Editor Comments

Received and published: 3 March 2016

Author Response: We sincerely thank the Editor for her thoughtful and thorough comments that will greatly improve the first version of our paper. We have added statements in **blue** below that detail our response to each comment. We feel that most of the comments were relatively minor in nature and we have addressed things below to the best of our ability.

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Nombre : 1 Auteur : Sujet : Commentaire sur le texte Date : 2015-12-21 11:40:55

There are too few main results provided in the abstract. For example the + or - 4% of DOM that was found to be bioavailable (and the absence of a trend onlong the continuum) is a fundamental discovery. Also interesting is the evidence of increased photolysis. And there are a few other points that could be put forward, at the expense of the usual general blabla.

We agree that the abstract could be vastly improved and as such, we have added details as per the above suggestions. In particular, we include the following: "However, despite our observations of downstream shifts in DOM composition, we found a relatively constant proportion of DOC that was bioavailable (~3–6% of total DOC) regardless of relative water residence time along the flow-path. This may be a consequence of two potential scenarios allowing for continual processing of organic material within the system, namely: (a) aquatic microorganisms are acclimating to a downstream shift in DOM composition; and/or (b) photodegradation is continually generating labile DOM for continued microbial processing of DOM along the flow-path continuum. Without such processes, we would otherwise expect to see a declining fraction of bioavailable DOC downstream with increasing residence time of water in the system."

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Nombre : 1 Auteur : Sujet : Commentaire sur le texte Date : 2015-12-21 11:43:29

is there any papers on precipitation of DOM as a loss process before reaching seawater (when DOM forms microgels?), especially when there is large concentrations of DOM such as in the presence of thaw slumps?

Although this is quite an interesting question, a literature search on this topic did not result in any studies related particularly to microgels/DOM and thaw slumps. As such, we have kept the list of DOM removal processes as is.

Nombre : 2 Auteur : Sujet : Commentaire sur le texte Date : 2015-09-24 13:16:06 -04'00'

There are so few studies on DOM photolysis in permafrost aquatic systems, I think it's worth citing (here or elsewhere) the paper by Laurion & Mladenov 2013, especially that it shows a slightly different trend as Cory et al., at least in terms of CO2 production

This is an excellent suggestion and we have added the Laurion & Mladenov (2013) reference to this list.

Nombre : 3 Auteur : Sujet : Commentaire sur le texte Date : 2015-09-22 16:22:19 -04'00'

and sedimentation?

We have added "sedimentation" to this statement.

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Nombre : 1 Auteur : Sujet : Commentaire sur le texte Date : 2015-12-21 11:48:39

(In line with referee 1 comment on oxygen content of water at start and during your incubations) Could there be chemical O2 consumption, especially from DOC-rich pore water? Was pore water oxic to start with? (upon in situ sampling)

The samples were allowed to equilibrate via filtering in a controlled laboratory environment at 15°C, after which t=0 was the start time of the incubations. At t=0, DO measurements were at concentrations expected at equilibrium with laboratory temperatures (~8.5–9.0 mg/L). Furthermore, bottles were wrapped tightly with paraffin such that physical degassing should have been minimal. We have added these clarifying statements to the text in this location.

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Nombre : 1 Auteur : Sujet : Commentaire sur le texte Date : 2015-09-24 14:04:16 -04'00'

how if only water is incubated in BOD?

Yes, the Winkler method for determining BOD is only performed on waters, but through its investigation one can understand how the water column may behave as it compares to sediment processes (determined through separate measurements). As such, we have added a clarifying statement here: "(through comparisons with sediment analyses)".

Nombre : 2 Auteur : Sujet : Commentaire sur le texte Date : 2015-09-24 13:52:21 -04'00'

I guess in separate bottles where no acidification was done? (i.e. not the same as DOC)

Yes, this is indeed the case and we have added the following clarifying statement: "CDOM absorbance was measured on filtered (precombusted Whatman 0.7 μm GF/F), unacidified waters stored in acid-washed HDPE bottles immediately after collection (within ~1 day) at the Northeast Science Station in Cherskiy using a Thermo Scientific GENESYS 10 UV/Vis Spectrophotometer across wavelengths 800–200 nm (1 nm interval) with a 1 cm quartz cuvette."

Nombre : 3 Auteur : Sujet : Commentaire sur le texte Date : 2015-12-21 11:50:33

isn't this the same?

Yes, we realize this statement is redundant and have edited it to read: "All sample spectra were blank corrected using Milli-Q water (18 Ω)."

Nombre : 4 Auteur : Sujet : Commentaire sur le texte Date : 2015-12-21 11:51:04

this is called null-point adjustment

Yes, indeed and we have added an additional clarifying statement to read the following: "Null-point adjustments were performed on all spectra, such that CDOM absorbance was assumed to be zero across wavelengths greater than 750 nm and the average absorbance between 750 nm and 800 nm was subtracted from each spectrum to correct for offsets owing to instrument baseline drift, temperature, scattering, and refractive effects (Green and Blough, 1994; Helms et al, 2008)."

Nombre : 5 Auteur : Sujet : Commentaire sur le texte Date : 2015-09-24 14:08:45 -04'00'

what was the criteria for diluting? ABS<X at Xnm

We have added the following statement here: "To avoid inner-filtering effects, several highly absorbing samples (primarily the soil pore waters) were diluted with Milli-Q water before analysis (to the point where A_{350} at a 1 cm path length was ≤0.02) to avoid saturation of the spectra at short wavelengths, where the final CDOM absorbance and therefore absorption coefficients were corrected for these procedures."

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Nombre : 1 Auteur : Sujet : Commentaire sur le texte Date : 2015-09-24 16:06:00 -04'00'

I suggest you consider applying Loiselle method for spectral slope calculations in the future, to avoid any effects of slope variations within the chosen wavebands, and more importantly to generate the spectral slope signature which has the potential to bring even more insights. Moreover, the use of a linear fit on log-transformed data could be problematic as it does not give the same weight to all data over the waveband

Yes, thank you for mentioning the Loiselle method and indeed it is an interesting approach that allows calculation of the spectral slope curve continuously over the spectrum rather than only looking at individual wavebands. Our reasoning for choosing our method was to be consistent with previous studies (and enable comparisons with published data, particularly in this same region). Of course the point of Loiselle's 2009 L&O paper was this new method should be standard so new studies can be better inter-compared (but unfortunately this hasn't quite caught on across the discipline yet). Perhaps this is something that can be explored in future studies (and comparison of the two methods with the same dataset can be made) to enable better comparisons among studies in the East Siberian/Kolyma region. To this end, we have added the following statement to this location in the manuscript: "As such, we chose this method for spectral slope calculations to be consistent with previous studies

to foster intercomparisons between datasets, however future studies may derive further insight utilizing methods that calculate a continuous spectral slope curve over the full 200–800 nm span (e.g., Loiselle et al., 2009) rather than only specific wavelength intervals as presented here.”

Nombre : 2 Auteur : Sujet : Commentaire sur le texte Date : 2015-09-24 14:17:21 -04'00'

please be careful thoughout the ms to distinguish between absorption coefficients (a) and absorbance (A). As you know, SUVA254 for example is calculated with A while other indices could be with a (for ex. apparently your a250:a365)

We have scoured the manuscript to ensure that “absorption coefficient” vs. “absorbance” are used correctly in each instance. In this particular location, we have changed absorbance to absorption coefficients, as we indeed are referring to “a” rather than “A”.

Nombre : 3 Auteur : Sujet : Commentaire sur le texte Date : 2015-09-24 14:21:33 -04'00'

does the second digit really mean something considering analytical errors?

Yes, we agree and we have changed all values referring to DOC, Bioavailable DOC, and percentage of bioavailable DOC to include only one decimal place.

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Nombre : 1 Auteur : Sujet : Commentaire sur le texte Date : 2015-09-24 14:27:01 -04'00'

an ANOVA would be better suited to test the "water type" effect all at once instead of pair by pair

Using one-way ANOVA may indeed be a cleaner, more elegant way of presenting these statistical results. As such, we have replaced each instance of “two-sample t-tests” with “ANOVA test” throughout the Methods section.

Nombre : 2 Auteur : Sujet : Commentaire sur le texte Date : 2015-09-24 15:16:02 -04'00'

then I guess you mean >

Yes, this is correct and we have made this change.

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Nombre : 1 Auteur : Sujet : Commentaire sur le texte Date : 2015-12-21 11:52:48

I guess you mean SUVA254??

Yes, this is correct and we have made this change.

Nombre : 2 Auteur : Sujet : Commentaire sur le texte Date : 2015-12-21 11:53:03

give this in a table instead, but here you could highlight the most interesting differences or averages that you will be discussing (if any is discussed)

We have created a new “Table 1” and incorporated the means into this table (instead of listing them in the paragraph), as well as highlighted a few of the interesting patterns in this same paragraph.

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Nombre : 1 Auteur : Sujet : Commentaire sur le texte Date : 2015-12-21 11:53:28

would it be more valuable to use stepwise regressions?

This is an interesting suggestion. However, in this case, we do not feel it would actually be more valuable to use stepwise regressions because that implies that we are investigating the use of multiple linear regression analysis to model biolability of DOM (i.e., using all parameters simultaneously). In this case, we are simply investigating the individual predictive ability of each CDOM parameter to explain biolability – and to be able to explain which of these individual metrics may be the most useful proxy indicator of this quality of DOM.

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Nombre : 1 Auteur : Sujet : Commentaire sur le texte Date : 2015-12-21 11:54:28

(In line with referees 1 & 2) What is the residence time (or transit time) of the water from soil to mainstem?

Unfortunately we did not determine residence times directly for our sampled sites. Accurate discharge/flow rate

data for streams and tributaries throughout the region are scarce if not nonexistent and tracer experiments (i.e., to directly determine residence times from soil pore waters downstream) have not been performed at these sites. However, we can refer to some previous studies that include information regarding residence times in the region. For instance, Vonk et al. (2013) estimate that in higher relief areas near Duvannyi Yar (adjacent to the Kolyma River mainstem), the transport time from permafrost thaw to entry into the Kolyma River may be less than one hour. Our study sites with lower relief may of course have longer transport times to adjacent streams/rivers. Furthermore, with respect to the mainstem, it has been estimated that water residence times in the Kolyma River from Duvannyi Yar to the river mouth may be ~3–7 days, assuming average mainstem velocities of 0.5–1.5 m/s (Holmes et al., 2012; Vonk et al., 2013). As such, permafrost-derived C may not be easily detectable at the river mouth, as this time is likely comparable to the rapid removal rates of highly labile permafrost C determined through incubation experiments (e.g., Holmes et al., 2012; Vonk et al., 2013). These examples give a range of possible residence times that may be experienced at our sampling sites as well. We have added these types of examples to the first paragraph in the Data and Methods section to give additional context to the potential residence times of waters in this study.

Holmes, R. M., et al. (2012), Seasonal and annual fluxes of nutrients and organic matter from large rivers to the Arctic Ocean and surrounding seas, *Estuaries Coasts*, doi:10.1007/s12237-011-9386-6.

Vonk, J. E., et al. (2013), High biolability of ancient permafrost carbon upon thaw, *Geophys. Res. Lett.*, 40, 2689–2693, doi:10.1002/grl.50348.

Nombre : 2 Auteur : Sujet : Commentaire sur le texte Date : 2015-09-24 16:47:45 -04'00'

you found in average 3-6% of total DOC putatively lost to remineralization; worth discussing that it's only a small fraction that is remineralized. It's only this fraction that is remineralized "well before waters reach the Arctic Ocean", right?

Yes, this is a good suggestion for clarification and we have included the following sentence in this location: "During this time of year, this amount of total DOC putatively lost to remineralization is a relatively small fraction (~3–6% depending upon water type), but indeed on par with similar studies across the Arctic (e.g., Holmes et al., 2008)."

Nombre : 3 Auteur : Sujet : Commentaire sur le texte Date : 2015-09-24 16:49:17 -04'00'

from which index can you say this? are you talking about your own study?

For clarification, we have added "in previous studies" to this location in the text. This sentence was intended to highlight the work in Spencer (2015), which is cited at the end of the sentence.

