Chaichana et al: Response to reviewers

We thank the reviewers for their comprehensive reviews and feel that the resulting manuscript is substantially improved. We reposed to their comments below. Reviewer's comments are in italics, our responses in red. Overall we

5 have reworked the manuscript to remove hypotheses, introduce a new synthesis of literature end-member concentrations to aid the analysis of DOM concentration changes over salinity gradients and restructured and extended the discussion, in line with the reviewers suggestions. A 'track changes' version of the revised manuscript can be found below the response to reviewers.

10 Reviewer 1

General Comments

This paper details a multi-year high-resolution sampling of DOM dynamics in the North Sea. The main conclusions of the work suggest that there is high spatial and temporal variability in the total concentrations and C:N ratio of OM over the sampled periods, and that this inter-annual variability has

- 15 strong implications for overall carbon budgets in the region. The implications of this work for carbon cycling in the region are important, and I found the paper to be generally well written. However, I struggle with the chosen focus on C:N ratios for elucidating DOM dynamics. I felt that novel portion of this work, that is, the elucidation of the impact temporal variability has on the overall carbon budget(s), was not emphasized enough.
- 20 We thank the reviewer for the positive summary of the paper and are pleased that they recognize the importance of this dataset, which we believe is of value and interest to the community. We agree with the reviewer that the inventory changes should have greater prominence in the manuscript and have tried to address this, as detailed in the responses to specific points below and in the manuscript. However, we would defend our approach of using C:N stoichiometry as a key indicator of the biogeochemical status of
- 25 shelf waters given the relatively contsant C:N ratio of the open ocean (out of the surface layer) and the low C:N of river inputs to the North Sea, the high C:N ratios observed, particularly in the first summer are, we argue, an important indicator of the state of the system. We address this more specifically in responses below and in changes to the text outlined below.

In particular, there are a few main facets of the work I feel need further development if they are to be

included in the final manuscript:

1) The objective that the C:N ratio is presented to address- and how this is interpreted and discussed. As mentioned in the work, many factors can affect this ratio! If this is the only metric you use to assess DOM dynamics, you need to be really careful. Can you really answer the larger objectives you outline with the

5 hypotheses that you pose? How does the C:N ratio compare to the chla concentrations, nutrients, and previous work in the region on tracking allochthonous vs autochthonous sources of OM? How does your end-member calculations compare to actual end-members from the literature, and OM composition from other work?

We absolutely agree that the CN ratio is highly variable (and state this in the manuscript), as a

- 10 consequence of the variable nature of DOC and DON. This is why we feel it is a useful indicator of the state of the system. We do not attempt to make any concrete inferences about the source / sink of DOC vs DON in the paper, because we do not have the appropriate observations at our disposal to do so. We had already looked at relationships with chlorophyll, nutrients etc but there is no evidence of significant relationships across the whole data set or in sub-sections of it. Therefore we did not present this data in
- 15 the paper.

Regarding the tracking of different sources of DOM, this was not really our initial aim, but have now included more discussion of this throughout the paper and have also conducted a synthesis of endmembers for the region (both river and open ocean) and furthermore compare these, and our data, with the global synthesis effort of Barron and Duarte (2013) and other temperate shelf environments. This has

20 provided a new and useful conceptual framework for the paper which hopefully addresses both reviewers' concerns and we feel has added usefully to the paper. In particular see changes to Sections 1.2 and 4.6, Tables S1 and S2 and new Figures 1 and 9.

2) Tie the POM work in better. How does this compare to the DOM, and what is this impact on the overall carbon budget?

25 It would be really good to do more with the POM but unfortunately we only have POM data for the second year of the study and therefore cannot compare the differences between the 2 years. We have included the POM data primarily to demonstrate that it is a small component of the budget, which is in line with other studies. In particular, the 'missing' carbon in 2012 cannot be stored in a large stock of POC – which

we can see is not present. We have stated this explicitly in the final paragraph of section 4.4.

The discussion and conclusions regarding the relationship of DOM with salinity. This relationship has been found to be conservative with mixing of the major water masses in the North-Baltic Seas transition, however major non-conservative processing on DOM does occur in the region (see eg. Osburn and

5 Stedmon, 2011 Marine Chemistry DOI: 10.1016/j.marchem.2011.06.007). I would like to see further development of this, including tying the current work into previous analyses of DOM composition, etc. What are the implications of local variability, in this context?

We have included much more discussion of DOM-salinity relationships in the revised manuscript as we agree with the reviewer that it is important. However, we would point out that the North Sea is under a

- 10 very different regime to the Baltic. The Baltic is an enclosed sea, with circulation dominated by salinity and a limited exchange of water with the ocean (the North Sea in this case). The North Sea however, is dominated by 'through-flow' of Atlantic water, via the English Channel and Malin shelf and out through the Norwegian trench. As such the open North Sea is subject to much smaller ranges of salinity (typically 30-35) and autochthonous processes are likely to be much more dominant. We make this case in the
- 15 introduction for the sake of clarity we would not expect strongly conservative behaviour and we do not believe that a significant component of the DOM in the N. Sea is of terrestrial origin in the summer, both because of the minor influence of freshwater on the main part of the North Sea but also because the long residence time will favour loss of terrestrial organic matter before reaching the higher salinity regions. This is discussed in Sections 1.2, 4.1 of the new manuscript.
- 3) This is perhaps the most important- I feel the discussion on C inventory should take center stage.We agree, and have made specific reference to this issue in the title of the piece and have expanded this section in the discussion.

How does this work advocate for or against high-resolution measurements?

25

We do not feel that this finding particularly advocates for or against high resolution measurements (although clearly they are often desirable) so have not commented on this.

How does it revise or promote our understanding of DOC cycling in the region? This is now covered in the discussion and conclusions section. In brief, DOC is probably the most variable pool of carbon in shelf water columns, given the inventory change observed here. The North Sea does not appear to be net-heterotrophic (certainly not in all years) as previously suggested by Bozec et al. The variable flushing time of the North Sea seems likely to be the control on DOC concentrations and stoichiometry.

5 How does this compare to other regions and/or the global budget?

We have introduced comparison with the global synthesis of Barron and Duarte (2015) and Vlahos et al study of the Mid-Atlantic Bight (MAB) section 4.2, Fig 9. This highlights 1) that the DOC concentrations in the North Sea and MAB are similar to each other and comparatively low at a given salinity compared to the global shelf average and 2) that the inventory change between the two years is therefore all the

10 more significant for the role of DOM in the carbon cycle in shelf seas.

What are the uncertainties with C budgets, and does this paper help to narrow these? We don't feel that this paper is the place to assess the uncertainties in carbon budgets of the North Sea however we do put our results in the context of the Thomas budget in sections 4.3, 4.5 and 5. Our study (as others also have) suggests net autotrophy and a DOC source to the open ocean, in contradiction to the

15 Thomas et al 2005 budget; so we are cautious about discussing 'narrowing' of uncertainty. The important point that we do make is that the dynamics of DOM clearly have a very important role to play in the export of carbon from the shelf.

Specific Comments

20 1 Introduction

The first paragraph starting on line 23, to me, is the motivation for this work.

We agree and are pleased to keep this paragraph despite reviewer 2's recommendation to remove it.

Clearly relate the following discussions, and set-up to the goals of the study relative to this. Be explicit upfront- what do you hope to find with this work, and how is it novel (e.g. lines 25-29)? Some of this is

25 outlined in later the introduction, but the narrative back to the main objectives of the work is lost throughout the rest of the paper.

We have now clearly stated the aim after the opening paragraph of the introduction, and also made it clear the constraints of the study – that it results from a PhD study on cruises of opportunity: 'In this study we

investigate the variability of the organic carbon inventory of a large and complex shelf sea by considering the evidence provided by two high-spatial-resolution summer surveys of organic matter concentrations, stoichiometry and deviation from conservative mixing between river and open ocean end members. These data were collected during cruises of opportunity during a PhD research programme, so our analysis is focussed on diagnostic,

5 geochemical approaches to understanding bulk concentrations and intentionally does not attempt to elucidate distinct sources or types of DOM, or determine process rates, given only *prima facie* evidence. 'We have not stated what we 'hope to find' as this seems pre-emptive of the findings.

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The authors attempt this tie by stating hypotheses and referring to them throughout. This causes the prose

- to be a bit awkward- and I suggest instead outlining the overlying research outcomes the authors hope the study will answer. As is, the hypotheses are too narrow to the stoichiometry work, and don't really address our gaps in understanding of the temporal variability of the C cycling in the region.
 We have removed the hypotheses and replaced them with aims and predictions in our re-structured introduction. Reference to hypotheses later in the paper are removed.
- 15 Perhaps a figure would help with synthesizing what we know, and what gaps this study addresses? We have considered this carefully, but in the end feel that this would start to make the paper more like a review paper than a report of field data and subsequent analysis, so have not made this change. We do however feel that the new Figure 1, presenting idealised salinity gradients and expected C:N ratios sets up the paper rather better than previously and goes some way to a synthesis figure at the start.
- 20 How has this sort of "high-resolution" work refined carbon budgets in other regions?
 To our knowledge regional surveys like this have not been conducted in other regions so we are unable to comment.

What are the processes affecting atmospheric CO2 draw down in regions such as shelf seas? We found that in order to bring this into the introduction in a meaningful way resulted in another long

25 paragraph that seemed tangential to the main point of the paper and so haven't included it in the end – again, if this were a review paper we would be dealing with such topics in great detail but for the purposes of this paper we feel it would be excessive detail.

How does this relate to the global carbon budget?

5

Again, we feel that going into more detail than we already do would require adding considerable additional length to the paper. Our opening sentence was chosen carefully to provide the context and references necessary for the reader to investigate this themselves if interested: "Coastal and shelf seas are generally more productive than the open ocean (Jickells, 1998; Simpson and Sharples, 2012), and through

5 various processes have been proposed as potentially disproportionately important for the drawdown of atmospheric carbon to the deep ocean (Bauer et al., 2013; Regnier et al., 2013; Thomas et al., 2005; Tsunogai et al., 1999)"

Why is the North Sea an ideal system to study in this regard?

20

The North Sea is complex and interesting but it is far from 'ideal'. We have extended the North Sea

10 description to cover a number of the points that the reviewers have raised, which we respond to below.We feel that this now sets the scene more effectively for the paper.

Page 2, Line 6- Is DIC really the only place for long term carbon storage in the ocean? Better tie in why you are looking at DOC, not DIC.

Actually we were making the opposite point – if it isn't broken down to DIC then it's stored for longer

15 (lifetime of refractory DOC >> DIC in the global ocean). We have tried to clarify: "The reactivity of DOM and in particular its availability for breakdown by marine microbes is a key factor controlling its resistance to degradation to inorganic carbon and thus capacity for long-term carbon storage as refractory, i.e. unreactive, DOC on a timescale of hundreds or thousands of years (e.g. Jiao et al., 2014)."

Page 2, Paragraph starting line 13- I would argue that C:N stoichiometry is a very small part of understanding allochthonous vs autochthonous OM sources, and especially reactivity of DOM.

We entirely concur, and don't believe that this paragraph suggests otherwise. We do not go on to use C:N
values directly as diagnostic of source or DOM reactivity. The point of this paragraph is to outline why
DOM stoichiometry might change in shelf seas, which is relevant as we do see and discuss C:N changes
in the results and discussion sections; and to outline how changing stoichiometry (for whatever reason)

25 may lead to changes in shelf carbon pump efficiency. This paragraph is substantially changed in the general re-working of the paper.

You acknowledge some caveats here, but how does more compound specific work (such as isotopes, biomarkers, etc) compare to C:N ratios (e.g. Kaiser and Benner, 2012 JGR-Oceans DOI:

10.1029/2011JC007141)?

The point we were making was about the large-scale recycling of N relative to C and carbon cycle response. In this context we don't feel that the isotope / biomarkers work is particularly relevant and to introduce them would add excessive length to the paper.

- 5 Convince the reader that the stoichiometry is an adequate tool for the objective you are outlining, ie. using C:N ratios to understand DOM source and reactivity.
 As is, I feel that the discussion and implications of the work rely too heavily on this.
 We feel that the reviewer has misunderstood this aspect of our paper at no point do we state that we are trying to understand the source or reactivity of DOM based solely on the C:N ratio. We do speculate on
- 10 the origin of the carbon-rich DOM in deep waters in 2011 in the paper, but do so on the basis of a range of evidence and reasoned argument rather than simply relating C:N to source and reactivity. We should have been clearer, and have added the following paragraph to this part of the introduction in order to deal with some of these issues.

'The carbon to nitrogen ratio of DOM therefore has the potential to be a useful diagnostic of the state of the shelf

- 15 system indicating the efficiency of nitrogen re-use throughout the microbial food web. However it is complicated by the interactions with river inputs at differing concentrations and probably variable stoichiometry, as well as seasonal and interannual variability. Some studies have used other parameters to elucidate sources of DOM, for example biomarkers and isotopic signatures (e.g. Kaiser and Brenner, 2012) or spectroscopic or fluorescent signatures (e.g. Painter et al., 2018). In some systems the N:C ratio can be used to determine the relative
- 20 contributions of terrestrial and marine sources to DOC, if endmembers are known and conservative mixing can be assumed (Perdue and Koprivnjak, 2007). In the absence of such techniques, the use of C:N alone as a diagnostic variable in shelf seas must be approached with caution. We explore in this paper its potential application to the North Sea case, in the context of other oceanographic measurements and observations.'

25

*Page 3 line 15- Add "climate" in front of cycles*Done (although this sentence has moved in the restructuring of the introduction)

2 Methods

In general, I feel the methods are well explained and analytically sound. An interesting paper recently came out in EST Letters that I feel the authors could benefit from regarding "DON" calculations-Saunders et al., 2017 DOI: 10.1021/acs.estlett.7b00416

We are aware of this work and does of course play an important role in interpreting the uncertainty in

5 DON measurement, which are already incorporated into our data processing, and we have historically taken the same approach as Saunders et al in our work, prior to the publication of their manuscript – hence not citing it. We now cite their paper in the relevant paragraph.

Page 4, lines 21-22- Why did you exclude the riverine-influenced sites? How does this impact your further discussion of sources and end-members and your hypotheses above?

10 As this study was conducted on a ship of opportunity, we did not have the opportunity to choose sampling locations, otherwise we would have sampled up the estuaries. We have changed 'Sampling focussed on the open waters...' to 'The cruise track focussed on...' to make this clear.

3 Results-

15 The results section includes a bit of interpretation in it (e.g. see paragraph on page 11 lines 11-17) and should be reworked to include only observations of the data.

This discussion relates to a hypothesis so the second half of the paragraph has been removed and the first part, describing the C:N ratios has been moved to join the paragraph preceeding it in the restructuring to avoid short paragraphs in response to reviewer 2.

- 20 Do you have the TS profiles? What about other property/property plots? We do not readily have access to complete T-S profiles for the cruise. We feel they would have been of limited additional value over the Temperature and Salinity data associated with the water sampling depths, unless we were to undertake detailed physical oceanographic analysis, which we felt was out of scope of this paper. We present numerous other property-property plots throughout the paper (i.e. original
- 25 manuscript Figures 4,5,7,8). In the process of the analysis we produced many more (DOC vs nitrate, DON vs Chlorophyll *a* etc) but have only presented those which show the most interesting and meaningful relationships, or absences of such, were of interest.

Page 7 line 21- What do you mean by noisy?

We meant that there is a lot of variability around the apparent mixing line in T-S space. This has been removed in the general reworking of the paper.

Page 8, lines 8-12- This is confusing, but is an important distinction. Be clear with your comparisons

5 here, and throughout the rest of the manuscript! Perhaps delineating the water bodies by type for comparisons of measurements over time (eg. Open Atlantic water)?

We agree that this could be clearer. We feel that we largely have delineated water bodies by type (Southern well-mixed, Northern Bottom, Northern Surface). Note that none of the water sampled is the Open Atlantic... The distinction here is that there is a body of water north of 59N but still in the North

- 10 Sea which was only sampled in 2011 and not 2012. We have reworded as follows: 'We investigated the potential bias due to the more northerly extent of the 2011 cruise potentially sampling waters richer in nitrate and phosphate. However statistical comparison (by t-test, p<0.05) of only the region of the 2011 cruise south of 59N (i.e. the section covered in both years), reveals a similar, and still statistically significant, difference. Similar statistical comparisons of only the region south of 59N have been made for DOC and DON; where we report
- 15 differences between years these are significant even after comparison on the same latitudinal basis.'

Page 9, lines 10-11- How does the spatial subset data compare?

Taking only the data that overlaps in space and comparing winter and summer leads to the same conclusions – we have removed the statement about different survey areas and river influence as later we make the point that the salinity is high in the winter data, so is clearly not strongly river influenced, or at

20 least the relationship is very complex.

Page 9, paragraph lines 20-29- I don't understand the point you are trying to make here.

Regressions of DOC and DON with salinity give intercept values that predict the zero salinity end member concentrations. Given that we have established in the introduction that conservative mixing of terrestrial DOM is unlikely, it is surprising that these end member extrapolations agree so well with the end-member

25 synthesis now presented in the introduction. One explanation is that there is an autochthonous coastal signal that results from riverine nutrient discharge (as outlined in introduction), which we cover in the second half of this sentence.

Additionally, the DOM-Salinity relationships, while significant, are not very strong (R2 < 0.5 for all

water bodies). Further discussion of conservative vs any potential non-conservative behavior is needed. Your salinity gradient is not that large- how does this impact your interpretations? We have extended the consideration of DOM-salinity relationships throughout the paper, particularly in

the introduction and discussion sections.

5 Page 10, line 9-14- I think this discussion would be better supported if depth were included on the figure. As is, I see no real linear relationship in the Winter 2012 samples and this discussion is not really supported by Figure 4- these relationships don't look particularly linear with salinity. Although we mention the relationship with depth with reference to the Hopkinson and Vallino (2005)

paper this is not relevant here – they consider processing with depth as a proxy for age in the open ocean.

10 This reference was included to justify the analysis of DOC/N gradients. In our case the variation is with salinity, not time/depth. This paragraph wasn't particularly clear and we have re-worded and moved to the discussion (section 4.1).

Page 10, line 28- What are the percent differences between these observations (i.e. interannual vs depth)? Is this statistically significant?

15 These differences are outlined in Table 2 Table 3 (previously Table 2) but we have now stated where these differences with depth are statistically significant in the text.

Page 11, line 20- "interesting differences"- what are these differences? Be explicit. This paragraph is confusing, perhaps by splitting up the observations into difference sentences would help for a more succinct narrative.

20 The second half of the sentence explained what they were. However, we have removed 'interesting' and made this whole paragraph clearer.

4 Discussion- I feel that much of the discussion should be reworked- I have a hard time following the structure of many of the arguments in the discussion, in particular the DOM-salinity (section 4.1) and the DOM variability (section 4.3) discussions.

25 We have reworked the discussion to address the clarity of the arguments and to adapt the discussion away from hypotheses and instead link back to the new sections of the introduction regarding DOM-salinity relationships and residence time / water exchanges.

Are the end-member data robust enough you could perform an actual mixing analysis (similar to the

approach in Perdue and Koprivnjak, 2007 Estuarine, Coastal and Shelf Science doi:10.1016/j.ecss.2006.12.021; See also the caveats outlined in using C:N ratio to determine terrestrial vs aquatic sources of OM outlined in this work)? How, specifically, does the nutrient data tie into this? The short answer is no... the endmembers are rather too uncertain and the production and loss processes

5 likely to be too significant to conduct such analysis. This is now covered in the introduction and discussion.

Section 4.1- I am missing the connection between the topic sentence and the following discussion. How does the lack of relationship between chla and POM support or refute your hypotheses? We have removed hypotheses so this question is no longer relevant. However the answer would be neither

- 10 it just demonstrates the multiple layers of complexity in DOM cycling we have changed this section to read: 'no direct relationship between either chlorophyll or POC/N (data not shown) was evident, demonstrating the complexity of multiple sources, sinks and lifetimes of DOM.' And in the conclusion: 'The analysis of DOM/salinity gradients here is constrained by our poor understanding of the lifetime of DOM in the North Sea, and of the source of high DOM in near-coastal waters (autocthounous, nutrient-driven vs riverine source). More measurements of
- 15 DOC/N in rivers and estuaries flowing into the North Sea, particualry transects from low to high salinity would be a valuable addition to our knowledge of low salinity DOM cycling and production in this region.'

Section 4.2 – This is your most interesting and novel finding. Do you see large spatial variations that might weaken the budget extrapolation?

As shown in Figure 5,6,7 and 10 (previously Figures 3-7) and Table 3 (previously Table 2), these

- 20 differences are spread throughout the domain, so we are confident about the inventory calculation. Are there any physical oceanographic work that support the shifts in exchange of water masses that you discuss? I think this section could be split and both paragraphs expanded upon significantly. More on the water exchange and residence time is included in the introduction and we have added extra discussion to this section to back up our findings and the possible explanations for them.
- 25

Section 4.3- The discussion of potential benthic inputs of OM must be further expanded upon-while this is an interesting hypothesis, the current arguments do not convince me. Do your turbidity or POC data support the nepheloid hypothesis?

Unfortunately we don't have any data that directly supports this hypothesis as our observations were very much focussed on the water-column. We don't have turbidity data and the POC is really dominated by the phytoplankton biomass and only available to 2012. Whilst we think it is an interesting possible explanation for some of the results we only have the circumstantial evidence from the ammonium and

5 phosphate concentrations and so rather than expand, we have shrunk this argument down and make the point in the conclusion that it is something that needs further investigation.

5 Conclusions

Again, I feel the focus here should be on the C budgets more than the DOM dynamics.

10 We have changed the balance of the discussion towards this aspect of the work, although we do think that the dynamics are also interesting and relevant.

Technical Corrections Comments for throughout the manuscript:

Make sure super and subscripts are correct (e.g. page 3 line 5, page 5 line 17). Check sentence structure for flow, spelling, and punctuation.

15 We have checked subscripts and superscripts throughout the manuscript and have considered sentence structure and clarity throughout as we have worked through the manuscript and feel it is now overall clearer for the reader.

Below are a few (nonexhaustive) examples:

Page 3, line 16 a comma is missing after "2007)" as on page 6, line 9 a comma is missing after "(LOD)".

20 Page 12, line 14 is missing a period.

Page 16 line 16 missing a "t" in "this".

Check paragraphs for run-on sentences, which confusing the meaning. Eg. Page 11 lines 19-23.

I feel many of the connecting sentences are awkward and should be reworded to flow better. E.g. page 12 lines 2-4: "In this discussion, we consider..."

25 Check that the citations are imported to the text properly (e.g. page 12 line 9).
Make sure the nomenclature is used consistently- ie. DOM, DOC, DON.
The above have been addressed as we have worked through the manuscript
Figure 1. This should be zoomed out and/or the land masses labelled. A compass-rose would help as well.

We have labelled land masses and given an approximate length scale to demonstrate the size of the North Sea Basin. Figure 1 is now Figure 2 in the new manuscript.

Figure 3. I find this figure hard to follow. Perhaps consider a different way to display this data, for example a temporal evolution plot such as those created in ODV?

5 As we have only 2 'time points' for this figure we don't see that temporal evolution is particularly useful. Whilst there are a lot of sub-plots we feel that these are important and that the gaussian smooth of the data provides a strong synopsis of the data, compared to often-used interpolation routines that can lead to apparent spatial details which are in fact artefacts of the interpolation method. Reviewer 2 is keen on this plot so we have decided to keep it as-is, with the addition of a fourth set of panels for salinity.

