Sources and Reactivity of VOC Emissions from Unconventional Oil and Gas Development

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Motivations

✓ Improvements in extraction techniques have significantly supported large increases in U.S. unconventional oil and gas development (UOGD), raising concerns about potential air quality and health impacts.

✓ Recent studies[a,b] have measured substantially increased emissions of C_8-C_{10} alkanes associated with the use of synthetic drilling muds. These heavier n-alkanes are more reactive and can enhance ozone production, while nonane is an air toxic.

Objectives

✓ Characterize volatile organic compound (VOC) emissions from a synthetic Neoflo drilling mud by laboratory headspace analyses to develop a synthetic drilling mud VOC tracer profile.

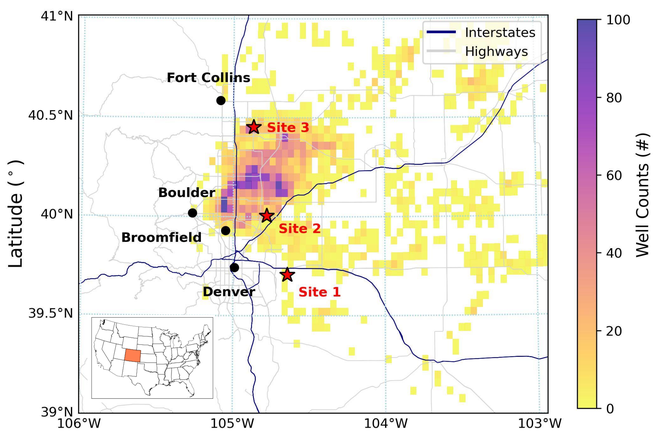
✓ Use positive matrix factorization (PMF) to identify characteristics of emissions from drilling mud volatilization in the field.

✓ Analyze hydroxyl radical reactivity of O&G and other sources to help assess contributions to regional ozone formation.

Conclusions

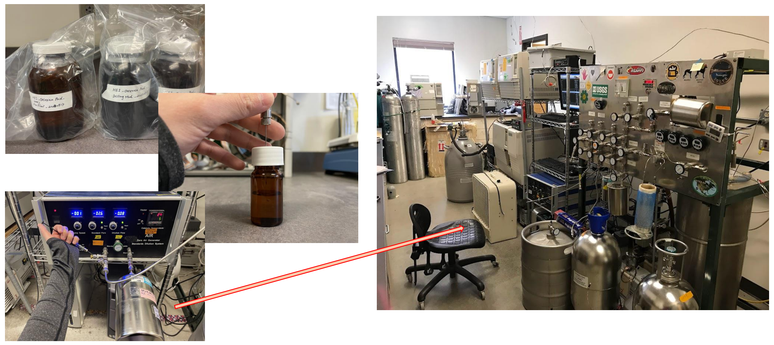
1. Fourteen VOCs were identified as major species outgassing from Neoflo-based drilling mud. The fractional composition matrix of these compounds is consistent across lab and field studies confirming this VOC "fingerprint" as a robust way to identify influence of Neoflo-based drilling mud VOC emissions in ambient air.
2. PMF analyses of VOC samples collected near UOGD operations identified 6 source factors. O&G-related factors contributed an average 48% O&G to OH reactivity across the study.

Measurements



▲ Samples were collected during UOGD pre-production and production activities at three locations (red stars) in the Denver-Julesburg basin.

Analysis Methods



▲ Neoflo-based drilling mud samples were provided by the operator at site 2. A series of headspace VOC analyses of both pure Neoflo drilling fluid and of a recycled drilling mud sample were conducted in our lab at CSU.

▲ The EPA positive matrix factorization (PMF) model was used to apportion sources of VOCs measured near UOGD operations.

▲ The OH reactivity for individual species and the total reactivity were calculated using the equations below.