Nombre : 4 Auteur : Sujet : Commentaire sur le texte Date : 2015-09-24 16:56:22 -04'00'

can you be more specific/explicit on why your results indicate so?
And is this (unchange in % bioavailable DOC) supporting the last sentence of previous paragraph?

Thank you for pointing this out and we have changed this sentence somewhat to be clearer about its intended meaning: "This suggests that continual microbial processing of organic matter is able to occur with similar rates during transit from headwaters throughout the Kolyma River drainage network to the Arctic Ocean concurrent with ongoing downstream CDOM compositional changes."

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why "highly bioreactive" if simply more in quantity but not more reactive in percentage bioavailable?

In this case, we do not mean that we are losing more C (i.e., the percentage bioavailable is obviously the same as downstream), but rather that we are likely losing a highly biologically available permafrost fraction of the bulk DOC pool. As such, we have slightly clarified this sentence to read: "The higher overall amounts of bioavailable DOC we measured in soil pore waters may reflect a highly bioreactive permafrost or aged surface soil derived fraction of the

bulk DOC pool (e.g., Vonk et al. 2013, Mann et al. 2014)."

Nombre : 2 Auteur : Sujet : Commentaire sur le texte Date : 2015-09-24 17:00:38 -04'00'

is it an adaptation or an acclimation? (depend on transit time, see question above)

We agree that a more accurate term would be "acclimate" and we have changed this in the manuscript.

Nombre : 3 Auteur : Sujet : Commentaire sur le texte Date : 2015-12-21 11:56:03

unless photolysis generates labile molecules, which needs time (exposure to light).
And that is what you are discussing in next paragraph, but unfortunately you do not make the link with lability (smaller molecules are known to be more labile than aromatic large molecules). Maybe the more abundant "virgin" bioavailable molecules upstream are replaced downstream by photobleached smaller molecules (originating from aromatic compounds), making the % used relatively constant or without any clear pattern overall?

We have completely reworked our Discussion and Conclusions section and I think hopefully is better organized to address these issues. In particular, we include the following as a new paragraph: "Photodegradation may indeed play an important and direct role in our observed consistent fraction of bioavailable DOC along the flow-path. Previous studies in the Arctic underscore the importance of residence times as well as a significant combined role for photo- and biological degradation along the flow-path in Arctic watersheds (Cory et al., 2007; Merck et al., 2012; Cory et al., 2013; Laurion and Mladenov, 2013). These previous results show that the photochemical "pretreatment" of stream DOM that occurs during export into lakes and coastal zones may impact the ability of microorganisms to mineralize DOM. Therefore, the residence times and flow-paths of waters should greatly influence the ultimate fate of DOM (e.g., DOM vs. CO_2) exported to the adjacent ocean. In our case, we find that our increasing S_R values downstream suggest important photodegradation processes are occurring along the flow-path continuum, where this photodegradation may potentially release significant quantities of labile DOM for continued microbial processing of DOM further downstream in these stream networks. In other words, the more abundant "virgin" bioavailable molecules upstream are replaced downstream by photobleached smaller molecules (originating from aromatic compounds), resulting in the fraction of DOC used relatively constant without any clear pattern overall. If this (or something similar) were not the case, we would expect to see a declining fraction of bioavailable DOC along the flow-path continuum."

Nombre : 4 Auteur : Sujet : Commentaire sur le texte Date : 2015-09-24 17:07:32 -04'00'

is this the correct word?

We refer so the slope as "shallower" as opposed to a steeper slope. Other terminology may be confusing since some report slopes as negative, whereas others report them as positive. However, in our study shallower slopes would also be lower (since they are all reported as positive values). In any event, we have clarified our terminology to avoid confusion and now say "shallower (i.e., lower)".

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Nombre : 1 Auteur : Sujet : Commentaire sur le texte Date : 2015-09-25 15:26:32 -04'00'

being correlated to the bioavailable portion of DOM does not mean it is related to the **rate** of decline of this fraction, does it?

Correct and to clarify we have removed the term "rate" here.

Nombre : 2 Auteur : Sujet : Commentaire sur le texte Date : 2015-12-21 11:58:04

this sentence needs to be clarified

We have changed this sentence to the following: "However, biological degradation has previously been shown to typically slightly decrease S_R values (Helms et al., 2008), which indicates that the opposite relationship observed here may instead be a consequence of co-variance with photodegradation of DOM, or demonstrate that S_R values may reflect a broader, more complex range of physical and biological processes than previously recognized."

Nombre : 3 Auteur : Sujet : Commentaire sur le texte Date : 2015-09-25 16:13:41 -04'00'

in DOM

Yes, we have added the clarifying statement here: "in DOM of waters".

Anonymous Referee #1

Received and published: 3 March 2016

Author Response: We sincerely thank Referee #1 for their thoughtful and thorough comments that would greatly improve the first version of our paper. We have added statements in **blue** below that detail our response to each comment. We feel that most of the comments were relatively minor in nature and we have addressed things below to the best of our ability.

This paper contains an interesting dataset of DOC in the Kolyma River watershed that follows closely from previous work by the authors in this system. In this paper, the authors build on their prior work on DOC and BDOC concentrations in the Kolyma River by also making these measurements on the soil waters draining into the small streams and eventually the main stem of the Kolyma. The data and methods are strong. A few ideas in the discussion and conclusions could be strengthened by comparing to similar findings in the arctic in other systems, and by broadening the interpretations as suggested below.

Methods:

It was not clear whether bioassay incubations were conducted on unfiltered water, or water with sediment? Also, bioassays were conducted at 15°C but no rational was provided for this temperature. How representative is this temperature of the soil waters, streams and the river studied here?

Waters used in the bioassays were filtered and treated the same as the DOC samples. We can make this more explicit in the Methods section. The bioassays were conducted at 15°C to mimic the standard BOD method, which was also the temperature of the laboratory the samples were handled in. A space heater in the laboratory was utilized occasionally to maintain this temperature on cooler days and/or overnight (which was the best that could be done given the available laboratory space). This temperature was only slightly warmer than environmental sampling conditions (i.e., the Kolyma River mainstem samples ranged from 11.40–13.90°C, river samples ranged from 10.70–14.20°C, and stream samples ranged from 4.40–13.80°C). However, again, we kept things at 15°C as is standard in the BOD method. This further allowed samples to be treated identically in the controlled experiment (as temperatures varied depending upon location as well as date/time of day, etc.). These further details were added to the Methods section.

Were the bioassays started right after sample collection, or were samples allowed to equilibrate with the atmosphere prior to incubation? The authors should provide information on whether any samples were sub or anoxic at the start of the experiment?

The samples were allowed to equilibrate via filtering in a controlled laboratory environment, such that all experiments were able to be carried out as close to 15°C as possible (and t=0 was the start time of the incubation, with temperatures at 15°C). Bottles were wrapped tightly with paraffin and laboratory temperatures were as close to 15°C as possible, so physical degassing should have been minimal. These further details were added to the Methods section.

Incubations were conducted at 15°C, but there was no information on how well the temperature was controlled over the course of the incubation, which is helpful to rule out influences from gas exchange (such as bubble formation if initial sample temperature at T0 in the BOD bottles is different than 15°C).

Again, the samples were allowed to equilibrate via filtering in a controlled laboratory environment, such that all experiments were able to be carried out as close to 15°C as possible (and t=0 was the start time of the incubation, with temperatures at 15°C). Bottles were wrapped tightly with paraffin and laboratory temperatures were as close to 15°C as possible, so physical degassing should have been minimal. There was great attention to detail in terms of potential degassing and temperature maintenance, so we do feel quite confident in our experimental results. These further details were added to the Methods section.

The extra information on Winkler titrations in this paragraph (lines 5-12) is out of place given that Winkler titrations are standard methods for O2 consumption; no further examples needed that were not used in this study.
We included this information in the paragraph to provide further information on the Winkler method and to further explain its utility and justify its usage in our methodology.

Results and discussion:

The authors mention relationship of DOC and BDOC concentrations with water residence time "in the system", is this the water residence time in soils, streams or the river? What are the residence times of water in these different systems (none were provided directly or in citations to previous work).
Unfortunately we did not determine residence times directly for our sampled sites. Accurate discharge/flow rate data for streams and tributaries throughout the region are scarce if not nonexistent and tracer experiments (i.e., to directly determine residence times from soil pore waters downstream) have not been performed at these sites. However, we can refer to some previous studies that include information regarding residence times in the region. For instance, Vonk et al. (2013) estimate that in higher relief areas near Duvannyi Yar (adjacent to the Kolyma River mainstem), the transport time from permafrost thaw to entry into the Kolyma River may be less than one hour. Our study sites with lower relief may of course have longer transport times to adjacent streams/rivers. Furthermore, with respect to the mainstem, it has been estimated that water residence times in the Kolyma River from Duvannyi Yar to the river mouth may be ~3–7 days, assuming average mainstem velocities of 0.5–1.5 m/s (Holmes et al., 2012; Vonk et al., 2013). As such, permafrost-derived C may not be easily detectable at the river mouth, as this time is likely comparable to the rapid removal rates of highly labile permafrost C determined through incubation experiments (e.g., Holmes et al., 2012; Vonk et al., 2013). These examples give a range of possible residence times that may be experienced at our sampling sites as well. We have added these types of examples to the first paragraph in the Data and Methods section to give additional context to the potential residence times of waters in this study.

Holmes, R. M., et al. (2012), Seasonal and annual fluxes of nutrients and organic matter from large rivers to the Arctic Ocean and surrounding seas, *Estuaries Coasts*, doi:10.1007/s12237-011-9386-6.

Vonk, J. E., et al. (2013), High biolability of ancient permafrost carbon upon thaw, *Geophys. Res. Lett.*, 40, 2689–2693, doi:10.1002/grl.50348.

The authors interpret decrease in DOC and BDOC concentrations from soil waters to small streams and rivers as evidence for rapid, in-stream processing, but the fraction of DOC that is labile is similar across all water types. If the most labile DOC is rapidly removed as water moves from small to large streams, how do the authors interpret that there is a consistent fraction of BDOC (% of DOC) in the waters studied? While the authors can't rule in or out the reasons for relatively consistent fraction of BDOC in their sites, they can do more to discuss alternative explanations within the context of the literature, such as photodegradation, changes in microbial community structure, or inputs of labile DOC along stream and river channels from soil waters.
This is an excellent comment by the reviewer and we agree that we could elaborate on potential mechanisms behind the consistent % bioavailable DOC pattern we observed across all water types. As the reviewer highlights, changes in DOM composition downstream may drive community structural differences leading to consistent microbially-driven DOC losses despite significant changes to DOM structure. An alternate (or additional) mechanism could be caused by continued sunlight exposure (and resulting photodegradation) acting to make a proportion of the DOM pool bioavailable during transit. A shifting microbial community downstream could also certainly lead to these types of results. As the reviewer suggests, including references to additional work (below) would strengthen this discussion of potential mechanisms for our observations of consistent % bioavailable DOC patterns across all water types. We have indeed included a full new paragraph in the Discussion section suggesting that the

photochemical “pretreatment” of DOM is important for continued microbial processing of DOM downstream in these stream networks.

For example, for photodegradation, the authors suggest that a decrease in CDOM slope ratio from streams to the river is consistent with photodegradation of DOC, which has previously been observed as a function of water residence times in arctic freshwaters (Cory et al. 2007 JGR-B, Merck et al. 2012 Hydrol. Proc.). The authors could strengthen their interpretation of CDOM and slope ration by comparing to these previously observed and similar patterns.
We appreciate the reviewer’s suggestion for including references to these studies, as they are quite relevant to our work in the Kolyma River basin. We agree that we can refer to these important studies in the context of our work and can easily add sentences in our Discussion section to describe this previous work. Cory et al. (2007) and Merck et al. (2012) demonstrate the importance of residence times as well as a significant combined role for photo- and biological degradation along the flowpath in Arctic watersheds. These previous results show that the photochemical ‘‘pretreatment’’ of stream DOM that occurs during export into lakes and coastal zones may impact the ability of microorganisms to mineralize DOM. Therefore, the residence time and flowpath of waters should greatly influence the ultimate fate of DOM (organic matter versus carbon dioxide) exported to the adjacent ocean. As such, in our case, we find that our slope ratio (S_R) values suggest important photodegradation processes are occurring along the flowpath continuum, and these previous studies suggest that this photodegradation may potentially release significant quantities of labile DOM for “continued” microbial processing of DOM further downstream in these Arctic stream networks. We have indeed reworked the entire Discussion and Conclusions section underscoring the importance of these issues above.

