This study reports on measurements of DOC quantity and quality, ferrous Fe, nitrate, P and pH in riparian soils for an agricultural headwater catchment in western France. Zero-tension lysimeters were installed in riparian soils at 15 cm depth. 17 lysimeters were sampled weekly to biweekly between November 2022 and June 2023. From data analysis, reductive Fe dissolution and the associated DOC mobilisation were found to be driven by the availability of nitrate. Redox driven mobilisation of DOC happed during the relatively cool and wet winter months.

General comments:

This is a well written paper that would benefit from the analysis of a few more aspects insufficiently addressed in the manuscript:

REPLY: We thank B. Selle for the postive evaluation of our work.

(i) The molar ratio at which Fe and DOC were mobilised should be reported and could be compared to ratios reported in the literature. This would indicate if the processes interpreted from the data are reasonable.

REPLY: The mean DOC:Fe(II) molar ratio was 142.4±285.5. This was higher than the DOC:Fe(II) ratio measured in experimental conditions (74.5±74.6) but similar than value measured on the field (134.4±25.6) by Lotfi-Kalahroodi et al. (2021) who aimed to investigate Fe reduction in the riparian area of our study catchment.

To compare our DOC:iron ratio it would have been necessary to measure Fe(III). However, if we consider a ratio between Fe_{tot} and Fe(II) of 4.8 based on Lotfi-Kalahroodi et al. (2021), our DOC:Fe ratio are 29.3±58.8. Keeping in mind that this is a rough estimation, the ratio at which DOC increases in soil waters is consistent with previous studies (e.g. Selle et al., 2019; Musolff et al., 2017; Grybos et al., 2009; Cabezas et al., 2013).

Following this comment, we plan to amend the manuscript, section 4.1:

“Regarding DOC, the mean DOC:Fe(II) molar ratio was 142.4±285.5. This was higher than the DOC:Fe(II) ratio measured in experimental conditions (74.5±74.6) but similar to value measured on the field (134.4±25.6) by Lotfi-Kalahroodi et al. (2021) who aimed to investigate Fe reduction in the riparian area of our study catchment. Fe(III) concentrations in soil waters were not measured, but, based on the work of Lotfi-Kalahroodi et al. (2021), we can estimate a ratio between total Fe and Fe(II) of 4.8. Keeping in mind that this is a rough estimation, our mean DOC:Fe ratio would be about 29.3±58.8, which is consistent with previous studies (e.g. Selle et al., 2019; Musolff et al., 2017; Grybos et al., 2009; Cabezas et al., 2013).”

(ii) Also, there may be an indirect mobilisation of DOC due to a pH increase with Fe reduction which could be evaluated from the data presented. Note that an indirect mobilisation of DOC with a pH increase would probably increase OC to Fe ratios compared to a pure mobilisation due to the dissolution of iron minerals.

REPLY: In fact the effect of pH on DOC mobilisation has also been investigated in the study site (Grybos et al., 2009). Results have shown that up to 60% of the release is due to DOC desorption caused by the pH increase that accompanies the reduction of Feoxyhydroxides in these soils. Although pH was variable among lysimeters, there was a positive relationship between DOC and pH (Figure 2), therefore supporting an indirect mobilisation of DOC linked to increasing pH associated with iron reduction.

Discussion will be modify to include these details:

“The nature of processes releasing DOC upon the reduction of soil-Fe oxyhydroxides in riparian soils of our study site has been studied in laboratory conditions (Grybos et al., 2009).

Results have shown that up to 60% of the release is due to DOC desorption caused by the pH increase that accompanies the reduction of Feoxyhydroxides in these soils, the remaining 40% being due to the dissolution of Fe-oxyhydroxides that strongly adsorb organic compounds previously bounded to surface minerals (e.g. Hagedorn et al., 2000). In good agreement with these results, soil DOC was positively related to pH (Supplementary Fig. S5)."

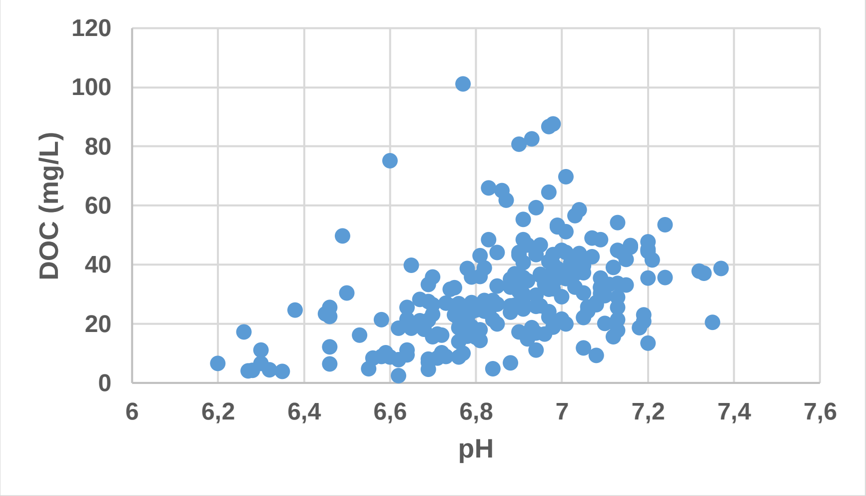

Figure S5 – DOC versus pH in our lysimeters.