$$OHR_{VOC_x} = k_{OH\&VOC_x} \times [VOC_x]$$

$$OHR_{total} = \Sigma(k_{OH\&VOC_x} \times [VOC_x])$$

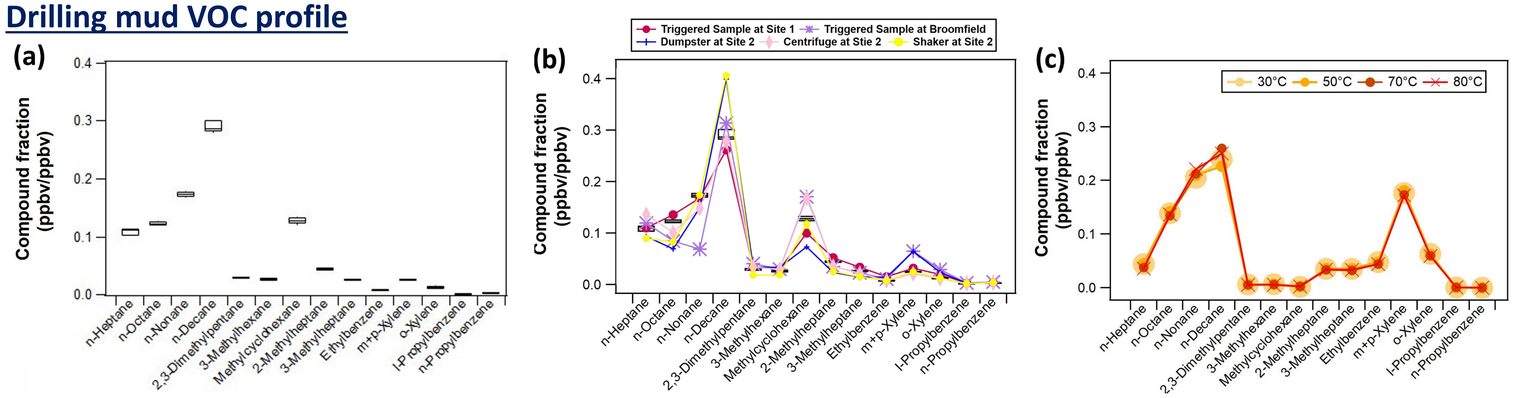
References

a. Ku, I.-T., Zhou, Y., Hecobian, A., Benedict, K., Buck, B., Lachenmayer, E., Terry, B., Frazier, M., Zhang, J., Pan, D., Low, L., Sullivan, A., Collett, J.L., 2024. Air quality impacts from the development of unconventional oil and gas well pads: Air toxics and other volatile organic compounds. Atmospheric Environment 317, 120187. https://doi.org/10.1016/j.atmosenv.2023.120187

b. Lachenmayer, E. K., Ku, I.-T., Hecobian, A., Benedict, K. B., Zhou, Y., Buck, B., and Collett, J. L., 2024. Source apportionment of airborne volatile organic compounds near unconventional oil and gas development. *Environ. Res. Commun.* **6** 101013. 10.1088/2515-7620/ad82b2

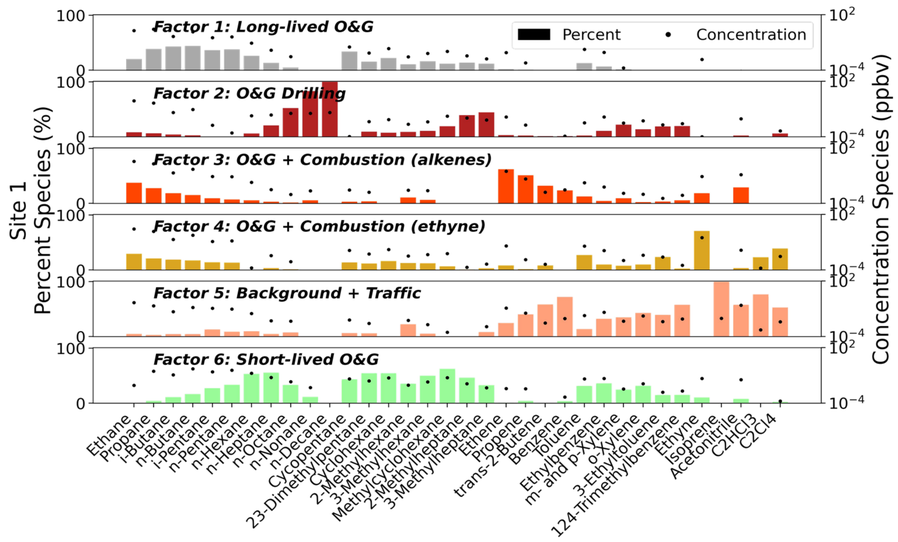
Results & Discussions

Drilling mud VOC profile

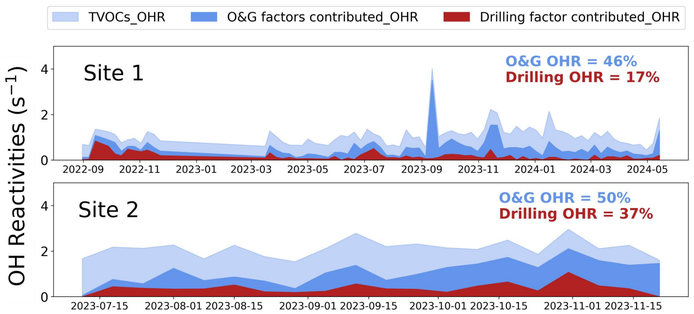


▲ (a) Fractional contributions of 14 key VOCs in replicate headspace analyses of recycled Neoflo-based drilling mud. (b) Fractional contributions of 14 key VOC in several drilling emission plume/source samples. (c) Compound profile variation in headspace samples at different temperatures.

Source appointment analysis and OH reactivity



◀ Six PMF source factors were identified from near-pad VOC analysis at Site 1. An O&G drilling factor (contained high C_8-C_{10} hydrocarbons) contributed an average of 18% to measured VOCs, highlighting the importance of this drilling mud outgassing source.



◀ Calculated OH reactivities. We see an average 48% O&G contribution to OH reactivity of measured VOCs across the full study. The drilling factor is a large contributor during drilling operations at sites 1 and 2.

Acknowledgements

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