Sources of hydroxyl radical photochemically produced in headwater streams from nitrogen-saturated forest

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Hydroxyl radical (·OH) is the most oxidative reactant among the active oxygen species and oxidation reactions with ·OH are involved in important biogeochemical processes. In this study ·OH photoformation rate ($R_{OH}$) was determined in headwater stream samples from nitrogen (N)-saturated forests, 1) to quantify the sources of ·OH in headwater streams and 2) to evaluate the nitrate ($NO_3^-$)-induced enhancement of ·OH formation in stream water caused by N saturation in forested watersheds. Stream water fulvic acid extracted from the forested watersheds was used to quantify the contribution of dissolved organic matter (DOM) to $R_{OH}$. The results showed that almost all (97%; 81-109%) $R_{OH}$ sources in our headwater stream samples were quantitatively elucidated; the photolysis of $NO_3^-$ (55%; 34-75%), nitrite [N(III)] (2%; 0.5-5.2%), and DOM-derived ·OH formation, from which photo-Fenton reactions (18%; 12-26%) and the direct photolysis of fluorescent dissolved organic matter (FDOM) (22%; 10-40%), was successfully separated. FDOM, which accounted for 53% (24-96%) of DOM in total organic carbon bases, was responsible for ·OH formation in our headwater streams. High $NO_3^-$ leaching caused by N saturation in forested watersheds increased $R_{OH}$ in the headwaters, indicating that N-saturated forest could significantly change photoinduced and biogeochemical processes via enhanced ·OH formation in downstream water.

Keywords: hydroxyl radical, dissolved organic matter, nitrate, photo-Fenton reaction, stream, photoinduced processes