

## Author Comments

### **Comments on the review by Reviewer #1**

Reviewer #1: “*The manuscript would be even more useful for the general scientific community if the authors would give a more thorough review on DOC concentrations in groundwater/springs in other parts of the world. DOC concentrations in Florida spring are among the lowest in the world. What is the level of DOC in groundwater world-wide? Numerous papers have reported surface water DOC concentrations. Although groundwater monitoring has been carried out in many countries, the knowledge on the level of DOC concentrations in groundwater is limited.*”

*Comment:* We agree that a comparison to DOC concentration in groundwater elsewhere will be of interest.

*Action:* We will add and discuss a table reporting DOC concentrations in groundwater across the world in the revised version of the manuscript.

Reviewer #1: “*Why are DOC concentrations so low in Florida springs? Is the overall conclusion that most/all DOC is biologically available, if the retention time is long enough.*”

*Comment:* Indeed, the conclusion should be that most DOC should be biologically available, although this does not imply that the DOC pool should be labile, as the long residence time of the Florida aquifer implies that even semi-labile DOC, which is used more slowly than labile DOC, would be depleted along the long residence in the aquifer. Moreover, the warm temperature in this aquifer (emerging at about 25 ° C) enhances respiration rates of prokaryotes, which should contribute to deplete the DOC pool.

*Action:* We will expand the discussion of this important aspect in the revised version of the manuscript.

Reviewer #1: p. 5255 "DOC concentration in most natural waters is a rather stable property – exhibiting only modest temporal variability". Why is DOC variability so low — is it linked mainly to the source, transport, reactivity?

*Comment:* We suggest that the reason for the low variability is the onset of an approximate steady-state between inputs and outputs in most aquatic ecosystems.

*Action:* We will expand the discussion of this important aspect in the revised version of the manuscript.

Reviewer #1: Although DOC shows very modest variability compared to many other elements, seasonal DOC variability e.g. in boreal streams is significant (e.g. Lepistö et al. 2008). Lepistö, A., Kortelainen, P. Mattsson, T. 2008. Increased organic C and N leaching in a northern boreal river basin in Finland. *Global Biogeochemical Cycles* Vol 22, GB3029, doi:10.1029/2007GB003175.

*Comment*: We agree.

*Action*: This and other references will be cited in the discussion of the revised manuscript.

Reviewer #1 3, 5, and 7, 14 I was missing references to DOC level in groundwater systems worldwide.

*Comment*: We agree that a comparison to DOC concentration in groundwater elsewhere will be of interest.

*Action*: We will add and discuss a table reporting DOC concentrations in groundwater across the world in the revised version of the manuscript.

### ***Comments on the review by Reviewer #2***

Reviewer #2 The introduction needs to be better tuned to the discussion section. For example, because the discussion lists these springs as 'the most organic-depleted waters yet reported in the biosphere', I expect that the introduction provides more information about DOC concentration in spring and necessarily also ground waters worldwide to the reader. I am curious about average DOC concentrations in spring/ground waters and other spring systems that show similar low DOC concentrations. Do these systems share similar characteristics?

*Comment*: We agree that further information on DOC concentration in groundwater systems and springs will improve the manuscript.

*Action*: We will add and discuss a table reporting DOC concentrations in groundwater across the world in the revised version of the manuscript.

Reviewer #2 (ii) The aspect of producing low-DOC reference material from these organic-depleted waters is to my opinion highly rewarding and needs a better discussion. The reader is a bit left alone with this final statement. The scientific community needs to be better convinced about a possible future initiative on producing Freshwater DOC reference standards. I have once produced my own ref standards from alpine lake water for a large lake sampling campaign, but would have been delighted if multiple tested and referenced standards would have been around.

*Comment:* We agree that the suggestion that waters with very low DOC from Florida springs could be used to produce reference materials for freshwater DOC analysis need be elaborated further.

