Review of the manuscript: 'Spatio-temporal patterns and drivers of terrestrial dissolved organic carbon (DOC) leaching to the European river network' by Celine Gommet and colleagues.

The manuscript addresses a significant topic that is interesting for different scientific communities studying the turnover of carbon in terrestrial and aquatic environments. As the authors also state in their introduction, OC loss from rivers has not traditionally been considered in terrestrial ecosystem budgets. It is therefore to be welcomed that this study makes a contribution to a cross-system synthesis. The manuscript is well written and presentation is clear. I comment from the perspective of an aquatic ecologist and question whether the model includes the relevant parameters for riverine DOC transport and whether the significant processes are reasonably represented. I recommend revision of the paper, addressing the points raised below. If the authors can address the listed issues in the manuscript, it would make the article interesting to a wider readership.

We thank the reviewer for her/his overall positive assessment of our work.

1. OC in the soil is represented by four different litter and three different SOC pools with different turnover rates. The SOC is subdivided into active, slow and passive pools (Figure 1). I understand that such a complex model is needed to describe the turnover of OC in the soil. However, one can critically question whether NPP and the amount of SOC in the catchment are significant criteria in determining how much DOC enters the river (see statement line 401). The proportion of DOC export relative to terrestrial NPP is low (on average 0.6%, line 630), but highly variable (~0.02% to 2%) and strongly related to runoff (Figure 12). This seems to suggest that NPP is likely not the rate limiting step and that hydrology is the key factor governing the transport of DOC to the stream, as also mentioned in the manuscript (lines 645-647). I would like to see a sensitivity analysis added to show how much the variability of the modeled parameters NPP, SOC, and pore water DOC as well as the input parameters determines the final result and if the parameters are significant. The multiple regression (equation 13) makes a step in this direction. But it would be more convincing if NPP was tested independently, not as a ratio DOC leaching / NPP.

We agree with the reviewer that it would be interesting to directly compare the impact of NPP vs. hydrology on DOC leaching. For that, we will add a table showing the partial correlations of DOC leaching vs. NPP, runoff, drainage, temperature. The analysis of this table indeed highlights that DOC leaching is mainly controlled by hydrology, while temperature and NPP have only a limited impact on the spatial variability of DOC leaching across Europe. We normalized DOC leaching to the NPP because our was to highlight that once, surface runoff, drainage (and their ratio) alone can explain most of the spatio-temporal variability in DOC leaching fluxes, temperature only playing a subordinate role. Performing a sensitivity analysis of DOC export to NPP is nevertheless not straightforward because in our model several modules are coupled and changing NPP may have indirect effects that are not easy to isolate from the direct effect.

PARTIAL CORRELATION	DOC leaching
Runoff	0.43
Drainage	0.54
Temperature	-0.17
NPP	0.18

2. It is well documented that the near-stream (riparian) areas are the main source areas of stream DOC (Inamdar and Mitchell 2006, Grabs et al. 2012), while large parts of the catchment remain hydrologically disconnected from the stream during most of the time. The upslope areas will be connected to the stream only occasionally during events (Stieglitz et al. 2003, Ocampo et al. 2006). In line with this, field investigations showed that the largest part of the DOC flux originated from only a few decimeters thick organic soil layer in the riparian wetland zones (Ledesma et al. 2015), which are near-infinite sources of DOC (Raymond and Hopkinson 2003). With this in mind, it seems questionable to assume the entire watershed as the source of the DOC in the model. It would be interesting here to see what the authors' views are on this issue. Should future models focus on riparian zones?

We agree with the reviewer that riparian zones are a main source of DOC to the stream-network. Note that the impact of riparian zones on DOC leaching through runoff to the river network is implicitly represented in the model (as described in Lauerwald et al. 2017). For this, a distinction is made between the riparian zones around smaller streams (stream order 1 to 3), which are not explicitly represented in the model because of the coarse spatial resolution, and the riparian zone along larger river stretches. For the small streams, it is assumed that the extent of the riparian zones, from which most of the DOC stems, scales linearly to the surface area of these small streams, both in time as well as in space (i.e. between different grid cells of our model grid). While the surface area of these small streams is not directly represented, Lauerwald et al. 2017 assumed that spatial and temporal variations in this stream surface area scale to the square root of discharge that is flowing through these streams (eqs. 1 and 2 below), roughly in line with empirical scaling laws (e.g. Raymond et al. 2012).

DOC leaching RO = RO * r_{gen} * r_{con} * $C_{DOC,top}$ (eq. 1)

r_{con} = f((RO+GW)^0.5) (eq. 2)

With:

DOC leaching RO	leaching of DOC with runoff
RO	runoff
GW	ground water outflow
r _{gen}	general reduction factor that implicitly accounts for the fact that some of the runoff represents excess throughfall that never entered the soil
r _{con}	reduction factor accounting for the connectivity between small streams and catchment
C _{DOC_top}	concentration of C in the top soil (here to 4.5cm)

Note that this connectivity issue only affects the leaching of DOC through runoff. Leaching of DOC through drainage is assumed to occur everywhere and is thus simply calculated as the product of DOC concentration in the last soil layer and drainage (see Lauerwald et al. 2017 for details).

For the larger rivers, for which the surface area is explicitly represented in the model, it is assumed that the riparian zone can temporally make up to 10% of the river water surface area, depending on the temporal variability of discharge. In the model, we simulate a direct input of DOC produced in the temporally inundated topsoils (assuming reduced SOC decomposition and DOC production due to inundation) into the river channel. For details, see Lauerwald et al. 2017.