Cory, R. M., D. M. McKnight, Y.-P. Chin, P. Miller, and C. L. Jaros (2007), Chemical characteristics of fulvic acids from Arctic surface waters: Microbial contributions and photochemical transformations, *J. Geophys. Res.*, 112, G04S51, doi:10.1029/2006JG000343.

Merck M, B. Neilson, R. Cory, and G. Kling (2012), Variability of in-stream and riparian storage in a beaded arctic stream. *Hydrological Processes*, 26, 2938–2950.

In addition, the authors seem to be interpreting the decrease in slope ratio from the streams to the river as evidence that photodegradation is important in this system. How might photodegradation influence the fraction of BDOC with distance downstream, given that light exposure has a substantial effect on DOC lability in bacteria in arctic freshwaters (for example, Cory et al. 2013 PNAS; Mladenov & Laurion 2013 Env. Res. Let).
We thank the reviewer for pointing out these additional previous studies (Cory et al., 2013; Laurion and Mladenov, 2013) that are quite relevant to our results in the Kolyma River basin. These studies additionally highlight the importance of photodegradation for “pretreating” DOM for further microbial degradation downstream in the system along the flowpath continuum. We certainly think it is important to highlight these additional studies in the context of our results. In particular, this previous work suggests that the consistent BDOC pattern we observed across all water types in our study is a result of photodegradation processes potentially releasing significant quantities of labile DOM for “continued” microbial processing of DOM further downstream in these Arctic stream networks. If this (or something similar) were not the case, we would expect to see declining % bioavailable DOC along the flowpath continuum. We have indeed reworked the entire Discussion and Conclusions section underscoring the importance of these issues above.

Cory, R. M., B. C. Crump, J. A. Dobkowski, and G. W. Kling (2013), Surface exposure to sunlight stimulates CO2 release from permafrost soil carbon in the Arctic, *Proceedings of the National Academy of Sciences*, 110(9), 3429-3434.

Laurion, I. and N. Mladenov (2013), Dissolved organic matter photolysis in Canadian arctic thaw ponds, *Environmental Research Letters*, 8, 035026.

Anonymous Referee #2

Received and published: 3 March 2016

Author Response: We sincerely thank Referee #2 for their thoughtful and thorough comments that would greatly improve the first version of our paper. We have added statements in **blue** below that detail our response to each comment. We feel that most of the comments were relatively minor in nature and we have addressed things below to the best of our ability.

The authors of this paper explored DOC quantity and quality along the fluvial network of the artic Kolyma River and present interesting results about changing patterns in concentration, bioavailability, and optical character of DOC from soils to the river mouth. Overall, this paper is an interesting study that addresses an important aspect of carbon cycling in the artic. DOC release from permafrost soils and the processing of DOC in the aquatic network are precursors of large CO2 and CH4 evasions from these systems, and the presented study particularly sheds light on the geographically large variability in soil DOC in contrast to the rather uniform DOC patterns in the main river, emphasizing the great potential of in-stream processing of DOC during artic summer. An additional strength of the paper is the highlighted potential in applying simple optical measurements to assess DOC in these artic systems on a larger scale. Future studies might benefit and build up on these findings. Overall, the paper is based on a robust dataset, it is well written and has clear illustrations. A few minor revision remarks are listed in the following:

1. In agreement with reviewer #1, I suggest to clarify what the water retention time of the different systems is. It will help to provide an idea about the different timescales of soil-, stream-, and river DOC processing.
Unfortunately we did not determine residence times directly for our sampled sites. Accurate discharge/flow rate data for streams and tributaries throughout the region are scarce if not nonexistent and tracer experiments (i.e., to directly determine residence times from soil pore waters downstream) have not been performed at these sites. However, we can refer to some previous studies that include information regarding residence times in the region. For instance, Vonk et al. (2013) estimate that in higher relief areas near Duvannyi Yar (adjacent to the Kolyma River mainstem), the transport time from permafrost thaw to entry into the Kolyma River may be less than one hour. Our study sites with lower relief may of course have longer transport times to adjacent streams/rivers. Furthermore, with respect to the mainstem, it has been estimated that water residence times in the Kolyma River from Duvannyi Yar to the river mouth may be ~3–7 days, assuming average mainstem velocities of 0.5–1.5 m/s (Holmes et al., 2012; Vonk et al., 2013). As such, permafrost-derived C may not be easily detectable at the river mouth, as this time is likely comparable to the rapid removal rates of highly labile permafrost C determined through incubation experiments (e.g., Holmes et al., 2012; Vonk et al., 2013). These examples give a range of possible residence times that may be experienced at our sampling sites as well. We have added these types of examples to the first paragraph in the Data and Methods section to give additional context to the potential residence times of waters in this study.

Holmes, R. M., et al. (2012), Seasonal and annual fluxes of nutrients and organic matter from large rivers to the Arctic Ocean and surrounding seas, *Estuaries Coasts*. doi:10.1007/s12237-011-9386-6.

Vonk, J. E., et al. (2013), High biolability of ancient permafrost carbon upon thaw, *Geophys. Res. Lett.*, 40, 2689–2693, doi:10.1002/grl.50348.

2. P12329 L19-22: It is stated twice here that no statistically significant results were found, however the p-value is given as <0.05. If you used the 0.05-level for significance, please check the results and correct either the p-value or the statement "...streams, rivers, and mainstem waters were not statistically different from one another (p < 0.05)....the percentage of bioavailable DOC....did not significantly decrease downstream (two-sample t tests, p < 0.05)".

The reviewer is correct and this is a mistype. Because these values were not statistically different from one another, we should refer to this with "$p > 0.05$". We have corrected this typo in these two locations.

3. P12330: L15-21: The enumeration of spectral slope values and other CDOM parameters is rather long, I suggest to present these values in a table instead.

This is an excellent suggestion by the reviewer and we agree that these values should be incorporated into an additional table that can simply be referred to in the text. We have included these data into a new table in the manuscript (Table 1).

4. P12334: L13 & 16-18: The CDOM parameter a250:a365 is here mistakenly referred to as a254:a365, please correct.

The reviewer is correct that there are four locations in these lines in the text where the CDOM parameter a_{250}:a_{365} was mistakenly referred to as a_{254}:a_{365}. These typos have been corrected.

5. P12327 L16: doubble spelling "using a using a Thermo"

The typo "using a using a Thermo" has been changed to "using a Thermo".

6. P12329 L28: "(Figs. 3a)" only one figure

"Figures 3a" has been changed to "Figure 3a".

7. P12329 L17-18: missing blank in "(two samplet tests...)"

We have edited these lines to refer to a "one-way ANOVA" instead and so this typo no longer exists.

Optical properties and bioavailability of dissolved organic matter along a flow-path continuum from soil pore waters to the Kolyma River mainstem, East Siberia

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Keywords: East Siberia, Kolyma River, permafrost, DOC, CDOM, biolability

Abstract

The Kolyma River in Northeast Siberia is among the six largest arctic rivers and drains a region underlain by vast deposits of Holocene-aged peat and Pleistocene-aged loess known as yedoma, most of which is currently stored in ice-rich permafrost throughout the region. These peat and yedoma deposits are important sources of dissolved organic matter (DOM) to inland waters that in turn play a significant role in the transport and ultimate remineralization of organic carbon to CO_2 and CH_4 along the terrestrial flow-path continuum. The turnover and fate of terrigenous DOM during offshore transport ~~will~~ largely depends upon the composition and amount of carbon released to inland and coastal waters. Here, we measured the ultraviolet-visible optical properties of chromophoric DOM (CDOM) from a geographically extensive collection of waters spanning soil pore waters, streams, rivers, and the Kolyma River mainstem throughout a ~250 km transect of the northern Kolyma River basin. During the period of study, CDOM ~~absorbance~~ absorption ~~values~~ coefficients were found to be robust proxies for the concentration of DOM, whereas additional CDOM parameters such as spectral slopes (S) were found to be useful indicators of DOM quality along the flow-path. In particular, ~~CDOM absorption at 254 nm showed a strong relationship with dissolved organic carbon (DOC) concentrations across all water types (r^2 = 0.958, p<0.01). The~~the spectral slope ratio (S_R) of CDOM demonstrated statistically significant differences between all four water types and tracked changes in the concentration of bioavailable DOC, suggesting that this parameter may be suitable for clearly discriminating shifts in organic matter characteristics among water types along the full flow-path continuum across this landscape. However, despite our observations of downstream shifts in DOM composition, we found a relatively constant proportion of DOC that was bioavailable (~3–6% of total DOC) regardless of relative water residence time along the flow-path. This may be a

consequence of two potential scenarios allowing for continual processing of organic material within the system, namely: (a) aquatic microorganisms are acclimating to a downstream shift in DOM composition; and/or (b) photodegradation is continually generating labile DOM for continued microbial processing of DOM along the flow-path continuum. Without such processes, we would otherwise expect to see a declining fraction of bioavailable DOC downstream with increasing residence time of water in the system. ~~The heterogeneity of environmental characteristics and extensive continuous permafrost of the Kolyma River basin combine to make this a critical region to investigate and monitor.~~ With ongoing and future permafrost degradation, peat and yedoma deposits throughout the Northeast Siberian region will become more hydrologically active, providing greater amounts of DOM to fluvial networks and ultimately to the Arctic Ocean. The ability to rapidly and comprehensively monitor shifts in the quantity and quality of DOM across the landscape is therefore critical for understanding potential future feedbacks ~~on~~ within the arctic carbon cycle.

1. Introduction

There is increasing evidence that inland freshwater ecosystems play a significant role in the global carbon cycle owing to the metabolism of terrestrially-derived organic matter as it moves through fluvial networks from land to ocean (Cole et al., 2007; Battin et al., 2009a, b). Recent research suggests that arctic watersheds may increasingly augment the role of freshwater ecosystems in the global flux of terrestrial carbon to the atmosphere (Walter et al., 2007; Denfeld et al., 2013; Vonk et al., 2013; Hayes et al., 2014; Spencer et al., 2015) and ocean (Frey and Smith, 2005; Frey and McClelland, 2009; Schreiner et al., 2014; Tesi et al., 2014) as a result of climate warming and changing regional hydrology. Terrestrial sources of organic matter generally dominate the energy and carbon fluxes through stream, riverine, and estuarine ecosystems (Mulholland, 1997; Holmes et al., 2008), but the lability and composition of this carbon remain poorly characterized. Headwater and intermediate streams dominate overall channel length in large dendritic drainage basins (e.g., Denfeld et al., 2013), thus the functional role of streams and intermediate rivers is magnified when assessing landscape controls on carbon and nutrient fluxes to the atmosphere and Arctic Ocean.

Following the publication of the "river continuum concept" (Vannote et al., 1980), there has been much research focused on the delivery and processing of terrestrially-derived organic matter within temperate stream ecosystems. Through these studies, it has been shown that biological processes within streams alter the transport of organic matter to downstream ecosystems (e.g., Webster and Meyer, 1997), but the fate of terrestrial organic matter in arctic streams and rivers has only more recently been explored (e.g., Frey and Smith, 2005; Neff et al., 2006; Holmes et al., 2008; Denfeld et al., 2013; Spencer et al., 2015). Furthermore, a variety of conceptual and pragmatic issues complicate the study of arctic rivers, including: (i) large seasonal variations in discharge accompanied by large seasonal variations in nutrient and organic matter inputs from rivers to the coastal ocean (e.g., McClelland et al., 2012); (ii) the heterogeneity of vegetation, permafrost extent, topography, and soil attributes within arctic watersheds (e.g., Frey and McClelland, 2009); and (iii) spatial and temporal inaccessibility hindering comprehensive sampling; among others.

