

Interactive comment on “Quantification of DOC concentrations in relation with soil properties of soils in tundra and taiga of Northern European Russia” by M.R. Oosterwoud et al.

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Author comments to reviewer #1

General comments

The regular mechanisms of the DOC release from tundra and taiga soils in view of the prospected climate warming in the area is of central scientific interest and consequently within the scope of Biogeosciences.

However, the ms needs mayor revisions, editing and language checking. There are a lot of uncertainties and shortcomings with regard to the methodology, the site description, the use of technical terms regarding the DOC fractions and with regard to the degree to which conclusions are supported by the data.

Response: we appreciate the reviewers interest in the topic and his positive, critical and constructive comments to help improve the quality of the paper.

Specific comments

The present title does not match the idea of this ms. Therefore, I suggest to change the title into “Variability of DOC concentrations related to soil properties of tundra and taiga soils along two topo-sequences in Northern European Russia”.

Response: we agree with the reviewer that the current title is too broad and we appreciate the suggestion. We will changed the title accordingly, as the suggested title is more precise.

Introduction

Please check the definitions you used on fulvic and humic acids on the one and hydrophilic acids on the other hand, or describe the fractionation method applied in more detail. So far, I have the feeling that this is a mix-up of two different methods fractionating DOC. Fulvic and humic acids are determined by the classical humus fractionation method using acids and based, whereas the term hydrophilic/hydrophobic acids/compounds is based on the Leenheer fractionation according to differences in molecular charge characteristics.

Response: DOC is a mixture consisting of high-molecular weight compounds collectively termed humic substances and low molecular weight hydrophilic compounds. Humic substances represent the hydrophobic fraction of DOC and consist of humic acids (HA) and fulvic acids (FA). Numerous methods have been developed for the isolation and quantification of humic substances (Hayes (1985), Thurman and Malcolm (1981), Leenheer (1981), Aiken (1985), Swift (1996)). Currently, the International Humic Substances Society (IHSS) uses the adapted extraction scheme of Aiken (1985), earlier described in detail by Thurman and Malcolm (1981), for the isolation of humic acids (HA) and fulvic acids (FA) from aqueous samples, and the method of Swift (1996) for solid materials.

Van Zomeren et al. (2007) developed a rapid batch procedure to quantify HA, FA, and Hy concentrations in both aquatic samples and solid materials based on the widely accepted procedures described in Thurman and Malcolm (1981) and Swift (1996). The new batch method can be performed within 1.5-4 h per sample, is easy to perform, and multiple samples can be processed simultaneously. This method is also

used by Ros et al., 2010, Speciation of water extractable organic nutrients in grassland soils, Soil Science.

With regard to the variety of already existing terms for different fractions of DOC please stick to the term WSOC, which is already established in ecosystem research, instead of this new one called EOC.

Response: we are aware of the already existing terms WSOC and WEOM. We agree with the suggested terminology and we will change the term EOC to WSOC.

Due to the low amount of new information, please leave Fig. 1 out.

Response: we agree and will remove Fig. 1 as suggested.

Please, use Corg for the organic matter content in soils instead of CT.

Response: we agree and will change CT to Corg as suggested.

Materials and methods

Site description and sampling strategy

Here, I miss climatic data on rain amounts and distribution and on the daily air and soil temperature during the sampling period in June and July 2008.

Response: we agree that the suggested climatic data would be a useful contribution to the ms. Unfortunately these data are only available to some extent, and not always from one source or equally reliable. It was out of the scope of this study to measure the suggested data ourselves. We will add climate data for the regions and provide some information below for the reviewer. Only for the tundra area we can provide monthly average precipitation and temperatures in June and July 2008 (unpublished data from project partner). Monthly average precipitation was 12mm in June and 53mm in July. Monthly average air temperatures was 8C in June and 16C in July, with a maximum air temperature of 29C in July. Soil temperatures at 5, 10, 20 cm below soil surface were on average 6, 5, and 3C respectively in June and increased to 12, 11, and 9C in July.

How big were the two catchments and where in these catchments were the soil transects established? At which locations, the stream samples were taken? Please make it clearer by supplying a map on the required topographic information.

Response: the size of the taiga catchment is approximately 71 km² and of the tundra catchment 49 km². We will provide more information about the two catchments in the form of a map with sample locations and major topographic information.

