

Source Influences on Ambient Ozone Precursor Concentrations in the Colorado Front Range

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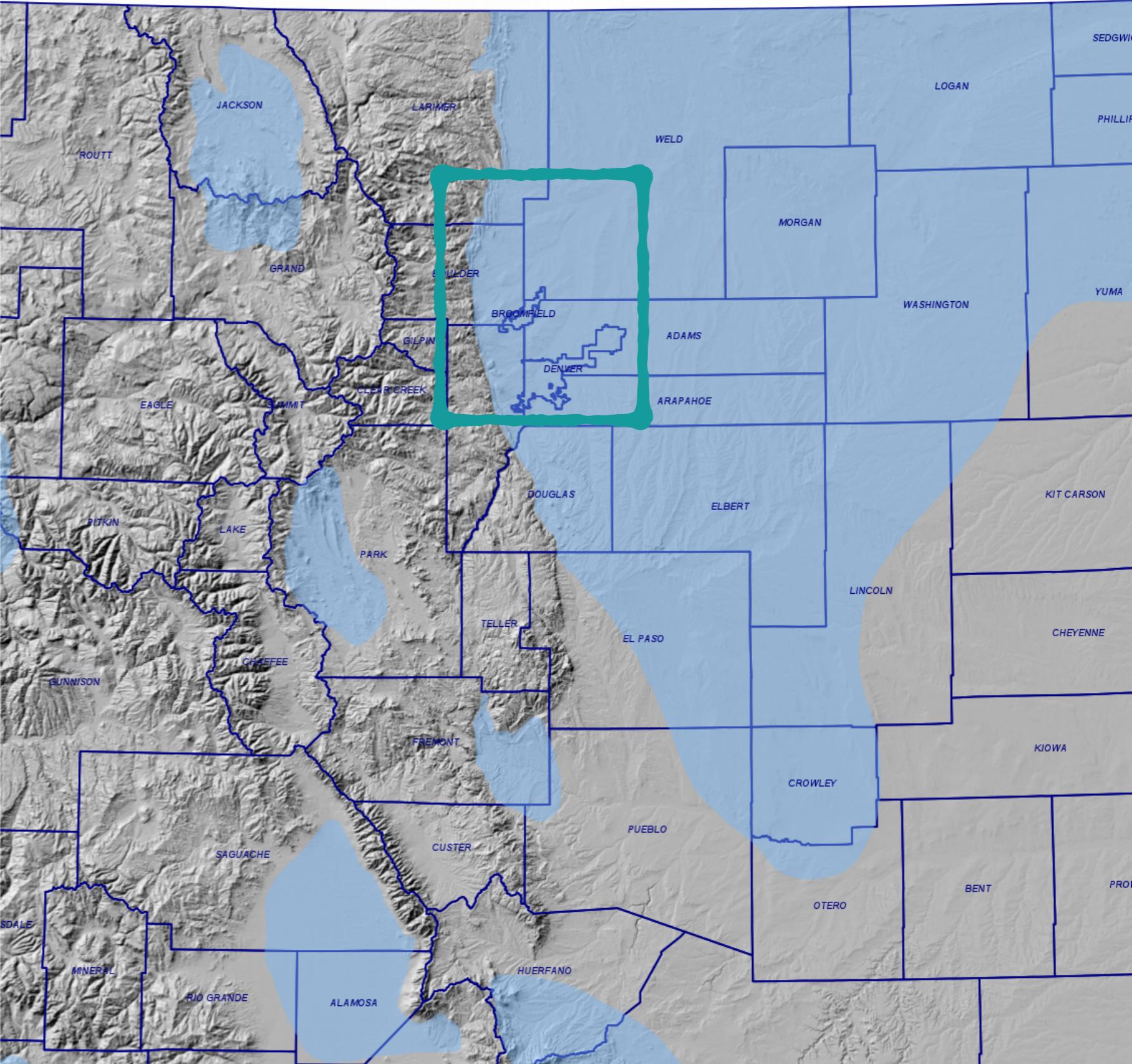
Colorado Front Range

Denver-Julesburg
Basin

Cities & Counties

Area of Interest

from Colorado Oil & Gas
Conservation Commission
(COGCC) Interactive Map



Measurement Campaign

- Conducted by Colorado Department of Public Health & Environment (CDPHE) Air Pollution Control Division Ozone Precursor Study

Samples	2013	2014
Denver	57	58
Platteville	51	56

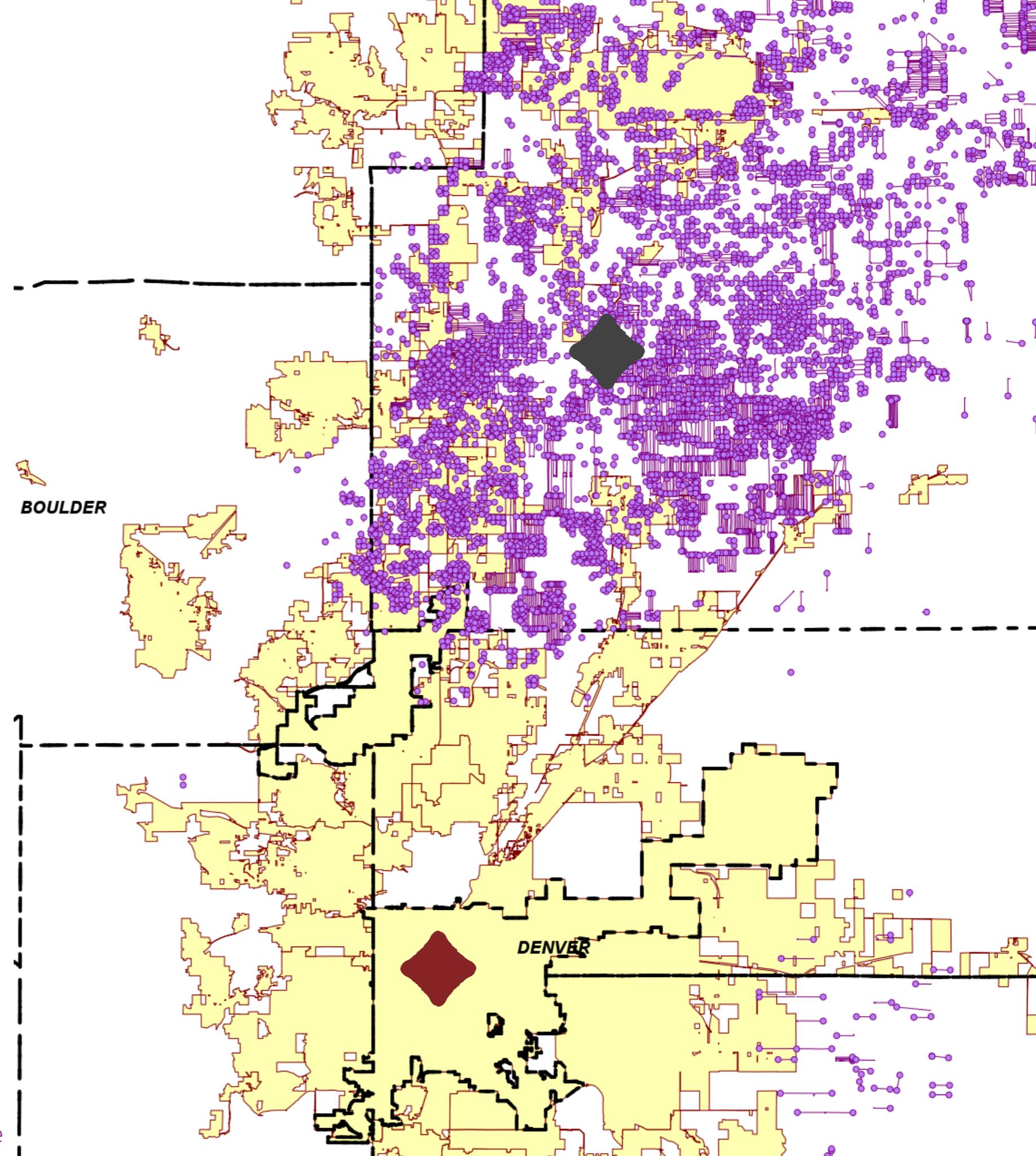
- Flasks analyzed for 79 non-methane organic compounds
 - co-elution of 1-butene and isopentane in sampling led to their exclusion
 - 3-hr samples acquired from 6 a.m. to 9 a.m. M.S.T.
 - methane and carbonyls separately measured and analyzed

Wells*

Cities

**Platteville
measurement site**

**Denver
measurement site**



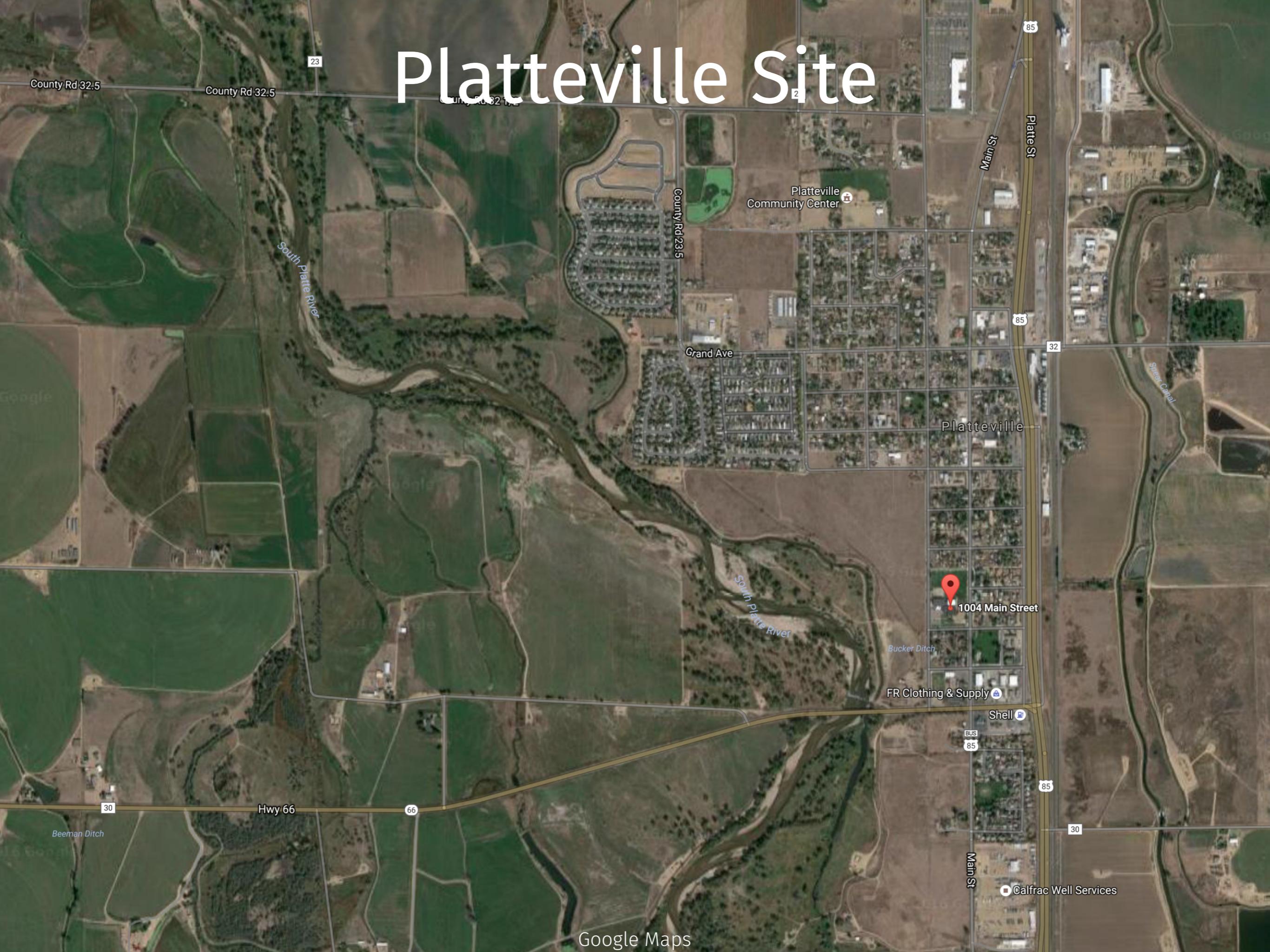
from COGCC Interactive Map (Oct 2016)

