

## ***Interactive comment on “Benthic fluxes of dissolved organic nitrogen in the Lower St. Lawrence Estuary and implications for selective organic matter degradation” by M. Alkhatib et al.***

**M. Alkhatib et al.**

moritz.lehmann@unibas.ch

Received and published: 18 August 2013

AC: We thank the referees for their valuable comments, which will be very helpful when preparing an amended version of the submitted manuscript. The most fundamental criticism (by Reviewer 1 and 2) was that “only two parameters” were measured “in only 9 down-core profiles” and that “it is an incomplete report”. Indeed, our study reports on the distribution of dissolved organic nitrogen (DON) and carbon (DOC) in sediment pore waters determined at nine locations along the St. Lawrence Estuary and in the Gulf of St. Lawrence. While the measurement as such could be considered “basic”, it is the context of the data set that makes it interesting. The estuary is characterized by

C4367

systematic changes in sediment organic matter reactivity and bottom water oxygenation. Hence it is a perfect environment to study the relationship between DON/DOC fluxes and the reactivity of the sediments, particularly in terms of potential elemental discrimination during hydrolysis and bacterial degradation. We demonstrate that DON from the sediments contributes significantly to the overall dissolved N exchange between the estuarine sediments and the water column, representing an important internal source of N to the ocean. Our results also suggest direct links between POM quality, aerobic remineralization and the release of DON to the water column. They furthermore underscore that both the sediment reactivity and the oxygen exposure time of organic particles after sedimentation influence the C/N ratio of hydrolysed dissolved organic matter, a finding which has important implications for the interpretation of bulk OM C/N ratios in sedimentary archives. As Reviewer 3 (Dr. Burdige, an internationally recognized expert in the field), points out, not much has been published on this topic in recent years, and the DON component has often been ignored in nitrogen budgets. Our results are also intriguing in that they confirm that variable preservation conditions and sedimentation regimes can result in variable early diagenetic C/N shifts that can compromise the use of C/N ratios of sedimentary OM as basic OM source indicator. The reviewers came to the conclusion that the quality of our study merits publication in Biogeosciences. Nevertheless, they asked for clarifications on some specific points and suggested corrections, which may help to further improve the manuscript. Below, we address the reviewers' concerns point-by-point (AC: author comment; RC: reviewer comment).

Referee #1

AC: General points: Some of the main points questioning the general value of our contribution have been addressed above. Another concern of Reviewer 1 was that the writing style was rather complex with long and hard to understand sentences. Whereas the other two reviewers think that “overall/generally, the manuscript is well-written”, we will do our best to further improve the writing style, and to break down long and com-

C4368

plicated sentences. We will shorten and simplify the text where necessary, particularly in the discussion, where we will remove sections that are rather speculative.

RC: It is also somewhat excessive using estimated DON fluxes from 9 locations in the St. Lawrence Estuary to extrapolate a total budget for continental shelves globally.

AC: The reviewer is right. We will clarify that this extrapolation is afflicted with large uncertainty. However, we consider the SL Estuary as an average/representative shelf environment, and not to attempt to do this extrapolation with the data in hand would be neglectful. The most important point that we want to make with this extrapolation, independent of the associated error, is that the global benthic DON flux likely is on the order of 50 Tg N per year, and hence an important component of the global N cycle.

RC: Based on these profiles, the diffusive fluxes were estimated and gave some interesting correlation between POM reactivity and oxygen exposure time. The origin of the latter is not clear, but it is certainly not from this study. . . It appears to me that the DOC and DON porewater data are leftovers from a larger project that did not fit into the other papers shown in the reference list (Alkhatib et al., 2012a,b).

AC: Chlorin- and amino acid based degradation indices were presented in Alkhatib et al. (2012a), and we will clarify the source of the data in the revised MS. This data set builds the foundation for the paper discussed here. Only through the study of Alkhatib et al. (2012a) we learned that a strong reactivity gradient exists along the Laurentian Channel. A logic consequence was to make use of this environmental setting to test the impact of sediment reactivity changes on the dissolved inorganic N isotope dynamics (Alkhatib et al. 2012b), as well as to assess its influence of dissolved OM exchange and element partitioning during OM remineralization (this study). Our DOC/DON data set is quite comprehensive, certainly not a leftover.

