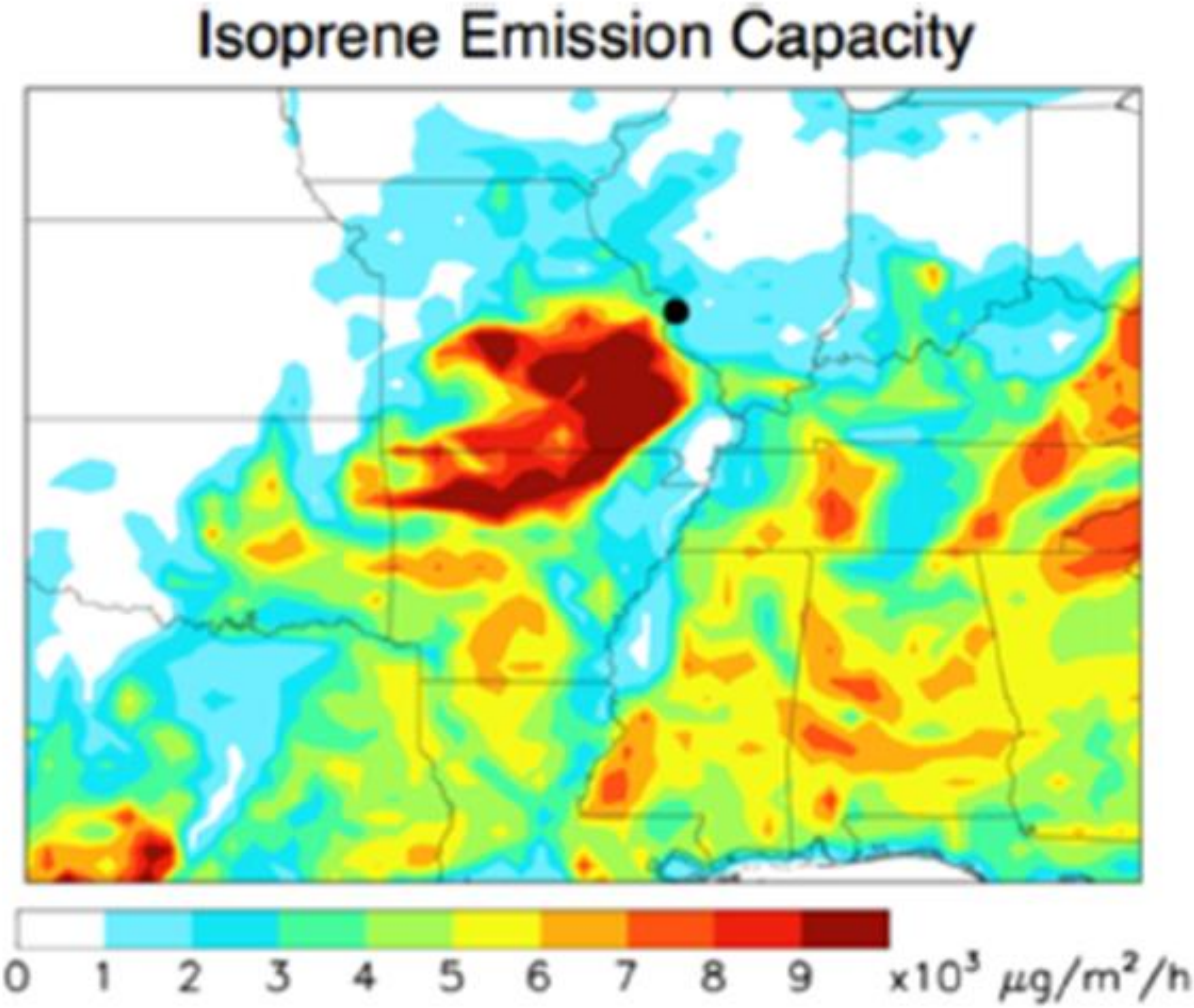
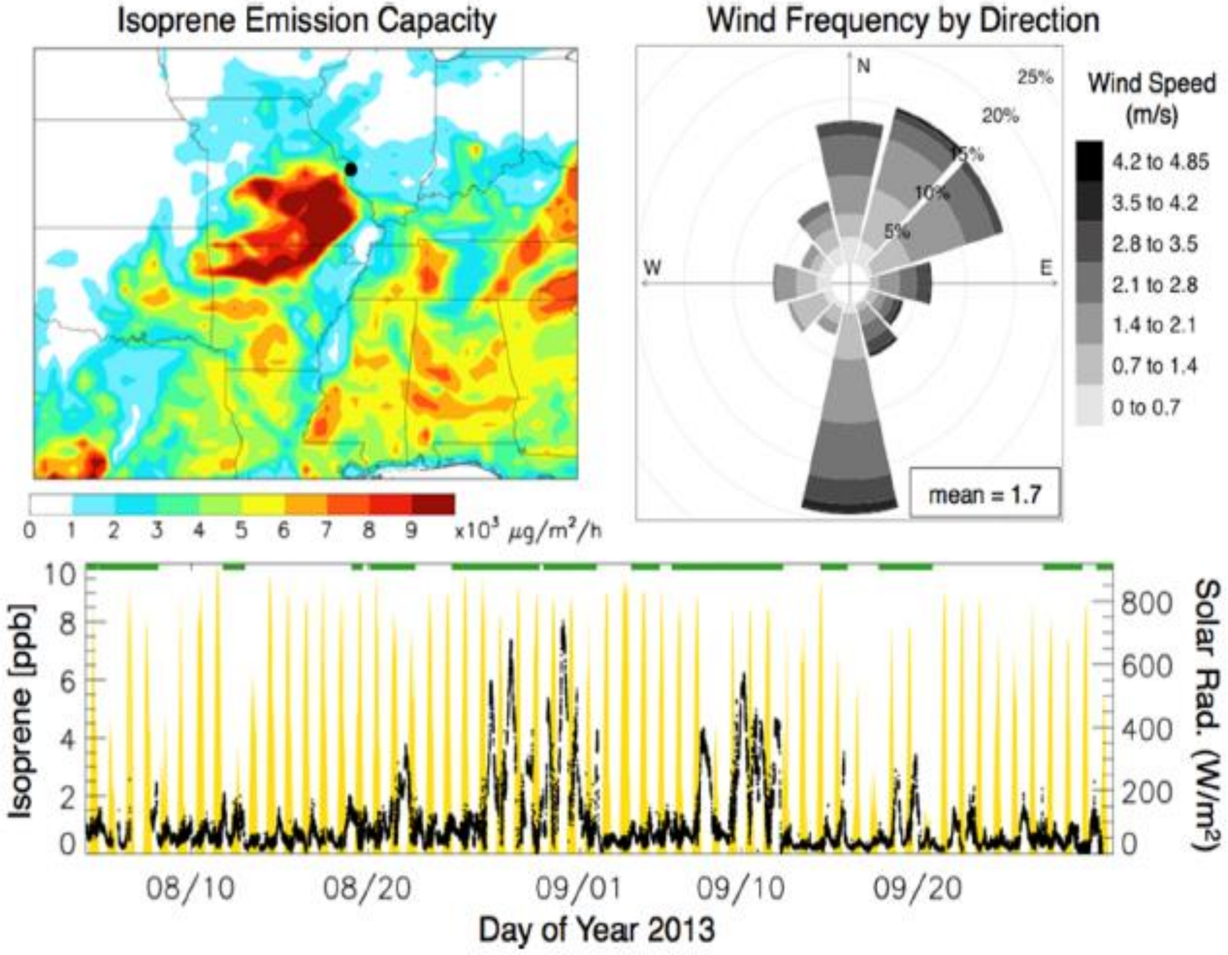
[||]Washington University in St. Louis, St. Louis, Missouri 63130, United States