10

Reviewer 2

The authors present results from three cruises that sampled the North Sea in August 2011/12 and January

- 15 2012. In addition to standard temperature and salinity data, nutrient (nitrate + nitrite, ammonium, phosphate, silicate) and dissolved organic matter (DOC, TDNDON) are also reported, being the focus of the manuscript. Particulate organic matter and chlorophyll collections are also described, however they seem to be of little focus to the manuscript and were not included in the results and discussion sections. Oxygen data, were either not collected or are not reported. Authors primarily consider salinity, nutrient,
- 20 DOM concentrations and DOC:DON, exploring relationships by cruise, region and surface/bottom samples.

We do not have access to oxygen data for the cruise. We do refer to POC and chlorophyll in the results and discussion but as no relationships could be discerned between these parameters and the DOM, which is the focus of the paper, we have not explored them further.

25 Much of the discussion is superficial, mentioning other/relevant papers without exploring prior results to gain insights and new findings from the reported data.

We are sorry that the reviewer feels this way. The Discussion section comprises 4 of the 16 pages of text in the original manuscript, plus both reviewers suggest that some discussion and interpretation had slipped

incorrectly into the results section, so overall a considerable proportion of the manuscript is devoted to discussion and interpretation. Quantity is no substitute for quality however, and we have tried to strengthen and clarify our arguments throughout. Inevitably this has resulted in a longer paper and extra figures, which may not have been this reviewer's intention... The manuscript as revised does we feel

5 elicit significant new insight in terms of distribution of DOM, and controls on its dynamics and inter annual variability.

It is mentioned that more data, particularly sampling other months/years, is necessary to complete analysis. As a result, reader is left wondering why the study was published if it is not complete and inconclusive.

This was a PhD project based on ships of opportunity. It is a reality of all science, but particularly timeand resource-limited postgraduate study, that datasets are limited. We strongly argue against limiting publication of manuscripts on the basis that 'more could be done'. Multiple years of dedicated cruises might answer some of the questions raised in this paper, but without publication of smaller datasets,

- 15 funding for such large studies could never be secured... We feel the dataset as it stands and the questions it raises are worthy of publication without waiting for further fieldwork that may never materialise. There is great potential to supplement limited data with satellite (temperature, chlorophyll, and even Aquarius salinity during the study period, however resolution may be too coarse), temperature (and oxygen?) data, and apparently measured but not reported POC/N and chlorophyll data, which should be
- 20 *done*.

10

We feel rather like this reviewer wants us to provide a synoptic biogeochemistry of the North Sea which is most definitely not our aim or desire. We do include temperature data (e.g. Section 3.1), and already make reference to the POC/N and chlorophyll data, but its use is limited in tackling the issue of DOM dynamics due to lack of observed correlations / relationships. Satellite data for this region is limited due

25 to cloudiness and, we would argue, is beyond the scope of this study. Interestingly, despite the limited data that the authors are working with, an excessive number of figures are included (both in the manuscript and as supplemental). In grand total, 13 figures are included with the manuscript, however discussion of them to the extent that would require so many figures is lacking, and it is recommended that figures be revisited to only include those that support key points/finds, and follow-up by elaborating on those points.

In the re-working of the paper we have ensured that these links back to the figures are made clearer. We note that the reviewer also requests *more* figures throughout their review so we have proceeded in or re-

5 working of the paper on the basis that quality and relevance of figures is more important than total number. Subsections (particularly in the Results section) disrupt flow, and much of the discussion is included in the Results section rather than in the Discussion section.

We have left subsections in in our resubmitted manuscript, partly to aid reference to places where changes have been made in response to reviewers' comments. We ask the editor to decide whether or not they

10 would like us to remove subsections and will make this change if necessary at the final stages of manuscript preparation.

In the reworking of the paper we have tried to move discussion out of the results section where possible. This study has great potential, however that potential is left to the reader's imagination.

We are glad that the reviewer recognises the value of the dataset. Given its limitations in time, space and
supporting data we are wary of 'over-analysing' but have worked to improve the narrative throughout in response to both reviewers' comments and hope it is now more coherent in the revised manuscript.

Focusing on and elaborating on the important points (mixing, rivers, significance of C:N, odd 2011/12 year) would greatly improve this manuscript and warrant its publication. The manuscript is written as a simple descriptive paper of the distribution of measurements made—as the title suggests—but much more

20 could be gained if reported data, available (satellite) data, and previous studied were considered and compared more critically.

We feel that there was significant discussion beyond a simple presentation of data in the original manuscript. However we recognise that a better framework for the paper aids the analysis and narrative and have made substantial changes in this regard. However we have not included additional data (other

25 than a summary of DIC data from other workers – see below) as it is either not available or adds little to the key points of the paper.

General comments

Paragraphs are often times short and disorganized. In general, paragraphs should be \geq 3 sentences long,

and flow from one to the next.

We have been through the paper and combined short paragraphs.

Punctuation throughout the manuscript could be improved. Specifically, there are many sentences that are either very long or very wordy that would benefit from including a coma or two.

- 5 We have tackled clarity and sentence structure in the re-working of the manuscript.
 Many times "well mixed" (and "carbon rich" and "near shore") is used as an adjective, and when it is used that way it should be hyphenated (i.e., should be written as "well-mixed").
 We have amended this in line with the reviewer's request
 When writing numbers, it is good to be consistent. For example, the authors switch between "2 years"
- 10 and "two years" many times. Generally, it is good practice to spell out the numbers. Exceptions could be dates, concentrations/units, and when doing math.

We have been through to improve consistency on this point where appropriate.

Include figure citation at the end of the sentence so flow is not disrupted.

This is stylistic and whilst we respect the recommendation and have given it consideration it has not

always been possible without unnecessarily complicating sentences.
It is not good practice to begin sentences with abbreviations and should be avoided.
We have avoided this where possible.

Many abbreviations (BML, CEND, CRM, CV, DOC, DON, ICES, LOD, POC, PON, SML, SRM, T-S, TDN, TOC) are either not defined, defined after they are used in the manuscript, or their meaning is

20 unclear.

All abbreviations are now clearly defined on first use.

When reporting averages, it seems that medians are randomly used without justification. Either justify why medians are used in those cases, or be consistent and always report mean values.

25 Our use of different types of averages is intentional, not random. In the results section we use the median specifically for ammonium concentration, which typically shows a strongly log-normal concentration distribution. Therefore median is a useful measure in this case for comparing values which are 'high' relative to what is typical. Box-and-whisker plots routinely present median and interquartile range as this

is a useful way of understanding the dirstribution of data. However we use mean data when presenting synoptic concentrations e.g. for DOC, as the mean is the value that one would use for e.g. calculating net fluxes or extrapolating inventories.

Often times tenses are incorrect (e.g., when referring to a cruise that took place in 2012, describing what happened on it should be written in the past tense—not present tense). Not as noticeable, but sometimes

5 happened on it should be written in the past tense—not present tense). Not as noticeable, but sometimes words are singular/plural when they should be opposite.

This has been addressed in the re-write of the manuscript.

"C:N" denotes C-to-N ratio, so writing "C:N ratio" is technically redundant.

We accept that the reviewer may be technically correct here but from a stylistic point of view we feel that

10 inclusion of the word ratio in most cases makes for easier reading. Looking back over the literature, we find many papers use 'C:N ratio' and have chosen to keep most instances of the term in this form, although some have been simplified to 'C:N' where this seemed more appropriate to us.

Virtually all sections are divided into subsections, which I feel disrupts the flow of the manuscript and delivery of its message overall, particularly in the Results section. I suggest restructuring manuscript

15 without subsections, reorganizing based on topics mentioned, and add subsections if necessary. Overall, I don't feel there is enough material to warrant subsections, as much of it as currently organized seems to be redundant.

We have extensively reorganised and rewritten the manuscript and in the process considered the need for subsections. We feel that the subsections are useful to break up the manuscript into coherent parts but

20 will happily take guidance from the editor on this.

There are many instances where names are written inconsistently. "North Sea" should always be capitalized, while when describing its regions that are referred to (i.e., Denmark, East Anglian coast, East Anglian plume, German Bight, Humber estuary, northern, southern, Southern Bight, Thames estuary, Wash, western, Western Approaches), they do not need to be capitalized.

25 Some of the examples given above do need be capitalised... 'the Wash', 'Thames', 'Denmark', etc are all proper nouns and we do capitalise them, as with North Sea. 'northern' etc should not be capitalised, and is not, throughout the revised manuscript. 'Western Approaches' is a grey area as is a proper name for a region of the shelf sea, like 'North Sea' so we leave this capitalised.

Do not abbreviate "North" as "N." (or "N") since "N" is used to denote nitrogen. We have removed all instances of the use of N as an abbreviation for North.

When referring to the "North Atlantic" it may be simply refer to it as the "Atlantic" to avoid overuse of

5 the word "North" (i.e., it is understood that the North Sea does not exchange with the South Atlantic).

Where we felt appropriate we have changed this

I do not like that hypotheses are included, as some of them are proven wrong. Perhaps this is not uncommon in journal publications, but I have only noticed this style of writing in proposals. Since this is not a proposal, I suggest restructuring/rephrasing the inclusion of hypotheses, as they may be misleading

10 to readers.

15

We are surprised that the reviewer has never come across hypotheses before other than in the proposal context. However, we agree with both reviewers that in this case they made the narrative more awkward and have reworked the paper to remove them.

Explain how your sampling efforts attempted to address the DOM vs. salinity relationship, seasonal variations, DOM stoichiometry, and anthropogenic/river influences, etc.

We are unclear about what specifically the reviewer means here? In our reworked introduction this should hopefully be addressed.

Keywords

Should you include "North Sea"? Carbon, Nitrogen, and Mixing are broad (i.e., not keywords).

20 We have added 'North Sea' to the key words

Tables

Inclusion of a table that lists cruise numbers and dates is recommended, which can be referred to throughout the manuscript to improve clarity.

We have added the following table, which also explains the 'acronym' CEND

25 Table 1. Summary of sampling cruises in the North Sea.

Cruises*	Dates	Season
----------	-------	--------

CEND 14/11	8 Aug – 7 Sep 2011	Summer 2011
CEND 02/12	20 Jan – 31 Jan 2012	Winter 2011
CEND 13/12	9 Aug – 23 Aug 2012	Summer 2012

*CEND is abbreviation used for research vessel Cefas Endeavour

Explain what "SML" and "BML" mean, either in captions or in text.

For this reviewer's reference, SML and BML are commonly used terms in shelf sea oceanography for Surface and Bottom mixed layer, respectively. However, these were left over from different terminology

5 used in an earlier draft of this manuscript and were left in Tables 1 and 2 (now Tables 2 and 3) in error, and have been changed to 'Northern Surface' and 'Northern Bottom' in keeping with the rest of the manuscript.

Label based on cruise number, in addition to season/region.

We don't feel the cruise numbers add anything to the text or figures – having included a table (Table 1)

10 for reference, we feel that no further change is needed.

Figures

For the most part, I don't feel that the supplemental figures are useful and can be omitted. Moreover, I feel that the number of figures included is excessive considering the limited number of times they are referred to. A better approach would be to limit to the most important figures and refer to them

15 frequently/when relevant, and omit the others.

We feel that most of the figures included are fundamental to the arguments we are making and, given that reviewer 1 did not feel they needed to be removed we prefer to keep them in, other than where stated below.

Figures are often times referred to as a/b/c/d etc., but figures are not labeled a/b/c/d etc. Please label

20 *them*.

Figures amended in this regard.

Figure 1: Referring to a map that shows the North Sea as a system—not exclusively as a sampling grid would be useful, including labeled geographical regions that are referenced throughout the manuscript (e.g., "northern North Sea" and "German Bight" etc. should be labeled). A bathymetric feature (a break?) can be seen at $\sim 54^{\circ}$ N in the west and $\sim 57^{\circ}$ N in the east—is this the northern/southern boundary that is referred to in the text?

We have removed references to these regions in the text as they weren't really necessary and allows us to keep the Figure simple. Whilst the boundary between well mixed waters in the south and seasonally

5 stratifying waters in the North does follow the bathymetry around the 40 to 50 m mark, we distinguish waters operationally in this study based on their temperature difference between surface and deep waters – as described in Section 3.1. We have added a note to this effect in the figure caption of Fig 1 Figure 1 (Figure 2 in the new manuscript).

Figure S1: Unnecessary and can be omitted.

10 We feel that this figure is essential in convincing readers that our between-year measurements are consistent and thus that the main finding of the work – that the interannual change in large – is reliable. We would prefer to keep this figure in the supplementary material..

Figure S2: Utilizing the colors better, this figure could be condensed into one panel, included in the manuscript and incorporated into discussion.

15 We have experimented with this but find that the data is much less clear as there are lots of overlapping points. As requested by this reviewer later in their review, this figure is now included as Figure 3 of the new manuscript.

Figures 2 and 6: I find these figures to be challenging to interpret and not all that useful. Furthermore, I find that claims made by authors based on these figures are often times incorrect due to the boxes

20 overlapping.

These figures are not simple, but we feel they are the only way to demonstrate the data that allows the reader to compare surface and bottom, different regions, and the winter data. We would prefer to keep them in. It is really important to point out though that in a highly variable dataset it is entirely possible for the mean concentrations to be statistically significantly different whilst the interquartile ranges

25 overlap. These boxes do not represent 'error bars'. This should have been stated explicitly in the figure captions for Figures 2 and 6 (Figure 4 and 7 in the new manuscript) and has now been amended: 'Box and whisker plots show statistical summary of the data where the thick horizonal line represents the median value, the extent of the boxes represents the interqartileinterquartile range and

whiskers represent the full range of data to 1.5 interquartile distances from the median. Any points outside this range are shown as discrete points.' Where we state differences in the text these are always on the basis of t-tests (p<0.05) to compare the mean values.

5 We have also added 'Northern' and 'Southern' to the Summer stratified and Summer well-mixed subplots to make nomenclature more consistent, and reduced the size of the 'outlying' points in the plots to make them less distracting from the boxes and whiskers which are more important.

I suggest omitting them and interpreting values with respect to depth (and perhaps adding shading to

10 *clarify ranges), similar to Figure 7.*

Unfortunately (as explained in Section 2) we only have 1 surface and 1 deep samples from each station, as these were the only ones taken during the cruise. We therefore cannot present depth profiles (Figure 7 also doesn't present such and only shows samples from the bottom layer). Figure 7 shows the data in a fundamentally different way to figure 6, and we feel that both have value in the presentation of data from

the study. Figure 7 is now included as Figure 8 of the new manuscript.
 Figure 3: Great, clear plots. I suggest doing this with T, S, nutrients, and oxygen. Also be good to include bottom.

We think these plots add a great deal to the paper, particularly the novel approach to showing a smoothed rather than interpolated background. We would note that the bottom data is already included in the plots

20 (second row of plots). We do not have oxygen data. As there is a greater focus on salinity trends in the revised manuscript we add a new panel showing salinity in the same manner. We could add plots of T, nutrients but don't feel these add a great deal to the analysis and increase the total number of plots, so have not made this change.

Figure 4: Great, but should be reevaluated with regressions (or similar statistical analysis), and a color

25 scheme with more contrast (e.g., red, green, orange, blue) would improve it. Label by cruise number in addition to season/year, and restate what is meant by northern/southern in the caption.

We have improved the colour scheme and labelling of this figure, although we have stuck to shades of brown and green to remain in keeping with Figures 4 and 6 which use similar colours to denote the same

(surface and bottom). Regressions clutter this figure and require an alternative approach with 3 x 4-panel plots rather than 3x 2 panel plots, which we include below for reference – if the reviewers or editor prefer we can produce these in high quality in the manuscript. However, regressions of these data are presented in Table 4 (previously Table 3) so we would prefer to keep the simpler figures. Cruise numbers are presented in the new Table 1 so we don't feel it is necessarynecessary or informative to repeat them on







Figure 5: Very nice, and I hope it is a focus of the/a discussion (sub)section.

This figure is already discussed in Section 3.4 and is now referred to in the extended discussion in Section

5 4.1 of the new manuscript. Figure 5 is now included as Figure 7 of the new manuscript. *Figure 6: I suggest omitting and refer to Figure 7 instead.*

As stated above Figure 6 and 7 are showing different things and Figure 7 will not substitute for Figure 6. Figure 7: Would be good to include additional colors to partition by region (northern/southern), and perhaps draw a line to specify surface/bottom samples or use different shapes (diamond = surface, square

10 = bottom).

As stated in the figure caption they are all bottom water samples. We could separate by different regions but generally, deeper water is more northern so it's a bit redundant to do this

Figure S3: Why is this figure supplemental? It seems fundament to the discussion of riverine input. Since

the lowest DOC concentrations are $\sim 50 \,\mu M$ (not $0 \,\mu M$), it would make sense for the color to reflect that. Also, please include units for DOC.

This figure is now included in the manuscript as Figure 11.

Salinity also doesn't appear to go below 33.5, or if it does those values can't be seen because they are

- 5 the same color as the depth colors. Please make these adjustments and include figure in manuscript. Caption should state that they are surface values. Can this be included/interpreted with respect to temperature and nutrients, in a similar manor as Figure 3, and included in the manuscript? The reviewer is correct that the salinity does not go very low (there is one point below 33.5 just south of the Humber Estuary). We have replotted these plots to improve the colour scales as requested and include
- 10 them in the main text. We have reworked and expanded the discussion to improve clarity, but we don't find much more can be said than we already have, given the data available.

Figure S4: Unnecessary.

Figure S4 has been removed.

Figure S5: There is nothing significant about any relationship plotted, and therefore there is no significant inverse relationship with salinity. This figure is unnecessary.

We have removed the figure and references to it in the text.

Figure 8/9: Unnecessary. The same information can be gained by referring to Figure 5.

Figure 5 and Figure 8, as numbered in the original manuscript, in our opinion show two important and distinct things. Firstly Figure 8 shows only the Northern bottom waters and so is really focused on the

- 20 cold, high saline waters which are closest in T-S properties to the open North Atlantic waters. They compare the two years against the Atlantic end members in DOC/N space which couldn't be done in the broader dataset. This comparison in DOC/DOC space is a novel analysis and we feel is the most important evidence that 2011 shows strong enrichment of DOC even at high salinity / low DON and that 2012 is more consistent with the open ocean end members. This is key in allowing us to draw our conclusion that
- 25 the 2011 northern bottom water data is indicative of the effect of autocthonous DOM processing on the shelf and thus the nature of the exported DOM (i.e. DOC rich, DON poor), but that this is not the case every year, probably because of changing residence time. Of all the figures, we feel this is the most important and would strongly argue to keep it in. Figure 5 and 8 are now included as Figure 10 and 12 of

the new manuscript.

Abstract

DOC and DON are not defined, while dissolved organic matter (DOM) is.

5 corrected

Lines 15-6: "...with higher DOC and lower DON in 2011 and lower C:N ratio and more moderate concentrations of DOC and DON in 2012." is confusing... higher [DOC] and lower [DON] in 2011 = higher C:N in 2011 than 2012, so why not just write that? Added detail on concentrations is superfluous unless sentence is restructured/point clarified.

10 *Changed to* 'with higher DOC and C:N ratio in 2011 than in 2012'

Line 16: Is it necessary to include "differences" twice in the sentence that begins with "Using other data we…"?

Second 'differences' changed to 'changes'

Introduction

- 15 Overall, the introduction brings up some interesting points but does not fully explore them and the papers citing, including them only in lists rather than by understanding and explaining prior, relevant findings. We feel that the introduction as originally presented provided a level of detail comparable to other papers presenting similarly sized datasets. We are wary of turning this paper into a literature review, but have found it useful to explore and expand the introduction somewhat – we feel it now improves the paper.
- 20 Page 1, lines 24-5: "... have been proposed as potentially disproportionately important for the drawdown of atmospheric carbon to the deep ocean." is very hard to read. "...may be more important for the drawdown of atmospheric carbon to the deep ocean, relative to the open ocean." Is that better? *Changed to* 'through various processes may be disproportionately important'
- 25 Line 26: "shelf carbon pump processes" would be clearer as "carbon pump processes on the shelf" Changed as suggested

Lines 27-8: Seems redundant to include "complexities" and "complex" when describing the same system.

I suggest replacing "complex" with "dynamic" or simply omit.

Removed.-sentence now reads: 'Our understanding of the mechanisms of carbon pump processes on the shelf and their relative importance is limited by observational data, the complexities of shelf circulation and interannual variability of both biological processes and physical drivers'

5 Lines 23-9: Are these two sentences (hardly a paragraph) necessary to begin the Introduction section? I suggest omitting them and directly begin with a subsection, or elaborate on the points made so paragraph is \geq 3 sentences. DOM and the continental shelf

Reviewer 1 felt this paragraph was essential to the paper so we have added more detail.

Page 2, lines 3-6: By definition, it is not "Marine DOM" if it includes "both terrestrial and marine

10 [material]". Sentence could be rephrased to begin as "In the marine environment, DOM..." or something similar so point on mixture can stay.

Changed to: 'In the marine environment, DOM can be is a complex mixture...'

Is "lifetime(s)" the correct word? Seems that "residence time(s)" is more appropriate. What is "Its" in reference to? Marine DOM? If so, DOM degrades to inorganic carbon explicitly? Perhaps "...its lifetime

15 in relation to degradation to inorganic carbon..." should be written as "...DOC's residence time prior to degradation to inorganic carbon..." Is "(e.g. Jiao et al., 2014)" necessary prior to the end of the sentence? Perhaps due to this citation disrupting sentence flow or a word or two being missing from it, I do not understand what is meant following the citation.

Sentence now reads: 'The reactivity of DOM and in particular its availability for breakdown by marine microbes is

20 a key factor controlling its resistance to degradation to inorganic carbon and thus capacity for long-term carbon storage as refractory, i.e. unreactive, DOC (e.g. Jiao et al., 2014).'

Line 13: Not good to begin a paragraph with "This..." Could you specify what "this" is? Do you mean "The export flux of DOM..."?

Now reads: 'The DOC export from continental shelf seas'

25 Line 14: The "production" itself is exported? Do you mean that newly produced DOM is exported? Changed to 'autochthonous DOM produced on the shelf...'

Lines 14-5: The portion of the sentence following the semicolon can be omitted, unless examples of previous studies that demonstrated this uncertainty can be provided.

Sentence now reads: 'The DOC export flux from continental shelf seas is composed of a combination of terrestrially-derived organic matter from rivers (allochthonous DOM) and autochthonous DOM produced on the shelf through in-situ autotrophic processes. The relative contributions from the different sources is uncertain, although there is strong evidence that much terrestrial organic matter is respired, photooxidised or buried in shelf

5 sea systems...'

Lines 15-6: Please provide examples of how the stoichiometry may be an important indicator. Including such examples would certainly be good justification for conducting this study.

Now reads 'The stoichiometry of exported DOM may also be an important indicator of the efficiency of the shelf carbon pump, with higher C:N organic material representing greater carbon fixation per unit nutrient and the export

10 of carbon-rich organic material off-shelf in particular contributing to nutrient retention on the shelf and a more efficient shelf pump (Humphreys et al., 2018).' Further discussion of stoichiometry is included in this section as justification

Line 19: The Redfield ratio is a indeed a "single fixed ratio," defined as 106:16:1 for C:N:P. These ratios have been further evaluated and C:N:P is not always 106:16:1—considering C:N:P does not make it a

15 the Redfield ratio.

Changed to 'C:N stoichiometry of particulate organic matter is not produced at a single fixed ratio even in primary production (Moore et al., 2013).'