*Action:* We will discuss further in the revised version of the manuscript the suggestion that waters with very low DOC from Florida springs could be used to produce reference materials for freshwater DOC analysis, including how this matterial could be used.

Reviewer #2 (iii) The authors miss to shortly explain why these spring water are so depleted in DOC? Does it also have anything to do with the geological setting, residence times, temperature? Is information on total N concentrations and discharge enough to predict DOC concentrations? This would help to clarify the unique status of these Florida springs.

*Comment:* Indeed, the causes for the low DOC concentration in Florida spring need be discussed. Most of the DOC pool should be biologically available, although this does not imply that the DOC pool should be labile, as the long residence time of the Florida aquifer implies that even semi-labile DOC, which is used more slowly than labile DOC, would be depleted along the long residence in the aquifer. The relationship with N concentrations, which affects DOM availability, also suggest that availability exerts a major control on DOC concentrations in the springs. Moreover, the warm temperature in this aquifer (emerging at about 25 ° C) enhances respiration rates of prokaryotes, which should contribute to deplete the DOC pool.

*Action:* We will expand the discussion of these important aspects in the revised version of the manuscript.

Reviewer #2 (iv) In which season were these spring samples obtained? The authors state that there is considerable variability in DOC concentrations among different discharge regimes. Did the authors also consider seasonal variability in regard to spring DOC concentrations and DOC accretion along downstream flow?

*Comment:* The springs were sampled in the late winter (February-March) and the results do not consider seasonal variability. We will, however, discuss seasonal changes in spring DOC concentration on the basis of a data base on DOC changes in some Florida springs available from the Florida Dept. of Natural Resources.

*Action:* We will discuss the issue of seasonal variability and will illustrate these changes on the basis of a a data base on DOC changes in some Florida springs available from the Florida Dept. of Natural Resources.

Reviewer #2 2. page 5254: improve discussion on DOC concentration in spring and necessarily also ground waters worldwide, inclusive better references to this information.

*Reply:* We will do so, including a table with a compilation of data on DOC concentration in groundwaters worldwide, along with the corresponding references.

Reviewer #2 3. page 5255: regards to modest variability in DOC concentrations I expect a better reference than Pairie unpublished data.

*Reply:* We agree, and will provide better and more appropriate references.

### ***Comments on the review by Reviewer #3***

Reviewer #3 There, however, needs to be some clarification both in setting up the scope of the discussion within the introduction and explanation for some key points made in the discussion itself. For example, there is a lack of background on spring waters and groundwaters worldwide to simply support the statement on the low DOC of these spring systems. Further, key statements such as the “stability” of DOC concentrations in most surface water environments is not well supported in the literature (seasonality in headwater stream DOC in temperate and boreal regions).

*Comment:* We agree that further information and background on DOC concentration in groundwater systems and springs as well as an improved discussion on variability of DOC in freshwater ecosystems that will improve the manuscript.

*Action:* We will add and discuss a table reporting DOC concentrations in groundwater across the world in the revised version of the manuscript, along with an improved discussion, better supported by references, on the variability of DOC in freshwater ecosystems, and the roles of discharge and the source of DOC on this variability

Reviewer #3 1. p.5254 lines 23-24. In the introduction provide more background on groundwaters and spring water DOC.

*Comment:* We agree that further information and background on DOC concentration in groundwater systems and springs.

*Action:* We will add and discuss a table reporting DOC concentrations in groundwater across the world in the revised version of the manuscript.

Reviewer #3 P.5255 lines 1-12. Explain what is meant by stable property. Temporal stability in DOC concentrations widely varies and for flowing systems can be quite “unstable” and highly dependent upon discharge which is a point raised in the discussion. Variation in DOC concentration with discharge is a common phenomena in headwater streams in general. Better referencing and more detail on this point needs to be made. The statement as provided is not well supported in the literature, however, the concept that the DOC pool can often be viewed as “stable” when in fact it is quite dynamic is a very important one. The point that systems such as these springs can help elucidate reactivity and processing of some pools of DOC is key and why I think the authors need to do a better job with this part of the introduction. The authors should consider discussing this in light of source and composition of DOC. Often the highly reactive portion of this pool is a small portion of the total particularly where DOC concentrations are very high.