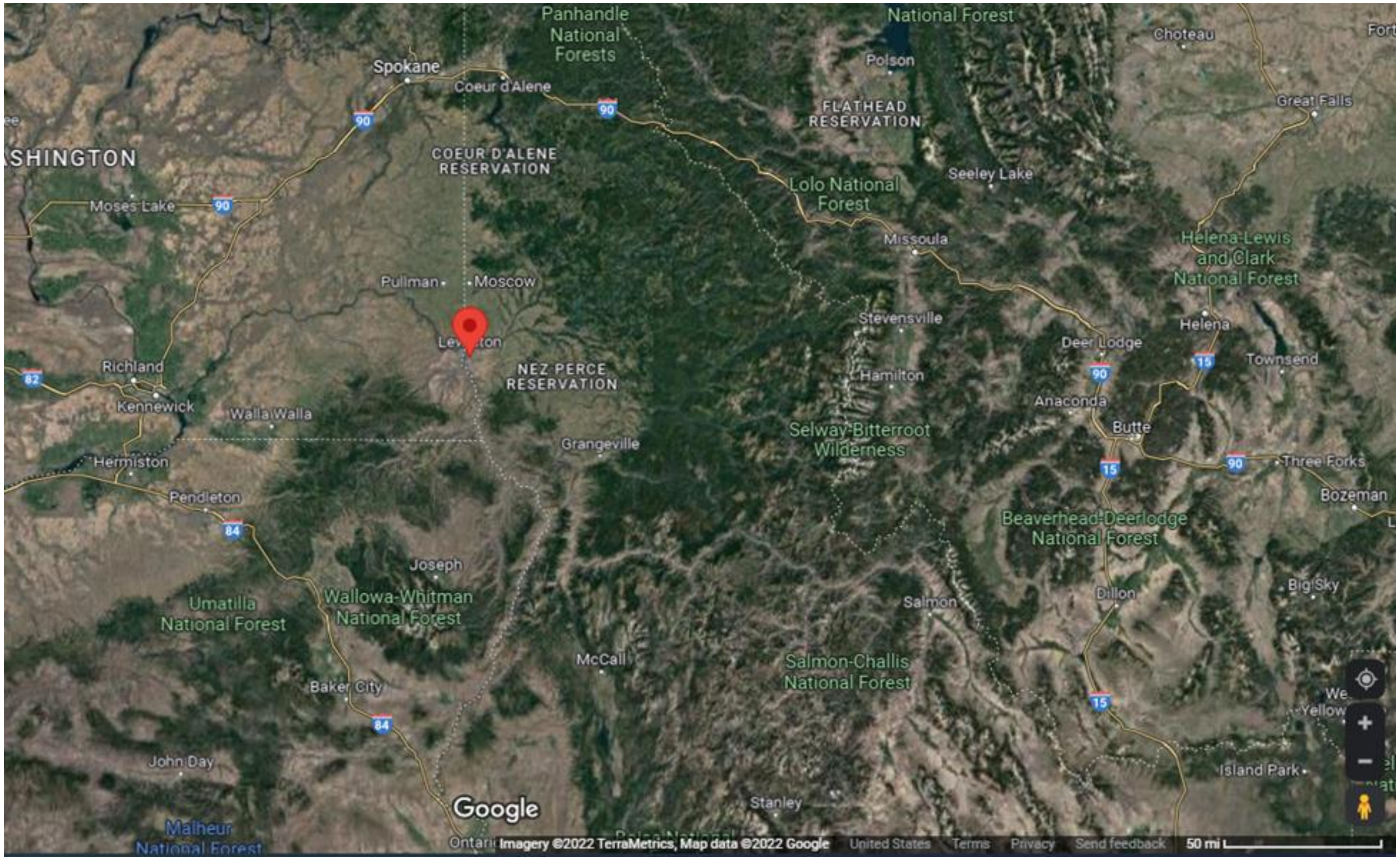


The St. Louis site lies near (~35 km) the oak forests of the Ozark Plateau

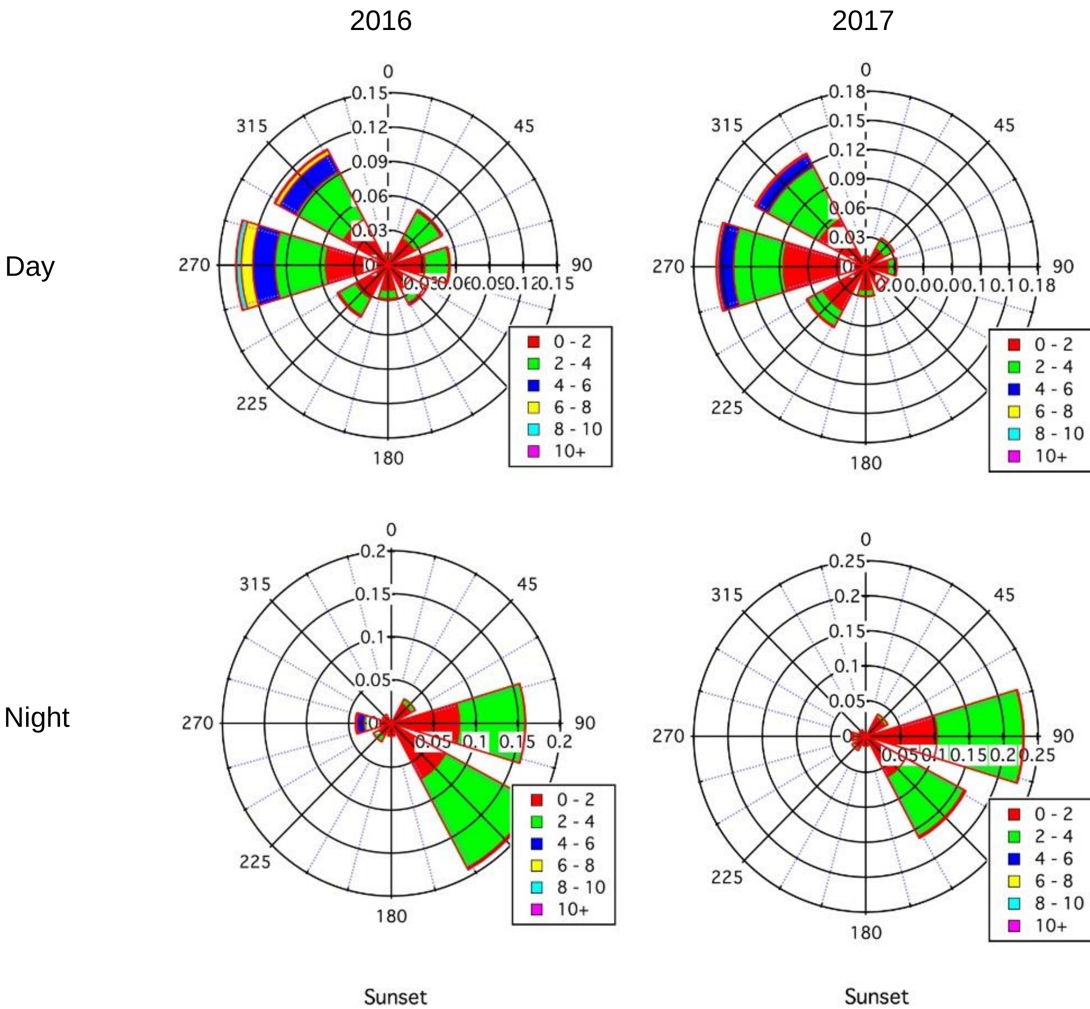


