Unveiling potent toxic chemicals associated to primary or aged (secondary) wood combustion particles: a bio-analytical approach

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Residential wood combustion (RWC) is a significant source of fine particulate matter ($PM_{2.5}$) in ambient air especially in winter. Due to large amounts of volatile and semi-volatile organic compounds (VOCs and SVOCs) emitted, this source also induces the formation, through atmospheric photo-(oxidation) processes, of secondary organic aerosols (SOA) which account for a significant fraction of $PM_{2.5}$. As PM are complex mixtures, chemical analyses alone cannot fully characterize them nor identify unknown bio-active species. Implementing complementary integrated strategies, combining effect-based assessment and analytical methods (bio-analytical approach) can allow to evaluate the overall PM biological activity and reveal the presence of potent toxicological compounds. In this context, the main objectives of this work were first, to assess and compare, using in vitro bioassays, the biological responses of the primary and aged RWC PM emissions, as well as of SOA formed from the oxidation of key precursors largely emitted by biomass burning processes namely PAHs and furans; and second, to identify, using effect-directed analysis (EDA), the key species involved in the observed biological responses. The daytime (OH radicals) or nighttime (NO_3 radicals) atmospheric aging of 4 pure PAHs and 3 furans, or RWC emissions, was simulated using a Potential Aerosol Mass - Oxidation Flow Reactor (PAM-OFR). RWC experiments have been carried out using two modern residential heating appliances (logwood and pellets stove) under different output conditions (nominal and reduced). The biological responses of the generated PAHs and furans SOA, as well as primary and aged RWC PM, were assessed using in vitro bioassays targeting different modes of action (aryl hydrocarbon receptor (AhR), (anti)estrogenicity, and (anti)androgenicity). Selected active samples were fractionated by liquid chromatography and fractions obtained were individually tested for their AhR activity. Non-targeted screening (NTS) chemical analyses were then performed by GC-MS and GC(×GC)-ToF-MS on the most potent fractions to identify the bioactive compounds. Results obtained showed that only the SOA formed from the oxidation of PAHs induced significant AhR-mediated activity, which was even higher when SOA were formed through NO_3 radical oxidation processes. The biological responses observed for RWC emissions, mainly AhR (and partial anti-androgenic), were dependent on the heating appliances and output conditions. They typically decreased, or remained comparable, after aging due to the degradation or inactivation of active primary ligands and/or the formation of new active compounds. Targeted chemical analyses of 45 PAHs, oxy- and nitro-PAHs explained only 1 to 23% of the observed AhR biological activity. Finally, EDA identified 18 AhR ligands that were confirmed for their individual activity, including 6 in PAH SOA samples and 2 in RWC emissions never reported before. Overall, this work has shown the relevance of combining effect-based methods with NTS chemical characterization to discover new key PM bioactive constituents that might be later monitored in ambient air as well as in combustion emissions.

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