*actual directional/horizontal well bottomhole

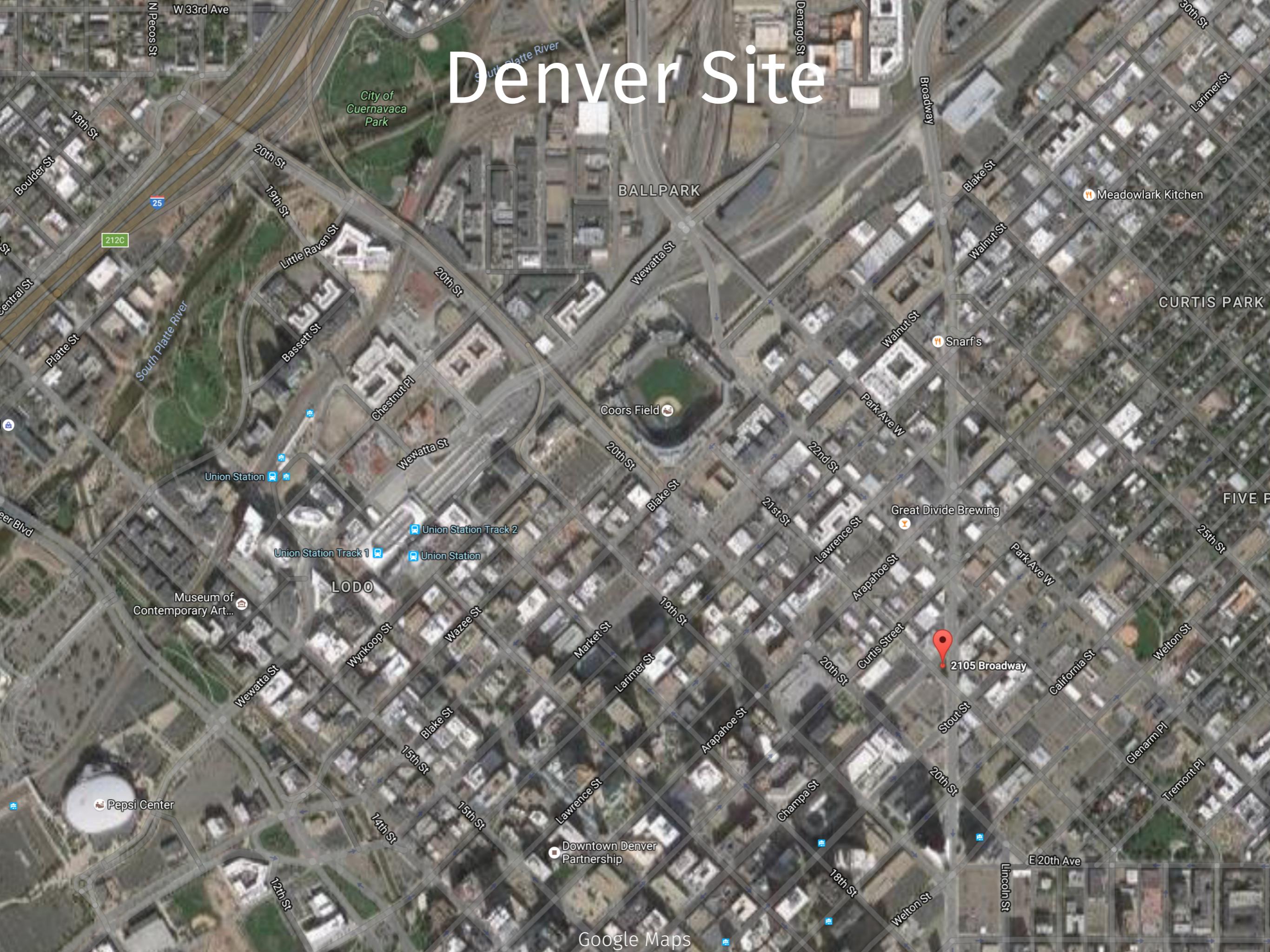
Platteville Measurement Site



Platteville Site



Denver Site



Denver Measurement Site

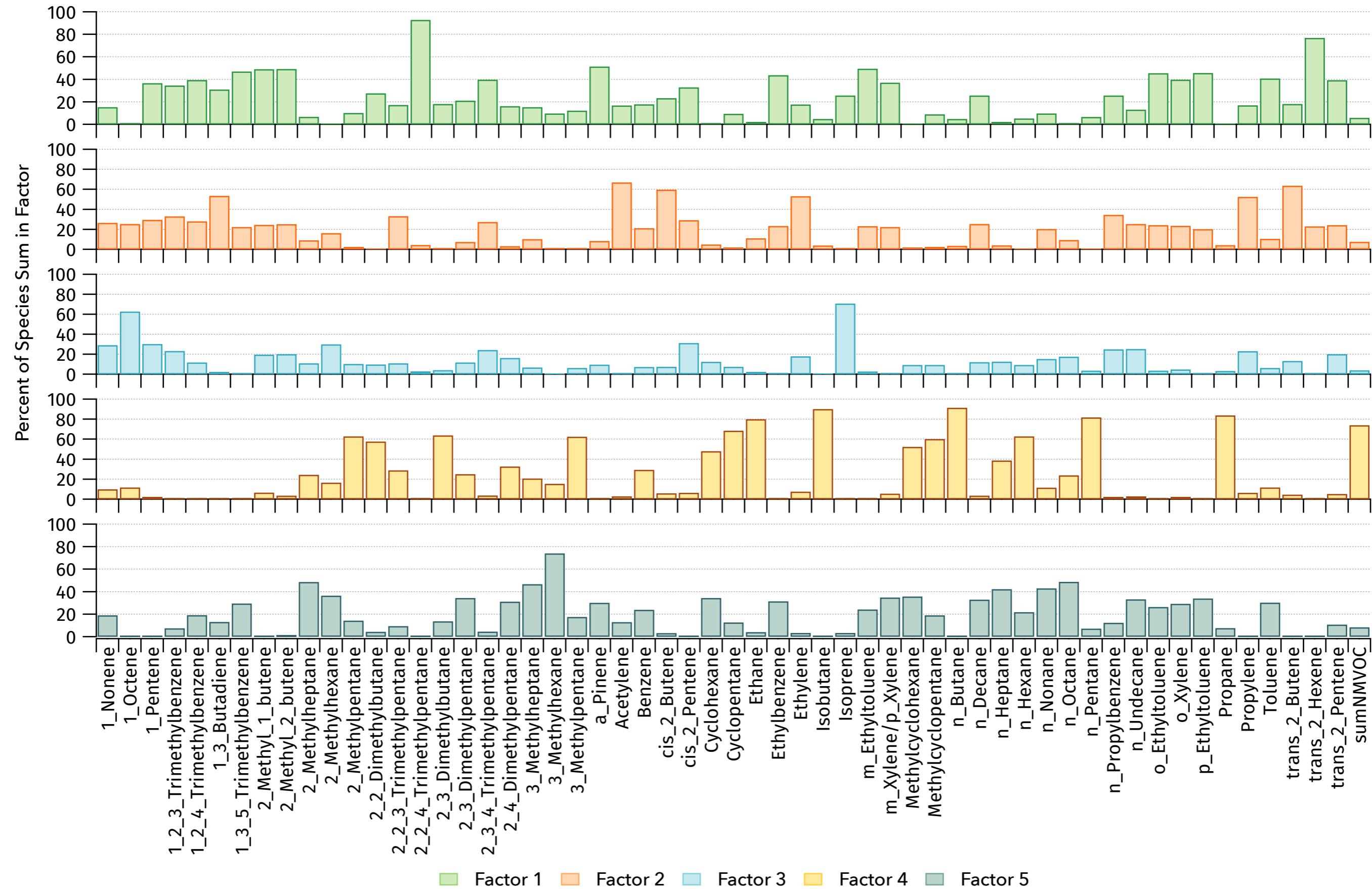


Evaluating Source Influences

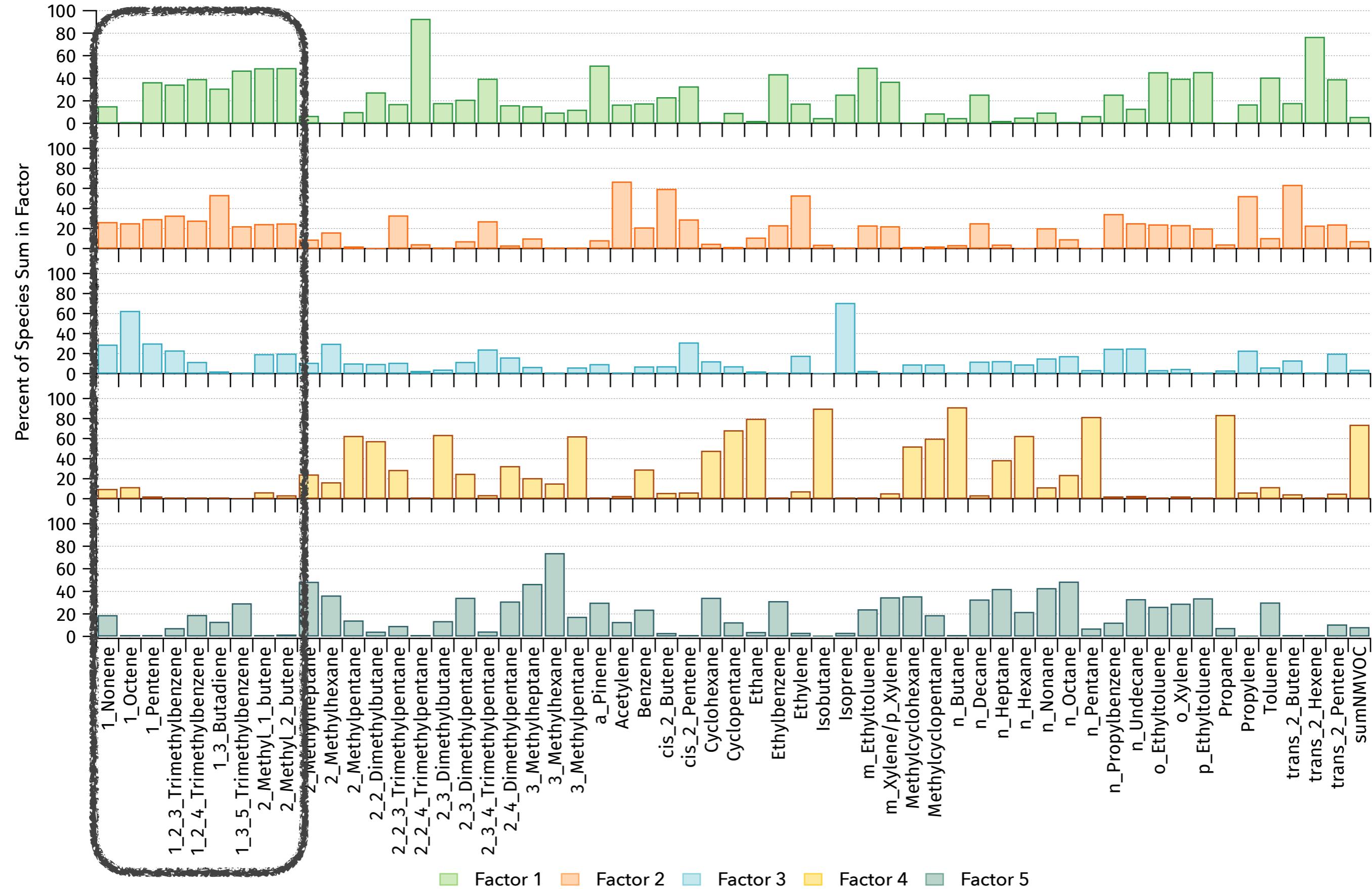
$$E_{ik} = \sum_{j=1}^p A_{ij} B_{jk} + \varepsilon_{ik} \quad i = 1, 2, \dots, m; k = 1, 2, \dots, n$$