Line 20: What is meant by "...as shelf seas process internally-produced organic matter..."? Do you mean "...as autochthonous organic matter degrades/is mineralized in shelf seas..."?

- 20 Actually our statement applied more broadly than just to autochthonous (i.e. 'internally-produced') organic matter so we have re-worded: 'Despite these caveats, a net enrichment of carbon relative to nitrogen as shelf seas cycle organic matter and nutrients implies re-use of the nutrient (i.e. nitrogen) to drive further primary production, thus decoupling organic matter processing from the relatively fixed stoichiometry of algal growth.' *Line 22: Surely dissolved organic carbon is carbon rich... Do you mean "Carbon-rich DOM..."*?
- 25 Yes, corrected

Line 26: Explain the jargon "refractory" better, in the context of DOM. Perhaps also useful to explain "labile" and why that would conversely not result in the marine environment being a sink for atmospheric carbon.

Now reads: 'refractory (i.e. resilient to degradation)' The North Sea system Could subsection simply be "The North Sea"? Changed as requested

studied, (un)productive systems so reader can grasp relative productivity.

Page 3, line 5: 25-30 m C/m²/yr is highly productive? Provide comparison(s) with other, perhaps better

We feel this is unnecessary detail and instead have removed the quantitative statement of southern North Sea carbon fixation.

Line 7: Is it "thought" to be or is it "understood" to be net autotrophic? Can you provide an additional citation to better show that efforts have been put forth to understand the system?

10 We have added numerous more key references for both the statement that it is thought to be net autotrophic and that it is a strong net sink for atmospheric CO2. We do not recognise a specific distinction between 'thought' and 'understood' but have changed to understood.

Line 8: Can you describe the seasonal stratification better, and how that results in net autotrophy? Seems out of place, perhaps due to "(i.e. ...)" Perhaps "driven by" would be better than "through its"

- 15 Paragraph now reads: 'The northern North Sea is a net sink for atmospheric CO₂, argued to be driven by seasonal stratification and the consequent vertical separation of surface autotrophy and respiration of exported carbon in the net-heterotrophic waters below the thermocline (Bozec et al., 2005; Clargo et al., 2015). In the 'classic' North Sea shelf pump mechanism, below-thermocline waters in the Northern North Sea then exchange with the deep ocean, so the accumulation of carbon there is thought to be an important mechanism in the shelf carbon pump (Bozec et al.)
- 20~ al., 2005; Thomas et al., 2004) '

5

Lines 10-1: Can you provide more context on this CO2 flux? What other region(s)/fluxes does this compare to that biogeoscientists/oceanographers might be familiar with?

We agree with the reviewer that providing quantitative detail without comparison to other regions is not good practice. However, as CO2 uptake mechanisms are not really considered in this paper we have

25 removed the quantitative detail in regards to this paragraph to simplify the manuscript. Is "Deeper waters" relative to the overlying waters? The southern North Sea? Please clarify what is meant by "deeper." Do you mean bottom waters, as I suspect they most readily overflow/exchange with the deep ocean. We do use the term deeper throughout the manuscript and have reviewed its use to make sure that it is clear what we're comparing to. In this case, in the rewording of the introduction, this sentence is no longer present.

5 Lines 12-3: What is "net DIC exchanges"? Either provide direction (net to ocean or net to North Sea) or omit "net".

This phrase removed in the re-writing of the introduction

Could DIC be introduced earlier? Inorganic carbon is referred to frequently, it seems, so an earlier introduction to DIC may be useful.

10 We considered this but given the paper is really about DOC, we felt bringing DIC in earlier would overcomplicate and lengthen the introduction.

Lines 14-7: Elaborating on these "Recent studies" and the interannual circulation variations would be useful for this paper/study. Please do so in a stand-alone paragraph, as this long sentence does not provide reader with enough information.

15 Done – a new paragraph dedicated to circulation forms part of the wider rewrite of the introduction Lines 19-20: Does the observed "minor net respiration of DOC" contradict the net autotrophy found in the northern North Sea, as stated in the previous paragraph?

No, there is no contradiction, the system can be strongly net autotrophic (transforming DIC into POC) and yet the inflow of DOC can be higher than the outflow, suggesting net respiration of DOC. That said,

20 we go on in the following sentence to mention other evidence which contradicts the Thomas et al budget.
Line 22: This decoupling is not "apparent" to reader—please elaborate.
Have added 'i.e. greater drawdown of carbon per unit nitrate uptake than would be predicted by the 'Redfield' ratio of 6.6:1 C:N'

Line 23: Is this "strong seasonality" limited to the northern North Sea? You've previously partitioned

25 the system into northern and southern regions, so any further discussion of the system should specify whether the entire system or its northern/southern regions are being considered.
We don't see a problem with the way this is phrased – this is a new paragraph on DOM in the North Sea

and no specification of northern vs southern has been made in this paragraph. To avoid over-wordiness

we would prefer to keep this as-is.

Line 24: "or so" is vague omit. Since "weeks" is plural, it could include a month (4 weeks), so stating "weeks to a month" is overly descriptive. Perhaps writing "weeks to months" or "weeks to a couple months" would be the most appropriate wording. An alternative could also be "1-6 weeks".

5 Changed to 'weeks to months'.

Lines 26-7: "impossible" is a strong word. Does this sentence suggest that it is impossible to determine whether or not the system is net heterotrophic or net autotrophic? Previous paragraph cited papers that showed that it is/isn't depending on region. Could this point be clarified, perhaps elaborating on distinctions between DOC, POC and DIC fluxes? A better description of the biological carbon pump, in

10 the context of this study/system, would be useful and strongly encouraged. Currently it is not possible to determine whether they system is overall net auto or heterotrophic. We are reluctant to enter into an extensive discussion of the biological carbon pump - there is extensive literature on this subject already.

15 Study area, sampling and analytical methods

Could simply be "Material and methods" I am surprised that oxygen was either not measured or is not reported here. Why is that?

O2 is not a particularly good diagnostic of DOM given the many sources and sinks, particularly in shelf environments. We therefore did not measure it. It could be 'materials and methods' but we would prefer

20 to keep the title of this section as-is.

Study sites and field sampling processes

Page 4, line 10: Ship names should be italicized.

Changed

Lines 10-1: Rather than listing cruises and dates in parentheses, include a table. What does "CEND"

25 mean? An abbreviation for RV Cefas Endeavour? If so, write "cruise no." in parentheses so reader is aware that "CEND 14/11" etc. are cruise numbers.

As described above, we have created the new table, **Table 1.** The meaning of CEND is explained below the table.

Lines 11-2: Which "two summer" cruises? You just introduced the cruises by number and date— refer to the cruises by name/abbreviation so stating that they "The two summer cruises were the summer surveys" is not redundant.

Having now moved details of the cruise names into a table, we would prefer to simply refer to them by

5 season/year as this is much more meaningful to the reader. Changed to 'The two summer cruises were surveys of...'

"ICES" should be in parentheses, following "International Council for the Exploration of the Sea" (outside of parentheses) and omit redundant "international."

Changed

10 Lines 12-3: "survey..." is used three times in this sentence. Can it be reworded/structured so "survey..." is only included once? What "sampling grid" are you referring to? The one illustrated in Figure 1? What is meant by "survey rectangles"?

Re-worded to use survey less and include a reference to explain the ICES survey rectangles. The sampling grid is determined by the ICES bottom trawl survey working group, the cruise had to comply with it and

15 our study had no opportunity to influence the sampling locations or regime. Line 16: Can you be more specific than "more northerly stations"? Is there a line of latitude or a bathymetric feature that was not crossed? Which cruise numbers? "2012" and "winter cruise" are vague considering your previous cruise number descriptions.

"more northerly stations" - we have specified '(North of approximately 58 N)""

20 We have specified "Summer 2012" to avoid confusion

Line 19: Only "Surface and bottom waters were sampled..."? What about intermediate depths? Figure 7 shows that many intermediate depths were sampled. Or are these sampled intermediate depths simply a result of a shallower water column? Please clarify.

It is quite evident from the paragraph that only surface and bottom samples were taken. To clarify though,

25 we have added 'The nature of the survey meant that only 2 water samples were taken at each station.' To the beginning of the paragraph. The caption to Figure 7 (Figure 9 of the new manuscript) clearly states: 'DOC, DON and DOM carbon to nitrogen ratios in bottom water samples, plotted against sampling depth (approximately 10m less than total water column depth). ' so we think it is quite clear that the sampled depths indeed vary

as a function of water column depth.

Lines 21-2: If standard seawater has a salinity of 35 and rivers have a salinity of 0, a minimum salinity of \sim 31 and majority of samples with salinity >34 does NOT suggest a "strong riverine influence." It suggests dilution, likely due to riverine influence (and precipitation > evaporation).

- 5 We explicitly state in that sentence that we DID NOT sample the regions with strong riverine influence and that the minimum observed salinity was 31.... In order to make it clearer the sentence now reads: The cruise track focused on the open waters of the North Sea (minimum observed salinity at DOM sampling points =30.9, 87% of samples had salinity >34.0) and did not sample near shore regions with stronger riverine influence. Precip / Evap is not considered a major influence on North Sea salinity compared to runoff/advection so
- 10 we do not consider it in our paper.

Line 25: Was nitrite measured, or was it only nitrate + nitrite? If not, please provide an example of a previous study that showed that nitrite values are negligible for purposes of this study (presumably they are), justifying nitrate + nitrite henceforth being referred to as nitrate. If nutrients are written out (e.g., "ammonium, phosphate ..."), "NO3- and NO2-" should also be written out.

- 15 This is pretty basic biogeochemistry away from anoxic waters nitrite is tiny compared to nitrate and the assumption that nitrate is small is made routinely in studies on and off the shelf. For the purposes of calcuating DON this ensures the inorganic nitrogen budget is closed DON = TDN – (ToxN + ammonium). Paragraph now reads. '... Note that nitrate was measured as total nitrate plus nitrite, and nitrite assumed a small fraction, as is common for oxic waters (e.g. Hydes et al., 2001; Suratman et al., 2008., Painter et al., 2018) '
- 20 POC (and PON) should be introduced when describing the biological carbon pump in the introduction section.

We do not discuss the biological pump in the introduction, we discuss the continental shelf pump, which is different. Although POC and PON do feature in our dataset and are briefly discussed they are not central to our analysis and we do not feel a further paragraph in the introduction is necessary for this.

25 Lines 26-8: Surely Tom Hull can provide you with a description of the "standard techniques" so readers are left informed, rather than clueless.

We are referring here to temperature and salinity measurements. It is not normal to provide references and details for these basic measurements when conducted as a matter of routine from a research vessel. Pers. Comm. to Tom Hull removed.

Analytical procedures

Page 5, line 2: "glass fiber filters, 47 mm diameter of nominal pore size 0.7 μ m..." could be reworded as "47-mm diameter glass fiber filters of nominal pore size 0.7 μ m (GF/F)..." (Note that the main reason

5 *for rewording is to include "GF/F")*

Changed as requested

Lines 4-5: "This storage regime..." has either not been described in the text or is unclear. Please elaborate on how samples were stored prior to analysis. "has previously been shown to be effectively preserve and not contaminate these analytes" should be rewritten as "effectively preserves these analytes

10 without contamination" (by the way, is "effectively" necessary?)

Changed to 'These filters and tubes have previously been shown to preserve these analytes without contamination (Chaichana, 2017; Suratman, 2007; Tupas et al., 1994).

Line 6: Omit "the water volume recorded." and/or move to appropriate place. omitted

15 The "a" in "Cholophyll a" is italicized while it is not on pg 4, line 25 — be consistent. All instances of the 'a' in 'chlorophyll a' are now italicized in the manuscript. Line 7: What is meant by "collected from a separate water sub-sample on the same type of GF/F…"? That chorophyll was also collected (from the same Niskin bottle) on a (separate) GF/F? Not clear as written.

20 Yes, that means chorophyll a was also collected (from the same Niskin bottle) on a (separate) GF/F. Simplified to: 'Chlorophyll *a* samples were collected on the same type of GF/F glass fibre filters (without combustion, gentle vacuum filtration ~10 kPa).'

"fibre" is used while on pg 5, line 2 "fiber" is used. The majority of this seems to be written in British English, so "fibre" should be used in both instances. Please be consistent.

25 One instance of 'fiber' corrected to 'fibre'

Lines 8-9: "immediately" is vague and likely not true, given its definition of "at once; instantly." I suggest rephrasing sentence to be similar to "All samples were filtered at sea and frozen (- 20°C for ...-60°C for ...) after filtration, until further analysis on laboratory on land."

'Immediately' has been removed, but we have otherwise kept our wording.

What is meant by "samples"? Are these seawater (liquid) or filters (particulate)?

"all samples" included both seawater (liquid) and filters (particulate) – changed this sentence to 'All samples (seawater and filters) were immediately frozen at -20 °C after filtration on board (-60 °C for chlorophyll *a* samples) until further analysis in the laboratory.'

Line 14: Elaborate on the mysterious "minor developments."

These minor developments are detailed on the following lines, this term was used simply to make it clear that the methods were not identical to those previously used. Instead of this term, which has clearly caused

10 confusion, we have reworded: 'The methods are similar to those we have reported previously (Johnson et al., 2013; Suratman et al., 2010) and are repeated here in brief.'

Line 15: "The combustion..." sentence is too short. How can this be included in another sentence/expanded upon?

Changed to 'Samples were oxidised over a catalyst at a combustion temperature of 750 °C.'

15 Lines 18-9: Try to avoid using parentheses whenever possible. "...acidification (adding ... 180 s)" could be changed to "...100 μl of 10% HCl was added to 6 ml of sample, spargingwith pure air for 240 seconds and stirring for 180 seconds..."

We have reviewed the manuscript for use of parentheses and tried to remove them where possible without compromising our own writing style.

- 20 Are the details on time necessary if these are automatic (and presumably default) settings? The times and settings used are not "default setting", the sparging time and stirring time used here have been tested and optimized to remove inorganic carbon in our seawater samples. Sentence changed: 'To eliminate inorganic carbon in samples, the TOC/N analyser was programmed to add 100 μl of 10% hydrochloric acid to each 6 ml sample, sparge using pure air for 240 s and stir for 180 s.'
- 25 Line 33-4: Sentence structure is odd. Should be "... (CRM) were used to verify DOC and TDN measurements: low carbon water..."

Rearranged as requested

5

Page 6, line 3: "Consensus values of DOC for DSR vary in each batch." Seems obvious and unnecessary.

Sentence removed

Line 4: "agreement" might be a more suitable word that "accord".

Changed as suggested

Line 15: "…analysis, the analysis…" redundant.

5 First 'analysis' removed

Lines 16-7: "in good agreement" loses meaning when used to describe the exact same value and a value within a range.

Changed "in good agreement with....." to "similar to"

Line 31: Since TDN includes inorganic nutrients, the paragraph on dissolved inorganic nutrients should

10 *come before the TDN paragraph.*

Inorganic nutrients moved up to second paragraph in this section

Pages 6-7, lines 34-1: "CRM" was previously defined as consensus reference materials (page 5, line 33), while Environment Canada provides certified reference materials.

All instances of 'CRM' have been replaced with the full name (certified or consensus, as appropriate).

15 Page 7, lines 1-2: "filters ... desiccator..." should be reorganized as "filters were placed in a desiccator overnight (12 hours) that was..."

This is a purely stylistic change and we chose on reflection to keep our wording.

8 Line 7: The detection limit of what? POC or PON or chorophyll or ???

This is the detection limit of Chlorophyll a. The sentence before this sentence explains the Chlorophyll a

20 measurement, so "the measurement" here is "the Chlorophyll a measurement". We have added 'chlorophyll' to the sentence to make it explicit.

Results

Much of this section is discussion and should be moved to the discussion section.

Although both reviewers are keen that results and discussion should be separate, and we have done our

25 best to accommodate their wishes, ultimately we feel this is stylistic and have found that the flow and readability of the paper is best served with an arrangement where some initial interpretation / discussion is conducted as results are presented. Higher level discussion is saved for the following section. However, in response to specific comments and as part of the request for more in-depth discussion there has been
considerable rearrangement of sections and new parts added, particularly to the discussion section.

Would be improved if subsections were omitted.

Whilst we have modified the results and discussion sections considerably, we have for now left the subsections in as we feel they are useful to separate out otherwise long sections covering multiple sub-

5 topics.

Physical oceanographic conditions

Line 10: List cruises by number and refer to suggested table (see previous comment). Now that a table (Table 1) explicitly linking cruises to seasons/year is included we feel that this is not necessary

10 Line 11: "biogeochemical" technically includes physical.

Technically the reviewer is of course correct. However, it is common practice to separate physical and 'other biogeochemical' properties out when referring to them and we follow this convention here. Line 15: Why is "Winter" capitalized?

A typo, now corrected

15 Line 18/Figure S2: If T-S diagrams provide key information for interpreting your data, these plots should not be supplemental. I think they are great and should be included.
 This plot has been redrawn and is included in the manuscript as the new Figure 3.

Line 19: warmer/fresher/colder/saltier relative to what? Are the "ers" necessary? Makes sense for winter data.

20 All of these terms are relative to each other i.e. warmer vs colder; fresher vs saltier. As this reviewer points out in an earlier comment, none of this water is 'fresh' and equally, the temperature range is relatively small. So Warmer/colder fresher/saltier is the appropriate way to phrase this in our opinion. *Lines 20-4: "Although..." could be moved to the discussion section.* This sentence removed in re-written manuscript

25 Inorganic nutrients

Lines 26-9/Table 1: Numbers in a table to not "show" what a figure can. I suggest showing these distributions as a figure with (profile or surface map) subplots, or perhaps just refer to Figure 2. We don't feel a further figure is necessary and instead make reference to Figure 4 (previously Figure 2)

which, along with the table Table 2 (previously Table 1), clearly demonstrate the trend we are describing. *Pages 7-8, lines 30-1/Figure 2: I see no reason for silicate to be excluded from Figure 2. Either include or don't bother mentioning. Why aren't data partitioned by region?*

We omit silicate because it is not critical to the analysis and would take up extra figure space. The data 5 are partitioned by region- southern well mixed vs northern stratified .

Page 8, line 4: Where is N:P shown? This should be included in Figure 2 if it is a result.N:P of inorganic nutrients is already shown in Figure 2 (now Figure 4).

Lines 5-7: This is discussion.

This is preliminary interpretation and important for building the framework of findings to feed into the

10 higher level discussion later or. We have not changed this.

Lines 10-1: Significant? Please demonstrate numerically/statistically.

Changed in response to reviewer 1 to 'We investigated the potential bias due to the more northerly extent of the 2011 cruise potentially sampling waters richer in nitrate and phosphate. However statistical comparison (by t-test, p<0.05) of only the region of the 2011 cruise south of 59N (i.e. the section covered in both years), reveals a

15 similar, and still statistically significant, difference (t-test, p<0.05).

Lines 14-8, 21-5: This is discussion.

We feel that this is preliminary interpretation and is necessary to present in the results

DOC and nitrogen concentrations

Pages 8-9, lines 31-8: This is, for the most part, discussion.

20 We have attempted to rationalise and make the manuscript more consistent in terms of what level of interpretation is done in results vs conclusions

Page 9, line 1: I disagree that hypothesis 1 is "confirmed" based on a salinity gradient of 31-6. I suggest reevaluating DOM-salinity relationships in the context of mixing/dilution rather than rivers.

Hypotheses have been removed and more discussion of mixing / dilution / end-members is now included

25 in the manuscript in relation to the comments by both reviewers.

Perhaps if a riverine end-member is used this can be assessed, but "confirm" is a very strong word. Ducklow et al. (2007) and Margolin et al. (2016) used a riverine end-member approach for the Black Sea that may be useful to consider, if an end-member is available. Ducklow et al. (2007) also considered C:N stoichiometry.

We have introduced a new synthesis of river and open-ocean end members in support of this manuscript, and make reference to these papers specifically.

Line 13: DOC is virtually always at least one order of magnitude lower than DIC – this is obvious and cited example is not needed.

Often DOC and DIC are considered separately so we believe it is useful here to briefly compare their concentrations.

Line 14: Actually, they are approximately 6 (approximately six or ~6) times smaller.

Corrected

5

10 *Line 15: How is this further demonstrated? Is there an example/citation to compare to? This is getting into discussion territory...*

The term 'further demonstrating' is used because in the previous sentence we give one comparison – DON is the dominant form of nitrogen in summer. Then in the sentence referred to we state it is 3 times the size of the PON pool – i.e. further demonstration that it is an important nitrogen pool. We don't see

15 the issue with the way that we have worded this.

Lines 20-9: For the most part, this would fit better in discussion.

We disagree- the calculated end member values are derived results which we need to use in the discussion later

DOM stoichiometry

20 Page 10, line 3: Where does the "expected North Atlantic endmember of 13-15" come from? Please cite and explain how that is expected.

The mean C:N molar ratio in the North Atlantic of 13-15 is from Aminot and Kérouel (2004). We also mention this on Page 4 (Line 7) and Page 11 (Line 28). It is now part of our end member synthesis so we make reference to this specifically at this point.

25 Lines 5-7: Omit hypotheses as this is not a proposal. Furthermore, this is not results—it is discussion! We have removed reference to hypotheses throughout the manuscript, but we consider this preliminary interpretation Section 4 is the discussion, so presumably most things mentioned in the results are discussed there! Reference to section 4 is removed

Line 9: A gradient of 6.5-7 is like a C:N of 106:15-16, which is very similar to, if not the same as, Redfield (106:16). Using those numbers (i.e., 106 for C) makes the comparison to Redfield easier and readers will

5 more readily grasp that.

That the gradient is similar to the C:N of Redfield is exactly the point we were making in this paragraph. We are used to seeing the 'Redfield' C:N presented as 6.6 (or approximated to 7) rather than 106:16 and don't feel this is a necessary change– we explicitly state that the Redfield C:N is 6.6 when we invoke it in this paragraph.

10 Lines 9-11: This sentence is discussion.

In the case of this paragraph on C:N gradients we agree and have moved this whole paragraph to the discussion. As a result we have removed section 3.4 on C/N ratios and moved the other paragraph from this to 'interannual differences' (previously 3.5, now 3.4)

Line 8: What is "low" salinity? Relative to other samples? Virtually all samples have salinities > 31, 15 which is high compared to many seas.

Lines 11-2: DOC in surface waters of the open ocean can reach \sim 70 μ M, and the lowest salinities in Figure 4 have DOC concentrations of \sim 60-120 μ M, which is not "more" than an order of magnitude. The sentence included here is false and misleading to readers.

This now sits in the discussion of conservative mining (Section 4.1). It has been reworded to be clearer:

²⁰ 'The concentration of DOM at zero salinity (from river data synthesis in Table S1 and apparent freshwater endmembers from regression analysis in Table 4) is more than an order of magnitude higher than the open ocean concentrations, so the slope of this line is, to first order, representative of the stoichiometry of DOM at low salinity.' *Line 15: Again, 106:16 is much clearer, as well as more precise.*

See our response above

25 Lines 14-20: This is discussion.

In the case of this paragraph on C:N gradients we agree and have moved this whole paragraph to the discussion. As a result we have removed section 3.4 on C/N ratios and moved the other paragraph from this to 'interannual differences' (previously 3.5, now 3.4)

Interannual differences

Lines 23-8/Table 2/Figure 6: I do not see "northern stratified" "northern surface" or "bottom waters" anywhere in Table 2 or Figure 6, making this text impossible to understand/interpret in this context. We have now been through the manuscript and made nomenclature consistent – Northern (stratified)

- 5 surface (summer), Norther (stratified) bottom (summer); Southern well-mixed (summer) and Well-mixed (winter) now describe the regimes considered. Terms in parentheses are used when needed for clarity. Line 30: I agree with this sentence, with exception of Jan 2012, despite not understanding what "SML" and "BML" are. However, the following sentence states it specifically rather than generally. I'd omit the "Generally" sentence because it makes the following (better/more descriptive) sentence redundant.
- 10 Agreed, 'Generally...' sentence deleted

Page 11, lines 1-9: This is, for the most part, discussion.