We admit that these important issues have not been very clearly described in our original submission. In the revised version, we will add the necessary information to the method section, and, moreover, we will add a paragraph to the discussion (in a new subsection on model limitations) addressing the importance of the riparian zone, which is only implicitly taken into account in the model. We think that this indeed remains a major shortcoming of large-scale land surface models such as ORCHILEAK. Moreover, we will discuss this issue as an important challenge for future model development, considering the useful references the reviewer kindly provided.

3. Figure 5 shows that DOC pore water concentrations decrease nonlinearly with depth, which is a reasonable result. However, the DOC in the topsoil was overestimated by 100% compared to reference sites. This can be a problem as the annual DOC exports are largely generated during events, when groundwater tables are high and the OC-rich topsoil layers become the main source of water and DOC to the stream (lines 590-595). The transmissivity feedback predicts that lateral hydraulic conductivities increase nonlinearly with increasing distance from the soil surface (Kendall et al. 1999, Bishop et al. 2004). Are there different lateral hydraulic conductivities assumed for different soil layers to connect the pore water DOC with the stream? In addition to Figure 5, I recommend including a graph showing the relationship between discharge and predicted DOC concentration in the stream. Typically, DOC concentration increases exponentially with discharge.

The representation of leaching processes in ORCHILEAK is highly simplified. Leaching occurs either from the topsoil, which in our configuration represents the top 4.5 cm of the soil column, or from the bottom soil, i.e. the lowest 50 cm of the 2 m soil profile.

The DOC leaching via runoff is calculated as described above in eqs. 1 and 2 (see also Lauerwald et al., 2017) for more details. The leaching is controlled by two reduction factors, a general reduction factor r_{gen} and a reduction factor r_{con} that represents the connectivity between streams and their catchment through the extent of the water saturated riparian zone. The general reduction factor r_{gen} accounts for the fact that some of the runoff represents excess throughfall that never entered the soil and thus corrects for the overestimated DOC concentration in the topsoil through . Note that the "runoff" is simulated as excess throughfall that is not infiltrating into the soil. ORCHILEAK is representing flows of water from land to the stream network only through surface runoff and drainage from the bottom soil. In other words, there is no representation of interflow, which is however of importance with regard to lateral solute transfers from catchment to the river network. For the implementation of DOC leaching in ORCHILEAK, it was thus assumed that the surface runoff exports the DOC from the topsoil (here defined as the top 4.5 cm), which we believe is reasonable as in reality the surface runoff, in particular in the riparian zone, contains some amount of interflow that exfiltrates where soil is saturated. This simple approach helps to overcome the limitation in the hydrology scheme which does not represent interflow.

We will describe the representation of DOC leaching more clearly in the method section, as this is a process which is very central to our study. We will further add a subsection on model limitations

where we discuss the potential importance of the process-details that are not represented in the model and how they might affect model performance.

The figure below reports the DOC concentration against discharge for the entire simulation period (one point for each month during 1979-2006) at the mouth of the Elbe and the Rhone rivers, model and observation. No clear correlation between the two variables can be observed (pearson correlation coefficient between 0.1-0.2) and this result is to be expected because DOC concentrations do not necessarily increase with discharge (flushing effect), another common response being just the opposite (dilution effect).



4. In the late 1980's the DOC concentrations started to increase in many European streams and rivers. Often the concentrations have doubled over the last decades. As possible causes a decrease of soil pH and ionic strength leading to a higher solubility of DOC (Monteith et al. 2007) and a decreasing stability of iron minerals and an accompanying release of formerly adsorbed OC are discussed (Ekström et al. 2016, Musolff et al. 2017). Is the model sensitive to the parameters discussed?

We agree with the reviewer that those are important processes. Unfortunately, these parameters and processes are not represented in our model, as there are still no reliable methods and forcing data to simulate the dynamics of soil pH and ionic strength at large scale. While the model accounts for the effect of soil pH on adsorption of DOC in the soil, soil pH is prescribed from a forcing file and does not change over time. We will add some discussion regarding these processes and the potential bias related to the fact that we do not represent the role of soil pH and ionic strength dynamically in our model. Note that we will add a new subsection on model shortcomings.

5. Application of manure was included (lines 216-226). Is there observational evidence that manure can contribute to stream DOC, except for cases when manure was applied on frozen ground or snow? On the other hand, discharge from wastewater treatment plants was not considered as a carbon source (lines 93-94). This can be questioned as the DOC concentrations in wastewater effluent are as high as in the streams (Griffith et al 2009) and, in contrast to manure this source is directly released to the stream. For the Sacramento River, Sickman et al. 2007 estimated that urban sources contributed 20% to total OC discharge. It can be assumed that wastewater-derived OC is also significant in other rivers with densely populated catchment areas.

There are indeed a couple of studies that have shown an increase in DOC flux with runoff and of DOC concentration in the river that is related to manure application (e.g., Royer et al., 2007; Delpla et al., 2011; Singh et al., 2014; Humbert et al., 2020). These studies have shown as well that the frequency and intensity of storm events in spring directly after manure application and exert an important control on the amounts of additional DOC leached to the river network. We will briefly summarize and discuss these findings in the revised version of our ms.

These processes are as well represented in ORCHILEAK. Note that the manure derived DOC is first entering the topsoil. There, a part of the DOC is decomposed, another part is transported to deeper parts of the soil column with percolating water, and finally a variable part of this DOC is flushed out of the topsoil with the runoff. Also in our model, runoff occurs mainly during storm events. The less of this manure added DOC is flushed out of the topsoil through runoff, the more of it will infiltrate deeper into the soil profile, and will be decomposed into CO2 and or contribute to the formation of particulate SOC.

To show that our model reproduces the behavior observed in the field studies mentioned above, we will further investigate in how far manure application affects DOC export in runoff vs DOC export in drainage, and we will further show during which months the manure increased DOC leaching is most intense. These findings will as well be added to the discussion in section 3.1.6.

