***Responses to* Referee #1*'s interactive comments on* "Carbon sources in the Beaufort Sea revealed by molecular lipid biomarkers and compound specific isotope analysis" *by* I. Tolosa et al.**

We appreciated the constructive comments of the reviewer #1 to our manuscript, which resulted in significant improvements. Below are given, the changes made in response to his comments and questions.

**Reviewer: The discussion is quite difficult to follow (jumps back and forth – though it's not an easy task to improve this given the complexity of the dataset), and there is room for a more critical interpretation of the data, and to put some more emphasis on the main new findings emerging from this particular study (go beyond the descriptive). I have detailed some suggestions and comments below.**
**The approach of assigning source contributions taken by the authors have some limitations. While obviously the compound-specific data can be used to obtain more detailed information than bulk measurements (d13C and D14C – due to overlap in signatures and a limited number of proxies), using the compound information to constrain contributions is complicated by the different degradability of different (groups of) compounds, and by their relative concentrations in each of the sources. This is not taken into account in this study. While the authors admit that their approach is only semi-quantitative (P 13945 L 15-20), I think this requires some extra effort. In particular, it is somewhat misleading to express results such as "we estimated that the fraction of terrestrial material preserved in the sediments accounted for 30–40% of the total carbon in the inner shelf sediments, 17% in the outer shelf and Amundsen Gulf and up to 25% in the slope sediments."**

**Reply:** We understand that the reviewer was confused about the qualitative and quantitative approach presented in our manuscript. In fact, the aims of sections 4.2 and 4.3 were to evaluate the quality and nature of the lipidic compounds by grouping the different lipid biomarkers into the different sources. For the algal component, we took into account the different degradability of the compounds to distinguish the fresh/labile algal component from that of refractory/detrital algal. In contrast to this source-specific approach, estimations of the fraction of terrestrial material preserved in the sediments and presented in section 4.5 are based on the concentrations of terrestrial biomarkers normalized to total organic carbon between the marine sediments and the river water.
This explains why the relative contributions of the terrestrial components (C3 plants+fossil) shown in Figure 8 differ from those obtained by the quantitative approach shown in Table 13. In fact, Fig. 8 shows the percentage of the terrestrial compounds within the total lipids, whereas the results of Table 13 are based on the concentrations of terrestrial compounds normalised to the total organic carbon.
To avoid confusions, we have now clarified and presented these two different approaches in the Introduction as:
*"Based on the contribution of different molecular markers (hydrocarbons, alcohols, sterols and fatty acids) characteristic of known organic matter sources and taking into account the different lability of the molecules, we evaluate the relative importance of different organic pools, such as fresh algal, refractory algal, fossil, C3 terrestrial plants, bacterial and zooplankton material. Additionally, a quantitative approach comparing the concentrations of allochthonous biomarkers normalized to the total organic carbon between marine sediments and river SPM allowed to reassess the fraction of allochthonous material preserved in the sediments of the Beaufort Sea."*
We have also changed the sentence of P13945 L 15-20:
*"We stress that this is an empirical approach because some of the compounds, such as sitosterol, might derive from more than one source (algal and/or terrestrial)."*

**Reviewer: Also, given that only surface sediments (upper 5 mm!) were sampled, the contribution of some sources will be overestimated given that further diagenesis is likely to occur for more labile compounds/markers. This makes it very difficult to compare the estimated contributions in this paper to earlier estimates, and might be the reason why for example, the fossil component is estimated to contribute so much in the current study compared to earlier results based on bulk measurements. A more critical discussion of these limitations seems warranted, in the intro (page 13928 L15-20) and in the Discussion. At the moment, results expressed as a relative contribution of a pool of biomarkers is a little weak.**

