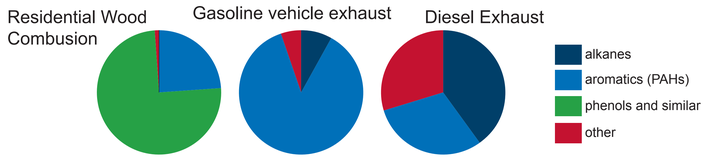
Contribution of Intermediate Volatility Alkanes and Polycyclic Aromatic Hydrocarbons to Organic Aerosol

Havala O. T. Pye, George A. Pouliot, Michael Lewandowski, John H. Offenberg, Tadeusz E. Kleindienst, Deborah Luecken
National Exposure Research Laboratory, US Environmental Protection Agency, Research Triangle Park, North Carolina

Introduction

Sources of organic compounds, such as wood burning, gasoline exhaust, and diesel combustion can emit gas-phase intermediate volatility compounds (IVOCs, saturation concentrations ~10^5 μg/m^3). These compounds include species such as long-chain alkanes (~C12-C19 n-alkanes) as well as polycyclic aromatic hydrocarbons (PAHs, e.g. naphthalene).



Species sampled and identified only in the gas-phase on the filter/PUF sampling train (indicative of IVOC volatility) from Schauer et al. [1999, 2001, 2002].

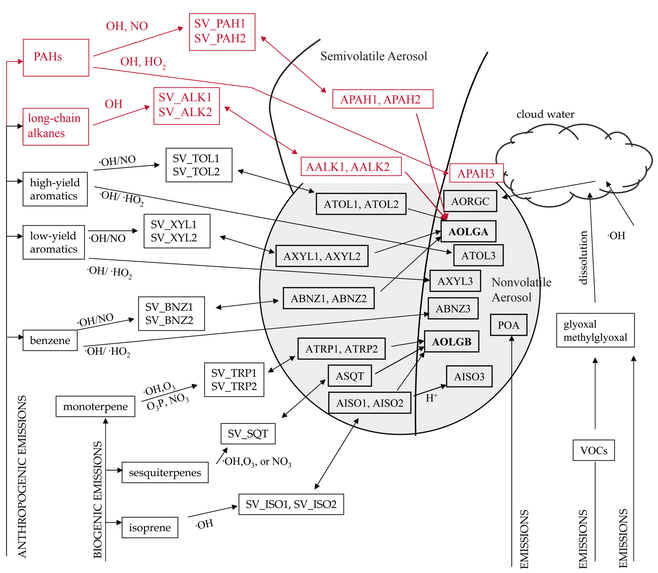
After emission to the atmosphere, these compounds can oxidize to form lower volatility compounds that partition to the aerosol phase. The yield of aerosol from these compounds depends on their structure as well as the conditions under which they are oxidized (high-NO_x vs low-NO_x).

Current CMAQ treatment of intermediate volatility compounds:
CMAQ v4.7.1 treats SOA from alkanes (including intermediate volatility alkanes) in the SAPRC mechanism. Although not explicitly treated, many PAHs are contained within existing emissions that have SOA yields based on xylene.

Objectives:
- Update the parameterization for SOA from alkanes to include information on the length and structure of the alkanes and add SOA from PAHs with yields according to a PAH surrogate species (naphthalene)
- Estimate the contribution of alkanes and PAHs to ambient organic aerosol

Updated CMAQ SOA Scheme

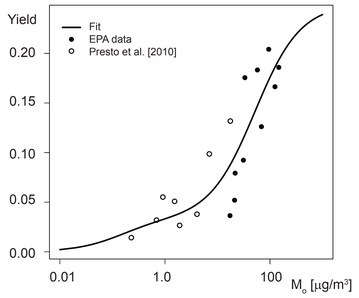
Based on Carlton et al. [2010] schematic of CMAQ v4.7.1 with updates shown in red



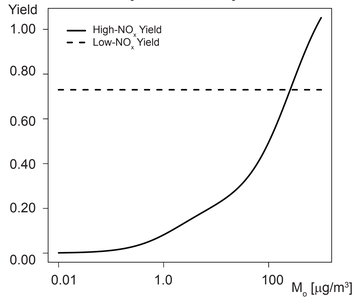
Baseline SOA Yields

Two species form the basis for the alkane and PAH SOA yields: n-dodecane ($C_{12}H_{26}$) for alkanes and naphthalene ($C_{10}H_8$) for PAHs.