RC: Since only DOC and DON are measured in this study, it is a pity that no Rhizon data on DOC are reported. No reason is given for that – they are just missing.

C4369

AC: When applying the Rhizon samplers, we unfortunately missed to use Teflon syringes, which is critical for sampling DOC pore samples. The proper procedure was followed when we extracted pore water using the WCS sampler. In an earlier version of our manuscript we have explained the reason for not having included Rhizon sampler DOC data, but we have decided to delete it. At the discretion of the editor, we can provide an explanation for the absence of Rhizon DOC data in the revised MS.

RC: Page 7918, lines 24-26: This sentence is poorly written and is almost impossibly to understand. AC: It will be rephrased

RC: Page 7919, line 1: What does “sedimentary archives” mean? Is it from the literature?

AC: Yes, this is a relatively common term used in paleolimnological and – oceanographic studies (e.g. Litt et al., 2011). It leans on the commonly used terms “paleoclimate or paleoenvironmental archives”, including sediments, speleothems, tree-rings, corals, ice cores. . .). We will clarify this, writing “sedimentary paleoenvironmental archives”.

RC: Page 7919, line 10-11: I disagree that estuarine sediments always exhibit uptake of dissolved inorganic N. In fact, most studies have shown a release of DIN from sediments.

AC: It is true that estuarine sediments are generally a source of ammonium. But often, the nitrate elimination in the sediments exceeds ammonium release, so that the sediments are net sinks of fixed N. Also, the reviewer seemed to have missed that we did not write “estuarine sediments” but “estuarine systems”. In any case, leaning on the papers by Seitzinger and colleagues (cited in the MS), it is fair to say that estuaries, through algal uptake and denitrification, can generally be considered efficient fixed N filters along the land-ocean continuum.

RC: Page 7919, lines 17-23: This sentence is very long and difficult to understand.

AC: See comment above. We will shorten/simplify.

C4370

RC: Page 7920, line 2: Not all forms of DON can be used by microorganisms for biosynthesis.

AC: we will write "...have the capacity to use some forms of DON as a source of N for biosynthesis"

RC: Page 7920, lines 7-8: First, delete "bottom" because it is where sediments always are. Second, does "...remineralized N as DON." mean that DON remineralized to DIN is re-assimilated and released as DON. This is true and not surprising as the gross mineralization in sediments usually is much larger than the measured net mineralization measured from DIN fluxes.

AC: "Bottom" will be deleted. Indeed, "remineralized N as DON" does not make sense. We will write "reflux of N as DON from particulate OM hydrolysis/lysis"

RC: Page 7920, line 15: What does "bioavailability of DOC from sediments with respect to DON" mean. It is hard to understand.

AC: This statement refers to the possibility of preferential consumption of specific dissolved organic matter molecules, which may contain relatively more or less N and C. We will clarify this in the revised MS, writing: "For example, the bioavailability for bacteria of dissolved organic components with high C/N ratios versus components with low C/N ratios, ..."

RC: Page 7922, lines 2-3: Oxygen loss is not only through aerobic microbial respiration. Chemical oxidation processes driven by anaerobic respiration can in certain areas contribute as much or even more than aerobic respiration.

AC: In the St. Lawrence system microbial respiration has been considered as the main route of oxygen consumption in the bottom water layer (Lehmann et al., 2009). However, we cannot exclude that the oxidation of reduced compounds contributes significantly to the O<sub>2</sub> consumption. We will change the text accordingly.

RC: Page 7922, lines 9-10: Where do these degradation indices come from? They are  
C4371

shown in Table 1, but there is no indication of the origin of the data. It is only referred that the indices are developed by Schubert et al. (2005) and Dauwe et al. (1999). These two authors have not presented the St. Lawrence data.

AC: See comment above. We will add references in Table 1

RC: Page 7922, line 12-14: How can we tell from Table 1 that the terrestrial content of OM decreases with distance from the head? No data is provided!!

AC: References will be added.

RC: Page 7922, line 16: Change "multiple" to "eight"

AC: "eight" will be inserted

RC: Page 7923, line 9: Wouldn't it be better using "DIN" here instead of "nutrient". Then any misunderstandings involving P can be avoided.