**Reply:** We do not completely agree with the reviewer but we thank him for this remark, which allows us to reconsider this point. Although, more labile compounds might be occurring in the upper most surface sediments compared to the deeper ones, most of the loss of the reactive components is taking place during settling through the water column. Therefore sampling more than 5mm should not make a great difference. As an example to support this statement, TOC measurements throughout a sediment core in the Beaufort Sea (Belicka et al., 2004) with a resolution of 4 mm exhibited a range of TOC values from 1.42 in the upper surface to 1.08 in the 0.8-1.2 cm. Other studies from the same area also showed a nearly depth-invariant organic carbon content through the sediment cores reflecting that sediments were dominated by the least reactive components of marine and terrestrial organic matter, i.e., refractory organic marine and terrestrial organic carbon (Magen et al., 2010). Taking into account a maximum overestimation of 20% in our TOC from the upper sediments, this would result in an increase of 4 to 12% maximum on the terrestrial contributions provided in Table 13. Therefore, we considered that sampling depths should not be the main reason for the observed differences among our samples and those from previous work.

Also, the reviewer says that the fossil component estimated in our study is much higher than those from earlier results, but this is not the case.

According to these arguments, we have accordingly amended and simplified the paragraph as:

*Compared to the study of Belicka et al, (2004), the carbon content of our sediments could have been overestimated by the relatively higher contribution of labile components due to the sampling of only the topmost layer (few mm). However, when taking into account a maximum overestimation of 20% in the TOC from our upper sediments, this would result in an increase of the terrestrial contribution of only 4 to 12%. Therefore more plausible reasons for the decrease of the terrestrial contribution in recent sediments are that the annual discharge of the Mackenzie river has actually decreased in the last years/decades (Durantou et al., 2012, this issue) and that primary production over the Canadian Beaufort Shelf has increased during the last decade.*

**Reviewer: The abstract should stress the fact that only surface sediments were sampled (in contrast to earlier studies?)**

**Reply**: This is already mentioned in the Abstract (L-4) and as it has been discussed before, we believe that there is no need to stress it particularly in the abstract.

**Reviewer: Page 13927 L17: specify for which area this production rate relates to.**

**Reply**: The value of ~250 Mt/year was for all the Arctic Ocean. Now, we have just focused on the Mackenzie shelf and delta and we changed accordingly the value to the concerned area:

*Marine organic carbon from primary and secondary production has been estimated at ~ 3.3 Mt C/year for the Mackenzie shelf/delta, but a large fraction of this marine carbon seems to be rapidly recycled in both the water column and the sediment/water interface (Macdonald et al., 1998).*

**Reviewer: Materials and methods: should describe how the CO2 aq data in Table 2 were obtained. Dito for nutrient concentrations etc. reported in Table 2.**

**Reply**: We have now included the required description with their appropriate references:

*"The other auxiliary parameters corresponding to the suspended particulate matter samples (Table 2) were obtained from the MALINA database where data and methods are fully described. Briefly,*

*temperature, pressure and salinity were measured using a Seabird Fastcast SBE-49. Suspended particulate matter (SPM) was obtained following the method described in Doxaran et al., 2012, this issue. Total Chl a was obtained by using the method described in Ras et al. (2008). Nutrient concentrations (nitrate, phosphate and silicate) were determined onboard using the methods described in Raimbault et al., (2008). The dissolved $CO_2$ concentration was derived from alkalinity, pH, temperature, salinity and the concentrations of silicate and phosphate using the CO2SYS program developed for $CO_2$ system (Lewis and Wallace, 1998). Total alkalinity ($A_T$) of water samples was measured by open-cell potentiometric titration (Mucci et al., 2010) and pH measurements on board were measured as described in Lansard, et al. (2012).*

*Doxaran, D., Ehn, J., Belanger, S., Matsuoka, A., Hooker, S. and Babin, M.: Optical characterisation of suspended particles in the Mackenzie River plume (Canadian Arctic Ocean) and implications for ocean colour remote sensing, Biogeosciences, 9, 3213-3229, 10.5194/bg-9-3213-2012, 2012.*