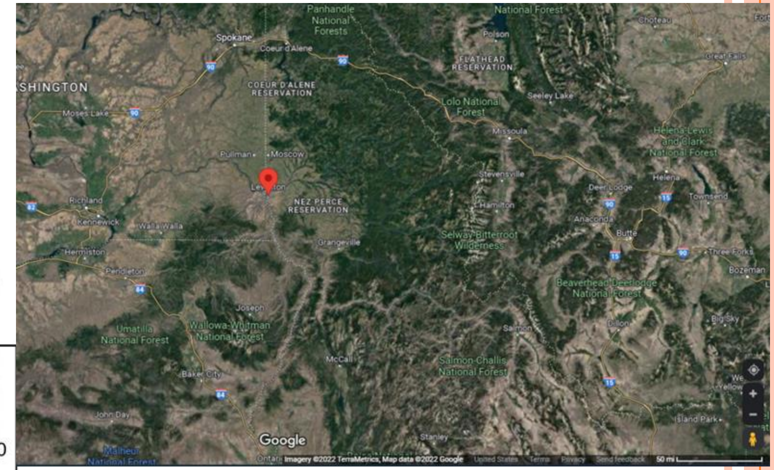
proton-transfer-reaction mass spectrometer (PTR-MS)

"We do not expect any measurement interferences for isoprene or MVK + MACR to impact the analyses"