Fig. 3: What do the different colors/gray tones mean (lacking legend)?

Response: we improved the legend of figure 3 to make it more clear. The colors represent the transition from continuous (dark blue) to discontinuous (blue) and sporadic (light blue) permafrost.

Please, add more detailed information on the sampling procedure: How many replicates, how long were the sampling intervals, what kind of suction was applied to gain which kind of soil solution from which pore sizes (macro-, meso-, micro pores)?

Response: soil and soil solution were sampled on the same day and therefore we can assume that soil solution composition represents the soil characteristics at the time of sampling. Stream water in tundra was sampled twice, once in the last week of June and once in the second week of July. The aim of this study was to get an impression

of the DOC concentrations in the study area, which was until now unknown. We did not intend to give a quantitative DOC budget for the area.

Rhizons are inserted in the soil such that the porous surface is in contact with the capillaries of the soil. When a vacuum is applied to the Rhizon, solution is drawn out of the capillaries into the syringe. We are aware of the fact that Rhizons are able to extract soil solutions that are maintained within the micro pores of the soil and consequently may be immobile. In our case Rhizons, with pore size of 0.45µm, were inserted horizontally in the soil, one for each distinctive horizon. A 30ml syringe was connected to apply a vacuum pressure of about 1 bar (tested with DPI 700 pressure measurer) and left overnight.

Chemical analysis

You stated that EOC was extracted from field moist soil using a soil to water ratio of 1:10. How did you correct the soil to water ratio for the differing soil water contents and did you related the EOC amounts to kg dry weight?

Response: we applied 1:10 soil to water ratio on the basis of field moist soil but expressed as EOC amounts to mg/l in soil solution and g/kg dry weight. For calculating the EOC amount to g/kg dry weight and mg/l in soil solution we did correct based on the following formula's:

$$\text{Moisture in subsample used for extraction (g)} = \frac{\text{field moist subsample used for extraction (g)}}{\text{mcf (-)}} * \text{moisture content (g g}^{-1}\text{)}$$

$$\text{Soil solution dilution caused by EOC extraction} = \frac{\text{water added for extraction (ml)} + \text{moisture in subsample used for extraction (ml)}}{\text{moisture in subsample used for extraction (ml)}}$$

$$\text{EOC in soil solution (mg/l)} = \text{soil solution dilution caused by extraction} * \text{EOC extracted (mg/l)}$$

$$\text{EOC in dry soil (g/kg)} = \frac{\text{EOC extracted (mg/l)}}{1000} * \frac{\text{water added for extraction (l)}}{\text{field moist subsample used for extraction (g)}} * 1000 * \text{mcf}$$

Please, describe the DOC fractionation method in more detail.

Response: we agree and will describe the fractionation method in more detail. See response on earlier comment on HA and FA definitions.

Results and discussion

Field description

In general, the description of the organic layers (main source for DOC), the soil types and the underlying bedrock are a little bit too short. So, what kind of "organic top layers" or forest floor did you identify? Mull, moder, raw-humus type?

Response: we agree that the description of the soil types is a little bit too short and we will provide a bit more information about the soil types.

From the litter layers the living material was removed before sampling, we defined the sampled organic layers as O horizons. In the taiga area we have relatively well drained conditions compared to the tundra area. We will therefore change the O horizons in taiga to F and H horizons. Based on our field observations we would describe most of the forest soils in the taiga area as moder soils. The soils in the tundra area are better represented by mor or raw humus type.

In most of the soil profiles there was a transition between litter layer and the mineral layers, which we defined as Ah. Only in the tundra area we found soil profiles without

a recognizable Ah layer. In the mineral horizons (B and C) we will give more information about presence of gley, frozen layers etc. by using the lower case designations (g, z, etc.).

Regarding soil type classification according to the WRB, the descriptions of the diagnostic horizons building up the different soil types appeared quite rough. Please, add some more information on the diagnostic properties of the soil horizons.

Response: we did not intent to give a detailed soil classification, which would be out of scope of this paper, but sampled the major distinctive soil horizons to give an impressions of the different soil characteristics with depth. The final soil type classification was done in combination with soil maps made for both the taiga and the tundra area within the project. We explicitly wanted to avoid sampling at fixed intervals and consequently grouping different horizons within one sample. See previous comment for some more information on the sampled soil types.

