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Biogeosciences Discussions

Interactive comment on "The impact of four decades of annual nitrogen addition on dissolved organic matter in a boreal forest soil" *by* M. O. Rappe-George et al.

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Referee #3

Referee comment 1

The authors found an accumulation of DOC in B but not O horizon soils, no responses to changes in pH or ANC from the long term N addition, and an increase in SUVA in B horizons of fertilized plots which they suggest is due to a mobilization of old SOM. Their best correlation of DOC was with tree biomass, which increased strongly when fertilized with N.The authors also found an increase in the DOC:DON ratio after fertilization ended, suggesting the N in SOM was getting consumed or leached.

However, several of us read it and do not think these are valid explanations. You could have an increase in aromaticity from the partially decomposed lignin components that are leaching into the soil from excess tree biomass (i.e. presumably if they are making more biomass they would be making more litter which they refer to in the discussion ref. Saarsalmi et al. 2007). Especially since the authors make the case in the introduction that the DOC input to the mineral soil can be large (refs Zech and Guggenberger 1996, Kleja 2008) and that DOM is a significant source of C in B horizons (Guggenberger et al. 1994). They say in the discussion that "As there were no treatment effects in O horizon leachates, the increased DOC in mineral soil requires an explanation other than increased leaching of DOC from the overlying O horizon." We disagree. The O horizon solution may already be C saturated, overall C stock is increasing in O horizon.

Author reply: We understand this comment as follows: The elevated dissolved organic carbon, DOC, concentration in mineral soil could be due to increased input of DOC (or a change in its quality) originating from overlying O horizon. However, our measurements do not support this hypothesis. We sampled soil water both within (Rhizon lysimeters) and immediately below (Zero tension lysimeters) the O horizon. These data did not show any treatment effects, neither on DOC quantity, nor on quality, in O horizon micro-, and macropores (and hence mineral soil DOC input from the overlying O horizon). We therefore concluded that the elevated DOC in mineral soil required an explanation other than increased leaching from overlying O horizon. We do not consider the O horizon soil solution to be C saturated, the values we report here are not extreme (see for instance Aandahl Raastad and Mulder, 1999). Also, the fact that DOC was higher in 2009 than in 1995 contradicts the hypothesis that the soil solution was C saturated in 1995.

Referee comment 2

I think it is fine to suggest that root exudation in the mineral horizon may be stimulating priming which could be the source of the DOC increase, but I think the authors cannot rule out just straight leaching from the increased tree biomass/litter.

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Author reply: The referee raises an interesting question. It is most likely that the increased biomass brought about an increased belowground production of litter, a point we stress in our manuscript (see discussion, page 12449 lines 3 – 9). It is possible that the elevated dissolved organic carbon, DOC, with a stronger aromatic signal in mineral soil solution originated from the root-litter directly. However, sorption of DOC to mineral phase favors the sorption of hydrophobic, aromatic DOC (Kaiser et al., 1996; Kaiser and Guggenberger, 2000). Therefore, aromatic DOC directly originating from root-litter would be rapidly and strongly adsorbed, leaving the less aromatic, more hydrophilic DOC in solution. This does not rule out the possibility that a source of elevated DOC with higher SUVA was decomposition of root litter, however. Furthermore, increased production of DOC from root litter could over time saturate the mineral phase, leading to less efficient sorption (Guggenberger & Kaiser, 2003), manifesting as increased DOC. Finally, addition of mineral N can induce suppression of the extracellular enzymes phenol oxidase and peroxidase, resulting in increased bulk DOC and soluble phenolics (Waldrop & Zak, 2006). However, our study does not enable an exact quantification of the contribution from these possible sources to observed DOC in mineral soil solution. We therefore suggest to substitute the text on page 12449 lines 6-18 with:

"The treatment effects on DOC in mineral soil could take on three possible explanations, alone or in combination. First, it is possible that elevated DOC with a higher SUVA at 254 and 280 nm in mineral soil solution originated directly from the decomposition of belowground root litter. However, sorption of DOC to mineral phase favors sorption of DOC with an aromatic structure (Kaiser et al., 1996; Kaiser and Guggenberger, 2000). Additionally, increased production of DOC from decomposition of root litter could over extended periods of time saturate the mineral phase, leading to less efficient sorption (Guggenberger & Kaiser, 2003) and manifest as increased DOC. Second, the increased root litter/exudates could act with a priming effect on SOM in the mineral B horizon. Root litter/rhizodeposition might be a relatively easily available C source that stimulated decomposition of old SOM found in the mineral soil (Kuzyakov, 2002), resulting in increased DOC. As SUVA (at both 254 and 280 nm) in mineral B

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horizon leachates increased in the fertilized plots, sampled DOM likely contained more aromatic moieties (Dilling and Kaiser, 2002). These compounds are important for long-term sorptive preservation of OM in mineral soil (Kaiser and Guggenberger, 2000). Third, addition of mineral N to hardwood forests in Michigan, USA, induced suppression of the extracellular enzymes phenol oxidase and peroxidase with a concomitant increase in DOC and abundance of soluble phenolics (Waldrop & Zak, 2006)."

Also, in the revised version of our manuscript we will replace the last sentence in the abstract (page 12434, lines 21-23) with: "We propose three possible explanations for the increased DOC in mineral soil: i) the result of decomposition of a larger amount of root litter, either directly producing DOC, or ii) indirectly via priming of old SOM, or iii) a suppression of extracellular oxidative enzymes."

In the discussion (page 12451, lines 10-13) we substitute the existing sentence with "The effect of long-term N addition on mineral soil C balance was unclear as the source of the increased DOC in N amended plots could not be fully determined. This is a matter in need of further research."

Furthermore, in the revised version of our manuscript we would like to replace a sentence in the conclusion section (page 12452, lines 10-12) with the following: "Increased DOC in both the ongoing and terminated N treatment are likely the result of decomposition of a larger amount of root litter, either directly producing DOC, or indirectly via priming of old SOM, or a suppression of extracellular oxidative enzymes."

Referee comment 3

Another argument the authors make about this is that (line 15 p. 9) is that in mineral B horizon leachates, the terminated N treatment, N2, had the highest DOC, not the ongoing N1 treatment, which demonstrated that ongoing N addition did not fuel DOC but that DOC was more related to the accumulated amount of added N.' BUT, once you have the higher tree biomass (which was still increasing in 2009, Fig 3), you have higher litter input and higher leaching from that increased amount of litter that could be

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the source of DOC increases in the B horizon.

Author reply: We trust the proposed changes made in response to referee comment #2, with three possible explanations presented and discussed, take care of this issue. In addition, mineral soil DOC was higher in the N2 than the N1 treatment whilst standing tree stock was of similar volume.

References used in author comment: Aandahl Raastad, I., and Mulder, J.: Dissolved Organic Matter (DOM) in Acid Forest Soils at Gådsjön (Sweden): Natural Variabilities and Effects of Increased Input of Nitrogen and of Reversal of Acidification, Water, Air, & Soil Pollution, 114, 199-219, 1999.

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