We agree with the reviewer that sewage water injection may be another significant source of DOC to the river network, which we do unfortunately not represent in our model due to the lack of forcing data related to the sewage water (e.g. time, place and amount of the sewage discharge, and the DOC concentration in the sewage). However, Meybeck (1986) showed that DOC from sewage is very labile and only affects the concentration within short distances downstream of water processing plants. We will again discuss briefly the possible implications introduced by this shortcoming in our new section dedicated to model limitations, in particular with regard to the potential biases that this omission might introduce in our model-data comparison.

Further comments

DOC is also produced by autochthonous photosynthesis in the stream. How important can production be compared to the terrestrial DOC modeled here. Or can we assume that the DOC is readily available and therefore most of it is quickly decomposed in the river itself?

Yes, most of the autochthonous DOC has a short turnover time within the river (Frajalla et al., 2009; Fonte et al., 2013), and thus won't contribute much to the net-C budget. Meybeck (1993*a*,*b*) found that soils were the major source of organic carbon, followed by rocks, with river-borne phytoplankton being negligible at the global scale. Autochthonous DOC would be important if river C cycling was represented in more detail. But in ORCHILEAK, we focus more on the role of fluvial DOC fluxes for the terrestrial C budget. We will make that point clear in the model description, and shortly discuss that shortcoming in the discussion section.

If the manuscript aims to provide an estimation of riverine organic carbon transport, particulate organic carbon (POC) cannot be ignored. Compared to DOC, concentrations are smaller, typically ranging between 10% and 30%. May briefly discuss the potential contribution of POC to OC flux.

We agree with the reviewer that fluvial POC transfers contribute to the terrestrial C budget, and should not be ignored. Building on the recent work by Zhang et al. (2018; 2021), we will give a short review of recent model developments and applications investigating the role of lateral POC fluxes in the terrestrial C budget and highlight the challenges that persist to implement these fluvial OC fluxes into a model like ORCHILEAK.

Figure 9: DOC export is the product of DOC concentration and discharge. What is the variability of DOC concentration compared to the variability of discharge? Figure 9 suggests that the exports largely depend on discharges. Would a similar result be obtained if a mean constant DOC release were assumed?

Of course discharge is the main contributor to inter-annual variability (IAV). But to fully answer the question of the reviewer, we will quantify the interannual variability in discharge, DOC concentration and DOC fluxes as coefficient of variance, which will allow to directly compare the variability in relative terms.

Table 1: May briefly explain 'topographic index' and the context of 'Floodplains and swamps'.

We agree that this needs clarification. Topographic index is an index controlling the flow velocity in each cell. "Floodplains" is defined as the maximum areal proportion of a grid cell that can be flooded when the river exceeds its bankful flow. "Swamps" represent groundwater fed wetlands in the the floodplain of a river. Depending on the areal extend of these swamps, a proportion of stream flow is simulated to feed into the soil moisture storage of the grid cell considered. Both parameters have an effect on the simulated river discharge and soil hydrology in the floodplains. Both parameters are prescribed by the forcing file.

Bishop K. et al. 2004. Hydrological Processes 18: 185-189.

Ekström S. M. et al. 2016. Journal of Geophysical Research: Biogeosciences 121: 479-493.

Grabs T. et al. 2012. Biogeosciences 9: 3901-3916.

Griffith D. R. et al. 2009. Environ Sci Technol 43: 5647-5651.

Inamdar S. P. and Mitchell M. J. 2006. Water Resources Research 42: W03421.

Kendall K. A. et al. 1999. J Hydrol 219: 188-205.

Ledesma et al. 2015. Global Change Biology 21: 2963-2979.

Monteith et al. 2007. Nature 450: 537-540.

Musolff A. et al. 2017. Global Change Biology 23: 1891-1901.

Ocampo C. J. et al. 2006. J Hydrol 331:643-658.

Raymond P. A. and Hopkinson C. S. 2003: Ecosystems 6: 694-705.

Sickman J. O. et al. 2007. Water Resources Research 43: W11422.

Stieglitz M. et al. 2003. Global Biogeochem Cycles 17: 1105.

References

Delpla I, Baures E, Jung AV, Thomas O. Impacts of rainfall events on runoff water quality in an agricultural environment in temperate areas. Sci Total Environ 2011;409(9): 1683–8. https://doi.org/10.1016/j.scitotenv.2011.01.033

Farjalla VF, Marinho CC, Faria BM, Amado AM, Esteves FA, Bozelli RL, Giroldo D (2009) Synergy of fresh and accumulated organic matter to bacterial growth. Microb Ecol 57(4):657–666. doi: 10.1007/s00248-008-9466-8

Fonte ES, Amado AM, Meirelles-Pereira F, Esteves FA, Rosado AS, Farjalla VF (2013) The combination of different carbon sources enhances bacterial growth efficiency in aquatic ecosystems. Microb Ecol 66(4):871–878. doi:10.1007/s00248-013-0277-1

Humbert, G., Parr, T.B., Jeanneau, L. *et al.* Agricultural Practices and Hydrologic Conditions Shape the Temporal Pattern of Soil and Stream Water Dissolved Organic Matter. *Ecosystems* 23, 1325–1343 (2020). <u>https://doi.org/10.1007/s10021-019-00471-w</u>

Meybeck Michel. Composition chimique des ruisseaux non pollués en France. Chemical composition of headwater streams in France. In: Sciences Géologiques. Bulletin, tome 39, n°1, 1986. Erosion. Transport par les cours d'eau. pp. 3-77; doi : https://doi.org/10.3406/sgeol.1986.1719

Meybeck, M. 1993*a* Riverine transport of atmospheric carbon: sources, global typology and budget. *Water, Air and Soil Pollution* 70, 443–463.