AC: We will insert DIN

RC: Page 7924, lines 16-24: How reliable are these flux estimates? Precise diffusive flux calculations can only be obtained from high resolution profiles (mm-scale). Furthermore, it is not possible from the current profiles to observe if any consumption or production of DOC and DON occurred near the sediment-water interface. There is often a dramatic shift in reactions when moving from the anoxic to the oxic surface layer. Some considerations justifying the approach are required. It is not enough stating that others have done the same.

AC: Yes, the resolution right at the SWI is a drawback of the method, and we may possible miss something. However, using porewater profiles based on whole-core-squeezing, this is the best we can do. The methods that we have applied are accepted by the scientific community. To our knowledge, there is no better way to obtain a greater porewater sample resolution than WCS. Net DON and DOM fluxes may have been more reliably determined with in-situ benthic chambers, but given the relatively

great water depth, such experiments are all but easy to do, and were not an option in this study. As for identifying the spatial separation of DOM production versus consumption: Again, there is no way to do better than using WCS sampling, and even benthic chamber flux measurements would have been of no help in this regard, as only net fluxes can be determined.

RC: Page 7925, lines 16-17: Which sampling approach provided these results?

AC: DON fluxes were calculated from data within the upper 2 cm of the profiles, and given the agreement between WCS and Rhizon-sampler in the upper 2 cm, we calculated and used the average of DON concentrations derived from both methods for this purpose. This will be clarified in the revised manuscript.

RC: Page 7926, lines 4-8: There is no explanation for the missing Rhizon DOC data. There must have been samples available since DON was analyzed. What have happened to those data?

AC: See comment above.

RC: Page 7926, lines 9-11: How was the DOC/DON ratio calculated? As average of samples from the upper cm or was it as a plot of DOC versus DON results from the upper cm. The latter provides good evidence for the production ratio because it automatically excludes the overlying water concentration. The authors should consider the best way to do this.

AC: We have calculated the C/N ratio from the upper cm by averaging the values of DOC and DON from the upper cm.

RC: Page 7926, line 15: Change to "Rhizon-based DON fluxes"

AC: It will be changed as suggested.

RC: Page 7927, lines 9-10: Bottom water DOC/DON ratios only increased from station 25 to station 20 and then decreased to station 16.

C4373

AC: Yes we have simplified the general trend and will more precisely describe the spatial changes in bottom water DOC/DON ratios.

RC: Page 7928, lines 1-7: These lines repeat what has been said before and could be omitted.

AC: In this paragraph, we address the suitability of our sampling methods for DOM flux determination. We think that the conclusion drawn here is important.

RC: Page 7928, lines 8-29 & page 7929, lines 1-9: The authors spend too much space here on sampling artifacts. This research was not designed for testing the sampling technique. If so, much more focus should have been on this from the start, and the approach should also have been different. The missing Rhizon DOC results are this respect puzzling.

AC: As for DOC Rhizon data, see comment above. As for the inclusion of the methodological aspects: We think that this is an important part of the paper. The comparison (and agreement within the upper 2 cm) between two fundamentally different sampling methods confirms the robustness of our results. At the same time, it begs the question of what could be the explanation for the disagreement between the two methods at greater sediment depth. What would be most puzzling in this regard is showing the profiles and not discussing the observed discrepancies.

RC: How can the authors conclude that Rhizon DOC results are best below 2 cm when there are no results?

AC: This is a general conclusion, which we drew from the DON Rhizon/WCS comparison. We think that the conclusion is valid, because the factors that control diffusivity are the same for both DOC and DON, i.e., molecular size/weight. It has been shown by other workers (eg. Burdige 1991) that the molecular size of DON and DOC is very similar. Nevertheless, we will generalize our statement, writing "...provides the best porewater DOM profiles".

C4374

RC: Page 7930, line 5-9: The data used to make these regressions shown in figures 6 and 7 (sediment particulate C/N ratios, degradation indices, dissolved oxygen concentration and oxygen exposure time) are not available from this study. Where are they from then? And why are they not made for DOC?

AC: See comment above. The data are from Alkhatib et al., 2012a (we will clarify the source of the data in the text). DOC concentrations along the St Lawrence Estuary have not shown any significant variability, that's why such regressions were not included. DOC (obviously, they are indirectly included in the DOC/DON transects). But, at the discretion of the Associate Editor, we could easily include such a regression graph.

RC: Page 7931 Lines 27-28 and page 7932, lines 1-2: This statement is unjustified and only relies on speculation. Should be omitted.

AC: We will take it out!