*Lansard, B., Mucci, A., Miller, L.A., Macdonald, R.W. and Gratton, Y.: Seasonal variability of water mass distribution in the southeastern Beaufort Sea determined by total alkalinity and $\delta^{18}O$, J. Geophys. Res., 117, C03003, 2012.*

*Lewis, E., and Wallace, D. W. R.: Program Developed for $CO_2$ System Calculations. ORNL/CDIAC-105. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, 1998.*

*Mucci, A., Lansard, B. Miller, L. A. and Papakyriakou T.: CO2 fluxes across the air-sea interface in the southeastern Beaufort Sea: Ice-free period, J. Geophys. Res., 115(C04003), DOI: 10.1029/2009JC005330, 2010.*

*Raimbault, P., Garcia, N. and Cerutti, F.: Distribution of inorganic and organic nutrients in the South Pacific Ocean − evidence for long-term accumulation of organic matter in nitrogen-depleted waters, Biogeosciences, 5, 281, 2008.*

*Ras, J., Claustre, H. and Uitz, J.: Spatial variability of phytoplankton pigment distributions in the Subtropical South Pacific Ocean: comparison between in situ and predicted data, Biogeosciences, 5, 353, 2008.*

**Reviewer: P13932 L15-16: specify if data from peaks lower than 0.5V are also included (or omitted) and if included, provide arguments against a possible bias in the d13C data**

**Reply:** We have taken into account this comment and we have modified the paragraph accordingly:

*"Most of the values reported here correspond to the $\delta^{13}C$ values of peak abundances higher than 0.5 V (m/z 44) where the standard deviation (S.D) was comparable to the instrument specifications (0.5‰). We also present some $\delta^{13}C$ values of peak abundances ≥0.3 V and ≤0.5 V with slightly higher variability (S.D.<2‰), which was validated by standards within this range.*

**Reviewer: P13933 L9-11: could this pattern also results from a mixture of different components with contrasting n-alkane patterns?**

**Reply**: The pattern we observed with the n-alkane profiles from $C_{23}$ to $C_{33}$ with no odd/even predominance (CPI~1) is mainly associated to a fossil component. However, some bacteria and diatoms producing even carbon-numbered n-alkanes below n-C22 might also synthesize n-alkanes with no carbon predominance in the n-C23-n-C34 range (Grimalt et al., 1988, Volkman et al., 1980). According to this point, we have included also the microbial sources, but the fact that we did not detect the other major compounds belonging to the short-chain alkanes makes this source less plausible:

*"All marine suspended particulate samples except for the most superficial one at 3 m depth showed traces of n-alkanes from $C_{23}$ to $C_{33}$ with no odd/even predominance (CPI~1), thus indicating the fossil component or microbial derived hydrocarbons (Grimalt et al., 1988,Volkman et al., 1980).*

*Grimalt, J.O., Torras, E. and Albaigés, J.: Bacterial reworking of sedimentary lipids during sample storage, Organic Geochemistry, 13, 741-746, http://dx.doi.org/10.1016/0146-6380(88)90096-4, 1988.*

*Volkman, J.K., Johns, R.B., Gillan, F.T., Perry, G.J. and Bavor Jr, H.J.: Microbial lipids of an intertidal sediment- I. Fatty acids and hydrocarbons, Geochimica et Cosmochimica Acta, 44, 1133-1143, http://dx.doi.org/10.1016/0016-7037(80)90067-8, 1980.*

**Reviewer: Results on sterol composition: unless I missed something it seems that no brassicasterol was detected, correct? Is this not unexpected given the contribution of diatoms mentioned elsewhere?**

**Reply:** Brassicasterol corresponds to 24-methylcholesta-5,22(*E*)-dien-3β-ol ($C_{28}\Delta^{5,22}$) which was certainly among the major sterols in our samples. To avoid this misleading, in the revised version we have also included the common name of brassicasterol next to its formal name, 24-methylcholesta-5,22(*E*)-dien-3β-ol as:

*"Sterol distribution in suspended particles from the deep chlorophyll maximum was dominated by 27-nor-24-methylcholesta-5,22(E)-dien-3β-ol (nor$C_{27}\Delta^{5,22}$), 24-methylcholesta-5,22(E)-dien-3β-ol ($C_{28}\Delta^{5,22}$, brassicasterol), 24-methylcholesta-5,24(28)-dien-3β-ol ($C_{28}\Delta^{5,24(28)}$) and the Z isomer of fucosterol (isofucosterol, 24-ethylcholesta-5,24(28)(Z)-dien-3β-ol; $C_{29}\Delta^{5,24(28)}$)".*

**Reviewer: P 13938 L12: alkanine: should be alkaline**

**Reply**: Thank you. Done

**Reviewer: P 13938 L15: provide a reference here for the C3 range of n-alkanes (eg. Papers by F. Rommerskirchen etc). The numbers cited seem somewhat on the high side?**

**Reply:** According to this comment, we have inserted the appropriate references and slightly modified the sentence as:

*"The $C_{27}$ and $C_{29}$ homologues were slightly lighter showing mean $\delta^{13}C$ values of -30 and -30.5 ‰, respectively, which fell into the high range of $C_3$ vascular plants (-29 to-39 ‰; Collister et al., 1994, Chikaraishi and Naraoka, 2003; Bi et al., 2005)".*

*Bi, X., Sheng, G., Liu, X., Li, C. and Fu, J.: Molecular and carbon and hydrogen isotopic composition of n-alkanes in plant leaf waxes, Organic Geochemistry, 36, 1405-1417, 2005.*

*Chikaraishi, Y. and Naraoka, H.: Compound-specific δD-$\delta^{13}C$ analyses of n-alkanes extracted from terrestrial and aquatic plants, Phytochemistry, 63, 361-371, 2003.*

*Collister, J.W., Rieley, G., Stern, B., Eglinton, G. and Fry, B.: Compound-specific $d^{13}C$ analyses of leaf lipids from plants with differing carbon dioxide metabolisms, Organic Geochemistry, 21, 619-627, 1994.*

**Reviewer: P 13938 L20 "sea ice proxy": be specific: marker for sea ice algae**

**Reply**: We agree and it has been changed

**Reviewer: P 13939 L13: provide a reference supporting the specificity of this marker.**

**Reply**: We have added the requested reference:

*Han, J. and Calvin, M.: Hydrocarbon Distribution of Algae and Bacteria, and Microbiological Activity in Sediments, PNAS, 64, 436-443, 10.1073/pnas.64.2.436, 1969.*

**Reviewer: P 13940 L6-9: Should look not only at d13C signatures of the markers, but also their relative concentrations in the sources may differ – so d13C in the "mixture" may be biased towards one source if it has higher concentrations.**

**Reply**: We agree with the reviewer for the n-alkane compounds, since their pattern indicates a mixture of long-chain n-alkanes derived from fossil and terrestrial plants. However, for the long chain n-alcohols, we have only the terrestrial plants contribution and their $\delta^{13}C$ values are usually in the same range as n-alkanes (Chikaraishi and Naraoka, 2007). We have slightly modified the paragraph to include this comment.

*"Although lignin and $\delta^{13}C$ data indicated that the major source of terrigenous material in this area consists of non-woody, $C_3$ angiosperm vascular plant vegetation derived from the tussock vegetation (sedges, cotton grass) (Goñi et al., 2000; Naidu et al., 2000), our relatively enriched n-alkanes and n-alkanols $\delta^{13}C$ values suggest that they are derived from gymnosperms. Angiosperms usually have long-chain n-alkyl compounds depleted in $^{13}C$ compared to gymnosperms, with n-alkane $\delta^{13}C$ values of -36 ‰ for angiosperms and -31.6‰ for gymnosperms (Chikaraishi and Naraoka, 2003, Chikaraishi and Naraoka, 2007)".*

