***Responses to* Referee #4*'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 #4 to our manuscript, which resulted in significant improvements. Below are given, the changes made in response to his comments and questions.

Reviewer: The study builds on several previous investigations in the region; including some that analyzed a subset of the biomarkers that were combined in the current work, and still others that applied stable and radioactive carbon isotopes. The authors should state clearly why this study improves upon previous investigations, and what new insight it offers.

The multitude of data while impressive is poorly presented and discussed. For example, statements such as "flagellates are the main contributor to SPM" or "reflecting post bloom conditions," or "fossil carbon is the main contributor to SPM," appeared in the text before any evidence/justification in support of such statements was provided. This gives the impression that these lipid distribution data are not being interpreted objectively. In my opinion the major shortcoming of the paper is that it lacks a clear statement explicitly addressing the assignment of certain classes of lipids to either a particular source or a process. For example, at the beginning of the discussion the authors could include a schematic, table etc that lists each relevant biomarker and its particular purported source. This table would be accompanied in the text by a description of the evidence (from the current study and previous studies) that supports each source assignment and the limitations of each assignment. ["In this paper we quantified the fossil contribution to SPM by integrating the area under the UCM (a region that occupied between x and y temperature range in the gas chromatogram). We assumed that everything in the UCM was derived from fossil organic matter, this assumption is valid because etc etc. Flagellate production was identified when the presence of 22:6 > 22:5 and 18:1 etc etc. Fresh diatoms were identified as…..We use "x-suite" of lipids to assign the detrital or refractory algal contribution…]. The remaining discussion could then be organized around this initial section to make the discussion more coherent.

My overall recommendation is to consider the following:

(1) What is the main (new) contribution of this study?

(2) Results and discussion points are mixed in the results section. This section should simply report data.

(3) A section that assigns particular lipids as proxies for particular source contributions should be included at the beginning of the discussion.

Reply: We have taken in account all 3 recommendations:

Concerning the (1), we have modified the introduction to better describe the new contribution of our study to the area:

"Several studies from the 1980's have partially characterized the Mackenzie-Beaufort Sea system using specific molecular compounds (Yunker et al., 1995; Yunker et al., 2002; Yunker et al., 2005; Yunker et al., 2011; Belicka et al., 2004; Goñi et al., 2000; Goñi et al., 2005, Drenzek et al., 2007). In particular, these studies all reported data on lipid biomarkers which are well suited to evaluate the supply of terrigenous organic matter (Bouloubassi et al., 1997, Saliot et al., 2002), but only a few have combined these analyses with compound-specific isotope determinations (Drenzek et al., 2007; Goñi et al., 2005). The approach using the $\delta^{13}C$ values of individual compounds is relevant since the isotope data provide additional evidence supporting the proposed origins of the biomarkers, and in

certain cases, this combination is essential for an accurate determination of the origin of the biomarkers. The present study combines a comprehensive list of biomarkers and compound-specific carbon isotope analysis on suspended particulate matter (SPM) and surface sediments collected in summer 2009. Here, the coupled data was used in the southeast Beaufort Sea to better understand the sources of carbon, the transport and the fate of organic matter from the Mackenzie river to the marine off-shore waters and surface sediments.. 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 and compare the relative importance of different organic pools, such as fresh algal, refractory algal, fossil, C3 terrestrial plants, bacterial and zooplankton material between the river SPM, marine off-shore SPM and surface sediments. Additionally, a quantitative approach comparing the concentrations of allocthonous 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".

Concerning the (2) recommendation, we have moved from the results section to the discussion section, all concerned statements and paragraphs related with discussion issues

Concerning the (3) recommendation, we have now introduced a new section under materials and methods (2.5. Background on lipid biomarker origins) to describe the relevant biomarkers used in our study with their main sources:

2.5. Background on lipid biomarker origins

Hydrocarbons from both natural and anthropogenic sources are very common in the environment. Among biogenic hydrocarbons, the n-alkanes exhibit a strong odd carbon-number predominance in living organisms where the carbon-number distributions vary depending on the source organism. Higher terrestrial plants are dominated by the long-chain (C_{25}-C_{33}) n-alkanes, lower terrestrial plants by the medium-chain (C_{23}-C_{25}) n-alkanes and aquatic algae by the short-chain n-alkanes (C_{17}-C_{21}) (Volkman et al., 1992, Baas et al., 2000). Other biogenic hydrocarbons include the polyunsaturated straight-chain alkenes, n-C21:6 and related isomers (n-C21:5, n-C21:4) derived from autotrophic marine and freshwater plankton (Volkman et al., 1992), the C_{25} monounsaturated hydrocarbon (IP_{25}) used as a sea-ice algae proxy (Belt et al., 2007) and retene, a diagenetic polycyclic aromatic hydrocarbon (PAH) from higher plants (Simoneit, 1977). In contrast to these biogenic sources, petroleum sources usually show a wide distribution range of n-alkanes with no predominance of odd or even carbon numbers. We use the carbon preference index (CPI) defined as the sum of the odd carbon-numbered alkanes to the sum of the even carbon-numbered alkanes to characterize the sources of n-alkanes (Bray and Evans, 1961). In fact, extant plants typically show CPIs > 5 (Rieley et al., 1991) while petroleum-derived n-alkanes have CPI values around 1 (Wang et al., 2003). Whenever both sources are mixed, terrestrial wax n-alkanes (C_{25}-C_{31}) are calculated by subtracting the fossil contribution resulting from the average of the next higher and lower even carbon numbered homologues as: Wax n-C = $[C_n]$ - 0.5$[C_{(n+1)} + C_{(n-1)}]$ (Simoneit et al., 1990). The presence of an unresolved complex mixture (UCM) defined as a hump in the hydrocarbon chromatograms is also a diagnostic tool of petroleum/fossil sources (Volkman et al., 1992).

Among alcohols, phytol is a marker for phototrophic organisms (Baker and Louda, 1983), short-chain (n-C_{14}-C_{20}) alcohols (SCOH) and short-chain monounsaturated alcohols (SCMUOH) might have multiple microbial sources (Robinson et al., 1984b), long-chain (n-C_{22}-C_{30}) even carbon numbered n-alcohols (LCOH) are markers of terrestrial higher plant waxes (Rieley et al., 1991), and long-chain (C_{20}-C_{24}) monounsaturated fatty alcohols (LCMUOH), biomarkers typical of zooplankton (Lee et al, 2006). Finally, α-amyrin (olean-12-en-3α-ol), is a specific triterpenoid for angiosperms and also present in peat (Hernes and Hedges, 2004).

Sterols occur in all eukaryotic organisms and the specificity of these compounds for different phytoplankton groups and vascular plants is well known (Volkman, 1986, 2003). The 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 24-ethylcholest-5-en-3β-ol (sitosterol, $C_{29}\Delta^{5}$) are common lipids in diatoms (Barrett et al., 1995, Volkman et al., 1998); $C_{28}\Delta^{5,24(28)}$ and the Z isomer of fucosterol (isofucosterol, 24-ethylcholesta-5,24(28)(Z)-dien-3β-ol; $C_{29}\Delta^{5,24(28)}$) is typical of prasinophytes (Volkman et al., 1994). Dinosterol (4α-23,24-trimethylcholest-22(E)-en-3β-ol ($C_{30}\Delta^{22}$) is commonly used as a biomarker for

dinoflagellates (Robinson et al., 1994a) and 27-nor-24-methylcholesta-5,22(E)-dien-3β-ol (norC$_{27}\Delta^{5,22}$) sterol together with C$_{28}\Delta^{5,22}$ predominate in the marine dinoflagellate Gymnodinium simplex (Goad and Withers, 1982) and in marine invertebrates (Volkman et al., 1981). Cholest-5-en-3β-ol (cholesterol, C$_{27}\Delta^{5}$) is considered a typical marker for zooplankton derived organic matter supply, but it is also present in many classes of algae (Harvey et al., 1987). The 24-methylcholesta-5-en-3β-ol (C$_{28}\Delta^{5}$); 24-ethylcholesta-5,22(E)-dien-3β-ol (C$_{29}\Delta^{5,22}$) and sitosterol have often been considered as terrestrial markers but they are also produced by both phytoplankton and aquatic plants (e.g. Volkman 1986, 2003).