Hydrologic flow-paths and organic matter transport in arctic regions dominated by permafrost are markedly different than temperate regions with well-drained soils. In particular, permafrost-dominated watersheds lack deep groundwater flow-paths owing to the permafrost boundary in soil that prevents deep groundwater movement (Judd and Kling, 2002; Frey et al., 2007). As a result, the delivery of terrestrial-permafrost organic matter to aquatic ecosystems may in fact lack significant terrestrial or groundwater processing. Once dissolved organic matter (DOM) enters aquatic ecosystems, multiple processes remove DOM from the water column: (i) photochemical reactions, where DOM is degraded to CO_2 or to compounds bioavailable for bacterial uptake (Moran and Zepp, 1997; Laurion and Mladenov, 2013; Cory et al., 2014); (ii) loss via aggregation of DOM owing to changes in ionic strength when freshwater mixes with sea water (Sholkovitz, 1976); (iii) DOM sorption to particles and sedimentation (Chin et al., 1998); and/or (iv) bacterial uptake and utilization of the bioavailable fraction (Bronk, 2002; Karl and Björkman, 2002; Mann et al., 2014; Spencer et al., 2015). Measurements of waters along a hydrologic flow-path may indeed give insight into the characteristics of DOM as it is modified through these various processes along the soil-stream-river continuum.

Recent work on the Kolyma River in Northeast Siberia has identified marked variation in annual discharge that is associated with large pulses of organic matter flux to the Arctic Ocean during spring freshet, providing detailed temporal characterization of DOM in the Kolyma River mainstem across the annual hydrograph (e.g., Mann et al., 2012). Furthermore, selective processing and loss of permafrost-derived DOM has been shown to occur via microbial metabolism throughout the Kolyma River basin, as waters move downstream through the fluvial network (Mann et al., 2014; ~~Spencer et al., 2015;~~ Mann et al., ~~in press~~2015; Spencer et al., 2015). Here, we complement these previous studies by providing extensive spatial characterization of DOM along a flow-path continuum from soil pore waters to the Kolyma River mainstem during mid-summer (July) baseflow. The heterogeneity of environmental characteristics and extensive continuous permafrost of the Kolyma River basin combine to make this a critical region to investigate and monitor. In particular, we measured the ultraviolet-visible absorption spectra

(200–800 nm) of chromophoric DOM (CDOM) from a geographically extensive collection of waters throughout a ~250 km transect of the northern Kolyma River basin, including samples of soil pore waters, streams, rivers, and the Kolyma River mainstem. ~~Absorbance values~~CDOM absorption and spectral slopes (calculated within log-transformed absorption spectra) were used to investigate contrasting water types and were found to be useful indicators of both the concentration and reactivity of DOM. ~~The heterogeneity of environmental characteristics and extensive continuous permafrost of the Kolyma River basin combine to make this a critical region to investigate and monitor.~~ With ongoing permafrost degradation and subsequent release of a long-term storehouse of organic material into the contemporary carbon cycle, the ability to easily and comprehensively monitor the quantity and quality of DOM across the landscape through ~~methods such as ultraviolet-visible absorption~~ investigation of its optical properties is becoming critical for understanding the global significance of the arctic carbon cycle. Here, we explore a full suite of CDOM parameters as well as concentrations of dissolved organic carbon (DOC) and bioavailable DOC as they vary across a full flow-path continuum in the Kolyma River basin in Northeast Siberia.

2. Data and Methods

The Kolyma River in Northeast Siberia is among the six largest arctic rivers and drains a ~650,000 km^2 region underlain by vast deposits of Holocene-aged peat and Pleistocene-aged loess known as yedoma, much of which is currently stored in ice-rich permafrost throughout the region (Holmes et al., 2012; Holmes et al., 2013). These peats and yedoma deposits are important sources of DOM to terrestrial waters that in turn play a significant role in the transport and ultimate remineralization of organic carbon to atmospheric CO_2 and CH_4 (e.g., Walter et al., 2006; Mann et al., 2012; Denfeld et al., 2013; Spencer et al., 2015). The Kolyma River basin and its subwatersheds exhibit extreme hydrologic seasonality, with ice breakup and peak river discharge typically occurring in late May or early June. In this study, sampling took place along the most northern ~250 km of the Kolyma River in the vicinity of Cherskiy, Sakha Republic, Russia (68.767°N, 161.333°E) during the mid-summer period of July 2009 (Figure 1). Samples were collected over a narrow temporal window from July 11–25, 2009 in order to capture a "snapshot" of observations during the mid-summer period. In total, 47 water samples were collected, including soil pore waters in shallow wetlands (n=9), small streams with watersheds <100 km^2 (n=15), major river tributaries with watersheds 900–120,000 km^2 (n=14), and Kolyma mainstem locations with watersheds >400,000 km^2 (n=9). Although we did not determine residence times directly for our sampled sites, Vonk et al. (2013) estimated that in higher relief areas near Duvannyi Yar (adjacent to the Kolyma River mainstem), the transport time from permafrost thaw to entry into the Kolyma River may be less than one hour. Furthermore, with respect to the mainstem, it has been estimated that water residence times in the Kolyma River from Duvannyi Yar to the river mouth may be ~3–7 days, assuming average mainstem velocities of 0.5–1.5 m/s (Holmes et al., 2012; Vonk et al., 2013). As such, permafrost-derived C may not be easily detectable at the river mouth, as this time is likely comparable to the rapid removal rates of highly labile permafrost C determined through incubation experiments (e.g., Holmes et al., 2012; Vonk et al., 2013).

Samples were collected by hand using a 1 L acid-washed high density polyethylene (HDPE) bottle as a collection vessel, where sample waters were used to rinse the bottle several times before filling. Soil pore waters were collected by depressing the soil surface within the wetlands and allowing the water to slowly seep into the collection vessel. In shallow streams, less than 0.5 m in depth, samples were collected approximately midway below the surface and the bottom. In larger tributaries and rivers, samples were collected at a depth of ~0.5 m. Water samples were then filtered through precombusted (450°C for 6 hours) Whatman 0.7 μm GF/F filters in the field and stored in acid-washed HDPE bottles without headspace to minimize degassing and algal growth. Upon returning to the laboratory (typically within ~1 day), DOC samples were acidified with concentrated HCl to a pH of ≤2 and stored refrigerated and in the dark until analysis via high-temperature combustion using a Shimadzu TOC-VCPH Analyzer (within one month of collection). DOC was calculated as the mean of 3 to 5 injections with a coefficient of variance less than 2%.

We additionally conducted a series of organic matter bioavailability assays to assess the total and relative amounts of bioavailable DOC in soil, stream, and river environments. These assays relied upon 5-day biological oxygen demand (BOD) ~~experiments~~incubations, with methods similar to those in Mann et al. (2014). Water samples were collected in triplicate glass 300 mL BOD bottles and filtered as DOC (above). The samples were initially allowed to equilibrate via filtering in a controlled laboratory environment at 15°C, after which t=0 was the start time of the incubations. The Winkler titration method was used to measure dissolved oxygen (DO) concentrations initially~~initial~~ (t=0) ~~dissolved oxygen (DO) concentrations~~ (i.e., in situ ~~dissolved oxygen~~DO) as well as after ~~a~~ 5-day incubations at 15°C ~~using water collected in triplicate glass 300 mL BOD bottles~~ ~~;~~, where bottles were kept in the dark in between measurements. At t=0, DO measurements were at concentrations expected at equilibrium with the 15°C laboratory temperature (~8.5–9.0 mg/L). This temperature was only slightly warmer than environmental sampling conditions (i.e., the Kolyma River mainstem samples ranged from 11.40–13.90°C, river samples ranged from 10.70–14.20°C, and stream samples ranged from

4.40–13.80°C). However, we maintained samples at 15°C as is standard in the BOD method, which allowed samples to be treated identically in the controlled experiment (in situ temperatures varied depending not only upon location but also date and time of day). Furthermore, bottles were wrapped tightly with paraffin such that physical degassing should have been minimal during the incubations. BOD was then calculated as the difference between DO concentrations at t = 0 and following the 5-day incubations. We assumed 100% of DO consumed was converted to CO_2 via aerobic respiration and that the carbon source respired was DOM, where resulting BOD measurements were used an analog for bioavailable DOC. The Winkler method we used here has been used extensively and is attractive for a variety of reasons, including: (i) enabling DO to be measured with precision of 0.01 mg/L, thus low respiration rates can be accurately measured; (ii) allowing for convenient replication of assays within habitats; (iii) permitting experimental manipulation of standard bioassays (e.g., N and P amendments, photolysis experiments, alteration of initial microbial consortia, and temperature manipulation; (iv) helping to segregate the relative roles of water column and sediment processes (through comparisons with sediment analyses); and (v) helping to inform more realistic ecosystem-level experiments that are much more laborious and time intensive.

In order to investigate the optical characteristics of the DOM in these samples, we additionally measured the ultraviolet-visible absorption spectra of CDOM from this broad collection of waters. CDOM absorbance was measured on filtered (precombusted Whatman 0.7 µm GF/F), unacidified waters stored in acid-washed HDPE bottles immediately after collection (within ~1 day) at the Northeast Science Station in Cherskiy using a ~~using a~~ Thermo Scientific GENESYS 10 UV/Vis Spectrophotometer across wavelengths 800–200 nm (1 nm interval) ~~using~~ with a 1 cm quartz cuvette. All sample spectra were blank corrected ~~and referenced against~~using

Milli-Q water (18 Ω). Measurements were made after samples had equilibrated to the laboratory temperature in order to minimize temperature effects. ~~CDOM~~ Null-point adjustments were performed on all spectra, such that CDOM absorbance was assumed to be zero across wavelengths greater than 750 nm and the average absorbance between 750 nm and 800 nm was subtracted from each spectrum to correct for offsets owing to instrument baseline drift, temperature, scattering, and refractive effects (Green and Blough, 1994; Helms et al, 2008). CDOM absorption coefficients were calculated as:

$$a(\lambda) = 2.303A(\lambda)/l \qquad (1)$$

where a is the Napierian ~~absorbance~~ absorption coefficient (m^{-1}) at a specified wavelength (λ, in nm), $A(\lambda)$ is the absorbance at the wavelength, and l is the cell path length in meters (Green and Blough, 1994). ~~Several~~ To avoid inner-filtering effects, several ~~samples with the highest CDOM concentrations~~highly absorbing samples (primarily the soil pore waters) were diluted with Milli-Q water before analysis (to the point where A_{350} at a 1 cm path length was ≤0.02) to avoid saturation of the spectra at short wavelengths, where the final CDOM absorbance ~~values~~ and therefore absorption coefficients were corrected for these procedures.

CDOM spectral slopes (S, nm^{-1}) between 290–350 nm ($S_{290–350}$), 275–295 nm ($S_{275–295}$), and 350–400 nm ($S_{350–400}$), calculated within log-transformed absorption spectra, were also utilized to investigate DOM characteristics of contrasting water types, and were calculated as:

$$a(\lambda) = a\,(_{\lambda ref})\, e^{-S\,(\lambda\,-\,\lambda ref)} \qquad (2)$$

where $a(\lambda)$ is the absorption coefficient at a specified wavelength, λ_{ref} is a reference wavelength, and S is the slope fitting parameter (Hernes et al., 2008; Helms et al., 2008; Spencer et al., 2009a). All slopes are reported here as positive values, such that higher (i.e., steeper) slopes indicate a greater decrease in absorption with increasing wavelength. Additional CDOM parameters investigated here include the spectral slope ratio (S_R), calculated as the ratio between $S_{275–295}$ and $S_{350–400}$; the ratio between CDOM ~~absorbance~~ absorption coefficients (a) at 250 nm and 365 nm (a_{250}:a_{365}); and specific UV absorbance (SUVA$_{254}$), determined by dividing UV absorbance (A) at 254 nm by the sample DOC concentration and reported in units of L mg C^{-1} m^{-1} (Weishhar et al., 2003). These six CDOM parameters ($S_{290–350}$, $S_{275–295}$, $S_{350–400}$, a_{250}:a_{365}, SUVA$_{254}$, and S_R) have been shown to provide insights for various DOM characteristics such as molecular weight, source waters, composition, age, and aromatic content for a variety of geographic regions (e.g., Weishaar 2003; Neff et al., 2006; Helms et al., 2008; Spencer et al., 2008; Spencer et al., 2009a; Spencer et al., 2009b; Mann et al., 2012). As such, we chose our method for spectral slope calculations to be consistent with previous studies to foster intercomparisons between datasets, however future studies may derive further insight utilizing methods that calculate a continuous spectral slope curve over the full 200–800 nm span (e.g., Loiselle et al., 2009) rather than only specific wavelength intervals as presented here.