Soil properties

In general, in Fig. 4, 6, 8, 9 which data were used for these regressions?

Response: all available data (see table 2 and 3) were used.

CEC

The CEC is determined by the soil texture (clay content), the humus content and principally by the pH. Since the soil pH varied considerably within the soil profiles, especially in the tundra soils, did you check for a relation between EOC and soil pH? Or a stepwise regression between EOC, pH, humus content (Corg multiplied by 1.72) and soil texture (if available)?

Response: we did check for a relationship between EOC in soil solution and soil pH. Remarkably, for taiga this resulted in a negative correlation ($r^2=0.50$) for tundra this resulted in a positive correlation ($r^2=0.50$). We did not do a stepwise regression but appreciate the reviewers suggestion. Multiple regression showed that the correlation between EOC in soil solution, pH and humus content did not improve.

Soil solution chemistry

The authors stated that "Soil solution of taiga soils have larger DOC concentrations than tundra soils, despite that both have comparable total organic carbon". What does this mean? Comparable Corg contents? To relate DOC concentrations to soil organic carbon or other soil properties, it would be more useful to calculate the Corg pool per horizon (taking into account the depth of every horizon and its bulk density) rather than the Corg contents. So, could you please provide the Corg pools for every horizon within the soil profiles and correlate this to (mean) DOC concentrations.

Response: The bulk density of the horizons is not determined. Therefore we are not able to calculate the C pools of the different horizons.

DOC concentrations are largely governed by the amount of rain water passing the soil profile and by the organic material from which they derive. Since data on rain or water fluxes and litter decomposition rate (e.g. litter bag experiments) are missing, the authors' assumptions on OC decomposition and DOC production are not tested and should be therefore left out.

Response: we are aware of the limited information on processes influencing leaching and decomposition but this is out of the scope of this paper. Therefore assumptions

are made based on literature from studies in comparable environments. More research in the study area on this topic is needed.

Soil solution leaching

In general, I do not understand the caption of Fig. 7. Where are the data of the tundra, where of the taiga site and what does “(b): June and, (c): July” mean?

Response: we will improve the caption of fig. 7. The upper row of graphs (a) shows the stream water chemistry at different sample locations, in downstream direction, of the taiga. Where the middle (b) and bottom (c) row of graphs show the stream water chemistry in June (b) and July (c) of the tundra.

How realistic are stream water temperatures between 5 and 23 C?

Response: we measured the water temperatures in the stream together with the pH using a combined pH electrode (WTW). The different temperatures are measured at different locations in the catchment. The high water temperature are from a thermokarst lake in the peat plateau with strongly colored water which adsorbs incoming solar radiation much stronger. The low water temperature is from a place in the stream where water was clearly upwelling.

The authors suggest different water flow paths for the tundra and the taiga transects through seasons affecting the DOC concentrations. However, studies on the water flow paths were not carried out. Additionally, solution sampling just covered two months, so that this statement appeared too far-reaching.

Response: we understand the concern of the reviewer regarding the spatial and temporal coverage of our sampling. Nevertheless we think we give a good representation by sampling along a slope in the direction of the stream and we are covering 70-80% of the soil types present in the catchment. Of course sampling each soil type once does not give detailed insight in the variability within the catchment but the most important for this study is that there is clear distinction between the soil types. We will rewrite this section of the ms to make it more clear and to give a better impression of the uncertainties as a result of our sampling strategy.

Potentially soluble organic carbon

The authors compare amounts of EOC and Ct (g/kg soil) rather than C pools (gC/m² and soil depth) therefore a comparison with regard to proportions EOC in Corg between soil profiles and experimental sites is not possible. This might be the reason by why the authors did not find a correlation between Corg and EOC.

Response: we agree with the reviewer that expressing concentrations in pools would be more appropriate but we do not have data on bulk density and therefore can not express amounts in pools.

Conclusions

To me the conclusions drawn from this study appear too generalizing and far-reaching. Besides, due to the short-term measurements of DOC concentrations and the lack of data on climatic conditions, hydrological flow-paths, soil organic carbon pools and decomposition rates, the comparability of results and thus the degree to which conclusions are supported by the data is not given.