Fatty acids are among the most abundant lipid biomarkers. Different group classes are distinguishable: The linearly saturated are used to separate marine from terrigenous sources through short chain C$_{14}$-C$_{18}$ (SCFA) and long chain C$_{22}$-C$_{30}$ (LCFA), respectively (Grimalt and Albaigés, 1990). Branched fatty acids (BrFA), composed of iso and anteiso branched compounds with odd chain lengths (e.g. C$_{15}$, C$_{17}$) are used as bacterial markers (Volkman et al., 1980). Vaccenic acid (C18:1ω7) is considered to be an indicator of bacterial input when 18:1ω9/18:1ω7 <1. However when this isomer ratio >1 then it suggests a dominant phytoplanktonic source (Thoumelin et al., 1997). Monounsaturated long-chain C$_{22}$-C$_{30}$ (LCMUFA), are typical of zooplankton (Lee et al., 2006). Polyunsaturated fatty acids (PUFA) are used as plankton biomarkers. Their presence indicates a fresh algal input because they are not resistant to degradation processes. Among the PUFA, the C18 are abundant in flagellates (green algae and cryptomonads), the C20:5 predominates in many diatom species and 22:6w3 dominates in dinoflagellates and flagellates (crytomonads) (Dalsgaard et al., 2003).

We estimated the relative contributions of OM constituents by grouping the different molecular lipid biomarkers into their different sources (fossil, algal, zooplankton, bacterial and terrestrial). We also took into account the different lability of the molecules to discern between fresh/labile and refractory/detrital algal. We assigned PUFA, phytol, IP$_{25}$, n-C21:6, C$_{28}\Delta^{5,24(28)}$, C$_{29}\Delta^{5,24(28)}$ within the fresh/algal component because these molecules are more labile bearing double bonds or oxygenated functionalities compared to the higher stability of the rest of biomarkers studied. These criteria yielded the following components: fossil (UCM, and petroleum hydrocarbons), fresh/labile algal (PUFA, phytol, IP$_{25}$, n-C21:6, C$_{28}\Delta^{5,24(28)}$, C$_{29}\Delta^{5,24(28)}$), refractory/detrital algal (SCFA, SCMUFA, rest of sterols, biogenic alkanes, SCOH, SCMUOH), zooplankton (LCMUFA, LCMUOH), bacterial (branched FA) and C$_3$ terrestrial plants (LCFA, LCOH, wax n-alkanes). 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). Hence, only relative changes among the stations and depths were evaluated.

Specific Comments.

Reviewer: P.13933 Lines 5-10. Is this discussion of CPI being ~ 1 based on what is shown in Table 3? I am not as familiar with this literature, but these data suggest that there is some odd preference. How accurate is the terrestrial n-alkane calculation?

Reply: Yes, the discussion is based on the ratio of odd- to even carbon *n*-alkanes (CPI) data shown in Table 3. In fact, extant plants typically show n-alkanes CPIs > 5 (Rieley et al., 1991) while petroleum-derived n-alkanes have essentially no odd-over-even carbon-number predominance with a CPI of 1. Therefore the CPI values ~1 obtained in the suspended particles samples indicates that there is no contribution from higher plants. As the concentration levels of n-alkanes in the marine suspended particles were very low and near the detection limit, the terrestrial contribution in these samples were below the detection limit. In contrast, in the freshwater sample and sediment samples, their peak areas were significant to integrate accurately the terrestrial n-alkane contribution.

Reviewer: Line 15. UCM used as a fossil indicator? Be specific.

Reply: Unresolved complex mixture (UCM) or "hump' of hydrocarbons is a common feature of gas chromatograms of crude oils and related products, and it is especially pronounced for weathered and biodegraded oils and oil-polluted sediment extracts. Therefore, UCM is usually linked to petroleum/fossil sources.

Reviewer: Line 17 – Does this discussion regarding the abundance of long-chain plant waxes pertain to the calculation in line 8? Or does the abundance reflect what was actually measured via GC-MS.

Reply: The abundance of long-chain plant waxes concerning discussion on line-17 reflect what was actually measured by GC.

Reviewer: In general it would be helpful to clean up this section. I would first report the abundance of n-alkanes as measured directly – this is what would be normally found in a results sections. The authors can then state their assumptions for "correcting" the data for a fossil contribution, and then report those abundance data separately. The way it is currently written I can't tell whether the calculated and measured data are both being discussed.

Reply: According to the reviewer's suggestion, we have now modified the presentation of the hydrocarbon results, introducing only the quantitative data obtained directly by GC. We have removed the statement concerning the calculations on wax n-alkanes, because it has already been included in the new section on "Background on lipid biomarkers origins".

Reviewer: Also, why don't the authors simply subtract the UCM contribution (e.g., a baseline subtraction) from each n-alkane peak rather than assume that a petroleum source is contributing the entire n-alkane series. I apologize for my limited familiarity with this topic, but it seems to me that the authors are using previous studies to assume that a fossil component is present. This is then extended to interpreting the GC-MS data.

