Response to referee 3

We thank the reviewer for his constructive comments. Below you find our answers to his comments and suggestions (in bold):

This manuscript focuses on using ïA¸d'13C-HMW DOC to trace the fate of terrestrial organic matter in the Baltic Sea. The authors concluded that terrestrial DOM contributes 43-83% DOM in the Baltic Sea, and that the terrestrial DOM is not subject to substantial removal once in the open Baltic Sea. The manuscript is well written and presented, and the data overall are solid. However, I feel that they over-interpreted the data a little bit, and this paper did not add much on what Alling et al. have previously presented.

The referee is correct that our study is closely related to the study of Alling et al. (2008). However, aim of the Alling et al. study was the test of a novel approach (δ34S-DOM) instead of δ13C-DOM to avoid the influences of estuarine produced DOM on the δ13C values. Furthermore their study was carried out during the winter months and it could be assumed that in our study during summer the DOCter distribution is significantly influenced by autochthonous DOC production from phytoplankton.
Additionally we used for the first time – to our current knowledge - the approach to combine the measured DOC concentrations together with the calculated share of DOCter to calculate concentrations of DOCter and plot them versus salinity which suggest a high DOC removal capacity of the Baltic Sea estuaries. Finally, we covered a much larger area by including the central parts of the Baltic Sea, called the Baltic Proper to our study. Thus this study represents the DOC dynamics of almost the entire Baltic Sea and is not restricted to its northernmost basin, the Gulf of Bothnia.

The authors used the HMW DOM to calculation the contribution of the total DOM pool, yet the recovery rates of the ultrafiltration were only in the range of 13.1-27.3%. It is known that HMW DOM is generally more labile than the LMW one (work from Benner's group), so their conclusions about the whole DOM may be flawed. This important fact was missed throughout the text.

We will change the text, to stress more clearly, that we only considered the HMW-fraction of the DOM pool and not the total DOM. Furthermore we will add a paragraph to the discussion section where we carefully discuss our results in context to the bioavailability question. Amon & Benner (L&O 41, 1996) developed the 'size reactivity continuum model' which suggests that the bioavailability of organic matter decreases from larger molecules or compounds to smaller ones. This means that the HMW-pool is more bioavailable than the LMW-pool. The model theory was approved by other studies (see the review by Sulzberger & Durisch-Kaiser, Aquatic Sciences, 71, 2009). However there were also studies showing contrary results (Rochelle-Newall et al., AME 39, 2004, Rosenstock et al., Microbial Ecology, 50, 2005).

The authors specifically chose the stations with salinities less than 7.5. I am wondering why they did not do the same on those stations with higher salinities. Those "real" coastal waters are more meaningful to the question about the fate of terrestrial DOM in marine environments. I do not feel very comfortable of making such a big deal out a dataset

within salinity of 2-7.5, and del13C values of -27.25 to -25.25 ‰ (Fig. 3b), unless you have very restricted end members.

In our study we wanted to focus on the central Baltic Sea which is characterized by a salinity range from 0-8. It was obvious from the 18O-H2O vs salinity plots, that we sampled two totally different systems. Whereas the central and northern parts of the Baltic Sea have relative stable conditions and long water-residence times in the order of several years, the western parts are very dynamic and show much shorter water residence times. Therefore the interpretation of the isotope data from the western Baltic Sea would have been really difficult and partly maybe speculative. For our data set the range of salinity as well as of the stable isotope data are in a typical for estuarine studies. Since the Baltic Sea is often described a large estuary we think our data basis is adequate.

In the introduction, the Carlson book chapter was cited many times. To me, it's more appropriate to credit the original research papers.

We will cite the original research papers.

P4487, line 3: The temperature is also important factor leading to isotopic fractionation.

The reviewer is correct. We will add the information to the text.

P4489: Sampling depth should be reported. I am curious how the depth profiles would change, and how their conclusions would be affected if the system is not homogenous in terms of depth.

The samples were taken from the surface which was between 1-5m depth, depending on the weather situation and the ship movement. We apologize that this information is not given in the text and will add it to the 'Material and methods' section. It is known from the study of Benner et al. (1997) that the δ13C-values of HMW-DOM do not change substantially with depth.