3. Results

Total DOC concentrations (and the variance among values within each water type) decreased markedly downstream along the flow-path continuum from soil pore waters to the Kolyma River mainstem (Figure 2a). Mean (±1 standard deviation) DOC values were 43.~~35~~ 3 ± 22.~~79~~ 8 mg L^{-1} (soil pore waters), 11.6~~3~~ ± ~~2.97~~3.0 mg L^{-1} (streams), 4.~~89~~ 9 ± 1.6~~1~~ mg L^{-1} (rivers), and 3.6~~1~~ ± 0.4~~1~~ mg L^{-1} (mainstem waters). Soil pore waters, in particular, showed highly variable DOC concentrations (ranging from 13.~~19~~ 2 to 64.74 mg L^{-1}) demonstrating the heterogeneous supply of DOM from terrestrial systems to streams. By contrast, DOC concentrations in the Kolyma mainstem along the ~250 km stretch sampled were remarkably similar (ranging from ~~2.97~~3.0 to 4.~~36~~ 4 mg L^{-1}) during this mid-summer July period (Figure 2a). Furthermore, DOC concentrations of the four water types sampled were found to be significantly different from one another (~~two~~one-way ANOVA~~sample t-tests~~, $p<0.05$).

Concentrations of bioavailable DOC showed similar patterns to DOC, declining downstream along the flow-path continuum with increasing water residence time in the system (Figure 2b). Bioavailable DOC concentrations averaged 0.9~~3~~ ± 0.24 mg L^{-1} (soil pore waters), 0.3~~3~~ ± 0.1~~15~~ mg L^{-1} (streams), 0.~~27~~ 3 ± 0.~~17~~ 2 mg L^{-1} (rivers), and 0.~~16~~ 2 ± 0.~~15~~ 2 mg L^{-1} (mainstem waters), and showed relative greater variability than DOC within the stream, river and mainstem water types. Concentrations of bioavailable DOC in soil pore waters were statistically different from the other three water types (~~two~~one-~~sample t-tests~~way ANOVA, $p<0.05$), although by contrast, streams, rivers, and mainstem waters were not statistically different from one another (p~~$<$~~$>$0.05). Importantly, the percentage of bioavailable DOC (i.e., calculated as the amount of bioavailable DOC divided by total DOC) did not significantly decrease downstream (~~two-sample t-tests~~one-way ANOVA, p~~$<$~~$>$0.05) and showed relatively similar values among the four water sample types along the flow-path continuum (Figure 2c), where percentages averaged 3.9~~3~~ ± 3.8~~1~~% (soil pore waters), 3.2~~1~~ ± 1.94% (streams), 6.2~~3~~ ± 4.3~~1~~% (rivers), and 4.~~46~~ 5 ± 4.5~~5~~% (mainstem waters).

CDOM absorption spectra (200–800 nm) showed clear separation between soil pore waters, streams, rivers, and the Kolyma mainstem, where soil pore waters exhibited values markedly higher than the other three water sample types (Figure~~s~~ 3a). CDOM absorption also clearly declined downstream from streams, rivers, to mainstem waters when assessing those waters only (Figure 3b). Furthermore, we investigated the potential for utilizing CDOM absorption as a proxy for DOC concentrations in these waters. Our data revealed that independent of water type along the stream-river-mainstem flow-path, CDOM absorption was strongly linearly correlated to DOC concentrations at 254, 350, and 440 nm (Figure 4). In particular, CDOM absorption at 254 nm had the highest predictive capability of DOC ($r^2 = 0.958$, $p<0.01$), with CDOM absorption at 350 nm ($r^2 = 0.855$, $p<0.01$) and 440 nm ($r^2=0.667$, $p<0.01$) less strongly predictive (Figure 4).

We additionally investigated the quantitative distribution of the six derived CDOM parameters ($S_{290–350}$, $S_{275–295}$, $S_{350–400}$, a_{250}:a_{365}, SUVA$_{254}$, and S_R) across the four water types (Figure 5; Table 1). In general, four parameters ($S_{290–350}$, $S_{275–295}$, a_{250}:a_{365}, and S_R) showed an increasing pattern along the flow-path continuum, whereas two parameters ($S_{350–400}$ and SUVA$_{254}$~~a_{250}:a_{365}~~) showed a decreasing pattern. ~~Spectral slope and other CDOM parameters for soil pore waters, streams, rivers, and mainstem waters averaged: (a) 15.35 × 10^{-3} nm^{-1}, 17.08 × 10^{-3} nm^{-1}, 17.17 × 10^{-3} nm^{-1}, and 18.10 × 10^{-3} nm^{-1}, respectively, for $S_{290–350}$ (Figure 5a); (b) 15.27 × 10^{-3} nm^{-1}, 17.39 × 10^{-3} nm^{-1}, 17.79 × 10^{-3} nm^{-1}, and 18.57 × 10^{-3} nm^{-1}, respectively, for $S_{275–295}$ (Figure 5b); (c) 18.65 × 10^{-3} nm^{-1}, 18.89 × 10^{-3} nm^{-1}, 18.19 × 10^{-3} nm^{-1}, and 17.50 × 10^{-3} nm^{-1}, respectively, for $S_{350–400}$ (Figure 5c); (d) 5.47, 6.44, 6.27, and 6.53, respectively, for a_{250}:a_{365} (Figure 5d); (e) 3.52 L mg C^{-1} m^{-1}, 2.94 L mg C^{-1} m^{-1}, 2.77 L mg C^{-1} m^{-1}, and 2.56 L mg C^{-1} m^{-1}, respectively, for SUVA$_{254}$ (Figure 5e); and (f) 0.82, 0.92, 0.98, and 1.06, respectively, for S_R (Figure 5f).~~ In terms of whether the values of the six parameters were statistically significantly different among water sample types, ~~two-sample t-tests~~one-way ANOVA tests (at the 0.05 level) revealed inconsistent results. Most commonly, soil pore waters were statistically different from all other water types for four of the parameters ($S_{290–350}$, $S_{275–295}$, a_{250}:a_{365}, and S_R), but no consistent pattern was observed in significant differences across other water types.

However, the spectral slope ratio (S_R) was the only CDOM parameter of the six investigated that showed statistically significant differences between all four water types (p<0.~~01~~05).

Lastly, we examined the relationships between CDOM optical properties and DOM bioavailability. To this end, we performed linear regressions between all six of our derived CDOM parameters and bioavailable DOC concentrations to determine the strength of their ability to predict bioavailable DOC. Our results indicated that five of the CDOM parameters ($S_{290–350}$, $S_{275–295}$, a_{250}:a_{365}, SUVA$_{254}$, and S_R) were statistically significant predictors at the 0.05 level (Table ~~1~~2). In particular, S_R showed the strongest relationship with bioavailable DOC concentrations (r^2 value = 0.45, p<0.01). The relationship between bioavailable DOC concentrations and S_R (Figure 6) showed a distinct negative trend (bioavailable DOC mg L^{-1} = -2.204(S_R) + 2.518), with the highest bioavailable DOC concentrations and lowest S_R values for soil pore waters, and lowest bioavailable DOC concentrations and highest S_R values for Kolyma River mainstem waters. We found a clear gradation in the relationship between S_R and bioavailable DOC down the flow-path continuum, as one would also expect by examining these parameters individually (e.g., Figures 2b, 5f). In summary, not only was S_R the only CDOM parameter that showed statistically significant separation between all four water types examined, but it also had the strongest relationship when compared with concentrations of bioavailable DOC.

4. Discussion and Conclusions

In this study, we present a full suite of DOC, bioavailable DOC, and CDOM parameters throughout the permafrost-dominated Kolyma River basin in Northeast Siberia with the purpose of helping to elucidate the processing of DOM along a full flow-path continuum from soil pore waters to the mainstem. Our findings show that average concentrations of DOC and bioavailable DOC generally decrease as waters travel downstream from soil pore waters, streams, rivers, and ultimately to the Kolyma River mainstem. This pattern suggests the occurrence of rapid in-stream processing of DOM and potential remineralization of DOC to atmospheric CO_2 ~~-~~during this July baseflow period well before these waters reach the Arctic Ocean (e.g., Denfeld et al., 2013~~,~~; Mann et al., 2015; Spencer et al., 2015~~, Mann et al., in press~~). The amount of total DOC putatively lost to remineralization is a relatively small fraction (~3–6% depending upon water type), but on par with similar studies across the Arctic for this time of year (e.g., Holmes et al., 2008). Although this may be a relatively small proportion, it is likely the permafrost-derived, ancient DOC found in headwaters that is contributing to permafrost carbon feedbacks to climate warming (Mann et al., 2015). ~~In general~~Moving downstream, the river continuum concept predicts that relative diversity of organic molecules decreases from the headwaters to the river mouth (Vannote et al., 1980). As energetically favorable compounds are converted to living tissue or respired as CO_2, bulk DOM in the Kolyma basin has indeed been shown in previous studies to become less diverse moving from headwaters to mainstem waters before exported to the Arctic Ocean (Spencer et al., 2015).

CDOM parameters presented in this study give further insight into characteristics of DOM along the full flow-path continuum throughout the Kolyma River basin. For instance, the specific ultraviolet absorbance ($SUVA_{254}$) has been shown to be correlated with DOM composition, where $SUVA_{254}$ values are positively correlated with percent aromaticity and molecular size of DOM (and for a given river have been shown to be greatest during spring flood) (e.g., Weishaar et al., 2003; Spencer et al., 2009a; Mann et al., 2012). In this study, we generally found progressively decreasing SUVA_{254} values along the flow-path from soil pore waters towards mainstem waters, suggesting that soil pore waters contain higher molecular weight, aromatic terrestrial DOM that generally becomes lower in molecular weight and aromaticity along the flow-path continuum towards the Kolyma River mainstem. In addition, the $a_{250}:a_{365}$ ratio has been shown to be negatively correlated to aromaticity and molecular size of DOM (Peuravuori and Pihlaja, 1997). In fact (similar to samples from the Yukon River, Alaska (Spencer et al., 2009a)), our data showed that the $a_{250}:a_{365}$ ratio is significantly negatively correlated with SUVA_{254} ($a_{250}:a_{365} = -0.947\ (\mathrm{SUVA}_{254}) - 0.947$; $r^2=0.49$, $p<0.01$). As such, the $a_{250}:a_{365}$ ratio may potentially be utilized as a first-order proxy for SUVA_{254} when DOC concentrations cannot be easily determined.

~~Despite~~ However, despite ~~these~~ our observations of downstream shifts in DOM composition ~~however~~, we find a relatively constant proportion of DOC that was bioavailable (~~~4.4~~3–6% of total DOC ~~averaged across all samples~~) regardless of relative water residence time along the flow-path. This suggests that continual microbial processing of organic matter is able to occur~~s~~ ~~over~~ with similar rates during transit from headwaters throughout the Kolyma River drainage network to the Arctic Ocean concurrent with ongoing downstream CDOM compositional changes. Microbial demand in headwater streams of the Kolyma River basin is subsidized by significant quantities of DOC specifically derived from permafrost and aged soils, yet the proportion of permafrost supporting DOC mineralization declines as waters move downstream through the fluvial network (Mann et al., ~~in press~~2015). Thus, our results importantly show that microbial metabolism continues at similar rates independent of dominant DOM source and radiocarbon age.

There may be several reasons for why microbial metabolism maintains this consistent rate along the flow-path, including the possibility that aquatic microorganisms are acclimating to a downstream shift in DOM composition. ~~The~~ The higher overall amounts of bioavailable DOC we measured in soil pore waters may reflect a highly bioreactive permafrost or aged surface soil derived ~~DOC~~ fraction of the bulk DOC pool (e.g., Vonk et al., 2013~~,~~; Mann et al., 2014). Further downstream in larger tributary and Kolyma mainstem waters, it has been shown that lower total amounts of bioavailable DOC is supported almost entirely from predominantly modern radiocarbon aged surface soils and vegetation sources (Mann et al., ~~in press~~2015). Aquatic microorganisms ~~must~~ may therefore be readily ~~adapt~~ acclimating to significant shifts in DOM composition caused by selective losses of unique DOM fractions (e.g., Kaplan and Bott, 1983; Spencer et al., 2015) alongside high-internal demand for labile DOM by stream communities in lower order streams, which ~~is~~ would otherwise generally be expected to result in decreased DOM lability with increasing water residence time (Stepanauskas et al., 1999a,b; Wikner et al., 1999; Langenheder et al., 2003; Sondergaard et al., 2003; Fellman, 2010; Fellman et al., 2014).