Reply: We believe that the reviewer misleads the contribution of petroleum and biogenic sources: First, hydrocarbon complex mixtures comprised resolved hydrocarbons (e.g. n-alkanes) which can be individually quantified and the unresolved complex mixture (UCM) which shows up as a baseline rise in the gas chromatogram of total hydrocarbons. Resolved components, such as n-alkanes, are integrated at the baseline of the UCM hump, which means that the baseline contribution of UCM is already subtracted for each n-alkane individual peak. To calculate the unresolved compounds (UCM), we trace the area underneath the resolved compounds and above the column bleed signal. Second, the quantified resolved n-alkanes might derive from fossil sources and also from biogenic sources. In order to discern these sources, the distribution of odd and even n-alkanes or the carbon preference index (CPI), which is a ratio of odd to even chain lengths gives information on their sources. In petroleum, the distribution of odd and even n-alkanes is uniform and the carbon preference index (CPI) is close to 1. In contrast, terrestrial plant waxes contain the odd numbered alkanes in the C23-C33 region exhibiting CPI> 5. Therefore within one individual n-alkane, we might have overlapped both sources and this is why calculation of the terrestrial wax n-alkanes was calculated by subtraction of the average of the next higher and lower even carbon numbered homologues. We hope that this explanation clarifies the concerns of the reviewer.

Reviewer: p.13936. Line 11. It is not accurate to attribute all fatty acids listed here to only a flagellate source. Just as with hydrocarbons for example, multiple sources can contribute many of these fatty acids. The authors should identify the suite of fatty acids that they think are indicative of flagellates (22:6, 18:4?). I see that they explain this later on p. 13941. They need to either move this explanation up to p13936 or remove the source attribution in the results section and simply report the ID and concentration of fatty acids found in each sample.

Reply: As suggested, we have removed the source attribution from the results section and moved to the discussion.

Reviewer: p.13937 – line 6. The conclusion that positive PC1 associated biomarkers are reflective of refractory marine and terrestrial OM seems tenuous to me. There is not much discussion in preceding sections that contributes to this conclusion. Could it be indicative of equally fresh secondary processes? In fact the attribution of +ve PC1 sources is not based on lipid composition but what comes later in the paragraph – that +ve PCI samples are from deeper depths. It seems that this discussion is backwards. I.e Line 14 -21 should come first.

Reply: The positive PC1 was associated to phytodetrital and terrestrial OM based on the presence of refractory biomarkers (both marine and terrestrial), and in contrast to the labile biomarkers which represented the fresh phytoplanktonic component in the negative PC1. In another words, we could say that the positive PC1 represents the contribution of heterotrophic (zooplankton and microbial) degradation products together with the terrestrial component represented by LCFA, whereas the negative PC1 represents the contribution of autotrophic organisms represented by fresh phytoplankton. From the viewpoint of an organic chemist, the attribution of the positive PC1 sources is consistent with the lipid composition, and after the introduction of the new section on "background on lipid biomarkers origins", we believe that there is no reason to backward the discussion. However, we have rewritten the paragraph to make it more logical:

"*Fig. 2 summarizes the PCA results. The plot (2A) distinguishes two groups which are characterized by typical factor loadings of their variables (2B). Phytol, nor$C_{27}\Delta^{5,22}$ sterol, C18 PUFA and C22:6ω3 representing fresh phytoplankton dominated by flagellates and dinoflagellates showed all negative factor loadings for PC1. The rest of sterols together with the short chain monounsaturated fatty acids (SCMUFA), the branched FA, the long-chain n-alcohols and FA, indicating refractory material from both marine and terrestrial sources showed all positive loadings. Similarly, the loadings for PC2 were positive for long-chain n-alcohols and n-fatty acids, branched FA, LCMUOH (C20-C24), C16:4ω1 and phytanic acid, indicating zooplanktonic, terrestrial, diatom and bacterial sources. From these loadings the two clusters in the plot represent a group with high negative PC1 loadings (fresh phytoplankton component) and a group with a high positive PC1 contribution (marine and terrestrial refractory material). The first group represents suspended particles from the DCM (60-85 m), except for the station 640-70 and the second group all the deeper suspended particles (≥ 100 m) and the superficial 640-70. Other scattered and particular samples included the Mackenzie River, with high contribution of terrestrial and refractory material; the 240-200 with high contribution of zooplankton material, the 130-3 with some refractory and diatom material, and the 135-40 with very low phytoplankton marker concentrations".*

Reviewer: Line 17-21. Here the authors point out samples that don't fit into their previously discussed trends. Instead of identifying the lipids that make these samples unique (as would be expected in a cataloguing of results) the authors attribute sources/processes to these samples without explicitly stating their reasons for doing so. The PCA does not identify sources, it simply examines similarities and differences in lipid "profiles."