We have left this as we feel it is the appropriate place to consider the reliability of the results Lines 14-7: If your hypothesis is "unfounded" it should not be included in a publication. Explain to readers what is gained from the data—reporting what is unfounded demonstrates incomplete

15 interpretation of data. Furthermore, this discussion does not belong in the results section.In the reworking and removal of hypotheses most of this paragraph has been moved or rewritten

DOM in bottom waters

Line 20: The word "interesting" does not belong in the results section—it is an opinion and belongs in the discussion section.

20 Removed.

Discussion

Pages 11-2, lines 30-4: A better place for these sentences may be the introduction, if they were to be rewritten slightly. At this point in the paper, the reader should already be aware of these points. Perhaps the abstract and/or conclusions would be a better place than introduction.

25 We have moved this text and incorporated it as suggested elsewhere in the manuscript*DOM-Salinity relationship*

Page 12, line 6: A salinity of ~ 30 is not "low salinity estuarine waters" This is simply a sea. Our meaning here is that the mixing between estuarine or near-coastal waters and the open ocean is a key control on the dynamics of DOM. We are not implying that we've measured them directly but as stated in the introduction and demonstrated in the end-member regressions in Section 3, it is possible to evaluate the contribution of low salinity waters to the DOM concentration. As we state in the introduction salinity in the North Sea is predominantly controlled by river inflows, with shelf-edge exchange also playing a

5 role. So a salinity of 30 represents a significant riverine component to any DOM signal seen in this 'low' salinity water (5*100/35.5 = 14% approx.). This sentence remains at the start of the discussion but is followed by a much fuller discussion of mixing and conservative vs non-conservative behaviour, as requested by both reviewers.

Lines 7-8: Again, DOC concentrations in the North Sea are not an order of magnitude higher than surface

- values found in the North Atlantic (~70 μM), but they are slightly higher (or perhaps double). A more convincing point is the gradient in surface DOC and DON concentrations shown in Figure 3, which clearly show that the waters further on the shelf/in shallower waters are more enriched in DOM. This was exactly the point we were trying to make. In the previous mention of low salinity we meant fresh (this wasn't particularly clear), but here we simply mean what we say, that the DOM on the shelf is
- 15 high relative to the N. Atlantic. This section is now greatly expanded so the sentence referred to has been removed.

Lines 12-4: Where does this information on the North Atlantic Bight come from? There should be a citation with this information. Can this NAB relationship be tested in the North Sea? That seems like an interesting discussion point.

20 This is a typo – should read the Mid-Atlantic Bight and the best reference is Vlahos et al 2002. We can indeed compare the relationship and now do so in this section, introducing a panel in a new figure 10 demonstrating the comparison.

Line 16: Can these "other controls on the concentrations of DOM" be elaborated on/discussed further? This is, after all, the discussion section!

25 We feel that the subsequent discussion on the following lines of the original manuscript unpacks the "other controls." However, we have expanded and reworked in the new Discussion section. *Line 18: What is hypothesis 2 again? I think it would be better to explicitly state the point rather than refer to hypotheses.*

Hypotheses are now removed

Significance of difference in DOC inventory between 2011 and 2012

Line 26: How is it significant? Statistically and biogeochemically speaking.

In this sentence we say 'significantly biogeochemically different' so clearly mean in terms of the biogeochemistry rather than statistics. It is however, also statistically significantly different, as presented

5 biogeochemistry rather than statistics. It is however, also statistically significantly different, as presented in results section 3.4 in the new manuscript, also Table 3, where we present statistically significant differences in concentrations.

Lines 27-8: By "apparent" do you mean "average"?

No, we mean apparent. As in, 'it is apparent from the data that'.

10 If average is what is meant, please be specific regarding average since both mean and median have been used throughout the manuscript.

N/A, also see above justficiation for intentional use of mean vs median

Was this change an increase or a decrease?

We avoided using such terms here as all we have is 2 snapshots not a time series. We could say apparent

15 decrease rather than apparent change but it's about the difference between the years not the direction of change really so we don't feel this change would achieve anything beyond the stylistic.

Looking at Figure 6, DOC boxes overlap slightly in the stratified plot, while the error lines do in the summer mixed, so I'm not sure how "significant" these differences are.

These are not error bars, and overlapping boxes do not mean that the differences are not significant. As

- 20 explained in the figure caption, the 'whiskers' mark the extent of the data within 1.5 x IQR (the interquartile range) from the median. Even if the boxes (representing the IQR) overlap this does not indicate that the means or medians are not significantly different. We have tested the differences in the means statistically as presented in the text. The relatively large number of samples means that the uncertainty range on the averages (whether medians or means) is quite small in most cases. As we state
- 25 in section 3.4 'The survey in 2011 presented significantly higher concentrations of DOC and DON than the summer 2012 survey in the whole water data set (all stations) (t-test, P <0.05), each data set separated by the three different water types (t-test, P <0.05), and each data set separated by two water types (whole surface data and whole bottom data) (t-test, P <0.05).'</p>

By also considering Figure 3, it is clear that the concentrations decreased for both DOC and DON, so this figure should be referred to.

We already did refer to Figure 3. But this section is about the DOC inventory change, so DON isn't the focus of this section. Also, the differences in DON are predominantly in the southern part of the survey,

5 with the range of value in the North being comparable (Figure 6, previously Figure 4)
Line 31: What percentage decrease is 10-20 Tg relative to the North Sea's DOC inventory? That seems like a useful and interesting way to interpret these numbers.

We have made an estimate of this (30-40%) and included it in the text (Section 4.4. end of first paragraph).

Line 32: This comparison with DIC is interesting, although you are referring to a decrease over a year

10 (Aug-Aug) while it seems Thomas et al. are referring to what is presumably an increase in 30 Tg C/year that is then consumed/replenished (i.e., in balance).

The DIC enrichment in the bottom layer of the norther North sea observed by Thomas is probably replenished by air-sea flux - this is the likely dirver of CO2 uptake in the system. There is also considerable interannual variability in air-sea CO2 uptake in the North Sea, so it's possible that this

15 difference in DOC dynamics results in a considerable difference in the air-sea flux over the two different years. We have extended the discussion on the differences between the years considerably in the revised manuscript.

Why is your change so large? Was it just an odd year? These points should be elaborated on!

This is the big question – much as we would like to be able to provide conclusive answers we don't have 20 the necessary data to be able to do so. We do however now provide a discussion of the possible explanations and how the evidence we do have supports / contradicts this. We have extended the discussion in Section 4.4 and 4.5 to cover this.

Page 13, line 2: If "our" best estimates, why do you cite Thomas et al? Please explain where the "our" (your interpretation of Thomas et al's data?) comes in, and where Thomas et al. come in.

25 We are referring here to the collective 'our' of the scientific community. We have amended to make this clearer.

Lines 3-4: Yes, just for the years concerned... This is potentially very interesting! Why is this paragraph

so short? It seems there is much to be discussed here regarding the contrasting Augusts. Are there climatological effects that would result in this, such as El Niño or NAO? Consider exploring satellite chlorophyll data before/after 2011/2012 to see if one of these years is anomalous or if there is a trend. There is much to explore and discuss, but where is that in this discussion section?

5 We have extended the discussion section considerably with an analysis of the various possible explanations and the evidence we currently have. As we discuss later on the same page, and at the end of the discussion section, NAO is a possible driver. It is also mentioned in the introduction. We have no reason to suspect ENSO.

Whilst we see the merit in conducting a satellite data study and extending this analysis, we feel that this

10 is beyond the scope of the original study and prefer to report the data we do have so that we or others can build on the current work with new analyses and investigations in the future. The idea of this paper is to report our observations and, as we feel we already did, explore possible explanations for the observations. We do not aim to solve all the problems at once!

Lines 9-10: High DOC coinciding with high salinity does not suggest that rivers are important, contradicting previous claims, as far as I understand.

This refers to the winter case which is rather different to the summer. This may be due to benthic sources, additional riverine transport (i.e. higher end member) or some other non-conservative processes. We feel these are discussed at various points throughout the discussion, but recognise that it could be set out more clearly – we have created a separate section on the winter case to bring these discussions together in the

20 reworked discussion section.

15

11Lines 13-5: This sentence is very hard to understand since the previous sentence referred to low DOC, and this sentence begins with high DOC. It is unclear whether authors are suggesting that high DOC values are coming in from the ocean or leaving to the ocean (or something else?)

We have re-worked this section to improve clarity

25 Lines 15-6: "observations...observed" redundant. amended

Is there a figure or table that could be referred to in order to guide the reader? We now refer the reader to Table 3

Lines 13-24: These sentences are a really great part of the discussion, although I feel much more thought could be put into the points made, as this is where new insights and understanding comes from. It is disappointing to see this subsection end/a new one begin just as new understanding begins to happen. We have addressed this in the re-worked discussion.

5 "confused" has previously been used to describe a graph, and I'm not exactly sure what it means. Do you mean unclear?

This sentence has been removed in the re-writing of the manuscript.

How are riverine inputs important? Looking at Figure S3, and am not convinced that they are.

10 Nor are we! Riverine inputs were mentioned as an additional factor after a paragraph discussing how the high DOC values in the south are likely associated with in-situ production from the previous summer. Although the role of rivers is discussed throughout the revised manuscript, this specific sentence is now removed.

Could the distribution in Figure S3 be due to it being in the winter?

15 Yes, of course. In the discussion of the winter data we are discussing the observations and evidence in the context of the winter regime (more run-off, different circulation) plus the influence of NAO in winter 'flushing' of the system. We have extended this discussion and reworded to make it clearer. What does this distribution look like in the August cruises? These points need to be discussed further

before changing to a new subsection of the discussion.

20 We didn't present salinity distribution previously as the DOC distribution and salinity are quite well correlated. However, we have now added a salinity distribution panel to Figure 5 (previously Figure 3) and it definitely adds value and insight to the dataset – in particular in influence of Norwegian Coastal Current/ Baltic input in lower salinities in the east of the North Sea.

DOM variability, C:N ratio and the seasonal signal

25 Line 27/Figure 5/Table 2: What are the R² values for the correlations? I agree that the correlation looks fairly good for the 2011 data, but it does not look great for 2012. More details are needed! Would be better to include regression equations (and R² values) in text and/or in a table. We have included the R² values in the text (Section 3.3).

C:N is as low as 5.9 and high as 36.5 in Table 2, so "roughly 9 to 17" is incorrect.

For C:N of DOM in Table 2 (Table 3 in the new manuscript), we state in the text Line 27 that "<u>Mean</u> C:N ratios of DOM (roughly 9 to 17, Table 2) were...". This sentence refers to the "mean" C:N values, not a minimum and maximum values showed in parentheses with low as 5.9 and high as 36.5 (Table 2).

5 Therefore, "roughly 9 to 17" is correct. However, we have changed 'roughly' to 'approximately' as this seems a more appropriate word to use here.

Line 30: Overall this paragraph is too short, and this sentence lacks discussion of comparisons made in previous sentence. What is the significance of comparing C:N between these systems? This needs to be discussed further here.

10 This was meant as in introductory paragraph to the section and the issues mentioned in it were dealt with in subsequent paragraphs in the section. We have tried to improve flow and expand discussion where appropriate in the reworking of the Discussion.

Lines 32-3: This sentence is unclear, and perhaps does not make sense.

We agree, and this paragraph was too short. it has been extended an incorporated into the wider discussion

15 of winter data

I don't see how Figure S5 supports what it stated here, as there is nothing significant about any relationship in Figure S5, as $R^2 = 0.15$ means there is no significant relationship, and therefore no inverse relationship.

The reviewer is incorrect. The R² value tells us what proportion of the variance can be explained by the

20 independent variable. It is not a measure of significance. Although the $R^2(0.15)$ is a low value (i.e. only 15% of the variance accounted for), there is a significant relationship in term of statistical test (P < 0.05), it is statistically significant due to the high n (60). However, we have removed Figure S5 as it didn't add a great deal to the discussion.

Page 14, lines 7-12: This could be discussed more.

25 We considered extending the discussion of benthic influence but ultimately we have no data to support any inferences or interpretations. Therefore, we have not extended the discussion of this but have made the point in the conclusions that the role of the sea bed in DOM dynamics in shallow seas is a key area for future study. Line 15: Why does it matter that you predicted this? It is not surprising that surface DOC is higher than deep concentrations, especially in the summer.

Making predictions and testing them (whether through hypotheses or narrative) is fundamental to testing our (as in the scientific community's) understanding and a key part of interpretation and discussion.

5 However, in the reworking of the manuscript and removal of hypotheses, we have omitted this part of the discussion altogether and it's not a major part of the narrative.

Lines 17-8/Table 2: Where are surface and/or summer values listed in Table 2? This is unclear, and renders table useless, especially if values are given in text. Either omit values in text and clarify table, or omit table (I suggest the former).

10 This confusion is due to our accidental use of SML / BML in Table 2 – now rectified (Table 3 in the new manuscript) as discussed above.

Lines 19-20: If this citation list is going to be included, the reported findings from listed papers should be compared/contrasted with yours, as this list means nothing to a reader, other than that if they want information they should look elsewhere.

15 The reported findings from listed papers were compared with our study, found to be similar and previously reported in the same section (section 4.3) on Page 13 Line 28-29 of the original manuscript. *Lline 21: Surely it is not impossible. This sentence is very wordy, which does not serve the manuscript well.*

We meant impossible given the data available to us. Of course, with a new study it could be possible. We

20 have clarified in the reworking of the discussion

Lines 24-5/Figure 6: I disagree, as I don't see any portion of the figure labeled as "northern" and many of the bars overlap, so it doesn't seem there is much of a difference.

The summer stratified values in Figure 6 are northern. We have made this explicit in the figure headings of Figure 7 (previously Figure 6) in the new manuscript. As before, these box and whisker plots are not

25 error bars and the differences in mean concentrations are significantly different as tested by t-test and reported elsewhere in the manuscript. See also Table 3 (previously Table 2).
Lines 24-8: I feel like this either has been covered, or should have been covered, in the results section—where is the deep, exploration and interpretation of your results?

Yes, the text on Line 24-28 here is similar to the text in the result section (section 3.5 on Page 10 Line 22-32 or original manuscript). However, the passage here (Line 24-28) is necessary as summary of the data to feed into the discussion. This is the difficulty with fully separating results and discussion. We have tried to remedy this in the reworking of the discussion section.

5 Line 28: Where is Figure 9?

This was supposed to refer to Figure 8. This is now Figure 12 in the revised manuscript.

Pages 14-5, lines 33-4: This sentence is too long. Discuss what this means/what can be learned from it. Agreed. This sentence is revised in the reworked discussion section.

Page 15, lines 7-12: This sentence is too long,

10 Agreed. This sentence is revised in the reworked discussion section.

and I don't see the point in mentioning all of these processes since results from other papers are not considered, and discussion/deduction of what the likely scenario is is lackling — rather you only provide this list of possibilities. These points need to be expanded upon and explored as a part of the discussion. We have tried to address this with the revised discussion, but it is difficult to go beyond recognising

15 possible explanations, as we only have the data that we have and cannot much further resolve the answer. Nonetheless we feel that considering possible explanations and highlighting areas for further study is a useful contribution.

Conclusion

Lines 31-2: I'm sorry, how does this support the claims from Barrón and Duarte? What were their claims

20 again? DOM negatively correlates with salinity is their major finding? I don't see the significance of this, as this trend is common.

We discuss why this is important in the introduction. It is not surprising that this is the trend, but it is interesting to assess to what degree this globlal pattern holds in a large and relatively slowly circulating shelf sea. Given the additional analysis of salinity relationships in the reworked manuscript we are able

25 to do a more detailed comparison with the Barron and Duarte, and other DOM-Salinity relationships and draw more detailed conclusions – see the reworked Discussion and Conclusions in the new version of the manuscript.

Page 16, lines 2-3: What freshwater end-members? Freshwater means salinity = 0!

We meant the apparent freshwater endmembers (i.e. those derived from our DOM-salinity relationships). 'apparent' now included in this sentence. The term 'apparent' in this context has been previously used by other workers (e.g. Vlahos et al 2002).

5 *Line 13: Should be "high C:N DOM"* Corrected

Interannual variability in the summer dissolved organic matter inventory of the North Sea: implications for the continental shelf <u>pump</u> Distribution and C/N stoichiometry of dissolved organic matter in the North Sea in summer 2011-12

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- 10 Abstract. We present the distribution and C:N stoichiometry of dissolved organic matter (DOM) in the North Sea in two2 summers (August 2011 and August 2012), with supporting data from the intervening winter (January 2012). This data demonstrates local variability superimposed on a general pattern of decreasing DOM with increasing salinitydistance from land, suggesting strong control over broad scale concentrations byconcentrations of DOM are controlled on large spatial scales by mixing between riverine sources and the open North Atlantic and either riverine sources or high DOM productivity in near-
- 15 shore coastal waters driven by riverine nutrient discharge. Given the large size and long residence time of water in the North Sea, we find concentrations are commonly modified from simple conservative mixing between two endmembers. We observe differences in dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) concentrations and land-ocean gradients between the two summers, leading to an estimated 10-20 Tg difference in the DOCM carbon inventory between the two2 vears, which is of the same order as the annual uptake of atmospheric CO2 by the North Sea system, and thus significant for
- 20 the carbon budget of the North Sea. <u>This difference is not consistent with additional terrestrial loading and is more likely to be due to balancing of mixing and in-situ production and loss processes across the North Sea.</u> Differences were particularly pronounced in the bottom layer of the seasonally stratifying <u>n</u>Northern North Sea, <u>with higher DOC and with higher DOC and lower DON in 2011 and lower C</u>:N ratio and more moderate concentrations of DOC and DONin 2011 than in 2012. Using other datadata, we consider the extent to which these differences in the concentrations and C:N ratio of DOM could be due to
- 25 differences changes in the biogeochemistry or physical circulation in the two2 years, or a combination of both. The evidence we have is consistent with a flushing event in winter 2011/12 exchanging DOM-rich, high C:N shelf waters, which may have accumulated over more than one year, with deep North Atlantic waters with lower DOC and marginally higher DON. We discuss the implications of these observations for the shelf sea carbon pump and the export of carbon rich organic matter off the shelf and hypothesise that intermittent flushing of temperate shelf systems may be a key mechanism in the maintenance of
- 30 the continental shelf pump, via the accumulation ad subsequent export of carbon-rich dissolved organic matter.

Keywords. Dissolved Organic Matter, Carbon, Nitrogen, Stoichiometry, Mixing, Continental Shelf Pump. North Sea

1 Introduction

Coastal and shelf seas are generally more productive than the open ocean (Jickells, 1998; Simpson and Sharples, 2012), and through various processes have been proposed as potentially<u>may be</u> disproportionately important for the drawdown of atmospheric carbon to the deep ocean (Bauer et al., 2013; Regnier et al., 2013; Thomas et al., 2005b; Tsunogai et al., 1999).

- 5 Our understanding of the mechanisms of such shelf carbon pump processes on the shelf and their relative importance is limited by observational data, the complexities of shelf circulation and interannual variability of both biological processes and physical drivers. This is particularly the case in complex systems such as the shelf sea systems such as the North Sea, which has complex physical circulation, involving large water exchange with surrounding seas and ocean; and strong anthropogenic forcing from surrounding land masses, especially via substantial river discharge (Bozec et al., 2005; Kühn et al., 2010; Simpson and
- 10 Sharples, 2012; Thomas et al., 2004, 2005b). The formation of dissolved organic matter (DOM) from inorganic carbon during primary production can lead to uptake of CO₂ from the atmosphere and, depending on the lifetime and ultimate fate of the DOM, this carbon may remain out of the atmosphere many hundreds or thousands of years (e.g. (Barrón and Duarte, 2015; Bauer et al., 2013).
- 15 In this study we investigate the variability of the organic carbon inventory of a large and complex shelf sea by considering the evidence provided by two high-spatial-resolution summer surveys. We consider organic matter concentrations and stoichiometry and deviations from conservative mixing between river and open ocean end members. These data were collected during cruises of opportunity during a PhD research programme, so our analysis is focussed on diagnostic, geochemical approaches to understanding bulk concentrations. It intentionally *does not* attempt to elucidate distinct sources or types of pool.
- 20 DOM, or determine process rates, given only prima facie evidence. -

1.1 Dissolved organic matter and the continental shelf pump

One potentially important mechanism of shelf carbon export to the deep ocean is via dissolved organic matter (DOM). In the marine environment, Marine DOM can be is a complex mixture of organic material from various sources both terrestrial and marine, with a spectrum of lifetimes from hours to millennia (Hansell, 2013; Nelson and Wear, 2014; Repeta, 2015). Its-The reactivity of DOM and in particular its availability for breakdown by marine microbes is a key factor controlling in its lifetime in relationresistance to degradation to inorganic carbon and thus capacity for long-term carbon storage; with refractory, i.e. unreactive, DOC having a lifetime of hundreds or thousands of years (e.g. Jiao et al., 2014). A recent synthesis of DOC in continental shelf seas observes a strong inverse relationship between distance from landrivers and decreasing DOC

concentration, with significant enrichment of DOC in nearshore waters relative to the open ocean (Barrón and Duarte, 2015).

30 This is consistent with a long term observational data set from the North Sea (Van Engeland et al., 2010) and results from the Mid-Atlantic Bight (Bauer et al., 2002; Vlahos et al., 2002) and Arctic (Wang et al., 2006). This seemingly ubiquitous gradient between low and high salinity is found by (Barrón and Duarte, (2015) leading to inferred global DOM flux across the shelf

break ranging between 7 and 29 Pg C yr-1to drive export of dissolved organic matter from shelf seas to the global ocean on a scale which is significant for the global carbon cycle. (Barrón and Duarte, 2015). This is consistent with a long term observational data set from the North Sea (Van Engeland et al., 2010) and results form the Mid Atlantic Bight (Bauer et al., 2002; Vlahos et al., 2002) and Arctic (Wang et al., 2006).

5

This <u>The DOC</u> export flux <u>from continental shelf seas</u> is composed of a combination of terrestrially-derived organic matter from rivers (allochthonous DOM) and production of autochthonous DOM <u>produced</u> on the shelf through in-situ autotrophic processes.<u>; although tT</u>he relative <u>contributions from importance of</u> the different sources in shelf sea systems is uncertain, although there is strong evidence that much terrestrial organic matter is respired, photooxidised or buried in shelf sea systems.