Meybeck, M. 1993b C, N, P and S in rivers: from sources to global inputs. In *Interactions of C, N, P and S Biogeochemical cycles and global change* (Wollast, R., Mackenzie, F. T. & Chou, L., eds). *NATO ASI Series,* 14. Springer-Verlag, Berlin, pp. 163–191.

Royer, I.; Angers, D. A.; Chantigny, M. H.; Simard, R. R.; Cluis, D. Dissolved organic carbon in runoff and tile-drain water under corn and forage fertilized with hog manure. J. Environ. Qual. 2007, 36, 855–863. doi: 10.2134/jeq2006.0355

Singh, S., Dutta, S., and Inamdar, S.: Land application of poultry manure and its influence on spectrofluorometric characteristics of dissolved organic matter, Agriculture, Ecosystems and Environment, 193, 25–36, https://doi.org/10.1016/j.agee.2014.04.019, 2014.Zhang, H., Goll, D. S., Manzoni, S., Ciais, P., Guenet, B., and Huang, Y.: Modeling the effects of litter stoichiometry and soil mineral N availability on soil organic matter formation using CENTURY-CUE (v1.0), Geosci. Model Dev., 11, 4779–4796, https://doi.org/10.5194/gmd-11-4779-2018, 2018.

This paper aims to reveal spatio-temporal patterns and drivers of DOC over Europe. It contributes to the current literature with main focus on the large-scale DOC variability. This paper has intensively compared the modelled values with different scales of observation data and tried to demonstrate the capability of the model in representing the European-scale soil and river DOC fluxes.

There are a few major concerns about this paper:

First, it is a really long paper and has been largely focused on the comparison with different observation data. The introduced new processes and the used parameters are staying as its original sources (except one parameter)? There is no sensitivity testing showing how different process/parameter interactively influence DOC concentration/fluxes. Is it real that water routing (or maybe some other hydrological) parameters introduced from Amazon basins (Lauerwald et al. 2017) can directly work on European basins? I am a bit surprised to see that without any systematic testing of these "new" parameters, the authors can already produce reasonable runoff and also DOC fluxes, as claimed.

We agree that our paper is on the long side because it includes a part on model evaluation and another, central part on model application targeting the spatio-temporal patterns of pan-European DOC leaching fluxes and their underlying drivers.

Regarding model parameter adjustment, ORCHILEAK (and its parent branch ORCHIDEE) is a model that has ultimately been developed for global-scale applications. Therefore, the overall philosophy of our modeling approach is indeed to try to minimize the number of parameters that need adjustments before reaching reasonable results.

Importantly, most of the hydrological parameters have actually been calibrated and evaluated against globally observed runoff (Ringeval et al., 2012; Yang et al., 2015) rather than only for the Amazon basin. That is why the model performs well when it is applied to different basins and this aspect will be clarified in the revised ms. Furthermore, to improve the model performance for European river networks, we have updated ORCHILEAK with the representation of hydrological processes from a more recent version of the ORCHIDEE LSM, which has been found to perform well for temperate regions in the US (MacBean et al. 2020). Therefore, a recalibration from our side was not necessary. Regarding the C fluxes, we adopted most of the configuration used in the Amazon and Congo River basins, but a few parameter adjustments were required. For instance, we adjusted two parameters which control the leaching of DOC from the top soils to the headwater streams (see r_{con} and r_{gen} in our response to comment #2 of reviewer #1). Given the length of the paper, it was decided to exclude the results showing how these parameter adjustments influence the simulations because the main aim of the paper is on the application, and not on the model itself.

Secondly, as also pointed out by authors that DOC is only tiny fraction of NPP, and the evaluation of NPP with the observation did not seem to be that important for me comparing to understanding DOC-related processes in regulating the spatial and temporal patterns. I would rather see how the modelled soil temperature and moisture compare with the observations or maybe also soil CO2 fluxes to indicate potential microbial activities. Then, I think the manuscript need to look into how these parameters used in simulating DOC influencing the simulated DOC fluxes and concentration.

The evaluation of NPP and SOC should probably not be in the main text (or at least reduce the length largely);

We believe that an evaluation of the NPP and SOC stocks is useful because a main aim of our research is to assess the extent to which the leaching fluxes influence the European terrestrial C budget across scales, from the basin to continental scale. Although indirect, terrestrial NPP is also found to be a key control factor of DOC leaching fluxes. However, we agree with the reviewer that other controlling factors of the DOC leaching fluxes come into play. Following her/his recommendation, our revised ms. will include a comparison of simulated temperature against the European Centre for Medium-Range Weather Forecasts reanalysis ERA5 dataset. For soil respiration, we compare with the data-driven global SHR dataset published by Yao et al. (2020).

Thirdly, the modelled data has been averaged at different spatial domains, i.e., climate zones, catchments, European continent and also at specific points. What are the motivation of presenting data at these many levels of scales? This is one of the reasons I think why the manuscript becomes so long and the current presentation is not super clear about the key message.

We agree with the reviewer, but unfortunately the model evaluation relies on observational data or previously published studies that have typically addressed different spatial scales. For the results of our study, we work on the cell scale and to visualize better the spatial distribution and the possible drivers, we choose to work with climate zones. In addition, each main spatial scale primarily serves a specific purpose: the grid and basin scales are the most relevant for the model evaluation; the climate zone scale is of interest for our research objective to identify the drivers of the spatio-temporal dynamics of the leaching fluxes, and the pan-European scale provides the basis for the implications of our results for the overall C budget. This rationale will be better explained in the revised version of our ms. and we will also improve the presentation to make sure that our multi-scale approach does not lead to confusion.