*Comment:* The reviewer is correct.

*Action:* We will improve the discussion on the variability of DOC in freshwater ecosystems, and the roles of discharge and the source of DOC on this variability

Reviewer #3 3. P. 5256 Lines 1-2. When were these samples taken? What is known about temporal variation in DOC in these springs? Given the focus of this study it is important to provide brief detail on these factors particularly in relation to the downstream inputs.

*Comment:* The springs were sampled in the late winter (February-March) and the results do not consider seasonal variability. We will, however, discuss seasonal changes in spring DOC concentration on the basis of a data base on DOC changes in some Florida springs available from the Florida Dept. of Natural Resources.

*Action:* We will discuss the issue of seasonal variability and will illustrate these changes on the basis of a a data base on DOC changes in some Florida springs available from the Florida Dept. of Natural Resources.

Reviewer #3 4. P. 5259. Lines 6-15. The general discussion on a younger versus slightly older water mass is not well supported as given. This is the most speculative part of the discussion and could be improved by providing better reference to information on the this aquifer system to explain the differences in DOC and TN provided here. For example, the authors do not explain why total N is higher in the older water mass as discussed here.

*Comment:* We agree

*Action:* We will improve the discussion on this point using all available information.

Reviewer #3 5. P. 5260 Lines 25-30. The one point about the need for reference materials for freshwater DOC measurements is important and points out something that is often done but individual labs but not with any formal consensus. This is brought up out of the blue in the discussion and needs to be incorporated into the discussion more.

*Comment:* We agree that the suggestion that waters with very low DOC from Florida springs could be used to produce reference materials for freshwater DOC analysis need be elaborated further.

*Action:* We will discuss further in the revised version of the manuscript the suggestion that waters with very low DOC from Florida springs could be used to produce reference materials for freshwater DOC analysis, including how this material could be used.

Reviewer #3 P. 5260 lines 22-23. The reference to long residence times should be better clarified since and any information regarding the Florida Aquifer residence time clearly cited. Obviously there are aquifers in the world which have much longer residence times than this aquifer. In few minor details.

*Comment:* We agree.

*Action:* We will improve the discussion on the residence time of the Florida Aquifer.

p. 5256. Lines 16-17. What was the resulting pH of the waters following acid addition. Low pH has been found to reduce DOC concentrations in natural samples.

*Comment:* The springs were sampled in the late winter (February-March) and the results do not consider seasonal variability. We will, however, discuss seasonal changes in spring DOC concentration on the basis of a data base on DOC changes in some Florida springs available from the Florida Dept. of Natural Resources.

*Action:* We will discuss the issue of seasonal variability and will illustrate these changes on the basis of a data base on DOC changes in some Florida springs available from the Florida Dept. of Natural Resources.

p. 5257 lines 21-25. Can the authors clarify this section? Net areal inputs are cited as conservative here given that no water inputs are accounted for but can and do occur in these systems. Increased water inputs would increase spring discharge variable used in this calculation but couldn't it also alter the DOC concentrations used to calculate

the accretion of DOC? Aren't the authors also assuming the DOC concentration of the water input as well when making this statement? In karst environments fractured flow paths can lead to increased inputs of various species including DOC. None of this renders serious problems with the generalized calculations made but it is important that ALL assumptions and their pros and cons be clarified briefly here.

*Comment:* We agree that these are important processes and factors that need be considered.

*Action:* We will better explain the assumptions of the calculations and the possible uncertainties associated with the calculations in the revised version of the manuscript.

p.5258 lines 23-24. One cannot obtain DOC concentrations from Table 2 only the figure.

*Action:* Concentrations will be provided directly in the revised version of the manuscript.