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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 NO3- (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