Last, I have listed a lot of detailed comments on the method and model description section. I think authors should definitely clarify in many parts and justify the reasons behind. In general, I would like to see testing/understanding of model process interactions, parameter values (and their sources) before digging into any spatio-temporal patterns.

It was decided not to focus on testing/understanding model process interactions and show how parameter adjustments influence the simulations because the main aim of the paper is on the application, and not on the model itself. We agree that parameters values and their sources should be written clearer in the main text.

Detailed comments:

Through the text, please consider to specify either **soil** DOC or **river** DOC fluxes/concentration, not using unspecified DOC fluxes/concentration. It becomes a bit unclear in some parts of text if it is describing soil or river processes.

Agreed. We will carefully check that this important point is fully addressed in our revised version.

L93-94, need studies to support the negligible point sources.

Meybeck (1986) showed that DOC from sewage is very labile and does only affects concentration within short distances downstream of water processing plants.

L151-152, how is soil carbon distributed in these 11 layers? In Fig 1, it says in each layer there are all of these 11 carbon pools? If so, in deeper soil, how these litter pools look like? A few comments about Fig. 1, I saw there is C feedbacks from passive SOC à active or slow SOC à active, what do these arrows mean?

For the litter pool we distinguish the metabolic and structural litter pool. Active, slow and passive represent three states of SOC that can decompose according to the soil moisture and soil temperature. The vertical soil profile is described by an 11-layer discretization of a 2 m soil profile, with geometrically increasing layer thickness from top to bottom (Fig. 1 and Lauerwald et al., 2017). In each soil layer, ORCHILEAK explicitly simulates the fresh litter input (depending on the simulated vertical root distribution), decomposition of each organic matter pool (including litter and SOC), C transformation between different organic matter pools (showed by arrows between different pools in Fig. 1), C transport and diffusion between neighboring soil layers, and the loss of DOC due to leaching. The organic matter decomposition scheme in ORCHILEAK follows the CENTURY model (Parton et al., 1987). For a specific organic C pool at each time step, only a fraction of the decayed C is respired as CO₂ to the atmosphere (mimics the microbial respiration), the remaining will be transferred to other organic pools (mimics the microbial growth and mortality). The arrows between different SOC pools denotes the transformation between different SOC pools during the microbial decomposition processes. Please see Parton et al. (1987) for detailed explanation on the biogeochemical mechanisms of the CENTURY model.

L156, Lateral leaching of DOC is not clearly marked in Fig.1, as advection is only markedly up and down, so where is runoff?

Agreed, this was confusing. In the revised ms., fig.1 (left panel) will be improved to better represent the lateral C fluxes associated to runoff and drainage. We will also show more clearly that the RHS of the figure is actually a zoom of the processes occurring within a given layer.

L157, "drainage" could often mean surface runoff, consider to call it subsurface runoff.

To avoid confusion, we will define precisely what each of these terms precisely mean: drainage or subsurface runoff is the water flux from the last layer soil (~2m) layer and runoff is the water flux from the topsoil surface.

L158-159, sorption-desorption also contribute to the soil DOC dynamics.

Agreed. The sentence will be modified as follows: "The DOC dynamics in the soil are controlled by production, decomposition, transport and sorption-desorption processes..."

L164-165, where did you get the diffusion coefficient and what is the value you used? It needs to be clear here.

The diffusion coefficient is from Ota et al. (2013) and is equal to $1.06*10^{-5} \text{ m}^2 \text{ d}^{-1}$.

L168-169, need to explain what is Fickian-type transport and how did you implement it in the model to represent bioturbation?

The effect of mixing by bioturbation on the distribution of soil properties is commonly represented in models as a diffusion-like process (e.g. Camino et al., 2018). In this case, the intensity of mixing of each variable (including solid species) is proportional to its concentration gradient, and the proportionality constant (the "bioturbation coefficient") was set to 2.74 * 10⁻⁷ m² d⁻¹, according to Koven et al. (2013). This description will be added to our revised ms.

L171, which time scale (daily?) do soil DOC concentrations reach equilibrium based on diffusion? And then is there an order how different processes (production, decomposition, bioturbation, diffusion, sorption-desorption, advection) were implemented?

The DOC profile is time-variant and does reach equilibrium (or steady-state). Its temporal evolution is simulated at the daily time-step, in the following order: First, production and decomposition fluxes are calculated, and the DOC stocks per soil layer and poll are updated accordingligy. Then flowwos the simulation of DOC advection in the soil column, followed by diffusion of DOC. Finally, the export of DOC through leaching from top- and bottom soil with runoff and drainage, respectively, are calculated. We will add those details to the model description in the method section.

L199-202, how did you separate solid and particulate litter and SOC pools? What do you mean "the production of DOC is dependent on leaching rates"? this is not what provided in equation 8. Please clarify this.

This sentence was confusing and will be changed to : "While preserving the basic structure of ORCHIDEE-SOM, we thus adapted the model in a way that organic C exchange occurs mainly among the litter and SOC pools, similar to the original Century model, while the production of DOC as side product of this C exchange is dependent on production rates as used in ECOSSE."

L211, As far as I know, this linear equilibrium is mainly tested for peatland soils, see Yurova et al.,(2008), which is not considered in this study. For mineral soils, it often uses Langmuir isotherm, see Lilienfein et al. (2004), Kothawala et al., (2008), and Tang et al., (2018). I would like to see some studies supporting of using linear equilibrium partition equations for mineral soils. Furthermore, equation 9 ignores the initial desorption term when the DOC concentration is zero. For sorption-desorption, which time step in the model can the equilibrium reach?

