Molecular Identities of Wildfire-Derived Quinones across Three North American Ecosystems

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Abstract

Wildfires generate pyrogenic organic matter, including redox-active quinones that influence carbon storage and turnover in soils. However, their molecular identity across ecosystems remains poorly constrained due to technical challenges. This study applied chemical tagging-enabled metabolomics to identify quinones in ash and soil samples from three North American wildfires occurring on temperate forest (Caldor fire, USA), boreal forest–wetland (Red Lake fire, Canada), and tundra (Kougarok fire, USA) ecosystems. Screening showed 112, 326, and 174 quinone candidates in ashes of each fire, respectively, with average molecular weights of 365.48, 327.30, and 293.10 Da. Quinones in Caldor and Red Lake ashes had higher average molecular weight compared to control soils, while Kougarok ash quinones showed lower average molecular weight. Ash quinones generally showed lower H/C ratios compared to controls in Caldor and Kougarok fires, consistent with greater aromaticity in fire-derived quinones. The boreal forest–wetland ecosystem (Red Lake) had the highest number of quinones detected compared to lower- or higher-latitude ashes. The ash-unique quinones ranged in the chemical space of [H/C 0.50–2.08, O/C 0.00–0.62] for temperate fire samples, while tundra quinones spanned [H/C 0.71–2.17, O/C 0.08–0.60]. Structure annotation uncovered a hydroxy-hydrazino long-chain benzoquinone (C14:1 side chain) ubiquitously occurring in all ashes across different ecosystems. Molecular networking analysis of the annotated candidates further revealed related quinone families through reactions spanning alkylation, oxidative aging, nitrogen incorporation, and partial reduction, with matrix-dependent distributions reflecting the interplay of combustion and post-fire soil chemistry. This study uncovered the molecular-level chemical properties of quinones in wildfire-impacted ashes and soils, as well as the structures for quinones ubiquitous to wildfires occurring across temperate to tundra ecosystems.