Specific comments:

L39-42: Isn't this a contradiction? DOC export cannot be source and transport limited at the same time.

L54-56: This indicates a source limited DOC export, which contradicts the transport limitation stated above. I am confused. Perhaps, the conceptual model of source and transport limitation for DOC export needs to be explained better.

REPLY: Considering this comment and the previous one, we realized that indeed the formulation was not easy do understand as the notion of source or transport limited are time-scale dependant. To make our introduction more clear and more focus on the time-scale of the study, we suggest the following changes in the introduction:

"Numerous research carried out in temperate and boreal catchments have shown that headwater catchments are the main entry point of DOM into fluvial networks (Ågren et al., 2007; Creed et al., 2015) and identified riparian areas as the dominant sources of DOM at the catchment scale owing to their location at the terrestrial-aquatic interface (Sanderman et al., 2009; Lambert et al., 2014; Laudon et al., 2012; Winterdahl et al., 2014). The flushing of shallow organic-rich soil layers during storm events typically represents the majority of annual DOC loads (Inamdar et al., 2006), and the DOC versus discharge relationships during storm events show that DOC export is transport-limited at the event scale (Buffam et al., 2001; Zarnetske et al., 2018). Although geomorphological and climatic conditions regulate DOC loads in stream waters (Winterdahl et al., 2014; Laudon et al., 2012), DOC export at the annual scale is commonly conceptualized as a two-steps process in which DOM is produced and stored in the catchment during the hot and dry period, and then exported toward surface waters during the wet and cold period (Boyer et al., 1996). This two-steps process model often described in temperate catchments (Deirmendjian et al., 2018; Strohmenger et al., 2020; Wen et al., 2020; Ruckhaus et al., 2023) is also supported by numerous studies carried out in tropical (Bouillon et al., 2014), boreal (Tiwari et al., 2022), Mediterranean (Butturini and Sabater, 2000) or Arctic fluvial networks (Neff et al., 2006). However the processes regulating the size of the pool of riparian DOM remain unclear (Tank et al., 2018 and references below).”

L79: hypothesis instead hypothese

REPLY: ok.

L179: Is DOC part of the mineral composition of soil waters?

REPLY: No, this is not. Text has been modified:

“A principal component analysis (PCA) coupled to a clustering analysis was used to discriminate and group lysimeters based on the occurrence or absence of iron biodissolution in soil waters in order to investigate the temporal pattern of each cluster that would help to identify patterns compared to individual time series. For this reason, data (DOC, NO3-, SRP and Fe(II) concentrations and the relative contribution of PARAFAC components) were aggregated for each lysimeters and normalized.”

L284: I am not sure if Skerlep et al. is an appropriate reference here: Does this paper report really on Fe reduction during winter periods?

REPLY: Indeed, this was a mistake. We added Knorr et al. (2013) and Selle et al. (2019) as more relevant examples.

L316: delete biodissolution

REPLY: ok.

L317: delete as long

REPLY: ok.

L364-372: Here you again discuss your conceptual model of source versus transport limitations of DOC mobilisation. Perhaps a sketch of the conceptual model would help the reader to better understand this.

REPLY:

L384: Do you equate DOC production with redox driven mobilisation of DOC here?

REPLY: No, ‘several’ should be replaced by ‘another’.

L386: delete main

REPLY: ok.

L409: Trends were not previously discussed but are mentioned now suddenly in the conclusion section.

REPLY: In

Figure 4: Why is relation between Fe and DOC is closer than between Fe and P?

REPLY: Likely because SRP is also controlled by soil properties such as phosphorus speciation. We modified the text:

"As a consequence, large release of DOC occurred in soils grouped in the first cluster. Iron biodissolution also affected SRP, but the relationships was weaker suggesting that the reductive dissolution of soil Fe was not the primary driver of SRP concentrations in soils. For instance, soil properties, and more specifically soil phosphorus content and speciation, have been shown to strongly regulate SRP in soil waters of the Kervidy-Naizin catchment (Gu et al., 2017)."

Reference

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