- 10-20 mi
- ~0-265
- NbE-WbS





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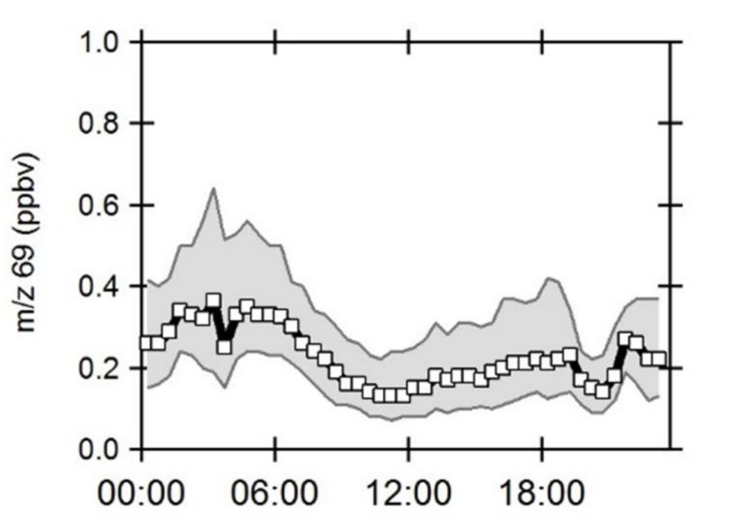
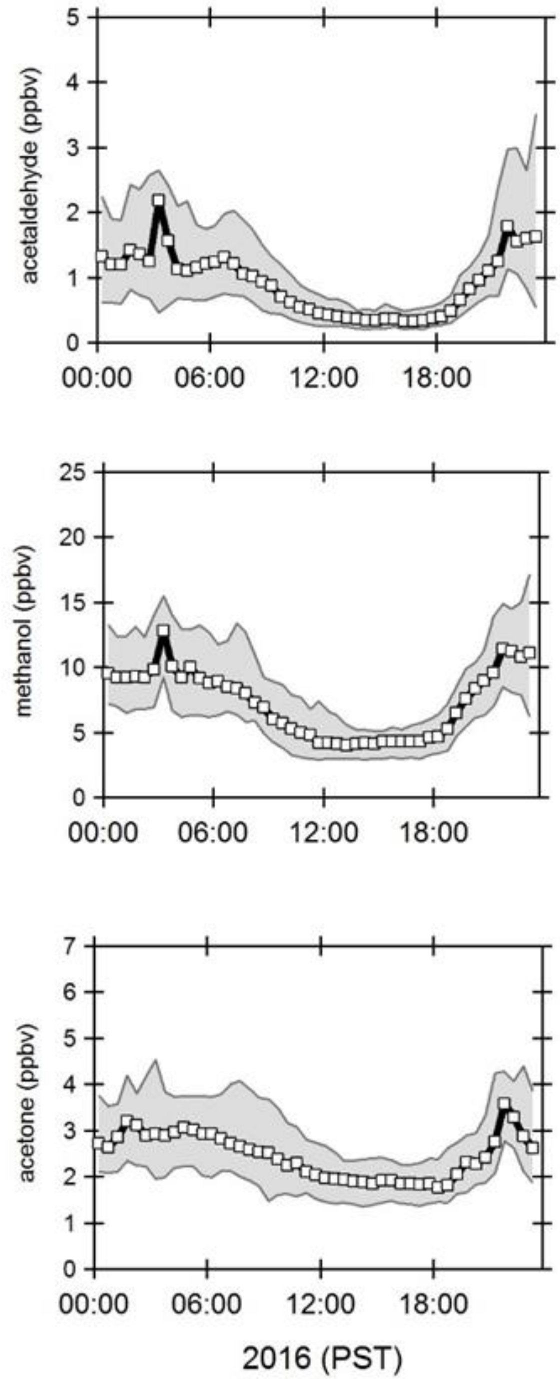