Additional mechanisms such as increasing photodegradation downstream may also account for our observed patterns in downstream DOM. Previous studies have indicated that CDOM spectral slopes (particularly $S_{290–350}$ and $S_{275–295}$) can serve as indicators of DOM source and composition, where a steeper spectral slope typically suggests lower molecular weight material with decreasing aromatic content and a shallower (i.e., lower) slope typically suggests higher molecular weight material with increasing aromatic content (Green and Blough, 1994;

Blough and Del Vecchio, 2002; Helms et al., 2008; Spencer et al., 2008; Spencer et al., 2009a). Furthermore, $S_{275–295}$ has been identified as a reliable proxy for dissolved lignin and therefore terrigenous DOM supply across Arctic Ocean coastal waters, as well as photobleaching history (Helms et al., 2008; Fichot et al., 2013). We found a general increase in $S_{290–350}$ and $S_{275–295}$ moving downstream through the network, indicative of progressive photodegradation of DOM alongside likely reductions in average DOM molecular weight and aromaticity. We found spectral slopes over longer wavelength regions ($S_{350–400}$) decreased through the network, also suggesting constant photochemical degradation of DOM as waters flowed downstream (e.g., Helms et al., 2008). The slope ratio (S_R) has also been shown to be a proxy for DOM molecular weight and source, where low ratios typically correspond to more allochthonous, higher molecular weight DOM (Helms et al., 2008; Spencer et al., 2009b; Mann et al., 2012). The advantage of S_R ratios over individual S values is apparent when each spectral slope responds to a process in an opposing manner, emphasizing the response in calculated S_R values. The clear increases in S_R we observed moving downstream in the fluvial network (from a minimum of 0.74 in soil pore waters to a maximum of 1.24 in the mainstem) indicate that during July summer conditions, soil pore waters contain higher molecular weight, aromatic terrestrial DOM that generally becomes lower in average molecular weight and aromaticity along the flow-path continuum towards the Kolyma River mainstem. The maximum S_R value of 1.24 we report in the Kolyma River mainstem is markedly higher than the range of S_R (0.82–0.92) reported in Stedmon et al. (2011) for the Kolyma from 2004 and 2005, demonstrating the heterogeneity of DOM properties even in mainstem waters and the necessity for greater temporal resolution in monitoring. Similar to spectral slopes, S_R values may also be indicative of photobleaching history (e.g., Helms et al., 2008) and our we observed increase in S_R downstream through the network suggests evidence of on-going photochemical degradation of surface water DOM during transit.

~~CDOM parameters presented in this study give further insight into characteristics of DOM along the full flow-path continuum throughout the Kolyma River basin.~~ ~~Previous studies have indicated that CDOM spectral slopes (particularly $S_{290-350}$ and $S_{275-295}$) can serve as indicators of DOM source and composition, where a steeper spectral slope typically suggests lower molecular weight material with decreasing aromatic content and a shallower slope typically suggests higher molecular weight material with increasing aromatic content (Green and Blough, 1994; Blough and Del Vecchio, 2002; Helms et al., 2008; Spencer et al., 2008; Spencer et al., 2009a). Furthermore, $S_{275-295}$ has been identified as a reliable proxy for dissolved lignin and therefore terrigenous DOM supply across Arctic Ocean coastal waters, as well as photobleaching history (Helms et al., 2008; Fichot et al., 2013). We found a general increase in $S_{290-350}$ and $S_{275-295}$ moving downstream through the network, indicative of progressive photodegradation of DOM alongside likely reductions in average DOM molecular weight and aromaticity. We found spectral slopes over longer wavelength regions ($S_{350-400}$) decreased through the network, also suggesting constant photochemical degradation of DOM as waters flowed downstream (e.g., Helms et al. 2008). The slope ratio (S_R) has also been shown to be a proxy for DOM molecular weight and source, where low ratios typically correspond to more allochthonous, higher molecular weight DOM (Helms et al., 2008; Spencer et al., 2009b; Mann et al., 2012). The advantage of S_R ratios over individual S values is apparent when each spectral slope responds to a process in an opposing manner, emphasizing the response in calculated S_R values. The clear increases in S_R we observed moving downstream in the fluvial network (from a minimum of 0.74 in soil pore waters to a maximum of 1.24 in the mainstem) indicate that~~

~~during July summer conditions, soil pore waters contain higher molecular weight, aromatic terrestrial DOM that generally becomes lower in average molecular weight and aromaticity along the flow-path continuum towards the Kolyma River mainstem. The maximum S_R value of 1.24 we report in the Kolyma River mainstem is markedly higher than the range of S_R (0.82–0.92) reported in Stedmon et al. (2011) for the Kolyma from 2004 and 2005, demonstrating the heterogeneity of DOM properties even in mainstem waters and the necessity for greater temporal resolution in monitoring.~~

Photodegradation may indeed play an important and direct role in our observed consistent fraction of bioavailable DOC along the flow-path. Previous studies in the Arctic underscore the importance of residence times as well as a significant combined role for photo- and biological degradation along the flow-path in Arctic watersheds (Cory et al., 2007; Merck et al., 2012; Cory et al., 2013; Laurion and Mladenov, 2013). These previous results show that the photochemical "pretreatment" of stream DOM that occurs during export into lakes and coastal zones may impact the ability of microorganisms to mineralize DOM. Therefore, the residence times and flow-paths of waters should greatly influence the ultimate fate of DOM (e.g., DOM vs. CO_2) exported to the adjacent ocean. In our case, we find that our increasing S_R values downstream suggest important photodegradation processes are occurring along the flow-path continuum, where this photodegradation may potentially release significant quantities of labile DOM for continued microbial processing of DOM further downstream in these stream networks. In other words, the more abundant "virgin" bioavailable molecules upstream are replaced downstream by photobleached smaller molecules (originating from aromatic compounds), resulting in the fraction of DOC used relatively constant without any clear pattern overall. If this (or something similar) were not the case, we would expect to see a declining fraction of bioavailable DOC along the flow-path continuum.

~~The specific ultraviolet absorbance (SUVA$_{254}$) has also been shown to be correlated with DOM composition, where SUVA$_{254}$ values are positively correlated with percent aromaticity and molecular size of DOM (and for a given river have been shown to be greatest during spring flood) (e.g., Weishaar et al., 2003; Spencer et al., 2009a; Mann et al., 2012). In this study, we generally found progressively decreasing SUVA$_{254}$ values along the flow-path from soil pore waters towards mainstem waters, suggesting that (similar to spectral slope parameters) soil pore waters contain higher molecular weight, aromatic terrestrial DOM that generally becomes lower in molecular weight and aromaticity along the flow-path continuum towards the Kolyma River mainstem. In terms of the remaining CDOM parameter investigated here, the a_{254}:a_{365} ratio has been shown to be negatively correlated to aromaticity and molecular size of DOM (Peuravuori and Pihlaja, 1997). In fact (similar to samples from the Yukon River, Alaska (Spencer et al., 2009a)), our data showed that the a_{254}:a_{365} ratio is significantly negatively correlated with SUVA$_{254}$ (a_{254}:a_{365} = −0.947 (SUVA$_{254}$) − 0.947; r^2=0.49, p<0.01). As such, the a_{254}:a_{365} ratio may potentially be utilized as a first-order proxy for SUVA$_{254}$ when DOC concentrations cannot be easily determined.~~

In this study, we have provided new and important findings with regards to the spatial distribution of DOM concentration, bioavailability, and optical properties during mid-summer hydrologic conditions throughout the Kolyma River basin in Northeast Siberia. Freshwater DOC measurements across the network were strongly positively correlated to CDOM absorption at 254 nm (r^2 = 0.958, p<0.01), confirming the utility of simple CDOM optical measurements for estimating carbon concentrations in arctic freshwaters (Spencer et al., 2008, 2009a; Stedmon et al., 2011) and across water types within the Kolyma River basin in particular. Furthermore, the optical parameter S_R proved to be the only CDOM compositional measure that showed statistically significant separation between all four water types examined during the study period, suggesting that this parameter may be useful for easily distinguishing characteristics and processes occurring in organic matter among water types along the full flow-path continuum. The significant increase in S_R values we observed downstream through the network suggests evidence of on-going photochemical degradation of surface water DOM during transit. Additionally, of all the CDOM parameters, S_R values were most closely related to concentrations of bioavailable DOC ($r^2 = 0.454$, $p<0.01$), suggesting that this value may be correlated with a ~~the rate of~~ decline in bioavailable DOC through the network. However, biological degradation has previously been shown to typically slightly decrease S_R values (Helms et al., 2008), which indicates that the opposite relationship observed here may instead be a consequence of co-variance with photodegradation of DOM, or demonstrate that S_R values may reflect a broader, more complex range of physical and biological processes than previously recognized. Garnering further insight from our measurements, the relatively constant proportion of DOC that was bioavailable regardless of relative water residence time along the flow-path may be a consequence of two potential scenarios allowing for continual processing of organic material within the system, namely: (a) aquatic microorganisms are acclimating to a downstream shift in DOM composition; and/or (b) photodegradation is continually generating labile DOM for continued microbial processing of DOM along the flow-path continuum. Without such processes, we would otherwise expect to see a declining fraction of bioavailable DOC downstream with increasing residence time of water in the system.

Unlike many previous studies that focus on only mainstem rivers in the Arctic, we focus here on a variety of waters along a full flow-path continuum, showing that CDOM metrics (in particular, S_R) reflect important compositional differences in DOM of waters along the transit from headwaters to the Arctic Ocean. The range in DOM properties of waters travelling downstream through the Kolyma Basin often spanned wider ranges than DOM compositional differences reported annually among the six major arctic rivers. For example, S_R values across the major arctic rivers over the years 2004 and 2005 spanned a minimum of 0.79 in the Yenisey River, to a maximum value of 1.11 in the Mackenzie River (Stedmon et al., 2011), compared to the range of 0.74–1.24 for waters in our study within a single basin. It is therefore essential that changes taking place in the quality of CDOM exported by these rivers be examined throughout entire river basins in order to adequately assess climate driven shifts in terrigenous carbon supply and reactivity. ~~.~~

Future work that includes both photo- and microbial degradation experiments may further elucidate the ability for S_R to serve as a direct proxy for these processes along a flow-path gradient. Our overall results thus far demonstrate promise for utilizing ultraviolet-visible absorption characteristics to easily, inexpensively, and comprehensively monitor the quantity and quality of DOM (over broad ranges) across permafrost landscapes in the Arctic. This is particularly critical for remote arctic landscapes such as those in Northeast Siberia, where the future fate of organic carbon currently frozen in permafrost soils (and whether it ultimately is released as CO_2 and CH_4) is tightly linked to the lability of this material.

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Table 1. Mean spectral slope and other CDOM parameters for soil pore waters, streams, rivers, and the Kolyma River mainstem.

	$S_{290–350}$ (× 10^{-3} nm^{-1})	$S_{275–295}$ (× 10^{-3} nm^{-1})	$S_{350–400}$ (× 10^{-3} nm^{-1})	a_{250}:a_{365}	SUVA$_{254}$ (L mg C^{-1} m^{-1})	S_R
Soil pore waters	15.35	15.27	18.65	5.47	3.52	0.82
Streams	17.08	17.39	18.89	6.44	2.94	0.92
Rivers	17.17	17.79	18.19	6.27	2.77	0.98
Kolyma Mainstem	18.10	18.57	17.50	6.53	2.56	1.06

Table ~~1~~2. Relationships between bioavailable DOC and each of the six CDOM metrics investigated. S_R shows the highest r-squared value, with a *p*-value of 0.00002.

	r^2	*p*-value
$S_{290-350}$	0.3560	0.00025
$S_{275-295}$	0.4497	0.00002
$S_{350-400}$	0.0443	0.23987
a_{250}:a_{365}	0.2645	0.00220
SUVA$_{254}$	0.1980	0.01376
S_R	0.4540	0.00002

Figure Legends

Figure 1. The northern reaches of the Kolyma River in East Siberia and the locations of the 47 water samples collected throughout the region in this study (including soil pore waters, streams, rivers, and the Kolyma River mainstem).