**Reviewer: P 13940 L11-14: mention d13C values for the LCFA's here. Can these learn us something on the relative contribution of higher/lower plants (trees vs. mosses etc)**
**Reply:** We have now added the requested $\delta^{13}C$ values for the LCFA (*-31 ‰):*
*"In addition to this aquatic production, the terrestrial component represented by the LCFA (n-$C_{22}$ to n-$C_{28}$) with $\delta^{13}C$ values of -31 ‰ confirms again the $C_3$ higher plants contribution".*
Unfortunately, the $\delta^{13}C$ values of C3-lower plants and higher plants can overlap and therefore $\delta^{13}C$ can not be source specific (Vogts et al., 2009). For that, the molecular contribution of n-C23 and n-C25 alkanes are a useful chemotaxonomic fingerprint for C3-lower plants, such as the Sphagnum moss (Brader et al., 2010).

Brader, A.V., van Winden, J.F., Bohncke, S.J.P., Beets, C.J., Reichart, G.-J. and de Leeuw, J.W.: Fractionation of hydrogen, oxygen and carbon isotopes in n-alkanes and cellulose of three Sphagnum species, Organic Geochemistry, 41, 1277-1284, 2010.

Vogts, A., Moossen, H., Rommerskirchen, F. and Rullkötter, J.: Distribution patterns and stable carbon isotopic composition of alkanes and alkan-1-ols from plant waxes of African rain forest and savanna C3 species, Organic Geochemistry, 40, 1037, 2009.

**Reviewer: Statement on P13941 L4-6 is overall not very well argumented.**
**Reply:** We have now rephrased the statement as:
*" Overall, the lipid composition of the Mackenzie river water was characterized by a major fossil component, important amounts of algal material dominated by diatoms and a terrestrial component mainly derived from the C3 emergent plants" .*
We have also added a sentence within this section to highlight the dominance of the fossil contribution:
*'This latter fossil signature is enhanced by the presence of a considerable amount of UCM, typical of fossil/petrogenic sources (Table 3). A confirmation of the fossil source was also obtained by mass fragmentograms (m/z191, not presented here), which exhibited a series of extended C32-C35 hopanes characteristic of oil-derived hydrocarbons".*

**Reviewer: Page 13942 L5: more enriched than ?**
**Reply**: We have rephrased and correct the sentence for clarity:
*"The most enriched δ13C values of phytol (Table 11) were measured at 3 and 60 m depths at sites 130 and 345, respectively, suggesting the highest growth rates".*

**Reviewer: Page 13942 L20: a bulk value of -28 per mil would still not result in values as low as -42.5 per mil in biomarkers ? Or provide literature data on Dd values for relevant markers to demonstrate that such large shifts are reasonable.**
**Reply**: We have added a new paragraph to demonstrate the large shifts between algal biomass and lipid biomarkers:
*"Also, the large isotopic offsets between algal biomass and eukaryotic lipid biomarkers ranging from -2 to 12 ‰ (Schouten et al., 1998, Hayes, 2001) are accounting for the relative depleted $\delta^{13}C$ of the biomarkers.*

Schouten, S., Klein Breteler, W.C.M., Blokker, P., Schogt, N., C. Rijpstra, W.I., Grice, K., Baas, M. and Sinninghe Damste, J.S.: Biosynthetic effects on the stable carbon isotopic compositions

of algal lipids: Implications for deciphering the carbon isotopic biomarker record, Geochim. Cosmochim. Ac., 62, 1397-1406, 1998.

Hayes, J.M., Fractionation of the isotopes of carbon and hydrogen in biosynthetic processes. In: Valley, J.W. and Cole, D.R., Editors, 2001. *Stable Isotope Geochemistry, Reviews in Mineralogy and Geochemistry* 43, Mineralogical Society of America, pp. 225–278, 2001.

**Reviewer: Page 13947 L 6: 24 per mil: -24 per mil.**
**Reply**: Thank you! It is done.