At night, the valley is located downwind of the national forests, and the easterly and southeasterly winds can transport isoprene emitted close to dust (with dropped OH levels) from the national forests to the site, leading to higher concentrations

At night, the easterly and southeasterly winds can transport other biogenic VOCs from the national forests to the site, leading to higher concentrations



The Biogenic Factor of PMF Modeling Results

- Isoprene, MVK, MEK, monoterpenes
- Methanol, acetone, acetaldehyde
- Benzenoids (e.g., benzene, xylene)
- Alkanes
- Question: Benzenoids are from fossil fuels or biogenic sources

SCIENTIFIC REPORTS

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Atmospheric benzenoid emissions from plants rival those from fossil fuels

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Despite the known biochemical production of a range of aromatic compounds by plants and the presence of benzenoids in floral scents, the emissions of only a few benzenoid compounds have been reported from the biosphere to the atmosphere. Here, using evidence from measurements at aircraft, ecosystem, tree, branch and leaf scales, with complementary isotopic labeling experiments, we show that vegetation (leaves, flowers, and phytoplankton) emits a wide variety of benzenoid compounds to the atmosphere at substantial rates. Controlled environment experiments show that plants are able to alter their metabolism to produce and release many benzenoids under stress conditions. The

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		Biogenic (MEGAN v2.1)		Biogenic (possible range)	Anthropogenic (EDGAR)	Biogenic SOA (mostly low NOx)	Anthropogenic SOA (mostly high NOx)
		Emission factor	Global emission	Global emission	Global emission	Potential global source range	Potential global source
Compound	Biogenic driver	μg m^{2} h^{-1}	Tg y^{-1}	Tg y^{-1}	Tg y^{-1}	Tg y^{-1}	Tg y^{-1}
toluene	multiple	9	1.5	1 to 6[b]	7.6	0.3 to 3.0	0.6 to 4.5
benzene	multiple	0	0	0.1 to 1	6.1	0.04 to 0.4	0.5 to 3.3
xylene	multiple	0	0	0.1 to 0.5	5.2	0.04 to 0.2	0.4 to 2.2
other[a]		37	6.6	3 to 33	5.5	1.0 to 11	0.2 to 1.8
Total		**46**	**8.1**	**4 to 40**	**24.4**	**1.4 to 15**	**2.0 to 12**
[a]*other biogenic benzenoids*							
homosalate	sunscreen	8.4	2.0	1 to 10			
ethylhexenyl salate	sunscreen	4.2	0.98	0.5 to 5			
cymene <para->	foliar, floral	7.5	0.9	0.5 to 5			
cymene <ortho->	foliar, floral	4.5	0.54	0.2 to 3			
methyl salicylate	stress	9	1.5	0.3 to 3			
p-cymenene (dimethyl styrene)	unknown	0.3 to 0.6	0.05	<0.1 to 1			
estragole (methyl chavicol)	floral, fruit conifer	0.9 to 1.65	0.18	0.1 to 5			
indole	stress	0.6	0.1	<0.1 to 0.2			
benzaldehyde	stress	0.15	0.05	<0.1 to 0.2			
methyl benzoate	unknown	0.15	0.05	<0.1 to 0.1			
m-cymenene	unknown	0.3	0.04	<0.1 to 0.1			
phenylacetaldehyde	unknown	0.15	0.05	<0.1 to 0.1			
anisole	floral	0.15	0.05	<0.1 to 0.1			
benzyl acetate	floral	0.3	0.1	<0.1 to 0.2			
benzyl alcohol	floral	0.15	0.05	<0.1 to 0.1			
eugenol	stress	0	<0.02	<0.1 to 0.2			
cinnamic acid	stress, floral	0	<0.02	<0.1 to 0.1			
coniferyl alcohol	unknown	0	<0.02	<0.1 to 0.1			
chavicol	floral	0	<0.02	<0.1 to 0.1			
safrole	unknown	0	<0.02	<0.1 to 0.1			
ethyl cinnamate	unknown	0	<0.02	<0.1 to 0.1			
salicylic aldehyde	stress	0	<0.02	<0.1 to 0.2			