- Positive Matrix Factorization (PMF)
- A_{ij} , source profile: loading of compound i on factor j
- B_{jk} , normalized source contribution: j^{th} factor's contribution for the total k^{th} observation
- p , total factors
 - [4-6 evaluated]
- i , compound observed and attributed
 - [79 NMVOCs]
- k , observation
 - [~55 per site per year]

Five Physically-meaningful Factors

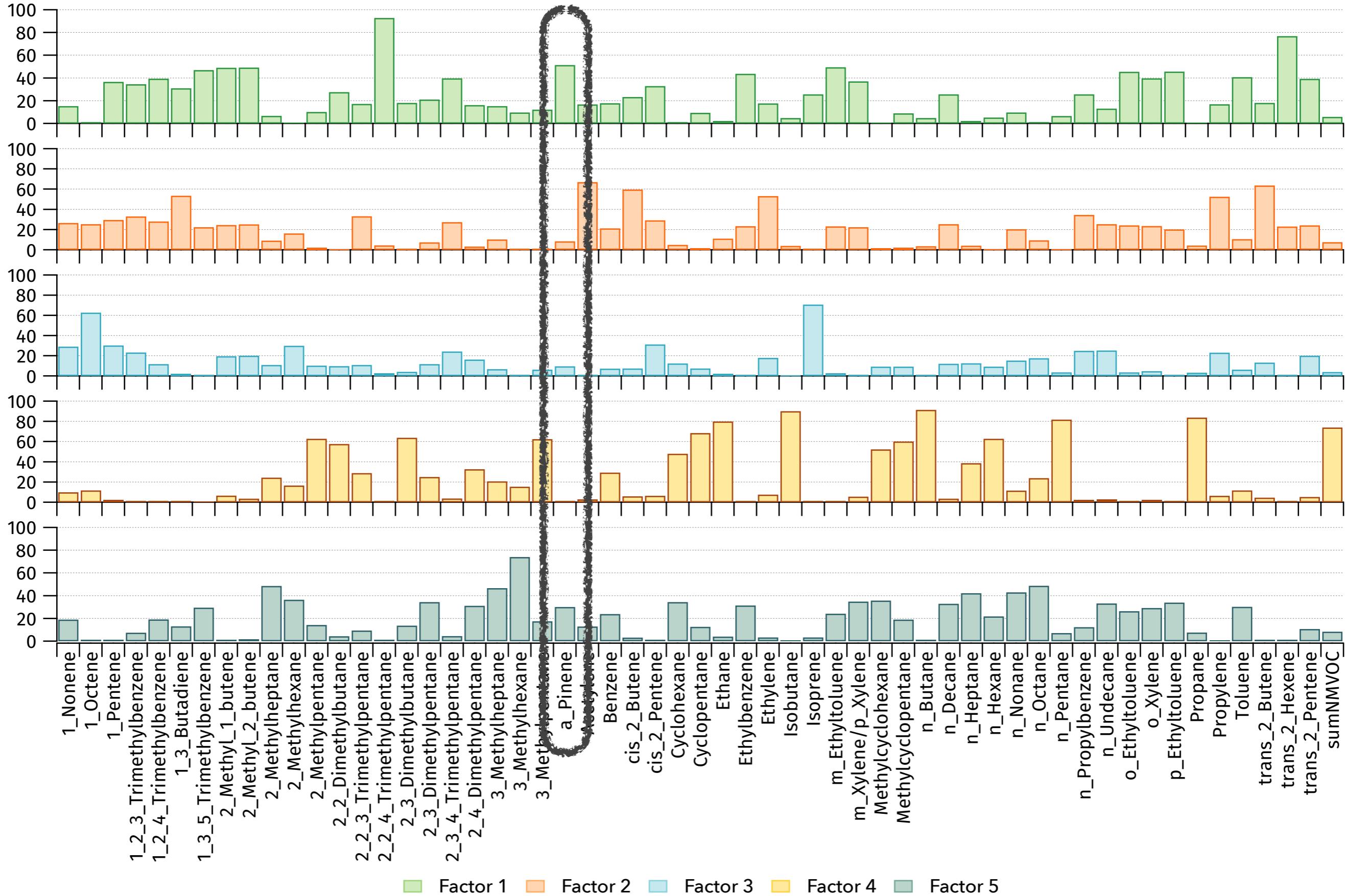


alkenes



α -pinene

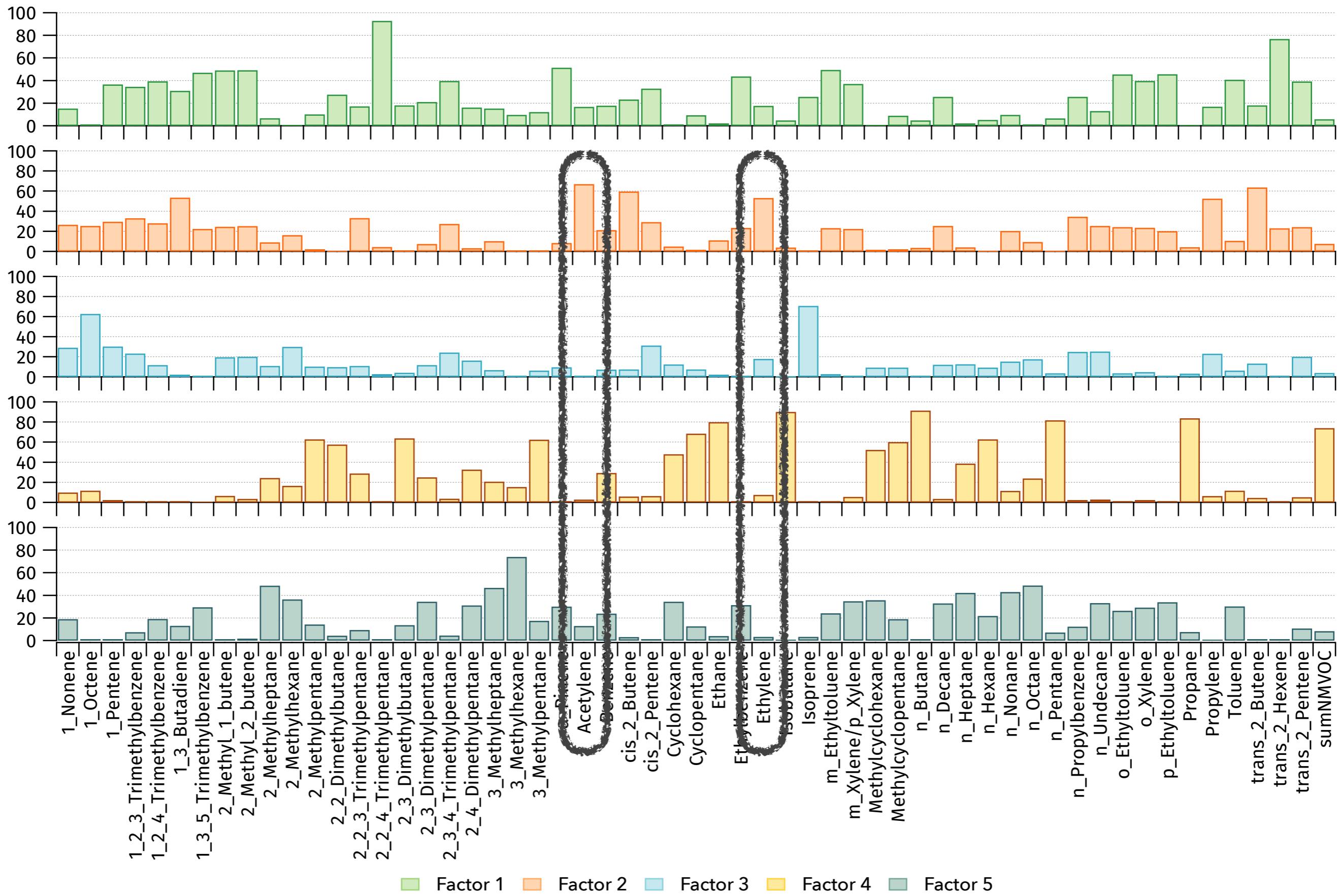
Percent of Species Sum in Factor



Legend: Factor 1 (light green), Factor 2 (light orange), Factor 3 (light blue), Factor 4 (light yellow), Factor 5 (teal)

