

Hopanes Degradation: New Observational Evidence and Their Incorporation into Chemical Mass Balance Source Apportionment of PM_{2.5}

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The chemically unstable and semi-volatile nature of molecular markers is among the major concerns in receptor model source apportionment of airborne fine particulates (PM_{2.5}). This hampers our way towards a more reliable estimation of source contributions, which is crucial for optimized air quality control in polluted areas. Vehicular exhaust (VE) is an important factor contributing to PM_{2.5} pollution in urbanized areas. Quantifying its source contribution estimate by receptor modelling has so far been relying mainly on hopanes, a group of molecular markers for fossil fuel combustion sources. Evidence for their atmospheric instability from both ambient measurements and chamber studies has been emerging. Overlooking atmospheric degradation would unarguably underestimate the source contribution, but studies about determining the bias has hitherto been scarce.

We will share some findings from analysing PM_{2.5} chemical speciation data, particularly C₂₇–C₃₁ hopanes and elemental carbon (EC), in two urban sites of the Pearl River Delta, a polluted co-urbanized region in China. Evidence for atmospheric hopanes degradation through investigating ratio-ratio plot normalized against EC will be shown. We will also present the first result of investigating the ratios between hopanes abundance normalized by the least reactive homologue in ambient PM_{2.5} and that in representative VE source profiles, to further corroborate hopanes degradation. This method could potentially be used in other regions to determine whether hopanes degradation exists.

We deployed the effective variance-chemical mass balance (CMB) model to apportion organic carbon (OC) in PM_{2.5} and subsequently total PM_{2.5}, with special emphasis on determining the bias arising from hopanes degradation. The effect was incorporated by applying degradation factors derived from pseudo-first-order atmospheric oxidation to ambient hopanes concentrations. The extent of degradation was individually determined for each sample through varying residence time between source and receptor until the statistical performance of CMB solution reaches the optimum. Our results reveal that accounting for hopanes degradation would increase the OC associated with VE by a factor of 2.1 ± 0.8 (average \pm standard deviation) from 1.00 ± 0.68 to $1.84 \pm 1.02 \mu\text{g}/\text{m}^3$ (9.0 vs. 16.7 % of total mass), corresponding to 4.30 ± 2.56 and $8.01 \pm 3.76 \mu\text{g}/\text{m}^3$ (8.7 vs. 15.1 %) of PM_{2.5}. The method we developed could be used to improve PM_{2.5} source apportionment in other urban locations with significant vehicular emissions.