Environmental Science: Atmospheres

Electronic supplementary information for

URMELL – Part II: Semi-explicit isoprene and aromatics gasSOA modelling

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Supplement S1

Supplement S1 contains a x-y diagram illustrating the enthalpy of vaporisation (ΔH_{vap}) fit function, schematics of URMELL aromatics and isoprene chemical degradation mechanisms leading to SOA, a plot showing the daily accumulated rain for the 18th and 19th of May 2014 and a brief summary of simulated gasSOA concentration for sesquiterpene, monoterpene, BIGALK and BIGENE.
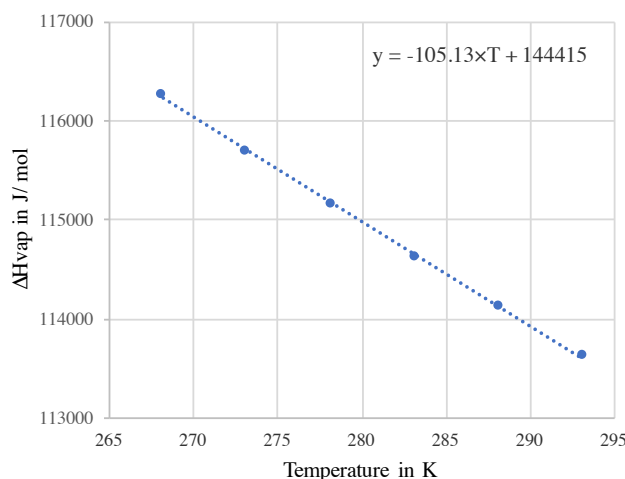
Fig. S1-1: Enthalpy of vaporisation ($\Delta H_{vap}(T)$) as a function of temperature (T) with the linear fit function for DHHPEPOX.

S1.1 Explicit gasSOA through phase partitioning of aromatic and isoprene oxidation products

A brief summary, providing the major changes of aromatics compared to JAMv2b[1] necessary for explicit gasSOA treatment with URMELL. The reaction of aromatic phenoxy radicals (C6H5O, CATEC1O) with NO_2 would produce no reaction products, while in URMELL[2], they lead to NPHEN and NCATECHOL, which are itself considered SOA precursor substances. Their further oxidation generates multiple even higher oxidized and non-volatile compounds. The latter are hydroperoxides with one or multiple hydroxyl and nitro groups, which are lumped into one non-volatile end product NAROMOLOOH, which is not undergoing further chemical degradation. Furthermore, the formation of organic nitrates (BENZN, TOLN, XYLNO3) from peroxy radicals of initial aromatic OH oxidation with NO is considered. Additionally, the SOA channel from the reaction of phenolic compounds (PHENOL, CRESOL) with NO_3 leading to NPHENOLOOH and NCRESOOH is included. The further reactions of bicyclic peroxy radicals from non-functionalised aromatics (BENZO2, XYLO2, TOLO2) leads to the production of furanones and from phenols (PHENO2, CRESO2) to quinones. MALANHY (leading to MALANHYOOH) is formed via further reactions of bicyclic peroxy radicals from nitrophenols and BENZOOH, but has also formation pathways not related to aromatic compounds, such as unsaturated organic acids (BIGACID1, BIGACID2, BIGAID3) and acyl peroxy radicals (DICARBO2, MALO2, MDIALO2). For more details on MALANHY pathways the reader is referred to Luttkus et al.[2]. For toluene and xylene, the reaction products are lumped into benzene or toluene product classes, where feasible to reduce the complexity.