We used a linear adsorption isotherm as in Neff and Asner (2001) and Wu et al. (2014). We assume that equilibrium between the dissolved and absorbed phases is instantaneous. Moreover, the work by Kothawala et al. 2008 showed that linear equation also performed fairly well and were parametrized on more observations than Langmuir equations.

Equation 4-11, there are a lot of constant used and also temperature and soil moisture dependent equations. I think it is important to present these parameter values (and the sources where these values are from). I would like to see how these k_L , k_{SOC} , k_{DOC} are modelled.

In the revised ms. a supplementary table with all parameter values along with appropriate references will be added.

L222-224, L225-226, There are many constants introduced in this section, I did not track if these cited studies are also from the same region, and it could be good to know. Depending on how valid these fractions are, the conclusion on manure impacts on DOC could vary, right?

Indeed, the type of manure input in different regions can be very different, and the physicochemical properties (e.g. C:N ratio and the ratio of dissolved and particulate organic matter) depends strongly on the specific type of manure input. However, current forcing data of manure only provide the amount of annual manure inputs, but not the specific composition and physicochemical properties of the manure. Therefore, following ORCHIDEE-CNP (Goll et al., 2017), we set the C:N ratio and DOC:POC ratio of manure to the mean value of previous observations.

L237-239, This sentence is not clear. Where is surface runoff? As it says water budget, it should also consider water content changes between two timesteps.

Of course. The paragraph will be altered as: "The water budget within the soil is determined by the infiltration rate, the evaporation and transpiration from the soil, runoff from the top soil and drainage at the bottom of the soil column. An imbalance between these fluxes leads to changes in water content within the soil."

Table 1. suggest to list the covering periods for some of the dataset. What do you mean by "After HSWD V1.1"? Then why not use soil texture data from HSWD, same as other soil properties?

We will delete 'After', and simply write the name of the source 'HSWD V1.1'. The 'After' was referring to the fact that the original data that has a higher resolution was aggregated to a 0.5 degree raster which is consistent with the other forcing data used. The fact that soil texture is taken from another source may seem odd, but is consistent with older applications of ORCHILEAK (Lauerwald et al. 2017, Hastie et al. 2019, 2021). We kept the Reynolds et al. (1999) as source for soil texture, as the soil hydrology model was calibrated to work with the soil classes used in that dataset.

L280-282, It definitely needs more details about which hydrological parameter values were based on Lauerwald et al., (2017). For me, I cannot imagine the tuned hydrological parameters for Amazon basin can "directly" work for different basins in Europe. Please justify this! Then where can we see how the calibration of surface roughness works, what values were used before and after calibration, and which discharge datasets used for this calibration? Was this discharge dataset used for calibration also included in the evaluation later in figures? Need clarification.

ORCHIDEE is a global model and the hydrology had been calibrated already. Nevertheless, we updated ORCHILEAK with a more recent hydrology scheme used in the recent standard version of ORCHIDEE (from ORCHIDEE 2.0). MacBean et al. 2020 has evaluated the model for temperate systems (see also comment 1 of rev 2)

L287-289: You had the climate forcing since 1978, why not looping period starting from 1978 for spinup? For spinup and transient periods, do you still run the model with 3-hour resolution or can the model run in coarser temporal resolution? If so, there are many other longer time series data can be used for these two periods to conquer the issues of inconsistent dataset, e.g., CO2 data from 1861 with the repeated climate forcing from 1980-2006.

There was a mistake in the ms. We'll change the paragraph about the spin up. We spun up over only a four year period (1979-1982) because the first year of forcing was not complete. After we did the spin up, we made a partly transient simulation with changing CO₂ and land cover until 1978, while looping over the years of climate forcing we had available (1979-2006). Then, starting from 1979 we did a fully transient simulation with the right climate forcing, land cover map and CO2 value for each year of simulation.

L315: suggest to provide NPP comparison maps in the appendix. I think the evaluation of NPP and SOC here and also later in the result section can be largely shortened in the main text.

We believe that this section is useful regarding the main aim of our research which consists in understanding how leaching fluxes influence the European terrestrial C budget. However, it is right that the paper is long so part of the section (comparison at the basin/climate scale) will be moved to supplementary.

L350, where were these measured fluxes measured? In soil profile? If so, I would suggest to look at soil DOC concentration instead. I assume there are more soil DOC concentration available in Europe, e.g., Camino-Serrano et al., (2016).

Our main results focus on DOC leaching flux, and we thus wanted to compare our results with observations of leaching fluxes, which to our knowledge were only measured for the EU by Kindler et al. (2010) for both top and bottom soil. We also compared DOC concentrations profiles in the soil with the study from Camino et al., 2014. Indeed, there are many more studies on DOC concentrations in the soil but we selected the one by Camino et al., 2014 because it provides a synthesis at the pan-European scale, and is thus ideal to extract "representative" concentration profiles over a sufficient large domain, compatible to the regional scope of our study. The rationale for doing the comparison with Camino et al., 2014 will be added to the revised version of our ms.

L353, you have shown in Fig 2d about the mismatch of river network between the data used in the model and the real river network. But I might miss the description about dealing with this mismatch when you do one to one comparison with discharge or other data at point level. please clarify this.

At the point level, we selected the cell from the routing scheme that corresponds to the coordinates of the gauging station. Since ORCHIDEE is a coarse resolution model, the river network is also represented at a coarse resolution. When a mismatch occurred, due to the coarse resolution, the cell corresponding to the observation was shifted by one grid.

Figure 4, the model seems doing rather good job, although hydrological parameters were originally from Amazon basin? How do you think these hydrological parameters should work across different basins? It could be nice to elaborate a bit on this.

ORCHIDEE is a global land surface model. Most of the hydrological parameters actually have been calibrated against globally observed runoff (Ringeval et al., 2012; Yang et al., 2015), rather than only in Amazon basin. That is why the model performs well when it is applied to other basins.