P4489, line 13: Do not start a sentence with a number; line 19: filtration rate well above 15? This is confusing.

The sentence will be changed to: In total 13 stations were sampled.

P4490, line 23: Should report the 4 values to show the variability. Also, how come in their opinion that this averaged end member can reflect the whole Baltic Sea? Evidences are needed to back this up.

We will add the 4 values (-27.1, -27.9, -28.5, -28.7, average -28.1 ± 0.7) to the text. Our chosen end member for terrestrial DOC is in the range of other values reported for terrestrial DOC from literature. Furthermore the values are comparable to the δ13C values reported from other rivers (see the review from Raymond & Bauer, Organic Geochemistry 32, 2001 and the literature values presented in Kaldy et al, Estuaries 28, 2005). From this it becomes obvious that the values of δ13C-HMW-DOC do not change very much between the

rivers. Therefore we think that our chosen end member is acceptable. We will add δ13C-HMW-DOM values from other rivers to the text.

P4492, line 6: The 3 stations in the Oder Bight were off (Fig. 2), and they interpreted this as melting water of the ice. From Fig. 2, these 3 points have about the same salinity, but drastically different del18O values. How exactly can this pattern be explained by melting water?

We agree with the reviewer that the different δ18O-H2O values at more or less constant salinities for the three samples of the Oder Bight are hardly to explain. Nevertheless we think that both the salinity measurements as well as the δ18O-H2O measurements are without errors. However we can only speculate about the reasons for these large differences in δ18O-H2O. A possible reason could be that isotope fractionation during the generation and melting of the ice in the Oder bight might have resulted in these large differences. During the formation of ice isotopic fractionation results in higher δ18O-values of the ice compared to the remaining water. Furthermore there will be differences in the δ18O values between ice that is coming out of the Oder Lagoon and ice that is formed in the Oder Bight. Since the sampling was in early march we assume that mixing of melt water and ice from these two different water sources can be responsible. Another option is estuarine mixing which however also not can explain the nearly constant salinities.

P4493: They argued that DOC and salinity have a weak correlation (Fig. 3a), but a very good one between del18C-HWM-DOM and salinity (Fig. 3b). But to me, there is not much difference between Fig. 3a and 3b. They need to show the regression equation of Fig. 3a to support their argument.

If isotope data is tested for mixing the visible mixing pattern must not necessarily be a straight line, but can also be a curve, since not only the isotope data but also the concentrations of the two mixed end member must be taken into account (see Fry 2002) In fact a straight line is the exception, since it only appears if both end member have the same concentration or if both end member have the same isotope values. Since the mixing of the DOC is linear and the mixing of the isotopes is non-linear it is not possible to compare the both datasets by simply calculating r^2 values or the regression equations. Therefore we decided to calculate the 'mean absolute percentage error' (MAPE) for each dataset. This will allow us to compare for both mixing calculations (Fig. 3a:DOC vs salinity; Fig 3b: d13C-DOC vs salinity) how close the measured values are from the calculated ones. A MAPE of 0 indicates a perfect fit between the calculated and measured values. For the mixing of the DOC (Fig. 3a) we calculated a MAPE of 5.39 and for the mixing of the HMW-d13C a MAPE of 1.12. Therefore we think that our statement, that DOC vs salinity shows a more weak correlation compared to d13C vs. salinity is valid. We will add this information to the text.

P4494, line 6: They argued that a "slight" deviation from the mixing curve (Fig. 3b). They further interpreted this as addition of DOC from marine sources. I do not think that the deviation they observed are statistically significant, considering the analytical errors involved and the assumption they made (end members).

The referee is correct, that the deviation we observed might be also influenced or maybe caused by our analytical errors. However, what becomes obvious is that nearly all of the samples in the open Baltic Sea showed higher 13C values than the calculated ones, which seemed like a pattern to us. Nevertheless we can add an additional sentence that the analytical precision might be also a reason for the deviation.

By the way, the line they drew on Fig. 3b does not seem to be a straight line, but a curve?

See our comment about the similarity of Figures 3a and b

P4494, line 21: Delete the comma after the fact.

Will be deleted

Fig. 2: The locations of SK, KT, BeS are not marked in the map (Fig. 1).

The locations will be added to the map