Species not implemented in the JAMv2b, but in URMELL, are highlighted in bold, semi- and low-volatile SOA precursor substances in blue and non-volatile products in red. Images for the chemical structures are e.g. taken from the MCM3.3.1 (https://mcm.york.ac.uk/MCM), Wennberg et al.[3], Vereecken et al.[4] or are created using GECKO-A (http://geckoa.lisa.u-pec.fr/index.php)
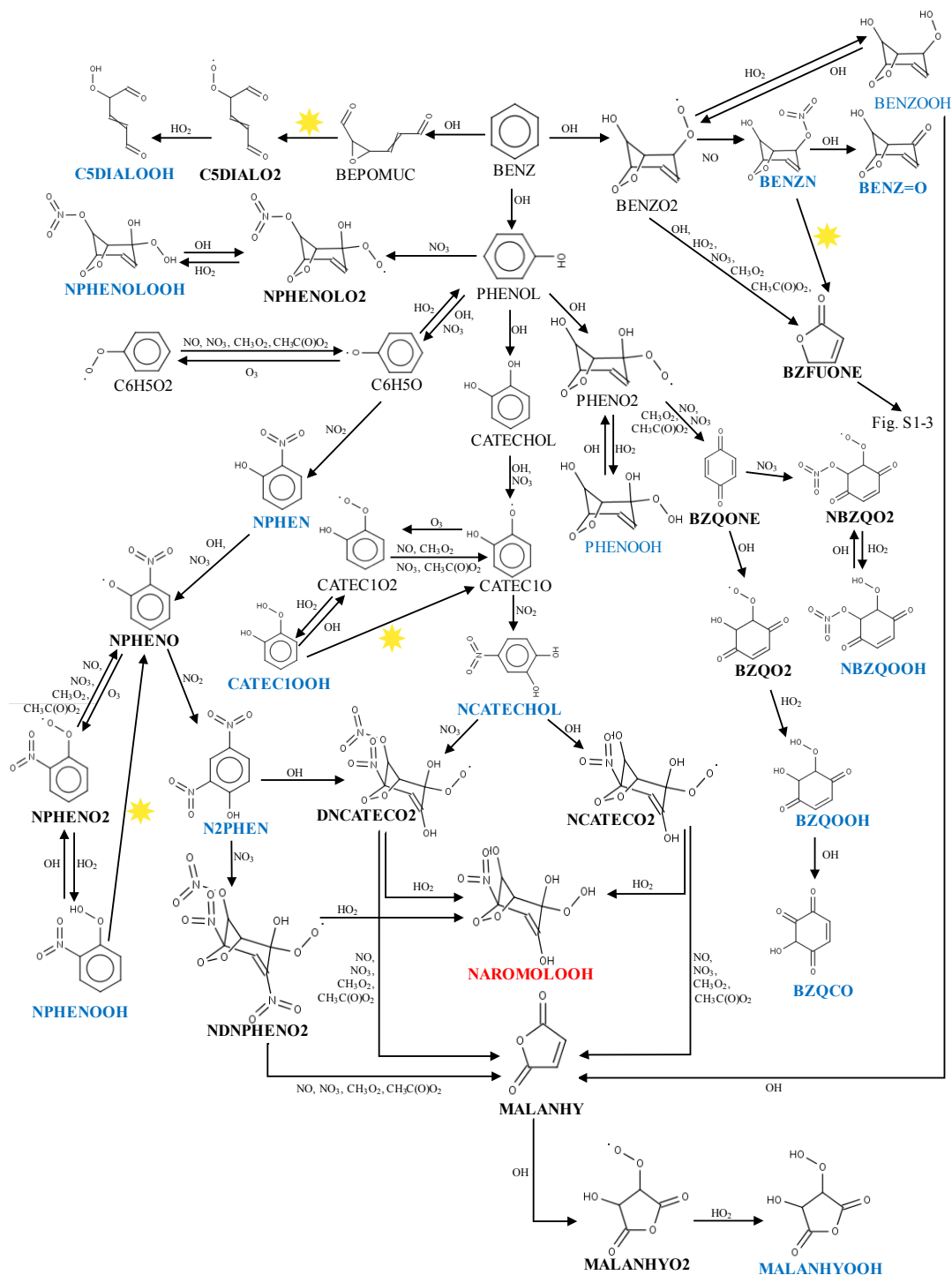