Figure 2. Concentrations of (a) dissolved organic carbon (DOC), (b) bioavailable DOC, and (c) percentage of total DOC that is bioavailable for the four water sample types. The mean (hollow squares), median (horizontal lines), ±1 standard deviation (gray boxes), and total range (whiskers) for each sample population are shown.

Figure 3. Chromophoric dissolved organic carbon (CDOM) absorption spectra from 200–800 nm for (a) all samples; and (b) streams, rivers, and the Kolyma River mainstem only.

Figure 4. Relationships between DOC and CDOM absorption at 254, 350, and 440 nm for streams, rivers, and the Kolyma River mainstem.

Figure 5. The six presented CDOM metrics, (a) $S_{290\text{–}350}$, (b) $S_{275\text{–}295}$, (c) $S_{350\text{–}400}$, (d) $a_{250}:a_{365}$, (e) SUVA_{254}, and (f) S_R, show the separation between soil pore, stream, river, and Kolyma main stem waters. The mean (hollow squares), median (horizontal lines), ±1 standard deviation (gray boxes), and total range (whiskers) for each sample population are shown.

Figure 6. The CDOM metric S_R shows a relatively strong relationship with concentrations of bioavailable DOC present in the sampled waters, with an r-squared value of 0.4540 and *p*-value <0.01.

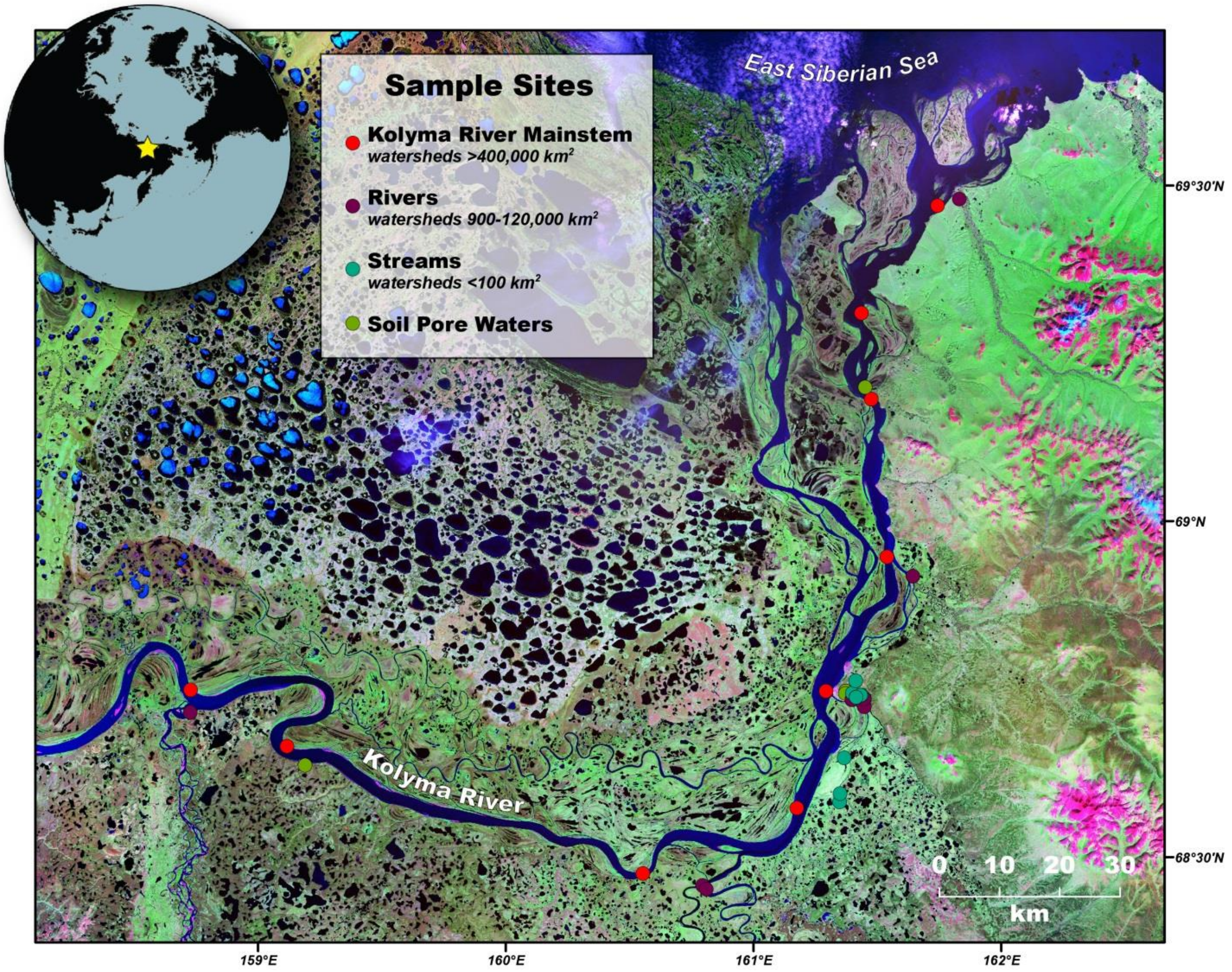

Sample Sites
Kolyma River Mainstem
watersheds >400,000 km^2
Rivers
watersheds 900-120,000 km^2
Streams
watersheds <100 km^2
Soil Pore Waters
East Siberian Sea
Kolyma River
69°30'N
69°N
68°30'N
159°E
160°E
161°E
162°E
0 10 20 30
km

Figure 1.

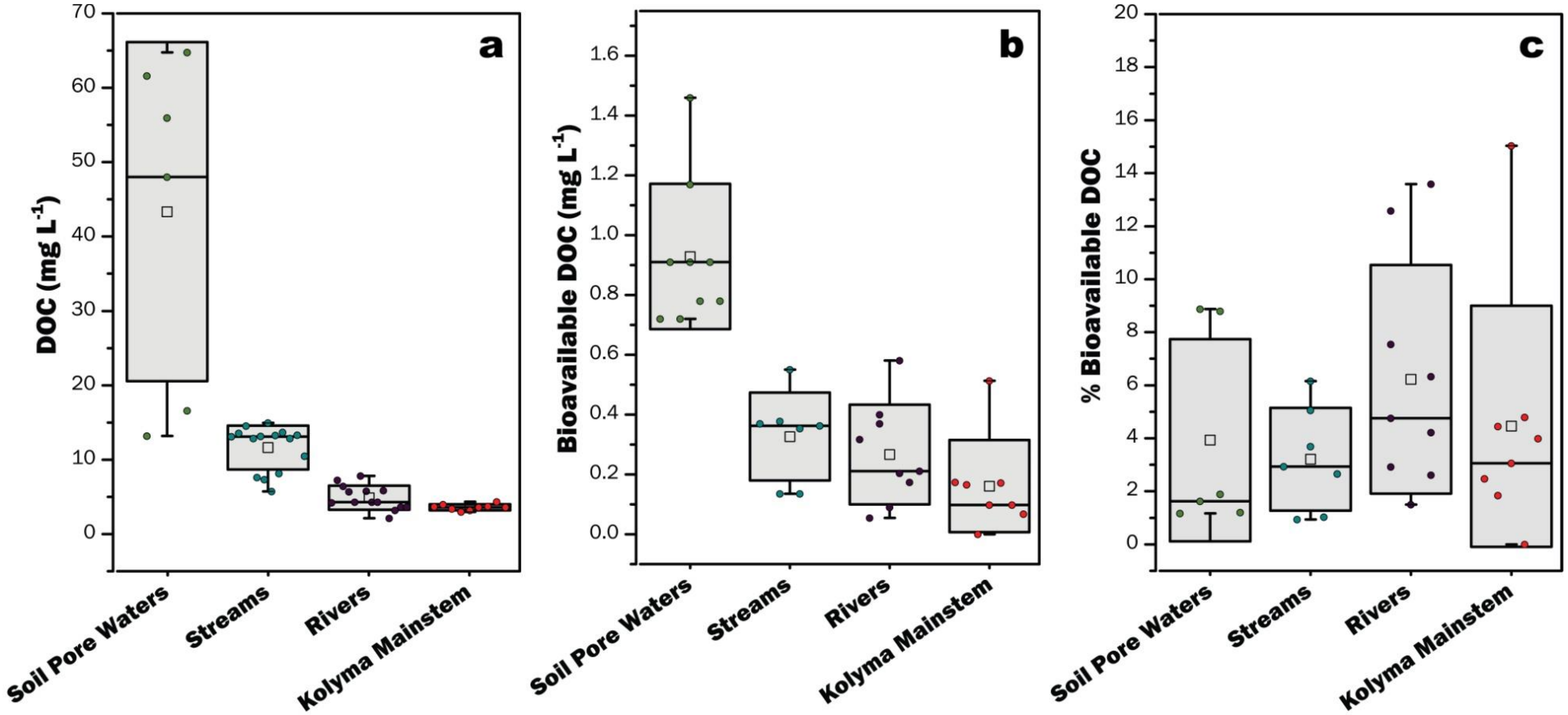

a
DOC (mg L-1)
70
60
50
40
30
20
10
0
Soil Pore Waters
Streams
Rivers
Kolyma Mainstem
b
Bioavailable DOC (mg L-1)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Soil Pore Waters
Streams
Rivers
Kolyma Mainstem
c
% Bioavailable DOC
20
18
16
14
12
10
8
6
4
2
0
Soil Pore Waters
Streams
Rivers
Kolyma Mainstem

Figure 2.

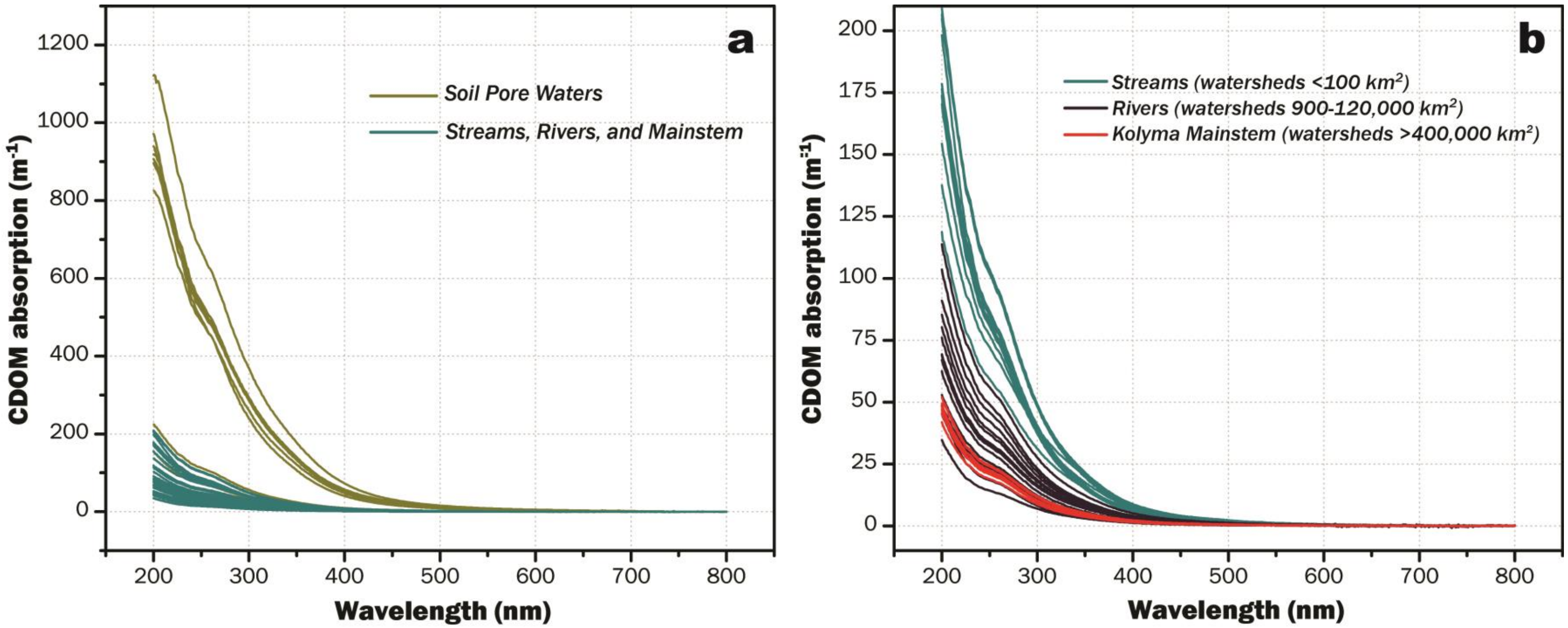

a
b
Soil Pore Waters
Streams, Rivers, and Mainstem
Streams (watersheds <100 km²)
Rivers (watersheds 900-120,000 km²)
Kolyma Mainstem (watersheds >400,000 km²)
CDOM absorption (m⁻¹)
Wavelength (nm)
1200
1000
800
600
400
200
0
200
175
150
125
100
75
50
25
0
200
300
400
500
600
700
800

Figure 3.