Response: we agree that on some parts the conclusions are too speculative. Therefore, we will partly rewrite the conclusions which is based only on our data.

Author comments to reviewer #2

General comments

Some discussions appear to be reasonable from the data referring previously published papers, but some are difficult to understand. Mainly authors try to explain the vertical distribution of DOC in soil profiles by sorption processes of DOC to sesquioxides. However sorptive control for DOC distribution in the conclusion seems to be just speculation from DOC distribution because there was no evaluation about sorption potentials in soils and there was no clear relationship between DOC and sesquioxides as sorbents. Some physical data such as specific surface area, clay content and particle size distribution would be possibly supportive to explain the sorptive control for DOC but nothing was provided. pH should also be taken into account for organic matter adsorption onto sesquioxides because of variable charges on the mineral surface depending on pH. In think that results were poor for the discussion of adsorption process of DOC in these soils.

Only the adsorption process is not enough to explain the fate of DOC from soils to the stream along with topography. The relationship between DOC and EOC presented in mg/l is not clear.

In consequence, I think this paper, especially the discussion, should be reconstructed based on the actual data and whole contents should also be revised logically.

Response: we highly appreciate the positive critical comments and suggestions made by the reviewer to improve the ms.

Specific comments

Abstract L23-26: this sentence is not necessary because it seems just authors impression.

Response: we agree and will remove the sentence as suggested.

P3192 L1: DOC adsorption by crystallized clay minerals also occurs...

Response: we will re-write the sentence to: The adsorption depends much on the content of sesquioxides and amount of carbon previously accumulated in soils (Kaiser et al., 2000). Furthermore adsorption of DOC by clay minerals is also of importance (Jardine et al., 1989; Kaiser et al., 1996; Stevenson, 1982).

P3193 L23: Rhizon samplers can collect soil solutions by suction. Was it effective in a organic horizon with dominance of gas phase?

Response: the effectiveness depends on the moisture content on the soil. In coarse textured soils with very low moisture content it is very difficult to sample soil solution with Rhizons. In our case it was not always possible to sample from a certain horizon, which is shown by “–“ in table 3.

P3194 L13: Shaking rotation of 9rpm is very slow being almost impossible to shaking. Is it correct?

Response: 9 rpm (end-over-end) is just enough to not have the soil clothing at the bottom of the tube but slow enough to prevent aggressive abrasion caused by shaking at larger rpm.

P3194 L14: Degassing of carbonate during filtration under vacuum can raise pH? It didn't influence pH measurement? Didn't use subsample solution?

Response: we agree with the reviewer that degassing of carbonates can take place when vacuum is used to sample soil solution. However, the vacuum slowly vanishes during sampling (overnight), when the syringe becomes filled with solution. We

therefore assume that the carbonates will dissolve again and therefore not affect the pH in the sampled soil solution. pH was measured in a subsample of the soil solution and discarded afterwards.

P3194 L19: Was determination of total organic carbons not affected by contamination of carbonates in the deeper horizons with high pH in the E position of tundra region?

Response: we checked all samples on presence of carbonates. See response to comment of reviewer 1 about Corg.

P3194 L20: How much concentration of BaCl₂ was used for extraction of cations?

Response: we used unbuffered 0.1M BaCl₂ based on the method of Hendershot and Duquette (1986).

P3195 L7: To the remaining solution after treatment with DAX-8 resin...

Response: we will change the sentence to: DAX-8 resin (Amberlite) was added (1:5 ratio) to the remaining supernatant to adsorb the FA fraction. (see also response on comments of reviewer 1 on fractionation method).

P3195 3.1: This section should be in the materials and methods section because of no experimental data in this description. Soils showing in Table 1 were not suitably named.

Response: we agree and will move this part to the materials and methods section. See response on comments of reviewer 1 on description of soil types.

P3197 L6-7: The sesquioxides of Al₂O₃ and Fe₂O₃ are not always much amount in the bottom horizons. Some are peaked at the middle horizon.

Response: this is explained in the text. Two rows down we make a statement about some soil profiles that show reverse trends or have large sesquioxides in the middle horizon. We will re-write these sentences to make this more clear.