Fig. S1-2: Schematic degradation mechanism of benzene (BENZ) in URMELL leading to SOA precursor substances. New species highlighted in bold, compounds partitioning into the particle phase in blue and non-volatile products in red.
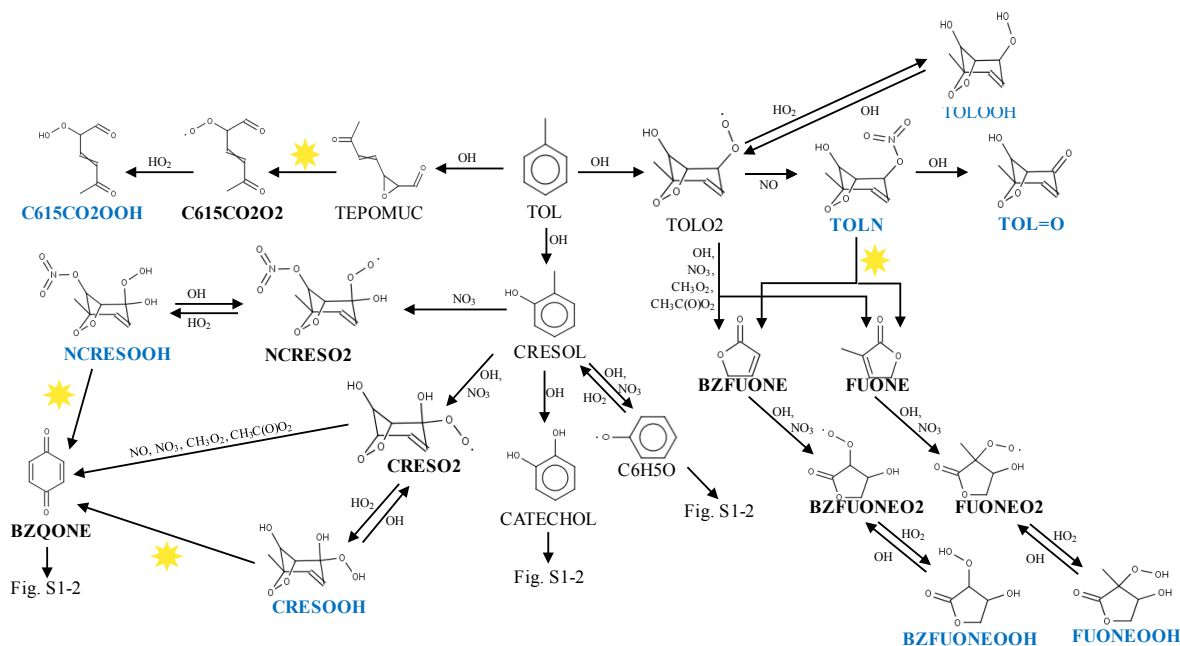
Fig. S1-3: Schematic degradation mechanism of toluene (TOL) in URMELL leading to SOA precursor substances. New species highlighted in bold, compounds partitioning into the particle phase in blue.
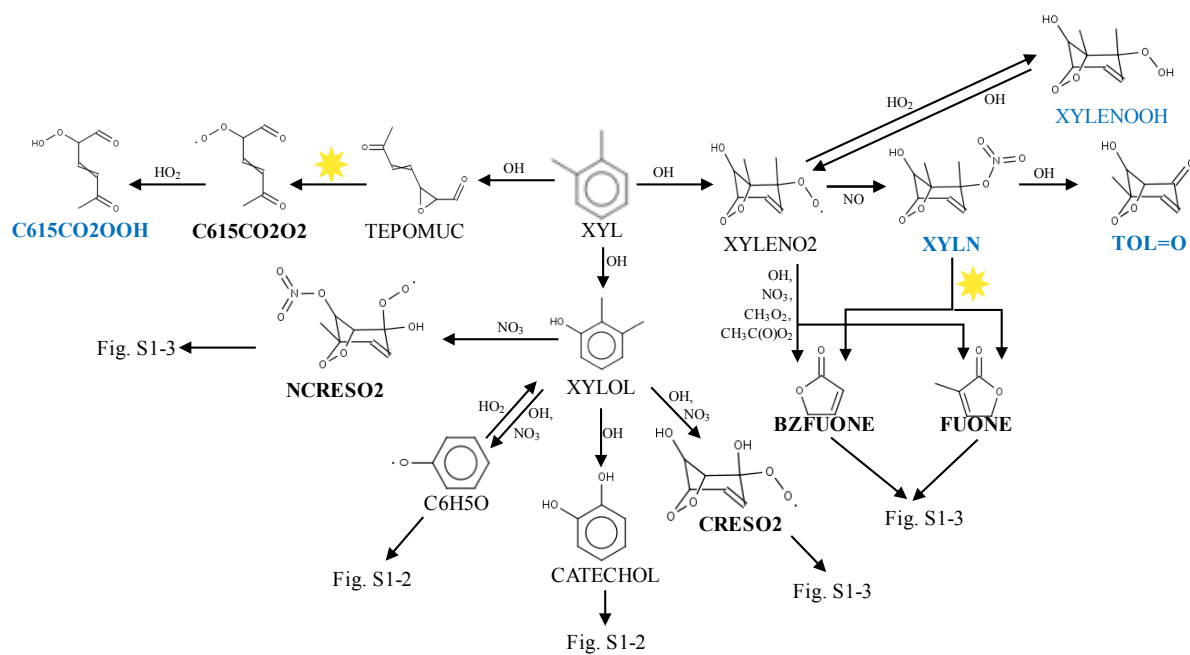

Fig. S1-4: Schematic degradation mechanism of xylene (XYL) in URMELL leading to SOA precursor substances. New species highlighted in bold, compounds partitioning into the particle phase in blue.