RC: Page 7932, lines 13-16: This statement tells nothing. Which "DOC-mineral interactions" played a role here?

AC: We referred to adsorptive processes. But again, this is a speculation and we will omit this sentence.

RC: Page 7932, line 28: Only CI is shown in figure 7!!

AC: We will delete "DI" in the text. (on a side note: an excellent agreement exists between the two degradation indices DI and CI)

RC: Page 7933, lines 3-19: These lines are speculative and not supported by the data. Should be omitted.

AC: We will omit (the most speculative) parts of this section. We tried to explain what the possible links between redox and C/N element partitioning are. Some of these links are proved and beyond speculation (the relevant literature is provided), and likely apply

C4375

to the situation in our study area.

RC: Page 7934, line 5: Where are the DIN data shown?

AC: Yes. The data were published in Thibodeau et al. (2010), as explained in line 6 of same page.

RC: Page 7934, lines 17-18: We have been told earlier how the present fluxes compare with other studies. Please omit.

AC: It will be changed as suggested by reviewer.

RC: Page 7934, line 19-27 and page 7935, line 1-2: This extrapolation to global continental shelves is too excessive. It is based on the unjustified assumption that the St. Lawrence Estuary is representative for all shelves, which is most unlikely. More data from different shelves and regions are required to do such extrapolation.

AC: See comment above. The basic assumption is that DON fluxes along the St. Lawrence Estuary and in the Gulf of St. Lawrence are within the range of values reported for various coastal marine environments, and can hence be considered "representative". We based this assumption on the huge data collection presented by Bronk and Steinberg (2008). Again, not to include some sort of more global assessment of benthic DON fluxes based on our data would be neglectful.

RC: Table 3: Such table providing a literature review of fluxes is not relevant here. The needed comparisons are given in the text. Please omit.

AC: We think it is a nice comparison to put the fluxes into a broader context. But this is not critical. At the discretion of the Associate Editor, we will be happy to take out the table.

RC: Figure 3: The sampling technique used is not mentioned in the legend.

AC: The sampling technique will be mentioned in the figure caption in the revised manuscript.

C4376

Referee #2

AC: General points: Some of the main points questioning the general value of our contribution have been addressed above. Another concern of Reviewer 2 was the correspondence between the reactivity and flux data sets, as well as the reproducibility of the flux data. The reactivity data previously published in Alkhatib et al. (2012) were generated during the same sampling campaign, using multiple cores at the same site, respectively. As for replication of porewater profiles: Indeed, within-site variability can be significant. We disagree however with the reviewer that there is no replication in the current data set. At least for DON measurements, we generated profiles from two different cores taken in close vicinity, using WCS sampling (multicore) and using Rhizons in a pushcore subsampled from a box core. The agreement with regards to the DON concentrations in the upper part of the profiles (relevant for flux measurements) was good, indicating not only that the approaches applied worked well, but also that spatial heterogeneity at a given site is relatively low. Reviewer 2 is also concerned about the fact that we extrapolate from 9 down-core profiles only. We already commented on this above. We fully agree that it is problematic that there is no temporal replication, so that extrapolation to the ecosystem and/or global levels is indeed dangerous. But putting a (limited) regional data set in a more global context may be very interesting nonetheless, and certainly valid if the associated short-comings of the approach are openly discussed. Again, the most important point that we want to make with this extrapolation, is that, although the regional/global estimates based on the St. Lawrence estuarine/Gulf data are highly uncertain, they suggest that benthic DON fluxes represent a key source of reduced N to the ocean, both at the eco-system scale and globally. We would like to keep section 4.4, but we will more clearly highlight the possible pitfalls associated with the calculation of global DON flux estimates based on local measurements.

RC: The abstract leads the reader to believe that this study presents data on denitrification, POM reactivity, OET etc. This data is actually from previous studies. This

C4377

should be made clear to the reader.

AC: We will clarify in the abstract what the data are from this study and what is known from previous work.

RC: Why wasn't the blank and for that matter concentrations for Rhizon sampling of DOC measured/calculated?

AC: We have done blank tests for DON oxidation using distilled water, and blank TDN concentrations were below detection levels. Similarly the DON and DOC blank from the filters and syringes used in the WCS sampling was below detection.

RC: What are the total errors for DON calculation (including the propagated errors associated with TDN, NO<sub>x</sub> and NH<sub>4</sub>)?