P3197 L10-11: Normally a B horizon contains larger content of secondary minerals as compared to the upper A horizon. However larger content of oxides in A horizon than C horizon is usual.

Response: We agree and this is given in the text at page 3197 first paragraph.

P3198 L8-12: Cation bridges are proposed for the retention of DOC to minerals. Can you present any data for the proof? Decayed plant materials could largely contribute to DOC production under such hydromorphic conditions over 100. How did authors take into account such over saturated water over 100.

Response: for proof on cation bridges for the retention of DOC to minerals we refer to Stevenson (1982). Production and decomposition processes are not within the scope of this paper. We did not do any decomposition experiments. Under saturated conditions decomposition of organic matter is slowed than by anaerobic conditions. The water content measured in our samples is based on weight (gravimetric) and therefore can exceed 100%.

P3198 L22: Why “sharpest” is in comparison of two items.

Response: in soil profiles of both taiga and tundra we found that CEC decreased with increasing depth. The slope of the decrease was however steeper for the taiga soil profiles than for the tundra soil profiles. We will replace “sharpest” by “steepest”.

P3199 L6: Authors found the significant (?) relationship between Ct and CEC. Despite of this correlation, why did authors say that “finer clay fractions contribute more to CEC without data of particle size distribution of soils?”

Response: we do not have an explanation based on experimental data other than field observations, but possibly a higher clay fraction contributes to the CEC. Therefore we will re-write the sentence to make it less speculative.

P3199 L10-11: pH as well as weathering stages is also one of the control for base cation content.

Response: we agree with the reviewer that pH is also important. We therefore changed the sentence to: The difference in major exchangeable cations can be explained by the different degree of weathering and pH between taiga and tundra soils.

P3199 L13-17: Can authors provide base, Ca, Fe, and Al saturation in CEC?

Response: Ca, Fe and Al contribution to CEC is given in text, see page 3199 line 7-17 and figure 5.

P3200 L20-21: Adsorptive capacity, specific surface area without covering organic matter, particle size distribution can be related to low retention of high concentration of DOC produced in the upper horizons of taiga soils. Such physical properties should be also taken into account.

Response: we agree and will mention this in the ms.

P3200 L23-24: There was a significant correlation between Ct and DOC in figure 6. It means that total C content and its quality seems to be a strong control for DOC production. Sorptive control was not dependent on sesquioxides but on total carbons. This means that DOC can in-situ produced in each horizon.

Response: Production of DOC is partly by microbial decomposition and partly DOC can be released from the soil by desorption, which is much faster than decomposition. The amount of EOC determines how much DOC can be released from the soil without decomposition playing a role.

P3201 L16-18: Is this correlation the positive liner regression? If this was the first linear regression, HY fraction occupied proportionally in DOC. It means that little change of the DOC composition with depth, giving contradiction of the discussion about HY degradation during the decomposition process.

Response: we agree that this is unclear and therefore this part is rewritten. the hydrophilic fraction contains the smallest molecules and is therefore more susceptible to decomposition than FA and HA. We assume that under warmer conditions (taiga) more decomposition takes place. Therefore also more FA will be transferred into smaller molecules like the HY fraction. In tundra decomposition is hindered by lower temperatures resulting in predominance of FA fraction.

P3201 L20-21: Is the fact that the higher rate of HY fraction than FA in DOC just for tundra or taiga or both? Here how did FA compounds change into HY? Authors

mentioned in the preceding sentence that substantial degradation of HY makes FA dominant.

Response: in both tundra and taiga we found higher abundance of HY in DOC with increase depth. In both tundra and taiga we find a good correlation between DOC and HY, only in tundra DOC has also a good correlation with FA.

FA adsorbs stronger causing predominantly HY to remain in solution. HY is vulnerable to decomposition because it consists of small molecules which are easily decomposable. Also FA can be decomposed, which results in the conversion of FA molecules into smaller compounds, resulting in more HY compounds available in soil solution.

P3202 L6: Why was “the most” (the superlative) here?

Response: we will re-write the sentence to: Therefore, HY is the dominant DOC fraction with increasing depth.

P3202 L23-24: Is this sentence the description for the stream in taiga? The area occupied by the peaty horizon (tundra B) can release low concentration of DOC. Not all histic horizons (which authors named) can contribute to high DOC output.