Fig. S1-5: Schematic degradation mechanism of initial OH isoprene (C5H8) oxidation in URMELL leading to SOA precursor substances. New species highlighted in bold, compounds partitioning into the particle phase in blue. Big arrows indicate similar pathways for multiple species marked by dashed boxes.
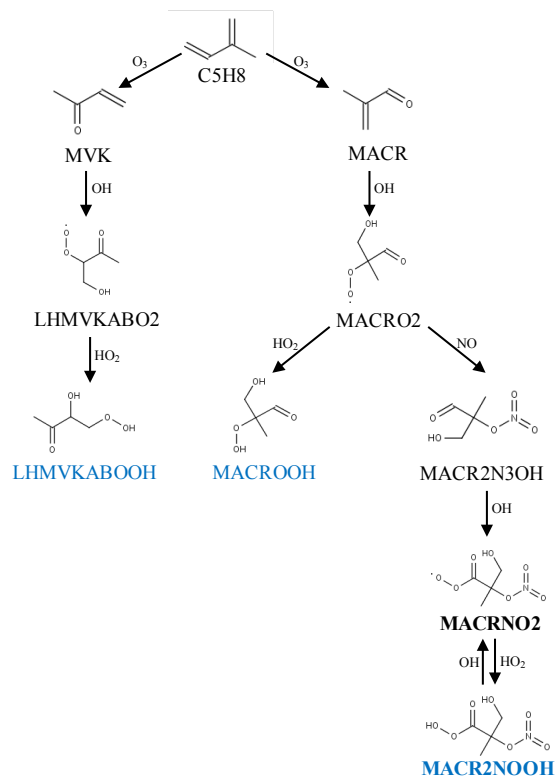
Fig. S1-6: Schematic degradation mechanism of isoprene (C5H8) ozonolysis in URMELL leading to SOA precursor substances. New species highlighted in bold, compounds partitioning into the particle phase in blue.
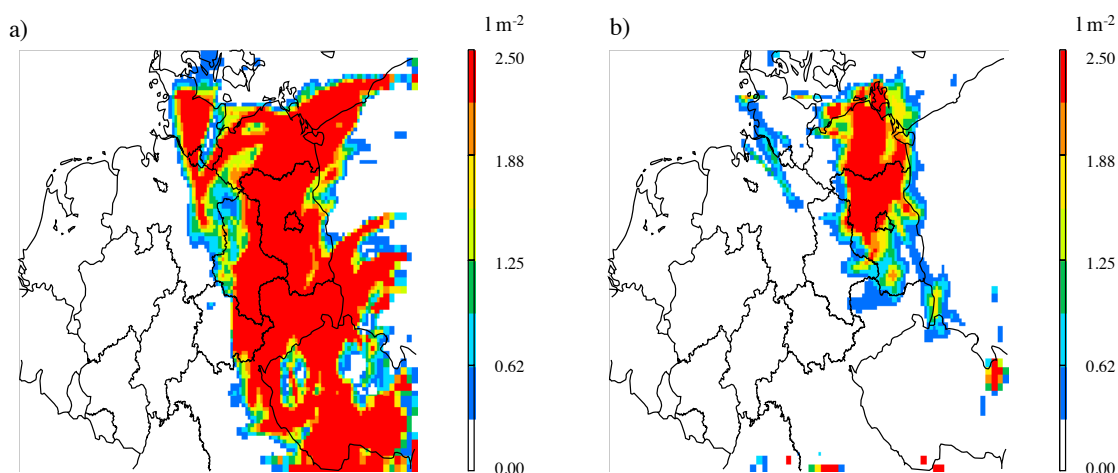
Fig. S1-7: Schematic degradation mechanism of initial NO₃ isoprene (C5H8) oxidation in URMELL leading to SOA precursor substances. New species highlighted in bold, compounds partitioning into the particle phase in blue. Big arrows indicate similar pathways for multiple species marked by boxes with dashed lines. IDHNBOO is produced via multiple pathways and marked with *. Its further degradation is only presented once (bottom left).

Fig. S1-7: Accumulated rain during the 18th a) and 19th b) of May 2024 for the model domain.

S1.2 Simulated gasSOA from other precursors

To provide a short outline and to emphasise future model development steps a brief summary of sesquiterpene, monoterpene, higher alkane and alkene SOA is given here. For sesquiterpenes (Fig. S4-1, S4-2), monoterpenes (Fig. S4-3, S4-4), alkanes (Fig. S4-5, S4-6) and alkenes (Fig. S4-7, S4-8), URMELL simulates lower SOA precursor and SOA concentrations. Especially for monoterpenes, there is a huge reduction in the north-east at 3 UTC in the area of heavy rain events (Fig. S4-3, S4-4). In general, the gas-phase analysis[19] already indicated restrictions with the currently implemented monoterpene chemistry mechanism and identified lower O_3 concentrations in monoterpene emission dominated areas (e.g. pine forests). Here, the lower amount of available oxidising partners also hinders the production of SOA precursor substances not just for monoterpenes but also for sesquiterpenes, which frequently react with O_3. Besides the differences for modelled oxidants, the slower reaction rate constants for monoterpenes in URMELL compared to RACM lowers also the production of SOA precursor substances. The applied SOA yields for the lumped species BIGALK und BIGENE as described in section 2.4. lead to one magnitude lower concentrations (Fig. S4-5 – S4-8). But as already stated, the yields for BIGALK and BIGENE should be seen as minimum contribution here. Extending the explicit SOA scheme to monoterpenes, alkane and alkene requires further chemical mechanism as well as SOA scheme development and will be addressed in the near future.