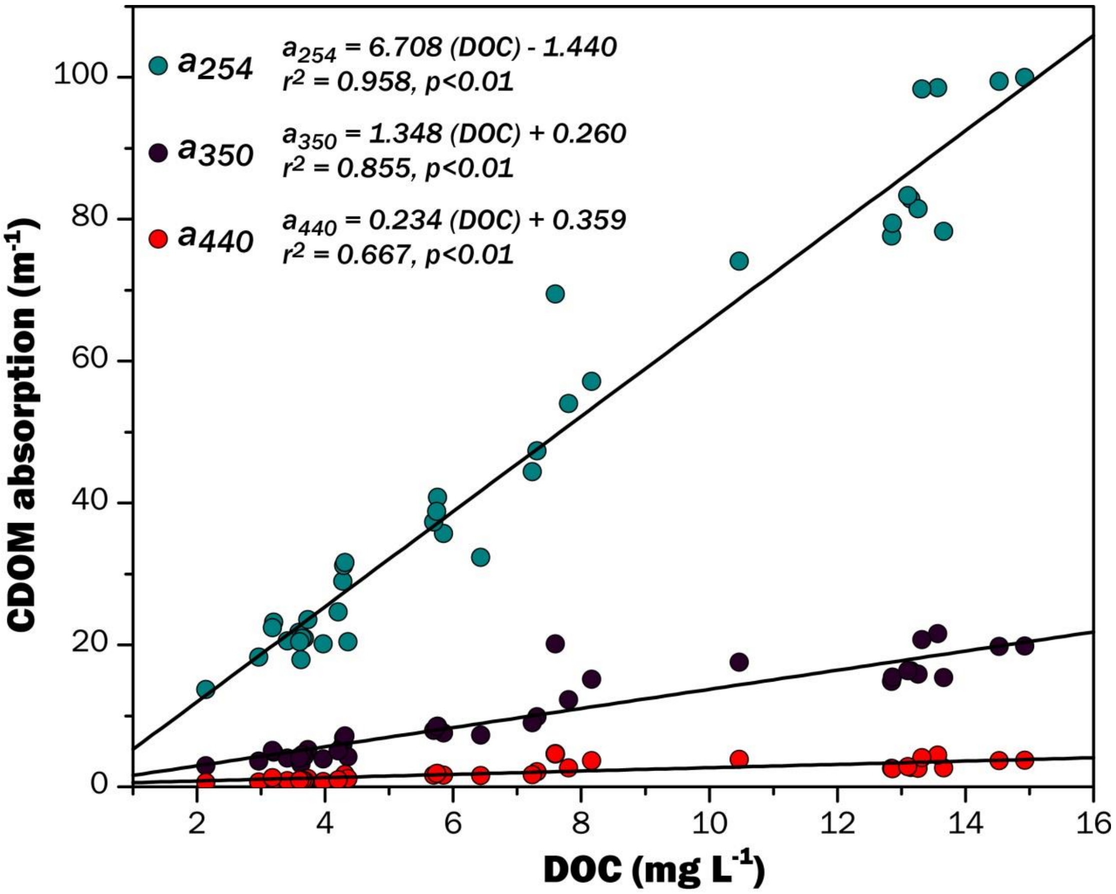
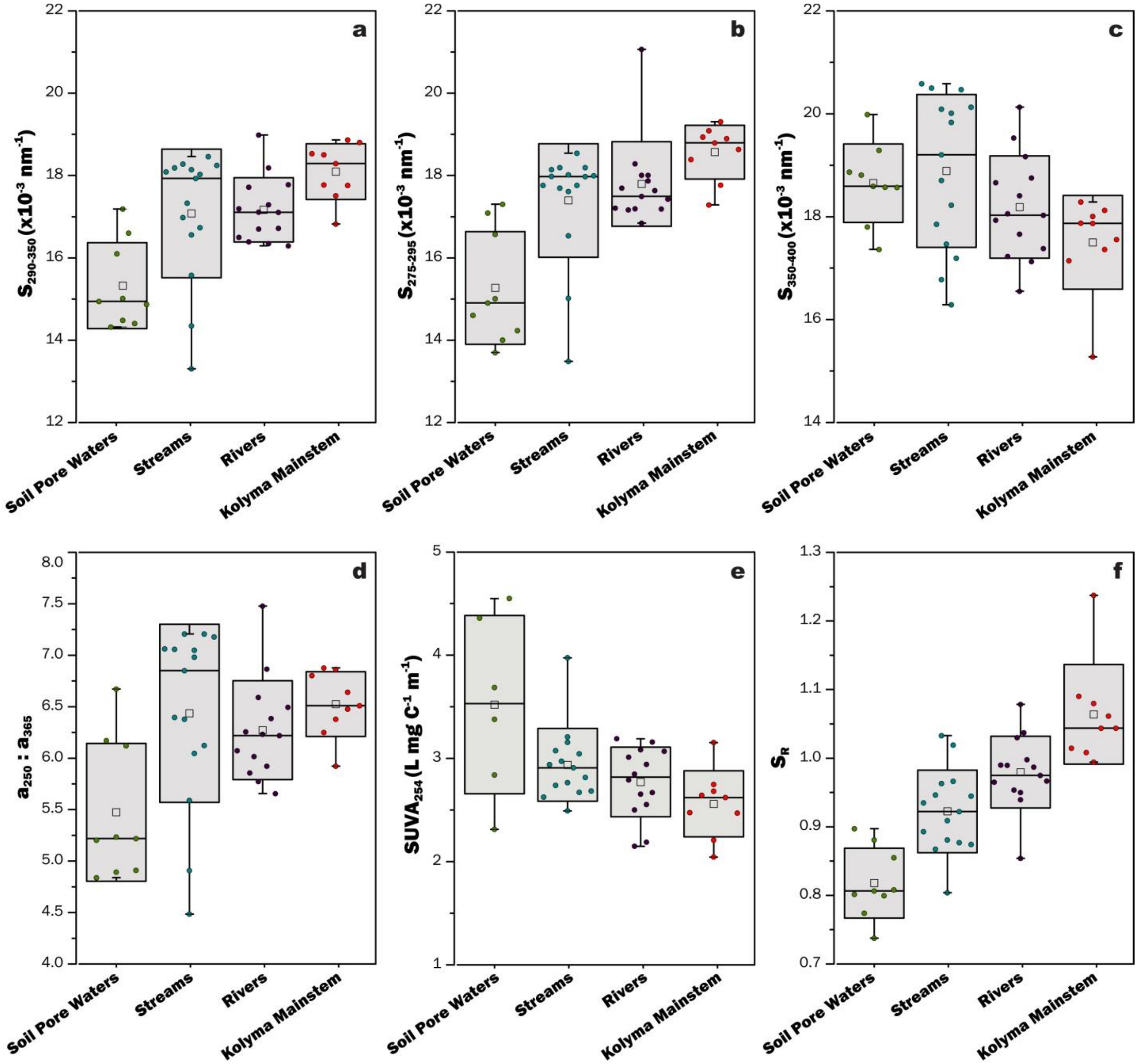

● a_{254}
a_{254} = 6.708 (DOC) - 1.440
r^2 = 0.958, p<0.01
● a_{350}
a_{350} = 1.348 (DOC) + 0.260
r^2 = 0.855, p<0.01
● a_{440}
a_{440} = 0.234 (DOC) + 0.359
r^2 = 0.667, p<0.01
CDOM absorption (m^{-1})
0
20
40
60
80
100
2
4
6
8
10
12
14
16
DOC (mg L^{-1})

Figure 4.



a
b
c
d
e
f
$S_{290-350}$ (x10^{-3} nm^{-1})
$S_{275-295}$ (x10^{-3} nm^{-1})
$S_{350-400}$ (x10^{-3} nm^{-1})
a_{250} : a_{365}
$SUVA_{254}$ (L mg C^{-1} m^{-1})
S_R
12
14
16
18
20
22
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
1
2
3
4
5
0.7
0.8
0.9
1.0
1.1
1.2
1.3
Soil Pore Waters
Streams
Rivers
Kolyma Mainstem

Figure 5.

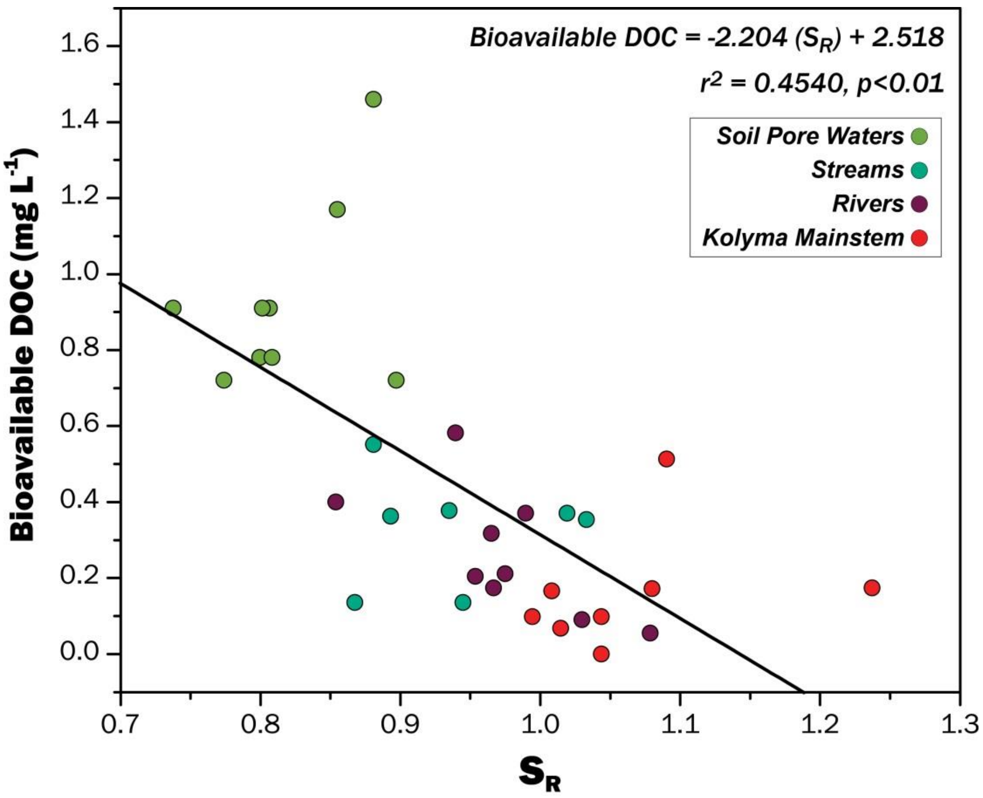

Bioavailable DOC = -2.204 (S_R) + 2.518
r² = 0.4540, p<0.01
Soil Pore Waters
Streams
Rivers
Kolyma Mainstem
Bioavailable DOC (mg L⁻¹)
S_R
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3

Figure 6.