- 10 (e.g. Asmala et al., 2016; Ward et al., 2017). Shelf seas with longer water residence times will therefore tend to deliver less terrestrial (dissolved and particulate) organic matter to the open ocean (Asmala et al., 2016; Barrón and Duarte, 2015). Rivers also deliver significant nutrient loading to the coastal zone. The consequent nutrient-driven primary productivity may be a source of new DOM produced in near-coast waters, which could also lead to the relationships between DOM and proximity to land observed by the abovementioned studies.
- 15

-The stoichiometry of exported DOM may also be an important indicator of the efficiency of the shelf carbon pump. <u>Higher</u> <u>C:N dissolved organic material represents greater carbon fixation per unit nutrient and the export of carbon-rich organic material off-shelf in particular contributing to nutrient retention on the shelf and a more efficient shelf pump (Humphreys et al., 2018). Where autochthonous production dominates the DOM pool, Tthis stoichiometrye C:N ratio is normallcan bey</u>

- 20 compared to the so-called Redfield ratio₂₇ and deviations of DOM stoichiometry from Redfield have <u>commonly</u> been observed (Abell et al., 2000; Aminot and Kérouel, 2004; Ducklow et al., 2007; Hopkinson and Vallino, 2005; Letscher and Moore, 2015; Pujo-Pay et al., 2011). <u>However</u>, <u>although it needs toit must be be</u> recognised that <u>the Redfield particulate organic</u> <u>matterratio is notis not produced at a</u> single fixed <u>C:N</u> ratio even in primary production<u>– (e.g.</u> Moore et al., 2013)<u>Moore et al.,</u> <u>2013)</u> and so DOM which deviates from Redfield may not necessarily have been modified from the stoichiometry of the
- 25 primary production from which it originates. Despite these caveats, -a net enrichment of carbon relative to nitrogen as shelf seas process internally producedcycle organic matter and nutrients implies possible re-use of the nitrogen_nutrient (i.e. nitrogen) to drive further primary production, thus decoupling organic matter processing from the relatively fixed stoichiometry of algal growth.
- 30 Carbon rich DOC-DOM that is carbon-rich relative to the Redfield ratio might be produced by the preferential remineralisation of phosphorus and nitrogen over carbon from DOM by bacteria (e.g. needing to meet their nutrient requirements for growth) (Lønborg et al., 2010)_ or via the 'overflow production' of carbon rich organic matter by phytoplankton under situations of nutrient limitation, also referred to as 'carbon overconsumption' (Prowe et al., 2009; Toggweiler, 1993). The bioavailability/ reactivity of exported DOM is also likely to impact the efficiency of the shelf pump₁₇ with e.g. aA change to more refractory

(i.e. resilient to degradation) DOM leading-would lead to accumulation in the marine system and subsequent-overall net removal of carbon from the atmosphere. The bioavailability of DOM in shelf environments has been proposed to be linked to nutrient availability, with higher nutrient (specifically, nitrogen) availability leading to greater remineralisation of <u>carbon-rich</u> refractory DOM which has low bioavailability as a result of its high C:N ratio and thus a decrease in microbial carbon pump

5 efficiency (Jiao et al., 2014).

The carbon to nitrogen ratio of DOM therefore has the potential to be a useful diagnostic of the state of the shelf system – indicating the efficiency of nitrogen re-use throughout the microbial food web. However, the interpretation of DOM C:N is complicated by the interactions with river inputs at differing concentrations and probably variable stoichiometry, as well as

- 10 seasonal and interannual variability. Some studies have used other parameters to elucidate sources of DOM, for example biomarkers and isotopic signatures (e.g. Kaiser and Benner, 2012) or spectroscopic or fluorescent signatures (e.g. Painter et al., 2018). In some systems the N:C ratio can be used to determine the relative contributions of terrestrial and marine sources to DOC, if endmembers are known and conservative mixing can be assumed (Perdue and Koprivnjak, 2007). In the absence of such techniques, the use of C:N alone as a diagnostic variable in shelf seas must be approached with caution. We explore
- 15 in this paper its potential application to the North Sea case, in the context of other oceanographic measurements and observations.

1.2 The North Sea system

- 20 The North Sea can be characterised by a shallow, well mixed water column in the south (Emeis et al., 2015), and a deeper seasonally stratifying system to the North (Van Haren and Howarth, 2004; Knight et al., 2002), with the boundary between these systems at roughly 55 °N and ~40m depth. The North Sea is a highly productive shelf sea, particularly the southern part which fixes 25 30 mol C m⁻² yr⁻⁴ (Emeis et al., 2015), although as in spite of this the southern North Sea, water columnwhich remains well mixed throughout the year, and is highly affected by riverine carbon fluxes may be net heterotrophic and a source of CO₂ to the atmosphere (Bozec et al., 2005; Prowe et al., 2009), respiration processes may mean it is a net source of carbon to the atmosphere (i.e. net heterotrophic). In contrast, the northern North Sea is thought to be net autotrophic (i.e. accumulates organic matter and is a net sink for inorganic carbon) The northern North Sea is a net sink for atmospheric CO₂, argued to be and tdriven byhrough its seasonal stratification and the consequent vertical separation of surface autotrophy and
- respiration respiration of exported carbon in the net-heterotrophic waters at depthbelow the thermocline (Bozec et al., 2005; 30 Clargo et al., 2015), is a strong net sink for atmospheric CO_2 (-2 mol m⁻² yr⁻¹ taken up at the air-sea interface) (Clargo et al.,
- 30 Clargo et al., 2015), is a strong net sink for atmospheric CO₂ (-2 mol m⁻²-yr⁻¹ taken up at the air-sea interface) (Clargo et al., 2015). In the 'classic' North Sea shelf pump mechanism, Deeper waters below-thermocline waters in the nNor-in the northern North Sea are thought tothen exchange with_the deep ocean, so the accumulation_of dissolved inorganic respiration products there (i.e. dissolved inorganic carbon, DIC) carbon in the deeper waters of the norther North Sea and its subsequent exchange

with the open Atlantic may-is thought to be an important mechanism in the shelf carbon pump (Bozec et al., 2005; Thomas et al., 2004). ____ These net DIC exchanges represent small differences between the large carbon fluxes representing primary production and respiration over the seasonal cycle. Recent studies have also noted that there can be important interannual variations of North Sea circulation and exchange with open Atlantic waters linked to cycles such as the North Atlantic

5 Oscillation (NAO, Salt et al., 2013; Sheehan et al., 2017) and possibly longer term shifts in patterns of production (MeQuatters-Gollop et al., 2007) which have the potential to alter the net DIC exchange fluxes.

The role of DOM in the carbon pump of the North Sea is <u>even</u>-less clear than that of <u>dissolved inorganic carbon (DIC)</u>. (Thomas et al., (2005a) observe inflows and outflows to the North Sea which suggest minor net respiration of DOC, based on

- 10 observations from a single year (spring and autumn cruises). However, (Prowe et al. (-2009) invoke the production of carbon rich organics via overflow production in the northern North Sea to explain the apparent decoupling of nitrate and DIC drawdown over a seasonal cycle, i.e. greater drawdown of carbon per unit nitrate uptake than would be predicted by the <u>'Redfield' ratio of 6.6:1 C:N</u>. Various studies also point to strong seasonality in the in-situ production of DOM by algae (especially during the spring bloom) and subsequent slow degradation (time scales of weeks to a month or somonths), albeit
- 15 with strong spatial variability and apparent patchiness (Van Engeland et al., 2010; Johnson et al., 2013; Suratman, 2007; Suratman et al., 2008, 2009). At the current level of knowledge and available data it is <u>not yet impossible</u> to determine whether the North Sea is a net source or sink for DOC in a typical year. In order to better understand the dynamics and stoichiometry of DOM, and whether or not there is the potential for an organic matter continental shelf pump for carbon (Barrón and Duarte, 2015; Thomas et al., 2005a)(Barrón and Duarte, 2015; Thomas et al., 2005b), a more detailed understanding of the spatial
- 20 variability and large-scale controls on DOM concentrations is thus required.

Unlike some enclosed coastal seas such as the Baltic or Mediterranean, the North Sea is characterised by a considerable 'through-flow' of seawater originating from, and returning to, the Atlantic Ocean. Except in the river estuaries flowing into the North Sea, and in the near-coastal zone of the southern North Sea, where river influence is greatest, salinity tends to range

- 25 between 30 and 35.5. The freshest part of this range is typically found in the Norwegian Coastal Current, in surface waters to the northeast of the study area, which combines local and regional river water with brackish water from the Baltic outflow (Winther and Johannessen, 2006). Sampling the North Sea is therefore analogous to sampling the high salinity portion of a large, extended estuary with strong ocean influence (e.g. Hydes et al., 1999), although complicated by circulation and seasonal stratification.
- 30

The horizontal gradient of salinity through the North Sea and also of any associated tracers of river or ocean, are determined by the exchange rate, or residence time of water. Water residence times in the North Sea are uncertain, but may vary between flushing on the timescale of <1 year to almost a decade (e.g. Blaas et al., 2001; Holt et al., 2009; Otto et al., 1990) depending on prevailing physical conditions on and off the shelf. (Sharples et al. (-2017) find the North Sea to have one of the longest residence times of shelf seas globally, due to its large size (specifically the width of the shelf) and its relatively high latitude, meaning that Coriolis force is strong so riverine inputs take a more circuitous route to the open ocean than they do at lower latitudes. They conclude as a result of this Coriolis effect that low latitude shelf seas are likely to be much more efficient at transporting riverine DOM to the open ocean than shelf seas at higher latitudes.

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Mixing and transport of riverine material through the North Ssea is ultimately driven by river flow and shelf-edge exchange of water with the open ocean. Recent studies have noted that there can be important interannual variations of North Sea circulation and exchange with open Atlantic waters linked to climate cycles such as the North Atlantic Oscillation (NAO, (Salt et al., 2013; Sheehan et al., 2017; Winther and Johannessen, 2006). This is both due to changing wind regime (strength and direction) driving shelf-edge exchange and circulation patters and also changing precipitation over land leading to greater

10 direction) driving shelf-edge exchange and circulation patters and also changing precipitation over land leading to greater runoff. Associated shifts in patterns of primary production have also been suggested, which have the potential to alter the net carbon exchange fluxes through both physical and biogeochemical processes (McQuatters-Gollop et al., 2007).

Comparison of DOM concentrations with idealised (i.e. conservative with salinity) mixing lines between riverine and open-

- 15 ocean end member DOC and DON concentrations has often been used to infer and even quantify in-situ loss and production rates (e.g. Asmala et al., 2016; Cauwet, 2002; Ducklow et al., 2007; Margolin et al., 2016). In combination with this, the N:C ratio is sometimes used to elucidate different sources of carbon, where DOM is known to be conservative with salinity (Perdue and Koprivnjak, 2007). Relationships with salinity can appear highly conservative, particularly in estuaries with short residence times or in unproductive regions (e.g. (Köhler et al., 2003). In other situations, they can be strongly non-conservative.
- 20 typically in long residence time systems, highly productive systems or simply where only a small part of the salinity gradient is observed (e.g. Asmala et al., 2016; Cauwet, 2002).— In the North Sea case, the degree to which DOM is conservative with salinity may be expected to vary considerably between periods of different circulation rate; particularly given that the system is highly productive, driven by terrestrial nutrients, and therefore high autochthonous production would be expected to substantially modify DOM concentrations in addition to the effects of terrestrial DOM degradation.

25

In a recent study of the North Sea in summer, (Painter et al. (-2018) applied fluorescence analysis to identify possible sources of DOM. In their study they identify two fluorophores (active regions of the excitation-emission spectrum), both of which decreased sharply with distance from land. One of these fluorophores was identified as representative of humic matter of

30 terrestrial origin, which showed a strong, near linear relationship with salinity over the range 30-35. Whilst strongly associated with salinity it was not correlated with bulk DOC or DON, suggesting strong autochthonous sources dominate DOM concentrations in the open North Sea, rather than riverine sources. They attribute this to high productivity and significant marine contribution to the organic matter pools. (Painter et al. (-2018) conclude that very little terrestrial organic matter reaches the open ocean via the North Sea due to its size and long residence time. The second fluorophore that was generally

higher nearer land was identified as being indicative of biological production of DOM. This is consistent with high levels of productivity in near-coastal seas due to riverine nutrient input and could explain the strong gradients going away from land without the need to invoke conservative mixing of terrestrial organic matter. As with the terrestrial signal, the influence of near-coast production on central and northern North Sea DOM appears to be small according to Painter et al. (2018),

5 reinforcing the idea that in-situ production probably dominates DOM composition in these regions also.

This current study has the following aims. 1) To determine the degree to which conservative mixing can explain the observed DOM distributions in the summer and winter survey data presented and to evaluate the possible reasons for any nonconservative behaviour. 2) To establish whether the North Sea is likely to be a source of DOC to the Atlantic Ocean, whether this DOC source is lower than the global average due to the long water residence time and how variable this source might be

10 this DOC source is lower than the global average due to the long water residence time and how variable this source might be interannually and seasonally. Finally, 3) to understand the potential role of C:N stoichiometry of the DOM on the effectiveness of carbon export from the shelf and how our results impact broader understanding of shelf pump mechanisms.

We undertook a spatial survey of the North Sea on cruises of opportunity in two summers (2011 and 2012) and the intervening
 winter to investigate the broad scale distribution and stoichiometry of DOMIn order to provide a reference for the observations
 presented below, we have conducted a synthesis of DOM end member concentrations from the literature with which to compare
 our results (detailed in Tables S1 and S2 of supplementary material). This synthesis is summarised in Figure 1, demonstrating
 the DOC, DON and resulting C:N ratio of DOM with salinity assuming purely conservative mixing. Two separate ocean end members are considered 1) 200-600m depth range in adjacent regions of the Atlantic and 2) those of deeper (>600m) waters

- 20 in the same region. The shallower depth range is assumed to be representative of winter concentrations in the surface Atlantic, relatively unaffected by in-situ seasonal production of DOM. Deeper values are likely to be more representative of older waters and the marine 'background' DOM (e.g. Hopkinson and Vallino 2005). Depending on the prevailing physical conditions and season, water moving from the open ocean onto the shelf may be of shallower or deeper origin (e.g. Blaas et al., 2001; Holt et al., 2012). The calculated C:N ratios presented in Figure 1 have a similar range to those directly observed by studies used in
- 25 the synthesis, which typically sit in the rage 113 to 165 (Aminot and Kérouel, 2004; Table S24 in supplementary material). (Aminot and Kérouel, 2004;),

on the working hypotheses that i) the dominant control on DOC/DON concentration would be salinity, and this would represent mixing of riverine or low salinity autochthonous marine DOM (Barrón and Duarte, 2015) with a relatively constant high

30 salinity end member, characteristic of the North Atlantic; ii) this signal would be complicated, particularly in summer, by internal processes in the open North Sea such as algal production and bacterial degradation (e.g Johnson et al., 2013); iii) that the stoichiometry of DOM in surface waters would show higher C:N than deeper waters due to carbon overconsumption due to nutrient limitation in summer and iv) given that agriculturally influenced rivers tend to have low C:N DOM, due to high nitrogenous inputs (Mattson et al., 2009), that the C:N ratio would increase with salinity, towards the characteristic C:N of DOM of N. Atlantic winter water of approximately 13-15 (Aminot and Kérouel, 2004).

2 Study area, sampling and analytical methods

2.1 Study sites and field sampling processes

- 5 Sampling (Figure 2) was conducted on three³ cruises of opportunity on board the RV Cefas Endeavour in August to September 2011, January 2012 and August 2012 (Table 1)(CEND 14/11, 8th August to 7th September 2011; CEND 02/12, 20th to 31st January 2012; and CEND 13/12, 9th to 21st August 2012). The two summer cruises were the summerwere surveys of thepart of the long-term ICES (International Council for the Exploration of the Sea), 2012), with the primary aim of surveying fish numbers.
- 10 The sampling grid is was determined by the needs of this survey, and aimeds to occupy one station in each of the ICES survey rectangles, with each station being close to the same location each year (ICES, 2012)(The International Council for the Exploration of the Sea (ICES), 20127). Due to time and weather constraints the more northerly stations of the survey (North of approximately 58 °N-) were not sampled in summer 2012 (Figure 2). The winter cruise surveyed a set predominantly of coastal sites in the well mixed southern and western North Sea.
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The nature of the survey meant that only two water samples were taken at each station. Surface and bottom waters_-were sampled from 10 litre Niskin bottles attached to a CTD rosette._ In general, surface and bottom water samples were collected at 2-4 meters below the surface and 5-6 meters above the seabed respectively. Sampling The cruise track focused on the open waters of the North Sea (minimum observed salinity at DOM sampling points =30.9, 87% of samples had salinity >34.0) and did not sample near shore regions with stronger riverine influence. (minimum observed salinity at DOM sampling points = 30.9, 87% of samples had salinity points

=30.9, 87% of samples had salinity >34.0).

Samples were collected at all stations for measurements of DOC and DON, along with dissolved inorganic nutrients (<u>nitrate+nitrite</u>, <u>phosphate</u>, <u>ammonium</u> and <u>silicate</u>the sum of NO₂⁻ and NO₂⁻ (henceforth nitrate), <u>ammonium</u>, <u>phosphate</u> and silicate). Additionally, chlorophyll *a*, <u>particulate organic carbon (POC)</u> and <u>particulate organic nitrogen (PON)</u> samples were collected during the summer 2012 cruises. Standard hydrographic measurements including temperature and salinity were recorded by the ship's water column profiling equipment and processed using standard techniques (Tom Hull, Cefas, pers. comm.).

2.2 Analytical procedures

30 Water samples were filtered immediately on-board upon collection to separate dissolved material (DOC, DON and inorganic nutrients) from particulate material (POC and PON). Filters and most of the filtration unit were combusted in a muffle furnace

before use (Kaplan, 1992; Sharp et al., 1993). Gentle vacuum filtration (~5 kPa) was used through pre-combusted (450 °C, 5 hours) glass fiber filters, 47 mm diameter glass fibre filters of nominal pore size 0.7 μ m (GF/F) with an ashed (550 °C, 5 hours) glass filtration unit. Filtrates were then collected in polypropylene sample tubes (FisherbrandTM polypropylene centrifuge tube 50_mL4, Fisher Scientific, UK) for DOC, total dissolved nitrogen (TDN) and inorganic nutrients analysis. This

- 5 storage regime-ese filters and tubes has have previously been shown to be effectively preserve and not contaminate these analytes without contamination (Chaichana, 2017; Suratman, 2007; Tupas et al., 1994). Filters were wrapped in aluminium foils for POC and PON analysis, the water volume recorded. Chlorophyll *a* samples were collected from a separate water subsample on the same type of GF/F glass fibre filters (without combustion, gentle vacuum filtration ~10 kPa) and the water volume recorded. All samples (seawater and filters) were immediately frozen at -20 °C after filtration on board (-60 °C for proceeding).
- 10 <u>c</u>Chlorophyll *a* samples) until further analysis in the laboratory.

Measurements of dissolved inorganic nutrients (nitrate, ammonium, phosphate and silicate) were performed using standard spectrophotometric methods (Kirkwood, 1996) using a Skalar San⁺⁺ autoanalyser (segmented flow analysis and colourimetric chemistry, Skalar analytical, Netherlands). The limit of detection for nitrate, ammonium, phosphate and silicate were 0.1, 0.2,

- 15 0.1 and 0.1 μM, respectively. Accuracy was assured by the use of Environment Canada certified reference materials with average measured values all within 10% or better of the expected value. Note that nitrate was measured as total nitrate plus nitrite, and nitrite assumed a small fraction, as is common for oxic waters (e.g., Hydes et al., 2001; Painter et al., 2018; Suratman et al., 2008).
- 20 DOC and total dissolved nitrogen (TDN) were determined by the high temperature catalytic oxidation method coupled with nitrogen chemiluminescence detectordetector system (high temperature catalytic oxidation (HTCO) total organic carbon (TOC) nitrogen detector (ND) system or HTCO-TOC-ND system) using a Skalar Formacs^{HT} combustion TOC/total nitrogen (TN) analyser (Skalar analytical, Netherlands) coupled with a Skalar nitrogen chemiluminescence detector (ND20, Skalar analytical, Netherlands). The methods involve minor developments of are similar to those we have reported previously
- 25 (Johnson et al., 2013; Suratman et al., 2010) and are repeated here in brief. The Samples were oxidised over a catalyst at a combustion temperature was of 750 °C. The catalyst was a layer of cobalt-chromiunchromium (CoCr, ~15 g sitting on quartz wool to prevent loss of the catalyst from the bottom of the combustion tube) and cerium oxide (CeO₂, ~2.5 g on top) in a quartz glass column. Carbon-free, high purity air (Zero grade air, BOC gases, England) was used as carrier gas (240 mL¹/min). To eliminate inorganic carbon in samples, the TOC/TN analyser was programmed to add , acidification (adding 100 µl of 10%)
- 30 hydrochloric acid to <u>each</u> 6 mLl of sample), <u>spargesparging</u> (using pure air for 240 s) and stirring for (180 s_) were performed automatically by the TOC/TN analyser_. The sample injection volume <u>s</u>-was 200 μ Ll and (the best <u>two2</u> injections were chosen automatically from <u>2</u>—4up to four injections to achieve the coefficient of variation (CV) better than 2 %).

Calibrations of the instrument were carried out by potassium hydrogen phthalate (KHP) $(0 - -300 \text{ }\mu\text{M})$ and a mixture of ammonium sulphate and potassium nitrate $(0 - 50 \mu M)$ dissolved in Milli-O water for DOC and TDN analysis respectively. The system blank was estimated by using acidified and sparged Milli-O blank injection which was $29.2 \pm 4.2 \mu M$ (n = 78) for DOC and was $0.6 \pm 0.6 \mu$ M, (n = 79) for TDN analysis. The value agreesd with the system blank reported in other previous studies (Álvarez-Salgado and Miller, 1998; Badr et al., 2003; Benner and Strom, 1993; Hopkinson et al., 1993; Koike and Tupas, 1993; Suzuki et al., 1992). The blank correction was applied to DOC and TDN data. Precision is expressed here as a eoefficient of variation (CV) obtained by replicate measurement of the same sample (Miller and Miller, 2010). A continuous

run of 40 standards in the same batch provided was used to determine the analytical precisions of about 2% and 4% for DOC

(used 100 µM) and TDN (used 10 µM standard) analysis, respectively.

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Two types of consensus reference materials (CRM):low carbon water (LCW) and deep seawater reference water (DSR). provided by the Hansell laboratory, the University of Miami (Hansell, 2005), were used to verify the DOC and TDN measurements: low carbon water (LCW) and deep seawater reference water (DSR), provided by the Hansell laboratory, the University of Miami (Hansell, 2005). For DOC analysis, a The consensus value concentration of DOC infor LCW is 1 µM.

- 15 The analysis of LCW in this study yielded a small negative value of DOC concentration as the DOC value for LCW is-was lower than the system blank value, therefore, sample concentrations wereas not corrected by the LCW value. Consensus values of DOC for DSR vary in each batch. The analysis of these DSR yielded mean concentrations of $42.6 \pm 2.9 \,\mu$ M (n = 98) and $42.4 \pm 2.6 \mu M$ (n = 66), which were in good accord agreement with the consensus values of $41 - 44 \mu M$ (batch 10 lot# 05-10, batch 13 lot# 02-13) and $42 - 45 \mu$ M (batch 14 lot# 01-14), respectively. The quantitative recovery of DSR relative to the
- 20 consensus values is was $(100 \pm 7\%, n = 98)$ and $(98 \pm 6\%, n = 66)$. The oxidation efficiency of KHP relative to urea was 93-105% (100 ± 3%, n=50) and 97 - 108% (100 ± 2, n=20) for 50 µM and 200 µM, respectively. This agrees with previous findings which showed the result $\sim 100\%$ for 200 µM KHP-glycine standard compared to urea (Watanabe et al., 2007). The limit of detection (LOD) estimated as the analyte concentration giving a signal equal to the blank signal plus three standard deviations of the blank (Miller and Miller, 2010) was 6 µM for DOC analysis. The mean of DOC concentrations for DSR 25 SRM is was similar between the analyses for the two² years, with median average values differing by less than 1 μ M and does not show a significant difference (t-test, p > 0.05) between the analysis for summer 2011 and summer 2012 (Figure-S1, supplementary material).