n-dodecane yield vs. organic aerosol loading



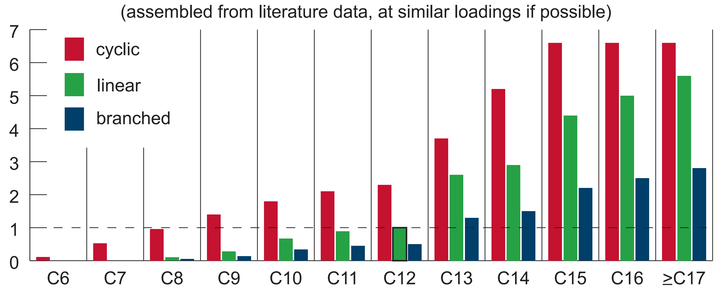
naphthalene yield vs. organic aerosol loading [Chan et al. 2009]



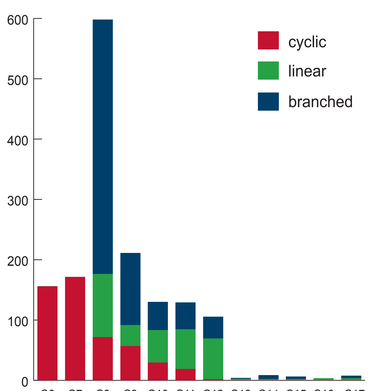
Adjustment for Alkane Structure

Since not all alkanes behave like n-dodecane, the dodecane yield/precursur emissions are adjusted to account for different length and structure (cyclic, linear, branched) alkanes.

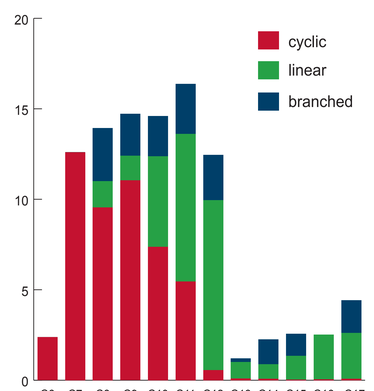
SOA yield relative to n-dodecane for different length and structure alkanes (assembled from literature data, at similar loadings if possible)



12km CMAQ CONUS Domain-wide emissions of alkane SOA precursors for 2006 (ktons/yr, based on NEI and SPECIATE)



Domain-wide contribution to alkane SOA by length and strucuture (percent, sum = 100%)



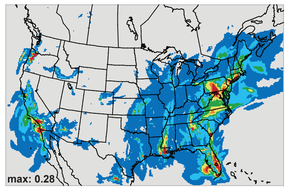
Emissions

SAPRC07 Species	Annual Domain Wide Emissions [kton/yr]	Fraction Forming SOA [% by mass]
ALK4	2470	11%
ALK5	1880	67%
ARO2	738	10% as PAH, 90% as xylene

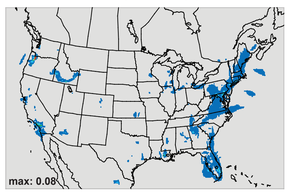
Surface Level Organic Aerosol

January 11-24, 2006

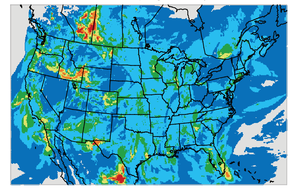
Maximum alkane SOA



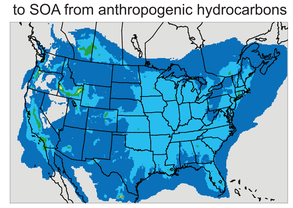
Maximum PAH SOA

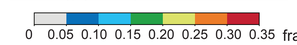


Maximum contribution of alkanes+PAHs to SOA from anthropogenic hydrocarbons



Mean contribution of alkanes+PAHs to SOA from anthropogenic hydrocarbons





Summary

- Cyclic alkanes (C6 to C19) are predicted to contribute about half of the alkane SOA due to their high yields.
- IVOC alkanes (C12 to C19) contribute about 25% of alkane SOA, but could contribute more if emissions were missing from the inventory.
- Alkanes and PAHs contribute modest amounts of aerosol; together they are predicted to constitute ~10 to 20% of SOA from anthropogenic hydrocarbons during January 11-24, 2006.

These parameterizations are expected to be part of CMAQv5.0.1.

Acknowledgements

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