AC: We will add more information on the analysis of errors, and we will include error bars.

RC: What is the precision/accuracy and errors associated of DOC analysis? These can be quite high, and accurate analysis of instrumental blanks is required for robust results. Some discussion on the uncertainties associated with the "best guess" estimate of DOC MW are needed, in particular what are the implications of this changing along the transect. It is likely that as the reactivity of the DOM pool changes, so does the MW of DOC.

AC: Blanks have been calculated for each DOC analysis run by measuring the DOC concentration distilled water samples with each set of samples. Thereby, blank samples were treated the same way as pore water sample. As mentioned above, in order to calculate DOC fluxes, we have adopted a single value for the MW of DOC from the literature (see Burdige et al. 1992, Lahajnar et al. 2005). Indeed, we cannot exclude that the MW of DOM changes with other OM characteristics along the Laurentian Channel, and we are aware of the fact that our approach is a simplification of the natural conditions. This will be highlighted in the revised MS. In any case, it is important to

C4378

note that the uncertainty in the MW has relatively little impact on the calculated fluxes, because of the inverse cube-root relationship between the diffusivity and MW (Burdige et al. 1992).

RC: Too much discussion on the potential artifacts associated with the methods. This should be restricted to a single paragraph.

AC: See comments above. We will try to reduce it; however, we think that this discussion is helpful in light of the ongoing debate regarding the dis-/advantages of different pore water sampling methods for DOM analysis.

RC: Water column respiration is given as the likely cause for no DOC increase along the transect, but this could also be driven by benthic respiration.

AC: See above. We will omit this section as it is quite speculative.

RC: The sediments are clearly heterotrophic (oxygen fluxes in table 1 indicate this) yet this is not adequately addressed. Is it possible that the flux of DOC might be overestimated due to bacterial respiration of DOC at the SWI?

AC: See comments above. The fluxes we estimate/profiles we see represent the net effect of DOM production and remineralization within the sediments/sediment porewater. We are limited by the sampling resolution constrained by the WCS technique (which is better than in any other discrete porewater sampling method). Thus we cannot exclude that there is a stark DOM sink right below the SWI, lowering the effective concentration gradient right at the SWI, which is relevant for the flux calculation. We will address this in the revised MS.

RC: The authors data could be integrated with previous studies to give an indication of the likely magnitude of global DON fluxes, but this requires consideration of a number factors that are likely to influence the fluxes including, but not limited to: sediment type, OM loading, depth, seasonality etc.

AC: As treated above, a spatial extrapolation has its pitfalls. We compared our fluxes

C4379

with those from other studies from different coastal marine areas. We came to the conclusion that they are within the range of previous reports, and thus representative for shelf environments. Thus our global estimates may be quite accurate. Anyway, they are not the focus of the paper, and we would like to not extend the discussion on global DON fluxes. Again, the goal was to provide a rough estimate of global benthic DON fluxes and to highlight the importance of DON fluxes from the continental shelf and coastal sediments.

D. Burdige (Referee)

RC: (7918, 9) - DON fluxes varied inversely with OET not positively (in Fig. 6, OET goes up and DON fluxes go down).

AC: Of course this will be corrected.

RC: (7920, 22-24) – This sentence is phrased in a somewhat confusion manner. I would argue that refractive OM by definition has a “lower potential for remineralization” as opposed to suggesting that because it is refractory it has “a lower potential”. Maybe I’m getting caught up in semantics but this seems redundant as written.

AC: Indeed what we have meant, and we will change the text accordingly.

RC: Section 2.1 – I assume (hope) these sediments are not bioturbated and/or bioirrigated? If they are bioturbated and/or bioirrigated, that’s a game-changer in terms of any interpretation of diffusive fluxes as is done here. Please state this in this section.