For TDN, <u>analysis</u>, the analysis of LCW yielded a concentration of 0 µM (no peak areas were detected during TDN analysis). 30 which was in good agreement with the consensus values of 0 µM. The analysis of the DSR yielded a mean concentration of $32.8 \pm 1.7 \,\mu\text{M}$ (n = 176), which was in good agreement with similar to the consensus value of $31 - 33 \,\mu\text{M}$. The quantitative recovery of DSR relative to the consensus values is $102 \pm 5\%$ (n = 176). The oxidation efficiency of the mixed standard relative to urea was 92 - 106 (98 ± 4 , n = 52) and 94 - 105 (99 ± 3 , n = 32) for 10 µM and 50 µM, respectively. The limit of detection for TDN analysis was 1 µM. DON was calculated by subtracting dissolved inorganic nitrogen (DIN) concentration (the sum of nitrogen in the form of nitrate and ammonium) from the TDN concentration. Therefore, the precision of DON is affected by the sum of uncertainties in TDN and DIN analysis. In this study, the precision of TDN, nitrate and ammonium, calculated as a coefficient of variation obtained by replicate measurements of the same samples (Miller and Miller, 2010) were 4%, 3% and 4%, respectively. The resulting uncertainty on DON depends on the relative concentrations of these analytes in a given

- 5 sample_(Saunders et al., 2017), but where DIN is low (e.g. in surface waters in summer) it roughly equates to the uncertainty on the TDN analysis (4%), whereas where DIN is high and DON is relatively low (e.g. deeper stratified <u>N</u>north <u>S</u>sea water and all winter samples), uncertainty can be significantly higher, up to +/- 30% at very low DON concentrations (less than 5 µM). However, in the context of the broad range of concentrations observed in this study, such uncertainties do not affect the findings or conclusions presented here.
- 10 Measurements of dissolved inorganic nutrients (nitrate, ammonium, phosphate and silicate) were performed using standard spectrophotometric methods (Kirkwood, 1996) using a Skalar San⁺⁺ autoanalyser (segmented flow analysis and colourimetric chemistry, Skalar analytical, Netherlands). The limit of detection for nitrate, ammonium, phosphate and silicate were 0.1, 0.2, 0.1 and 0.1 μM, respectively. Accuracy was assured by the use of Environment Canada CRMs with average measured values all within 10% or better of the consensus value.
- 15 For POC and PON<u>analysis samples</u>, filters were placed overnight (12 hours) in a desiccator saturated with concentrated hydrochloric acid (HCl, 36% w/v) fumes to remove inorganic carbon (carbonate). The filters were then dried for 24 hours at 60 °C. POC and PON were determined by the dry oxidation method using the Exeter Analytical CE440 Elemental analyser (Exeter analytical Ltd.,UK). The precision as the coefficient of variation (CV) was about 1% for C and 4% for N. Chlorophyll *a* filters were extracted by acetone and measured by spectrofluorometric method (Holm-Hansen et al., 1965; Parsons et al.,
- 20 1985) using spectrofluorometer (Perkin Elmer LS45, USA). The detection limit of the <u>chlorophyll a</u> measurement was 0.1 μ g/L.

3 Results

3.1 Physical oceanographic conditions

During the summer cruises there was a clear difference between southern, well mixed waters and northern, stratified waters in both physical and biogeochemical parameters, as expected. By comparing surface and bottom temperatures we divide the summer cruise data up into <u>three3</u> sets (henceforth 'water types') for further analysis: '(southern) well_-mixed', '(northern) (stratified) surface layer' and '(northern) (stratified) bottom layer'. <u>This approach to water mass classification is commonly used in synoptic scale studies of the North Sea (e.g. Queste et al., 2013). We consider the limited winter cruise data as a whole, on the basis that it is mostly in the permanently well mixed southern part of the North Sea, and given that the whole system is vertically well-mixed in <u>wWinter. (Queste et al., 2013)</u>.</u>

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Surface waters were generally warmer in summer 2012 than in 2011 (<u>Table 2</u>; Fig<u>ure S23</u>), and the stratified bottom waters show mostly colder but more variable temperatures in 2011 than in 2012. <u>Temperature-salinity (T-S)</u> diagrams (Fig<u>ure-S2 of supplementary material3</u>) of the whole dataset reveal a dominant pattern of mixing of warmer, fresher water with colder, saltier water <u>in summer</u>, with some colder, fresher water observable in the winter data, <u>highlighting the disproportional seasonal</u>

- 5 warming / cooling on the shelf relative to the open ocean (Tsunogai et al., 1999). Although 2011 and 2012 northern bottom waters appear to sit within the same (noisy) mixing line between these end members, there is little overlap in T-S space between the 2 years suggesting considerable renewal of water in the bottom layer between the 2 years. Some of the highest salinities in the dataset are observed relatively close to the coast, in the winter cruise, suggesting possible inflow into the southern North Sea from the English Channel. Summer salinity distributions in both years reveal a strong east-west gradient in surface water
- 10 salinity with the lowest salinity waters (of 31-33) being found along the east coast of the North Sea and particularly in the region of the Nowegian Coastal Current (Figure 5d). In bottom water samples, the pattern was of higher overall salinity and a south-east to north-west salinity gradient.

3.2 Inorganic nutrients

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Inorganic nutrient concentrations, summarised in Table 2 and Figure 4.1 show the typical pattern expected for the North Sea, with relatively high concentrations in the winter, and at depth in the northern North Sea, and low concentrations in summer surface waters, presumably due to utilization by phytoplankton. Northern surface waters tend to be more depleted in nutrients than southern well mixed waters, due to the greater re-supply of nutrients from the benthos, river and possibly atmospheric inputs to the latter. Figure 4 presents nitrate, phosphate, ammonium concentrations by cruise and water type. Note that silicate (not shown) follows a similar pattern to phosphate except for apparently reaching limiting concentrations in all surface waters 20 in both summers.

Nitrate and phosphate concentrations and inorganic N:P ratios in the northern bottom waters were significantly higher in 2011 than 2012. This suggests differences between the two years which may reflect differences in water exchange with the open Atlantic, differences in productivity, plankton community and nutrient limitation in the spring and summer before sampling or a combination of all of these.

Note that the data are potentially skewed<u>We investigated</u> by the <u>potential bias due to the</u> more northerly extent of the 2011 cruise <u>potentially</u> sampling waters richer in nitrate and phosphate. However statistical comparison (by t-test, p<0.05) of only the <u>portion-region</u> of the 2011 cruise south of 59°N (i.e. the section covered in both years), reveals a similar, and still statistically significant, difference (t-test, p<0.05). The sameSimilar statistical comparisons of only the region south of 59°N

30 have been made for DOC and DON; and where we report differences between years these are significant even after comparison on the same latitudinal basis.

Ammonium concentrations were high (median values >1 μ M) and variable in northern deep waters and not significantly different in the two summers, probably suggesting high levels of remineralisation and heterotrophy in deep waters in both years. In well-mixed waters in 2012 most observations were at or below detection limit. However, in summer 2011 concentrations in well-mixed waters were substantially elevated with a median concentration comparable to that of northern

5 bottom waters (~1.2 μM). Ammonium concentrations have previously been suggested as being diagnostic of the trophic state of the marine system, with periods of decoupling of respiration from photosynthesis leading to accumulation in ammonium concentrations over large areas of the ocean (e.g. Johnson et al., 2007). Higher concentrations were generally observed in southern well-mixed waters in 2011 at the bottom of the water column and not in the surface.

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- 10 periods of decoupling of respiration from photosynthesis leading to accumulation in ammonium concentrations over large areas of the ocean (e.g. (Johnson et al., 2007) Johnson et al., 2007). Ammonium concentrations were high (median values >1 μM) and variable in northern deep waters and not significantly different in the two summers, probably suggesting high levels of remineralisation and heterotrophy in deep waters in both years. In well mixed waters in 2012 most observations were at or below detection limit; however in summer 2011, concentrations were substantially elevated with a median concentration
- 15 comparable to that of northern bottom waters (-1.2 μM), but these high concentrations were generally observed at the bottom of the water column and not in the surface. This is possibly indicative of a strongly net heterotrophic state, either due to remineralisation of sinking organic material, or resuspended benthic material in the southern North Sea in 2011 that was not the case in 2012. These elevated ammonium concentrations coincide with- phosphate concentrations being higher in well mixed waters (surface and bottom) in 2011 than 2012. This elevated phosphate is also consistent with greater heterotrophy relative to autotrophy in 2011 than 2012, or potentially the influence of benthic resuspension.

3.3 Dissolved organic carbon and nitrogen concentrations

Figure 3-5 (a-c) shows the geographic distribution of dissolved organic carbon and nitrogen over the survey area in both summers. Statistical summary of the concentrations is presented in Table 23. In general, higher concentrations were seen in the coastal zones particularly in the the Southern Bight, the German Bight and surrounding the East Anglian plume (the Thames estuary, the Humber estuary and the Wash) for both surface and bottom water, and around the coast of Denmarksouth and east of the study area, representing the regions most influenced by river and possibly Baltic Sea inflows. , and ILowerwest concentrations were generally observed in higher salinity waters in the North. This is consistent with previous observations in the Southern -North Sea (Van Engeland et al., 2010) and the summer North Sea distribution pattern reported by (Painter et al., 2018) Painter et al., 2018; and implies that mixing of riverine/estuarine DOM with open ocean waters is a major control on DOM concentration across the gradient from river to open ocean. The lowest salinity waters observed are

found around the Baltic inflow to the North Sea (Figure 5d) in surface waters and are associated with intermediate DOC concentrations.

Figure 4-<u>6</u> presents DOC and DON concentrations with salinity and serves to confirm hypothesis 1<u>further supports the idea</u> that the gradient in DOM from low salinity, river influenced water to high salinity open-ocean water is a major characteristic of DOM concentrations in the North Sea. Superimposed on the simple mixing- relationship is considerable variability <u>in DOM</u> concentrations, which we suggest reflects production and consumption of DOM produced in situ (hypothesis 2). The inverse

- 5 relationship between salinity and DOC is particularly clear in southern well mixed waters and northern bottom waters, with surface waters in the stratified north-region showing considerable deviation from the trend, presumably due to in situ consumption and production by microorganismsparticularly in the low salinity waters in the Norwegian Coastal Current (NCC). All data in our study with S<33.5 occurs in the NCC, which appears to have a much shallower DOC/salinity gradient than the other waters, The sameSimilar patterns are observed is the case for DON in summer 2011 but in summer 2012</p>
- 10 (Figure- 64d) the salinity relationships is more confused, with northern stratified bottom waters appearing to show a positive relationship with salinity (albeit over a very limited salinity range). The limitednear-coast winter data (Table 3) show high, but also highly variable DOC concentrations. DON concentration in winter was of a similar magnitude to the summer values but was also highly variable. However, the winter data reflects a limited survey area mostly very near to river inputs, so may not reflect conditions in the wider North Sea.
- 15

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DOC average concentrations are an order of magnitude smaller than DIC (e.g. (Clargo et al., 2015) Clargo et al., 2015), and POC average concentrations are <u>approximately six6</u> times smaller than DOC (<u>Table 3</u>). Hence DIC dominates the carbon inventory in the water. This is not the case for DON₃₅ however, which becomes the dominant fror of nitrogen in summer and hence its degradation rate has the potential to influence nutrient availability and phytoplankton productivity. PON is about three3 times smaller than DON in terms of average concentrations, further demonstrating the important role of DON as a nitrogen reservoir in nutrient cycling in shelf environments.

From-By regression of the DOM vs salinity relationships, it is possible to derive apparent zerolow salinity end-members and associated uncertainties -for DOC and DON and these vary by water type and season (Table 43). The estimated zero-salinity

- 25 concentrations were 420 µM DOC and 40 µM DON for the combination of two surveys in summer<u>the two summer surveys</u> combined, giving a source C:N ratio of about 10₂- It is not possible to say from these data whether the high<u>These values are</u> consistent with either <u>DOM</u> concentrations at low salinities are river-derived (allochthonous) <u>DOM</u>, or <u>DOM</u> produced in estuaries or the near-coastal zone (autochthonous), fed by the riverine delivery of inorganic nutrients. Given the low range of salinities observed, ed and the high in-situ variability, and the seemingly different relationship with salinity in the NCC, the
- 30 end member values derived here are highly uncertainsubject to large uncertainty, but nonetheless their values are consistent with typical global riverine DOC and DON observations (Agedah et al., 2009; Markager et al., 2011; Neal and Robson, 2000) and also with the synthesis of North Sea river end members in Table S1 of the supplementary material. The slope (~10) and y intercept (~420) for the DOC vs salinity relationship estimated here for the North Sea are also quite similar to those estimated by Bauer et al., 2013 (11.5 slope 455 intercept) for the Mmid_Atlantic Bight region off the US east coast.

DOC and DON are generally well correlated with each other in summer data (Figdure: 7) with R-squared values of 0.62 and 0.27 for 2011 and 2012 respectively (both relationships significant at p < 0.001). Mean C:N ratios of DOM (approximately 9 to 17, Table 3) were comparable to those previously reported in in the southern North Sea (10.8 – 14.8) (Van Engeland et al.,

5 2010) (Van Engeland et al., 2010) and other continental shelf waters (11 – 19) (Bates and Hansell, 1999; Hansell et al., 1993; Hopkinson et al., 1997, 2002; Kim and Kim, 2013; Wetz et al., 2008). -The weaker relationship in 2012 appears to be due to high salinity waters having lower DOC and higher DON concentrations than waters of similar salinity in 2011 and is thus associated to the apparent increasing DON with salinity observed in northern bottom waters in Figure- 6.

10 3.4 DOM stoichiometry

The change in C:N ratio with salinity (Fig. 4 e and f) reveals striking differences between 2011 and 2012, with C:N increasing with salinity in 2011 to values above the expected North Atlantic endmember of 13-15, particularly seen in bottom waters of the stratified northern north sea. In 2012 however the C:N ratio decreases to below 10 at high salinities in bottom waters, due to the combination of higher DON and lower DOC than in the previous year. This therefore appears to contradict our hypothesis

(iv) of C:N ratio being dominated by mixing line between riverine and open ocean C:N and is investigated further in Section
 4.

Plots of DOC vs DON for both summers (Fig. 5) reveal a gradient of between 6.5 and 7. Hopkinson and Vallino (2005) interpret such element/element plots in a study of depth profiles of DOM in the open ocean as indicative of the stoichiometry of DOM breakdown and processing over time. In our dataset, where the concentration of DOM at low salinity is more than an order of magnitude higher than the open ocean concentrations, the slope of this line is, to first order, representative of the stoichiometry of DOM at low salinity (note in Figure 5 that the general pattern is one of increasing salinity with decreasing DOM concentration, particularly in 2011). Thus the gradient could be indicative of autochthonous production of DOM by phytoplankton at or near the Redfield C:N of 6.6:1, in estuarine or coastal waters, driven by riverine nutrient input. However,
Mattsson et al., (2009) note in a synthesis of riverine DOM C:N ratios that rivers flowing through catchments with high levels of intensive agriculture commonly have low C:N, likely due to the high inputs of inorganic nitrogen in fertiliser. Thus the C:N of ~7 is potentially consistent with an allocthanous (i.e. terrestrial) DOM source also.

3.5-4 Interannual differences

Consistent with the strong spatial freshwater/seawater_coastal to open ocean mixing-gradients, higher DOC concentrations are observed in southern well mixed than northern stratified waters in both 2011 and 2012, although this is not the case in 2012 for DON, where average concentrations in all waters of survey area are very similar (Figure 7, Table 32). In 2011 southern well mixed waters demonstrated statistically significantly (t-test, p<0.05) higher concentrations of DOC and DON than either</p>

northern surface or bottom waters ($\underline{\text{Table 2}\underline{\text{Table 3}}}$, Figure <u>67</u>). In the northern stratified waters DOC and DON concentrations were generally slightly higher in surface waters than at depth (statistically significant only in 2012). Larger differences in DOM concentrations however, are observed between the <u>two</u>2 years than between surface and bottom concentrations within either of the years.

5

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Generally, DOM concentrations were elevated in 2011 compared to 2012. The survey in 2011 presented significantly higher concentrations of DOC and DON than the summer 2012 survey in the whole water data set (all stations) (t-test, P <0.05), each data set separated by the three different water types (t-test, P <0.05), and each data set separated by two water types (whole surface data and whole bottom data) (t-test, P <0.05). Figure 6 demonstrates that these differences are not related to sampling different salinity ranges on the same DOM/salinity gradient, but rather that concentrations of DOC for all water types, and

DON for all but northern bottom waters are elevated in 2011 vs 2012 for a given salinity.

Given the challenges associated with DOM analysis it is essential that we demonstrate that this apparent

difference cannot be due to a systematic analytical error in DOC measurement. We have demonstrated (Section 2, Figure S1)
that repeat measurements of CRMs-consensus reference materials do not vary systematically in their DOC concentration between the analyses for 2011 and 2012 samples, so we are satisfied that this is not the case and we conclude that this DOC enrichment is a real feature of the North Sea in 2011.

20 The C:N ratios of DOM in northern stratified waters show a particularly large difference between the two summers, dominated by the C:N ratio of DOM in the bottom waters. Whilst C:N ratio in the surface is the same in both years (11.3 +/- 1.4 in 2011, 11.7+/- 2.3 in 2012) the bottom water C:N changes from being higher than surface values in 2011 (13.4+/- 3.6), to being lower than surface values in 2012 (9.3+ 1.8). Thus our working hypothesis iii), that carbon rich DOM production in surface in summer would lead to enhanced C:N in the surface compared to deep waters is demonstrated to be unfounded. A DOM C:N

25 ratio of 11 is consistent with greater than Redfield C:N DOM production, in both years, but the relative C:N is dominated by the bottom water signal.

3.56 DOM in bottom waters

In order to further investigate bottom water DOM, we We investigate the change in bottom water DOM concentrations with water column depth in Figure 8, which. The relationship between bottom water DOM concentrations and depth (Fig 7) reveals

30 interesting differences between the years, with <u>DOC concentrations are elevated elevated DOC</u> throughout bottom waters in 2011 relative to 2012 (typically 20 to 40 µM higher concentrations than in 2012) and with a pattern of more elevated DOC concentration in shallower regions in 2011, compared to 2012 (in which bottom waters across the survey region appears to have similar DOC concentrations irrespective of depth, except for the shallowest waters). The pattern for DON in bottom

waters in 201<u>2 shows 2 is similar with little variation with depth of water column</u>. However, DON in 2011 behaves very differently, with shallower waters showing -enrichment in DON relative to the following year (typically 10 μ M compared to 5 μ M in 2012), but with deep waters showing similar or even lower DON concentrations than in 2012. Consequently, deep bottom waters with relatively high DOC and low DON in 2011 show elevated C:N ratios (Figure 7eFigure 89c);₅ in a substantial number of cases higher than the typical North Atlantic end member of ~13-1513-15 (Aminot and Kérouel, 2004).

4. Discussion

5

4.1 Is DOM conservative with salinity?

The data presented above demonstrates that mixing between high DOM, lower salinity coastal waters and low DOM, higher salinity ocean waters is an important component of DOM dynamics in the North Sea. This does not necessarily mean that
 DOM is conservative with salinity, however. Figure 9 a) and c) compare our observations of DOC and DON respectively with the range of values consistent with conservative mixing based on our end member synthesis (Figure-1). We can consider the data in two distinct subsets based on salinity range: all salinities of less than 33.5 observed during this study were associated with surface waters in the NCC, which is strongly influenced by Norwegian rivers and Baltic outflow (Winther and Johannessen, 2006). Salinities greater than 33.5 are all outside the NCC and can be considered to synthesise the high salinity

15 portion of the river-ocean continuum across the wider North Sea.

The DOC and DON concentrations in the NCC do not appear to sit on the same mixing line as the rest of the corresponding year's data, with concentrations well below what would be expected based on the gradients in the high salinity data. This may be due to lower DOM concentrations in the river inputs from the Norwegian rivers, or potentially photochemical degradation

20 in the shallow, salinity stratified surface waters of the NCC. Alternatively, this may represent the influence of surface brackish water outflow from the Baltic. We do not have the data available to resolve this, so for the rest of the discussion we focus on the waters of the main part of the North Sea with salinity of 33.5 and higher.

As noted earlier, the DOC-salinity relationship seen here is similar to that seen in the Mid-Atlantic Bight (e.g. (Vlahos et al., 2002), which drains a catchment with some climatological and land use similarities to the North Sea. (Vlahos et al., (2002)) find an apparent zero salinity endmember of ~400 µM DOC, and an open Atlantic endmember of 47 µµM, so conservative mixing lines predicted in both their study and this one are very similar (Figure 9-b). Furthermore, they observe a typical excess of DOC above the conservative mixing line of 10 to 40 µµM of DOC. This leads to observed DOC concentrations at high salinity (>35) of greater than 50 but less than 100 µµM, consistent with our summer 2011 data, but somewhat higher than the

30 2012 summer observations presented here. Overall there is good agreement between (Vlahos et al. (-2002) data and our 2011 data across a similar range observed salinities (Figure-9b).

By averaging observations across different salinity 'bins' - an approach previously taken by (Barrón and Duarte (-2015) - we can see trends in the data which are otherwise obscured by the high variability. Mean DOC with salinity (Figure 9a) shows

- 5 distinctly different trends between years: in 2011 mean values lie slightly above the highest predicted conservative mixing line but lie broadly parallel to it, whereas summer 2012 data is systematically lower and strongly consistent with the range of conservative mixing values predicted for mixing to a deep Atlantic endmember. Mean DON (Figure- 9c) is broadly consistent with predicted range of conservative mixing vales, however the uncertainty on the open ocean endmember values are large compared to DOC so it is difficult to draw any conclusions from this. Nonetheless there is a clear difference between summer
- 10 2011, -where minimum DON is associated with maximum salinity and summer 2012 where minimum DON concentration occurs a salinity of around 34.5 and then increases to a higher value at open ocean salinity. Furthermore, the summer 2012 pattern is similar to the data from the intervening winter, although in winter the overall concentrations are higher. A minimum in DON concentration at salinity of ~34.5 suggests a possible sink for DON, associated with an open ocean source of DON to the shelf waters, in 2012. Overall, the trends observed in summer 2012 in DOC, DON and DOM C:N with salinity, above
- 15 <u>S=34.5</u>, suggest mixing with deep Atlantic water containing the most -N-rich-/ low C:N DOM that could possibly be consistent with the data collated in our open ocean end member synthesis (Table S2).

Observations of DOC and DON tend to be *consistent with or above* predicted conservative mixing values in 2011, but *consistent with or below* predicted conservative mixing values in 2012 (Figure 9). This is potentially indicative of greater net

autochthonous production of DOM in the waters sampled in 2011 and greater net consumption of DOM in 2012. Both of these processes are expected to occur in the North Sea. (Painter et al. (,-2018) see strong indication of breakdown of terrestrial and coastally-produced DOM in the wider North Sea; and multiple studies observe or predict in-situ production and degradation of DOM by plankton and bacteria in the North Sea during spring and summer (Van Engeland et al., 2010; Johnson et al., 2013; Suratman, 2007; Suratman et al., 2008, 2009). In this, as in other datasets (e.g. (Johnson et al., 2013; Painter et al., 2018), no direct relationship between either chlorophyll *a* or POC/N (data not shown)

was evident, demonstrating the complexity of the multiple sources, sinks and lifetimes of DOM.