Response: in both the taiga and tundra area the streams have their source in a peatland. In taiga there is a fen situated in the upstream part of the catchment, where in tundra there is a peat plateau situated upstream in the catchment. We will provide more information about the two catchments in the form of a map with sample locations and major topographic information. See response to comment of reviewer 1 on sample locations.

P3203 L4: Al and Fe in taiga didn't have negative but a positive correlation in Fig. 8.

Response: we agree with the reviewer that there is a mistake in the ms. Ca has negative correlation, Al and Fe have positive.

P3203 L12 Table 3.

Response: needs to be corrected to table 3

P3203 L12-14: Which data can show the good relationship between DOC in soil solutions in gleysols and in stream water?

Response: composition of gleysols (DOC, cations) is comparable to concentrations found in stream. See page 3203 L11-14, for the data see table 2 and figure 7.

P3204 L10-12 and L23-25: In upper part, organic rich soils contribute to larger rate of FA in stream DOC, while the soil adjacent to the stream seems to be responsible for DOC in the stream. Both are contradictory.

Response: up stream in the catchment more organic matter rich soils are found. This is where the source of the stream is and therefore in the upstream parts of the river larger DOC concentrations are found.

All the water running down along the hill slope from the peat plateau in the direction of the stream contains large amounts of DOC in the beginning but along its way down it loses DOC by decomposition and adsorption. Especially the soil in the riparian zone function as filter for DOC before it enters the stream.

P3205 L7-9: EOC is also originated from soil organic carbon. Actually, EOC is correlated to Ct (L23). Why did authors expect the EOC increase depending on soil

depth? The rate of EOC in CT is depending on depth probably due to organic matter quality.

Response: we expect EOC to increase with increasing depth because we know that more oxides are available in the mineral soil layers. Comparatively to the total carbon content in the soil there is more EOC in the mineral layers than in the organic. Therefore relatively more carbon in the mineral layers will be able to desorb and potentially available for solution.

P3206 L3-4: Please show calculation for conversion from g/kg to mg/l in EOC.

Response: please see comments reviewer 1.

P3206 L9: Why did authors conclude high SOC turnover in taiga soils? Which data could support it?

Response: Taiga has a warmer climate, from literature we know that this often results in higher decomposition.

P3206 L26: Lower EOC in the soil nearby the stream was explained strong adsorption of EOC onto mineral. The expected EOC is actually not the EOC because the carbon was not extracted. It's just soil organic carbon strongly adsorbed onto minerals. Furthermore authors can't say degree of strength just with the data of amorphous oxide content.

Response: the reasoning is that we found less EOC in soil solution and more Fe oxides in the riparian zone profile compared to the other soil profiles in the transect which resulted in the conclusion that in the riparian zone the organic carbon is stronger adsorbed resulting in less carbon being available as EOC We will re-write this sentence to make it more clear and less speculative .

P3207 L7-9: Please clearly explain the calculation.

Response: the %DOC of EOC was calculated using the following equation:

$$\frac{\text{DOC}}{\text{EOC in soil solution}} * 100 = \% \text{DOC of EOC}$$

P3208 4: Most of the descriptions were highly speculative. It can be revised after reevaluation the data taking into account these comments.

Response: we agree that on some parts the conclusions are to speculative. Therefore, we will partly rewrite the conclusions which is based only on our data.

P3208 L7: Deeper active layer after regression of permafrost could be oxic and amorphous sesquioxides can be crystallized, leading to less adsorptive capacity. Authors also explained this in comparison between taiga and tundra mineral soils.

Response: we agree with the reviewer and appreciate his comment on the effect of deeper active layers on crystallization of amorphous sesquioxides.

Table 1: Reconsider Histic and Folic horizon.

Response: the soil type classification was done in combination with soil maps made for both the taiga and the tundra area within the project. Therefore we believe that the given soil type in table 1 are realistic.

Table 2: How did pH determined? With water or with neutral salt solution? Which type of description adopted for the soil survey?

Response: pH was determined in subsample of soil solution sampled with Rhizon.

Fig. 1: It isn't informative to explain the soil organic matter.

Response: we agree and we will remove the figure.

Fig. 7: This caption is not clear.

Response: we agree and we will change the caption of this figure.