AC: There certainly is bioturbation (Belley et al. 2010) and its effect on non-diffusive exchange is uncertain. This always is the disadvantage of profile-based estimates versus benthic chamber based estimates. However, we are confident to state that bioturbation/bioirrigation has unlikely contributed to the observed trends in (diffusive) DOM fluxes along the Lower Estuary and the Gulf. Belley et al. (2010) found that the macrobenthos surface-trace density was highest at the head of the channel (Sta. 25 and Sta. 23) and that it decreased noticeably eastward along the LC. This observation

C4380

was explained by the fact that the hypoxic area of the Laurentian Channel is now in a transition phase, where suspension feeders, non-tolerant to hypoxia, are progressively replaced by low-oxygen tolerant deposit feeders that are mainly responsible for surficial benthos traces (e.g. *Ophiura* sp.). Again, the possible effect of bioturbation/bioirrigation on dissolved organic matter fluxes therefore remains uncertain. Bioirrigation in general facilitates the DOM exchange between the bottom and pore waters, and thus may allow “deeper” DOM to escape from the sediments, by-passing the diagenetically active reaction zone right below the SWI. At the same time, oxygen is supplied to anoxic regions within the sediments, pushing down the active interface zone, and can probably introduce DOM produced from older and less reactive POM with different nature than that produced from more reactive POM at the surface sediments. We included a section on bioturbation in an earlier draft of the MS, considering these factors, but given the overall length of the MS we decided to exclude it. At the discretion of the Associate Editor, we can easily re-add the paragraph.

RC: (7922, 12-14) – What parameter(s) were used to determine the terrestrial content of the organic matter? This is not clear from Table 1.

AC: The parameters were introduced in Alkhatib et al. (2012a). The assessment of terrestrial OM content was based on the  $^{13}\text{C}/^{12}\text{C}_{\text{org}}$  distribution in POM, OM C/N ratios, as well as the lignin concentrations along the Laurentian Channel as published by different authors (e.g. Louchouart et al. 1997)

RC: Some of the discussion in section 4.1 could be cut back and/or better focused.

AC: We will condense section 4.1.

RC: (21,7928) – How high is the pressure exerted by the WCS relative to the original in situ pressure the cores experiences before being brought to the surface? Does this have an impact on the discussion here? Also does high pressure really favors DOM desorption?

C4381

AC: We assume that the pressure inside the WCS can be significantly higher, particularly within the deeper sediments. However, given additional experimental evidence, we plan to cut back this part of the discussion. The effect of varying pressure on organic chemical chemisorption is probably small. Recent experiments by one of the co-authors (Y. Gelinac and colleagues), where porewater was extracted at different pressures (slicing + squeezing; 4 pressures in triplicates) on fresh box cores, yielded results (DOC adsorption) that were not significantly different. This topic has not been studied much, but it seems safe to assume that the effect of the differences in pressure is negligible.

RC: (7928, 29) – Is there data in the Lalonde et al. (2012) paper on concentrations of nanophase ferrihydrite – I don't recall seeing it, but maybe I missed it (I have a similar concern about line 10, p. 7932).

AC: In modern sediments, the highly reactive iron phases are typically found as nanospheres of ferrihydrite  $<10\text{Å}$  in diameter, as shown by van der Zee et al. (2003). The correct reference will be included in the revised MS. There is no data on amorphous or nanophase ferrihydrite in Lalonde et al. (2012), as their iron extraction method (citrate-dithionite-bicarbonate) targeted all reducible forms of iron.

RC: (7930, 8) – Rather than say DON fluxes correlated linearly with OET, tell us there was an inverse relationship. The inverse relationship is far more important, interesting and relevant to the discussion here than simply knowing that DON flux and OET correlate with one another.

AC: The text will be revised as suggested.

RC: Another possible explanation for the links between DON fluxes and redox controls involves possible redox controls on DON (or DOC) consumption, regardless of (or in addition to) any redox controls on DOC production during the initial stages of POM degradation. I talk about this in my 2001 *Org. Geochem.* paper as well as my 2002 review article in the Hansell and Carlson DOM book. This might be worth considering

C4382



here.

AC: We have briefly discussed the issue of selective vs. non-selective consumption in relation with oxic conditions and reactivity of DOM, and addition, we will consider the reviewer's suggestion in the revised manuscript.

RC: (3, 7932) – After reading this paragraph I wondered why surface reactions might only affect DOC molecules and not DON molecules. Also, if DOC molecules do preferentially stick to sediment particles is this consistent with the close tracking of the different elemental ratios shown in Fig. 5?