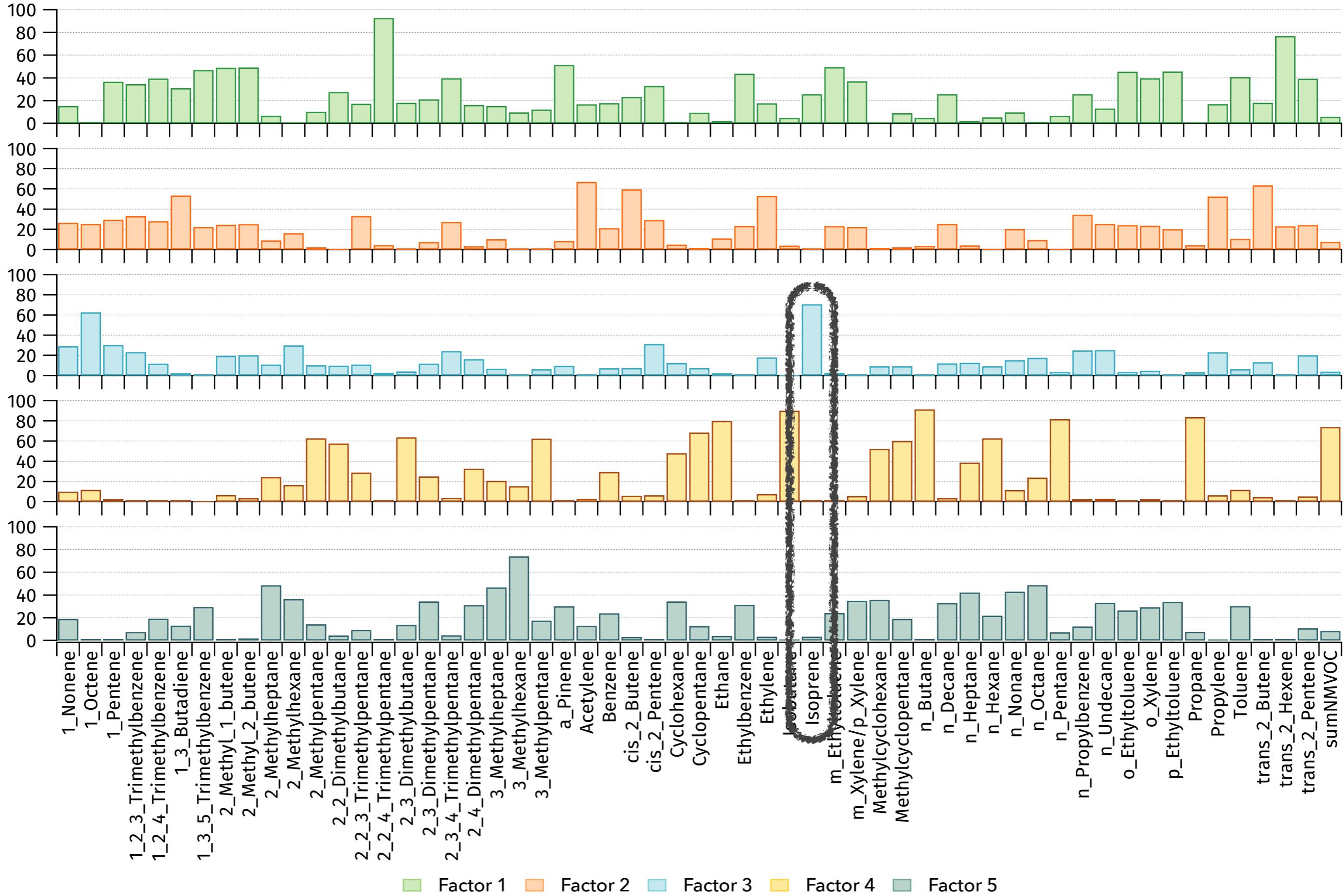
acetylene and ethylene

Percent of Species Sum in Factor



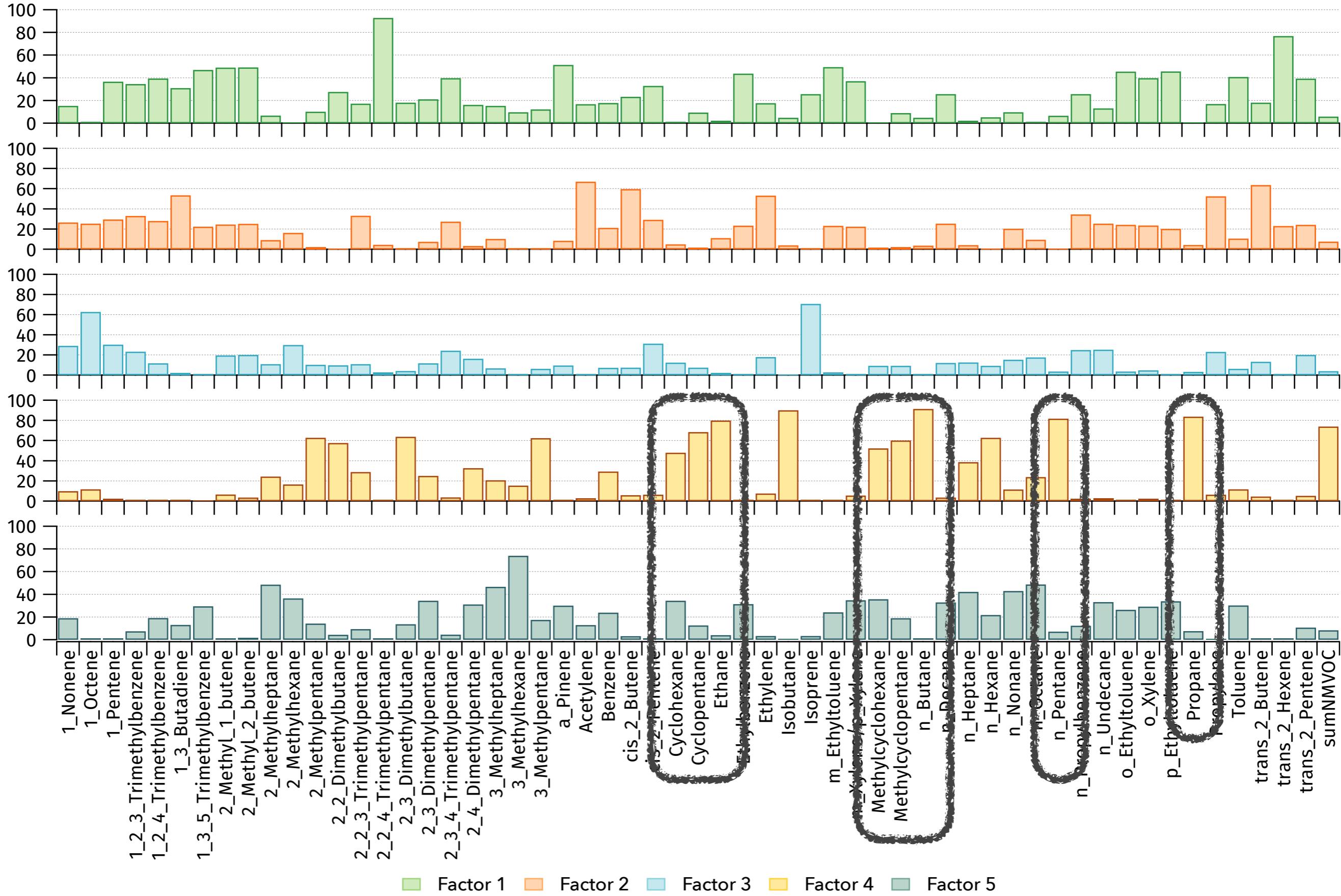
isoprene

Percent of Species Sum in Factor



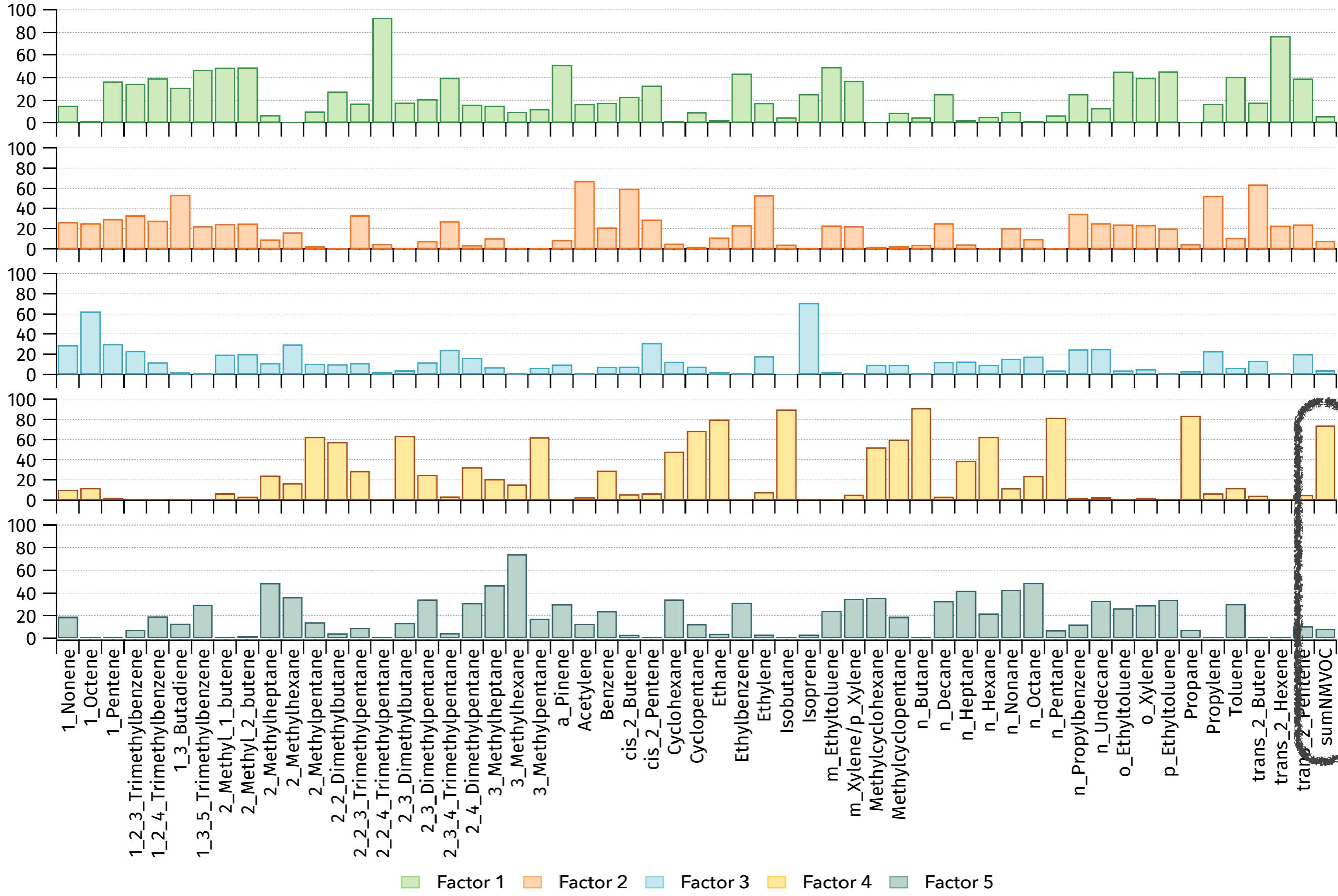
lighter, branched, and cyclic alkanes

Percent of Species Sum in Factor