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EMISSION RATES OF ORGANICS FROM VEGETATION IN CALIFORNIA'S CENTRAL VALLEY

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(*First received* 22 *February* 1991 *and in final form* 21 *January* 1992)

Table 2. Compounds identified* as emissions from the agricultural and natural plant species studied

Isoprene

Monoterpenes
- Camphene
- 2-Carene
- Δ^3-Carene
- Limonene
- Myrcene
- *cis*-Ocimene
- *trans*-Ocimene
- α-Phellandrene
- β-Phellandrene
- α-Pinene
- β-Pinene
- Sabinene
- α-Terpinene
- γ-Terpinene
- Terpinolene
- Tricyclene or α-thujene (tentative) †

Sesquiterpenes
- β-Caryophyllene
- Cyperene
- α-Humulene
- Other isomers ‡

Alcohols
- *p*-Cymen-8-ol (tentative) †
- *cis*-3-Hexen-1-ol
- Linalool

Table 2. (Contd.)

Acetates
- Bornylacetate
- Butylacetate (tentative) †
- *cis*-3-Hexenylacetate

Aldehydes
- *n*-Hexanal
- *trans*-2-Hexenal

Ketones
- 2-Heptanone
- 2-Methyl-6-methylene-1, 7-octadien-3-one (tentative) †
- Pinocarvone (tentative) †
- Verbenone (tentative) †

Ethers
- 1,8-Cineole
- *p*-Dimethoxybenzene (tentative) †
- Estragole (tentative) †
- *p*-Methylanisole (tentative) †

Esters
- Methylsalicylate (tentative) †

n-*Alkanes*
- *n*-Hexane
- $C_{10} \rightarrow C_{17}$

Alkenes
- 1-Decene
- 1-Dodecene
- 1-Hexadecene (tentative) †
- *p*-Mentha-1,3,8-triene (tentative) †
- 1-Pentadecene (tentative) †
- 1-Tetradecene

Aromatics
- *p*-Cymene

Atmos. Chem. Phys., 9, 81–92, 2009
www.atmos-chem-phys.net/9/81/2009/

Atmospheric Chemistry and Physics

Are biogenic emissions a significant source of summertime atmospheric toluene in the rural Northeastern United States?

M. L. White[1], R. S. Russo[1], Y. Zhou[1], J. L. Ambrose[1,2], K. Haase[1,2], E. K. Frinak[1], R. K. Varner[1], O. W. Wingenter[3], H. Mao[1], R. Talbot[1], and B. C. Sive[1]

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- Dynamic branch enclosure measurements of loblolly **pine trees:** vegetative emissions of 12 pptv d^{-1}
- Static chamber measurements: **alfalfa** (5 pptv d^{-1})
- **Measured biogenic fluxes were on the same order of magnitude as the influence from gasoline evaporation and industrial sources (regional industrial emissions estimated at 7 pptv d−1) and indicated that local vegetative emissions make a significant contribution to summertime toluene enhancements**.

frontiers in Plant Science

ORIGINAL RESEARCH
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Diversity and Interrelations Among the Constitutive VOC Emission Blends of Four Broad-Leaved Tree Species at Seedling Stage

Anne Charlott Fitzky[1], Arianna Peron[2], Lisa Kaser[2], Thomas Karl[2], Martin Graus[2], Danny Tholen[3], Mario Pesendorfer[1], Maha Mahmoud[1,3], Hans Sandén[1] and Boris Rewald[1]*

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TABLE 1 | Constitutive VOC emission rates (nmol m^{-2} s^{-1}) of *Q. robur, F. sylvatica, B. pendula*, and *C. betulus* seedlings (Mean ± SD).