AC: These reactions, if present, probably do not only affect DOC. Obviously, it is not the content of C or N that matters, but it seems reasonable to assume that there maybe some element partitioning associated with preferential adsorption/desorption (e.g., as a function of the polarity of functional groups) of specific organic molecules, which lead to a preferential adsorption of DOC versus DON. Solid affinity for different kinds of DOM may be highly variable. A good example of such elemental partitioning would be the sorption of polysaccharides on reactive iron oxide phases. Also, organic dipoles and large C-rich organic ions may be preferentially adsorbed at particle surfaces primarily because their hydrocarbon parts have a low affinity for the aqueous phase (Stumm and Morgan). But Dr. Burdige is right, the parallel trends of the C/N ratio in DOM in the porewater and in the bottom water (as shown in Fig. 5 of the discussion paper) seem to speak against such physico-chemical constraints on element partitioning. However, we need to keep in mind that the size of the bottom water DOM pool and the sediment porewater pool is very different. There could be selective partitioning in the porewaters, with no discernable effect on the bottom water DOM, simply because its contribution is too small. We will modify the text accordingly.

RC: section 4.3 – If the explanations here involves differences in the reactivity of N-rich (versus N-poor) POM or DOM, it may be better to frame the discussion in terms of comparisons of N/C (rather than C/N) ratios (see, for example, Perdue and Koprivnjak.

C4383

2007. *Est. Coastal Shelf Sci.*, 65-72). I also wonder if revising this discussion in this way helps to better explain some of the uncoupling in the behavior of DOC and DON benthic fluxes from St. Lawrence estuarine sediments (which in my mind, is a very interesting aspect of these results).

AC: We will consider this when preparing the revised manuscript

RC: (3, 7933) – Again this may be an issue of semantics, but the discussion here gets a little muddled with regards to terminology. At least from my perspective, the “initial depolymerization” of sediment POM can occur in either two ways: hydrolysis or oxidative cleavage. Given this perspective, some of the text here needs to be cleaned up.

AC: We agree with Dr. Burdige, and will modify the text accordingly.

RC: (5, 7936) – I assume you mean here water column inorganic N pools? If so, you might be specific.

AC: It will be changed to “DIN (NO<sub>3</sub><sup>-</sup> + NH<sub>4</sub><sup>+</sup>)”, as suggested by reviewer.

RC: In Table 1 is the Corg flux the carbon rain rate to the sediment surface or the remineralization flux (i.e., the depth-integrated rate of organic carbon remineralization)?

AC: This parameter depicts the rate of Corg supply to the sediments (vertical flux).

#### References

Alperin, M. J., Martens, C. S., Albert, D. B., Suayah, I. B., Benninger, L. K., Blair, N. E., and Jahnke, R. A.: Benthic fluxes and porewater concentration profiles of dissolved organic carbon in sediments from the North Carolina continental slope, *Geochim. Cosmochim. Ac.*, 63, 427–448, 1999.

Belley, R., Archambault, P., Sundby, B., Gilbert, F., and Gagnon, J.M.: Effects of hypoxia on benthic macrofauna and bioturbation in the Estuary and Gulf of St. Lawrence, Canada, *Cont. Shelf Res.*, 30, 1302–1313, 2010.

C4384

Holcombe, B. L., Keil, R. G., and Devol, A. H.: Determination of porewater dissolved organic carbon fluxes from Mexican margin sediments, *Limnol. Oceanogr.*, 46, 298–308, 2001.

Jahnke, R. A.: A simple, reliable, and inexpensive porewater sampler, *Limnol. Oceanogr.*, 33, 483–487, 1988.

Lehmann, M. F., Barnett, B., Gélinas, Y., Gilbert, D., Maranger, R. J., Mucci, A., Sundby, B., and Thibodeau, B.: Aerobic respiration and hypoxia in the Lower St. Lawrence Estuary: Stable isotope ratios of dissolved oxygen constrain oxygen sink partitioning, *Limnol. Oceanogr.*, 54, 2157–2169, 2009.

Litt, T., Anselmetti, F.S., Cagatay, M.N., Kipfer, R., Krastel, S., Schmincke, H.-U., Sturm, M., 2011. A 500,000-year-long sediment archive drilled in eastern Anatolia. *EOS Transactions, American Geophysical Union* 92, 477–479. doi:10.1029/2011EO510002.

van der Zee, C., Roberts, D. R., Rancourt, D. G. & Slomp, C. P., 2003. Nano-goethite is the dominant reactive oxyhydroxide phase in lake and marine sediments. *Geology* 31, 993–996.

---

Interactive comment on *Biogeosciences Discuss.*, 10, 7917, 2013.