<u>Regressions of DOC vs DON for both summers (Figure</u>, 10) reveal a gradient of between 6.5 and 7. The concentrations of DOC and DON at zero salinity (from river data synthesis -in Table S1 and apparent freshwater endmembers from regression

30 analysis in Table 4) are more than an order of magnitude higher than the open ocean concentrations, so the slope of this line is, to first order, representative of the stoichiometry of DOM at low salinity. Thus the gradient could be indicative of autochthonous production of DOM by phytoplankton at or near the Redfield C:N of 6.6:1, in estuarine or coastal waters, driven by riverine nutrient input. However, it could also be consistent with freshwater DOM inputs: (Mattsson et al. (-2009) note in a synthesis of riverine DOM C:N ratios that rivers flowing through catchments with high levels of intensive agriculture such

as the southern North Sea commonly have C:N of <10, likely due to the high inputs of inorganic nitrogen in fertiliser enriching DOM with nitrogen. Thus the C:N of ~7 is potentially consistent with an allochthonous (i.e. terrestrial) DOM source also.

We conclude from the above analysis that DOM is not conservative with salinity in the North Sea i.e. simple dilution of

- 5 riverine DOM with open ocean water cannot be assumed. However, much of the deviation from conservative mixing, due to production and degradation processes is evened out by averaging to reveal trends with salinity that are broadly consistent with what would be expected from conservative mixing. Given that we expect most riverine DOM to be degrades relatively close to the coast (e.g. Painter et al. 2018) we suggest these trends are likely related to autochthonous production of DOM driven by nutrient availability, which follow a similar decreasing trend with salinity (e.g. Hydes et al. 1999). The interannual differences
- 10 <u>are substantial, with summer 2012 data indicating both a different open ocean endmember value (more consistent with deeper</u> waters of the North Atlantic) and less autochthonous production of DOM compared to 2011.

4.2 Does the North Sea export organic carbon -to the open ocean?

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Conservative mixing of freshwater DOM (or any other tracer) with the open ocean, by definition, must result in a concentration equal to that of the ocean end member at open ocean salinity (i.e. \geq 35.5). Direct exchange of water of equal salinity between open ocean and shelf waters under this situation would not result in any net DOM transport off-shelf. However there must be net transport of DOM from fresh to ocean waters in conservative mixing as there is a concentration gradient along which

- 20 mixing occurs. The rate of any such conservative-mixing driven export must be directly related to the rate of mixing (i.e. water exchange) through the system in question. Any elevation of DOM concentrations on the shelf at open-ocean salinity (i.e. S ≥ 35.5) must represent an autochthonous on-shelf source that will lead to net 'enhanced' export of organic matter to the open ocean if this water were to be exchanged across the shelf break. Figure 9a demonstrates that summer 2011 satisfies this enhanced export: any mixing of water at the shelf break will result in export of DOC. Given that summer 2012 appears to be
- 25 quasi-conservative above S=34 for DOC (i.e. binned average data in Figure. 9a sit in a straight line very close to the predicted conservative mixing line), this implies that the export of DOC will be lower for given mixing rate than for 2011. As the DON-salinity gradient is positive above S=34.5, this suggests a net on-shelf transport of nitrogen in DON at this time. However, the exchange across the shelf break in summer tends to be low compared to winter so summer fluxes might be expected to be small irrespective of the magnitude or direction of the concentration gradient. In this case it might be more appropriate to think
- 30 of the 2012 case as 'recently mixed' with the open ocean vs the 2011 case as representative of a period of time when autoethonousautoethonous production was rapid relative to mixing. The low DON at salinity of around 34.5 would then be representative of in-situ degradation during the summer period, presumably of relatively bio-available, N-rich DOM of marine origin.

The global synthesis of shelf sea DOC concentrations by (Barrón and Duarte (,-2015)<u>Barron and Duarte (2015)</u> leads to much greater predicted enhancement of shelf DOC concentration at $S \ge 35.5$ relative to open ocean concentrations than those observed in summer 2011 in the North Sea, or in the Mid-Atlantic Bight (MAB) in the data of <u>Vlahos et al.</u>, (2002) (Vlahos et al.)

- 5 al. (-2002), as demonstrated in Figure- 9b. Given the relatively small width of the MAB shelf relative to the North Sea, the difference with the global synthesis is unlikely to be purely due to the size of the North Sea relative to the average shelf (and therefore longer residence time leading to more degradation of terrestrial DOC).- Both the MAB and the North Sea are temperate shelf seas, and a significant proportion of the studies contributing to the Barron and Duarte (2015) (Barrón and Duarte (-2015) synthesis are sub-tropical or tropical seas. This is consistent with the suggestion of Sharples et al., (2016)
- 10 (Sharples et al. (-2017) that low latitude shelf seas are significant exporters of allochthonous organic matter due to weak Coriolis-driven circulation and greater DOC loading from tropical than temperate rivers. This, however, does not directly explain the greatly enhanced concentration at open ocean salinity implied by the global synthesis; although, all else being equal the sum of autochthonous plus allochthonous DOM would be greater if less allochthonous DOM was degraded. DOC concentrations at high salinity in the North Ssea are lower than the values presented by Barrón and Duarte (2015), which
- 15 potentially implies a considerably smaller net DOC flux per unit area of shelf for the North Sea (and the MAB) than the global average. Nonetheless the evidence from this study strongly suggests that the North Sea- is a source of DOC to the open Atlantic, although the strength of this source appears interannually variable. It is not clear from our data or other studies whether the North Sea is a source of sink for open ocean DON, but it appears possible that the direction of net flux might change depending on prevailing conditions.
- 20

4.34 Differences in carbon inventory between 2011 and 2012

The two summers observed appear to be significantly biogeochemically different, not least in the concentration and C:N ratio of DOM observed, but also in nutrient regime, and physical oceanography. The apparent change in DOC concentration across

- 25 the whole of the North Sea basin between August 2011 and August 2012 is between 20 and 40 μM. There is little spatial variability in this pattern, with higher DOC in all regions-/ depths within this range (Figures 5-9, Table 3). Therefore we are confident in assuming a uniform change throughout the entire North Sea volume of ~42 x10³ km³ (the volume used in the carbon budget for the North Sea by (Thomas et al. (-2005a)) for the purposes of extrapolating the carbon inventory change. Taking 20 and 40 μM as the lower and upper estimates of interannual difference, this represents a change in the carbon
- 30 inventory of the North Sea of approximately 10 to 20 Tg (or about 1 to 2 Tmol), or roughly 30 to 40% change in the DOC inventory on the basis of our observations.

This compares to the strength of the DIC enrichment pump for the North Sea estimated by (Thomas et al. (-2005a) of -30 Tg C yr⁻¹. This enrichment pump represents the accumulation of DIC in the bottom waters of the northern North Sea as a result of POC export from the surface. Could it be possible that the interannual difference in DOC observed is simply a difference in the partitioning of carbon between the dissolved inorganic and organic forms in the two years? If so, we might expect to see

- 5 higher DIC in the 2012 than in 2011 by a similar magnitude to the DOC change (20-40 μʉM). DIC data collected as part of the UK Ocean Acidification programme (Naomi Greenwood pers. comm.) from the same cruises as our summer data shows no significant difference in concentration between the two years (t-test, p<0.05), so the change we observe is not likely to be due to a change in partitioning between dissolved inorganic and organic pools.
- 10 We do not have particulate organic matter ()POC measurements for summer 2011, so cannot compare the particulate organic carbon pool between the two years. However, as POC in 2012 had an average concentration of $\sim 2 \mu M$ and maximum concentration of 5.9 μM , the largest potential POC change (i.e. from zero in 2011 to 5.9 μM in 2012) cannot possibly account for the lower DOC of 20-40 μM in 2012. We discount the idea of a transfer of carbon between the DOC and particulate inorganic carbon on the basis of no obvious mechanism or direct link between these pools and therefore we conclude that the
- 15 DOC difference is a real change in water column inventory of total carbon between 2011 and 2012.

Spread over the entire surface area of the North Sea the difference in DOC inventory would represent a carbon flux of between 1.5 and 3 mol m⁻², which is the same order of magnitude as the best estimates for annual net CO₂ uptake by the nNorthern North Sea (Thomas et al., 2005b; Wakelin et al., 2012). This change in DOC inventory is, therefore, potentially an important

- 20 change in the carbon budget of the North Sea, at least for the years concerned. Depending on the source and fate of the DOM, this could represent a substantial change in the magnitude of air-sea CO₂ flux and/or carbon export form the North Sea to the deep ocean between these two years, and is indicative of a system whose carbon cycling demonstrates considerable interannual variability. It is therefore important that we try to understand why this might have occurred and we offer some possible explanations below.
- 25

The data presented in this paper demonstrate that there is significant complexity in the DOM dynamics in the North Sea both satially and inter-annually, although through this the expected pattern of decreasing DOM with salinity is still discernible. The results also demonstrate that there are considerable (and interannually variable) inventories of

30 carbon and nitrogen in DOM in the North Sea. In this discussion, we consider the various potential controls on DOM concentrations, stoichiometry and interannual variability in the following sections, as well as considering the significance of DOM for nitrogen cycling and carbon uptake in the North Sea.

4.1 DOM-Salinity relationship

The data presented above demonstrates that mixing between high DOM, low salinity estuarine swater 4.45 Why are the two summers so different? and low DOM, high salinity ocean waters is an important component of DOM dynamics in the North Sea. Given the relatively high concentrations of DOM on the shelf relative to the North Atlantic, the DOM data presented

- 5 here generally supports the suggestion by (Barrón and Duarte, 2015) that shelf sea regions have the potential to export DOC from the continental shelf water to the open ocean. The shelf sea DOC concentrations in the North sea are lower than the global average values compiled by those authors and hence this implies a smaller net DOC flux per unit area of shelf than suggested by those authors. As noted earlier, the DOC salinity relationship seen here is similar to that seen in the North Atlantic Bight, which drains a catchment with some climatological and land use similarities to the North Sea, suggesting that the
- 10 patterns seen may have wide ranging applicability

The noisiness of the relationships with salinity demonstrate that there are clearly other controls on concentrations of DOM, consistent with previous data which observes in situ production and degradation by plankton and bacteria of DOM in the North Sea during spring and summer, and supporting hypothesis 2 (Van Engeland et al., 2010; Johnson et al., 2013; Suratman, 2007;

15 Suratman et al., 2008, 2009), although no direct relationship between either chlorophyll or POC/N (data not shown) was evident.

However, as discussed by Johnson et al. (2013) the spring bloom in the North Sea is associated with a DOM maximum which decays away on a timescale of a few months, a situation similar to that described for open ocean and Antaretic systems (Carlson et al., 1994, 1998). Hence by the time of these surveys in late August, the main effects of this seasonal DOM concentration maximum may have decayed away, leaving the river/ocean mixing signal dominant.

The difference between summer 2011 and summer 2012 could be due to within-year factors. Marginally lower temperatures in 2011 might have inhibited the remineralisation of DOM. Higher primary productivity might have led to greater DOM production (nutrient levels in northern bottom waters suggest a greater inorganic nutrient inventory to drive spring

25 phytoplankton growth and temperatures indicate weaker stratification in 2011); and subsequently stronger N limitation relative to P (as suggested by higher levels of unutilised P in surface waters in 2011) may have caused greater overproduction of carbon-rich DOM. Greater release from sediment DOM pools is also possible and would be consistent with elevated ammonium concentrations in well-mixed southern waters in 2011.

20

Given that the largest differences in DOC concentration occur at the highest salinities (Figure- 6), where ocean influence is greatest, -it is likely that there is a strong physical driver for the difference. DOC concentrations observed in winter 2011/12 in shallow coastal stations mostly in the southern part of the North Sea are among the highest observed in this study, of up to

³⁰
and above 100 µM. These observations also coincide with some of the highest salinities observed in the study (comparable to deep northern North Sea bottom water, Table 2). The winter salinity distribution (Figure 11a) shows highest salinity waters to the south (presumably inflow from the English Channel) and a northward gradient of increasing salinity from low salinities around the UK coast north of 52 °North. The higher salinities to the north of the winter survey areas were associated with the

- 5 lowest DOC concentrations observed during the cruise (Figure 11b). Overall these data indicate very high DOC, high salinity waters flowing in to the southern North Sea via the English Channel and low DOC (extrapolated open ocean endmember of \sim 50 μ M) to the North, mixing with the river outflows along the east coast of the UK. This is different to the observations of the previous summer, where high salinity northern bottom waters had DOC concentrations of about 70 μ M (Table 3). This may indicate a flushing and renewal of North Sea waters with N. Atlantic water from the North, whilst the high DOC (75-150)
- 10 μM), high salinity water flowing in from the South, possibly represents the remnants of summer waters being pushed into the North Sea from the Channel and Western Approaches. If this is so, then the winter exchange in 2011/12 may have been responsible for a significant delivery of DOC to North Atlantic as the shelf system was flushed. (Bai et al., 2014; Hurrell, 2017) (Salt et al., 2013)
- 15 Winter 2011/12 had a strongly positive NAO index (Bai et al., 2014; Hurrell, 2017), consistent with a strong shelf-edge exchange and flushing circulation of the North Sea basin (e.g. Salt et al., 2013; –Sheehan et al., 2017). (Winther and Johannessen (–2006) find that short periods of positive NAO can enhance on-flow of surface water onto the shelf in shallow regions such as the Malin shelf, but sustained periods of NAO forcing are required to drive onwelling of deep water through the Norwegian trench. Given that the DOC concentrations in 2012 were consistent with the deep North Atlantic endmember,

20 it is quite plausible that such onwelling may have occurred over winter 2011/12 during a period of intensely positive NAO.

The preceding three years were a period of strongly negative NAO index (Bai et al., 2014; Hurrell, 2017), suggesting relatively little exchange between the waters of the NW European Shelf and the North Atlantic over this period and small output through the Norwegian trench. Elevated DOC concentrations throughout the survey in 2011 might then represent the accumulation of

- 25 DOC over multiple years of productivity, which was then mixed off-shelf in the winter of 2012; explaining substantial enhancement of DOC concentrations over the predicted conservative mixing line in summer 2011. In a period of high shelf-edge exchange associated with NAO this water would be refreshed with water more consistent with the North Atlantic endmember, resulting in a net export of DOC of approximately the magnitude of the annual CO₂ uptake. (Section 4.3). Without the full northerly extent of the survey in 2012, however, it is not possible to resolve these details conclusively and further years
- 30 of summer data are needed to resolve the interannual variability and stoichiometry of DOM processing in the North Sea. However this mechanism is strongly consistent with the conclusions of a recent study of the Celtic sea, which concludes that differences between observations of DIC and inorganic nutrients between 2014 and 2015 can be explained by a flushing event which exported carbon-rich organic matter which had potentially accumulated over multiple years from the shelf and simultaneously imported new nutrients onto the shelf to reset the system (Humphreys et al., 2018). As such our data adds

further weight to the concept that irregular flushing of carbon-rich organic matter off the shelf is a potentially key element of the continental shelf pump, at least on the NW European shelf.

5 4.56 C:N stoichiometry of DOM

As identified by (Humphreys et al. (-2018), the stoichiometry of the organic matter pool is potentially important for the efficiency of carbon uptake on the shelf and subsequent export. The C:N ratio in all surface waters in summer in both

- 10 years of our study has a rather similar average value of (-11.3 ± 1.4 and 11.7 ± 2.3) (Table 32), which is consistent with surface DOM production as previously observed in other studies in the North Sea 2010) (Van Engeland et al., 2010) and other continental shelf waters (Bates and Hansell, 1999; Hansell et al., 1993; Hopkinson et al., 1997, 2002; Kim and Kim, 2013; Wetz et al., 2008). The bottom water C:N changes from being higher than surface values in 2011 (13.4 ±+/- 3.6), to being lower than surface values in 2012 (9.3 ± +-1.8). DOM is therefore depleted in nitrogen relative to primary production in both
- 15 years (note the POC:PON in 2012 of about six to seven, as expected for primary production), but DOM in bottom waters is N-poor in 2011 and N-rich in 2012 relative to surface waters. This is potentially due to the greater breakdown of POM to yield DOM with lower C:N in 2012, but this cannot explain the strong trend of increasing DON with salinity in northern stratified bottom waters.

20 4.2 Significance of difference in DOC inventory between 2011 and 2012

The two summers observed appear to be significantly biogeochemically different, not least in the concentration and C:N ratio of DOM observed, but also in nutrient regime, and physical oceanography. The apparent change in DOC concentration across the whole of the North Sea basin between August 2011 and August 2012 is between 20 and 40 μM (Figure 6). Assuming a uniform change throughout the entire North Sea volume of 42.3 x10³ km³ (the volume used in the carbon budget for the North

- 25 Sea by Thomas et al. (2005b)), this represents a change in the carbon inventory of the North Sea of approximately 10 to 20 Tg (or about 1 to 2 Tmol). This compares to the estimated strength of the DIC enrichment pump for the North Sea estimated by Thomas et al. (2005b) of ~30 Tg C yr⁻¹. Spread over the entire surface area of the North Sea the difference in DOC inventory would represent a carbon flux of between 1.5 and 3 mol m⁻², which is the same order of magnitude as our best estimates for annual CO₂ uptake by the Northern North Sea (Thomas et al., 2005a). This change in DOC inventory is, therefore, potentially
- 30 an important change in the carbon budget of the North Sea, at least for the years concerned. Depending on the source and fate of the DOM, this could represent a substantial change in the magnitude of air sea CO₂-flux and/or carbon export form the North Sea to the deep ocean between these two years, and is indicative of a system whose carbon cycling demonstrates considerable interannual variability.

DOC concentrations observed in winter in shallow coastal stations mostly in the southern part of the North Sea shows among the highest observed in this study, of up to and above 100 µM. These observations also coincide with some of the highest salinities observed in the study (comparable to deep northern North Sea bottom water, Table 1). The salinity distribution (Fig S3a) shows highest salinity waters to the south (presumably inflow from the Channel) and higher salinity waters to the north.

- 5 with low salinities around the East Anglian Coast. The higher salinities to the north of the winter survey areas were associated with the lowest DOC concentrations observed during the cruise (Fig S3b). This is suggestive of high DOC waters flowing in to the southern North Sea via the Channel and low DOC (35.5 salinity endmember --50 μM) waters flowing in from the North. This is at odds with the observations of the previous summer, where high salinity northern bottom waters are observed to have DOC concentrations of about 70 μM. This may indicate a flushing and renewal of North Sea waters with N. Atlantic water
- 10 from the North, whilst the high DOC (75-150 μM), high salinity water flowing in from the South, possibly represents the remnants of summer waters being pushed into the North Sea from the Channel and Western Approaches. If this is so, then the winter exchange in 2011/12 may have been responsible for a significant delivery of DOC to North Atlantic as the shelf system was flushed. Winter 2011/12 had a strongly positive NAO index (Bai et al., 2014; Hurrell, 2017), consistent with a strong shelf-edge exchange and flushing circulation of the North Sea basin (Salt et al., 2013). Given the confused relationship between
- 15 DOC and salinity (Fig S4), it is likely that other processes played an important role in the DOC concentrations in winter, including riverine inputs and likely interaction with sediments, which are known to be a source of DOM (Fitzsimons et al., 2006).
- 20 4.3 DOM variability, C:N ratio and the seasonal signal The change in C:N ratio with salinity (Figure: 6-e and f, Figure: 9-d) reveals striking differences between 2011 and 2012, with C:N increasing with salinity in 2011 to values above the expected North Atlantic endmember of 112-16 (see end member synthesis in Table S2-Table 1- of Supplementary Information), particularly seen in bottom waters of the stratified northern Nnorth Ssea. In 2012, howeverhowever, the C:N ratio decreases to below 10 at high salinities in bottom waters, due to the combination of higher DON and lower DOC than in the previous
- 25 year. This signal is consistent with the deep North Atlantic endmember, although there is large variability in the literature in observations of deep North Atlantic DON, from 2.7 to 7.7 μ#M so the range of potentially consistent values is correspondingly large. DON concentrations at the higher end of this range are seen at 35 °N in the open North Atlantic by Kahler and Koeve (2001) (Kähler and Koeve (2001), but also in deep waters of the Faroe-Shetland channel, associated with Norwegian Sea / Arctic Ocean outflow by (Kramer et al., (2005). Lower DON concentrations are observed offshore in the bay of Biscay by
- 30 (Aminot and Kérouel_(-2004) and in the open North Atlantic between Greenland and Portugal by (Álvarez-Salgado et al., 2013). In the case of northern, high salinity waters in this study, relatively high DON of 6 to 7 μuM at high salinity in 2012 is in good agreement with deep waters from the Norwegian Sea/ Arctic Ocean outflow, which would likely be advected onto the shelf if deep Atlantic waters were advected to the North Sea via the Norwegian trench under strong NAO winter conditions, as suggested by (Winther and Johannessen (-2006). The low C:N values in 2012 are thus consistent with on-flow of water

with low C:N DOM. As such, it is possible that water exchange with the Atlantic between 2011 and 2012 led to a net export of DOC from and a net import of DON into the North Sea.

The significant difference between the northern bottom waters in the two years is further explored in Figure 12, which

- 5 compares DOM stoichiometry in the northern bottom waters in 2011 and 2012 with literature values of the subsurface North-Atlantic end member, representing relatively old water not expected to show interannual variability (e.g. (Hopkinson and Vallino, 2005). -We compare the location of samples in DOC–DON space with possible Atlantic end members from the studies synthesised in Table S2. In 2011, high salinities tended to be associated with lowest DOC and DON concentrations, and all high salinity values can be seen to be very inconsistent with end member data, with elevated DOC at all DON concentrations
- 10 relative to the end member ranges. In 2012,- hHigh salinities were associated with some of the highest concentrations of DON observed in northern bottom waters, and these high salinity, low DOC (<50 μHM) waters with DON concentrations of 6-7 are strongly consistent with the deep Atlantic background concentration observed by (Kähler and Koeve, (-2001) and somewhat consistent with the deep waters of Arctic Ocean origin observed by (Kramer et al. (-2005), although with lower DOC. We therefore conclude that the northern bottom waters in 2012 are likely to be strongly influenced by the on-flow of new, deep</p>
- 15 water of Atlantic or Arctic Ocean origin, supporting our hypothesis that flushing with new, deep water in winter 2011/12 substantially changed DOM composition and concentration in the North Sea between the two summers.

DOC and DON are generally well correlated (Fig 5). Mean C:N ratios of DOM (roughly 9 to 17, Table 2) were comparable
 to those previously reported in in the southern North Sea (10.8 – 14.8) (Van Engeland et al., 2010) and other continental shelf waters (11 – 19) (Bates and Hansell, 1999; Hansell et al., 1993; Hopkinson et al., 1997, 2002; Kim and Kim, 2013; Wetz et al., 2008). There are however some differences in DOC/N relationships with season and location.