Reply: We identified and explain the singularities of the samples scattered in the PCA based on the data and statements already presented in the preceding results sections. We also consider that the PCA provides a summary of the data, providing clusters of samples and exploring the interactions of the variables. We agree that PCA does not directly identify sources but provides the correlations with the variables, which are then interpreted by the expert in the area.

Reviewer: p.13938 The d13C Results section demonstrates some of the difficulties that I experienced when trying to decipher this paper. The first two paragraphs present results on the extremely depleted d13C value of certain lipids in marine SPM. However, on line 16 the authors discount the possibility of aquatic plant input to odd, mid-chain n-alkanes because d13C values are depleted (-30 and -31 per mil in this case), and such a depletion is indicative of terrestrial origin (not aquatic origin). Given the source

ambiguity of 13C depleted isotope signatures – a fact the authors themselves point out several times – if it not correct to use depleted isotopic values in one case to say that only terrestrial inputs are relevant, and in another case to say that in fact, an aquatic source with an unusually depleted signature is implicated. I am sure the authors have a good reason for making this statement, but the reasoning has to be stated more explicitly.

Reply: We discount the possibility of C3 aquatic plant input for the odd, mid-chain n-alkanes because 13C values of submerged aquatic plants have usually more enriched values and similar values to C4 plants (Chikaraishi and Naraoka, 2005). In order to support our statement, we have now added a reference for that.

Chikaraishi, Y. and Naraoka, H.: δ13C and δD identification of sources of lipid biomarkers in sediments of Lake Haruna (Japan), Geochimica et Cosmochimica Acta, 69, 3285-3297, 2005.

Reviewer: p.13938 .Again on line 23, the authors state that heavy isotope values for IP25 are entirely consistent with OM of planktonic origin (e.g. phytol). But it appears from the data that the values are only consistent with phytol in the sediments and not all phytol. Incidentally, "indistinguishable" appears to assume that there is no difference between a value of -17 per mil and -27 per mil (line 6).

Reply: The reviewer misunderstood this paragraph. Our 13C values of IP25 in sediments are similar to those reported for the same compound in sediments of the Franklin Bay (Belt et al., 2008) and their enriched values (-17 to -21 per mil) are very different (distinguishable) from those of the OM of planktonic origin (phytol: -27 to -29 per mil). This is why the isotopic values of biomarkers derived from sea ice algae are very unique (enriched) and different from planktonic biomarkers from the water column.

Reviewer: Also, it is curious that only a subset of data that appears in the discussion section is directly presented in the results - e.g., the isotopically depleted c-17 n-alkane is the first topic tackled in the discussion, yet it is absent from the results (except in the table). Again, this speaks to lack of coherence.

Reply: We agree that in the result section 3.6, we did not present the 13C of hydrocarbons from the Mackenzie River since they were presented and discussed together with their molecular abundance (Fig. 3A) in section 4.1. According to the reviewer's concern, we have now specified in the text that carbon isotope ratios of selected lipid biomarkers are also displayed together with their molecular abundances in Figures 3, 4, 6 and 9.

"Additional 13C data is also displayed together with their molecular abundances in Figures 3, 4, 6 and 9"

Discussion

Reviewer: p.13939. Line 14. Which lipids are considered in the "fossil alkane" category and where are these data presented? Does a value or -32.7 really contrast with the -30 per mil figure?

Reply: As it has already been explained in previous questions related to hydrocarbon sources, the fossil n-alkanes show a uniform distribution of odd and even n-alkanes with a carbon preference index (CPI) close to 1. This data profile is shown, as explained in the text, in Figure 3A, where we can see the fossil contribution (odd+ even n-alkanes) overlapped with the biogenic derived n-alkanes (odd n-alkanes), such as, n-C17 (algal) and C25, C27, C29 (from terrestrial waxes). From Fig.3, it is obvious that the 13C value of n-C17 (-32.7) is different from those obtained for the fossil n-alkanes (even n-alkanes). To make the text more clear, we have now specified "even fossil n-alkanes" in the text.