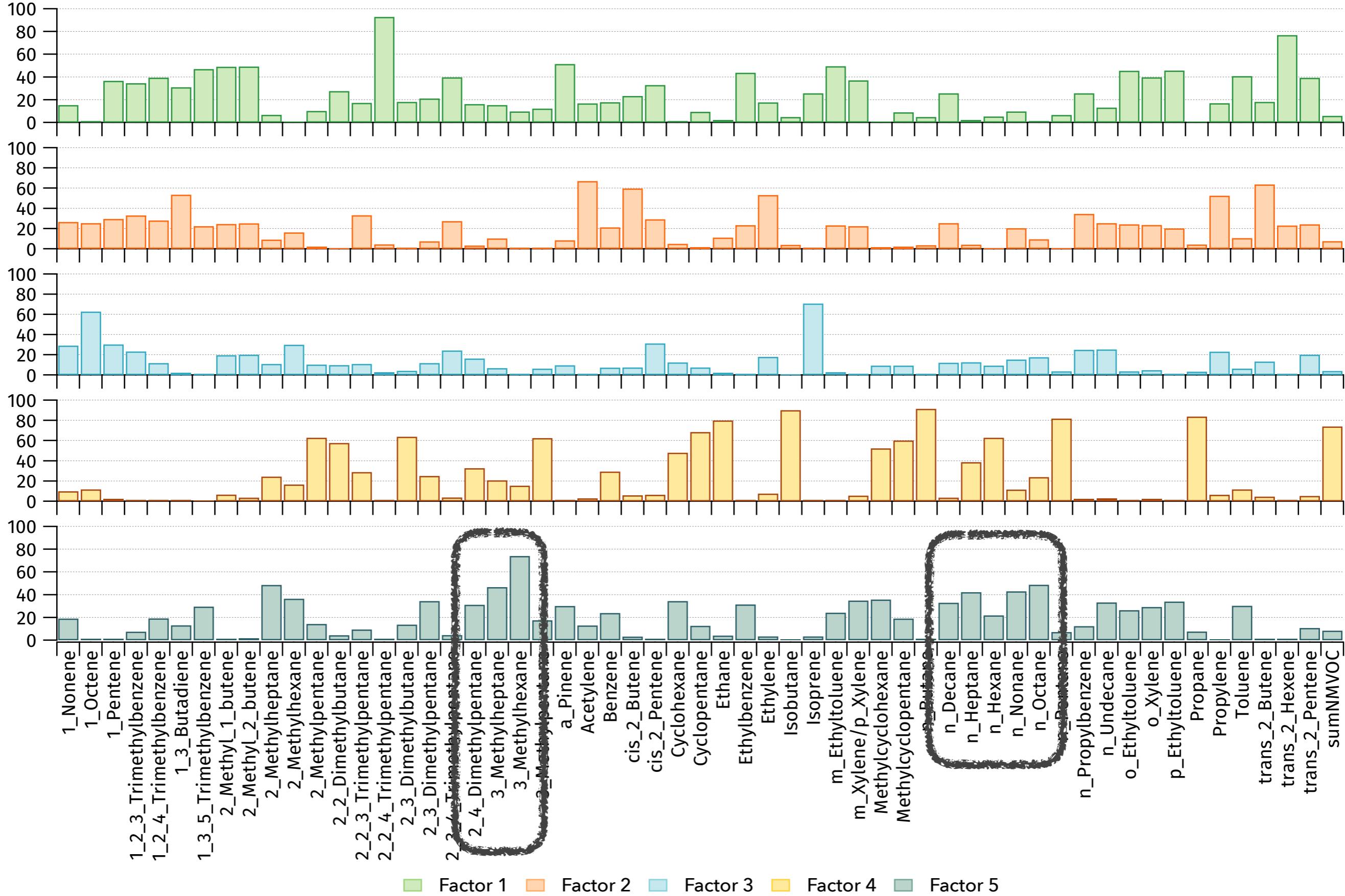
sum of the VOCs

Percent of Species Sum in Factor

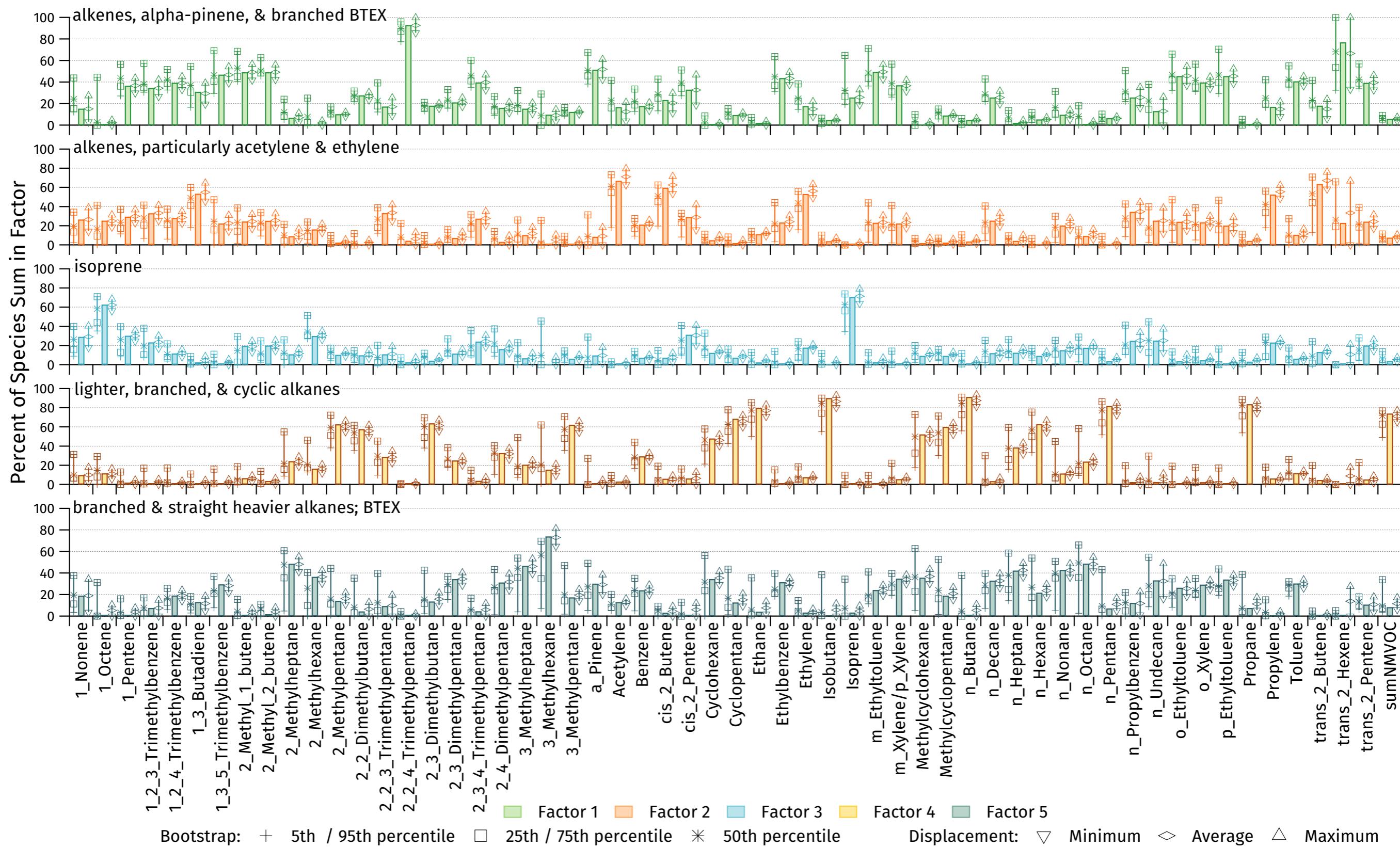


branched and straight heavier alkanes

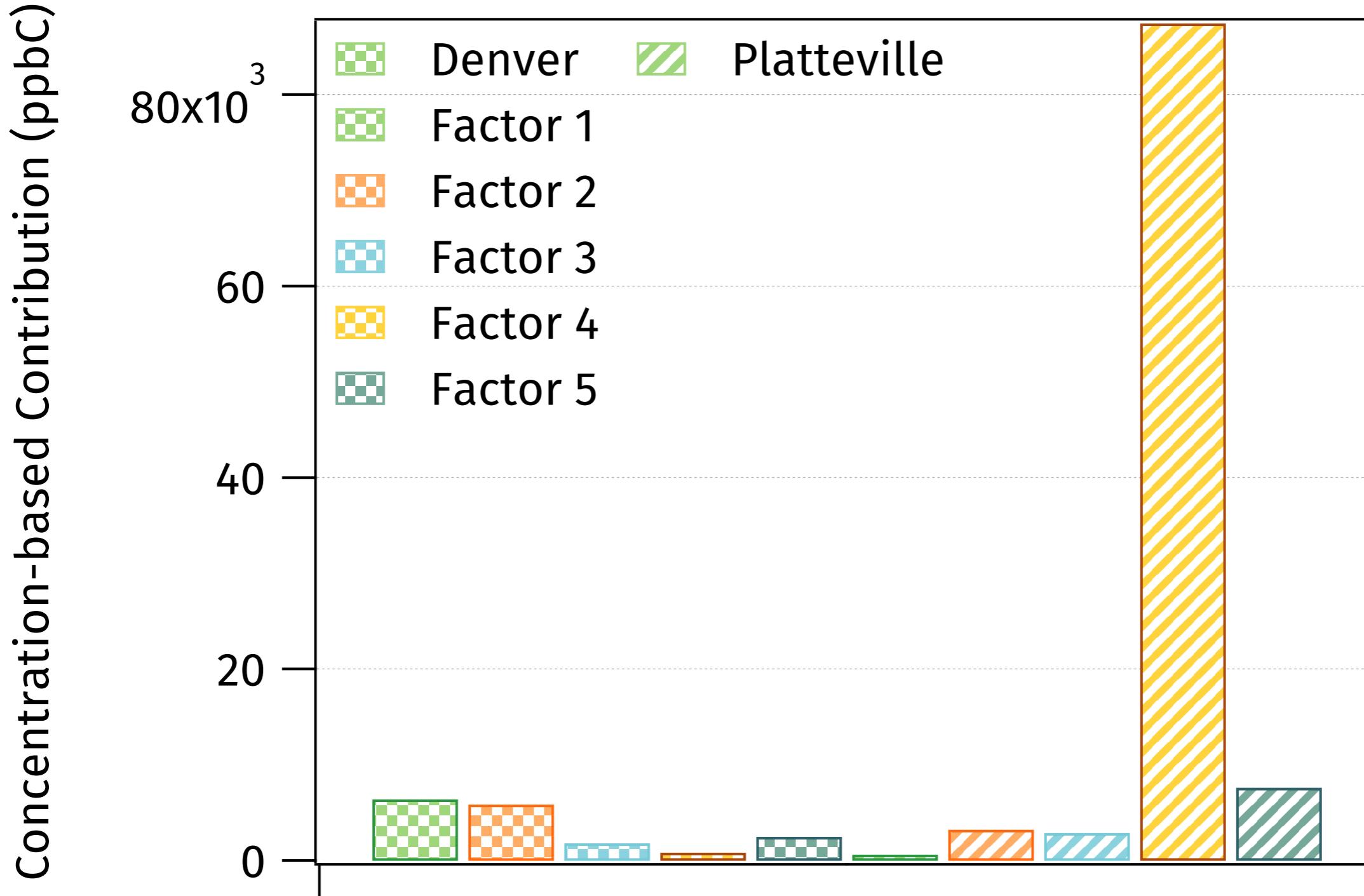
Percent of Species Sum in Factor



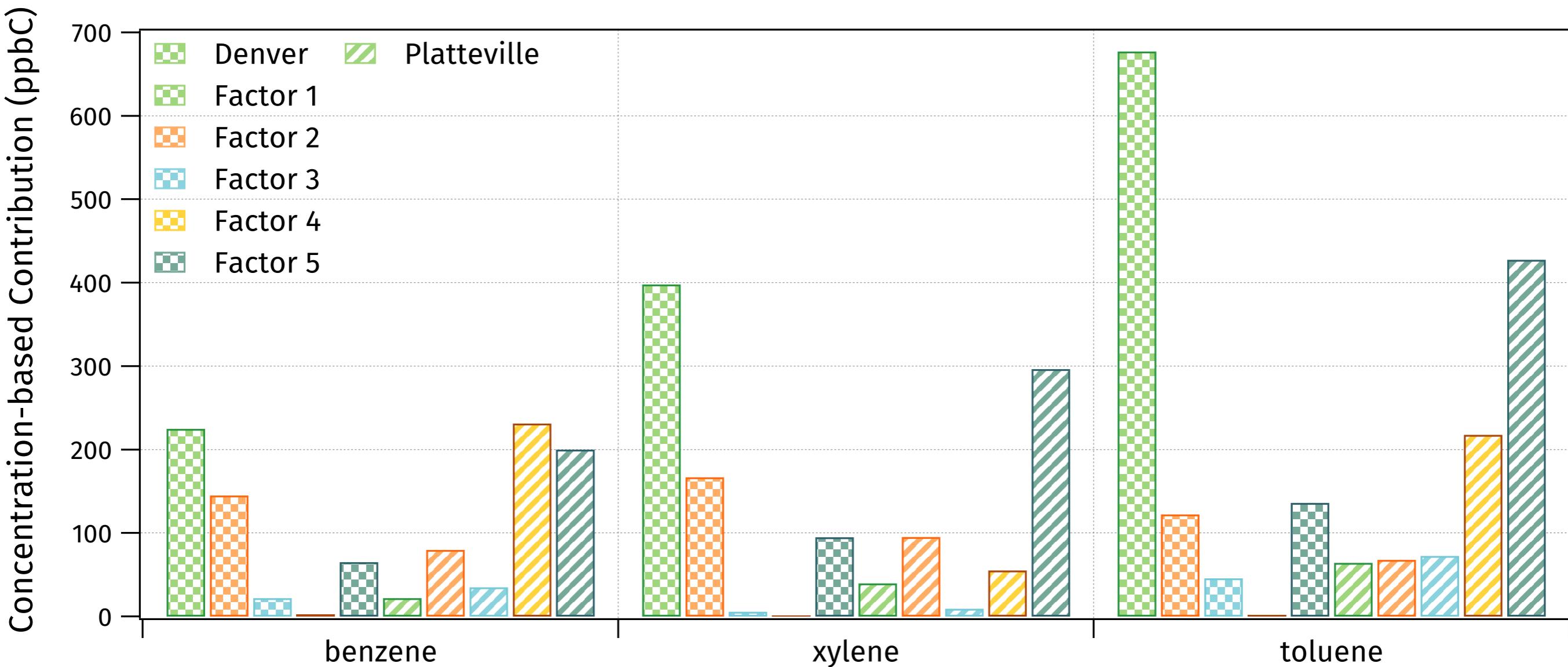