***m/z* ratio**	**Chemical formula**	**Assigned compound(s)**	**Constitutive VOC emission rates (nmol m^{-2} s^{-1})***			
			Quercus robur	***Fagus sylvatica***	***Betula pendula***	***Carpinus betulus***
Oxygenated VOCs						
33.034	$(CH_4O)H^+$	Methanol	0.039 ± 0.115	0.061 ± 0.111	0.913 ± 0.571	0.313 ± 0.372
47.049	$(C_2H_6O)H^+$	Ethanol	0.002 ± 0.002	0.004 ± 0.008[§]	0.004 ± 0.003	0.011 ± 0.013
45.034	$(C_2H_4O)H^+$	Acetaldehyde[Std]	0.018 ± 0.008	0.023 ± 0.010	0.025 ± 0.010	0.020 ± 0.007
61.028	$(C_2H_4O_2)H^+$	Acetic acid	0.010 ± 0.003	0.015 ± 0.003	0.043 ± 0.020	0.014 ± 0.003
59.049	$(C_3H_6O)H^+$	Acetone	0.037 ± 0.025	0.012 ± 0.016[§]	0.129 ± 0.020	0.013 ± 0.007
LOX-pathway						
101.096	$(C_6H_{12}O)H^+$	Hexanal	0.0002 ± 0.0001[§]	0.0001 ± 0.0001[§]	0.0006 ± 0.0002[§]	0.0003 ± 0.0001[§]
99.080	$(C_6H_{10}O)H^+$	Hexenals	0.0005 ± 0.0001	0.0005 ± 0.0002[§]	0.001 ± 0.001[§]	0.0010 ± 0.0003[§]
85.101	$(C_6H_{12})H^+$	Hexene	0.0004 ± 0.0003[§]	0.0002 ± 0.0002[§]	0.0002 ± 0.0002[§]	0.0001 ± 0.0002[§]
143.107	$(C_8H_{14}O_2)H^+$	Hexenyl acetate	0.0010 ± 0.0002	0.0010 ± 0.0002[§]	0.0010 ± 0.0003[§]	0.0010 ± 0.0002[§]
145.122	$(C_8H_{16}O_2)H^+$	Hexyl acetate	0.0001 ± 0.0001[§]	0.0001 ± 0.0002[§]	0.0002 ± 0.0001[§]	0.0002 ± 0.0001[§]
57.069	$(C_4H_8)H^+$	Butyl	0.005 ± 0.004	0.001 ± 0.002[§]	0.002 ± 0.001[§]	0.001 ± 0.001[§]
MEP-pathway						
69.069	$(C_5H_8)H^+$	Isoprene[Std]	20.831 ± 4.837	0.008 ± 0.004	0.019 ± 0.007	0.007 ± 0.003
71.049	$(C_4H_6O)H^+$	MVK/MAC	0.004 ± 0.001	0.001 ± 0.001[§]	0.003 ± 0.001	0.0010 ± 0.0003[§]
73.065	$(C_4H_8O)H^+$	MEK	0.006 ± 0.007	0.004 ± 0.007[§]	0.011 ± 0.005	0.003 ± 0.003[§]
87.080	$(C_5H_{10}O)H^+$	MBO	0.017 ± 0.004	0.005 ± 0.002	0.011 ± 0.003	0.006 ± 0.001
137.132	$(C_{10}H_{16})H^+$	Sum of MTs[Std]	0.029 ± 0.027	0.390 ± 0.359	0.080 ± 0.030	0.072 ± 0.110
93.069	$(C_7H_8)H^+$	F MT/toluene	0.001 ± 0.001	0.006 ± 0.005	0.002 ± 0.001[§]	0.001 ± 0.001[§]
MVA-pathway						
205.195	$(C_{15}H_{24})H^+$	Sum of SQTs[Std]	0.007 ± 0.011	0.013 ± 0.012	0.022 ± 0.021	0.006 ± 0.003[§]
Shikimate-pathway						
79.054	$(C_6H_6)H^+$	Benzene	0.0010 ± 0.0003	0.001 ± 0.001[§]	0.001 ± 0.001[§]	0.001 ± 0.001[§]
107.049	$(C_7H_6O)H^+$	Benzaldehyde	0.0010 ± 0.0001	0.0005 ± 0.0002[§]	0.0006 ± 0.0002[§]	0.0010 ± 0.0002[§]
153.055	$(C_8H_8O_3)H^+$	Methyl salicylate	0.002 ± 0.002	0.003 ± 0.002[§]	0.003 ± 0.002[§]	0.047 ± 0.053
165.092	$(C_{10}H_{12}O_2)H^+$	Eugenol	0.0001 ± 0.0001[§]	0.0001 ± 0.0001[§]	0.0002 ± 0.0001[§]	0.00010 ± 0.00003[§]
TOTAL VOC			21.383 ± 5.054	0.552 ± 0.546	1.295 ± 0.700	0.525 ± 0.584