"*Its δ13C value of -32.7 ‰ contrasts with those measured for the even n-alkanes, which are fossil derived ($\delta^{13}C$ of ~ -30 ‰)*".

Reviewer: p. 13941 - Last paragraph of section 4.1. The preceding section did not allude to the dominance of fossil lipid at all. How did the authors arrive at this conclusion? Is this based on n-alkane concentrations? Isotope values? As far as I can tell n-alkane isotope values are not unique and concentrations are quite low compared to other lipids. Based on what is said later the authors must be referring to the "size" of the UCM "peak." Is the UCM a definitive indicator of fossil inputs in aquatic SPM or is it simply an indicator of sample complexity. I would venture to guess that without some other indicator of high petroleum/fossil input it is difficult to definitively assign the UCM to fossil OM. If nothing else, some qualifications or justifications should be provided. It was frustrating to review this paper for exactly this reason. I found myself having to jump from one section to another over and over again to figure out whether I had missed something.

Reply: We agree with the reviewer that, we did not emphasize the high contribution of fossil sources in section 4.1. Now we have modified the text to include the importance of the UCM concentrations and also supported by the presence of hopanes which are also characteristic of fossil sources:

A higher abundance and lower $\delta^{13}C$ values of the odd chain alkanes compared to the even alkanes can also be observed. This highlights the terrestrial contribution of the odd n-alkanes (n-C27, n-C29, n-C31, with $\delta^{13}C$ values of -31 ‰), overlapping the petroleum-derived alkanes. 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: p.13942 – Why is there a big difference between SPM samples and the upper 5mm of sediments in terms of phytol-d13C?

Reply: The difference of $\delta^{13}C$ values of phytol between SPM samples and the sediments is certainly accounted for by differences in growth rates between phytoplankton in the water column and that already sedimented in the upper sediment. In fact, periods of high algal growth rates are typically associated with 13C enrichment because carbon isotope fractionation decreases as the rate of fixation relative to the supply of CO2 across the membrane increases. Therefore, our enriched 13C values in sediments reflects the already sedimented phytoplankton bloom, whereas the depleted 13C values in the water column indicates the post bloom conditions.

Reviewer: p.13943 line 18. Here is another one of those statements that seemingly come from nowhere – "post bloom conditions" – what is the basis for this statement? Line 20 – if you are in post bloom conditions would CO2 be replete?

Reply: The lipid composition in the SPM is dominated by flagellates and dinoflagellates markers and together with the low 13C values seems to indicate the post bloom conditions, which were also confirmed by microscopic counts. In post-bloom conditions, the water column might be replete with CO2 if mineralization in the water has occurred. However, in the text we refer to the commonly repleted concentrations of CO2 that occur in cold waters. We have modified the text to make it more clear:

" Overall, the specific composition of the particulate matter from off-shore waters indicating the importance of dinoflagellates and prasinophytes together with the low phytoplankton biomarker concentrations and low $\delta^{13}C$ suggests post-bloom conditions during the survey. The low $\delta^{13}C$ (Fig. 4, Table 11) might result from the reduced growth rates that favour the assimilation of the lighter isotope and also from the repleted concentrations of CO_2 in the cold waters".

Reviewer: Line 24. Aerosols appear in the discussion for the first time. Is this really an important discussion point? The interpretation may certainly be correct but there is no independent evidence in support of this statement.

Reply: We believe that the particular composition of the upper sample (3m depth), which was the only marine SPM sample evidencing the terrigenous material, merited the discussion referring to the aerosols likely deposited on the ice. As wax particles are easily sloughed off the leaf surfaces by wind, they are found in aerosols from remote ocean areas. Moreover, this atmospheric transport linked to ice melting has been already evidenced in other works, such as that from Pfirman et al. (1995).

"The suspended particulate sample from the upper PML (3m) of site 130 stands out among all other SPM samples. It contains biogenic material dominated by diatoms plus terrigenous material (wax n-alkanes, LCOH, LCFA). A likely explanation for the presence of this material could be the deposition of aerosols on the ice. Plant waxes readily form aerosols and are subject to atmospheric transport. This together with ice melting and subsequent release of particles results in the transfer of terrigenous material from the shelf and land to the offshore waters (Pfirman et al., 1995)''.

Reviewer: p.13944. Line 5. "Higher growth rates at depth compared to DCM." Do you mean higher growth rates for zooplankton? There are some isotope data for alcohols in Figure 4 but there is no depth information here. How different are the values? If the authors are referring to phytoplankton growth rates then I am even more confused as to why growth rates would be higher below the DCM.