Key Species Robust to Error Testing



Contributions from Each Factor & Site to Sum of the NMVOCs

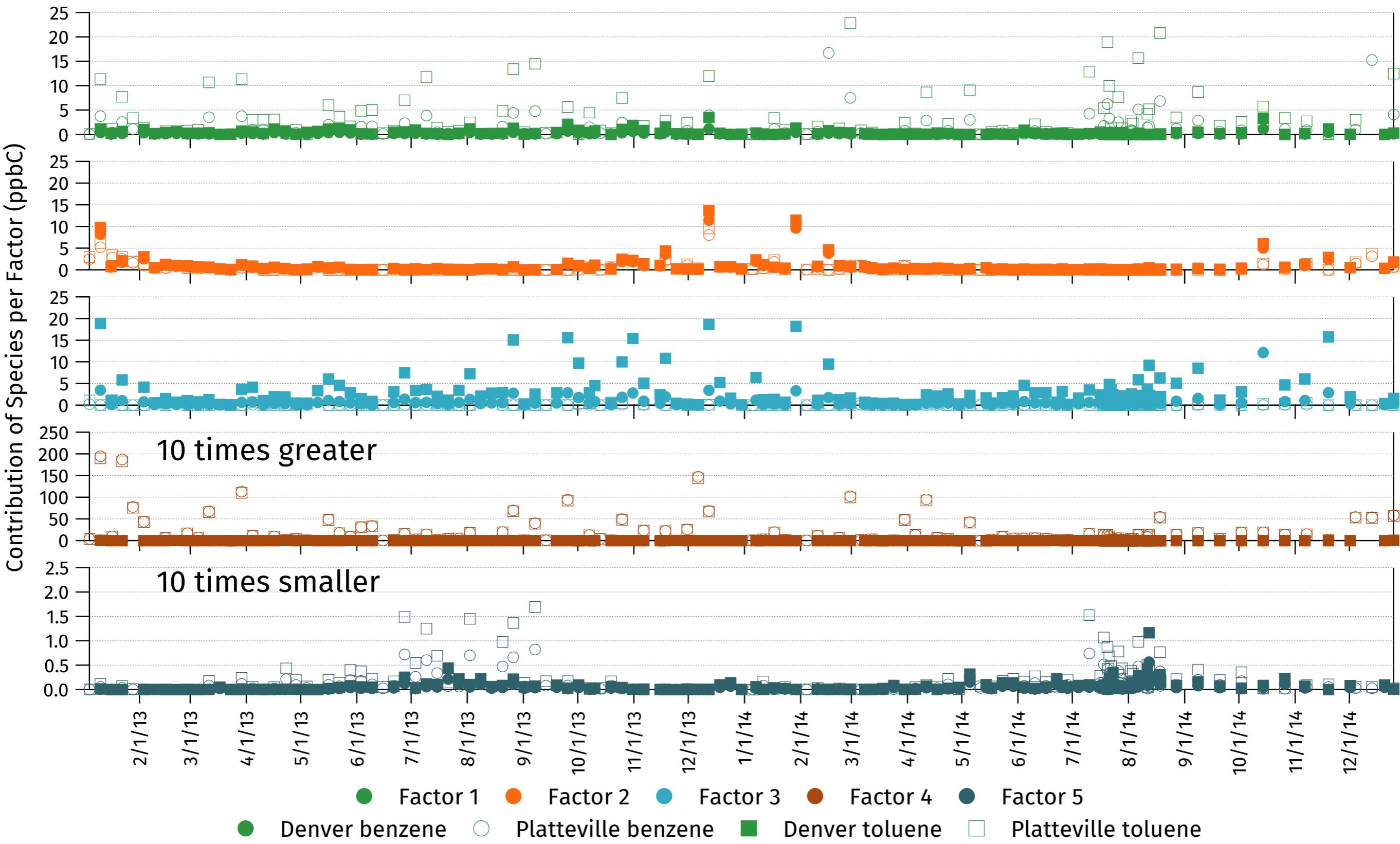


Contributions from Each Factor & Site to BTEX Compounds

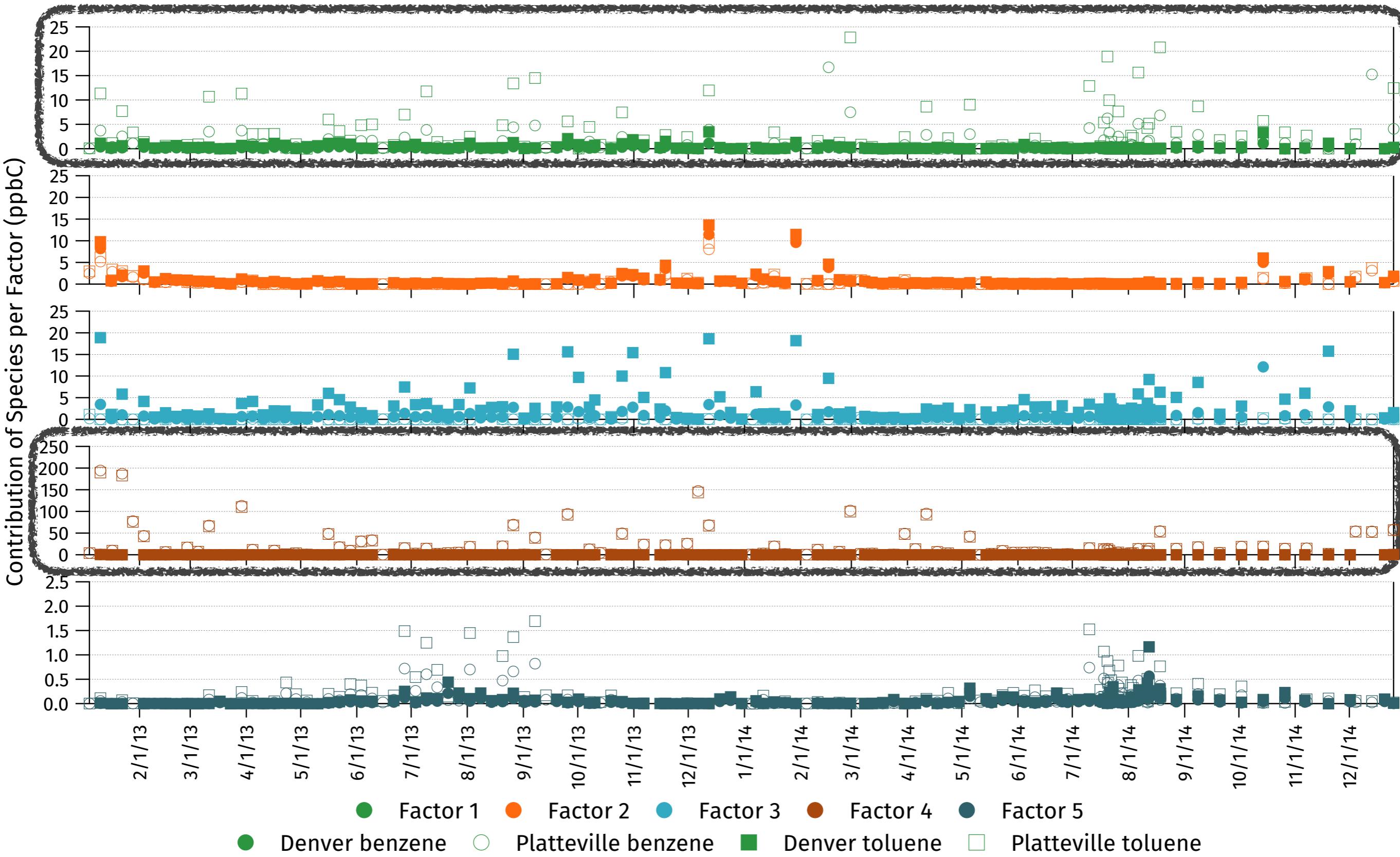


Time Series of Contributions:

Benzene and Toluene

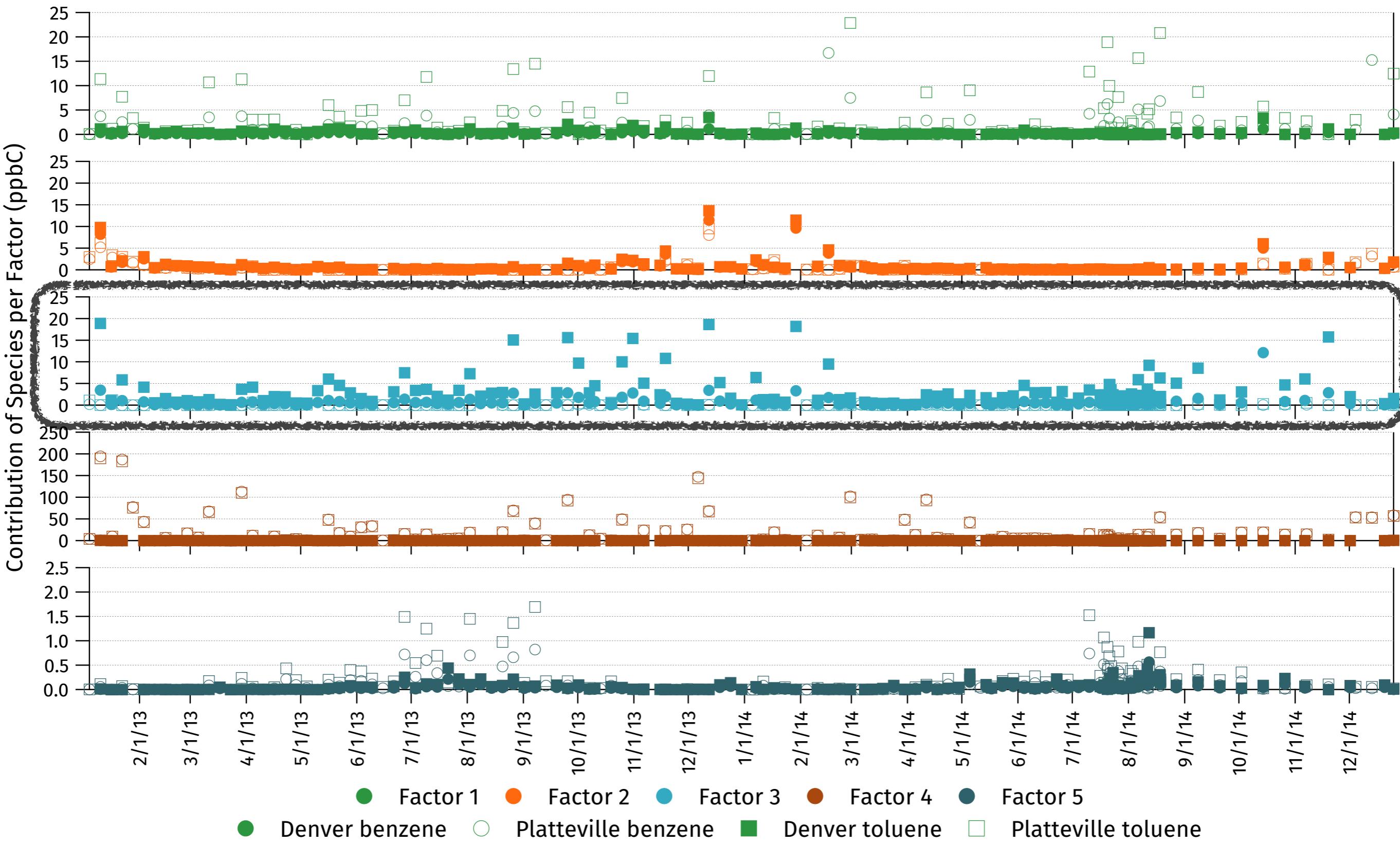


Time Series of Contributions: Benzene and Toluene

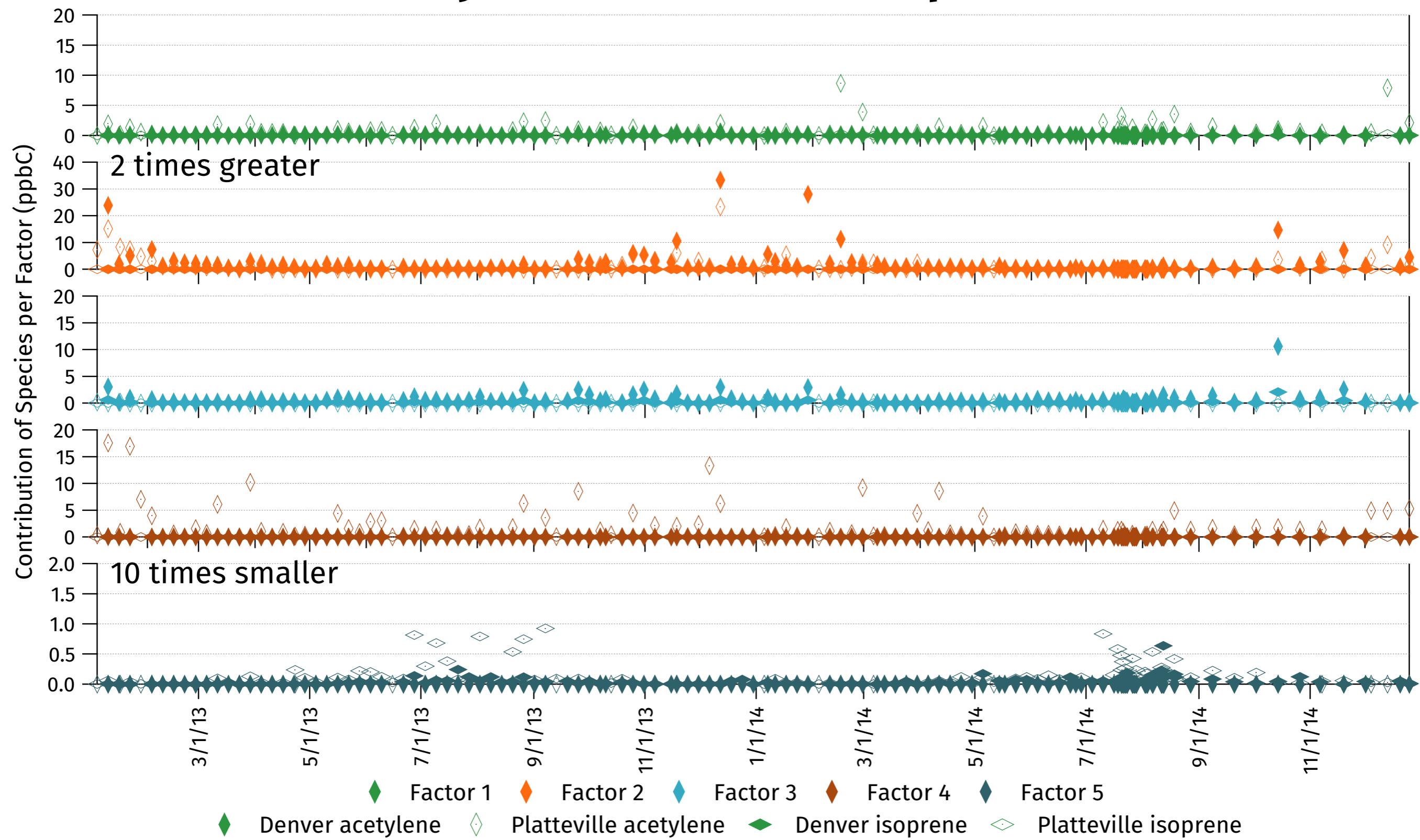


Time Series of Contributions:

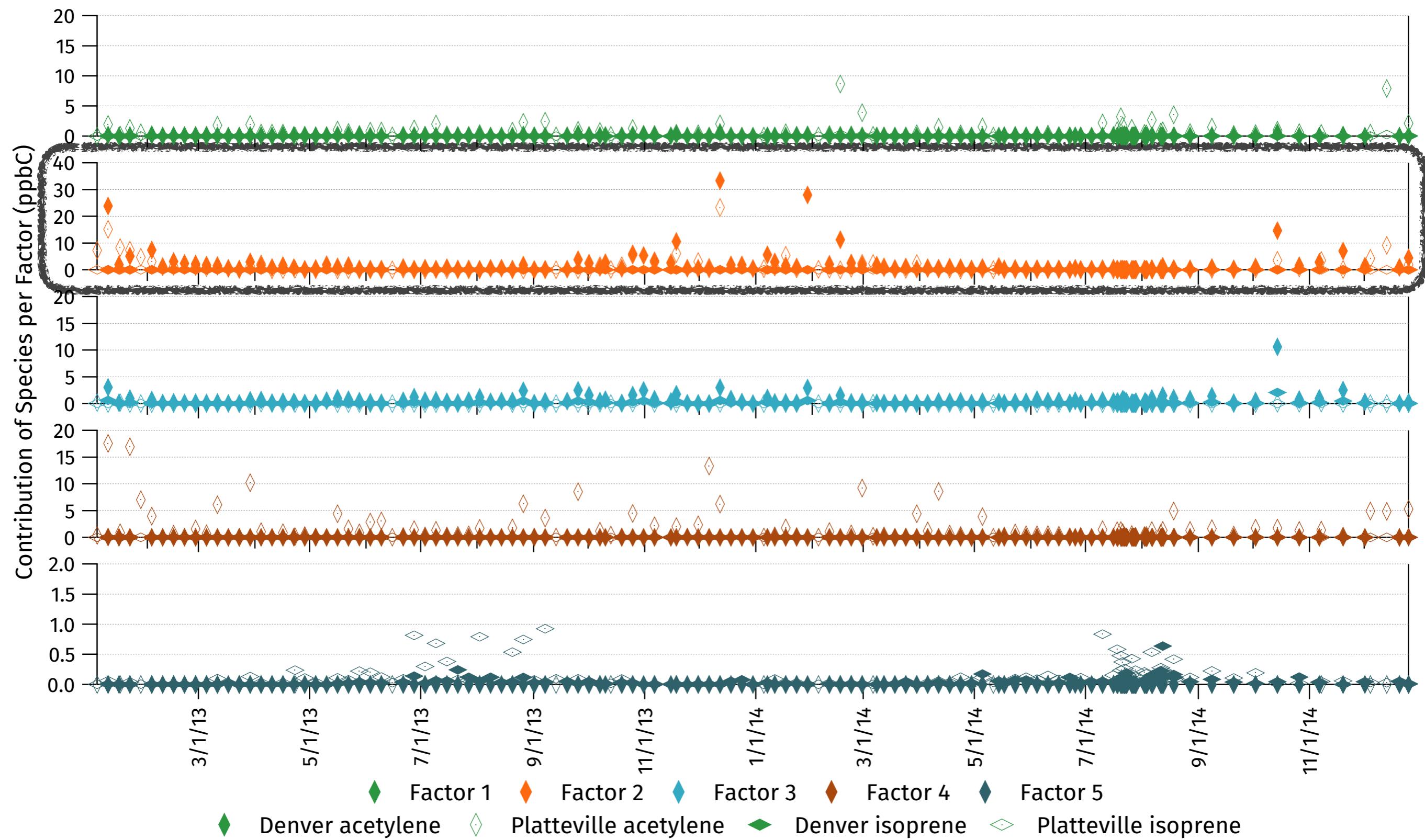
Benzene and Toluene



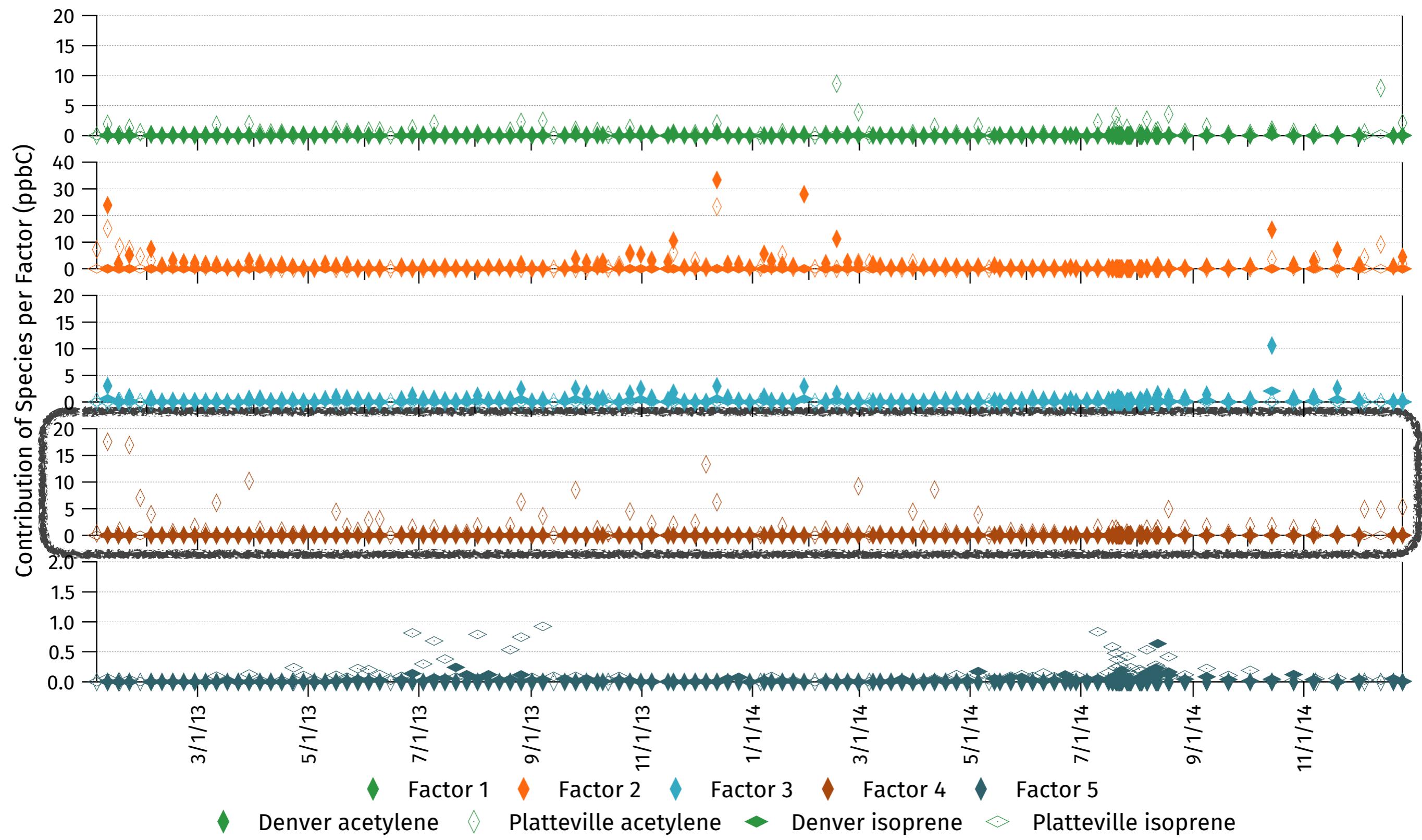
Time Series of Contributions: Acetylene and Isoprene



