

Answer to Anonymous Referee #1

We would like to thank Anonymous Referee #1 for the very constructive comments. The manuscript has been modified and will be uploaded when required from the editorial system. Below, find our response to the suggestions from Referee#1.

This manuscript presents the findings of a study on the geochemistry and benthic in-fauna in sediments across a gradient of oxic to anoxic conditions in the Black Sea, which is topical given current interest in the effects of hypoxia on biogeochemical processes. The data set is well presented and the paper is generally well written. The key finding, which surprises me somewhat is that most of the oxygen consumption within these sediments is driven by the (inferred) direct oxidation of organic matter (including faunal respiration) as opposed to the oxidation of reduced solutes. One of the key conclusions is that organic matter is more efficiently mineralised in the oxic sediments which is generally consistent with current understanding, however, I am not convinced that this is to the extent inferred here.

Referee#1: A change of 100% to 10% of organic matter mineralization seems extreme and should be backed up with some other measurement - %OC and sedimentation rates for example. The way things stand; these values are based on the assumption of constant organic matter deposition at all sites – how valid is this? How do you rule out gradients of water column productivity as you move off-shore?

Reply: We have combined several methods to test this. We assessed publicly available ocean colour satellite data (variation in chl a content of surface waters over 10 years, i.e. 1 cm sedimentation, http://marine.copernicus.eu/web/69-mycean-interactive-catalogue.php?option=com_csw&view=details&product_id=OCEANCOLOUR_BS_CHL_L3 REP OBSERVATIONS 009_071) and found there was no regional difference (now mentioned in the MS; data are not shown; chapter 4.1.). Also the transect was with around 30-40 km length relatively short and showed barely any slope (p6450, l 6), so different deposition rates are not likely. We provided sediment accumulation rates and found they were rather similar across all zones (P6463, L4). We now also include the Corg concentrations of the different zones (in Methods, Results, Discussion, Table 2) in the manuscript, that show the same effect, i.e. in the oxic station much more organic carbon has been consumed than in the other zones.

Referee#1: The study would have benefitted greatly from DIC flux measurements (as well as profiles). If these were undertaken this would have enabled respiration quotients to be determined which would have greatly assisted in the interpretation. If, as the manuscript concludes, that the mineralization of organic matter was the dominant carbon degradation pathway, then this should be close to 1. I think that the RQ could be >1, particularly under hypoxic conditions, which implies the burial of reduced material, most likely sulfides. Many studies which have measured the RQ in coastal sediments (see for example Berelson, Hammond and Devol to name a few) and it would be nice to have a bit more literature context on what others have measured and their interpretations. It would be particularly nice if the authors could find such data for sites with high rates of Fe reduction as I suspect is occurring here (see below).

Reply: We agree with the reviewer that both DIC flux measurements as well as DIC profiles would have been a great addition to this manuscript. We originally aimed at measuring the DIC fluxes in the chamber, however, using flow injection measurements and having a relatively small volume sample for DIC measurements left from the chamber samples, we found the results from our DIC measurements not accurate enough to reliably determine the carbon flux rates. Thus we focussed on oxygen consumption. As Referee #1 states correctly, a RQ of >1 often implies that you have an active iron and sulfate cycle, where sulfide is not consumed by oxygen, but precipitating with iron and thus is not included in the O₂ budget. However in our case it is obvious that in the sites where we have an active iron cycle (oxic station), measured sulfate reduction rates (Table 3) are very low. Vice versa where some sulfate reduction was measured, the solid phase iron profiles show that the iron cycle has mostly ceased due to lack of bioturbation. This is as well reflected in the relatively low AVS/CRS concentrations compared to other measurement in the Black Sea e.g. Joergensen et al. 2004, GCA 68, 2095-2118 or Wijsman et al. (2001), Marine Chemistry, 74,261-278. Thus we concluded that we should use the widely used value for RQ = 1.

Referee#1: Following on from above, is burial of reduced solutes a significant fraction of ODU? Can you do a mass balance of the oxygen equivalents buried in the reduced sulfur species measured here in combination with the sedimentation rates and add this to table 3?

Reply: Similar as above, geochemical results indicate that the sulfide-precipitation with iron is not necessarily important in our study. As visible in Fig. 5 of the original manuscript, for the stations where the iron cycle could be important (oxic and oxic-hypoxic zone) the amount of reduced sulfur species and sulfate reduction rates are generally low in the upper 5 cm of the sediment (Fig. 5g, n, original manuscript). This can be the result of bioturbation activity causing transport of iron-sulfides into the oxic zone, which are oxidized here and thus are included in the O_2 budget, eventually. Nevertheless, we now state that iron-solid mineral concentrations are generally low (in chapter 4.1: Effect of oxygen availability on remineralization rates and reoxidation processes) and we assume that this does not have a large effect on the RQ.

Referee#1: I was also surprised that there is no data on the sediment carbon content, this information would help confirm the postulated differences in carbon mineralization, hence preservation across the study sites.

Reply: We now include the organic carbon content in the first cm in the Methods, Results, Table 2 and the Discussion to strengthen the discussion in this regard.

Referee#1: The high concentrations of Fe^{2+} combined with the relatively high concentrations of solid phase iron suggest that there is very active iron reduction taking place at St462 and to a lesser extent St487. I was surprised that iron reduction was not mentioned or discussed. Could it be that a lot of oxidation of reduced iron takes place on a time and spatial scale missed by the microsensors? For example there are some nice examples of profiles here showing O_2 penetration to 1 cm (clearly mediated by irrigation), yet the profile interpretations are all undertaken on the mm/diffusive scale. Can you constrain this a little better? For example can you use the relationship between poorly crystalline Fe and %Fe reduction shown in (Jensen et al. 2003) to estimate the likely contribution of Fe reduction?

REPLY: It is generally accepted that dissolved iron from dissimilatory iron reduction gets oxidized by O_2 (e.g. Canfield et al. 1993, Glud et al. 2008). To calculate the contribution of iron reduction to organic carbon degradation is a very interesting suggestion, however, due to a extend dataset already included, we think that splitting up the organic carbon degradation pathways is in this case beyond the scope of the paper, and would rather refrain from including this here. A statement about "ceasing of the iron and manganese cycling upon low bottom water oxygen" is included already (p6467, l21-23), and to underpin that iron cycling might be important in the oxic zone, will be added here.

Referee#1: There is no mention of denitrification. This is probably not significant, but should be justified based on measured NO_3^- concentrations.

REPLY: Nitrate in the sediment is close to detection limit (1 μM) in the first cm of sediments at the station in the permanently oxic and oxic-hypoxic zone and nitrate concentrations were below detection limit in the sediments at the station in the hypoxic-anoxic and the anoxic zone. We now included this information in the Methods, Results and mention in the Discussion that denitrification most likely is not significant in our study, due to the very low nitrate concentrations. However, similar as in the comment above, we rather would not go into the splitting up into different organic carbon degradation cycles in detail, due to the extent of the dataset already included.

Ref cited. Jensen, M. M., B. Thamdrup, S. Rysgaard, M. Holmer, and H. Fossing. 2003. Rates and regulation of microbial iron reduction in sediments of the Baltic-North Sea transition. *Biogeochemistry* 65: 295-3