Reply: Looking at the 13C values of the phytoplanktonic biomarkers of site 240 (Table 11), we observed more enriched 13C values at 200m depth than at 70m (DCM). These differences in 13C ranging between 2 and 5 per mil indicates that the suspended particles collected at 200m are likely derived from a previous phytoplanktonic bloom developed in the DCM and settling down the water column. As we already explained in previous questions, periods of high algal growth rates are typically associated with 13C enrichment. The fact that the suspended particles at 200m depth contain also high concentration of zooplankton biomarkers indicates high abundance of zooplankton at this depth, and together with the enriched 13C values of the phytoplankton markers at this depth it can be deducted that zooplankton is likely grazing on remnants of phytoplankton produced at high growth rates (or bloom conditions). As phytoplankton is certainly not developing at 200m depth, we have now specified in the manuscript that zooplankton is likely grazing on *remnants* of phytoplankton and not just phytoplankton.

Reviewer: p. 13944, Line 10-13. "herbivorous grazing on phytoplankton." Based on what we know from foodweb studies this should take place, but how is that tied to what your data show? What exactly allows you to draw this conclusion? The presence of both diatom biomarkers and zooplankton biomarkers in suspended POM, at a particular depth, does not necessarily mean there is a connection between the two or does it? Are the authors assuming that diatom biomarkers can only get to depth once they are repackaged by zooplankton grazing? I think these organisms could contribute independently to the sinking flux. Again, it is not outlandish to suggest a connection, but either sticking with the evidence or being more explicit about the conclusion would be more satisfactory. Also, this is not a big deal. I would be more than happy to let one statement like this stand. However, in the case of this paper these seemingly subjective conclusions are relatively commonplace.

Reply: As the reviewer stated correctly, from foodweb studies and even from common sense, we know that the simultaneous presence of predator and prey in nature implies a more than likely occurrence of predation. So the question whether there is a connection is rather rhetoric. Of course, as the reviewer states, both phyto- and zooplankton may independently contribute to sinking flux. This latter question has not been subject of our discussion. We have now adapted the text trying to avoid such confusions:

"All these parameters point out that post-bloom conditions prevailed in the euphotic layer of site-240, whereas the important signal of zooplankton and diatom markers below the euphotic layer gives evidence of the opportunistic behaviour of predators grazing on the sinking flux of remnants of phytoplankton produced during bloom conditions in the euphotic layer."

Reviewer: Line 24. This belongs in section 4.1
Reply: According to the reviewer, we have moved it to section 4.

Reviewer: p.13945 – paragraph starting on Line 9. This is the most coherent and realistic section of the discussion. In fact, I don't think the preceding discussion is really necessary. A slight expansion of this section (to include a brief statement as to why each lipid is assigned to a particular category) would make a better discussion. Alternatively, a general section that assigns each lipid to a source based on composition, other indices, and stable isotopes could precede this section (as I pointed out previously).
Reply: We thank the reviewer for this comment, but we believe that the preceding discussion is worth to keep in order to understand and better constrain the sources of OM in the SPM. Nevertheless, as suggested by the reviewer, we have added the new section on "Background on lipid biomarker origins" summarizing the biomarkers and biochemical indices discussed within the manuscript together with their putative sources.

Reviewer: p.13946 – Line 16-19. Then why do you see such a big difference in d13C values between sediments and the water column?
Reply: As we have already explained, the more enriched 13C values measured in the sediments indicate lipid biomarkers derived from phytoplankton with higher growth rates than those measured during the study from the water column where the 13C values were more depleted. All together suggests again post-bloom conditions in the water column, and ungrazed diatoms derived from the bloom were already deposited on the surface sediment.

Reviewer: p.13946, Line 22-24 I don't understand how these things are connected?
Reply: The fact that the 20:5w3 biomarker, typical of diatoms predominates over the flagellate biomarker (22:6w3) in sediments, together with their more enriched 13C values (higher growth rates) compared to the water column, suggests the sinking of ungrazed diatoms derived from a previous bloom or from ice algae mats released when ice melts (enriched 13C values from sea ice algae). Also the dominance of flagellates in the water column together with their more depleted 13C values indicates the post bloom conditions in the water column.