L442, How about soil moisture comparison?

Soil moisture is directly linked to soil temperature and soil respiration (see comment #2 reviewer#2).

L446-448, "the underestimation of SOC stocks ... " If I get this correctly, the underestimation of SOC stocks were checked at catchment level, but the comparison of DOC stocks are at a few points?, if so, it is difficult to put these two comparisons together to argue too high decomposition rates, right? Please justify this.

In this paragraph, the DOC stock refers to an average for all forests, and we observe a significant overestimation in the top soil compared to the observations. Since we diagnosed previously that SOC stocks were underestimated while DOC stocks appear here overestimated, one plausible explanation would be to assume too high SOC decomposition rates.

L461-464, on L350-353, the authors mentioned the difficulty/impossibility of comparing with these local measurements, but why it is then correct/possible to compare these 17 points with the modelled average leaching fluxes over Europe. It did not seem correct for me.

We agree that comparing model results to observations at the local scale, as shown in figure 6, is difficult (and indeed large discrepancies between observations and model results at point level can be diagnosed). This is why we choose to compare the 17-point average against the model-averaged result. But we agree that even in this case, the data-averaged value should be considered with care, taken the limited amount of observations. In the revised ms., we will insist on the limits of the model evaluation for the DOC leaching fluxes.

Fig. 6. There are low DOC leaching values along the coast, such as along Italy, UK, France? Why this pattern occurs?

We normalized by the area of the whole cell (even when the cell was not entirely covered by land). Thus when the land only accounts a small fraction (e.g. 25%) of the $1^{\circ}*1^{\circ}$ grid cell, then the DOC leaching from the 25% land is averaged to the whole grid cell. So that averaging can impact the results for "coast cells". We will clarify this point in the revised ms.

L491-492 "labile and refractory DOC", I did not recall from the method section there is a separation of different DOC pools. please clarify it in the method how the model deal with these two pools?

Indeed, this distinction should already have been included in the method section. DOC degradation in the river considers two different pools (labile and refractory), each one having a different decay constant. The methods section will be amended to include this description.

Section 3.1.6, a bit confused here: so all the comparisons earlier has included manure implementation, right? If so, I don't think the authors need a separate section to describe the impacts, and it breaks the flow a bit.

Agreed. We will move this section on manure impacts to the supplementary.

Section 3.2, please justify the reason behind to look at the drivers of DOC leaching at climatic zones, instead of at catchments? And here I guess DOC leaching refer to leaching from soil? Please specify.

The grid and basin scales were the most relevant for the model evaluation. However, when searching for potential drivers of soil DOC leaching, temperature, runoff and drainage (driven by precipitation) were diagnosed and, therefore, a climatologic segmentation of the European domain can capture the spatial variability of these physical variables.

L586-587, Litter and SOC are the sources for DOC production, not NPP. NPP cannot be important control on DOC leaching fluxes either.

Yes, but Litter and SOC stocks are fed by NPP and, thus, indirectly DOC leaching depends on the terrestrial NPP. This indirect effect will be clarified in the revised ms.

L587-590, Did the normalization implemented at annual scale? It cannot use NPP to normalize DOC at monthly scale.

Yes, the normalization was implemented at the annual scale. This will be clarified in the revised ms.

L596-597, the higher leaching to NPP ratios could be also related to more organic soils and lower NPP.

More SOC or litter is actually also due to the low temperature. Thus lower temperatures lead to longer turnover times of organic C in the soil.

L605- 609, please consider to move most of these part of text into the method section. How did the authors end up choosing these three variables? Why not doing a sensitivity testing on the model first? What are the benefits of only using these three variables in comparing with the whole model? not clear why we need this section.

In our opinion, the predictive equation results from an analysis of the model results and is thus not already explained in the methods section which describes the model. Regarding the variables, it was found in the result section that DOC leaching is correlated to the total runoff (figure 11). Our hypothesis was that temperature could also affect the leaching through its control on the DOC production and decomposition rates.

The main purpose of this section was to highlight that once normalized to the terrestrial NPP, surface runoff, drainage (and their ratio) alone can explain most of the spatio-temporal variability in DOC leaching fluxes, temperature only playing a subordinate role.

L641-642, "our lower value may come from xxx", I don't think peatlands in UK and Scandinavia area the reasons why the model underestimated the whole region averages. Please elaborate on the uncertainties of the included processes.

We believe that the exclusion of peatlands is at least part of the explanation but the reviewer is right that uncertainties in the processes included or omitted could also explain some of the discrepancy. In the revised version, a new section on model shortcomings will be added that will reflect more broadly and comprehensively on the various sources of uncertainties. The statement in lines 641-642 will be toned down.

Reference

Yurova, A., Sirin, A., Buffam, I., Bishop, K., and Laudon, H. (2008), Modeling the dissolved organic carbon output from a boreal mire using the convection-dispersion equation: Importance of representing sorption, Water Resour. Res., 44, W07411, doi:10.1029/2007WR006523.