The elevated C:N molar ratio in the winter cruise may be due to the riverine input of high C:N materials as a significant inverse

- 25 relationship with salinity in C:N molar ratio (R2 = 0.15, P < 0.05, n = 60) is seen (Fig S5). However given the apparent decoupling of DOC and DON concentrations in winter (no statistically significant correlation between DOC and DON were found at the 95% significance level in winter 2011 (P > 0.05)), it maybe that benthic interactions also play an important role particularly in winter (Suratman et al., 2008).
- 30 In summer 2012 little variation between surface and bottom concentrations of DOC and DON is seen in well mixed southern waters (Figure 6). In 2011, however, these waters show a different pattern, with bottom samples having significantly elevated DOC (and DON) concentrations relative to surface samples, and with a lower C:N ratio. This observation suggests that there is a source of DOC from the shelf sediments in the Southern North Sea in 2011 or remineralisation of accumulated DOM at

sufficient rate not to be mixed out by the overturning of the water column. This is consistent with the coincident observations of elevated concentrations of ammonium and phosphate (Figure 2d), suggesting strong remineralisation rates of benthicderived DOM near the bottom of the water column, potentially associated with a nepheloid layer or similar (Burdige et al., 1999; Burdige and Homstead, 1994; Fitzsimons et al., 2006), either not present or not captured by sampling in 2012.

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On the basis of previous observations and the assumption that DOC-rich DOM would be produced in surface waters over the summer and broken down at depth, we predicted that DOC concentrations would be elevated in surface compared to bottom waters in summer. In seasonally stratifying water this seems to be the case in both years, although with a much stronger difference between surface and bottom waters in 2012. The C:N ratio in all surface waters in summer in both years has a rather similar average value of $(11.3 \pm 1.4 \text{ and } 11.7 \pm 2.3)$ (Table 2), which is consistent with surface DOM production as previously observed in other studies in the North Sea (Van Engeland et al., 2010) and other continental shelf waters (Bates and Hansell, 1999; Hansell et al., 1993; Hopkinson et al., 1997, 2002; Kim and Kim, 2013; Wetz et al., 2008). However, it is impossible to disentangle local seasonal effects from the broad scale dominance of mixing along the salinity gradient from coast to open ocean.

15

The substantial differences between surface and bottom waters in the northern stratified part of the surveys in the two years is clear in Figure 6. In 2011 surface DOC is only marginally elevated over bottom DOC, but DON is considerably higher (and less variable) at the surface. In 2012, however, the DOC is much lower in the bottom compared to the surface, but the DON is not significantly different. This leads to differences in C:N in northern bottom waters between 2011 (13.4 ± 3.6) and 2012 (9.3 ± 1.8). The significant difference between the northern bottom waters in the 2 years is explored in Figure 9, which compares DOM stoichiometry in the northern bottom waters in 2011 and 2012 with literature values of the subsurface N. Atlantic end member, representing relatively old water not expected to show interannual variability (e.g. Hopkinson and Vallino, 2005). As low DOM concentrations correspond to high salinities in deep northern waters (Figure 4), we can consider these properties to co vary with salinity and thus, the location of samples in DOC — DON space can be compared to possible end members as indicated by the subsurface open ocean values from the literature. This indicates that northern bottom waters in 2012 tended of the subsurface open ocean values from the literature.

- towards and were entirely consistent with the N. Atlantic observations of both Álvarez Salgado et al. (2001) covering a transect from Ría de Vigo (the eastern North Atlantic upwelling system, 42 – 43°N) and Aminot and Kérouel (2004) who considered depth profiles (surface layer – 4000 meters) from the Bay of Biscay (the eastern North Atlantic); other than the surface observations of Aminot and Kérouel (2004), defined by those authors as the top 200m, which appear relatively enriched in
- 30 DOC compared to the 2012 waters.

On the basis of previous observations and the assumption that DOC rich DOM would be produced in surface waters over the summer and broken down at depth, we predicted that DOC concentrations would be elevated in surface compared to bottom waters in summer. In seasonally stratifying water this seems to be the case in both years, although with a much stronger

difference between surface and bottom waters in 2012. The C:N ratio in all surface waters in summer in both years has a rather similar average value of (11.3 ± 1.4 and 11.7 ± 2.3) (Table 2), which is consistent with surface DOM production as previously observed in other studies in the North Sea (Van Engeland et al., 2010) and other continental shelf waters (Bates and Hansell, 1999; Hansell et al., 1993; Hopkinson et al., 1997, 2002; Kim and Kim, 2013; Wetz et al., 2008). However, it is impossible to

5 <u>disentangle local seasonal effects from the broad scale dominance of mixing along the salinity gradient from coast to open</u> <u>ocean.</u>

Northern bottom waters in 2011, however appear inconsistent with the likely North Atlantic end-member suggesting very different conditions. This may be due to within year factors such as lower temperatures (inhibiting the remineralisation of DOM), higher primary productivity leading to greater DOM production (nutrient levels in northern bottom waters suggest a greater inorganic nutrient inventory to drive spring phytoplankton growth), stronger N limitation relative to P (as suggested by higher levels of unutilised P in surface waters in 2011) leading to greater overproductivity (temperature differences release from sediment DOC pools, or weaker stratification leading to higher summer productivity (temperature differences between surface and bottom were greater in 2012).

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It may also be possible that there is a multi-year component to this signal. We have seen that the winter data suggests high salinity waters entering the southern North Sea from both the south and north in winter 2011/12 and noted that this winter period was associated with a very high NAO index, which is associated with greater cross shelf exchange (Salt et al., 2013; Sheehan et al., 2017). Furthermore, higher salinities to the north in the Winter data are associated with much lower DOC concentrations than the previous summer, all suggestive of flushing of the North Sea over the winter of 2011/12. The preceding

- 20 concentrations than the previous summer, all suggestive of flushing of the North Sea over the winter of 2011/12. The preceding 3 years were a period of strongly negative NAO index (Bai et al., 2014; Hurrell, 2017), possibly suggesting less exchange between the waters of the NW European Shelf and the North Atlantic over this period. Elevated DOM concentrations throughout the survey in 2011 might then represent the accumulation of DOM over multiple years of productivity, which was then mixed off shelf in the winter of 2012. Northern bottom waters in 2011 then would be representative of the 'processing'
- 25 signal' of organic matter in the North Sea / NW European shelf; and be indicative of DOM carbon enriching processes. In a period of high shelf edge exchange associated with NAO this water would be refreshed with water more consistent with the North Atlantic endmember at a similar salinity, resulting in a net export of DOC of approximately the magnitude of the annual CO₂ uptake (section 4.2). Without the full northerly extent of the survey in 2012, however, it is not possible to resolve these details conclusively and further years of summer data are needed to resolve the interannual variability and stoichiometry of
- 30 DOM processing in the North Sea.

5. Conclusion

The data presented in this paper demonstrate that there is significant complexity in the DOM dynamics in the North Sea both spatially and inter-annually, although there is a strong spatial gradient of decreasing DOC and DON concentrations with distance from land and with decreasing salinity. *[It has been indicated that shelf sea regions have the potential to export DOC*]

- 5 from the continental shelf water to the open ocean (Barrón and Duarte 2015). Higher DOM concentrations are observed in inner shelf rather than the outer shelf and both areas this study having higher than average surface DOC concentrations in the North Atlantic Ocean (~ 60-80 μM) (Aminot and Kérouel 2004, Carlson et al. 2010, Kähler et al. 2010). This is taken to suggest that DOC in the North Sea is potentially in this study exported to the North Atlantic Ocean over the summer period. However, further research to quantity the export is required i.e. a mathematical modelling.
- 10]The observed DOM concentrations show a strong spatial gradient of decreasing DOC and DON concentrations with distance from land and with decreasing salinity, strongly supporting the conclusions of the data synthesis for global shelf seas of (Barrón and Duarte, 2015). This gradient may arise in the North Sea from estuarine and coastal DOM production by marine phytoplankton or represent the transport and processing of terrestrially-derived material in the coastal zone. The apparent freshwater end members are consistent with either a fluvial (i.e. allochathonous) source or near-coastal autochthonous
- 15 production driven by riverine nutrients. Data from another study (Painter et al. 2018) suggests that the contribution of terrestrial sources to the DOM pool in the open North Sea is small, so we suggest that nutrient-driven autochthonous production is the more likely explanation. The analysis of DOM/salinity gradients here is constrained by our poor understanding of the lifetime of DOM in the North Sea, and of the source of high DOM in near-coastal waters (autochthonous, nutrient-driven vs riverine source). More measurements of DOC/N in rivers and estuaries flowing into the North Sea, particularly transects from low to
- 20 <u>high salinity would be a valuable addition to our knowledge of low salinity DOM cycling and production in this region.</u>

Overall, DOC concentrations are lower in the North Sea than average values in the global synthesis of shelf DOC concentrations by (Barrón and Duarte (,-2015). Long residence times in the North Sea, compared to the global shelf average may help to explain the lower-than-average DOC concentrations, with little or no terrestrial DOM reaching the shelf break (e.g. (Painter et al., 2018). Longer residence time also means longer for the production and processing of autochthonous organic matter, so the oldest, most saline waters of the northern North Sea may provide a good synthesis of shelf processes or even some 'memory' of multi-year organic matter processing signals during periods of low exchange with the Atlantic.

30

The spatial pattern (i.e. dominated by mixing) is the same similar in both years but the actual concentrations, particularly of DOC, are different. High interannual variability appears to dominate the DOC/DON, particularly in the deep bottom waters in the northern North Sea, which are those that are most likely to be leaving the shelf the following winter. The source of elevated

DOC concentrations in 2011 is potentially the same as the high DOC signal seen by <u>Thomas et al. (2005b)</u> (Thomas et al. <u>(</u>-2005a), in their study attributed to onwelling water; but we establish that at least in 2011 the elevated DOC is inconsistent with the open ocean DOC concentration, suggesting an <u>in-situon-shelf</u> source (Figure-<u>98</u>), and in disagreement with the budget of (Thomas et al. (-2005a) which suggests net respiration of ocean DOC in the North Sea overall. Simultaneous measurements

- 5 of DON sheds more light on this than observations of DOC alone:- in 2011 at least, high DOC in deep waters appears associated with high C:N ratio (i.e. depleted DON). This is consistent with in-situ production of high DOC organics, and/or the preferential remineralisation of N over C from DOM. Either way this high C:N DOMC is a potentially a very-important component of the shelf carbon pump, allowing greater carbon uptake for a given winter stock of inorganic nutrient than for non-carbon enriched (i.e. Redfieldian) DOM production. The differences between 2011 and 2012 described here suggest
- 10 important interannual differences in the scale of shelf sea carbon export in this region, and perhaps at other shelf sea boundaries. We note that the DOC concentrations observed by Painter et al. (2018) in summer 2016 in the North Sea are comparable in magnitude and distribution to those in 2011, suggesting that the apparent accumulation of DOC in the North Sea may be a regular occurrence. Further years of data and greater seasonal detail are needed to quantify this effect and understand the complex interaction roles of role of mixing, benthic interaction and nutrient limitation in the system.
- 15

The data and subsequent analysis we present here leads us to hypothesise that intermittent flushing of the North Sea may be a key driver of both the variability in the carbon inventory and also the strength of the shelf pump for carbon in the region, and possibly elsewhere. Periods of low exchange with the open ocean are associated with reduced nutrient inputs to the system and would be characterised by high C:N dissolved organic matter, which represents an accumulation of carbon in the system

- 20 and thus continued uptake of atmospheric CO₂ in spite of reduced carbon export to the deep ocean via circulation. This high C:N DOM could accumulate -via preferential remineralisation of DOM nitrogen over carbon and/or nutrient stress leading to overflow production of carbon rich organics by phytoplankton (e.g. (Humphreys et al., 2018; Lønborg et al., 2010; Prowe et al., 2012). Either of these mechanisms are likely to be compounded by increased periods of relative isolation of shelf waters from the open ocean, when nutrient inputs are reduced and the total nitrogen inventory is likely to decrease due to loss from
- 25 denitrification in sediments. Our data is strongly supportive of this hypothesis, providing both circumstantial evidence of a flushing event based on winter salinity data and comparison with open ocean endmembers and evidence of elevated DOC concentrations, low DON and high C:N in the high-salinity shelf waters in summer 2011 prior to the proposed winter flushing event. The change in the DOC inventory observed here suggests that DOC may represent the most variable pool of carbon in the shelf water column and therefore the biggest control on annual CO₂ uptake and subsequent off-shelf export. Greater
- 30 understanding of the dynamics of DOM production, degradation and stoichiometry is needed. In particular, the interacting roles of -sediment-water interactions, nutrient limitation and variable water residence times/ flushing events needs to be better understood. This is an important area of future study in better quantifying and predicting the role of shelf seas in carbon uptake and export to the deep ocean.

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by upper DOC- divided by lower DON and vice versa gives an unreaslitically unrealistically large range of values.





Figure 42.÷ The North Sea study area, showing sampling points from each of the <u>three3</u> cruises (note that the <u>two2</u> summer cruises occupy notionally the same stations, each in separate ICES grid square, each year hence the close overlap). Also shown is bathymetry, with 40 m, 50 m, 100 m, 200 m, 400 m, 600 m and 1000 m contours shown in light grey. -<u>Note that the division between well mixed southern waters and the seasonally stratifying norther region follows the bathymetry, approximately at the 40 m countour running from around 54 N on the UK coast to approximately 57 N on the Danish coast.</u>



Figure 3. Temperature-salinity plots divided by location-/ season and cruise. Grey points show the whole data set from all other water types / seasons.





5 Figure <u>42</u>. Summary of inorganic nutrient observations demonstrating the differences between surface and bottom samples, different mixing regimes, seasons and years. a) nitrate, b) phosphate, c) nitrate to phosphate ratio and d) ammonium concentration. Box and whisker plots show statistical summary of the data where the thick horizonal like represents the median value, the extent of the boxes represents the intergartile interguartile range and whiskers represent the full range of data up to 1.5 interguartile distances from the median. Any points outside this range are shown as discrete points.





Figure 53. Distribution of a) DOC, b) and DON, c) and C:N ratio of DOM and d) salinity for surface and bottom waters in summer 2011-2012. Points represent discrete observations and the underplotted colour gradient is a 2-dimensional Gaussian smooth of the discrete data to demonstrate the spatial trend.



5 Figure 4. Property-salinity plots for a) DOC₁ and b) DON c) C:N ratio of DOM for both summer cruises.



Figure 6. Property-salinity plots for a) DOC, c) DON and e) C:N ratio of DOM for summer 2011. Corresponding plots for summer 2012 are shown in panels b), d) and f). Note that regression analysis for property-salinity relationships is presented in Table 4.





Figure <u>105</u>. Element-element plots of DOC vs DON for summer surveys a) August 2011; b) August 2012. Points are coloured by salinity. Lines represent application of standard linear least squares regression models to the relevant data; equations for which are quoted on the plots.





Figure <u>76</u>. Summary of DOM concentrations a) DOC, b) DON<u>and</u>, c) DOM C:N ratio<u>. Box and whisker plots show statistical</u> 5 <u>summary of the data where the thick horizonal like represents the median value, the extent of the boxes represents the</u> <u>intergartileinterguartile range and whiskers represent the full range of data to 1.5 interguartile distances from the median. Any</u> points outside this range are shown as discrete points.





Figure <u>87</u>. DOC <u>(a)</u>, DON <u>(b)</u> and DOM carbon to nitrogen ratios <u>(c)</u> in bottom water samples, plotted against sampling depth <u>(approximately 10 m less than total water column depth)</u>. Red points from summer 2011, green points from summer 2012, blue from the intervening winter cruise.



Figure 9. Comparison of a) DOC, and c) DON and d) C:N relationships with salinity, compared to conservative mixing
 predictions. Small points represent discrete observations and large points are binned averages spaced at 1/3 of a salinity unit. The solid and dotted grey lines/areas represent predicted conservative mixing lines between rivers and the shallow and deeper Atlantic

end members, respectively. In panel b) DOC data form this study is compared to the data (black dots) and salinity relationship (dot-dash line) of Vlahos et al. (2002) in the Mid-Atlantic Bight, as well as the mean (long dash) and median (long dash – short dash) relationships from the global synthesis of Barrón and Duarte (2015). Barron and Duarte (2013).





Figure <u>12</u>. DOM stoichiometry from northern stratified bottom water samples in <u>summer</u> 2011 (red) and 2012 (green), compared with open North Atlantic concentrations as follows. <u>from A13:</u> Álvarez-Salgado et al. (2013); <u>AK04:</u>-and <u>Aminot and Kérouel</u> (2004); <u>K05: Kramer et al. (2005); KK01: Kähler and Koeve (2001)</u>. These 'end member² ranges' were constructed in DOC/DON space based on the ranges of concentrations of DOC and DON quoted in the relevant papers, constrained by limiting possible combinations of DOC and DON that were consistent with the quoted range of observed C:N ratios (in the absence of the full dataset). <u>TEffectively the full range of DOC concentrations observed in the studies is covered by these derived end-members, and the large majority of the DON concentrations.</u>
Table 1. Summary of sampling cruises in the North Sea.

Cruise number	Dates	Season
<u>CEND 14/11</u>	<u>8 Aug – 7 Sep 2011</u>	Summer 2011
<u>CEND 02/12</u>	<u>20 Jan – 31 Jan 2012</u>	<u>Winter 2011</u>
<u>CEND 13/12</u>	<u>9 Aug – 23 Aug 2012</u>	Summer 2012

CEND is abbreviation for the research vessel Cefas Endeavour in its cruise naming nomenclature.

	Temperature	Salinity	DIN <u>a</u>	DIP_b	DISi_c
	(°C)		(µ <u>M</u> mol l-	(µ <u>M</u> mol 1-1)	(µ <u>M</u> mol_l-
			4)[U2]		1)
August 2011					
Southern well-mixed	15.5 ± 1.7	34.3 ± 0.5	1.5 ± 1.1	0.2 ± 0.1	2.2 ± 1.5
	(10.4-17.8)	(33.0-34.9)	(0.2-4.7)	(0.1-0.5)	(0.4-7.7)
Northern stratified SML surface	14.2 ± 1.0	34.3 ± 1.0	0.7 ± 1.1	0.2 ± 0.1	1.3 ± 0.6
	(12.2-16.0)	(31.8-35.4)	(0.2-4.7)	(0.1-0.5)	(0.5-3.7)
Northern BMLstratified bottom	8.4 ± 1.6	35.1 ± 0.2	9.9 ± 4.4	0.8 ± 0.3	4.5 ± 1.6
	(6.7-12.4)	(34.6-35.4)	(0.9-16.2)	(0.1-1.1)	(0.3-6.8)
January 2012					
WSouthern well-mixed	7.2 ± 0.9	34.8 ± 0.4	8.8 ± 3.3	0.6 ± 0.1	5.4 ± 1.0
	(5.7-8.7)	(33.3-35.4)	(5.3-23.0)	(0.4-0.9)	(4.1-8.9)
August 2012					
Southern well_mixed	16.2 ± 1.7	34.5 ± 0.5	0.8 ± 1.2	0.2 ± 0.1	1.5 ± 1.0
	(11.0-18.5)	(33.1-35.1)	(0.4-8.3)	(0.1-0.4)	(0.3-5.2)
Northern SMLSurface	16.3 ± 0.8	34.3 ± 1.0	0.5 ± 0.3	0.1 ± 0.0	0.9 ± 0.5
	(13.2-17.4)	(30.9-35.2)	(0.4-1.5)	(<lod-0.2)< td=""><td>(0.1-1.6)</td></lod-0.2)<>	(0.1-1.6)
Northern BMLBottom	8.8 ± 0.6	35.0 ± 0.2	5.5 ± 3.0	0.6 ± 0.2	3.2 ± 0.8
	(7.5-10.5)	(34.6-35.4)	(0.4-11.2)	(0.2-0.9)	(1.2-5.1)

Table 21. Summary of physical and inorganic nutrient parameters during the 3 cruisesthis study.

Mean values are presented in mean \pm SD, SD is standard deviation. Range values are showed in parentheses. Limit of detection (LOD) is 0.1 μ M for phosphate in August 2012 samples. For parameters presented < LOD, the half of detection limit was used to calculate the mean value.

5 <u>a DIN = the sum of nitrogen concentration in the form of nitrate (total nitrate plus nitrite) and ammonium</u>

^b DIP = phosphate concentration

^c DSi = silicate concentration

	DOC	DON DOC:DON	DOC:DON	POC	PON	POC:PON
	(<u>µMµmol−l</u> -	(<u>µM</u> µmol		(<u>µMµmol l</u> ⁻	(<u>µM</u> µmol	
	¹)[U3]] +)		⁴)	± [⊥])	
August 2011						
Southern well_mixed	97.5 ± 13.7	9.0 ± 1.8	11.1 ± 1.6	-	-	-
	(77.1-134.5)	(6.1-13.7)	(8.3-14.3)			
Northern SMLSurface	73.8 ± 11.6	6.6 ± 1.0	11.3 ± 1.4	-	-	-
	(51.2-104.2)	(4.8-8.7)	(8.0-15.3)			
Northern BMLBottom	73.8 ± 14.7	5.9 ± 2.1	13.4 ± 3.6	-	-	-
	(53.3-120.1)	(3.0-11.7)	(7.4-23.3)			
January 2012						
Southern wWell-mixed	107.5 ± 29.6	6.7 ± 2.0	17.3 ± 6.2	-	-	-
	(56.2-224.8)	(3.7-12.3)	(5.9-36.5)			
August 2012						
Southern well_mixed	65.5 ± 16.4	5.3 ± 1.3	12.6 ± 2.8	16.0 ± 9.3	2.2 ± 1.3	7.7 ± 1.8
	(36.3-124.4)	(2.8-9.8)	(8.9-21.3)	(5.8-43.8)	(0.6-5.9)	(5.0-13.2)
Northern SMLSurface	60.7 ± 13.0	5.3 ± 1.1	11.7 ± 2.3	10.5 ± 4.2	2.0 ± 0.7	5.9 ± 3.1
	(32.7-99.5)	(3.0-7.5)	(7.2-16.4)	(2.7-21.8)	(0.6-2.9)	(1.1-14.2)
Northern BMLBottom	46.9 ± 6.8	5.2 ± 1.0	9.3 ± 1.8	7.3 ± 3.5	1.5 ± 0.7	6.0 ± 3.9
	(36.8-61.2)	(3.5-7.5)	(6.4-13.8)	(1.1-16.2)	(0.3-2.7)	(0.7-16.8)

Table 32. Summary of dissolved organic carbon and nitrogen observations during the 3 cruises in this study.

Mean values are presented in mean \pm SD. Range values are showed in parentheses.

5

Parameters	Surveys	Water mass ^a	R-square (R ²)	Slope	y-Intercept \pm uncertainty	n ^b
DOC	Summer 2011	NS	0.2594	-5.7	270.1 ± 47.9	50
		SM	0.1661	-11.1	477.7 ± 129.9	45
	Winter 2011	SM	0.0830	-20.0	805.5 ± 304.6	60
	Summer 2012	NS	0.4062	-8.1	338.3 ± 63.5	30
		SM	0.2871	-18.7	711.0 ± 153.4	46
DON	Summer 2011	NS	0.1973	-0.4	20.6 ± 4.1	50
		NB	0.3009	-5.1	183.7 ± 39.5	49
		SM	0.3037	-1.9	75.3 ± 15.3	45
	Summer 2012	NS	0.2535	-0.5	23.4 ± 5.9	30
		SM	0.4047	-1.8	67.1 ± 11.3	46
POC	Summer 2012	SM	0.1004	-6.3	233.6 ± 98.2	46
PON	Summer 2012	SM	0.1469	-1.0	37.8 ± 12.9	46
0 117	NG		.1	•		<u><u><u></u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u></u>

Table 3. <u>Table 4.</u> Regression analysis of DOC, DON, POC and PON with salinity in each water mass. Note only significant correlation (at the 0.05 confidence level) is presented.

5 а Water masses: NS = stratified northern surface water, NB = stratified northern bottom water, SM = southern well-mixed water

^b Number of sample (n)