Reviewer: p.13947. The results of this mass balance were used to inform the discussion about sitosterol in section 4.2. There it was out of place. Again, I reiterate, this makes the paper very hard to follow. Conclusions should only be drawn after they have been empirically (in this case) justified.
Reply: Sitosterol has always been a biomarker commonly associated with terrestrial vegetation but it might be also abundant in phytoplankton. As terrestrial material is generally more refractory, due to the presence of protective lignin structures, than algal material, sources of sitosterol in the suspended particles from the water column might not mirror the sources of sitosterol in the sediments due to the different degradability of the biomarkers depending on the source (terrestrial or algal). This is why the mass balance used for sediments in section 4.3, should not be applied to the water column and therefore other different approaches, e.g. correlation with other biomarkers, were applied to constrain the sources of sitosterol in the water column and sediments separately.

Reviewer: p. 13948. Line 1. I am assuming that by 'deep sediments" you mean "sediments underlying a deeper water column." All your sediment samples came from the top 5 mm?

Reply: Yes, the reviewer is right and we modified the text as suggested. Yes, sediment samples were from the top 5 mm.

Reviewer: Line 11. Does this discussion confirm or weaken your discussion point in the previous page (line 15-20) where you determine that between 55-60% of sitosterol in your "marine" sediments is derived from algal sources. These two discussions again show a lack of coherence -- data from different biomarkers are interpreted individually rather that being used together to provide a unified view.

Reply: First, we would like to correct the calculation from 55-60 % to 44-60 % of sitosterol in sediments derived from algal sources. Second, we believe that the correlation of terrestrial biomarkers gives a first insight into the dominance of sitosterol and this is in line with the results derived from the mass balance. Altogether, they confirm the mixing of terrestrial and marine derived sitosterol in all sediments, excepting site 390, which is typically marine derived. Third, we agree with the reviewer that both discussions should be together and we have now moved the discussion of the mass balance next to the correlation discussions to be more rational:

However, when site 390 is excluded, all other sediment samples showed relatively good correlation between sitosterol and long-chain terrestrial biomarkers, confirming the dominant terrestrial origin of sitosterol in these sediments. Also, the $\delta^{13}C$ value of sitosterol in the sediment 390, -24 ‰, typically of marine sources contrast with the more depleted values of the rest of sediments (~28 ‰) and that of the Mackenzie river (-31 ‰). Assuming the isotope ratio of the Mackenzie River (-31 ‰) as the terrestrial and the value from sediment at site 390 (-24 ‰), as marine end-member, we estimate that 66 % of sitosterol in sediments of the site 690 is terrestrial, whereas it was only 39% at the site 260, and 45% in the slope and deeper sediments.

Reviewer: Line 28 – again "with depth" is misleading here. I would recommend "with water column depth."

Reply: We have now modified.

Reviewer: Section 4.4. There appears to be a significant amount of speculation in this section. E.g., "This is consistent with the well-known fact that picoplankton is efficiently recycled within the food web and only large phytoplankton is exported." Isn't it possible that flagellate-associated carbon had not yet been exported at the time that these data were collected?

Reply: Yes, this is possible and was even evidenced by sediment traps (data not shown). However, it is commonly known that microplankton, which is large phytoplankton mostly dominated by diatoms, is the main contributor to the export of marine material to the sediments. In contrast, nano and pico-plankton, usually dominated by flagellates, are minor contributors of the export material. Therefore, our observations based on the pattern distribution of lipids throughout the water column and sediment are in line with this fact, giving clear indication of the post-bloom conditions in the water column, whereas sediments exhibited a solid signal of diatom markers likely derived from a previous diatom bloom.

Reviewer: p. 13951. Line14. I am still a little unclear about whether the terrestrial n-alkanes are quantified based on what is measured directly (i.e., integrating the area under the peak) or only after making the petroleum-derived n-alkane correction? If the discussion refers to the latter then wouldn't it be better to use a biomarker whose abundance has not manipulated in this way.

Reply: The values shown in Table 13 were based on the wax-n-alkanes, which take into account the corrections for the petroleum-derived n-alkane contribution. We prefer to leave the discussion and Table as it was, because conceptually it is more accurate. However, to

assure the reviewer, calculations without the corrections of petroleum-derived n-alkanes give slightly lower values differing from 1 to 5 %.

Reviewer: P. 13952 . Line 11 etc. I am not sure that these studies are comparable.
Reply: We believe that we can compare directly our data with those obtained using the same approach of lipid biomarkers, such as Belicka et al., (2004), and just report the data obtained using other approaches for information. Concerning this concern, which was also reported by reviewer's 1, we 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.