Lilienfein, J., Qualls, R.G., Uselman, S.M. and Bridgham, S.D. (2004), Adsorption of Dissolved Organic Carbon and Nitrogen in Soils of a Weathering Chronosequence. Soil Sci. Soc. Am. J., 68: 292-305. https://doi.org/10.2136/sssaj2004.2920

Kothawala, D.N., Moore, T.R., & Hendershot, W.H. (2008). Adsorption of dissolved organic carbon to mineral soils: A comparison of four isotherm approaches. Geoderma, 148, 43-50

Tang, J., Yurova, A.Y., Schurgers, G., Miller, P.A., Olin, S., Smith, B., Siewert, M.B., Olefeldt, D., Pilesjö, P., & Poska, A. (2018). Drivers of dissolved organic carbon export in a subarctic catchment: Importance of microbial decomposition, sorption-desorption, peatland and lateral flow. Science of The Total Environment, 622-623, 260-274

Camino-Serrano, M., Graf Pannatier, E., Vicca, S., Luyssaert, S., Jonard, M., Ciais, P., Guenet, B., Gielen, B., Peñuelas, J., Sardans, J., Waldner, P., Etzold, S., Cecchini, G., Clarke, N., Galić, Z., Gandois, L., Hansen, K., Johnson, J., Klinck, U., Lachmanová, Z., Lindroos, A.-J., Meesenburg, H., Nieminen, T. M., Sanders, T. G. M., Sawicka, K., Seidling, W., Thimonier, A., Vanguelova, E., Verstraeten, A., Vesterdal, L., and Janssens, I. A.: Trends in soil solution dissolved organic carbon (DOC) concentrations across European forests, Biogeosciences, 13, 5567–5585, https://doi.org/10.5194/bg-13-5567-2016, 2016

References

Camino-Serrano, M., Guenet, B., Luyssaert, S., Ciais, P., Bastrikov, V., De Vos, B., Gielen, B., Gleixner, G., Jornet-Puig, A., Kaiser, K., Kothawala, D., Lauerwald, R., Peñuelas, J., Schrumpf, M., Vicca, S., Vuichard, N., Walmsley, D., and Janssens, I. A.: ORCHIDEE-SOM: modeling soil organic carbon (SOC) and dissolved organic carbon (DOC) dynamics along vertical soil profiles in Europe, Geosci. Model Dev., 11, 937–957, https://doi.org/10.5194/gmd-11-937-2018, 2018.

ERA5-Land Hourly Data from 1981 to Present C3S ERA5-Land reanalysis (2019); <u>https://cds.climate.copernicus.eu/cdsapp#!/dataset/reanalysis-era5-land?tab=overview</u>

Goll, D. S., Vuichard, N., Maignan, F., Jornet-Puig, A., Sardans, J., Violette, A., Peng, S., Sun, Y., Kvakic, M., Guimberteau, M., Guenet, B., Zaehle, S., Penuelas, J., Janssens, I., and Ciais, P.: A representation of the phosphorus cycle for ORCHIDEE (revision 4520), Geosci. Model Dev., 10, 3745-3770, https://doi.org/10.5194/gmd-10-3745-2017, 2017.

Jian, J., R. Vargas, K.J. Anderson-Teixeira, E. Stell, V. Herrmann, M. Horn, N. Kholod, J. Manzon, R. Marchesi, D. Paredes, and B.P. Bond-Lamberty. 2021. A Global Database of Soil Respiration Data, Version 5.0. ORNL DAAC, Oak Ridge, Tennessee, USA. <u>https://doi.org/10.3334/ORNLDAAC/1827</u>

Koven, C. D., Riley, W. J., Subin, Z. M., Tang, J. Y., Torn, M. S., Collins, W. D., Bonan, G. B., Lawrence, D. M., and Swenson, S. C.: The effect of vertically resolved soil biogeochemistry and alternate soil C and N models on C dynamics of CLM4, Biogeosciences, 10, 7109–7131, https://doi.org/10.5194/bg-10-7109-2013, 2013. MacBean, N., Scott, R. L., Biederman, J. A., Ottlé, C., Vuichard, N., Ducharne, A., Kolb, T., Dore, S., Litvak, M., and Moore, D. J. P.: Testing water fluxes and storage from two hydrology configurations within the ORCHIDEE land surface model across US semi-arid sites, Hydrol. Earth Syst. Sci., 24, 5203–5230, https://doi.org/10.5194/hess-24-5203-2020, 2020.

Meybeck Michel. Composition chimique des ruisseaux non pollués en France. Chemical composition of headwater streams in France. In: Sciences Géologiques. Bulletin, tome 39, n°1, 1986. Erosion. Transport par les cours d'eau. pp. 3-77; doi : https://doi.org/10.3406/sgeol.1986.1719

Neff, J. C. and Asner, G. P.: Dissolved organic carbon in terrestrial ecosystems: Synthesis and a model, Ecosystems, 4, 29–48, https://doi.org/10.1007/s100210000058, 2001.

Ota, M., Nagai, H., and Koarashi, J.: Root and dissolved organic carbon controls on subsurface soil carbon dynamics: A model approach, J. Geophys. Res.-Biogeosc., 118, 1646–1659, 2013.

Parton, W.J., Schimel, D.S., Cole, C.V. & Ojima, D.S. (1987) Analysis of Factors Controlling Soil Organic Matter Levels in Great Plains Grasslands1. *Soil Science Society of America Journal*, 51, 1173-1179.

Ringeval et la., 2012 Modelling sub-grid wetland in the ORCHIDEE global land surface model: evaluation against river discharges and remotely sensed data. Geosci. Model Dev. 5, 941-962, 2012

Wu, H., Peng, C., Moore, T. R., Hua, D., Li, C., Zhu, Q., Peichl, M., Arain, M. A., and Guo, Z.: Modeling dissolved organic carbon in temperate forest soils: TRIPLEX-DOC model development and validation, Geosci. Model Dev., 7, 867–881, https://doi.org/10.5194/gmd-7-867-2014, 2014.

Hui Yang, Shilong Piao, Zhenzhong Zeng, Philippe Ciais, Yi Yin, et al.. Multicriteria evaluation of discharge simulation in Dynamic Global Vegetation Models. Journal of Geophysical Research: Atmospheres, American Geophysical Union, 2015, 120 (15), pp.7488 - 7505. ff10.1002/2015JD023129ff. ffhal-01806099f