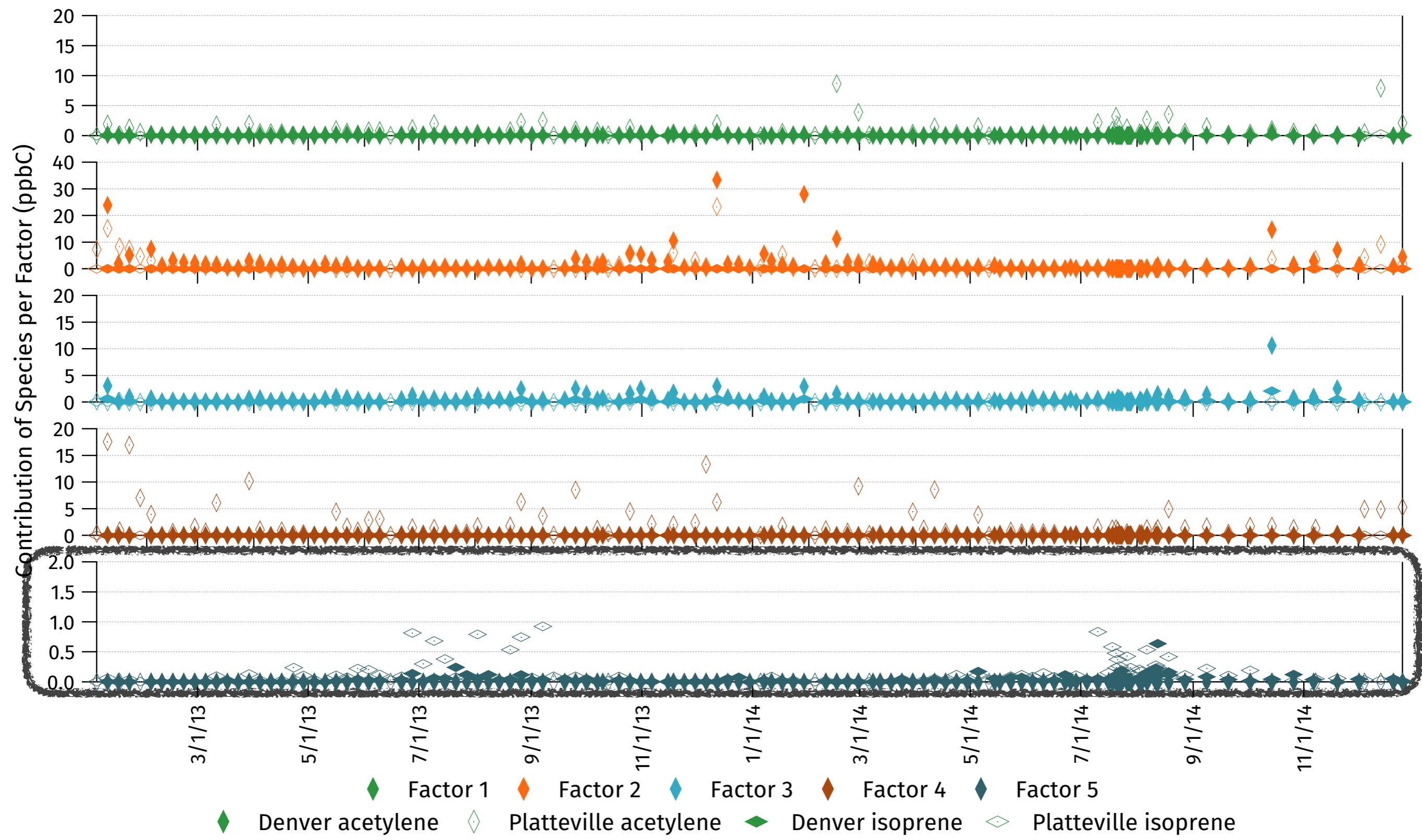
Time Series of Contributions: Acetylene and Isoprene



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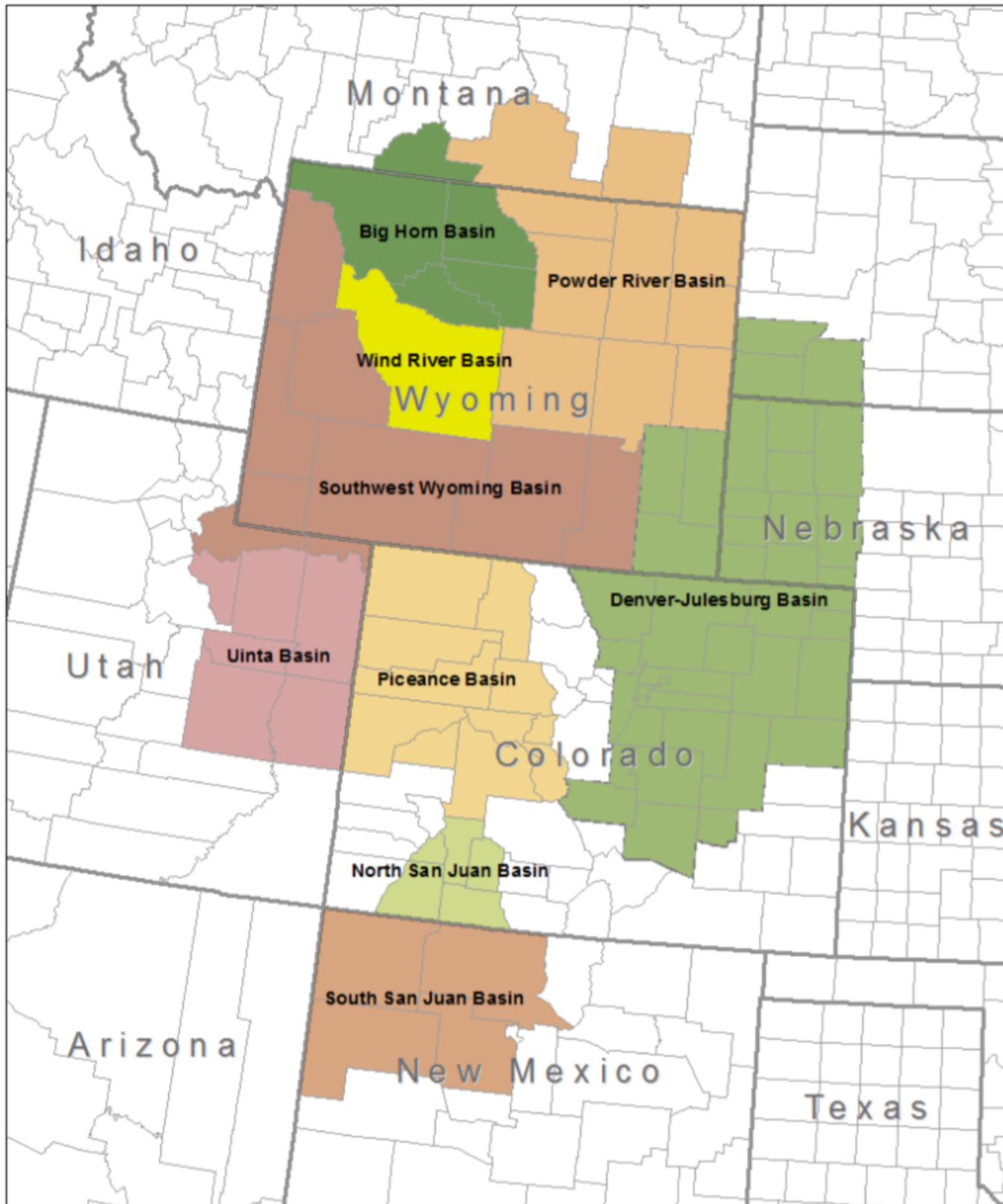


Time Series of Contributions: Acetylene and Isoprene



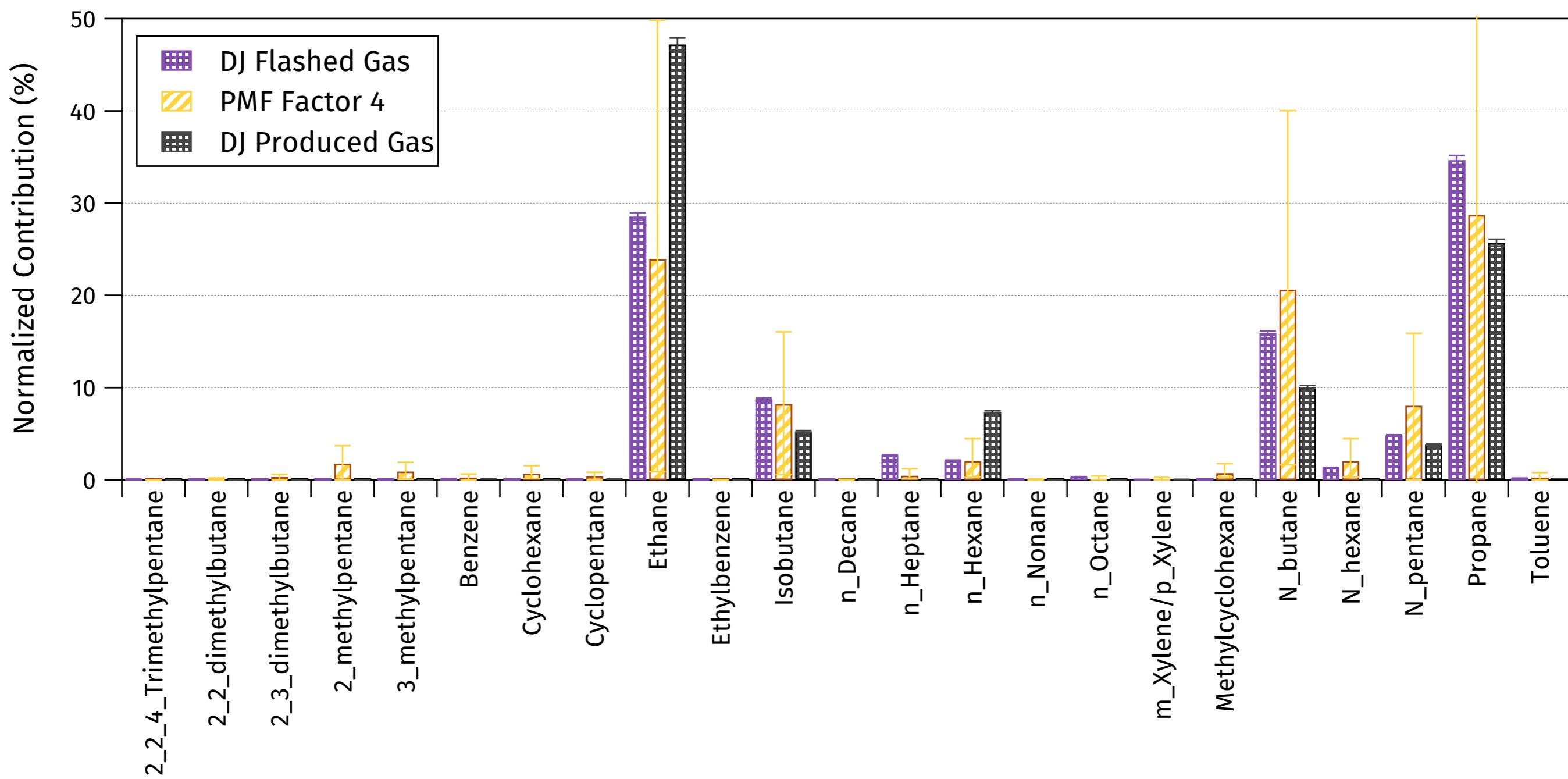
Western Regional Air Partnership

Phase III O+G Speciation Profiles



- Surveyed O+G producers in intermountain west basins for gas chromatography / mass spectrometry-based speciation
- Provided SPECIATE profiles with molar VOC content standard deviation to U.S. EPA (Shah et al., memo, 2015)

Evaluation of VOC Profile for DJ Flashed and Produced Gas Emissions



DJ Flashed and Produced gas VOC profiles from the Western Regional Air Partnership
Error bars: 1.45% standard deviation for DJ profiles | bootstrap 5th / 95th percentile

Conclusions & Next Steps

- 2013-2014 observations of factors composed of VOCs characteristic of oil and gas development were much higher in Platteville than in Denver.
- PMF suggests that BTEX compounds arise from other sources in addition to the oil and gas activity.
- The WRAP Phase III VOC emissions profiles for the Denver-Julesburg flashed and produced gas align well with the oil and gas factor from PMF.
- *Consider 2015 observations and implications for ozone based on VOC reactivity.*

Acknowledgements

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AirWaterGas



Sustainability
Research
Network