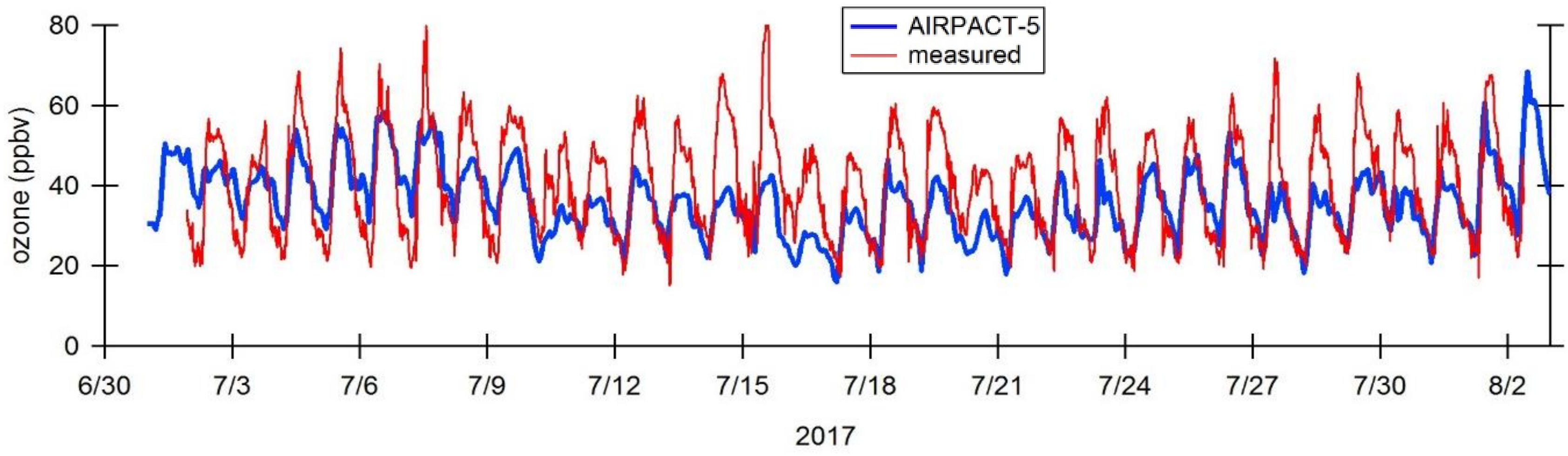
Mass-to-charge ratios (m/z) are assigned to VOCs: their chemical formula and the compound name. The measured VOCs are sorted in oxygenated VOCs, and VOCs synthesized by the LOX-, MEP-, MVA-, and Shikimate pathways and the respective catabolites, respectively. See ***Supplementary Tables 2, 3*** *for ANOVA and Tukey HSD test, respectively, on SQT and total VOC emissions.*

F, fragment; MBO, 2-methyl-3-buten-2-ol; MVK, methyl vinyl ketone; MAC, methacrolein; MEK, methyl ethyl ketone; MT, monoterpenes; SQT, sesquiterpenes.

[Std]Standardized emission rates of isoprene, the sum of monoterpenes and sesquiterpenes, and acetaldehyde are marked with "Std."

**Concentrations under the limit of quantification (LOQ < 0.05 ppbv) are marked with an "§."*

Implications for future studies on ozone and $PM_{2.5}$ in the region



- Biogenic emissions models (e.g., MEGAN v2.1) do not simulate some VOCs (e.g., benzene, xylene)
- VOCs can affect ozone and secondary organic aerosols
- AIRPACT-5 significantly underestimates the peaks of ozone concentrations at the Sunset site (up to 30-40 ppb)
- This region: small towns; not many vehicles; huge national forests
- Possible factor? Missing emissions of VOCs from national forests and local trees?

Summary and Conclusion

- Performed data analyses and literature review to understand how the sources and wind circulations affect the observed behaviors of many compounds such as isoprene, formaldehyde, SO_2, H_2S, acetaldehyde
- VOCs in the area are influenced by national forests and wind circulations
- The paper mill may have contributed to the decadal HCHO decline
- The emissions from the paper mill cause high formaldehyde spikes in the early morning
- Implications for future studies on ozone and $PM_{2.5}$ (secondary organic aerosols)